

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

Division of Environmental Remediation, Remedial Bureau C

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October 15, 2019

Via Email

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Brown and Caldwell
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Ramsey, NJ 07446

Timothy R. Roeper, P.G.
Tetra Tech
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RE: Emerging Contaminants
Site Investigation Work plan October 2019
Nepera Inc.-Harriman, Site No. 3-36-006

Dear Mr. Caputi and Mr. Roeper:

The New York State Department of Environmental Conservation (the Department) has received the Emerging Contaminants Site Investigation Work plan dated October 2019 and prepared by Cornerstone PLLC and Brown and Caldwell Associates for the above referenced site. The Department has approved this work plan.

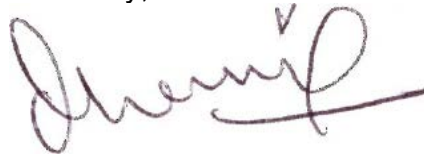
The Department understands that the Conceptual Site Model will be revised or refined as more site-specific data is available. Please note that the conceptualized ground water flow path presented, does not preclude the Department from requiring additional soil and groundwater evaluation along the certain site boundary or other locations.

Please submit the detailed schedule of implementation of the work plan within seven-day days of this letter. Please place the approved work plan in the document repository established for the site. If you wish to discuss this matter, please contact me at 518-402-9662 or email me at paraq.amin@dec.ny.gov.



Department of
Environmental
Conservation

Sincerely,

A handwritten signature in dark ink, appearing to read 'Parag Amin', with a stylized flourish at the end.

Parag Amin P.E.
Project Manager
Remedial Bureau C
Division of Environmental Remediation

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October 2, 2019

Parag Amin, P.E.
Project Manager
Remedial Bureau C
Division of Environmental Remediation
New York State Department of Environmental Conservation
625 Broadway, 11th Floor
Albany, New York 12233-7014

153734

Subject: Per- and Polyfluoroalkyl Substances (PFAS)
Site Investigation Work Plan – August 2019
Nepera Inc. – Harriman, Site No. 3-36-006

Dear Mr. Amin:

Brown and Caldwell Associates (BC) is transmitting the revised work plan on behalf of the Corporate Defendants; Cornerstone Engineering, Geology and Land Surveying, PLLC (Cornerstone); and ELT-Harriman. The parties have modified the work plan to address the comments received in the Department's September 3, 2019 letter.

As requested, a redline-strikeout version of the text is provided in addition to the modified work plan, which now is titled Emerging Contaminants Site Investigation Work Plan. Responses to comments are attached to this letter.

Please do not hesitate to contact us with any questions or comments.

Very truly yours,

Brown and Caldwell Associates

A handwritten signature in black ink, appearing to read "Jeffrey R. Caputi".

Jeffrey R. Caputi, P.E.
Managing Director

cc: K. Carpenter
C. Clark
V. Dittman
S. Levine
K. Peluso
A. Perretta
M. Robinson
T. Roeper
R. Schott
M. Schuck
T. West
T. Wolff

Attachment

RESPONSE TO COMMENTS
Per- and Polyfluoroalkyl Substances (PFAS) Site Investigation Work Plan August 2019
Nepera Inc. - Harriman, Site No. 3-36-006

1. Please revise the title of the work plan from the “Per- and Polyfluoroalkyl Substances (PFAS) Site Investigation Work Plan’ to Emerging Contaminant Site Investigation Work Plan”. Where necessary in the work plan make changes to reflect above.

The title of the work plan has been revised in accordance with this comment, as have been applicable portions of the text.

2. The work plan must include investigation of 1,4-Dioxane, which the Department understands has not been performed for the site. Where necessary in the work plan, include the details of the 1,4-Dioxane investigation. You may elect to sample selected existing ground water monitoring wells to evaluate the need for further investigation.

The requested changes have been made to the revised work plan. Please note that specifics with respect to the groundwater investigation will be provided as an addendum as called for in the work plan. It is understood that soil sampling for 1,4-dioxane may be required based on the groundwater sampling results.

3. Certification Statement: Please revise the statement to remove the words “as to soil aspects” and “as to ground water aspect” from the Caputi’s and Roeper’s statement respectively.

As discussed via phone on September 5, 2019, the certification statements are correct with reference to the work completed by each of the certifying individuals, and it would not be appropriate for an individual to certify work for which they were not responsible. As discussed during the call, however, these certifications are not intended to place the Department in a position of having to direct one entity or another to perform a given task. The Corporate Defendants and ELT-Harriman have agreed to work cooperatively to complete the work and will coordinate as needed to respond accordingly.

4. Section 2.1, Site Hydrology: The estimate of 38 degrees for Kmax which corresponds to the general axis of the outwash deposits and is stated to have the most significant impact to the direction of groundwater flow is an oversimplification as that angle appears to vary significantly depending on which portion of the site being viewed.

The statement that the angle appears to vary significantly depending on which portion of the site is being viewed appears to focus on the channel and approximate extent of thicker sequences of sand and gravel as shown on Figure 2-5. While the orientation of the channel does vary, the estimate of 38 degrees represents both the thickest section of the channel and a conservative (i.e., low) angle from north. For example, using the orientation of the channel within the southwest side of the site (i.e., closest to the railroad tracks) yields an estimate of approximately 78 degrees. The greater the angle is from north, the more influence the orientation of the sand and gravel deposits has on groundwater flow direction. The conservatively low angle of 38 degrees results in less influence on groundwater flow direction as compared to an estimate of 78 degrees. Therefore, the resultant groundwater flow direction is based on conservative assumptions. A brief explanation in this regard has been included in the revised work plan.

5. Section 2.1, Site Hydrology: The Vector Inspector in the excel results for the eastern side of the site indicates there is a difference of approximately 90 degrees between the hydraulic gradient vector and the groundwater velocity vector, but the Figure 2-10 shows a smaller angle between the two. Please recheck the calculations and ensure that the figure matches the excel spreadsheet.

The angle visually depicted in the Vector Inspector was distorted due to the scaling factors. The scaling factors have been revised to reflect the suggested scaling factors provided by the Excel spreadsheet program and the revised figure has been included in the Work Plan. Please note that this error was in the visual depiction (Vector Inspector) only. The calculated angles as shown in Figure 2-8 did not change and the average angle between the hydraulic gradient and groundwater velocity vectors shown in Figure 2-10 remains correct.

6. Section 2.1, Site Hydrology: The text indicates that the analysis are simplifications of the conditions present in the field and that there will be differences from location to location across the site. As a result, it is unclear how much value could be placed on the conceptualized ground water flow path presented in the work plan. To have confidence in the conceptualized ground water flow path, more analysis using combination of different wells is warranted. Please note that the conceptualized ground water flow path presented, does not preclude the Department from requiring groundwater evaluation along the certain site boundary or other locations.

The referenced differences refer to the differences between the gradient and groundwater flow vectors. The more the gradient direction aligns with the direction of maximum hydraulic conductivity, the less the difference between the two vectors, and vice versa. The direction of the groundwater flow vectors, however, will be similar. This is evident in the hydraulic head data provided on Figure 2-8. Two dates; October 1, 2007 and September 5, 2018, are shown in the table at the bottom of the figure. While the direction of the hydraulic gradient between these two dates varies by almost 24 degrees (101.19 degrees as compared to 77.34 degrees) the difference in the groundwater flow vectors only varies by approximately 1 degree (39.82 degrees as compared to 38.75 degrees). This would be similar throughout the site. In addition, the wells selected to represent the west and east sides of the site, respectively, were selected to represent the approximate full range of hydraulic gradient directions observed across the site (gradients on the west side are to the north and those on the east side are to the west). These two examples cover the range of gradient directions observed at the site and groundwater flow vectors would fall in between these ranges. However, as noted above, there is very little change in the groundwater flow vectors over the range of gradient vectors observed at the site. Therefore, additional analysis will not change the outcome.

More significantly, these vector analyses serve to confirm the conceptual groundwater flow paths evident from the COC distribution as summarized at the bottom of Section 2.1 of the work plan and first presented in the 2008 Supplemental Remedial Action Work Plan. Collectively, these data indicate that the flow paths presented in the conceptual model do provide value in understanding fate and transport, even with some degree of expected variability.

It is acknowledged that the conceptual site model does not preclude potential investigation along certain site boundaries or at certain locations. However, the conceptual site model does establish preferential flow paths. As noted in the work plan, proposed groundwater sample locations will be provided in a Work Plan Addendum prepared with the benefit of the results of the soils investigation.

7. Section 2.1, Site Hydrology: Within the context of the site conceptual model presented in the work plan, please include explanation of the detection of the PFAS in well MW-24S during 2017 sampling event.

The detected PFAS compounds in MW-24S will be a subject of the soil and groundwater investigation, so additional information will be forthcoming. However, from the perspective of the site conceptual model, there are no other potential sources of PFAS compounds beyond those identified in the work plan. The PFAS detected in MW-24S may be the result of preferential flow paths along sewer lines (assuming a source, see work plan Figure 1-2) or may be from an off-site influence. For example, the Orange County Sewer District No. 2 wastewater treatment plant discharges to the Harriman Pond, which represents an artificially high-water surface due to the dam located northwest of MW-24S on the west side of Route 17. Given the artificially high-water surface, it is plausible that surface water radially discharges to groundwater and migrates to the southeast towards MW-24S.

8. Section 4.2.1, Soil: The area in the vicinity and the area immediately upgradient of the well MW-16S where the maximum PFAS groundwater contamination was identified must be investigated. Also, soil borings are recommended in the areas which could have potentially caused PFAS detection at MW-24S.

Soil borings have been added in the vicinity and immediately upgradient of MW-16S as shown on Figure 4-1. A soil boring also has been added in the vicinity of MW-24S.

Additionally, at a minimum the ground water around the tank farms connected to the foam tank should be investigated. Soil sampling may be required, if ground water sampling results from those areas indicate the presence of source of [sic] PFAS contamination.

Proposed groundwater sampling locations will be included in the Work Plan Addendum.

9. Section 4.2.1, Soil: Specify the datum (below vegetative cover, below the existing debris layer, below the slab etc.) from which the 0-2" sample will be collected.

The datum has been specified as 0-2" beneath the debris layer, slab, pavement or vegetative cover depending on the conditions at each sample location.

10. Section 4.8, Report: The individual PFAS concentrations in soil must be compared to 1ppb. 1, 4-Dioxane concentration in soil must be compared to unrestricted use soil cleanup objective (SCOs) and applicable restricted use SCOs specified in 6 NYCRR Part 375-6. Ground water data should be evaluated against the values presented in the enclosed document. All exceedances must be highlighted in the summary table. The report must include the figure showing the location of the public and private water wells within ½ mile radius of the site. The figure must also depict the conceptualized ground water flow direction.

The work plan text has been revised to clarify that the report will include this information.

11. Table 4-2: Please include target reporting limits (RL) consistent with the Department guidance.

A new table (Table 4-3) has been added to include the target RLs.

12. Append the Leggette, Brashears & Graham, Inc. (LBG) reports referred to in Cornerstone's letter dated December 4, 2017.

The referenced LBG reports have been added to the appendix.

Emerging Contaminants
Site Investigation Work Plan
Former Nepera Plant Site
Harriman, New York
Site #3-36-006

Prepared for
ELT Harriman, LLC and Nepera, Inc. &
Warner-Lambert Company Corporate
Defendants
October 2019

Emerging Contaminants
Site Investigation Work Plan
Former Nepera Plant Site
Harriman, New York
Site #3-36-006

Prepared for
ELT Harriman, LLC and Nepera, Inc. & Warner-Lambert Company Corporate Defendants

October 2019



Brown and Caldwell Associates
500 N. Franklin Turnpike, Suite 306
Ramsey, New Jersey 07446



100 Crystal Run Road, Suite 101
Middletown, New York 10941

Certification Statement

I, Jeffrey Caputi, certify that I am currently a NYS registered professional engineer, and that this Site Investigation Work Plan, as to soil aspects, was prepared in accordance with all applicable statutes and regulations and in substantial conformance with the DER Technical Guidance for Site Investigation and Remediation (DER-10) and any DER-approved modifications.



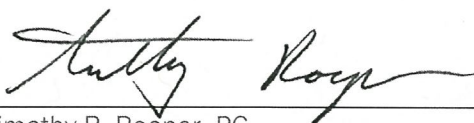
Jeffrey R. Caputi, P.E.
N.Y.P.E. License Number 082196



10/1/19

Date

I, Timothy R. Roeper, certify that I am currently a NYS registered professional geologist, and that this Site Investigation Work Plan, as to groundwater aspects, was prepared in accordance with all applicable statutes and regulations and in substantial conformance with the DER Technical Guidance for Site Investigation and Remediation (DER-10) and any DER-approved modifications.



Timothy R. Roeper, PG
N.Y.P.G. License Number 000307

October 1, 2019

Date

]

Brown AND Caldwell



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Section 1

Introduction

This Site Investigation Work Plan has been prepared on behalf of ELT Harriman, LLC (“ELT”) and Nepera, Inc. and Warner-Lambert Company (the “Corporate Defendants”) in response to the request from the New York State Department of Environmental Conservation (the “Department” or “NYSDEC”) to conduct an investigation of Per- and Polyfluoroalkyl Substances (PFAS) and 1,4-dioxane (emerging contaminants) in soils and groundwater at the Nepera-Harriman Site, also referred to as the Former Nepera Plant Site (the “Site”). The purpose of this Site Investigation is to assess potential sources of emerging contaminants at the Site and to further assess the nature and extent of these compounds in groundwater.

Sampling and analysis conducted by the NYSDEC in June 2017 detected perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) in on-site groundwater monitoring wells and in surface water samples collected from Mary Harriman Park Lake and the West Branch of the Ramapo River. Sampling conducted by the New York State Department of Health (NYSDOH) detected PFOA and PFOS in public water supply wells located at the Mary Harriman Park. The results of the NYSDEC’s and NYSDOH’s sampling are presented in the Department’s September 12, 2017 letter (Appendix A). In a letter dated December 4, 2017, Corporate Defendants provided an analysis of Site-related investigations and investigations and data specific to the Village of Harriman groundwater supply concluding that PFAS detected in the Mary Harriman wells is unrelated to the Site. A copy of this letter and the referenced attachments is also provided in Appendix A. Investigation of the presence of 1,4-dioxane has not been completed to date.

The Site Investigation described in this Work Plan will be conducted in two phases. The initial phase will include soil sampling and analysis for emerging contaminants at building locations where potential PFAS containing products such as fire-fighting foam may have been stored or used. The subsequent phase will include sampling and analysis of groundwater. The results of the soil investigation will inform the selection of locations for groundwater sampling, which are expected to include a combination of existing and new monitoring wells. Following the receipt of soil sampling data, a Work Plan Addendum will be submitted to the Department with the preliminary soil sampling results and proposed groundwater sampling locations. A report presenting the results of soil and groundwater sampling will be submitted following the receipt of groundwater sampling data.

The Nepera-Harriman Site is located on NY Route 17 in the Village of Harriman, Orange County, approximately one mile west of Exit 16 of the New York State Thruway (Figure 1-1). The Site was used for the manufacture of pharmaceutical and specialty chemicals from 1942 until operations were discontinued in 2005. The facility is currently inactive and the buildings, tank farms, distilling operations, and other manufacturing areas have been decommissioned and demolished. The layout of the Site prior to demolition activities is presented in Figure 1-2.

The site history has been extensively described in prior work plans and reports including the *Site-Wide Characterization Summary Report* (Brown and Caldwell Associates and Cornerstone Engineering and Land Surveying, PLLC, March 2011) and is not reproduced in this work plan. The site hydrogeology and conceptual site model are described in Section 2. The investigation objectives are outlined in Section 3. The proposed investigation activities and procedures are detailed in Section 4. The schedule is provided in Section 5.

Reservation of Rights

The preparation and submission of this Site Investigation Work Plan is subject to a full reservation of rights by all the private parties, including ELT and the Corporate Defendants. Nothing in the work plan or the discussions and submissions related thereto will be cited or construed in support of or against any position regarding which parties are responsible for any environmental liabilities or remediation at the Nepera-Harriman Site, including without limitation the presence of emerging contaminants and any of the costs associated with investigation and the potential remediation of such compounds.

Section 2

Site Hydrogeology and Conceptual Site Model

The site hydrogeology and conceptual site model (CSM) were previously submitted to the NYSDEC in the report *Conceptual Site Model and Supplemental Remedial Action Work Plan (HydroQual, May 2008)*, which was approved by the NYSDEC in a letter dated June 18, 2008 (see Appendix C). The conclusions of the above-referenced report are summarized below along with additional calculations, as requested by the Department, to support the understanding of the predominant direction of groundwater flow and that groundwater flow is not perpendicular to equipotential lines due to anisotropy. These calculations, as well as water quality data that further support anisotropic groundwater flow directions are presented in this section.

2.1 Site Hydrogeology

The site is underlain by a layer of fill material overlying a complex sequence of glacially derived clay, silt, sand and gravel. Near surface, immediately underlying any fill material, is a fine grained Clay and Silt with interbedded, discontinuous layers of Silt and fine Sand. This fine grained unit represents a glacial lacustrine or lake deposit that is present throughout the entire site with the exception of the area near PZ-1 near the southwest-central portion of the facility. Underlying the Clay and Silt deposits is a glacial outwash or stream deposit that varies across the site from fine to coarse Sand. Generally speaking, the sand is finer near the southeast end of the facility and coarser and thicker near the central portion. Also, within the central portion of the facility, the coarse Sand deposits immediately overlie bedrock. Within the northeast side of the site, the glacial lacustrine and glacial outwash deposits are underlain by a kame or esker deposit which is characterized by a mix of clay, silt, sand and gravel that is weakly cemented. Glacial till, consisting of a dense silt and clay matrix with lesser amounts of sand and gravel, is present intermittently at various locations immediately overlying bedrock. The entire site is underlain by fractured dolomite bedrock.

Figure 2-1 presents a map of the site along with the orientation of three cross sections that are presented in Figures 2-2 through 2-4. These figures are reproduced from the HydroQual 2008 Report referenced above and the cross sections illustrate the relationship between the various glacially derived deposits and visually depict the layer of glacial lacustrine silt and clay overlying the coarser-grained sand and gravel as well as the kame and glacial till deposits. Figure 2-5, also reproduced from the HydroQual 2008 Report, presents an isopach map of the thickness of the glacial outwash deposits. This map illustrates a thicker sequence of sand and gravel underlying the central portions of the facility as generally illustrated by the shading.

The variations in grain size and the thickness of the glacial deposits described above and illustrated in Figures 2-2 through 2-5 represent the controlling factors relative to groundwater flow beneath the facility. Water levels collected on October 15, 2007 are plotted on the cross sections presented in Figures 2-2 through 2-4 and are used as control points for construction of the equipotential lines illustrated in blue. Note that water level data plotted on Figures 2-2 through 2-4 have not been updated with more recent data as the monitoring wells completed in the fine grained aquitard and the underlying bedrock are no longer monitored. However, these existing figures consistently indicate principally

vertical (downward) flow paths within the near surface, fine grained glacial lacustrine deposits and more horizontal flow paths in the coarser-grained outwash deposits. Collectively, this indicates that the finer grained silt and clay deposits represented by the glacial lacustrine deposits, glacial till and to a slightly lesser degree the kame deposits, serve as aquitards, limiting the volume of water moving through them and principally demonstrating downward, vertical flow paths.

Hydraulic conductivity estimates of the near surface glacial lacustrine deposits, at 10^{-6} cm/sec, further support this interpretation (*Remedial Investigation, Harriman Site, Conestoga-Rovers & Associates, November 1995*). Conversely, the coarser-grained outwash deposits represent an aquifer with the ability to transfer larger volumes of water in a preferentially horizontal orientation. This is supported by aquifer tests completed within the thicker, more coarse-grained portions of the outwash channel, which suggest permeability on the order of 5×10^{-2} cm/sec (Conestoga-Rovers & Associates, November 1995). Note that this estimated permeability is likely high in that the referenced aquifer test was completed in an area where the outwash is in direct hydraulic communication with the bedrock, and therefore, the resulting hydraulic conductivity represents a combination of both the bedrock and the outwash. In addition, as one moves out of the channel of thicker coarse-grained outwash to where finer-grained sands predominate, the hydraulic conductivity will further decrease.

Hydrogeologically, the data indicate that the glacial lacustrine deposits represent an aquitard while the outwash deposits serve as an aquifer. As illustrated in the cross sections, both units underlie the majority of the site. However, the extent to which the aquifer can transmit significant volumes of water is dictated by grain size and thickness. Accordingly, greater flow volumes are anticipated near the central portion of the site where the outwash is thickest and coarse grained. Conversely, lower flow volumes will be present where the outwash is finer grained and thinner. The extent to which the channeling of the coarser grained outwash deposits influences groundwater flow is further evident in the southeastern portion of the site where the aquifer is apparently blocked, or at least limited, by the abrupt intersection of the glacial outwash with the glacial till as shown in Section C- C' (Figure 2-4). This observation, coupled with water quality data discussed further below, and the knowledge that thicker, coarse-grained outwash deposits are present to the north of this area underlying the central portions of the site, suggest that groundwater flow is diverted around the low permeability till towards the central portion of the site before again moving eastward.

Monitoring wells completed within the overburden aquifer (i.e., outwash deposits) were used to construct a potentiometric surface map as illustrated in Figure 2-6 reproduced from the HydroQual 2008 Report and updated in Figure 2-7 to include additional monitoring wells installed since 2008 (i.e., the MW-100 series of wells) and with data collected September 5, 2018. Notably, the addition of MW-103 within the southern quadrant of the site noticeably changes the orientation of the groundwater contours to depict groundwater flow in a more northerly direction in Figure 2-7 (2018 data) as compared to Figure 2-6 (2008 data). The more northerly direction of groundwater flow is consistent with the conceptualized groundwater flow path shown on Figure 2-6 due to anisotropy.

In a homogeneous, isotropic aquifer, groundwater flow paths would be oriented perpendicular to the equipotential lines (i.e., in the direction of the hydraulic gradient). As noted above, however, the system is not homogeneous or isotropic, therefore, groundwater flow would not be perpendicular to the equipotential lines, but rather at a resultant vector (angle) to the equipotential lines as influenced by the direction of highest hydraulic conductivity.

The influence of anisotropy (i.e., the hydraulic conductivity is higher in one direction (k_{\max}) than it is in another (k_{\min})) on groundwater flow can be evaluated using the USEPA spreadsheet tool 3PE (3PE: A Tool for Estimating Groundwater Flow Vectors, EPA 600/R-14-273, September 2014). Input to the spreadsheet includes the coordinates and groundwater elevations for three monitoring points, hydraulic conductivity in the k_{\max} and k_{\min} direction and the orientation of k_{\max} in degrees from north.

For this assessment, data was input for MW-25S, MW-20S, and MW-8S, which form an approximate triangle near the eastern half of the site. MW-25S and MW-20S are completed within the glacial outwash overburden deposits but on the edges of the thicker, coarse-grained deposits underlying the central portion of the Site as shown on Figure 2-5, while MW-8S is located within the thicker coarse-grained deposits that represent the overburden deposits with the highest hydraulic conductivity. The K_{\max} and K_{\min} hydraulic conductivity values were taken as the maximum and minimum hydraulic conductivity values estimated for the overburden aquifer in the Remedial Investigation report (CRA, November 1995) of 5.6×10^{-2} and 9.0×10^{-4} cm/sec, respectively. The orientation of K_{\max} from north was estimated at 38 degrees as a line drawn along the center of the outwash deposits as shown in Figure 2-5. The estimated angle represents the axis of the thickest sand and gravel deposits underlying the northeast portion of the site and is the most conservative with respect to how these sand and gravel deposits influence groundwater flow. Specifically, use of a higher angle such as that represented by the axis of the sand and gravel deposits underlying the southwest portion of the site, would result in a larger deviation in groundwater flow direction (the greater the angle (orientation) of K_{\max} from north the greater the influence on groundwater flow). Finally, groundwater elevations from October 2007 and September 2018 for each of the three wells were also entered.

A second spreadsheet was also prepared to represent the western half of the site using data from wells MW-9S, MW-20S, and MW-24S. Note that none of these wells are located within the thick coarse-grained outwash deposits depicted in Figure 2-5. As such, the K_{\max} values used in the spreadsheet may be overstated (i.e., the spreadsheet value may be higher than actual field conditions). Reducing the K_{\max} value by an order of magnitude reduces the effect of the anisotropy on the direction of groundwater flow such that the deviation from north would be less (less than 10 degrees different). However, the direction of groundwater flow is most significantly influenced by the orientation of K_{\max} with respect to the hydraulic gradient so that even with an order of magnitude decrease in K_{\max} , the resultant groundwater flow direction is diverted easterly toward the center of the Site and the orientation of the glacial outwash channel that represents the maximum hydraulic conductivity (i.e. K_{\max}).

Data input (green shaded cells) and output (blue shaded cells) are shown in Figures 2-8 and 2-9 for each of the above scenarios. The vector plot (Vector Inspector) in Figures 2-8 and 2-9 shows the direction of the hydraulic gradient (i.e., the direction of flow in an isotropic medium) as a blue arrow and the direction of flow due to anisotropy as a red arrow. Also shown under the headings "Hydraulic Gradient" and "Groundwater Velocity" are the orientation of these flow arrows in degrees from north. As shown, the direction of groundwater flow from north ranges from 37.08 to 39.82 degrees with the resultant flow direction influenced by the high hydraulic conductivity outwash deposits depicted in Figure 2-5. Using an average hydraulic gradient and groundwater flow direction from north as derived from the October 2007 and September 2018 data sets described above (see Figures 2-8 and 2-9) the resulting vectors representative of the west and east sides of the site, are overlain on the potentiometric surface maps as shown in Figures 2-10 and 2-11. As shown, even though the orientation of the equipotential lines are different on the western half of the site as compared to the eastern half, the resultant groundwater flow is generally along the same orientation as K_{\max} .

It should be stated that both the equipotential maps and the spreadsheet analysis are simplifications of the conditions present in the field and that there will be subtle differences from location to location across the site. However, by completing the analysis representative of gradients present within both the western and eastern sides of the site and as measured by water levels collected over two events, the approximate range of observed conditions are accounted for and the analysis shows that there is very little change in the groundwater flow vectors over the range of gradient vectors observed at the site. The analysis serves to confirm the water quality data described below, illustrates the influence of the coarse-grained outwash deposits on overall site groundwater flow and provides a more representative direction of groundwater flow for consideration in the selection of groundwater monitoring points.

As noted above, the flow direction as a consequence of the anisotropy is evident in the water quality data. For example, although the gradient would suggest groundwater flow from the OW-6/OW-7/MW-25S area (wells with some of the highest benzene concentrations) towards MW-12S and MW-13S, the site COC concentrations at these two wells have historically been non-detectable (ND) to trace level ("J" qualified). This is true as far back as 1985 prior to any remedial actions. The water quality data thus provides further evidence of the effects of anisotropy on groundwater flow and supports the direction of groundwater flow as previously stated (HydroQual, 2008) and as calculated by the USEPA spreadsheet tool.

Groundwater flow along the northwest, downgradient boundary of the site (adjacent to the West Branch of the Ramapo River) is also likely locally influenced by surface water associated with the Harriman Park Pond that is dammed immediately northwest of the Site. The Orange County Sewer District No. 2 wastewater treatment plant discharges to this pond and as a consequence of this discharge and the damming of this pond, there is likely radial groundwater flow within the surrounding area. While additional information will be forthcoming as part of the groundwater investigation, it is plausible that surface water radially discharges to groundwater and migrates to the southeast towards MW-24S. Under this scenario, groundwater quality at MW-24S may partially be influenced by off-site water quality.

2.2 Conceptual Site Model

On the basis of the above, the conceptual site model (CSM) may be summarized as follows:

- Groundwater flow in the near surface glacial lacustrine deposits (aquitard) is principally vertical with discharge into the underlying glacial outwash. Horizontal flow in the aquitard is limited to localized and discontinuous lenses of sand.
- A channel of coarser-grained sand and some gravel outwash, underlying the central portions of the site, is the primary conduit for groundwater flow and contaminant transport. While the outwash aquifer is present underlying most, if not all of the site, these deposits thin and become finer grained to the west and east, thus limiting their ability to transmit groundwater.
- The variable thickness and grain size of the outwash aquifer deposits result in a nonhomogeneous, anisotropic aquifer. As a consequence, groundwater flow is not perpendicular to the equipotential lines. Rather, groundwater flow will travel at an angle to the equipotential lines toward the coarser-grained, thicker deposits underlying the central portion of the site.
- Groundwater flow through the glacial outwash aquifer is generally to the northeast, generally parallel to the direction of maximum hydraulic conductivity represented by the channel of coarse-grained sand and gravel, with discharge to surface water (West Branch of the Ramapo River) and adjacent wetlands.
- Groundwater travel times vary depending on the grain size and associated permeability of the aquifer material.

Section 3

Investigation Objectives

The investigation objectives are as follows:

- Investigate potential sources of emerging contaminants at the Site via sampling of soils at the locations of former buildings or activities where potential PFAS containing products such as fire-fighting foam were stored or used
- Further assess the nature and extent of emerging contaminants in groundwater via sampling of temporary and permanent monitoring wells at the Site

The NYSDEC identified four former building locations for investigation of PFAS compounds. The buildings include the former emergency center (Building 52) where fire equipment was stored, a former fire pump house (Building 26), a former storage building (Building 2A), and the former foam house (Building 72). ELT interviewed former plant employees to obtain information regarding the storage and use of potential PFAS containing materials at the Site. The interviews yielded the following information:

- Aqueous foam was stored in a tank located inside Building 72. The foam tank was connected via piping to the tank farms in this part of the plant. In the event of a fire, valves could be opened to disperse a mixture of water and foam. There were no fires for which this system would have been deployed. The contents of the tank were removed from the Site during plant decommissioning.
- Foam was not stored or used at Buildings 2, 26 or 52. The pump located in Building 26 was part of the backup sprinkler system that was connected to the large water tank in the rear of the plant. Dry chemical fire extinguishers were stored in Building 52.
- The facility had its own fire truck that dispensed dry chemical powder (monoammonium phosphate).
- Fire training exercises were conducted in an open area between Building 67 and Arden House Road. These exercises involved the use of dry chemical fire extinguishers.
- No other locations were identified in which potential PFAS containing materials were stored or used at the Site.

This information is helpful in selecting soil sampling locations, which are described in Section 4. The area surrounding former Building 72 is of greatest interest. Samples are proposed at this location to assess the potential presence of PFAS in the surrounding soil. The tank farms that were connected to the fire suppression system also are areas of interest. These areas will be investigated as part of the groundwater sampling program to assess if PFAS compounds are present and if subsequent soil sampling is warranted.

The other building locations are unlikely to be potential PFAS source areas. Limited sampling is proposed in these areas to confirm the absence of PFAS compounds. Although aqueous foam reportedly was not used in training exercises, samples are proposed in the former training area to confirm the absence of PFAS compounds.

The NYSDEC also requested that soil samples be collected in the vicinity and upgradient of MW-16S and in the areas which could have potentially caused PFAS detection at MW-24S. A soil sample is proposed in the vicinity of MW-16S and a second soil sample is proposed adjacent to the Building 64 tank farm, which is hydraulically upgradient of this well. The former buildings located upgradient of MW-24S consisted of offices and warehouses, which are unlikely to have been a source of PFAS. As discussed in Section 2.1, groundwater quality at MW-24S may partially be influenced by off-site water

quality. Thus, PFAS compounds detection in this well may be attributable to an off-site source. A sample is proposed in the vicinity of MW-24S to assess whether PFAS is present within unsaturated zone.

There are no known or suspected sources of 1,4-dioxane at the site. 1,4-Dioxane was not used as a raw material and is most commonly associated with chlorinated solvents. The contaminants of concern at the site are benzene, toluene, xylene, pyridine, alpha-picoline and 2-aminopyridine, none of which are chlorinated solvents. Chlorinated solvents (specifically chlorobenzene) have only be detected sporadically in groundwater and at low levels based on review of historic water quality data.

The results of the soil investigation for PFAS will inform the selection of locations for groundwater sampling, which are expected to include a combination of temporary, existing and new monitoring wells. The groundwater sampling program will include 1,4-dioxane, in addition to PFAS compounds. Soil sampling may be required for 1,4-dioxane based on the groundwater sampling results.

Section 4

Proposed Investigation Activities and Procedures

The initial phase of investigation will include the collection of soil samples at each of the target locations, which are shown on Figure 4-1 and described in Table 4-1. Sample locations will be identified in the field prior to sampling through use of a licensed surveyor. Locations may be adjusted in the field based on access constraints or observations regarding potential impacts.

Groundwater sampling locations will be proposed in a Work Plan Addendum to be submitted following the receipt of soil sampling data. Details regarding the procedures for the collection and analysis of soil and groundwater samples are described in the following sections.

4.1 Health and Safety

A health and safety plan (HASP) will be prepared in accordance with the standards set by the Occupational Safety and Health Administration as stated in 29 CFR with emphasis on the relevant provisions of the following subsections, as well as other applicable federal and state statutes and regulations:

- 1910.120 Hazardous Waste Operations and Emergency Response
- 1910.1000 Toxic and Hazardous Air Contaminants
- 1910.1200 Hazard Communication, Employee Right-to-Know Law
- 1904 Recording and Reporting Occupational Injuries and Illnesses
- 1990 Identification and Regulation of Potential Occupational Carcinogens
- 1926 Safety and Health Regulations for Construction)

Existing HASPs prepared for prior soil and groundwater sampling activities at the Site may be used, if current, or updated, as necessary, for the planned field activities. Each entity performing work at the Site will be solely responsible for the health and safety of its employees, and will have a site-specific health and safety plan in place for its work.

4.2 Sample Collection Procedures

Standard operating procedures and NYSDEC guidance for PFAS sampling are provided in Appendix B. If alternative sample collection methods are required due to field conditions, NYSDEC will be notified, and approval obtained prior to sample collection. The PFAS Sampling Checklist will be strictly adhered to and completed by the field team leader on each day of sampling activities.

4.2.1 Soil

Proposed locations for the collection of soil samples for analysis of PFAS compounds are shown on Figure 4-1. As described below in Section 4.2.2, proposed locations for the collection of groundwater samples for PFAS and 1,4-dioxane analysis will be submitted to NYSDEC as part of a Work Plan Addendum following the receipt of the soil sampling results. If additional soil sampling is required for

emerging contaminants based on the soil or groundwater sampling results, a Work Plan Addendum will be submitted to NYSDEC specifying the proposed sampling locations and analyses.

Surficial soil samples will be collected manually utilizing a pre-cleaned stainless-steel spoon or hand auger. Deeper soil samples will be collected using one of two methods: GeoProbe® (macro core) or 2-inch stainless steel split-spoons. If soil samples are collected via GeoProbe®, a new acetate liner will be used for each sample. If sampling is performed using a 2-inch stainless steel split-spoon, the split-spoons will be field decontaminated prior to each use.

Both surficial and deeper soil samples will be homogenized in a stainless steel bowl prior to being put in sample containers. After the completion of sample collection, any excess soil will be carefully placed back in the borehole. The remainder of the borehole will be restored to grade with additional soil.

Further detail regarding sample collection methodology is provided in the Standard Operating Procedure provided in Appendix B.

Target Intervals

At each of the sample location, a minimum of two soil samples will be collected unless otherwise noted. A soil sample will be collected from the 0-2-inch interval, below any debris, slab, pavement, or vegetative cover depending on the conditions at each sample location. The deeper sample will be collected from the 1-foot interval above soil saturation unless evidence of potential impact is apparent at a different depth interval, in which case the sample will be collected from that interval.

The soils will be transferred into the sample container using a laboratory decontaminated high density polyethylene (HDPE) or polypropylene trowel or spoon or directly by dedicated new nitrile gloved hand. The sample containers will be unlined HDPE or polypropylene and will be placed in a cooler that will be maintained at 4°C. The samples will be packaged so as to minimize the potential for breakage and cross contamination. Glass jars will be wrapped with protective packaging prior to placement in the cooler for transport. Plastic bags filled with wet ice and sealed, will be placed inside each cooler with the samples to ensure that the preservation temperature is maintained. The sample coolers will be transferred, in accordance with the chain of custody procedures, to a courier for same day delivery to the analytical laboratory.

4.2.2 Groundwater

On the basis of the soils analytical data and the understanding of groundwater flow and quality as described above, proposed locations for the collection of groundwater samples for PFAS and 1,4-dioxane analysis will be submitted to NYSDEC as part of a Work Plan Addendum. It is anticipated that groundwater samples will be collected from a combination of temporary locations advanced with a GeoProbe® as well as from selected existing monitoring wells. Additionally, the installation of new permanent monitoring well locations will also be considered, again in the context of the soils analytical results and potential PFAS source areas. As stated above, there are no known or suspected sources of 1,4-dioxane.

Groundwater samples collected through the use of a GeoProbe® will be obtained by advancing GeoProbe® rods equipped with a retractable screen (decontaminated using Alconox and potable water between each boring location) to the selected depth (see Target Intervals below). Upon reaching the selected depth, the rods will be pulled back to expose the screen and the groundwater within the rods and adjacent to the screened interval will be purged using a peristaltic pump and HDPE tubing. The HDPE tubing will be dedicated to each location. Purging will continue until there is no noticeable improvement in the turbidity of the water, with the objective of reducing turbidity to the greatest extent possible. Once the turbidity has visually stabilized, the tubing will be connected to a flow through cell for the measurement of field parameters (pH, conductivity, turbidity, temperature, ORP). Once the field

parameters stabilize, a sample for PFAS and 1,4-dioxane analysis will then be collected directly from the same tubing into laboratory provided sample containers. The collected samples will then be stored on ice pending shipment to the laboratory.

Groundwater sampling at monitoring well locations will also be completed using a peristaltic pump and HDPE tubing, with the tubing again dedicated to each individual location. Field parameters will be monitored through a flow through cell for stabilization, followed by collection of a sample for PFAS and 1,4-dioxane analysis directly from the same tubing into laboratory provided sample containers. The collected samples will then be stored on ice pending shipment to the laboratory. In the event that water levels drop to a depth beyond the limits of the peristaltic pump (not anticipated), a disposable HDPE bailer will be used for sample collection.

Target Intervals

At each location selected for the collection of groundwater samples from a temporary well location (i.e., GeoProbe® boring) a groundwater sample will be collected from the shallowest depth that yields sufficient volume for purging and groundwater sampling. This will be determined by advancing the GeoProbe® rods to the anticipated depth of the water table, pulling back the rods, and checking for free standing water. If the borehole contains water, the peristaltic pump will be used to purge the borehole. If the borehole yields 500 milliliters per minute or more, purging and sampling will continue as described above. If the borehole does not yield this minimum amount, the rods will be advanced deeper, and the above assessment will be completed again. If the shallowest sample is collected from a depth consistent with the shallow aquitard (i.e., fine grained Clay and Silt with interbedded, discontinuous layers of Silt and fine Sand as described in Section 2.0 above), then a second sample will be collected from a depth consistent with the underlying aquifer (see Section 2.0 above). In this manner up to two individual samples will be collected from each temporary boring. Note that it may not be feasible to collect a groundwater sample from the aquitard at all locations.

Samples from permanent monitoring wells will be collected from locations that are representative of both the aquitard, aquifer and bedrock units.

Groundwater samples will be stored, handled and shipped to the laboratory under chain of custody consistent with the procedures described above for soil samples.

4.3 Chain-of-Custody Procedures

Custody requirements address sample custody and handling in the field and during laboratory receipt, analysis and disposition. All samples will be subject to complete custody documentation.

In the field, samples will be in physical possession or in view of the sampler/custody holder (typically the field sampling team leader). The sample may also be placed in a (designated) secure area by the custody holder.

Before sending samples to the analytical laboratory (typically by lab courier pick up), appropriate sections of the Chain-of-Custody (COC) will be filled out. Sample containers will be labeled and must contain at least the following information: sample ID, sample date and time, and requested analysis. The COC will accompany the samples to the analytical laboratory; a copy of the COC stays in custody of the sampler.

The laboratory personnel will be responsible for the care and custody of samples from the time of receipt until the sample is exhausted or disposed. Custody rules will apply throughout the life of the sample in the laboratory. Documentation of sample custody within the laboratory will become a permanent part of the laboratory project files. The laboratory will submit an analytical report, including custody documentation.

4.4 Sample Analyses

Analytical services will be performed by a laboratory certified for analysis of emerging contaminants under the New York State Environmental Laboratory Approval Program (ELAP). Soil and groundwater samples will be analyzed for the following analyte groups, using the method listed below:

- PFAS Target Analyte List (NYSDEC, April 2018) –EPA Method 537, revision 1.1 (modified)
- 1,4-dioxane – SW846 Method 8270 SIM with Isotope Dilution
- PFAS Synthetic Precipitation Leaching procedure (SPLP) – Method 1312 – Contingent analysis for samples where PFOA or PFOS concentrations exceed 1 ppb.

Table 4-2 provides a summary of each sample type, quantity, analyte, container, holding time and preservation method. Table 4-3 provides the reporting limits for the analyses.

4.5 Survey

Upon completion of the sampling activities, each of the soil and groundwater sample locations will be surveyed by a New York-certified land surveyor. The survey will utilize the New York State Plane coordinate system (NAD'83, East Zone, Feet). Vertical elevations will be references to NAVD '88.

Surveying of any permanent, new groundwater monitoring wells would include vertical elevations of the inner and outer casings, as well as the adjacent ground surface, using the same datum referenced above for the soil samples.

4.6 Data Management Plan

4.6.1 Sample Nomenclature

Each sample collected will receive a distinct sample identifier. The sample identifier will consist of three parts; the first part will identify the area the sample was collected from within; the second part will identify the sample matrix; the third part will identify the specific sample. A complete list below identifies the different area and matrix identifiers. As an example, a soil sample collected using a split spoon or a macro core in Area A from Boring 1 would be designated A-B-001. The “A” designates the area, “B” identifies the sample as a soil boring, and “001” identifies the specific boring number. Each boring identifier will additionally have the depth interval added to the end of the identifier. In the example above, if the sample was collected from the 1-2 foot interval the sample identifier would be “A-B-001-01-02”.

Groundwater samples collected from temporary GeoProbe® locations may or may not be collocated with a specific soil sampling location. Groundwater sample locations will be identified with the area, consistent with the above description for soils, followed by “GW” to identify the sample as a groundwater sample followed by a sequential number and depth interval; for example, A-GW-01-08-10'. Groundwater samples collected from permanent monitoring wells will be identified with the monitoring well location ID (e.g., MW-25S).

The Quality Assurance/Quality Control (QA/QC) samples will also be identified in three parts; sample type, date, and a unique number if more than one type is collected in a single day. For example, a duplicate would be identified as “DUP-mmddyy” and a second duplicate collected on the same day would be “DUP-mmddyy-1”.

Below are the matrix/sample codes:

- “B” indicates a soil boring
- “GW” – indicates groundwater sample collected from a temporary location

- “MW” – indicates groundwater sample collected from a permanent monitoring well
- “FB” indicates a field blank
- “DUP” indicates a duplicate

4.6.2 Data Record

Data will be received from the laboratory as both a hard copy and as an electronic data deliverable. Data will be imported and stored in a database, which will include a minimum of three data tables. These three main data tables will be a results table, a parameter table, and a sample table. The results table will have each of the sample results stored; the parameter table will contain details regarding the analysis; and the sample table will contain information about the sample.

Data collected in the field, including PID data, will be stored electronically with the soil boring log data.

4.6.3 Tabular and Graphical Displays

Data will be presented in tables generated using the database and spreadsheets. Graphical displays, maps, figures, and boring logs will be generated using survey data from the database and GIS or CAD depending on the application. Boring logs will be presented using Gint® or other similar logging software.

4.7 Quality Assurance Plan

4.7.1 Data Quality Objectives

Method analyses that are selected must, at a minimum, have detection limits that meet the relevant standards, criteria or guidance.

4.7.2 Quality Assurance/Quality Control Samples

The field QA/QC samples to be collected are as follows:

4.7.2.1 Field Duplicates

Field duplicates are a second aliquot of a field sample. Variations in the sample and duplicate can be indicative of possible inaccuracy or imprecision of laboratory methodologies. One Field Duplicate will be collected for every 20 samples of the same matrix (i.e., soils or groundwater).

Field duplicates for soil samples will be collected by homogenizing the sample volume in plastic bowls with plastic spoons, or by kneading the material in a plastic bag (e.g. Ziploc® bag). Once homogenized, the material will be evenly distributed into the sample containers. Sample collection materials (bowls, spoons, plastic bags, gloves) will be laboratory decontaminated or single use. Field duplicates for groundwater samples will be collected by concurrently filling sample and duplicate sample containers at a randomly selected location.

4.7.2.2 Field Blanks

Field blanks, also referred to as equipment blanks, are used to determine if the sampling equipment used in the field might contribute appreciable concentrations of constituents to the samples. Laboratory certified PFAS free water is run over, or through, the sampling equipment and collected in the same type of sample containers as other samples. Ideally, the results for this analysis will show non-detects for the constituents analyzed. One field blank will be collected every day that samples are collected, or one per 20 samples, whichever is greater.

4.7.2.3 MS/MSD Samples

Matrix Spike/Matrix Spike Duplicate (MS/MSD) samples will be used to determine if there are groundwater matrix interferences that may affect the groundwater analytical results. MS/MSD samples are obtained by collecting three times the required sample volume from a given sampling location. One set of MS/MSD samples will be collected for every 20 groundwater samples.

4.7.3 Test Methods

The following methods will be used for analysis:

- PFAS Compound Target Analyte List (NYSDEC, April 2018) – EPA Method 537 Revision 1.1 (modified)
- 1,4-dioxane – SW846 Method 8270 SIM with Isotope Dilution
- PFAS Synthetic Precipitation Leaching procedure (SPLP) – Method 1312 – Contingent analysis for samples where PFOA or PFOS concentrations exceed 1 ppb.

Data will be reported in Category B format along with the required quality assurance data on the required forms and with raw data including calibration data, blank data, chromatograms, quant reports, sample prep logs, sample run logs and percent moisture work sheets (as applicable) and will be provided in electronic format. Soil samples will be reported on a dry weight basis.

4.7.4 Data Validation

4.7.4.1 Qualitative Data Validation

Data validation services will be performed by a qualified data validator. For each data package a Data Usability Summary Report (DUSR) will be produced.

The criteria for qualitative data validation include the following:

- Data Completeness
- Sample Temperatures
- Holding Times
- Analytical Detection Limits and Sample Quantitation
- Surrogate Recovery
- MS/MSD Review
- Laboratory Control Sample (LCS)
- Review of QA/QC Samples
- Overall Evaluation of Data
- Gas chromatograph/mass spectrometer/GC/Electron Capture Detector (GC\MS\GC\ECD) Instrument Performance
- Initial Calibration
- Continuing Calibration
- Internal Standards
- Target Compound Identification
- System Performance
- Serial Dilution

4.7.4.2 Qualitative Data Validation Criteria

Data Completeness

The data completeness criterion incorporates a checklist of what should be found in a data package. It also identifies the types of forms used for certain analyses. A complete data set is considered to have the following: case narrative, data summary, surrogate recovery summary, MS/MSD summary, and LCS summary. In addition to identifying missing components of the data package, the data completeness check also includes verifying the following criteria: proper analytical method selection and documentation, use of the proper analytical data sheets, appropriate report formats, sample preservation documentation, and documentation clarity.

Sample Temperatures

Most environmental samples are required to be held within a temperature range of 2-6°C. The rationale for this range is that temperature affects various chemical and biological degradation processes, including solubility. Freezing of samples should be avoided as well.

Holding Times

Various parameter groups have different allowable holding times. Holding times are a function of solubility, rates of decay, evaporation, and other factors that are function of time and potentially affect the concentrations of contaminants. The following lists the holding times for the constituents included in the various levels of data validation.

- PFAS Compounds – 28 days
- 1,4-dioxane – 14/7 (soil/water) days to extraction, 40 days after extraction for analysis

The results of samples that are tested outside of the holding time ranges are considered estimates, since there may have been sufficient time for a constituent loss or a reduction in concentration to have occurred.

Analytical Detection Limits

Various analytes and various concentrations require different detection limits. This review focuses on whether or not the detection limits are sufficiently low to detect relevant concentrations of the samples by comparison to DQOs or project action limits and examines diluted samples. As a sample is diluted to bring the concentration within the calibration curve the detection limit changes as a multiple of the dilution factor. This elevated detection limit will be avoided to the extent practical; however, in some cases the elevated detection limit may not impact the DQOs.

Surrogate Recovery

Surrogate recoveries are performed on each organic sample. Surrogate recoveries are one of several ways to examine the potential for matrix interference. Chemicals that are not specifically analyzed for are added (spiked) to the sample matrix in a known quantity, and the laboratory analyzes the sample.

The result is weighed against the known quantity added, and the percent difference between the spiked concentration and the analytical result provides a measure of possible matrix interference. Surrogate recovery data are reported as a percentage. The Relative Percent Difference (RPD) may be reported if a surrogate recovery duplicate is performed.

In general, if a lab has recoveries that are too low, then the results for that analysis are considered to be biased low, and if too high, the results are considered to be biased high. In each case the results should be considered an estimate and are qualified as such. In extreme cases where the recoveries are poor, in that they have a zero recovery, the data should be considered for rejection.

MS/MSD

MS/MSDs are similar to the surrogate recovery in that they are spiked samples performed in the sample matrix. There are several distinct differences, however. One difference is that the chemicals added are the same chemicals that are being analyzed for; moreover, MS/MSDs are performed on each constituent group analyzed in the samples, not just organic compounds. MS/MSDs also address whether or not the matrix interferes with the analysis.

As with surrogate recoveries, low MS/MSD recoveries indicate that the results may be biased low, and high recoveries indicate results that may be biased high. As with surrogate recoveries, MS/MSD data are reported in the form of percentages.

Laboratory Control Sample

Laboratory control samples examine the laboratory's accuracy and precision, where the focus is on the laboratory equipment and procedures. Unlike the MS/MSDs and the surrogate recovery analyses, the LCS analysis is performed with laboratory grade de-ionized water. The LCS results are reported in percentages, with low results indicating that the results may be biased low, while high results indicate the results may be biased high.

Laboratory Case Narrative

The laboratory case narrative describes inconsistencies observed by the laboratory during analysis. The case narrative states what was done differently, if anything, from prescribed methods, identifies holding time violations if any, and outlines other difficulties the lab may have encountered.

Analytical Detection Limits and Sample Quantitation

For organic compounds, the accuracy of the contract required quantitation limits (CRQL) and the reported quantitation results are calculated through a series of equations. Quantitation results are a function of the mass and area of internal standard ion added, the amount of dilution, the volume of water purged during the process and the relative response factor (RRF). The RRF is a ratio of the internal standard concentration and ion area to the target ion's concentration and ion area. The CRQL is adjusted simply by multiplying by the dilution factor.

Overall Evaluation of Data

The overall evaluation of the data is a holistic assessment of all the data. The entire data package and data review results are reviewed, and a narrative is prepared outlining concerns and comments about the quality of the data. Rarely are additional qualifications or rejections made based on the overall evaluation.

GC/MS/GC/ECD Instrument Performance

GC/MS/GC/ECD instrument performance, also referred to as "tuning", is designed to demonstrate accurate mass resolution, identification, and sensitivity of the equipment. Instrument performance is evaluated using standard solutions and rarely results in rejections.

Initial Calibration/Continuing Calibration

Initial and continuing calibrations are standards for instrument calibration ensuring that the instruments are detecting the appropriate concentration ranges and produce a linear calibration curve. The initial calibration demonstrates that the equipment is capable of detecting the appropriate ranges and is producing the proper calibration curve. The continuing calibration produces 12 hour relative response factors (RRF) and checks the instrument daily throughout its use on the SDGs. The RRF is used to calculate quantitation and must be greater than 0.05, and produce percent differences within a range of plus or minus 25%.

Internal Standards

Internal standards evaluate GC/MS sensitivity and responses for stability. The internal standard areas must not vary by greater than a factor of two from the calibration standard, and the retention time within the columns must not vary by more than thirty seconds.

Target Compound Identification

Target compound identification examines the GC/MS results for false readings. The ions are scrutinized for concentration variances; the ions present within the standard mass spectrum with a relative percent intensity greater than 10% must also appear in the sample spectrum. If the ions that have a relative percent intensity greater than 10% are not in the sample spectrum they must be accounted for. Ions that are in both the standard and sample spectrum must have a relative percent intensity that is within 20% of each other.

System Performance

System performance examines the accuracy of the instrumentation. As samples are analyzed, changes may occur that will impair the various instruments ability to accurately analyze data. Sudden, severe shifts in the Reconstructed Ion Chromatogram (RIC) baseline can indicate decreasing resolution of the calibrated zero concentration. Inexplicable peaks, split peaks, or unusually high background readings can all also indicate problems with the instruments and may lead to inaccurate readings.

Serial Dilution

The serial dilution examines matrix interference from physical or chemical sources. One serial dilution must be performed for each type of sample matrix, concentration level, or SDG, depending on what would be more frequent. Field Blanks must not be used. The dilution must be within 10% of the original concentration if that concentration is greater than 50 times the instrument detection limit (IDL).

A complete copy of the DUSR, signed by the reviewing validator, will be provided to the NYSDEC.

4.8 Report

A Site Investigation Report will be prepared following the receipt of all laboratory data. The report content will include:

- Technical overview of findings including description of work performed, findings and results, and conclusions and recommendations
- Sample location maps
- Map illustrating public and private wells within a half mile radius of the site and a depiction of conceptualized groundwater flow direction
- Tables and figures summarizing sampling results including location, media, sample interval, identification numbers, analytical results and comparison to guidance values with exceedances highlighted, as follows:
 - Soil:
 - Individual PFAS compounds – 1 ppb
 - 1,4-dioxane – unrestricted and applicable restricted use soil cleanup objectives in 6 NYCRR Part 375-6
 - Groundwater:
 - PFOA/PFOS – 10 ng/L
 - Other PFAS compounds (NOT PFOA/PFOS) - >100 ng/L

- Total PFAS compounds (all) >500 ng/L
 - 1,4-dioxane - 1 µg/L
- Soil boring and monitoring well logs
- Field data sheets including PFCs sampling checklist
- Electronic data deliverables
- Data usability summary reports

Section 5

Schedule

The Site Investigation will be conducted in two phases as described in the preceding sections. Soil sampling will be scheduled within three weeks following receipt of NYSDEC approval of this Work Plan and is anticipated to require less than one week in the field. Analysis of soil samples is anticipated to require three-to-four weeks. The Work Plan Addendum will be submitted to NYSDEC within three weeks of receipt of soil sampling data.

A schedule for groundwater sampling activities will be provided in the Work Plan Addendum. The groundwater investigation schedule will depend upon the number of wells to be sampled, the number of new wells to be installed, driller availability, and if off-site wells are included off-site access agreements or approvals. The Site Investigation Report will be submitted within six weeks of receipt of validated groundwater sampling data.

The NYSDEC will be notified at least five business days in advance of each sampling event.

Section 6

References

Brown and Caldwell Associates and Cornerstone Engineering and Land Surveying, PLLC, March 2011. "Site-Wide Characterization Summary Report, Former Nepera Facility, Harriman, New York".

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EPA 600/R-14/273, September 2014. "3PE: A Tool for Estimating Groundwater Flow Vectors".

HydroQual, Inc., May 2008. "Conceptual Site Model and Supplemental Remedial Action Work Plan".

New York State Department of Environmental Conservation, May 3, 2010. "DER-10/Technical Guidance for Site Investigation and Remediation; NYSDEC Program Policy".

New York State Department of Environmental Conservation, June 2019. "Sampling for 1,4-Dioxane and Per- and Polyfluoroalkyl Substances (PFAS) Under DEC's Part 375 Remedial Programs".

Tables

TABLE 4-1
SAMPLING AND ANALYSIS SUMMARY
FORMER NEPERA PLANT SITE
HARRIMAN, NEW YORK

Location	Sample Location	Sample IDs	Matrix	Rationale	Sample Depths (see notes)	Analytes (see notes)
<u>Soil Samples</u>						
Building 2A	2A-B-001	2A-B-001-0-1, TBD	Soil	Former Storage Building	2 Samples/Boring	PFAS, 1,4-Dioxane
Building 2A	2A-B-002	2A-B-002-0-1, TBD	Soil	Former Storage Building	2 Samples/Boring	PFAS, 1,4-Dioxane
Building 26	26-B-002	26-B-002-0-1, TBD	Soil	Fire Pump House	2 Samples/Boring	PFAS, 1,4-Dioxane
Building 26	26-B-003	26-B-003-0-1, TBD	Soil	Fire Pump House	2 Samples/Boring	PFAS, 1,4-Dioxane
Building 52	52-B-002	52-B-002-0-1, TBD	Soil	Fire Equipment Storage	2 Samples/Boring	PFAS, 1,4-Dioxane
Building 52	52-B-003	52-B-003-0-1, TBD	Soil	Fire Equipment Storage	2 Samples/Boring	PFAS, 1,4-Dioxane
Building 64	64-B-002	64-B-002-0-1, TBD	Soil	Tank Farm Upgradient of MW-16S	2 Samples/Boring	PFAS, 1,4-Dioxane
Building 72	72-B-002	72-B-002-0-1, TBD	Soil	Foam House	2 Samples/Boring	PFAS, 1,4-Dioxane
Building 72	72-B-003	72-B-003-0-1, TBD	Soil	Foam House	2 Samples/Boring	PFAS, 1,4-Dioxane
Building 72	72-B-004	72-B-004-0-1, TBD	Soil	Foam House	2 Samples/Boring	PFAS, 1,4-Dioxane
Building 72	72-B-005	72-B-005-0-1, TBD	Soil	Foam House	2 Samples/Boring	PFAS, 1,4-Dioxane
Area B	B-B-105	B-B-105-0-1, TBD	Soil	Vicinity of MW-24S	2 Samples/Boring	PFAS, 1,4-Dioxane
Area F	F-B-008	F-B-008-0-1, TBD	Soil	Fire Training Area	2 Samples/Boring	PFAS, 1,4-Dioxane
Area F	F-B-009	F-B-009-0-1, TBD	Soil	Fire Training Area	2 Samples/Boring	PFAS, 1,4-Dioxane
Area F	F-B-010	F-B-010-0-1, TBD	Soil	Fire Training Area	2 Samples/Boring	PFAS, 1,4-Dioxane
Area F	F-B-011	F-B-011-0-1, TBD	Soil	Fire Training Area	2 Samples/Boring	PFAS, 1,4-Dioxane
Area G	G-B-105	G-B-105-0-1, TBD	Soil	Vicinity of MW-16S	2 Samples/Boring	PFAS, 1,4-Dioxane

NOTES:

PFAS compounds to be analyzed by Modified Method 537 for PFAS Target Analyte List per DEC guidance titled *Sampling for 1,4-Dioxane and Per- and Polyfluoroalkyl Substances (PFAS)* dated June 2019. Samples to be collected at the 0-2 inch depth interval, and the 1 foot interval above soil saturation unless another depth interval is selected based on visible indication of potential impacts. Details regarding groundwater sampling will be provided in a Work Plan Addendum following receipt of soil sampling data.

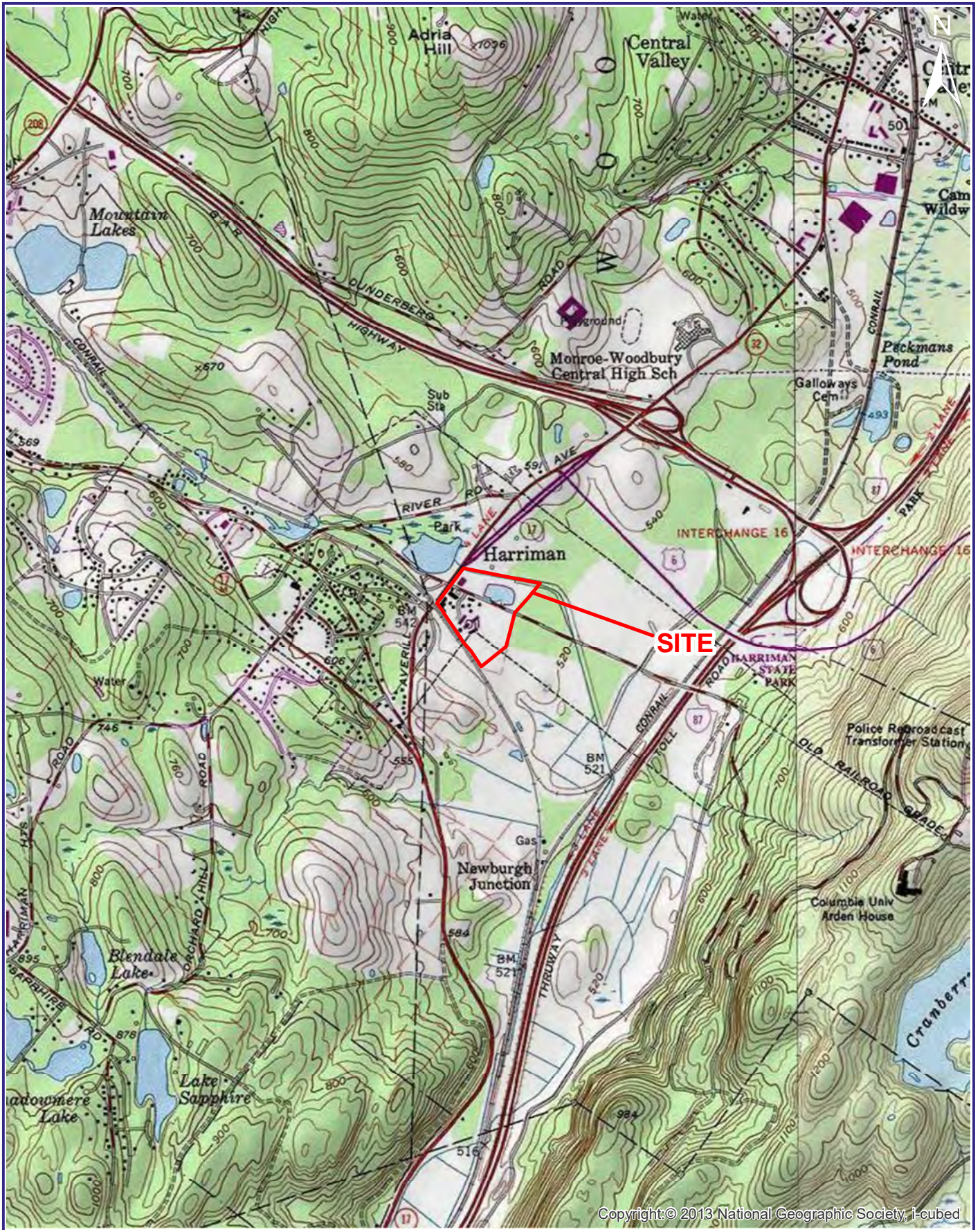
TABLE 4-2
ANALYTICAL METHODS AND HOLDING TIMES
FORMER NEPERA PLANT SITE
HARRIMAN, NEW YORK

Matrix	Number of Samples	Parameters	Analytical Method	Container Type	Preservative	Holding Time
Soil	28	PFAS Compounds	Modified USEPA Method 537, Revision 1.1 (Modified)	8 oz. HDPE Container	Cool, 4 deg C	28 Days
Soil	28 (contingency analysis)	PFAS Compounds - Synthetic Precepitation Leachate Procedure	EPA Method 1312	8 oz. HDPE Container	Cool, 4 deg C	28 Days
Soil	TBA	1,4-Dioxane	EPA Method 8270 SIM	8 oz. Glass Jar	Cool, 4 deg C	7 Days Extraction, 40 Days Following Extraction for Analysis
Groundwater	TBA	PFAS Compounds	Modified USEPA Method 537, Revision 1.1 (Modified)	8 oz. HDPE Container	Cool, 4 deg C	28 Days
Groundwater	TBA	1,4-Dioxane	USEPA Method 8270 SIM w/Isotope Diluton	1 L. Amber Glass	Cool, 4 deg C	7 Days Extraction, 40 Days Following Extraction for Analysis

TABLE 4-3
ANALYTICAL REPORTING LIMITS
FORMER NEPERA PLANT SITE
HARRIMAN, NEW YORK

Analyte	CAS Number	Aqueous (ug/l)	Non-Aqueous (mg/kg)
1,4-Dioxane		0.2	0.00167
PFAS Compounds			
Perfluorobutanesulfonic acid	375-73-5	0.002	0.002
Perfluorohexanesulfonic acid	355-46-4	0.002	0.0006
Perfluoroheptanesulfonic acid	375-92-8	0.002	0.0006
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	0.002	0.0006
Perfluorodecanesulfonic acid	335-77-3	0.002	0.0006
Perfluorobutanoic acid	375-22-4	0.005	0.002
Perfluoropentanoic acid	2706-90-3	0.002	0.0006
Perfluorohexanoic acid	307-24-4	0.002	0.0006
Perfluoroheptanoic acid	375-85-9	0.002	0.0006
Perfluorooctanoic acid (PFOA)	335-67-1	0.002	0.0006
Perfluorononanoic acid	375-95-1	0.002	0.0006
Perfluorodecanoic acid	335-76-2	0.002	0.0006
Perfluoroundecanoic acid	2058-94-8	0.002	0.0006
Perfluorododecanoic acid	307-55-1	0.002	0.0006
Perfluorotridecanoic acid	72629-94-8	0.002	0.0006
Perfluorotetradecanoic acid	376-06-7	0.002	0.0006
6:2 Fluorotelomer sulfonate	27619-97-2	0.005	0.002
8:2 Fluorotelomer sulfonate	39108-34-4	0.003	0.003
Perfluorooctanesulfonamide	754-91-6	0.002	0.0006
N-methyl perfluorooctanesulfonamidoacetic acid	2355-31-9	0.002	0.002
N-ethyl perfluorooctanesulfonamidoacetic acid	2991-50-6	0.003	0.002

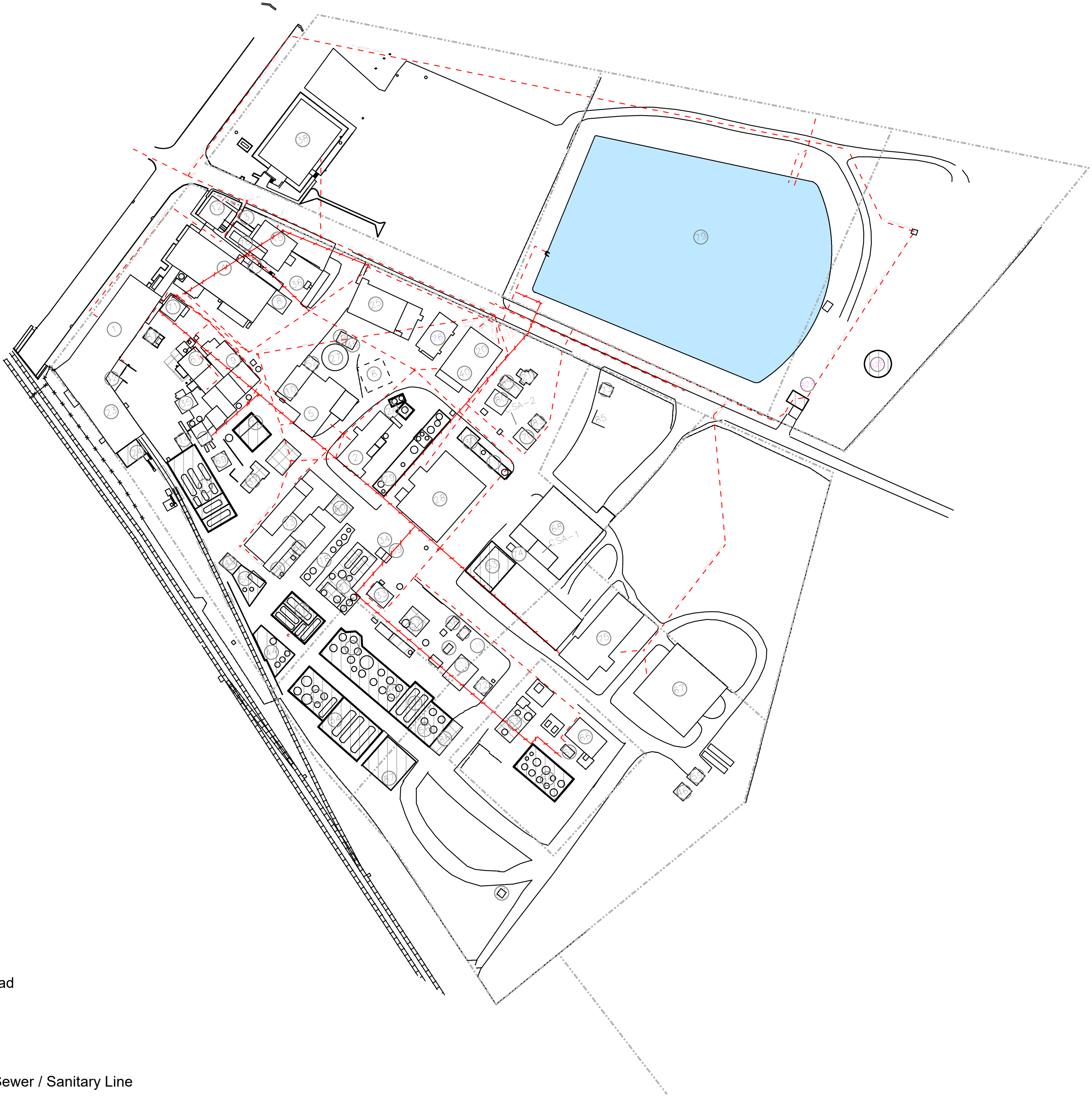
Figures





Legend

- Site Area Boundary
- Former Building
- Former Containment Pad
- Former Tank Farm
- Lagoon
- Abandoned Industrial Sewer / Sanitary Line
- Industrial Sewer / Sanitary Line



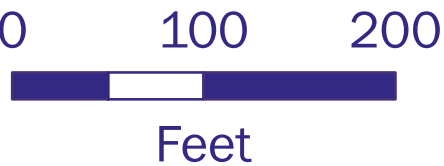
FORMER BUILDING INDEX

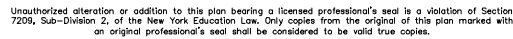
- 1 WAREHOUSE
- 2 MFG DEPT A (2AP)
- 2A TANK FARM - BLDG 2
- 3 SUBSTATION
- 4 MFG/WAREHOUSE
- 5 STOCKROOM
- 6 PYRIDIUM STORAGE (REMOVED)
- 7 SUBSTATION #2
- 8 ENGINEERING OFFICES
- 9 BOILER HOUSE
- 10 SHIP/REC, PROD/MAINT, STOCKROOM
- 11 TANK FARM
- 12 MATERIALS MGMT OFFICES/ PURCHASING
- 13 MFG - AMIDE/ CONTROL ROOM
- 14 OLD PUMP HOUSE
- 15 OPERATIONS/ENVIRON/SAFETY OFFICES
- 17 #1 COOLING TOWER
- 18 TANK FARM -WASTE WATER
- 19 TANK FARM
- 20 LABORATORY
- 21 HIGH PRESSURE LAB
- 22 TANK FARM - FUEL OIL
- 23 WAREHOUSE/ WATER FILTRATION
- 24 WAREHOUSE
- 25 LOCKER-LUNCH ROOM/SECURITY
- 26 ELECTRIC FIRE PUMP
- 27 WATER TANK - FIRE SYSTEM
- 28 MFG - AMIDE/BATCH
- 29 TANK FARM
- 30 SUBSTATION #3
- 31 CRUDE BASE - DISTILLATION
- 32N TANK FARM
- 32S TANK FARM
- 33 #2 COOLING TOWER
- 34 VALVE HOUSE - FIRE SYSTEM
- 35 COOLING TOWER
- 36 TRUCK SCALE
- 37 OLD CYANO REACTOR
- 38 ADMINISTRATION OFFICES
- 39 YARD EQUIPMENT STG
- 40 PILOT PLANT
- 41 SUBSTATION #3
- 42 FREIGHT ELEVATOR
- 44 TANK FARM
- 45 #1 DIESEL PUMP
- 46 STG BLDG
- 47 SOUTH WELL PUMP
- 48 TANK FARM
- 49 DISTILLATION
- 50 TANK FARM/PROCESS
- 51 ORGANIC INCINERATOR
- 52 EMERGENCY CENTER
- 53 HYDROGEN TUBE TRUCK AREA
- 54 TANK FARM
- 55 TANK FARM
- 56 TANK FARM
- 57 CRUDE BASES REACTOR AREA
- 58 #4 & 5 COOLING TOWERS
- 59 STORAGE BLDG
- 60 DISTILLATION PAD
- 61 INCINERATOR
- 62 SUBSTATION #5
- 63 CYANO REACTOR PAD
- 64 TANK FARM
- 65 #6 COOLING TOWER
- 66E MCC
- 66W HYDROGEL STG
- 67 MAINTENANCE SHOP
- 68 DRUMMING STATION/ DRUM WAREHOUSE
- 69 AIR COMPRESSOR BLDG
- 70 FIRE TRUCK GARAGE
- 71 EMERGENCY GENERATORS
- 72 FOAM HOUSE
- 73 #2 DIESEL PUMP
- 74 MCC -BLDG 68
- 75 HYDROGEL BLDG
- 76 HYDROGEL OFFICES
- 77 ENGINEERING TRAILER
- 78 TRAINING CENTER
- 79 LAGOON
- 80 VAPOR PHASE R&D
- 81 TANK FARM - FUELS
- 82A DELUGE PUMP
- 82B DELUGE COLLECTION
- 83 ERT GARAGE
- 84 LAB CYLINDER STORAGE
- 85 IRM BLDG
- 86 TRUCK LOADING STATION
- 87 ACS PYRIDINE TANK FARM

Note:
Former plant buildings demolished in 2015



FIGURE 1-2
SITE PLAN
FORMER NEPERA PLANT SITE, HARRIMAN, NEW YORK





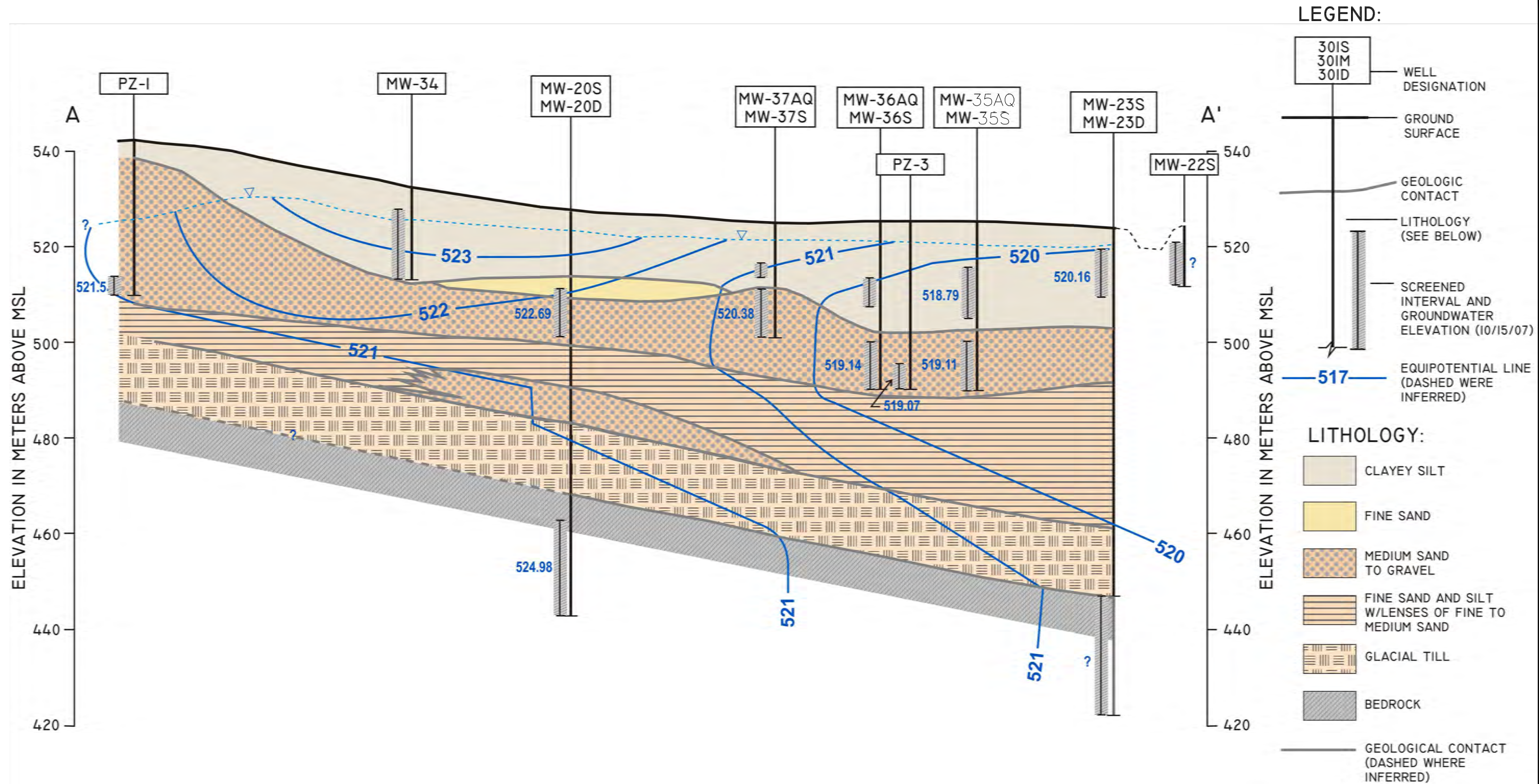
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FIGURE NO.
2-1
PROJECT NO.
180552

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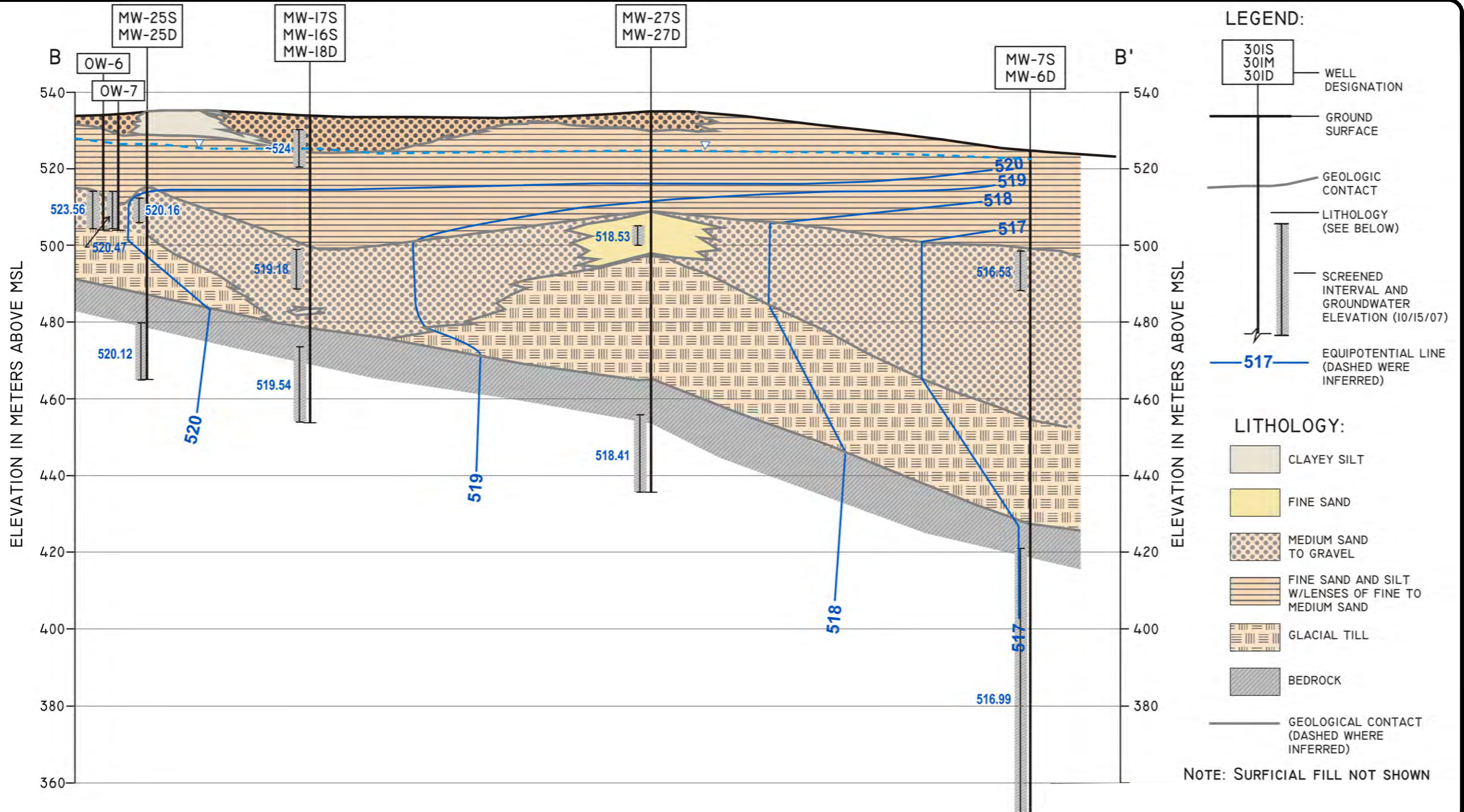
FORMER NEPERA PLANT SITE
HARRIMAN, ORANGE COUNTY, NEW YORK

HYDROGEOLOGIC CROSS SECTION A-A'

FIGURE NO.
2-2

PROJECT NO.
180552

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0 20 40
SCALE IN FEET

SOURCE:
CONCEPTUAL SITE MODEL AND
SUPPLEMENTAL REMEDIAL
ACTION WORK PLAN,
HYDROQUAL MAY 2008.

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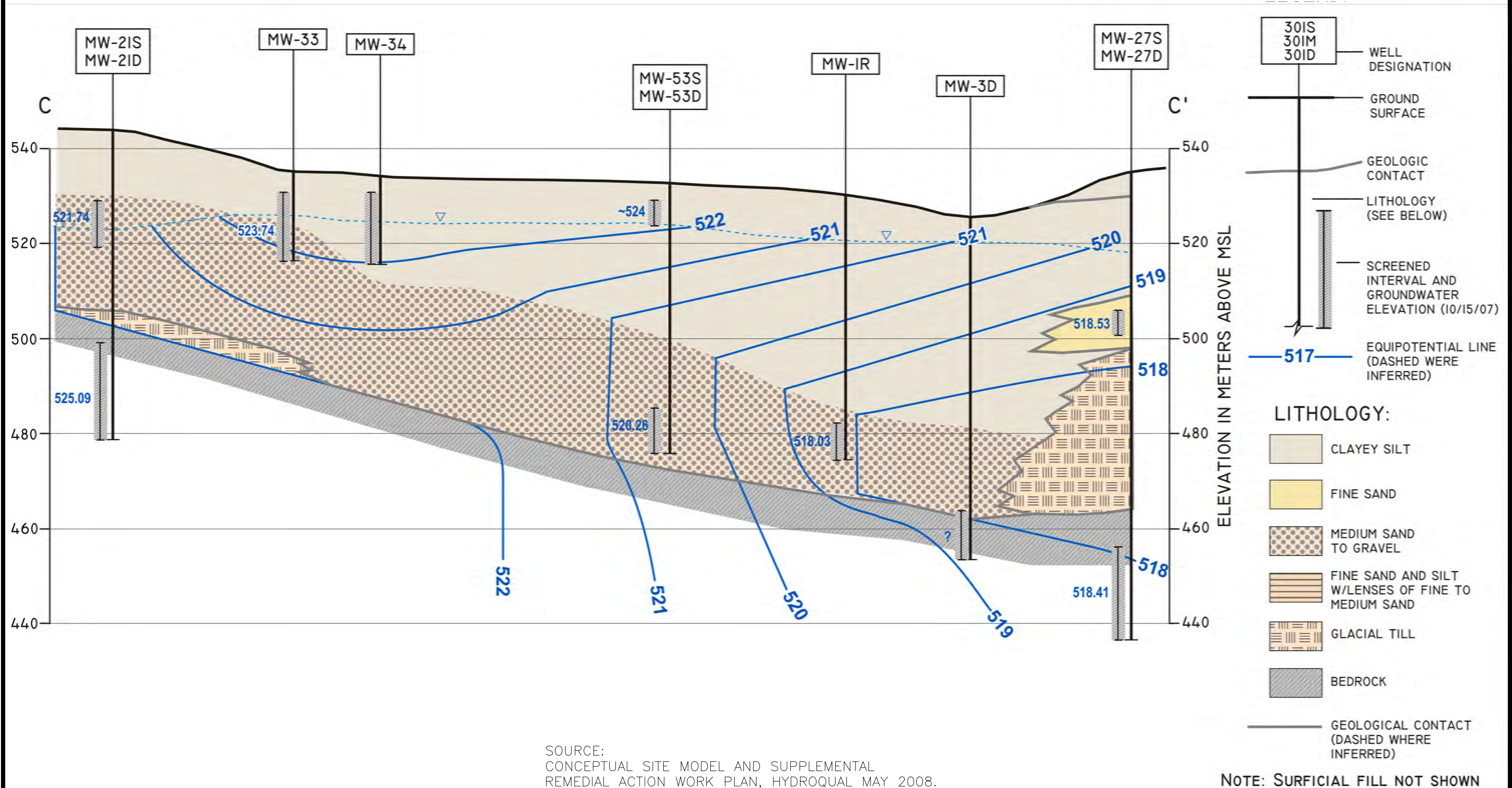
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FORMER NEPERA PLANT SITE
HARRIMAN, ORANGE COUNTY, NEW YORK
HYDROGEOLOGIC CROSS SECTION B-B'

FIGURE NO.
2-3
PROJECT NO.
180552

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FORMER NEPERA PLANT SITE
HARRIMAN, ORANGE COUNTY, NEW YORK

HYDROGEOLOGIC CROSS SECTION C-C'

FIGURE NO.
2-4

PROJECT NO.
180552

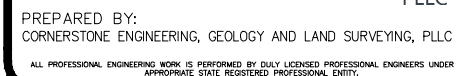


- MW-36AQ  MONITORING WELL IN
OVERBURDEN AQUITARD
- MW-37S  MONITORING WELL IN
OVERBURDEN AQUIFER
(SAND & GRAVEL)
- MW-23D  MONITORING WELL
IN BEDROCK
- (44) APPROXIMATE SAND AND GRAVEL
THICKNESS OBSERVED AT
BORING LOCATION
-  20 APPROXIMATE OUTWASH
THICKNESS (DOES NOT INCLUDE
KAME DEPOSITS)
-  APPROXIMATE EXTENT OF
THICKER SEQUENCE OF SAND
& GRAVEL UNDERLYING CENTRAL
PORTIONS OF THE FACILITY

SOURCE: CONCEPTUAL SITE MODEL AND SUPPLEMENTAL
REMEDIAL ACTION WORK PLAN, HYDROQUAL MAY 2008.

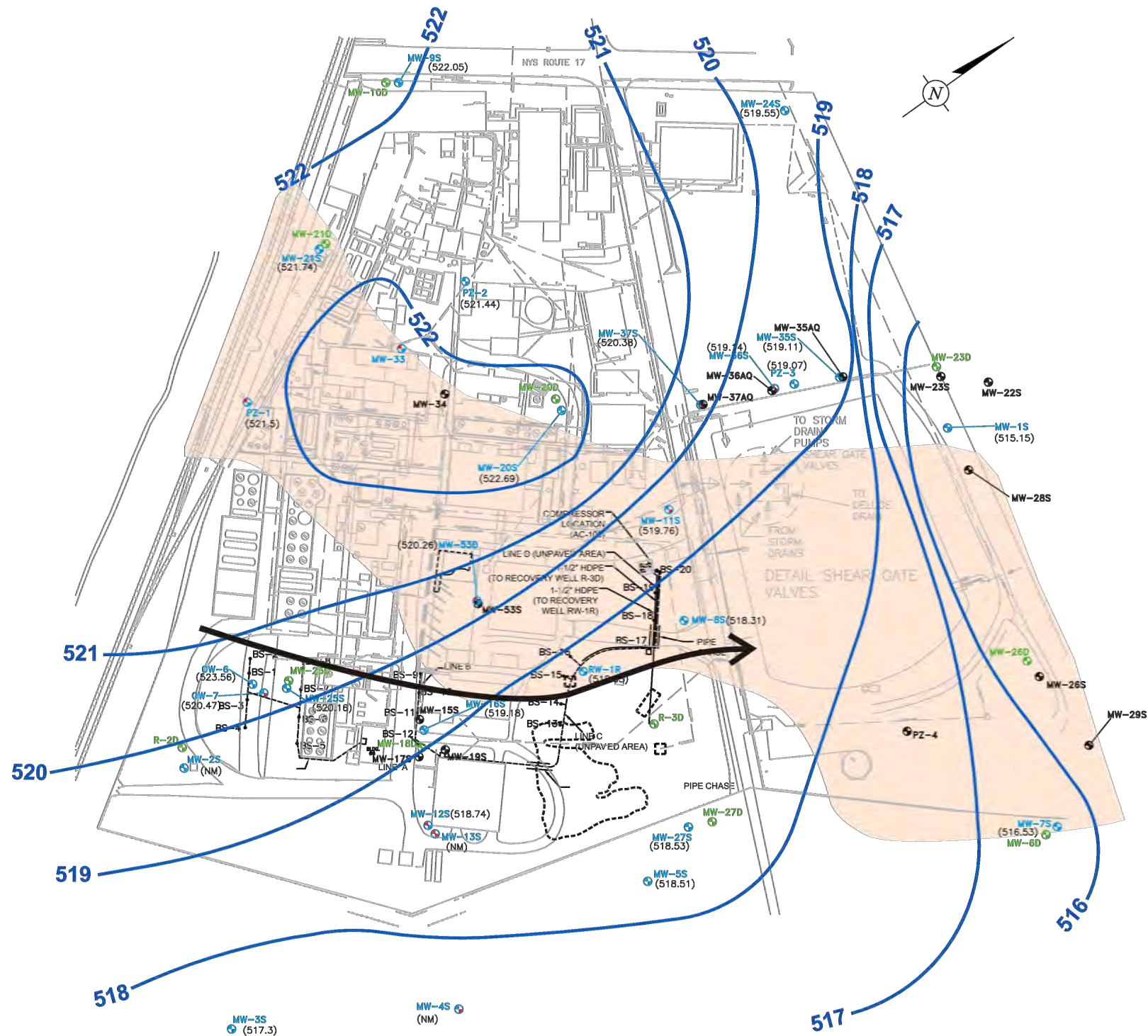
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ISOPACH MAP OF GLACIAL OUTWASH DEPOSITS (OVERBURDEN AQUIFER)

FIGURE NO.
2-5
PROJECT NO.
180552




LEGEND:

- MW-36AQ  MONITORING WELL IN OVERBURDEN AQUITARD
- MW-37S  MONITORING WELL IN OVERBURDEN AQUIFER (SAND & GRAVEL) WITH OCTOBER 2007 GROUNDWATER ELEVATION
- MW-23D  MONITORING WELL IN BEDROCK
-  APPROXIMATE EXTENT OF THICKER SEQUENCE OF SAND & GRAVEL UNDERLYING CENTRAL PORTIONS OF THE FACILITY
-  CONCEPTUALIZED GROUNDWATER FLOW PATH DUE TO ANISOTROPY. SEE TEXT FOR DISCUSSION
- 516  GROUNDWATER ELEVATION CONTOUR (OCTOBER 2007)

SOURCE: CONCEPTUAL SITE MODEL AND SUPPLEMENTAL REMEDIAL ACTION WORK PLAN, HYDROQUAL MAY 2008.

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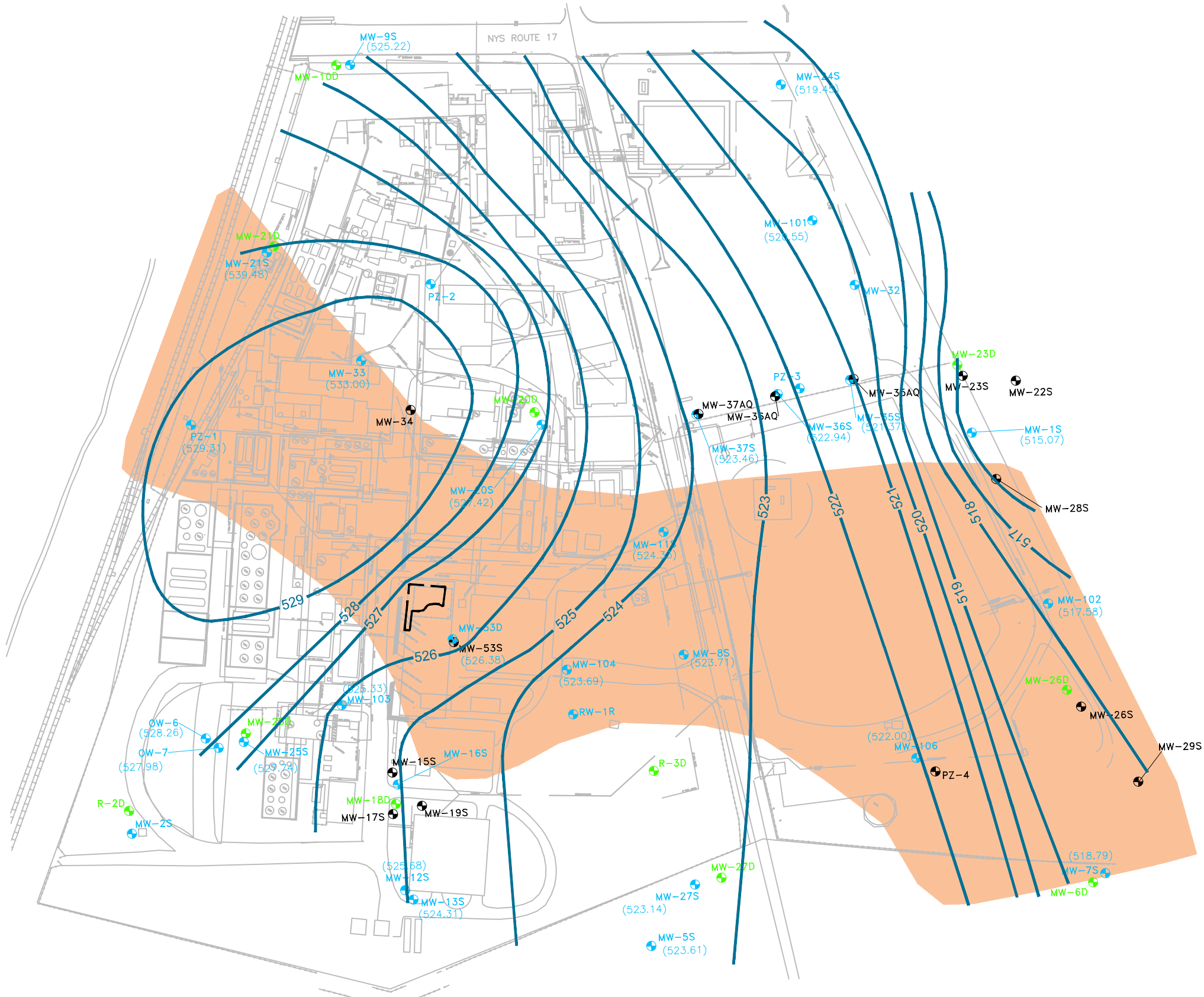
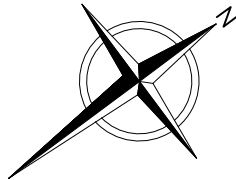
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FORMER NEPERA PLANT SITE
HARRIMAN, ORANGE COUNTY, NEW YORK

**OVERBURDEN AQUIFER POTENTIOMETRIC
SURFACE, OCTOBER 2007**

FIGURE NO.
2-6

PROJECT NO.
180552

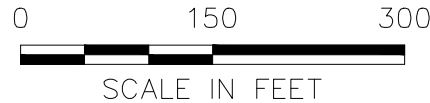


LEGEND:

- MW-36AQ MONITORING WELL IN OVERBURDEN AQUITARD
- MW-37S MONITORING WELL IN OVERBURDEN AQUIFER (SAND AND GRAVEL)
- MW-23D MONITORING WELL IN BEDROCK
- 522 GROUNDWATER ELEVATION CONTOURS (SEPTEMBER 2018)
- APPROXIMATE EXTENT OF THICKER SEQUENCE OF SAND & GRAVEL UNDERLYING CENTRAL PORTIONS OF THE FACILITY

NOTE:

BASE MAP TAKEN FROM DRAWING TITLED "PROPOSED ENHANCED OVERBURDEN AQUIFER MONITORING PROGRAM - PHASE I" PREPARED BY ARCADIS IN 2007.



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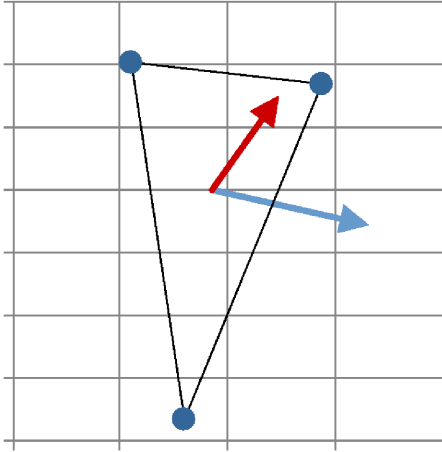


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FORMER NEPERA PLANT SITE
HARRIMAN, ORANGE COUNTY, NEW YORK

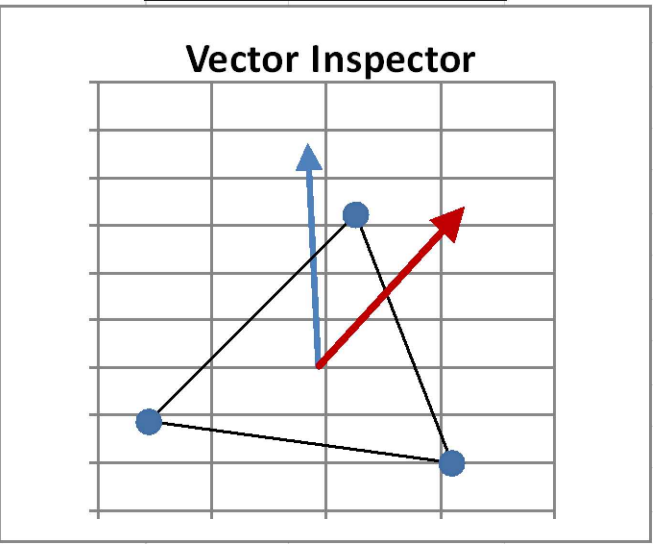
**OVERBURDEN AQUIFER POTENTIOMETRIC
SURFACE MAP - SEPTEMBER 5, 2018**

FIGURE NO.
2-7
PROJECT NO.
180552

Project:	Nepera, Harriman							10/1/07 12:00 AM				
Location:	Eastern Side of Site											
Date:												
	Well Location											
Well Name	X Coordinate (L)	Y Coordinate (L)			Vector Inspector Row of Interest:	22						
MW-25S	590,516.97	901,235.30	1		Must be between 22 and 23							
MW-20S	590,419.85	901,801.25	1									
MW-8S	590,775.19	901,767.86	1		Statistics							
				Head (L)	MW-25S	MW-20S	MW-8S	<div>Vector Inspector</div> 				
Principal Hydraulic Conductivity Components				Maximum =	527.74	527.42	523.71					
Kmax =	0.0560	(L/T)		Minimum =	520.16	522.69	518.31					
Kmin =	0.0009	(L/T)		Average =	523.95	525.06	521.01					
Orientation of Kmax =	38.00	(degrees from N)		Range =	7.58	4.73	5.40					
θ =	52.00	(degrees from X axis)										
					Hyd. Grad. (L/L)	Velocity (L/T)		Hydraulic Gradient Vector is BLUE				
Effective Porosity =	0.30	(-)		Maximum =	0.012336	0.001578		Groundwater Velocity Vector is RED				
				Minimum =	0.010932	0.001039		Hyd. Grad. Scale Factor =		23,989.00	23,989.66	
User input cells are shaded green.				Average =	0.011634	0.001309		Velocity Scale Factor =		187,501.00	187,501.34	
HYDRAULIC HEAD DATA SET MUST NOT CONTAIN BLANK LINES												
	Hydraulic Head (L)			Hydraulic Gradient		Groundwater Velocity		Angle Between Vectors		Planar Equation Constants		
Date/Time	MW-25S	MW-20S	MW-8S	Magnitude (L/L)	Direction (deg)	Magnitude (L/T)	Direction (deg)	(deg)		A	B	C
10/1/07 0:00	520.16	522.69	518.31	0.012336	101.19	0.001039	39.82	61.37		-0.012101294	0.00239373	5508.8658
9/5/18 0:00	527.74	527.42	523.71	0.010932	77.34	0.001578	38.75	38.59		-0.010665825	-0.0023957	8985.1803
				#VALUE!	#VALUE!	#VALUE!	#VALUE!	#VALUE!		#VALUE!	#VALUE!	#VALUE!
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File: X:\PROJECTS\MAYBROOK HARRIMAN TRUST\180552 - NEPERA-HARRIMAN TRUST\Drawings\180552-F-09-GW FLOW CALC.DWG Layout: SHEET 2-9 User: loris.chizhov Jul 16, 2019 - 11:37am


Location:		Western Side of Site								<div><div>Vector Inspector</div></div>		
Date:		Date Range for Data or Other Information										
		Well Location						Vector Inspector Row of Interest: 22				
Well Name		X Coordinate (L)	Y Coordinate (L)					Must be between 22 and 23				
MW-9S		589,888.90	901,886.03	1								
MW-20S		590,419.85	901,801.25	1								
MW-24S		590,252.37	902,323.76	1								
						Statistics						
						Head (L)	MW-9S	MW-20S	MW-24S			
						Maximum =	525.22	527.42	519.55			
						Minimum =	522.05	522.69	519.45			
						Average =	523.64	525.06	519.50			
						Range =	3.17	4.73	0.10			
							Hyd. Grad. (L/L)	Velocity (L/T)				
						Maximum =	0.014786	0.001952				
						Minimum =	0.005932	0.000842				
						Average =	0.010359	0.001397				
</												



Hydraulic Gradient Vector is BLUE		Suggested	
Groundwater Velocity Vector is RED		Scaling Factors	
Hyd. Grad. Scale Factor =	79,000.00		19,239.40
Velocity Scale Factor =	500,000.00		145,722.20

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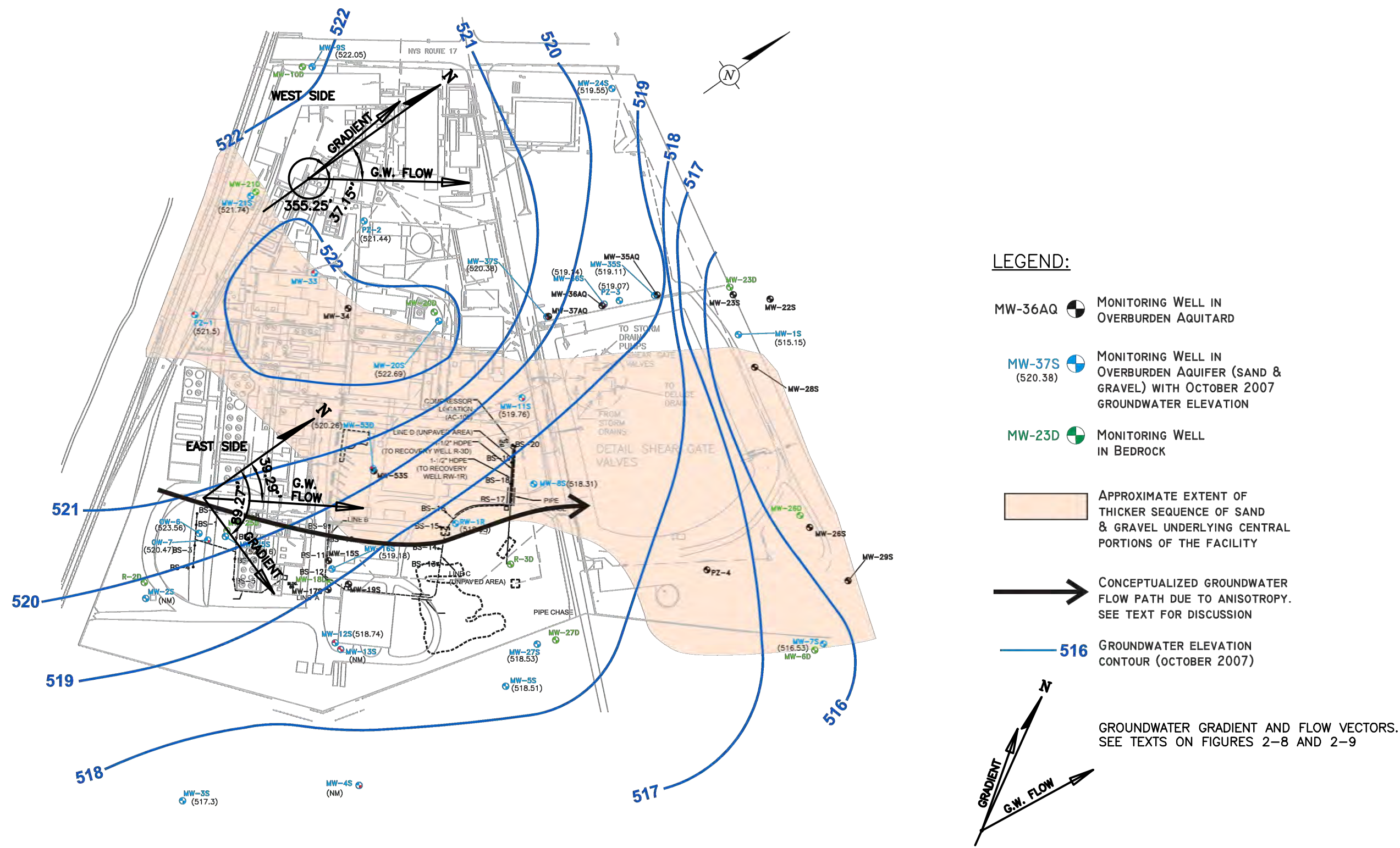
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FORMER NEPERA PLANT SITE
HARRIMAN, ORANGE COUNTY, NEW YORK

**ANISOTROPIC GROUNDWATER FLOW
CALCULATIONS**

FIGURE NO.
2-9
PROJECT NO.
180552



0 200 400
SCALE IN FEET

SOURCE: CONCEPTUAL SITE MODEL AND SUPPLEMENTAL
REMEDIAL ACTION WORK PLAN, HYDROQUAL MAY 2008.

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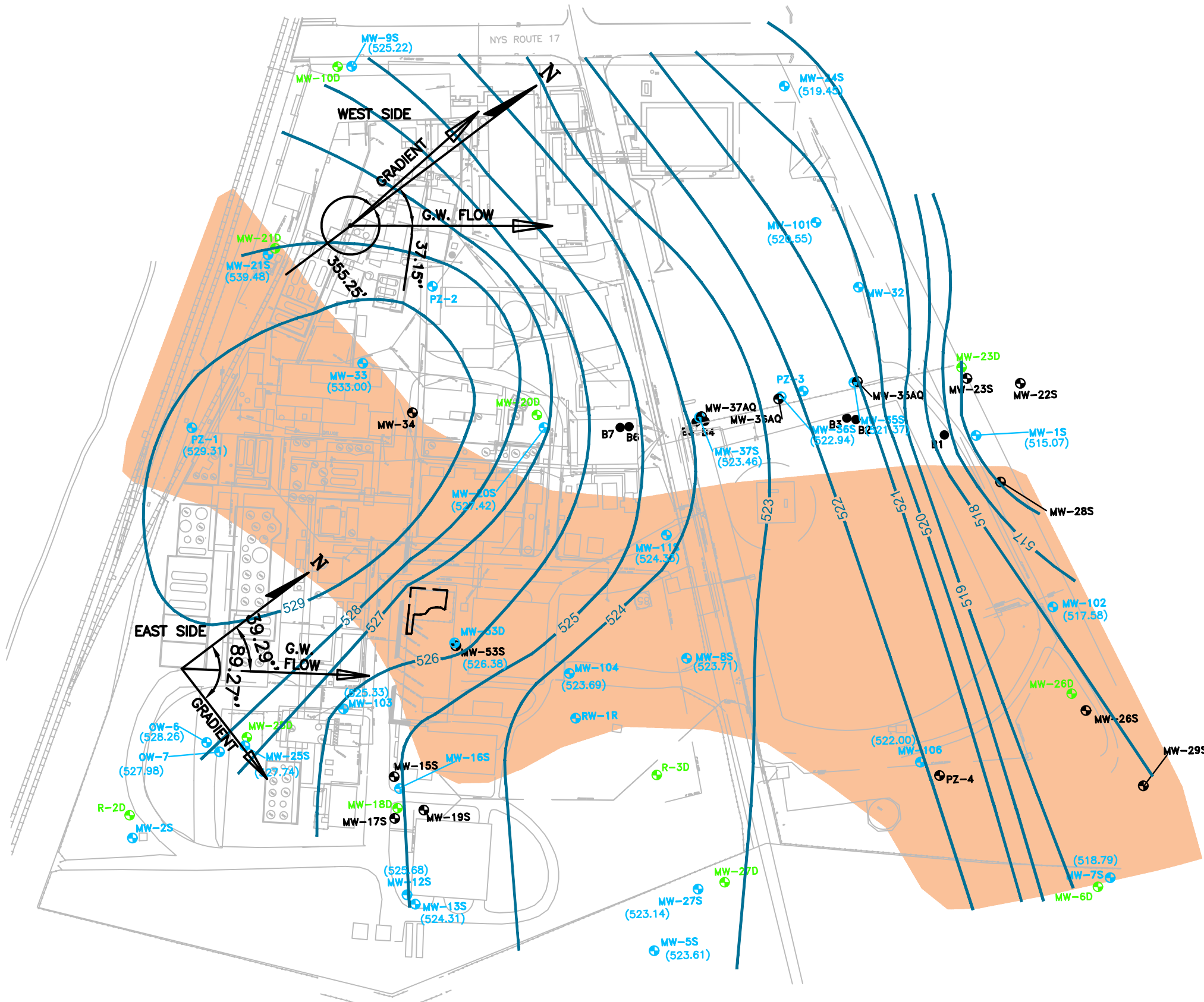
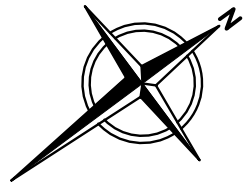
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FORMER NEPERA PLANT SITE
HARRIMAN, ORANGE COUNTY, NEW YORK

**OVERBURDEN AQUIFER POTENTIOMETRIC
SURFACE MAP GRADIENT AND FLOW VECTORS
OCTOBER 2007**

FIGURE NO.
2-10

PROJECT NO.
180552



LEGEND:

- MW-36AQ MONITORING WELL IN OVERBURDEN AQUITARD
- MW-37S MONITORING WELL IN OVERBURDEN AQUIFER (SAND AND GRAVEL)
- MW-23D MONITORING WELL IN BEDROCK
- 522 GROUNDWATER ELEVATION CONTOURS (SEPTEMBER 2018)
- APPROXIMATE EXTENT OF THICKER SEQUENCE OF SAND & GRAVEL UNDERLYING CENTRAL PORTIONS OF THE FACILITY
- GROUNDWATER GRADIENT AND FLOW VECTORS. SEE TEXTS ON FIGURES 2-8 AND 2-9


NOTE:

BASE MAP TAKEN FROM DRAWING TITLED "PROPOSED ENHANCED OVERBURDEN AQUIFER MONITORING PROGRAM - PHASE I" PREPARED BY ARCADIS IN 2007.

0 150 300
SCALE IN FEET

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FORMER NEPERA PLANT SITE
HARRIMAN, ORANGE COUNTY, NEW YORK
OVERBURDEN AQUIFER POTENTIOMETRIC
SURFACE MAP GRADIENT AND FLOW VECTORS
SEPTEMBER 5, 2018

FIGURE NO.
2-11
PROJECT NO.
180552

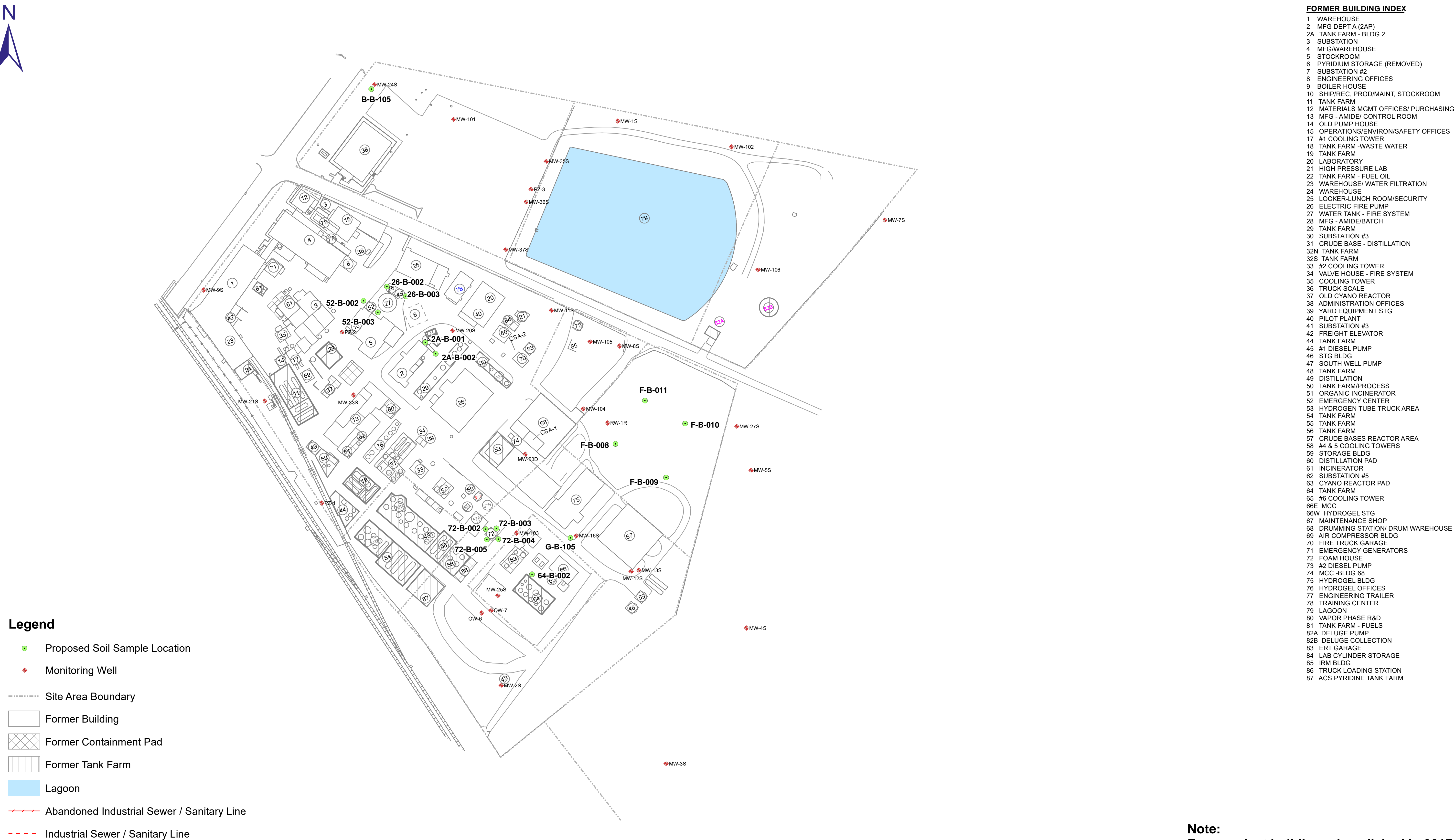


FIGURE 4-1
PROPOSED SOIL SAMPLE LOCATIONS
FORMER NEPERA PLANT SITE, HARRIMAN, NEW YORK

Appendix A: NYSDEC Correspondence

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

Division of Environmental Remediation, Remedial Bureau C

625 Broadway, 11th Floor, Albany, NY 12233-7014

P: (518) 402-9662 | F: (518) 402-9679

www.dec.ny.gov

(via e-mail and US Mail)

September 12, 2017

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Ted Wolff
Manatt, Phelps & Phillips, LLP
7 Times Square
New York, NY 10036

**RE: Perfluorinated Compound Sampling
Nepera-Harriman, Site No. 3-36-006**

Dear Messrs. Pike, West, Levine, Peluso, Erickson and Wolff:

As you are aware, on June 28 and 29, 2017, the New York State Department of Environmental Conservation (Department) collected groundwater and surface water samples from the Nepera/Harriman Site, as well as the Mary Harriman Park. These water samples were analyzed for perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS). PFOA and PFOS are part of a group of chemicals known as perfluorinated compounds (PFCs). The analytical results from that sampling are attached to this letter. As shown in the attached summary and reports, surface water sample results ranged from 7.2 to 9.4 parts per trillion (ppt) for PFOA and 5.3 to 6.3 ppt for PFOS; and the on-site groundwater monitoring well results ranged from 3.4 to 55 ppt for PFOA and 1.9 to 580 ppt for PFOS. The combined levels of PFOA and PFOS in two on-site monitoring wells (MW-20S and MW-11S) were 140 ppt and 608 ppt respectively. The highest detection found at the site was in close proximity to Building 72, which is identified as the "Foam House" on facility drawings. Firefighting foam is a documented source of PFCs, particularly PFOS, which is the predominant PFC found at the Nepera site.



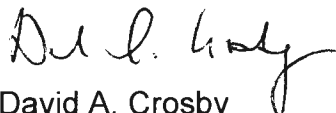
Department of
Environmental
Conservation

The PFOS and PFOA levels found in groundwater beneath the Nepera/Harriman Site exceed the United States Environmental Protection Agency (USEPA) health advisory level (HAL) for these two compounds in drinking water of 70 ppt, either individually or in total. Further, PFOS and PFOA were detected above the 70 ppt HAL in the Mary Harriman #1A supply well of the Harriman Village Public Water Supply, located approximately 1,500 feet from the Nepera site boundary. Also, effective March 3, 2017, the Department amended 6 NYCRR Part 597, Hazardous Substances Identification, Release Prohibition, and Release Reporting, to include the addition of PFOA and PFOS to the list of hazardous substances.

Based on a review of the June 2017 sampling results, and the detection of these hazardous substances in a nearby public supply well, the Department, in consultation with the New York State Department of Health, has determined that additional investigation regarding the presence of PFCs at and adjacent to the Nepera/Harriman Site is required. Pursuant to Paragraphs V(E)(32) and V(G)(35) of the May 21, 1998 Consent Decree, the Department requires additional investigation and the installation of additional sentry wells for the purpose of protecting human health. Specifically, the Department requires the submittal of a PFC Investigation Work Plan to determine the extent of PFC contamination potentially emanating from the Nepera/Harriman Site which may be contributing to contamination in Mary Harriman well 1A. The Department requires the submittal of this work plan within 60 days of the date of this letter.

Please contact me at 518-402-9642 or Tanya Lahr, the Department's project manager at 518-402-9581 if you have any questions.

Sincerely,



David A. Crosby
Chief, Remedial Section B, Remedial Bureau C
Division of Environmental Remediation

Attachments (Electronic only)

cc: Matt Robinson, ELT
Christopher Clark, Pfizer
Thomas Mesevage, Vertellus
Jeff Caputi, Brown and Caldwell
Gary DiPippo, Cornerstone
Dan Wheeler, Cornerstone
Maureen Schuck, NYSDOH – Albany
Michael Murphy, DEC OGC
George Heitzman, DEC DER
Ed Moore, DEC Reg. 3
Tanya Lahr, DER PM

Attachment

Summary of PFOA and PFOS Results from NYSDEC Sampling Done on June 28, 2017 and June 29, 2017
Harriman/Nepera Detection Summary for PFOA and PFOS

Sample Number	Results (ng/l = ppt)	
	Perfluorooctanoic Acid (PFOA)	Perfluorooctanesulfonic Acid (PFOS)
Harriman/Nepera_MW-20S-62017	55	85
Harriman/Nepera_MW-20D-62017	27	38
Harriman/Nepera_MW-16S-62017	28	580
Harriman/Nepera_MW-11S-62017	3.4	1.9
Harriman/Nepera_MW-8S-62017	7.1	10
Harriman/Nepera_MW-23D-62017	2.2	ND
Harriman/Nepera_MW-24S-62017	28	35
Harriman/Nepera_MW-26D-62017	3.8	4.0
Mary Harriman Park Lake SW-1-62017	7.2	6.3
Below Mary Harriman Park Lake Dam (Nepera side of Rte. 17) SW-2-62017	9.8	5.3
West Branch Ramapo River by Bridge on Arden House Road SW-3-62017	9.4	6.0

100 Crystal Run Road, Suite 101, Middletown, NY 10941
T 877.294.9070 | F 845.692.5894 | W www.cornerstoneeg.com

December 4, 2017

Via Electronic Mail

David A. Crosby, P.E.
New York State Department of Environmental Conservation
Division of Environmental Remediation, Remedial Bureau C
625 Broadway, 11th Floor
Albany, New York 12233-7014

Re: Harriman Inactive Waste Disposal Site #336006
NYSDEC Letter of September 12, 2017
Perfluorinated Compound Sampling

Dear Mr. Crosby:

On behalf of the Corporate Defendants, Nepera, Inc. and Warner-Lambert Company, this letter is in response to the above-referenced New York State Department of Environmental Conservation (NYSDEC) letter dated September 12, 2017. The NYSDEC's September 12 letter established a 60-day schedule for submittal of a "PFC Investigation Work Plan" (Work Plan). In a letter dated October 16, 2017, Cornerstone, on behalf of the Corporate Defendants, requested an extension of the time frame to respond. The schedule extension was requested to provide time for receipt of responses to New York State Freedom of Information Law (FOIL) requests to the NYSDEC and the New York State Department of Health (NYSDOH). The NYSDEC responded to the FOIL request on October 20, 2017. The NYSDOH responded to the FOIL request on November 10, 2017, indicating it needed until January 18, 2018 to complete the FOIL process. We assume this means there is a certain volume of relevant documents in the NYSDOH's files.

In addition to the NYSDEC and NYSDOH FOIL requests, an informal request for information was made to the Village of Harriman, and the Village through its consultant, Leggette, Brashears & Graham, Inc., provided information that was essential to the preparation of this letter. Pending a response to the NYSDOH FOIL request and additional relevant information that may be provided, if any, the Corporate Defendants reserve the right to make a supplemental response to the NYSDEC's September 12 letter.

As of the date of preparation of this letter, notwithstanding the delayed NYSDOH FOIL response, the NYSDEC did not respond to the request for a schedule extension. In accordance with the October 16, 2017 letter, the Corporate Defendants have been operating under the assumption that an absence of a response is implicit agreement to an extension.

In response to the Department's request for a Work Plan, investigations completed at the Nepera Site, as well as investigations and data collected on behalf of the Village of Harriman with respect to its groundwater supply, have been reviewed to assess the potential for the Nepera Site to contribute to the PFCs found in Mary Harriman well 1A (MH-1A). As discussed in detail below, the NYSDEC's sampling data, coupled with the Conceptual Site Model of groundwater flow, understanding of the distribution of contamination at the Harriman site, hydrogeologic and water quality studies conducted on behalf of the Village of Harriman, and the presence of known contamination immediately up gradient of MH-1A, all indicate that the Nepera Site is not a source of PFCs found in Well MH-1A and that absent additional nexus information there is no need for a PFC Investigation Work Plan associated with the former Nepera Harriman site.

Investigations and Data Specific to the Former Nepera Site

The Conceptual Site Model (CSM) of groundwater flow at the Nepera Site has been submitted to the NYSDEC, and approved, in two documents:

- The June 2014 *Supplemental Remedial Investigation/Feasibility Study Work Plan* (approved June 3, 2014); and
- The May 2008 *Conceptual Site Model and Supplemental Remedial Action Work Plan* (approved June 18, 2008).

As documented in the CSM, groundwater flow at the site is summarized as follows:

- Groundwater flow in the near surface glacial lacustrine deposits (aquitard) is principally vertical with discharge into the underlying glacial outwash. Horizontal flow in the aquitard is limited to localized and discontinuous lenses of sand.
- A channel of coarser-grained sand and some gravel outwash, underlying the central portions of the site, is the primary conduit for groundwater flow. While the outwash aquifer is present underlying most, if not all of the site, these deposits thin and become finer grained to the north and south, thus limiting their ability to transmit groundwater.
- The variable thickness and grain size of the outwash aquifer deposits result in a non-homogeneous, anisotropic aquifer. As a consequence, groundwater flow is not perpendicular to the equipotential lines. Rather, groundwater flow will travel at an angle to the equipotential lines toward the coarser-grained, thicker deposits underlying the central portion of the site.
- Groundwater flow through the glacial outwash aquifer is generally to the northeast with discharge to surface water (West Branch of the Ramapo River) and adjacent

wetlands. However, due to the contribution to flow from the upstream Harriman Wastewater Treatment plant, portions of the stream can be losing (i.e., flow is downward from the stream into groundwater), *although overall the surface water and wetlands are the ultimate discharge point for groundwater* [emphasis added].

Figure 2-6 of Appendix A to the June 2014 *Supplemental Remedial Investigation/Feasibility Study Work Plan* has been excerpted and attached to this letter. As this figure illustrates, groundwater flow is generally to the northeast with discharge to the West Branch of the Ramapo River and the adjacent wetlands. This groundwater flow configuration demonstrates that the former Nepera Harriman site is not associated with the PFCs found in Well MH-1A.

The PFC data collected by the NYSDEC is also consistent with the CSM and understanding of the distribution and fate of contamination at the site. As described in the CSM, the lower permeability fine sands and silts of the aquifer and silt and fine sand of the aquitard that exist in the former plant area retain diffuse, residual levels of contaminants. However, groundwater monitoring has been consistently performed since approval of the 2008 *Supplemental Remedial Action Work Plan* and to date, has demonstrated that this diffuse, residual contamination with a low flux rate from the fine-grained deposits is not contributing to groundwater contamination at levels that cause contravention of groundwater quality standards at sentinel wells. As such, the presence of PFCs in the former operations area, and in particular at monitoring well MW-16S, is not surprising. As described in the CSM, MW-16S is situated in these fine-grained deposits, and exhibits some of the highest concentrations of site-related contaminants at the site. However, this does not mean, as noted above, that the flux of these contaminants is sufficient to cause down-gradient contamination above the groundwater quality standards.

Figure 1, attached, is a plot of the perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) analytical results from the NYSDEC's June 2017 sampling event. The down-gradient wells in this figure, and at which the NYSDEC collected samples for PFC testing, include MW-24S, MW-23D, and MW-26D. As shown on this figure, each of these sample results is below the USEPA lifetime health advisory level (HAL) for combined PFOA and PFOS of 70 ng/L (parts per trillion, ppt). This is consistent with the history of sentinel wells at the site meeting groundwater quality standards. While the USEPA HAL is not a groundwater quality standard, it is currently the comparative concentration in use for combined PFOA and PFOS. Further, with the understanding of groundwater flow at the site, monitoring wells MW-8S and MW-11S are located in the higher permeability outwash deposits and are down-gradient of monitoring well MW-16S. Both MW-8S and MW-11S have combined PFOA and PFOS concentrations well below the 70 ng/L HAL, again indicating the absence of PFC flux sufficient to have a down-gradient impact.

The site specific data presented above demonstrates that the former Nepera Harriman site is not associated with contamination by PFCs of the Well MH-1A. This conclusion is further supported by hydrogeologic and water quality investigations performed on behalf of the Village of Harriman as discussed below.

Investigations and Data Specific to the Village of Harriman Groundwater Supply

Leggette, Brashears & Graham, Inc. (LBG), as consultant to the Village of Harriman, has completed a number of water supply and water quality studies for the Village of Harriman. Reports that specifically address the Mary Harriman Park Wellfield, which includes wells MH-1, MH-1A and MH-3, include:

- *Ground-Water Supply Assessment, Village of Harriman, Orange County, New York, April 1989.*
- *Well Redevelopment Report, Village of Harriman, Harriman, New York, January 1996.*
- *Mary Harriman Park Well Field, January 2017 Sodium and Chloride Sampling, Letter Report dated February 14, 2017.*

The Mary Harriman Wellfield is located to the northwest of the Nepera site, immediately west-northwest of Mary Harriman Park as shown in the attached figure excerpted from the LBG, February 14, 2017 Letter Report. Also excerpted from the same LBG report is a figure illustrating the location of production wells and monitoring wells within the Wellfield. Production wells MH-1 and MH-1A are completed within stratified sand and gravel deposits. MH-1A represents an original production well that was taken out of service in 1984 when replacement well MH-1 was completed. MH-1A was redeveloped in 1995 and subsequently returned to service. Both wells are currently active. MH-3 is completed within the underlying bedrock and is also active. There is no well MH-2 (a test well was installed but the location was never completed as a production well). All of the monitoring wells are completed within stratified sand and gravel.

LBG (April 1989) describes the sand and gravel deposits as stratified glacial drift consisting of coarse-grained sand and gravel deposits interbedded with gray silty and clayey lenses that occur in contact with till. These deposits likely occur as valley-fill deposits in channels or former meltwater streams originating from glacial melt back. The “channelized” and “stratified” nature of these deposits are evident in the variable yield obtained from individual wells and the aquifer response observed during pumping.

This is clearly evident in the data collected from MH-1 and MH-1A. MH-1 is completed approximately 10' to the north of MH-1A. However, the original estimated yield of MH-1A was 350 gpm, while the yield at MH-1 was 75 gpm. These yields have dropped off with time, however MH-1A continues to yield roughly twice that of MH-1. More significantly,

even though these wells are only 10' apart, pumping of MH-1A only results in two feet of drawdown at MH-1, leading LBG to conclude that both wells can be pumped simultaneously without problematic water level interferences (LBG, January 1996). In other words, both wells can be pumped simultaneously at their respective design rates, without impacting the yield at either location. Subsequently, water levels collected from monitoring wells on January 6, 2017, while MH-1A was in operation, indicate the lowest groundwater elevation is at monitoring well MHP-MW-5 (LBG, February 14, 2017), located to the east-northeast of MH-1A (see attached figure from LBG). Collectively, and further supported by water quality data discussed below, these data indicate that the cone of depression developed by MH-1A is an ellipse oriented east-northeast to west-southwest, and intersecting the West Branch of the Ramapo River to the north. The elliptical cone of depression is consistent with "channelized" deposits as described above and coupled with the limited drawdown interference between MH-1A and MH-1, indicates the source of water to MH-1A is from coarse grained sand and gravel deposits that are oriented in the same east-northeast to west-southwest direction. This orientation is roughly parallel to and north of the sand and gravel deposits and direction of groundwater flow observed at the former Nepera Harriman site and provides no evidence to suggest that the cone of depression, much less the zone of capture associated with MH-1A, intersects the former Nepera site. In other words, there is no hydraulic connection with the former Nepera site and; therefore, no pathway for PFCs detected at the former Nepera site to be transmitted to well MH-1A.

The above conclusion is further supported by water quality data, as well as potential sources of PFCs that are within the zone of capture developed by MH-1A. Specific to water quality, LBG concluded that the main contributing source of elevated levels of sodium and chloride observed in the Mary Harriman Park wellfield production wells (i.e., wells MH-1A, MH-1 and MH-3) appears to be recharge from the nearby Ramapo River (LBG, February 14, 2017). This clearly demonstrates a hydraulic connection between the wellfield and the Ramapo River. LBG further notes the upstream discharge into the Ramapo River of the Village of Kiryas Joel Wastewater Treatment Plant, which could be a potential source of PFCs to the Ramapo River. In fact, NYSDEC's testing indicates the presence of PFCs in both the Mary Harriman Park Lake (sample SW-1-62017), which is fed by the Ramapo River and immediately downstream of the Mary Harriman Park Lake dam (Sample SW-2-62017). Both of these locations are upstream of the former Nepera site and indicate that the Ramapo River may be a source of PFCs to the wellfield. However, the NYSDEC's surface water sampling data does not indicate that the former Nepera site is a source of PFCs via stormwater runoff to the West Branch of the Ramapo River. There is no significant difference in the concentrations of PFCs detected in the surface water samples upstream of the former Nepera site by comparison to the concentrations of PFCs detected downstream of the site (i.e., sample SW-3-62017).

Additionally, historical water quality results for both MH-1A and MH-1 have indicated the presence of low concentrations of trichloroethene (TCE), which are attributed to the Gaess Site located upgradient, and immediately adjacent to the wellfield to the south (LBG, January 1996). The Gaess Site was listed on the NYS Registry of Inactive Hazardous Waste Disposal Sites until June 2013, when it was delisted. The site was operated as a waste handling service and the principal contaminants of concern were tetrachloroethene (PCE), 1,1,1-trichloroethane, and TCE (NYSDEC Environmental Site Remediation Database). Based on the records reviewed and the date of investigation, it is unlikely that PFCs were specifically tested for at this site. However, given its historical use, it represents a potential source of PFCs to the wellfield.

Last, the records provided by the NYSDEC from its Class B Fire Suppression Foam Usage Survey indicate that the Monroe Joint Fire District has “stored and/or used” Class B fire suppression foam. The Monroe Joint Fire District has a fire station at 2 South Main Street, upgradient and along the axis of the cone of depression of the Mary Harriman well field.

Overall, the available information indicates that there are other more likely sources of PFCs found at the Mary Harriman well field and any detections of PFCs at the former Nepera site are not in any way connected to the PFCs found at well MH-1A.

Summary and Conclusion

In response to the Department’s request, investigations completed at the Nepera Site, as well as investigations and data collected on behalf of the Village of Harriman with respect to its groundwater supply, have been reviewed to assess the potential for the former Nepera site to contribute PFCs to the Mary Harriman well MH-1A. The data indicate that there is no hydraulic connection between the former Nepera site and well MH-1A, and other more proximate and hydraulically connected potential sources of PFCs exist, unrelated to the former Nepera site, that are the more probable sources of PFCs found in well MH-1A. Therefore, no further investigation of the Nepera Site is required in this regard. Data supporting this conclusion and discussed in greater detail above include the following:

- Groundwater flow at the Nepera Site is well understood and has been documented to flow to the north-northeast with discharge to the West Branch of the Ramapo River and/or the wetlands to the northeast.
- The Mary Harriman Park Wellfield is located to the west-northwest of the former Nepera site and is, therefore, up and cross gradient to the former Nepera site with respect to groundwater flow and upstream with respect to the Ramapo River.
- Groundwater flow at the former Nepera site and the Mary Harriman Park Wellfield is controlled by stratified and channelized sand and gravel deposits that are parallel

to each other and oriented in a generally northeast to southwest direction. Given the geology and hydrogeology of the area, there is no hydraulic connection between the two locations and, therefore, no pathway for contaminant transport between the former Nepera site and the Mary Harriman Park Wellfield.

- The NYSDEC's PFC testing at the former Nepera site show that sentinel wells contain PFCs well below the USEPA HAL and, therefore, could not be contributing to the PFC levels detected in well MH-1A.
- Studies conducted by LBG indicate that groundwater quality at the Mary Harriman Park Wellfield is influenced by surface water infiltration from the Ramapo River.
- The Village of Kiryas Joel Wastewater Treatment Plant discharges to the Ramapo River upstream of the Mary Harriman Park Wellfield and studies by NYSDEC document the presence of PFCs in the Mary Harriman Park Lake, which is fed by the Ramapo River, and just below the Mary Harriman Park Lake dam. This discharge, as well as any other potential sources upstream of the Wellfield (e.g., the Monroe Joint Fire District station at 2 South Main Street and the Gaess waste disposal site), represent more likely potential sources of PFCs to well MH-1A

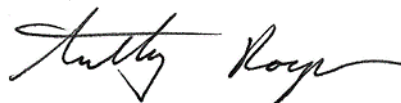
The Corporate Defendants, therefore, respectfully disagree that a Work Plan is needed, but will supplement this letter in the unlikely event that the NYSDOH file information reflects otherwise. The NYSDEC currently has sufficient information to conclude that the former Nepera Harriman site cannot be the source of PFCs detected in Mary Harriman well MH-1A.

Sincerely,

CORNERSTONE ENGINEERING AND LAND SURVEYING, PLLC



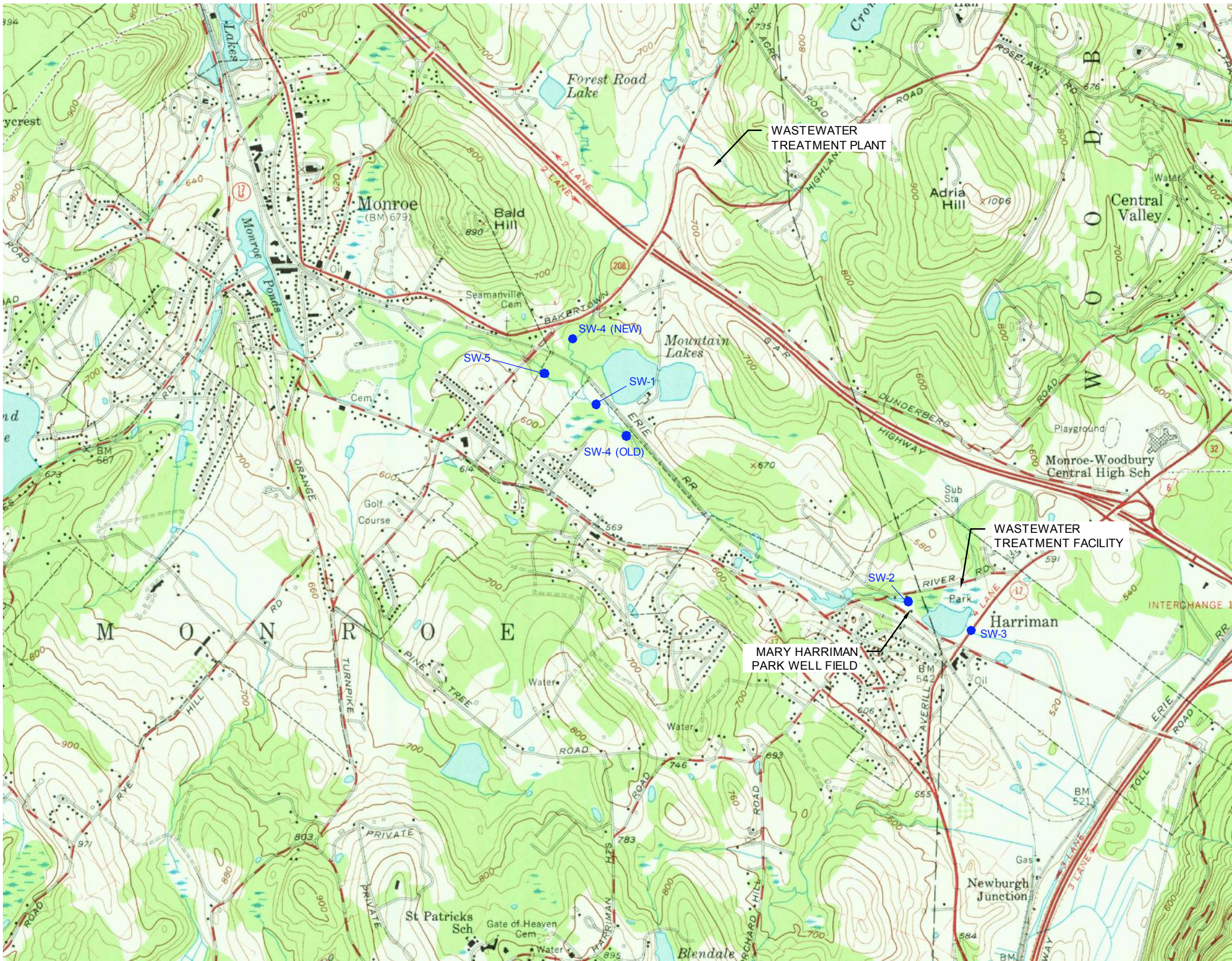
Gary J. DiPippo, P.E.
Client Services Manager



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LEGEND

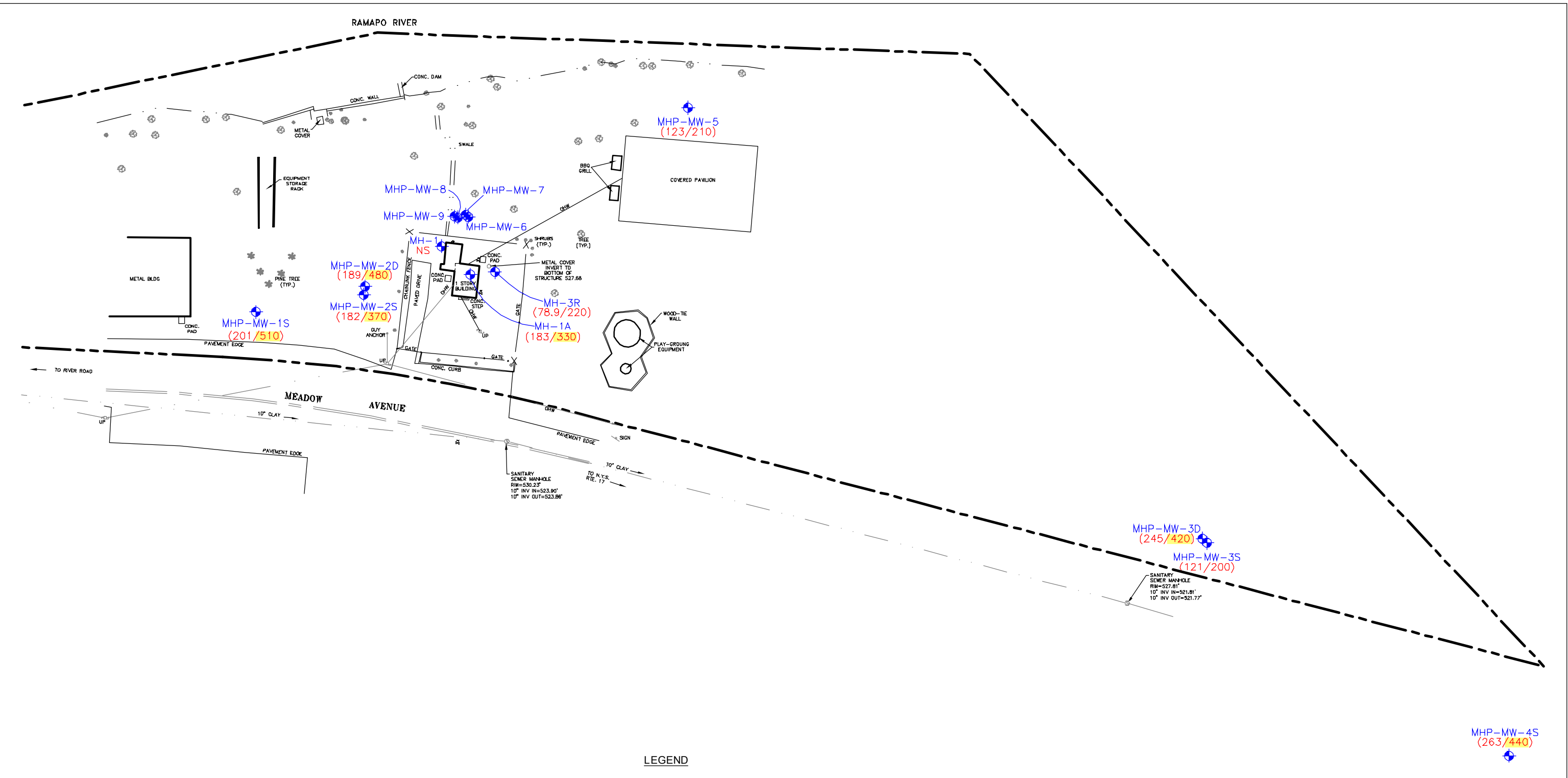
● SW-3 SURFACE WATER SAMPLE LOCATION

MARY HARRIMAN WELL FIELD
HARRIMAN, NEW YORK

RAMAPO RIVER SURFACE WATER SAMPLING LOCATIONS

DATE	REVISED	PREPARED BY: LEGGETTE, BRASHEARS & GRAHAM, INC. Professional Groundwater and Environmental Engineering Services			
		 4 Research Drive Suite 204 Shelton, Connecticut 06484 (203) 929-8555			
DRAWN:	RAC	CHECKED:	SS	DATE:	01/20/17
				FIGURE:	2

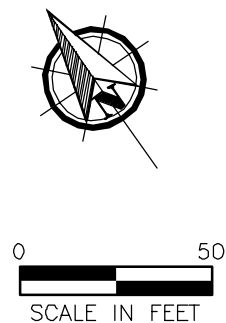
O:\DWG\ Village of Harriman\ Mary Harriman Well Field\2017\F1Jan2017.dwg, Layout1, 1/19/2017 3:45:40 PM, AcroPlot.pc3



SOURCE:
LANC & TULLY "MAP PREPARED FOR A PORTION OF MARY W HARRIMAN MEMORIAL PARK"
SHEET 1 OF 1, DATED NOVEMBER 12, 2010, REVISED SEPTEMBER 3, 2014.

LEGEND

- PROPERTY BOUNDARY
- MONITORING WELL LOCATION
- SODIUM/CHLORIDE CONCENTRATION OF WELL IN MILLIGRAMS PER LITER
- NOT SAMPLED
- HIGHLIGHTED NUMBER INDICATES CONCENTRATION EXCEEDS NEW YORK STATE DEPARTMENT OF HEALTH DRINKING WATER STANDARD MAXIMUM CONTAMINANT LEVEL FOR CHLORIDE



MARY HARRIMAN WELL FIELD HARRIMAN, NEW YORK

SITE PLAN - SODIUM AND CHLORIDE CONCENTRATIONS
JANUARY 6, 2017

DATE	REVISED	PREPARED BY:	LEGGETTE, BRASHEARS & GRAHAM, INC.			
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DRAWN:	RAC	CHECKED:	SS	DATE:	01/19/17	FIGURE: 1

**GROUND-WATER SUPPLY ASSESSMENT
VILLAGE OF HARRIMAN
ORANGE COUNTY, NEW YORK**

Prepared For:

The Village of Harriman

April 1989

LEGGETTE, BRASHEARS & GRAHAM, INC.
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GROUND-WATER SUPPLY ASSESSMENT
VILLAGE OF HARRIMAN
ORANGE COUNTY NEW YORK

INTRODUCTION

The Village of Harriman retained Leggette, Brashears & Graham, Inc. (LBG) in February of 1989 to provide a hydro-geologic assessment of an area within the Village of Harriman, New York. The emphasis of LBG's investigation would be to determine the adequacy of the existing water supply and its ability to meet present and future demands. Recommendations would be made to develop additional ground water to augment Harriman's existing water supply.

It should be noted that the Village of Harriman currently has imposed water-use restrictions and has implemented a water-service connection moratorium. The actions have been undertaken so that the Village officials can evaluate the Village's water needs and sources.

EXISTING GROUND-WATER SUPPLY

Well Supply in Service

Based upon information supplied by John Karl, Water Superintendent, we understand that the Village currently operates five production wells completed either in sand and gravel or bedrock aquifers. These wells are located on figure 1. The present well yield capacities are listed on table 1.

Well Supply Not in Service

In February, the Village drilled the Freemont Well and Mary Harriman Well 3 under the supervision of LBG. LBG also investigated the feasibility of placing Harriman Heights Well 3 and Layne Well 1 online. Both the Harriman Heights

Well 3 and the Layne 1 are presently inactive.

Data collected on all four of these wells indicates that additional water supply could be developed from these sources. These wells are located on figure 1. The estimated yield capacities of these available wells are listed in table 2.

Proposed ICC Well Supply Service Agreement

The Town of Woodbury, Village of Harriman and Interchange Commerce Center Associates (ICC) are proposing an Inter-municipal Water Agreement. Five wells have been developed on the ICC site and completed in the bedrock. These wells are located on figure 1 and the estimated yield capacities of the wells are listed in table 3. LBG has reviewed the reports submitted to the Village by CA Rich Consultants, Inc. (Rich) on these wells. Pumping test data and well construction is detailed in the CA Rich reports.

The five wells developed on the ICC site are proposed to be incorporated in the Village of Harriman's existing water distribution system.¹¹ The surplus water not utilized by the ICC site would be available to the municipalities and utilized solely at their discretion; the Village receiving one-third and the Town of Woodbury receiving two-thirds. The water requirements for the ICC project are 275,000 gpd. The Village shall be entitled to withdraw one-sixth of any water production from a well for general consumption for the residences of the Village of Harriman (table 3).¹¹

The five wells developed on the ICC site have been estimated to have a maximum yield capacity of approximately 600,000 gpd (table 3). With the nearby Nepera Inc. (Nepera) ground-water contamination and without remediation activities at Nepera fully active, a prudent ground-water management practice was recommended by Rich. Rich recommended the wells be pumped at "Safe Yield Capacities" (table 3). In a letter report to Steven Deutsch, P.E., dated March 3, 1989, Rich

states "the safe yield of an aquifer is defined as the quantity of ground water which can be safely withdrawn without undesirable results". An undesirable result of excessive pumping of the five wells developed on the ICC could, over time, result in the induced migration of contaminated ground water from Nepera toward one or several of the wells developed on ICC site. The feasibility of pumping the ICC wells at yield capacities higher than the safe yield capacities could be justified if favorable information were generated after the wells are placed in service. The data needed for review would be more definitive ground-water flow mapping, collection of historical ground-water quality data, and the status of Nepera's remediation activities.

WATER SUPPLY DEMAND

With all of the existing wells in service pumping simultaneously, the present supply meets the average seasonal peak summer demand estimated to be about 400,000 gpd (gallons per day) or 280 gpm. However, to meet the peak summer demand the North Main well and Mary Harriman Well 1 are pumped continuously on a daily basis, and the remaining wells are pumped at 12 to 18 hour cycles, which allows wells to recover in off-peak hours. The continuous pumping of the North Main well and Mary Harriman Well 1, is generally necessary during the summer peak-demand period. With the North Main well out of service, the best well, the system is not capable of meeting peak summer demands (table 1).

During non-summer months, the combined pumping of the North Main well with any other supply well, with the exception of Harriman Heights Well 1, would likely meet the off peak average demand of 240,000 gpd or 165 gpm. Similarly, with the North Main Well out of service, the simultaneous pumping of all the remaining supply wells can meet the off-peak demand.

For new community water supplies developed from ground water, the NYSDOH (New York State Department of Health) requires development of two sources, each capable of the average daily demand of the system. In effect, this guideline requires that a community water supply can yield double the average system demands. Although this guideline is not directly applicable to a municipal public supply system, it represents a prudent goal for a system supported by wells.

Wells having a combined pumping capacity of at least 480,000 gpd or 335 gpm would be required for the Village of Harriman to supply double its off-peak demand. If the existing supply wells are pumped at maximum yield capacity at rates above the recommended safe yield of certain wells under continuous pumping conditions, the supply would likely meet 480,000 gpd. Although the wells have demonstrated their ability to meet a water demand greater than 480,000 gpd under emergency conditions, it is not desirable to pump certain wells higher than their recommended safe yield.

The Village should develop the wells listed in table 3. The Harriman Heights Well 3, Layne Well 1, Freemont Well and Mary Harriman Well 3 would likely develop an additional 200 gpm or about 300,000 gpd to augment the existing wells and provide a total combined capacity of about 575 gpm, or about 825,000 gpd. If the wells recommended for development were placed online with the existing well supply, this would enable the Village supply to meet peak summer demand without over-pumping the wells and with the best well out of service.

GEOLOGY

Surficial Materials

A map of soils within the Village, taken from the Soils Survey of Orange County, New York (Olsson, 1981) is shown in figure 2. The majority of the surficial soils formed in

glacial till deposits derived from sandstone, shale and slate. Glacial till generally consists of clayey deposits which usually contain an unsorted mixture of sand, pebbles, cobbles and boulders. Logs of wells located in the study area indicate that the unconsolidated deposits in the southwestern portion of the Village are relatively thin, 10 to 15 feet in thickness. The area within the Village to the northeast have a moderately thick unconsolidated deposits reported to be 60 to 120 feet in thickness.

Sand and Gravel Aquifer

Stratified glacial drift consisting of coarse-grained sand and gravel deposits occur in contact with the till. The sand and gravel aquifer material within the Village and surrounding region consists of fine to medium sand, some gravel and angular rock fragments. The aquifer material is not continuous vertically, but occurs in layers interbedded with gray silty and clayey lenses. These probably occur as valley-fill deposits in channels or former meltwater streams originating from glacial meltback. The fine-grained materials were deposited by sluggish streams capable of transporting only silt and clay-size particles. However, at times, the streams were regenerated and during these periods of higher flow, coarse-grained materials were deposited. In general, the areal extent and thickness of coarse-grained aquifer materials in the Harriman region is not well known, as the subsurface in large parts of the Village has not been explored. The areal extent of the sand and gravel aquifer has been mapped by Frimpter (1985) in a report "Ground-Water Resources of Orange and Ulster Counties, New York". Utilizing the map in the Frimpter report, combined with more recent geologic data, figure 3 gives an approximate boundary of the sand and gravel aquifer. It is likely that a majority of the sand and gravel aquifer would not be suitable for ground-water development.

The sand and gravel aquifer in the vicinity of the Village of Harriman offers a large potential for ground-water development. The Village of Harriman has several wells completed in this aquifer. Frimpter inventoried the original Mary Harriman Well 1, presently inactive, with a reported yield of 350 gpm (gallons per minute).

Six test borings were drilled and three monitor wells installed on the Bailey Farm property northwest of Melody Lane just outside the Village. Three of the borings were terminated at shallow depths because of bedrock. Sand and gravel aquifer material was reported at all locations. Three monitoring wells were installed at locations where the sand and gravel aquifer materials was reported to be deep and thick enough to be considered for production well development. A 6-inch diameter production well was also drilled. The well was drilled to a depth of 74 feet, with a 6-inch diameter stainless steel screen installed 64 to 74 feet below land surface. The well can be operated at rates up to 70 gpm.

Figure 3 locates test borings, monitoring wells and production wells completed in the sand and gravel aquifer regionally.

The sand and gravel aquifer underlying the Bailey Farm tract and the Village of Harriman is most likely hydraulically connected to one of the most prolific aquifers in the region, the Ramapo River Valley aquifer to the east-southeast.

BEDROCK AQUIFER

The Village of Harriman and most of the region north of the Village is underlain by layered sedimentary bedrock covered by unconsolidated glacial deposits. The uppermost bedrock formations is the Wappinger Group, consisting of a dolostone and limestone carbonate unit. The Wappinger Group averages about 160 feet thick along the southern boundary and

about 600 feet thick along the northern boundary of the Village. Immediately south, southwest of the Village, metamorphic rocks dip beneath the younger sedimentary rocks (figure 4).

The Wappinger Group, comprised of thin to massive, blocky beds of carbonate rock is considered to be a relatively prolific aquifer. Some beds are highly fractured and weathered and, as the formation is moderately soluble, these openings are commonly enlarged by dissolution of the rock. This results in a high secondary permeability and, in some places, the rock is an excellent aquifer, producing large quantities of water. There are several wells in Orange County that produce in excess of 200 gpm from bedrock units in the Wappinger Group, and this aquifer offers large potential for ground-water development in the region of the Village. The Village's best well in service, the North Main Well, is completed in the limestone aquifer and yields in excess of 170 gpm.

The older metamorphic rocks which dip beneath the younger sedimentary rock is another aquifer tapped by wells locally. The metamorphic rock consist of undifferentiated gneisses. Although, regionally the gneiss bedrock is not as prolific as the overlying dolostone, wells tapping this aquifer commonly yield from as little as 0.5 gpm to as much as 75 gpm. During ground-water development for the proposed Applecross project in Monroe several wells were completed in the gneiss bedrock aquifer. One well developed for Applecross reported to have a safe yield of up to 75 gpm based on a 72-hour pumping test. The gneiss has little primary porosity or permeability. Some zones in the gneiss are highly fractured, causing the rock to have a relatively high secondary permeability. The highly fractured zones are the most prolific water-bearing zones in the formation.

Several wells locally have been reported to yield water from the contact zone between the gneiss and dolostone bedrock

units.

Two steep, essentially-vertical faults have been mapped trending north and northwesterly through the Village and continuing deep into the region (figure 4). The Lizda Well and two production wells located on Bailey Farm were drilled in the approximate area of the fault zone. The bedrock within the fault zone is a prolific aquifer. The Lizda Well yields 75 gpm and the two wells developed in the Bailey Farm yield 150 and 160 gpm, respectively.

GROUND-WATER AVAILABILITY

Ground water in the sand and gravel and bedrock aquifers is a renewable resource that is continuously replenished by precipitation on the local watershed. The sand and gravel aquifer in the Village is recharged from precipitation which falls directly on the surface of the aquifer, from ground-water flow from surrounding hills, mountains and most importantly from water in the Ramapo River.

There are no precipitation data available for the Village of Harriman. Records for nearby Gardnerville, New York indicate that the average annual precipitation there is 41 inches (figure 6).

The amount of rainfall which becomes ground-water recharge is difficult to measure directly. An estimate developed by the USGS (United States Geological Survey) for recharge to similar sand and gravel deposits in the nearby Fishkill-Beacon area (Snively, 1980) is an average recharge rate of 1,000,000 gpd (gallons per day) per square mile, or about 21 inches annually. R.E. Wright (1982), in his report on the Upper Delaware River Basin, estimates that recharge to local multi-textured sand and gravel deposits during a year of normal precipitation is 790,000 to 985,000 gpd per square mile or about 16.5 to 20.5 inches. Ground-water recharge to

till-covered bedrock similar to that beneath local hills and mountains is estimated to be about 400,000 gpd per square mile or 8 inches per year during periods of normal precipitation (Snively, 1980).

Figure 6 shows that precipitation during a one-year-in-thirty drought (3.3 percent probability of recurrence) decreases to about 27 inches or 66 percent of the average annual precipitation in the vicinity of the study area. If ground-water recharge from precipitation decreases at the same rate as precipitation, recharge from precipitation during a one-year-in-thirty drought would be about 11 to 14 inches to the sand and gravel and 5 inches to the till-covered bedrock within the watershed. During extreme drought conditions the USGS has estimated recharge to decrease to as little as 40 percent of the average rate.

The area of the watershed to the Village well fields is shown on figure 7. The area is approximately 3.4 square miles. Of this area, approximately 40 percent is underlain by moderately thick mixture of silt, sand and gravel and 60 percent is underlain by till-covered bedrock. Recharge which infiltrates this sediment readily recharges the bedrock aquifer. Considering these indications, it is our view that a gross average ground-water recharge of 10 inches to both the sand and gravel and bedrock within the study area is appropriate. Therefore, ground-water recharge from precipitation on the watershed to both aquifers would be about 1.6 mgd (million gallons per day) in an average year and 1.0 mgd during a one-year-in-thirty drought.

The recharge actually available for ground-water supply from the Village well field may be much greater than the amount contributed from precipitation on the watershed. Because of the moderate permeability of the sand and gravel deposits and their inferred hydraulic connection with the water in the Ramapo River, ground-water withdrawals from the

sand and gravel and bedrock are presumed to induce some recharge from the river. The volume of this induced recharge is not measurable without extensive studies but it would increase as the withdrawal rate increases.

For these reasons, LBG concludes that the ground-water recharge available to both aquifers is more than sufficient to meet the present and future demands of the Village of Harri-man. Further, the proposed near-future increase in withdrawals will have no significant impact upon the local ground-water system.

FRACTURE-TRACE ANALYSIS

One of the techniques employed by LBG in evaluating the potential for developing water supplies from the bedrock in the vicinity of the Village was a fracture-trace analysis. For this purpose stereo pairs of aerial photographs were obtained. Using a stereo viewer, structural features call lineations were identified. These features frequently are surficial indications of fracture zones within the bedrock. The fracture-trace analysis method does not always provide successful results, but it does afford an additional useful tool in selecting favorable well sites. Figure 5 shows numerous lineation within the Village and outside the Village which were identified by fracture-trace analysis. None of these lineations are mapped on property owned by the Village which have not already been developed by a well supply. Figure 5 shows existing wells for the Village which are located on or near lineations.

The yield of a bedrock aquifer can be determined only by drilling test wells and conducting pumping tests. If a mapped locations is to be considered, LBG recommends that 6-inch diameter test holes be drilled into the bedrock at the intersections of two or more lineations shown on figure 5. The proper length of temporary casing should be installed, un-

grouted, into competent rock. Wells should be drilled to a minimum depth of 300 feet. A hydrogeologist should decide whether or not to continue drilling beyond 300 feet and determine the final depth of the well.

The proposed wells would be drilled by the air-rotary method, which is relatively fast and efficient in the type of rock found in the region. A 6-inch diameter, 300-foot deep well can usually be drilled in two days. A hydrogeologist would examine the drill cuttings as they as they are flushed from the borehole, and determine the depths at which water enters the hole by observing the flow from the borehole during drilling. The depth of the water-bearing fractures is useful information when interpreting the results of a pumping test and in determining the depth at which to set the permanent pump.

Following the drilling, it will be necessary to convert the 6-inch diameter test well to a 6 or 8-inch diameter production well. The size of the production well will depend upon the flow from the well during drilling. In general, test wells that flow in excess of 50 gpm during drilling require reaming from 6 to 8-inch diameter to accommodate a pump capable of delivering the yield of the well. Test wells must be converted to production wells by installing the proper length of casing and, if necessary, grouting it into place to achieve a water-tight seal, as required by NYSDOH guidelines.

WELL SUPPLY

Table 1 summaries the available information on wells located in the Village well fields, including additional wells proposed to be placed online at some time in the future (table 2 and 3). Data regarding the inactive wells for the Village are limited. This information was obtained from

interviews with Water Department personnel, contacts with well drillers who have worked on the Village wells, review of available reports, and file searches at the Village of Harriman Water Department and Orange County Health Department.

SAND AND GRAVEL WELLS

Original Mary Harriman Well 1 (inactive)

The inactive Mary Harriman Well 1 (MH-1) was reported to be drilled in 1947. The well was completed in the sand and gravel aquifer and supplied water to the Village of Harriman until 1984. Well construction details are given in table 4. The pumping assembly is still in place and in good working condition. The pump is a 40-hp (horsepower) vertical turbine pump. The well, when drilled, was reported to yield 350 gpm and was equipped with a 250-gpm pump. The pump discharged 220 gpm to the 200,000-gallon storage tank on Harriman Heights Road. An initial test on the well reported that, at a pumping rate of 250 gpm, the resultant water-level drawdown was only 13 feet. This would indicate a specific capacity of 19 gpm/foot at a pumping rate of 250 gpm.

In the early 1980's, the yield in the presently-inactive MH-1 began to drop off. The Water Superintendent reported that well was only yielding 80 gpm in 1981. Indications are that the well was never redeveloped since it was placed online in 1947. A letter to the Orange County Department of Health in January of 1981 indicated that "the well's intake screen capacity is being reduced because of it becoming clogged or corroded". It was reported that the problem would be remedied with redevelopment of the well.

In 1984 the Village decided to abandon the well and drill a replacement well. Redevelopment of the well was not considered for several reasons: first, because of the age of the well, it was felt that the well screen was too corroded and could not be replaced; second, because the well was located in

a pump house, not easily accessible; and finally, the Village felt that it could not be without water from the well for any prolonged period of time, as necessary during a redevelopment program.

In 1984 a replacement well was completed in the sand and gravel aquifer. The replacement well was drilled approximately 10 feet outside the existing pump house from the original MH-1. The replacement well has been yielding approximately 75 gpm since its connection.

On February 22, 1989, approximately five years since the original MH-1 was abandoned, a short pumping test was conducted on the well. Utilizing the existing 40-hp turbine pump for the well, which was found to be in excellent working condition, the discharge pipe was adapted to flow freely outside the pump house. No valve was installed to allow regulation of flow rate. When the pump was started the well discharge extremely dark-colored water at a rate estimated between 150 to 180 gpm for approximately 24 seconds before breaking suction. The water level in the well was allowed to recover for 10 minutes at which time pumping was restarted. Again the well yielded 150 to 180 gpm for approximately 24 seconds. This was repeated several times over the next hour. The discharge eventually became less turbid, appearing to clear. There was no evidence during the test of a collapse of the well screen. Due to the inability to decrease the pumping rate with a valve, LBG was not able to sustain a lower pumping rate for a longer pumping duration.

Although there is no documentation of who actually drilled the original MH-1, it is reported to have been drilled by the Lauman Company which was based on Long Island. This firm has since reorganized. During a conversation with Fred Lehman of Eastern Well Drilling, a former employee of the Lauman Company, he felt certain that the Lauman Company was constructing sand and gravel wells with welded well screens fabricated of Everdur. The Everdur well screens manufactured

by Johnson were continuous-slot wire-wrapped affording extra strength and made of Everdur bronze, making them resistant to unusually corrosive waters. Everdur is known to be extremely resistant to acid treatment (Johnson, 1985).

Present indications are that the well screen on the original MH-1 has not collapsed. The gradual decline in the yield of the well is likely a result of clogging of the water-bearing formation around the well, in the gravel pack and around the well, seriously reducing the capacity. This would result in gradual decline of well yield. The well was reported to be constructed with an Everdur well screen. This type of screen is strong and durable. During a recent conversation with Raymond Schreurs of Johnson Division of UOP Inc., Mr. Schreurs suggested that if the well was properly redeveloped, the well screen would likely last an additional 30 years. If redevelopment is successful, the well could likely be placed back online at a pumping rate between 150 to 250 gpm.

Layne Well 2

In 1967, the Village developed two wells under a guaranteed contract with Layne New York Company, Inc.; one being a gravel well (Layne Well 2) and one adjacent rock well (Layne Well 1). The 10-inch diameter sand and gravel well was drilled to a depth of 52 feet and was reported to have a safe yield of 104 gpm. The available well construction details are given in Table 4. No additional information is available. At present it is not possible to determine which of the two 10-inch diameter well drilled by Layne in 1967 is the sand and gravel or the bedrock well. The village abandoned both these wells during the 1970's due to their low yields. In addition the sand and gravel well (Layne Well 2) was reported to be discharging turbid water during pumping. The Village felt it was better to concentrate its efforts on higher producing wells rather than several low yield wells.

Mary Harriman Well 1 (replacement well)

In 1984, an 8-inch diameter natural-pack sand and gravel well was drilled by Eastern Well Drilling (Eastern). The well was located approximately 10 feet outside the pump house for the original MH-1. The available well construction details are given in table 4. When the original MH-1 was abandoned, the 8-inch diameter replacement well drilled by Eastern became known as MH-1. The replacement MH-1 has been producing 75 ppm since connected into the Village's distribution system. The well was last redeveloped by Turnbull Well Drilling, Inc., (Turnbull) in April 1989 under the supervision of LBG.

On February 21, 1989, MH-1 had a non-pumping static water level of 9.05 feet. On February 27, 1989, following a pumping duration of approximately 72 hours at a rate of 75 gpm, MH-1 had a stabilized pumping level of 17.75 feet below top of casing. The total observed drawdown was 8.7 feet indicating a specific capacity of 8.7 gpm/foot.

MH-1 presently averages 98,000 gpd during a 24-hour pumping cycle. The well is shut off whenever possible, usually one to possibly two days a week.

Mary Harriman Well 2

Mary Harriman Well 2 (MH-2) was drilled by Eastern in 1984. The 6-inch diameter well was drilled to a depth of 42 feet. The available well construction details are given in Table 4. The well log indicates that the borehole drilled through broken-up weathered limestone and coarse gravel between 39 and 42 feet. The open-hole well casing was set in the broken-up weathered limestone and gravel, as an open-end completion.

A preliminary test conducted by Eastern on MH-2 indicated a safe yield of 50 to 60 gpm with less than 10 feet of drawdown. An additional 72-hour pumping test indicated a safe yield of 45 gpm with only 5.88 feet of drawdown. The specific capacity of MH-2 was 7.6 gpm/foot at a pumping rate of 45 gpm.

MH-2 was never placed online for two reasons. First, the well is located only a few hundred feet from Nepera Inc. Present reports indicate significant ground-water contamination on the Nepera property. In addition, water-quality analyses conducted on the well reported elevated concentrations of both chloride and sodium at levels as high as 246/120 ppm (parts per million), respectively. The concentrations for chloride is just under the maximum permissible concentration allowed by the NYSDOH which is 250 ppm. The concentration of sodium in the well is above the recommended guideline of 20 ppm for people on a diet severely restricted in sodium. Water containing more than 270 ppm of sodium should not be used for drinking by those on diets moderately restricted in sodium.

During a site visit to the well in February, LBG observed that the well had been vandalized. The well cap had been removed, and the borehole filled with gravel, almost to the top of casing.

BEDROCK WELLS

Harriman Heights Well 1

The Harriman Heights Well 1 (HH-1) is located outside the Village on Village-owned property. The available well construction details are given in table 4.

HH-1 was drilled in 1928. The well is reported to tap the gneiss bedrock aquifer. When the well was originally drilled, it was estimated to yield over 100 gpm. The well was reported to yield 70 gpm in November of 1971 and 60 gpm in January of 1981. Based on present pumping records, the well yield has dropped off to 30 gpm. It is manually-controlled and used as a supplementary water supply for the Village on an as-needed basis.

Due to the close proximity of HH-1 and Harriman Heights Well 2 (HH-2), under simultaneous pumping conditions both

wells are reported to interfere severely with each other. Therefore, HH-1 and HH-2 are only pumped simultaneously under emergency conditions. LBG was not able to collect water-level data on HH-1. The present well cap will not allow access to take a measurement of the depth to water. The air line presently installed is not operable.

Harriman Heights Well 2

HH-2 was drilled in 1971. The available well construction details are given in table 4. The well is reported to tap the gneiss bedrock aquifer.

In November of 1971, a 48-hour controlled pumping test was conducted on HH-2. The static water level prior to the start of the test was reported to be 132 feet below ground level. After pumping the well for 12 hours, the water level stabilized at approximately 222 feet below ground level at a rate of 102 gpm. The water level stabilized and the pumping rate was maintained for the remaining 36 hours of the test. The specific capacity of the well during the November 1971 pumping test was 1.1 gpm/foot at a pumping rate of 102 gpm.

During a site visit to HH-2 in March of 1989, LBG was not able to collect water-level data.

HH-2 presently averages 39,000 gpd during two six-hour pumping cycles on a daily basis.

North Main Street Well

The North Main Street Well (North Main) was drilled by Eastern in 1977. The available well construction details are given in table 4. The well is reported to tap the limestone bedrock aquifer.

A 72-hour controlled pumping test was conducted on North Main in April of 1977. The water level in the well was reported to flow over the top of casing prior to the start of the test. The well was pumped at rates as high as 200 gpm. The water level eventually stabilized at a pumping rate of

171 gpm for the the last 12.5 hours of the test at a depth of 313 feet. The specific capacity of the well during the April 1977 pumping test was 0.55 gpm/foot at a pumping rate of 171 gpm.

During a site visit to North Main on March 30, 1989, the pumping water level was 292.2 feet at a pumping rate of 145 gpm, indicating a specific capacity of 0.50 gpm/foot.

North Main presently averages 190,000 gpd during a 24-hour pumping cycle.

Lizda Well

In 1984 an 8-inch diameter well completed in bedrock was drilled by Eastern. The available well construction details are given in table 4. The well is reported to tap the limestone bedrock aquifer.

In December of 1984 a 72-hour controlled pumping test was conducted on the Lizda Well. The static water level prior to the start of the test was 54 feet below top of casing. The pumping water level in the well was reported to stabilize at 159 feet, for a drawdown of 105 feet at a rate of 75 gpm. The specific capacity of the well during the December 1984 pumping test was 0.71 gpm/foot at a pumping rate of 75 gpm.

During a site visit to the Lizda Well on March 30, 1989, the pumping water level was 145.3 feet at a pumping rate of 75 gpm, indicating a specific capacity of 0.82 gpm/foot.

The Lizda well presently averages 101,000 gpd during an 18-hour pumping cycle.

Mary Harriman Well 3

In February of 1989, under the supervision of LBG, Turnbull drilled an 8-inch well completed in bedrock. The well is located approximately 5 feet outside the pumphouse for the original MH-1 and known as Mary Harriman Well 3 (MH-3). MH-3 is located approximately 8 feet from the original MH-1 located in the pumphouse and 25 feet from the replacement MH-1 presently online.

Well construction details are given in table 4. The well is reported to be completed in both the limestone and gneiss bedrock aquifer.

During the drilling, Turnbull reported the well yielded little water until at a depth of 505 feet below grade, the drill bit entered a water-bearing zone which produced an estimated 40 gpm. Drilling was terminated at a depth of 520 feet. The driller's log is included in Appendix A.

On February 27, 1989 LBG conducted a preliminary 18-hour pumping test on MH-3. The static water level was 16 feet from the top of the measuring point. The well was pumped at the maximum capacity off the temporary pump installed in the well. The well was tested at a rate of 33 gpm which was held for the entire duration of the test. Just prior to shutdown the pumping water level was 96.4 feet from the top of the measuring point for a total drawdown of 80.4 feet. Although the pumping water level in the well had not stabilized, just prior to shut down the water level appeared to begin to decline at a much slower rate of decline during the last 3 hours of the test. If the test had continued, the water level would likely have stabilized at some lower depth.

The test on MH-3 was conducted to confirm the yield estimate during drilling. In addition, it was necessary to determine if during the pumping of MH-3, damaging water-level interference would affect the yield of MH-1. The preliminary test conducted was ended prior to obtaining a stabilized water level at the constant rate of 33 gpm. A 72-hour pumping test is scheduled for the near future to determine the actual safe yield of the well. MH-1 was monitored during the preliminary 18-hour pump test. The non-pumping water level in MH-1 remained at 10.5 feet from the top of casing prior to and during the entire test conducted on MH-3. Present data indicate that the sand and gravel aquifer tapped by MH-1 is not hydraulically connected with the deep water-bearing fractures

in the bedrock tapped by MH-3, so that both wells could be pumped simultaneously without serious mutual interference.

Harriman Heights Well 3

Harriman Heights Well 3 (HH-3) is an 8-inch diameter well completed in bedrock on Village-owned property. The available well construction details are given in table 4. The well is reported to tap the gneiss bedrock aquifer. The well has been considered to be placed online and connected to the Village distribution system for the past several years. However, to date, the well is still inactive.

LBG has reviewed the available data on HH-3. Once online, the well will likely supply up to 50 gpm to the Village's water system, but probably not on a continuous basis. A 72-hour controlled pumping test was conducted on HH-3 in June of 1984. The data for the well indicate that the pumping rate was reduced several times during the 72-hour test, to achieve stabilization of the the water level in the well. The final pumping water level in the well was 393 feet, with a constant pumping rate of 50 gpm and stabilized water-level maintained for the last 4.5 hours of the test. The specific capacity of the well during the June 1988 pumping test was 0.17 gpm/foot at a pumping rate of 50 gpm.

The pumping water levels were reported in feet rather than feet and inches. The NYSDOH guideline requires a constant pumping rate and stabilized water level for at least the last five hours of a pumping test. Pumping test data for HH-3 was reviewed by the NYSDOH in Albany, and Orange County Department of Health. Although the pumping test data indicate that the minimum guidelines of the NYSDOH have been satisfied, no offsite well monitoring program was conducted during the testing. Further, water samples to allow determination of ground-water quality were not collected from HH-3 during the test. There is some concern from both regulatory agencies that the aquifer in which HH-3 is completed will still yield up to 50 gpm, since the test was conducted in 1984.

To eliminate present concerns expressed by both the NYSDOH and the Orange County Department of Health, LBG recommends that HH-3 be retested so that additional data can be submitted.

Freemont Well

In February of 1989, Turnbull drilled a well completed in bedrock on Village-owned property. Well construction details are given in table 4. The well is reported to be completed in both the limestone and gneiss bedrock aquifer. The drillers log for the Freemont Well is included in Appendix B.

During the drilling, Turnbull reported the well yielded little water until at a depth of 187 feet below grade, the drill bit entered a water-bearing zone which produced an estimated 56 gpm. Drilling was terminated at a depth of 340 feet.

The Village is presently considering developing the Freemont Well site. However, at present the Freemont well site does not meet NYSDOH guidelines requiring ownership of a 100 foot radius or a 200 foot radius of sanitary control from the well. The Village may be able to obtain a sanitary easements on the adjacent properties.

WELL MONITORING PROGRAMS

Nepera reportedly disposed of drums and chemicals onsite between 1942 and 1976, which were discovered during excavation of a new building in 1981. The contamination was remediated upon its discovery. The most toxic of the chemicals found is benzene. Benzene is classified as a hazardous chemical and carcinogen by the U.S. Environmental Protection Agency (EPA). The EPA recommends that the maximum concentration of benzene permissible in drinking water must not exceed one part per billion.

LBG has reviewed the existing well monitoring program which is to identify ground-water contamination of wells in the region surrounding Nepera. Five wells are presently sampled and analyzed quarterly for the potential presence of volatile organic compounds. Two of these wells, Mary Harriman Well 1 and the Lizda Well, supply ground water for the Village of Harriman. The three remaining wells supply ground water for Automotive City, Tom Sullivan Chevrolet and the motel. To date, these five wells have indicated no presence of volatile organic compounds.

Ground water sampled from several shallow monitoring wells completed in the overburden materials and located on Nepera property indicate traces of benzene. In addition samples collected in July of 1988 showed that monitoring wells that had tested clean in the past have benzene levels as high as 500 parts per billion. The data collected July 1988 indicates that the contamination was continuing to spread northward and to the Ramapo River, and perhaps eastward. The results of the March 1989 sampling have not been resubmitted to LBG prior to submitting this report. The extent and possible continuing spread of the contamination is being further investigated.

An "early warning monitoring well network" being required as a special condition to New York State Department of Health's and Environmental Conservation's Permit for the OR-7 well is being completed along the southeastern boundary of ICC and Nepera. The OR-7 well and eleven small-diameter monitoring wells are scheduled to be sampled and analyzed quarterly for contamination with volatile organic compounds such as benzene, pyridene, and annually for all 128 priority pollutants. Once OR-1, OR-3, OR-5 and OR-6 are placed online these wells are also scheduled to be sampled and analyzed for the same above-mentioned parameters.

The five presently-monitored supply wells, OR-7, including proposed supply wells OR-1, OR-3, OR-5 and OR-6 and

the eleven small-diameter monitoring wells are located on figure 8.

Five of the eleven small-diameter monitoring wells have not been constructed. The drilling of the five wells D-2, D-3, S-3, D-4 and S-4 is scheduled to be completed within the next month.

To date all of the wells sampled in the early warning monitoring all tested below the detectable levels for benzene which is one part per billion, except MW-1 on the Nepera property. On December 30, 1988, MW-1 was reported to show 330 parts per billion of benzene. Additional water quality data are scheduled to be collected from the six wells to be completed next month.

CONCLUSION

The five wells in service pumping simultaneously meet the average seasonal peak summer demand estimated to be about 400,000 gpd. During non-summer months, the combined pumping of the North Main Well with any other supply well with the exception of Harriman Heights Well 1, could meet off-peak summer demands of 240,000 gpd, as would the simultaneous pumping of all remaining wells with the North Main well out of service.

However, to meet the peak summer demands a majority of the wells are pumped continuously on a daily basis which is not a recommended practice. With any of the following wells out of service, Mary Harriman Well 1, Harriman Heights Well 2, the Lizda Well or North Main Well, the system is not capable of meeting average peak summer demands. With the North Main Well out of service, the system is capable of meeting off-peak summer demands, however marginal.

LBG concludes that the supply problem experienced by the Village during the Summer of 1988 probably resulted from prolific water use during a period of low rainfall, combined

with mechanical problems with water storage equipment. The storage tanks are presently being equipped with low level and high level probes to regulate water storage.

The pumping data collected on the existing supply wells for the Village during the Summer of 1988 indicated no loss in yield capacity during the low rainfall. Several of the wells were able to sustain continuous pumping over a period of several weeks.

The sand and gravel and limestone aquifers are the most prolific and most suitable aquifers in the region of the Village for development. Although, the gneiss bedrock aquifer is suitable for ground-water development, historically, wells completed in this aquifer indicate a substantial loss in yield capacity over time.

The ground-water recharge available to both the sand and gravel and bedrock aquifers is more than sufficient to meet present and future demands of the Village. Further, the proposed increase in withdrawals will have no significant impact upon the local ground-water system.

At present, the Village is reviewing the Inter-municipal Water Agreement with ICC and the Town of Woodbury. If the Agreement is accepted, the Village will incorporate five wells developed on ICC into their existing water distribution system. The Village shall be entitled to withdraw one-sixth of any water production from a well for general consumption for residences of the Village of Harriman.

LBG is in general agreement with the "safe yield capacities" determined by CA Rich listed in table 3. The feasibility of pumping the ICC wells at yield capacities higher than the "safe yield capacities" could be justified if favorable information were generated. The data needed for the review would be more definitive ground-water flow mapping, collection of historical ground-water quality data and the status of Nepera's remediation activities. It should be understood that the collection of the above-mentioned data may also require the lowering of certain well yield capacities or

even result in the abandonment of one or several of the supply wells developed on the ICC site. If the ICC wells become contaminated, treatment of the contaminated water could be an alternative, however, costly.

LBG has reviewed the "early warning monitoring well network". The monitoring program covers an extensive area with scheduled sampling and analysis to detect migration of contaminants from the Nepera site.

RECOMMENDATIONS

Following a review of the current water demand of the Village of Harriman and review of the existing ground-water supply, LBG offers the following recommendations to secure additional ground water for the future.

As additional water supplies are developed and placed in service, the Village should evaluate the ability to eventually eliminate water-use restrictions and review the availability to provide water service connections.

Data collected on the Harriman Heights Well 3, Layne Well 1, Freemont Well and Mary Harriman Well 3 indicate that if all four wells are placed in service, an additional 300,000 gpd would likely be developed. Due to the close proximity of the Layne Well 1 and Mary Harriman Well 3 to the existing water distribution system, these wells can be more readily developed.

Consideration should be given to rehabilitating the original Mary Harriman Well 1, presently inactive. Qualified Drilling Contractors should be contacted to give cost estimates for the proper redevelopment work necessary to place the well back in service. Cost estimates provided by the drillers

would be evaluated to better determine the feasibility of placing the well back online. It is likely that if redevelopment is successful, the well could be placed back online at pumping rates between 150 to 250 gpm.

The fracture-trace analysis conducted by LBG did not locate any promising well locations on Village-owned property not already developed by a well supply. The Village could obtain drilling options on favorable property not presently owned.

LBG recommends that a test well be drilled on Village-owned property located between James Street and South Main Street. The parcel is located on tax map block no. 3, and designated as parcel no. 4. The fracture-trace analysis indicate no mapped lineation of this parcel. However, this parcel is adjacent to the parcel owned by William Roarke. A well located on the Roarke property drilled 180 feet in depth indicated during a preliminary pumping test to have a yield capacity of 175 gpm. The well is presently utilized for domestic use. Subsequently a well drilled on the Village's parcel may tap the same water bearing fractures tapped by the Roarke well on the adjacent parcel.

The Village should review the water storage tanks capabilities in relation to present and future water demands to determine if the present tanks are adequate for the water storage requirements.

All wells presently in service for the Village, including any well placed in service in the future should have a dip tube installed in the well to allow easy access for taking measurements of the depth to water using a clean electric dropline. Static and pumping water levels should be recorded on a regularly scheduled basis.

The test results from the wells presently available for sampling indicate that there is no immediate threat to local

well
on
the
adjacent
property
is reported
to
yield
175 gpm

drinking water supplies from the ground-water contamination on the Nepera site. The Village of Harriman should exert pressure on Nepera and the NYSDEC to expedite remediation activity of this site.

LEGGETTE, BRASHEARS & GRAHAM, INC.



Thomas P. Cusack
Senior Hydrogeologist

Affirmed by:

R. G. Slayback, CPG
President

gmm
April 26, 1989
pi-har

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Frimpter, Michael H., 1972, Ground Water Resources of Orange and Ulster Counties, New York, U.S. Geological Survey Water-Supply Paper 1985.

Frimpter, Michael H., 1970, Ground-Water Basic Data: Orange and Ulster Counties, New York, U.S. Geological Survey and the State of New York Conservation Department, Water Resources Commission.

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Snavelly, Deborah S., 1980, Ground-Water Appraisal of the Fishkill-Beacon area, Dutchess County, New York, United States Geological Survey Water Resources Investigation Open File Report, 80-437.

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T A B L E S

TABLE 1

VILLAGE OF HARRIMAN

Well Supply in Service
and
Present Yield Capacity of Wells

Well	Present Yield		Maximum Yield
	Capacity (gpm)	Average (gpd)	Capacity (gpd)
North Main	170	190,000	225,000
Mary Harriman 1	75	98,000	104,000
Harriman Heights 1	30 80	0	16,000
Harriman Heights 2	52	39,000	55,000
Lizda Well	75	101,000	135,000
	TOTAL:	428,000	535,000

TABLE 2

VILLAGE OF HARRIMAN

Well Supply Not In Service
and
Estimated Yield Capacity of Wells

Well	Estimated Yield Capacity (gpm)
Harriman Heights Well 3	50*
Layne Well 1	69*
Freemont Well	50**
Mary Harriman Well 3	40**
TOTAL	----- 209 gpm or 300,960 gpd

* Tested well capacity

** Estimated yield capacity

TABLE 3

VILLAGE OF HARRIMAN

Interchange Commerce Center Associates
Proposed Well Supply for Service
and
Yield Capacity of Wells

Well	Safe Yield Capacity* (gpm)	Surplus Water Available for Village Residence Use (gpm)	Maximum Yield Capacity* (gpm)
OR-1	75**	12.5	100
OR-3	70**	11.6	100
OR-5	32**	5.3	75
OR-6	25**	4.1	45
OR-7	50***	8.3	100
	-----	-----	-----
	252 gpm or 362,880 gpd	41.8 gpm or 60,192 gpd	420 gpm or 604,800 gpd

* CA Rich Consultants, Inc.

** applied for yield capacity on NYSDEC Water Supply
Application

*** Permitted yield capacity, NYSDEC WSA No.: 8150

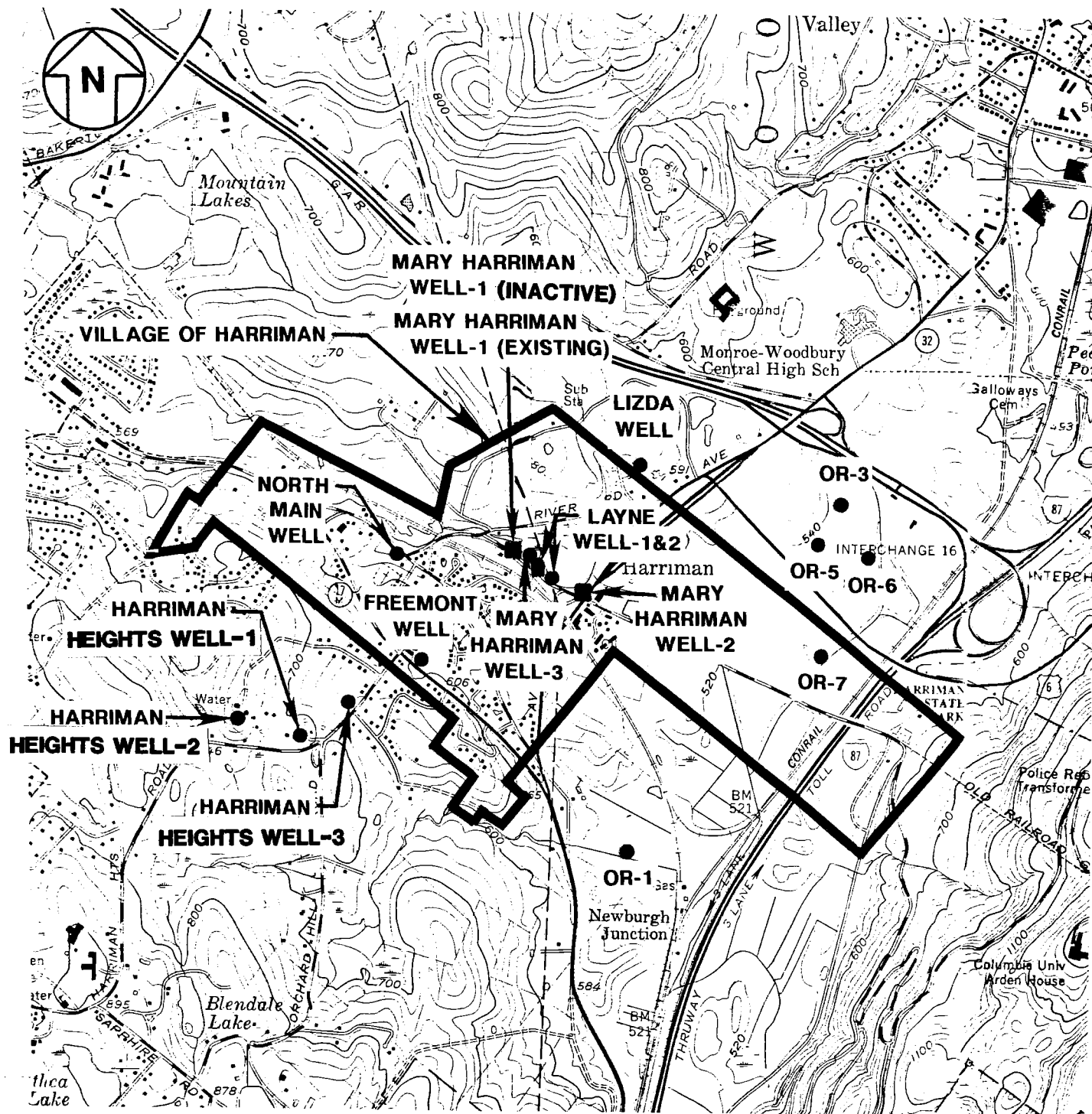
TABLE 4
VILLAGE OF HARRIMAN
Summary of Well Data

Well	Use	Reported Yield (gpm)	Depth of Well (feet)	Diameter (inches)	Length of Casing (feet)	Screen Length (feet)	Aquifer	Date Drilled
Mary Harriman Well 1 (original)	inactive	350	34	12	24	10	sand & gravel	1947
Layne Well 2	inactive	104	52	10	NA	NA	sand & gravel	1967
Mary Harriman Well 1 (replacement)	supply	75	52	8	48	10	sand & gravel	1984
Mary Harriman Well 2	inactive	45	42	6	41	--	broken-up weathered limestone; coarse-gravel	1984
Harriman Heights Well 1	supply	30	328	10	NA	--	bedrock	1928
Harriman Heights Well 2	supply	52	400	8	130	--	bedrock	1972

TABLE 4
(continued)
VILLAGE OF HARRIMAN
Summary of Well Data

Well	Use	Reported Yield (gpm)	Depth of Well (feet)	Diameter (inches)	Length of Casing (feet)	Screen Length (feet)	Aquifer	Date Drilled
North Main Well 1	supply	171	400	8	NA	--	bedrock	1977
Lizda Well	supply	75	350	8	153	--	bedrock	1984
Layne Well 1	inactive	69	205	10	40	--	bedrock	1967
Mary Harriman Well 3	test well	40	520	8	50	--	bedrock	1989
Harriman Heights Well 3	test well	50	400	8	NA	--	bedrock	1989
Freemont Well 1	test well	56	340	6	40	--	bedrock	1989

F I G U R E S



LEGEND


- WELL COMPLETED IN SAND AND GRAVEL AQUIFER
- WELL COMPLETED IN BEDROCK AQUIFER

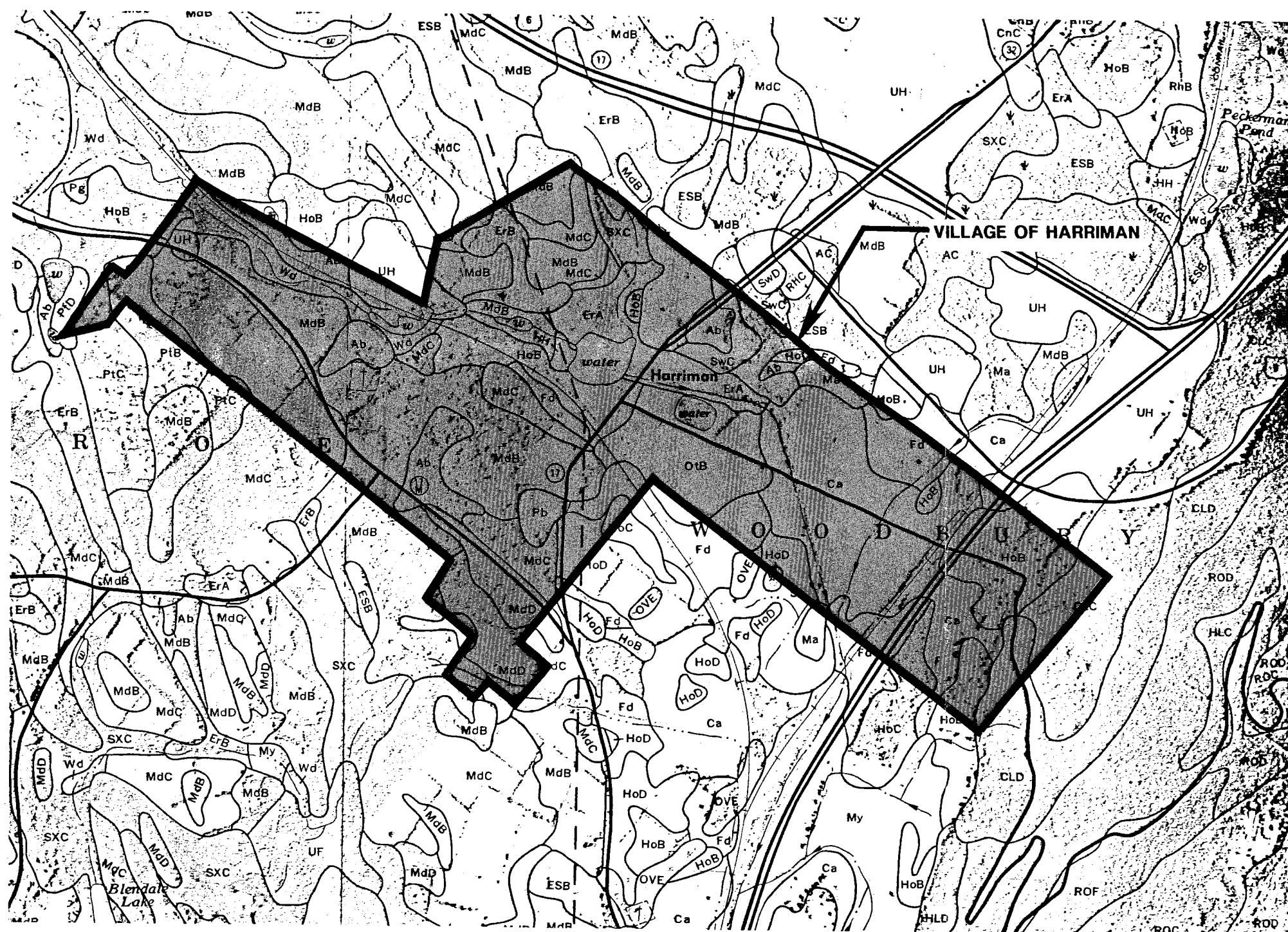
0 2000

 SCALE IN FEET

VILLAGE OF HARRIMAN ORANGE COUNTY, NEW YORK

WELL LOCATION MAP

DATE	REVISED	PREPARED BY:
		 LEGGETTE, BRASHEARS & GRAHAM, INC. Professional Ground-Water Consultants 1123 Route 52, Suite 38 Fishkill, NY 12524 914-897-2970
DATE: 4/17/89		FIGURE 1



LEGEND

- Ab ALDEN SILT LOAM
- Ca CANANDAIGUA SILT LOAM
- ErA ERIE GRAVELLY SILT LOAM, 0 TO 3 PERCENT SLOPES
- ErB ERIE GRAVELLY SILT LOAM, 3 TO 8 PERCENT SLOPES
- Fd FREDON LOAM
- HH HISTIC HUMAQUEPTS, PONDED
- HoB HOOSIC GRAVELLY SAND LOAM, 3 TO 8 PERCENT SLOPES
- HoC HOOSIC GRAVELLY SAND LOAM, 8 TO 15 PERCENT SLOPES
- HoD HOOSIC GRAVELLY SAND LOAM, 15 TO 25 PERCENT SLOPES
- Ma MADALIN SILT
- MdB MARDIN GRAVELLY SILT LOAM, 3 TO 8 PERCENT
- MdC MARDIN GRAVELLY SILT LOAM, 8 TO 15 PERCENT SLOPES
- OtB OTISVILLE GRAVELLY SAND LOAM, 0 TO 8 PERCENT SLOPES
- OVE OTISVILLE AND HOOSIC SOILS, STEEP
- Pb PALMS MUCK, PONDED
- SwC SWATSWOOD GRAVELLY LOAM, 8 TO 15 PERCENT SLOPES
- SwD SWATSWOOD GRAVELLY LOAM, 15 TO 25 PERCENT SLOPES
- SXC SWATSWOOD AND MARDIN VERY STONY SOILS, SLOPING
- UH UDORTHENTS
- Wd WAYLAND SILT LOAM

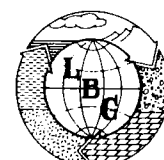
SOURCE: OLSSON 1981



0 2000
SCALE IN FEET

VILLAGE OF HARRIMAN ORANGE COUNTY, NEW YORK

SOIL TYPES

DATE	REVISED	PREPARED BY:
		 LEGGETTE, BRASHEARS & GRAHAM, INC. Professional Ground-Water Consultants 1123 Route 52, Suite 38 Fishkill, NY 12524 914-897-2970
DATE: 3/29/89		FIGURE 2



LEGEND

- ▲ TEST BORING ENCOUNTERING SATURATED SAND AND GRAVEL MATERIAL
- MONITORING WELL(S) COMPLETED IN SAND AND GRAVEL AQUIFER
- PRODUCTION WELL(S) COMPLETED IN SAND AND GRAVEL AQUIFER

0 2000

SCALE IN FEET

VILLAGE OF HARRIMAN ORANGE COUNTY, NEW YORK

SAND AND GRAVEL AQUIFER, TEST BORING AND WELL LOCATION MAP

DATE	REVISED

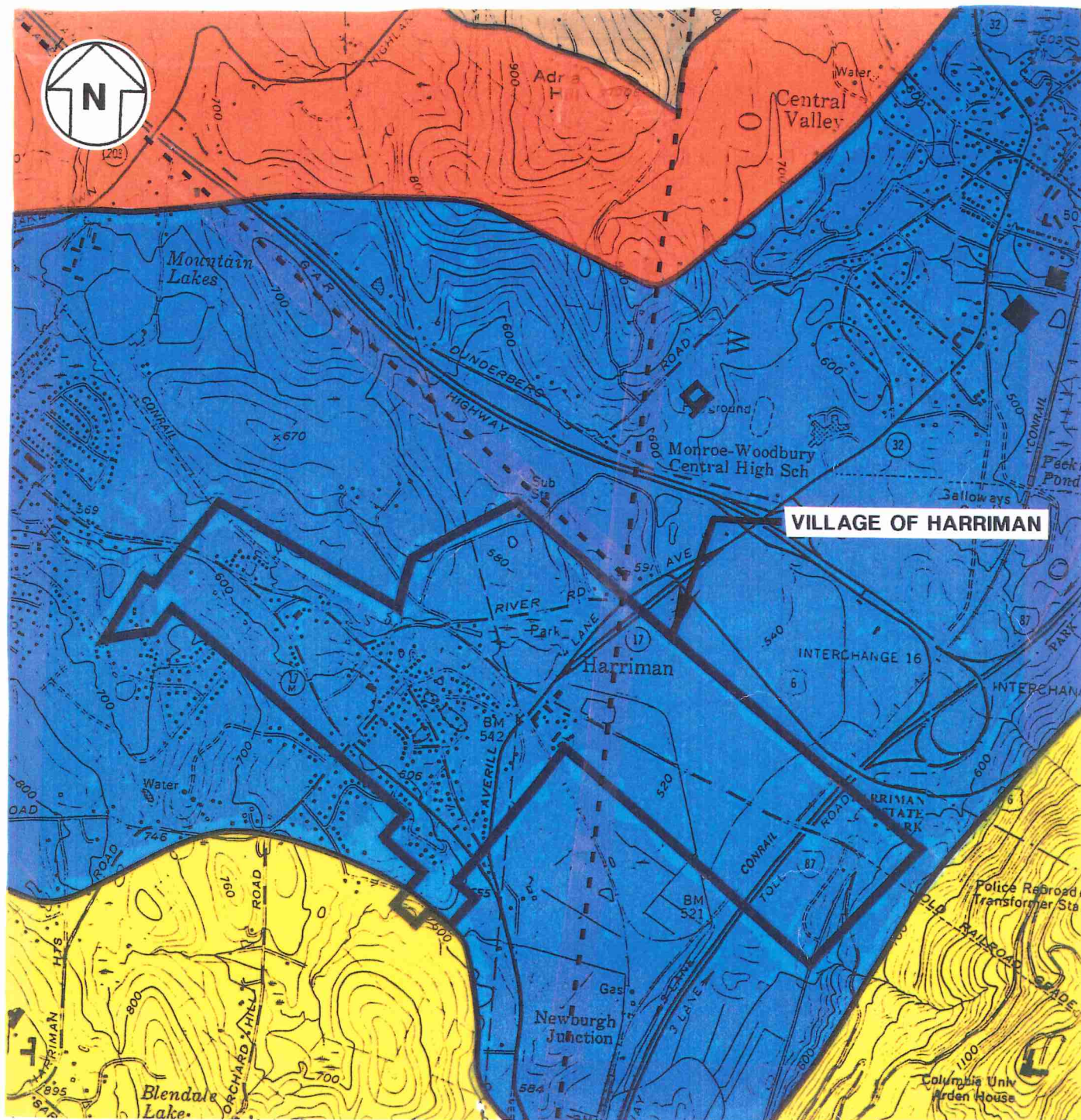
PREPARED BY:



LEGGETTE, BRASHEARS &
GRAHAM, INC.
Professional Ground-Water Consultants
1123 Route 52, Suite 38
Fishkill, NY 12524
914-897-2970

DATE: 3/29/89

FIGURE 3



SOURCE: JAFFEE 1973

LEGEND

- UNDIFFERENTIATED GNEISS
- WAPPINGER GROUP
- CONCEALED DEVONIAN, SILURIAN, ORDOVICIAN STRATA
- ESOPUS FORMATION
- FAULT


0 2000

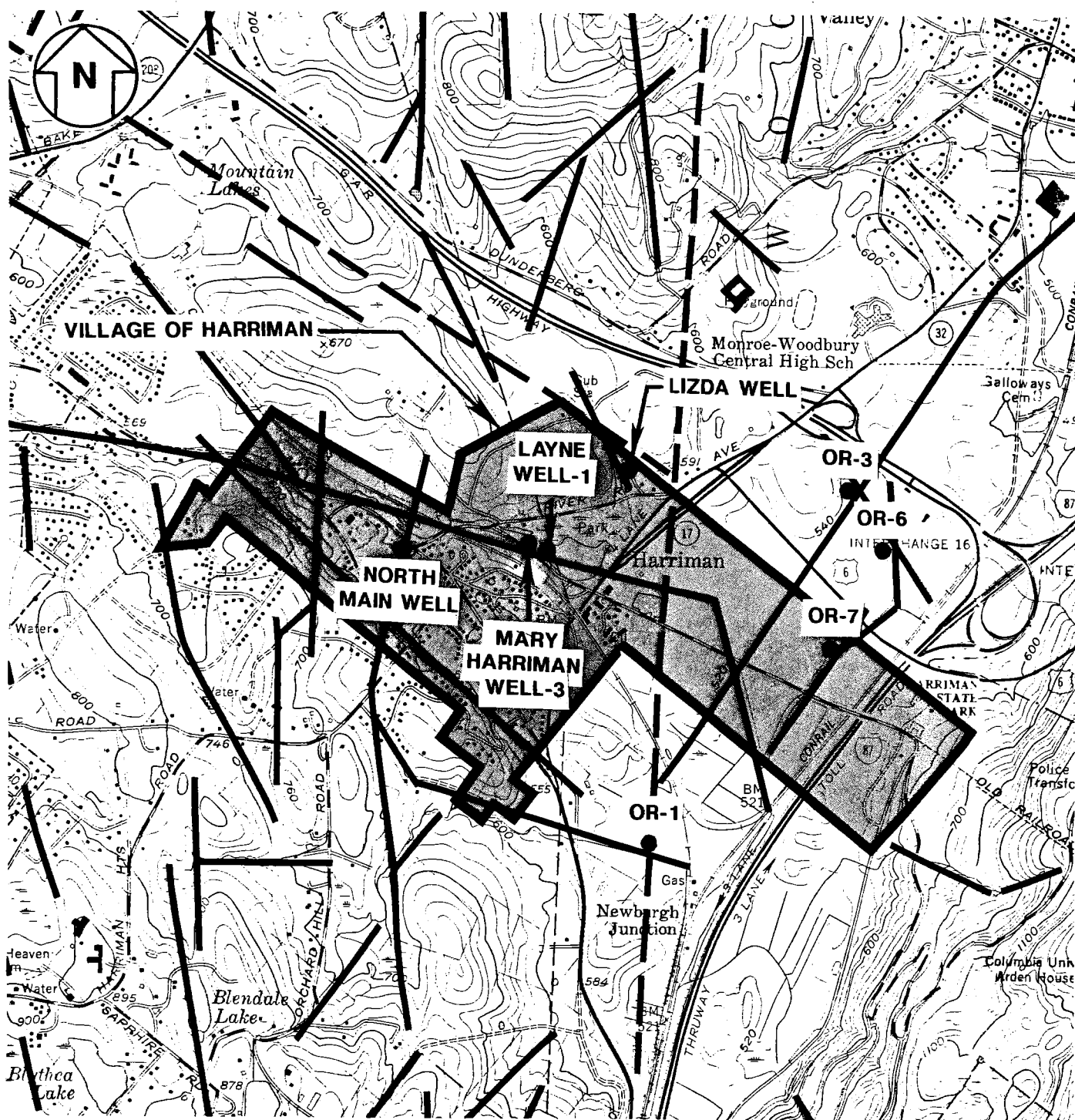


SCALE IN FEET

VILLAGE OF HARRIMAN ORANGE COUNTY, NEW YORK

GENERALIZED GEOLOGIC MAP

DATE	REVISED	PREPARED BY:
		 <p>LEGGETTE, BRASHEARS & GRAHAM, INC. Professional Ground-Water Consultants 1123 Route 52, Suite 38 Fishkill, NY 12524 914-897-2970</p>
DATE: 3/29/89		FIGURE 4



LEGEND


- FAULT**
- FRACTURE TRACE**
- WELL LOCATION**

0 2000

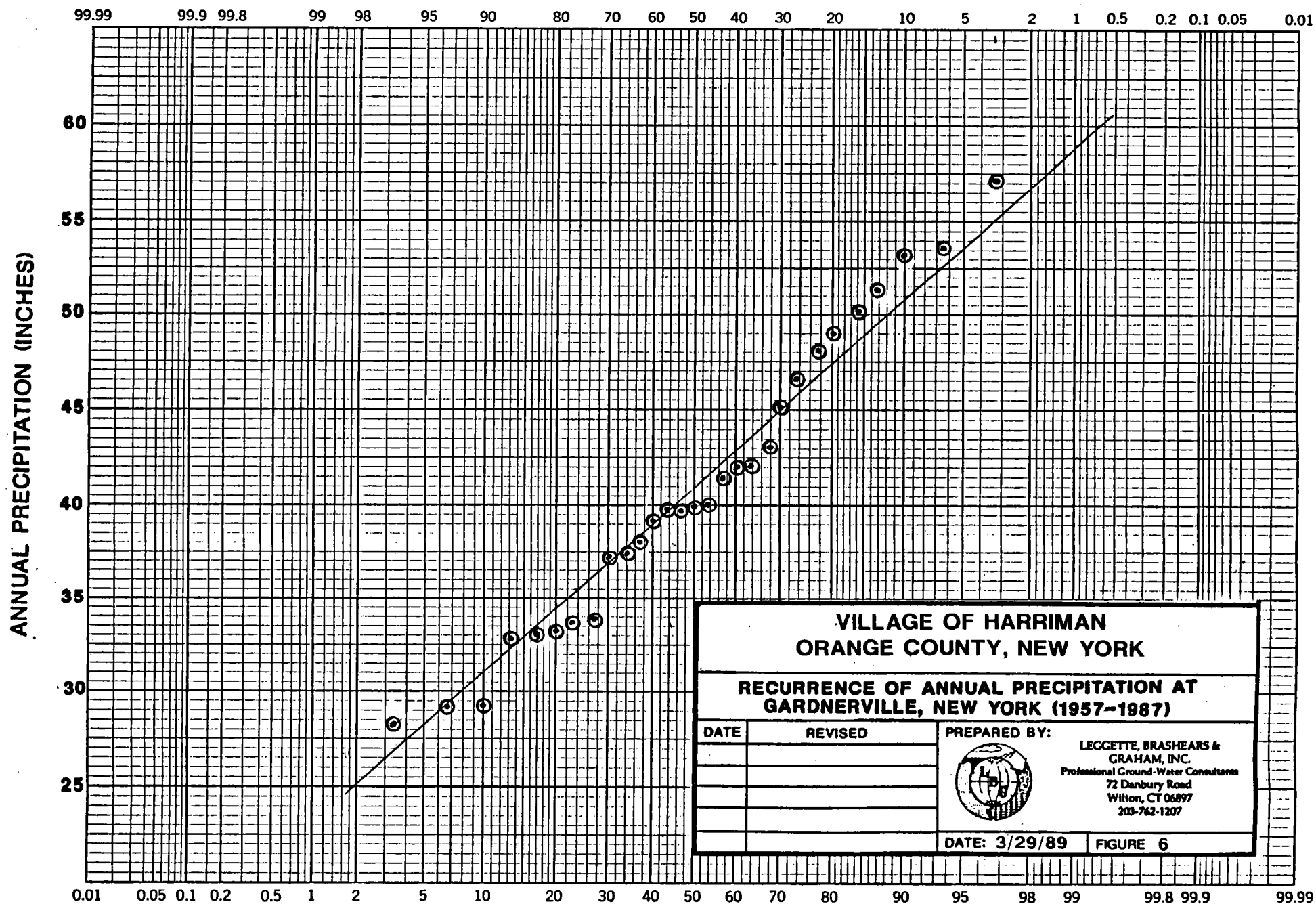
SCALE IN FEET

VILLAGE OF HARRIMAN ORANGE COUNTY, NEW YORK

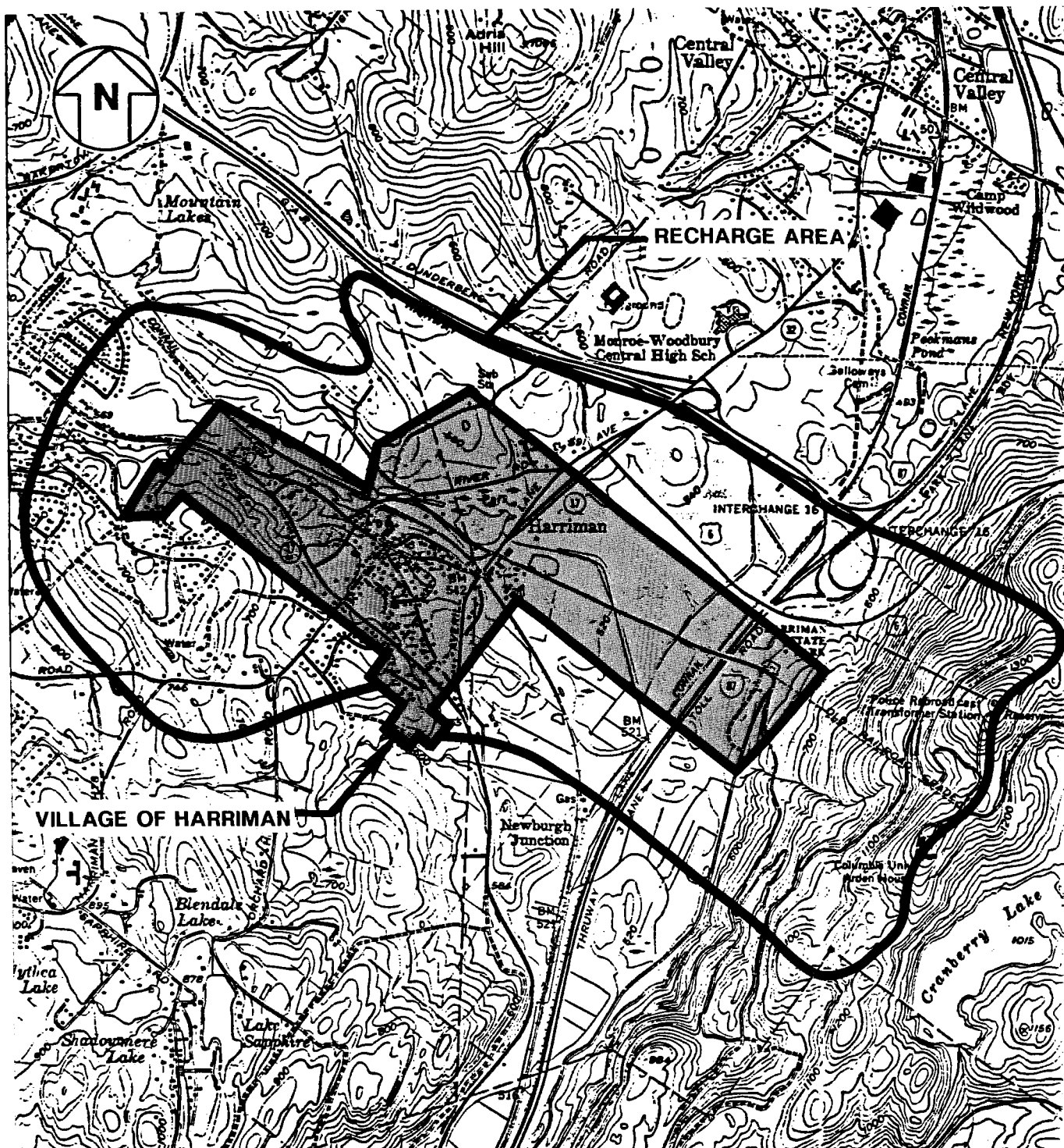
FRACTURE TRACE ANALYSIS

DATE	REVISED	PREPARED BY:
		 <p>LEGGETTE, BRASHEARS & GRAHAM, INC. Professional Ground-Water Consultants 1123 Route 52, Suite 38 Fishkill, NY 12524 914-897-2970</p>
DATE: 4/17/89		FIGURE 5

PERCENT PROBABILITY THAT ANNUAL PRECIPITATION IS GREATER THAN GIVEN AMOUNT




PERCENT PROBABILITY THAT ANNUAL PRECIPITATION IS EQUAL TO OR LESS THAN GIVEN AMOUNT

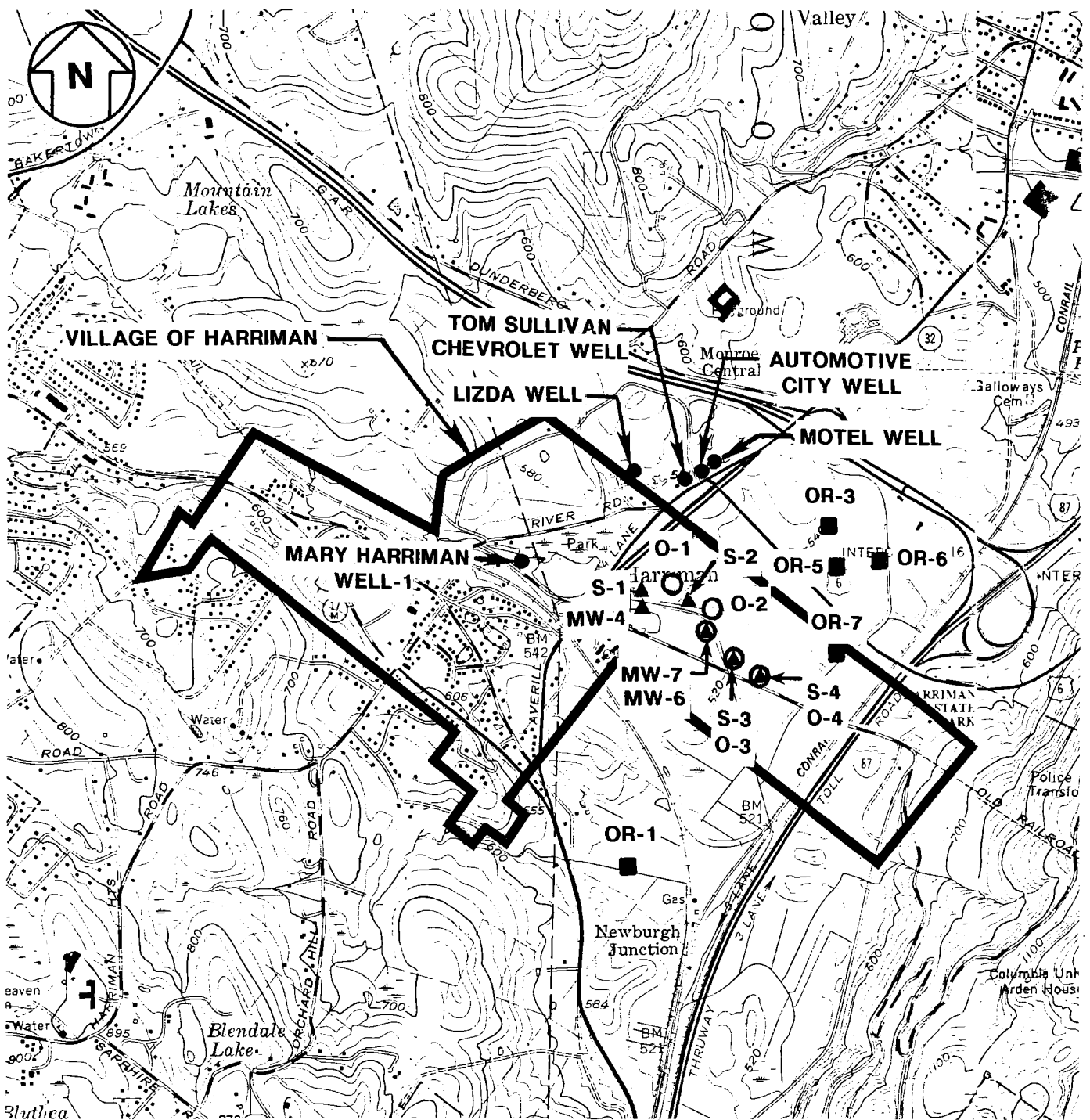


VILLAGE OF HARRIMAN ORANGE COUNTY, NEW YORK

AREA OF RECHARGE TO VILLAGE WELL FIELDS

0 2000
SCALE IN FEET

DATE	REVISED	PREPARED BY:
		 <p>LEGGETTE, BRASHEARS & GRAHAM, INC. Professional Ground-Water Consultants 1123 Route 52, Suite 38 Fishkill, NY 12524 914-897-2970</p>
DATE: 3/29/89		FIGURE 7



SOURCE: CA RICH CONSULTANTS INC.

LEGEND

MONITOR WELLS

- ▲ OVERBURDEN WELL
- BEDROCK WELL

SUPPLY WELLS

- SUPPLY WELL NOT IN SERVICE
- SUPPLY WELL IN SERVICE


0 2000



SCALE IN FEET

VILLAGE OF HARRIMAN ORANGE COUNTY, NEW YORK

MONITORING WELL LOCATIONS FOR NEPERA AND ICC PERIMETER MONITOR WELL SYSTEM

DATE	REVISED	PREPARED BY:
		 <p>LEGGETTE, BRASHEARS & GRAHAM, INC. Professional Ground-Water Consultants 1123 Route 52, Suite 38 Fishkill, NY 12524 914-897-2970</p>
DATE: 4/17/89		FIGURE 8

A P P E N D I X A

Drilling Log

TURNBULL

WELL DRILLING

DRILLING LOG

RECEIVED

APR 17 1989

ALSO

JOB # DRILL RIG # 2

JOB NAME VILLAGE OF HARRIMAN

WELL # MARY HARRIMAN #3

TOWN

DATE STARTED 2/13/89

DATE COMPLETED 2/21/89

HOUR METER START

HOUR METER FINISH

HOURS RIG RAN

CASING DATA

	FT.	IN.
1st LGTH.	20	0
2nd LGTH.	20	0
3rd LGTH.	10	0
4th LGTH.		
5th LGTH.		
6th LGTH.		
TOTAL	50	0

7th LGTH.		
8th LGTH.		
9th LGTH.		
10th LGTH.		
11th LGTH.		
12th LGTH.		
TOTAL		

PLAIN END

DRIVE SHOE

FT. OF 8" IN HOLE 50

WELDED CASING

—
X
50
—

WELL COMPLETION DATA

TOTAL CASING 50 FEET

TOTAL DEPTH 530 FEET

TEST YIELD 40⁺ G.P.M.

WATER LEVEL 15 FEET

BIT SIZE 8" INCHES

RED ROCK TO FEET

TRAP ROCK TO FEET

GRANITE ROCK TO FEET

ROTARY BIT

ROTA TOOL

DIESEL FUEL

QTS. OIL DIESEL

QTS. OIL COMPRESSOR

NOTE: LIST BELOW MISC. DATA
AND RECORD REPAIRS

SAND TO ROCK AT 40'

5 G.P.M. AT 60'; NO

MORE WATER UNTIL 505'

ROCK CHANGES AT 410' & 500'

DRILLER John Turnbull

HELPER

HELPER

A P P E N D I X B
Well Driller's Log and Report

FREEMONT well
 Well at **FITNESS CTR.** In **V. OF HAZRIMIN** County of **ORANGE**
 Name of place City, village or town

Owner **HAZRIMIN/ULLAGE** P.O. Address.....

Depth of well **340** ft. Diameter **6** in. Yield **60** gpm. Was well disinfected? **yes or no**

Amt. of casing above ground **16** in. Below ground **40** ft. Well seal **DRIVE SHOPE & cement grout**

Draw a well diagram in the space provided below and show the depth and type of casing, the well seal, kind and thickness of formations penetrated, water bearing formations, diameter of drill holes with dotted lines and casing(s) with solid lines.

Well Diagram		Depth in ft.	Formations Penetrated		Remarks
Diameter, inches			Kind, thickness and if water bearing		
		Grade			Type of well..... Hammer Drilling method..... Hammer Was well dynamited?..... NO
		20'			Pumping Tests
		25			Details
10	0	25			Static water level, in ft. below grade
10	0	40			10'
6	0	50			Pumping rate in g.p.m.
					Pumping level in ft. below grade
6	0	75			Duration of test, in hrs.
					Water at end of test:
6	0	100			Clear.... Cloudy.... Turbid....
		125'			Recommended depth of pump in well, feet below grade.....
6	0	150			Wells in sand & gravel:
		165'			Sand Eff. size.....mm
6	0	183'			Unif. Coef.....
		200/182			Length of screen.....ft.
		205'			Diam. of screen.....in.
		201			Type of screen.....
6	0	250			Screen openings.....x.....
					Comments: MAIN SUPPLY OF WATER AT 183-187
6	0	300			
6	0	340			

Show cross-section of well & formations penetrated above. Draw a sketch of the property on the back of this sheet locating the well and sewage disposal systems within 200 feet.

Drilling started **2/13/89** Completed **2/15/89**
 Well Driller **Mark Teimbull**
 Signature

Figure 8. WELL DRILLER'S LOG AND REPORT

WELL DATA

Project

HARIMAN / FREEMONT WELL

Project No.

Date

2-16-89

Well No.

1

Recorded by

J.B.D.

Latitude

Longitude

Owner:

VILLAGE OF HARIMAN / TOWN OF DEERNA SP.

Address:

HARIMAN NY.

Well Owner No.:

H.F. 1

Depth to Pump Intake:

Ground Surface
Elevation:

Screened
Formation:

Total Well Depth:

340

Static Water Level:

181-0" TO CASING TOP
10.50 AM

Well Yield:

50-60 GPM

Specific Conductance:

Temperature:

pH:

Lithologic Log, Well Specifications, Well Location, and Remarks:

(Use back of sheet if more space is needed)

* SEE TURN BOLL DRILLING WELL LOG
CASING "STICK UP" IS 14.0"

**GROUND-WATER SUPPLY
WELL PUMPING TEST REPORT
VILLAGE OF HARRIMAN
ORANGE COUNTY, NEW YORK**

Prepared For:

The Village of Harriman

June 1989

LEGGETTE, BRASHEARS & GRAHAM, INC.
Professional Ground-Water Consultants
1123 Route 52, Suite 38
Fishkill, NY 12524

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Mary Harriman Well 3.	2
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Long-Term Yield of MH3.	4
WELL MONITORING PROGRAM.	5
WATER QUALITY.	6
CONCLUSIONS.	6
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TABLE
(at end of report)

Table 1 **Well Data of Monitoring Wells**

FIGURE
(at end of report)

Figure 1 **Well Location Map**

GROUND-WATER SUPPLY
WELL PUMPING TEST REPORT
VILLAGE OF HARRIMAN
ORANGE COUNTY, NEW YORK

SUMMARY

In February of 1989, under the supervision of Leggette, Brashears & Graham, Inc. (LBG), Turnbull Well Drilling (Turnbull) drilled an 8-inch well completed in bedrock. The well was terminated at a depth of 530 feet at which time the well yielded an estimated 40 gpm (gallons per minute). The well is known as Mary Harriman Well 3 (MH3).

From May 31 to June 3, 1989 the Village of Harriman, under the supervision of LBG, conducted a 72-hour pumping test on MH3. The data from the pumping test indicate that MH3 is a reliable well source and could be pumped at rates up to 50 gpm. The well would provide an additional 72,000 gpd (gallons per day) for Village use.

During the test on MH3 an onsite and offsite well monitoring program was conducted. Water levels were measured in ten selected nearby wells. The data indicate the pumping of MH3 at a maximum pumping rate of 50 gpm would not significantly affect water levels and yields of adjacent public supply wells for the Village and other existing wells in the region.

INTRODUCTION

LBG was retained by the Village of Harriman to conduct a 72-hour pumping test on the recently drilled Mary Harriman Well 3. The purpose of the investigation was to determine the maximum yield capacity of MH3 based on the test. Special attention was directed to the long-term potential of the well to provide reliable water supply and to the possibility of water-level interference in adjacent Village public-supply wells and offsite wells located in the region.

Mary Harriman Well 3

In February of 1989, under the supervision of LBG, Turnbull drilled an 8-inch well completed in bedrock. The well is located approximately 5 feet outside the pumphouse for the original Mary Harriman Well 1 (MH1) and MH3 (figure 1). MH3 is located approximately 8 feet from the original inactive MH1 located in the pumphouse and 25 feet from the replacement MH1 presently online.

Well construction details are given on well logs located in Appendix A. The well is completed in the bedrock aquifer consisting of both limestone and gneiss.

During drilling, Turnbull reported the well yielded little water until the drill bit entered a water-bearing zone, at a depth of 505 feet below grade, which produced an estimated 40 gpm (gallons per minute). Drilling was terminated at a depth of 530 feet. The driller's log is in Appendix A.

On February 27, 1989 LBG conducted a preliminary 18-hour pumping test on MH3. The static water level was 16 feet from the top of the measuring point. The well was pumped at the maximum capacity of the temporary pump installed in the well. The well was tested at a rate of 33 gpm which was held for the entire duration of the test. Just prior to shutdown the pumping water level was 96.4 feet from the top of the measur-

ing point, for a total drawdown of 80.4 feet. Although the pumping water level in the well had not stabilized, just prior to shut down the water level appeared to begin to decline at a much slower rate during the last three hours of the test. If the test had continued, the water level would likely have stabilized at some lower depth.

The test on MH3 was conducted to confirm the yield estimate during drilling. In addition, it was necessary to determine if during the pumping of MH3, damaging water-level interference would affect the yield of MH1. The preliminary test was ended prior to obtaining a stabilized water level at the constant rate of 33 gpm. A 72-hour pumping test was scheduled for the near future to determine the actual safe yield of the well. MH1 was monitored during the preliminary 18-hour pumping test. The non-pumping water level in MH1 remained at 10.5 feet from the top of casing prior to and during the entire test conducted on MH3. Data indicate that the sand and gravel aquifer tapped by MH1 is not hydraulically connected with the deep water-bearing fractures in the bedrock tapped by MH3, so that both wells could be pumped simultaneously without serious mutual interference.

May 31 to June 3, 1989 Pumping Test

In May, Doncar, Inc. of Flanders, New Jersey, installed a 20-hp (horsepower) Grundfos submersible pump in MH3 at a depth of 403 feet. The pump intake is set at 405.5 feet. A 1-inch diameter access tube for manual measurements of water-level was installed to a depth of 403 feet. An air line for pressure reading to determine water-level was installed to a depth of 403 feet. The pump shut-off probe was set at 402 feet and the re-set probe at 150 feet.

MH3 was pumped at rates of 40, 45 and 50 gpm. The water-level declined at a moderate rate during the 40-gpm interval, from a pre-test level of 13.6 feet to 121.75 feet in

22.5 hours. The water level appeared to trend toward a generally slow rate of decline during this interval from 1270 to 1350 minutes into the test. At this time the pumping rate was increased to 45 gpm and the water level continued to decline, however, again at a moderate rate of decline. The water level again appeared to trend toward a generally slow rate of decline to a depth of 193.7 feet; at 2010 minutes into the test. At this time the pumping rate was increased to 50 gpm and held at this rate for the remainder of the test. The water level continued to decline, however, the yield and drawdown remained stabilized for at least the last six hours of the test. The final pumping water level was 315.9 feet, resulting in a final drawdown of 302.3 feet.

When the pumping stopped, the water level in MH3 recovered rapidly and was 15.5 feet below the measuring point in less than five hours after shut down. Recovery continued and in approximately 48 hours the water level recovered to a depth of 14.4 feet from the measuring point, only 0.8 feet lower than the pre-test static level of 13.6 feet.

The data from the pumping test and water-level plots are in Appendix B.

Long-Term Yield of MH3

The data from the pumping test indicate that MH3 is a reliable well source and could be pumped at rates up to 50 gpm. The test data indicate that at a rate of 50 gpm, the pumping water-level in three days would likely stabilize at approximately 315 feet below the measuring point. Any additional water-level decline would be minimal due to the very slow stabilized rate of decline, even over the long term. The data from the test indicate that the pumping water-level stabilized at approximately 90.5 feet above the pump intake and 190 feet above the major water-bearing fractures penetrated by the borehole during drilling at 505 feet.

WELL MONITORING PROGRAM

During the May 31 to June 3, 1989 pumping test on MH3, an onsite and offsite well monitoring program was conducted. Water levels were measured in ten selected nearby wells. The wells monitored are shown in figure 1. The data from the monitoring wells and water levels are given in Appendix C.

Table 1 summarizes the available well data on the ten wells monitored.

The purpose of the well monitoring program was to determine if pumping MH3 for 72 hours at maximum pumping rates would significantly affect water level and yield on adjacent public supply wells for the Village and other existing wells in the surrounding region.

Water level data for the Mary Harriman Well 1 and Layne Well 1 show a slow gradual decline in water level resulting from pumping MH3. Water levels generally stabilized at a very slow rate of decline approximately 48 hours into the test. The data indicate a maximum drawdown of only 2.9 feet in Mary Harriman Well 1 and 1.9 feet in Layne Well 1 as a result of pumping MH3 at rates as high as 50 gpm.

The water-level data for the remaining wells, MW10, MW6, Lizda Well, Amato Well 1, Amato Well 2, North Main Well, Freemont Well and Harriman Heights Well 2 indicate no decline in water level resulting from pumping MH3. The water levels in the North Main Well, Lizda Well and Amato Well 2 show some fluctuation caused by pumping. The North Main Well and Lizda Well were on a pumping cycle of approximately 18 to 24 hours daily. The Amato Well 2 was pumped sporadically for domestic use. These wells experienced no loss in yield capacity during the test on MH3. The water-level measurements prior to, during and following the test on MH3 indicate a region water-level decline over an eight-day period from May 26 to June 3, 1989.

WATER QUALITY

Water samples were collected from MH3 near the end of the 72-hour test. The samples were sent to Envirotest Laboratories, in Newburgh, New York. Envirotest is a New York State Department of Health certified laboratory. The water-quality results will likely be available the first week in July.

CONCLUSIONS

Based on the results of the 72-hour pumping test on MH3 and the interference study conducted during the test, LBG draws the following conclusions.

1. Pumping test data for MH3 indicate a maximum yield capacity of 50 gpm. MH3 would provide an additional 72,000 gpd for Village use.

2. Minimal drawdown of less than 3 feet was measured in the Layne Well 1 and Mary Harriman Well 1 at the end of the 72-hour test on MH3. The data for both wells indicate that the water level in each well generally stabilized at a very slow rate of decline by the end of the test. The observed drawdown did not affect the yield capacity of Mary Harriman Well 1 during the test. Layne Well 1 is presently inactive. The pumping of MH3 at a maximum pumping rate of 50 gpm would not significantly affect water level and yield on adjacent public supply wells for the Village and existing wells in the region.

3. The evaluation conducted indicates that MH3 could be pumped simultaneously with the existing public supply wells online for the Village. In addition the data indicate that MH3 could be pumped simultaneously with Layne Well 1 and Freemont Well proposed to be placed online in the near future.

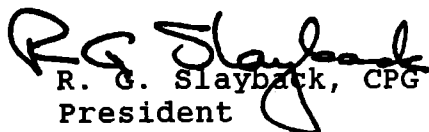
4. No drawdown interference was observed in MW6 or MW10 located on Nepera, Inc. property. Present data indicate that the Nepera, Inc. property is not within the area of drawdown created by MH3.

LEGGETTE, BRASHEARS & GRAHAM, INC.



Thomas P. Cusack
Senior Hydrogeologist

Reviewed by:



R. G. Slayback, CPG
President

gmm
June 19, 1989
vilhar

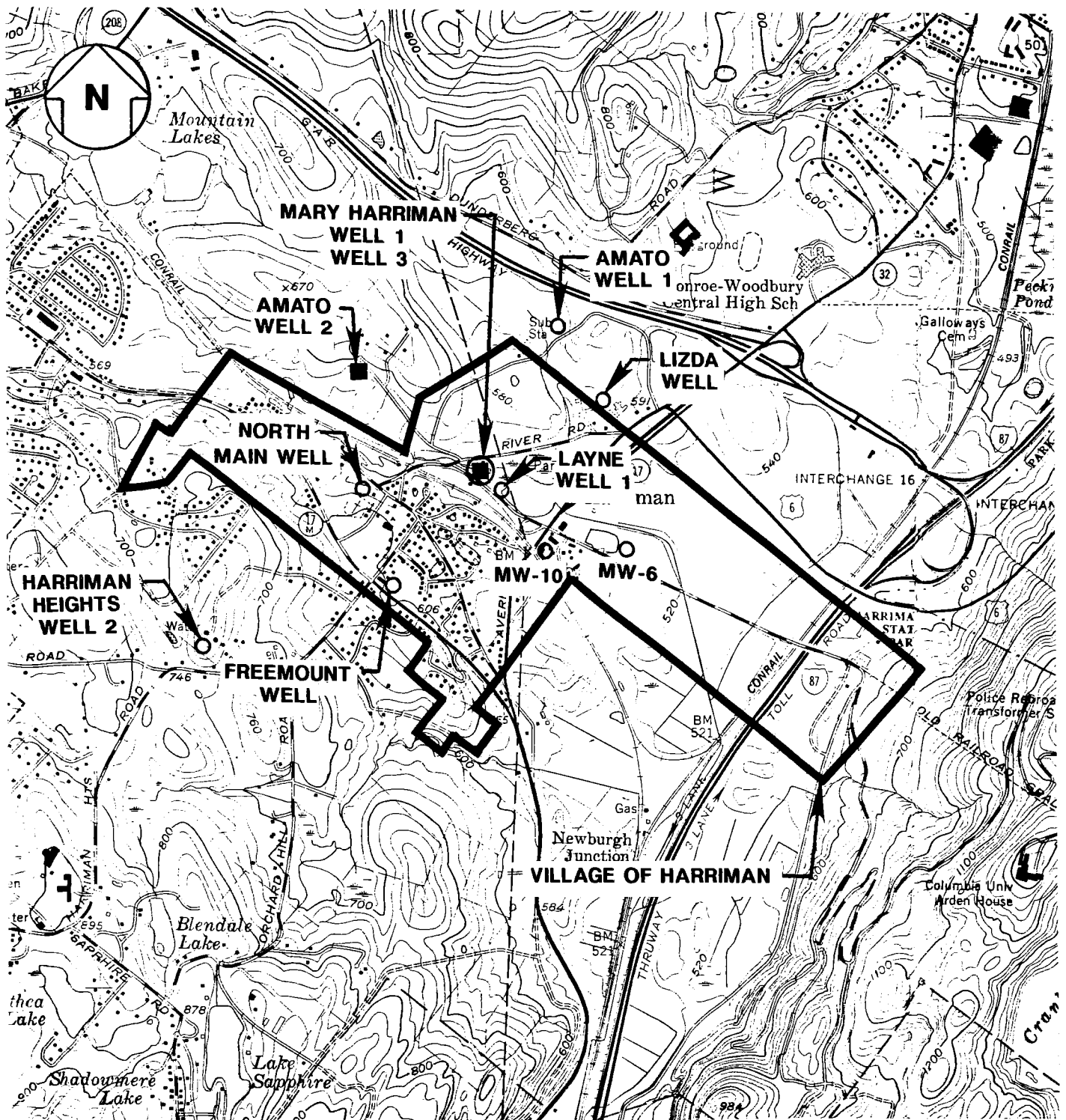
T A B L E

TABLE 1
VILLAGE OF HARRIMAN
ORANGE COUNTY, NEW YORK

Well Data of
Monitoring Wells

Monitoring Well Identification	Well Owner	Well Depth (feet)	Aquifer
MW10	Nepera, Inc.	80	bedrock
MW6	Nepera, Inc.	173	bedrock
Layne Well	Village of Harriman	318	bedrock
Lizda Well	Village of Harriman	350	bedrock
Amato Well 1	Joseph Amato	600	bedrock
Amato Well 2	Joseph Amato	74	sand and gravel
Mary Harriman Well 1	Village of Harriman	52	sand and gravel
North Main Well	Village of Harriman	400	bedrock
Freemont Well	Village of Harriman	340	bedrock
Harriman Heights Well 2	Village of Harriman	400	bedrock

F I G U R E



LEGEND


- WELL COMPLETED IN SAND AND GRAVEL AQUIFER
- WELL COMPLETED IN BEDROCK AQUIFER

0 2000

 SCALE IN FEET

VILLAGE OF HARRIMAN ORANGE COUNTY, NEW YORK

WELL LOCATION MAP

DATE	REVISED	PREPARED BY:
		 LEGGETTE, BRASHEARS & GRAHAM, INC. Professional Ground-Water Consultants 1123 Route 52, Suite 38 Fishkill, NY 12524 914-897-2970
DATE:		FIGURE 1

A P P E N D I X A

TURNBULL

WELL DRILLING

DRILLING LOG

RECEIVED

APR 17 1989

AMC

JOB # _____ DRILL RIG # 2

DATE STARTED 2/13/89

JOB NAME VILLAGE OF HARRIMAN

DATE COMPLETED 2/21/89

WELL # MARY HARRIMAN #3

HOUR METER START _____

TOWN _____

HOUR METER FINISH _____

HOURS RIG RAN _____

CASING DATA

	FT.	IN.
1st LGTH.	20	0
2nd LGTH.	20	0
3rd LGTH.	10	0
4th LGTH.		
5th LGTH.		
6th LGTH.		
TOTAL	50	0

7th LGTH.		
8th LGTH.		
9th LGTH.		
10th LGTH.		
11th LGTH.		
12th LGTH.		
TOTAL		

PLAIN END	-
DRIVE SHOE	X
FT. OF 8" IN HOLE	50
WELDED CASING	-

WELL COMPLETION DATA

TOTAL CASING 50 FEET

ROTARY BIT

TOTAL DEPTH 530 FEET

ROTA TOOL

TEST YIELD 40+ G.P.M.

DIESEL FUEL

WATER LEVEL 15 FEET

QTS. OIL DIESEL

BIT SIZE 8" INCHES

QTS. OIL COMPRESSOR

RED ROCK TO _____ FEET

TRAP ROCK TO _____ FEET

GRANITE ROCK TO _____ FEET

NOTE: LIST BELOW MISC. DATA
AND RECORD REPAIRS

SAND TO ROCK AT 40'
5 G.P.M. AT 60', NO
MORE WATER UNTIL 505'
ROCK CHANGES AT 410' & 500'

DRILLER

HELPER

HELPER

John Turnbull

WELL LOG

LEGGETTE, BRASHEARS & GRAHAM, INC.

CONSULTING GROUND-WATER GEOLOGISTS

72 DANBURY ROAD

WILTON, CT. 06897

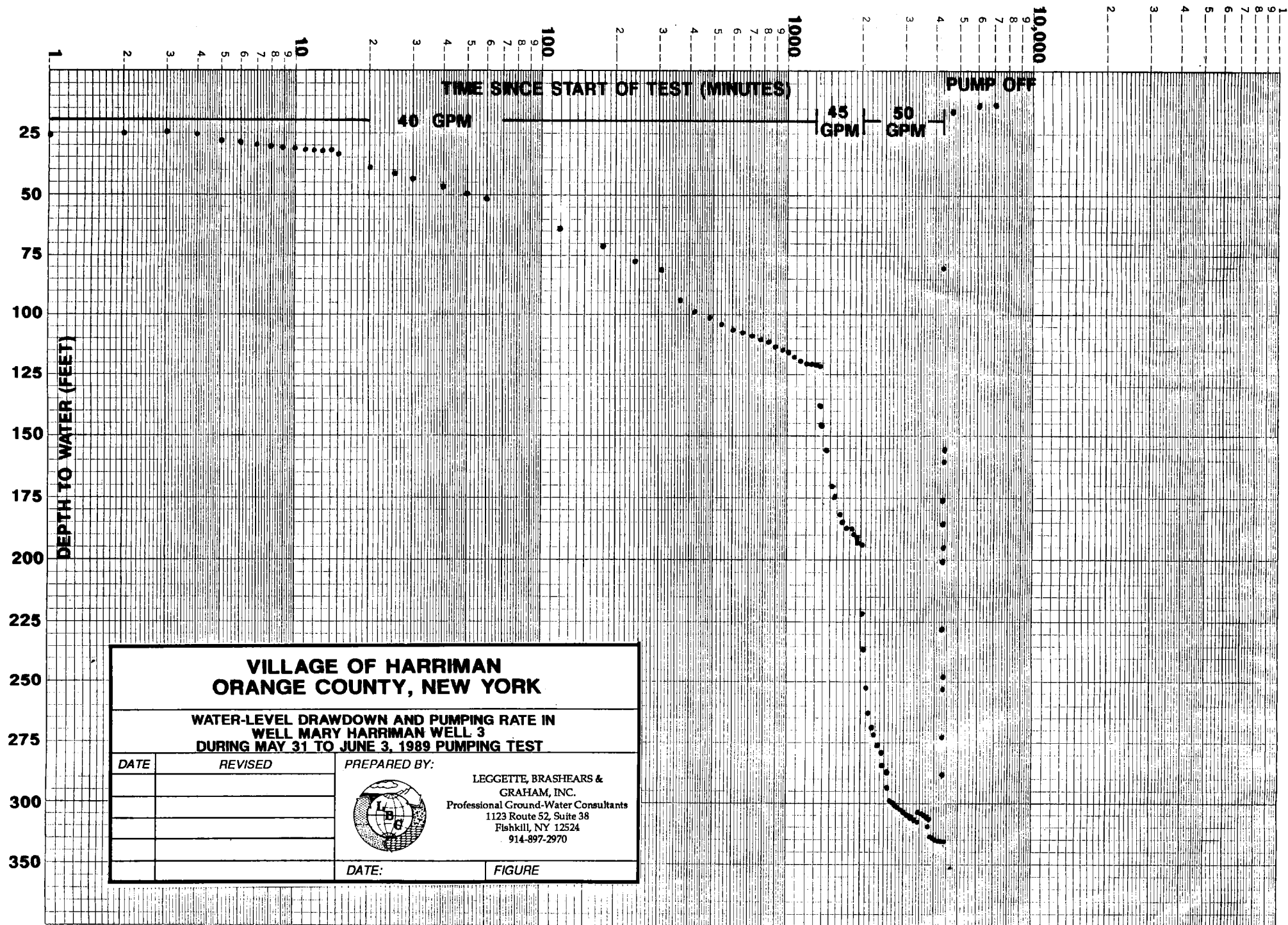
OWNER Village of Harreman

WELL NO. Mary Harreman Well 3

DATE _____ PAGE _____ OF _____ PAGES

	DEPTH IN FEET		DESCRIPTION
	FROM	TO	
LOCATION <u>Village of Harreman</u>			
<u>Mary W. Harreman Memorial Park</u>	0'	40'	Salty clay lenses in contact with
DATE COMPLETED <u>2/21/89</u>			saturated sand some gravel.
DRILLING COMPANY <u>Turnbull Well Drilling</u>	40'	410'	limestone (bedrock)
DRILLING METHOD <u>Air Rotary</u>	410'	530'	gneiss (bedrock)
SAMPLING METHOD <u>wash cutting</u>			
SAMPLES EXAMINED BY <u>Tom Cusack</u>			major water bearing fracture at
REFERENCE POINT <u>grade level</u>			505' → yielded 40+ gpm
ELEVATION OF R.P. _____			
WELL CONSTRUCTION SCREEN TYPE <u>Bedrock</u>			
DIAM. _____ SLOT NO. _____			
SETTING _____			
GRAVEL PACK SIZE _____			
CASING <u>8" diameter ; 50 feet</u>			
DEVELOPMENT <u>air method</u>			
PUMPING TEST DATE <u>May 31 - June 3, 1989</u>			
DURATION <u>72-hour</u>			
STATIC WATER LEVEL _____			
PUMPING WATER LEVEL _____			
YIELD <u>50 gpm</u>			
REMARKS <u>50' casing installed,</u>			
<u>driven 10' into</u>			
<u>competent rock, grout</u>			
<u>Sealed.</u>			

A P P E N D I X B



TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data
MH-3
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Time in minutes since start of test	Remarks
05-31-89	1040	13.60	0	Start up 40 gpm
	1041	26.44	1	
	1042	25.00	2	
	1043	24.90	3	
	1044	26.45	4	
	1045	28.06	5	
	1046	28.90	6	
	1047	29.65	7	
	1048	32.05	8	
	1049	31.05	9	
	1050	31.25	10	
	1051	31.55	11	
	1052	31.56	12	
	1053	32.05	13	
	1054	32.25	14	
	1055	34.15	15	
	1100	39.99	20	
	1105	41.64	25	
	1110	43.10	30	
	1120	46.05	40	
	1130	49.29	50	
	1140	52.13	60	
	1240	64.78	120	
	1340	72.20	180	
	1440	77.20	240	
	1550	86.10	310	
	1640	93.80	370	
	1740	98.10	430	
	1840	101.08	490	
	1940	104.14	550	
	2040	106.06	610	
05-31-89	2140	107.05	670	40 gpm

TABLE
(continued)

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data
MH-3
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Time in minutes since start of test	Remarks
05-31-89	2240	109.34	730	40 gpm
	2340	111.05	790	
06-01-89	0040	112.13	850	40 gpm Q increased to 45 gpm
	0140	114.58	910	
	0240	115.08	970	
	0340	115.68	1030	
	0440	118.00	1090	
	0540	119.27	1150	
	0640	120.15	1210	
	0740	120.88	1270	
	0840	121.50	1330	
	0900	121.75	1350	
	0915	137.41	1365	
	0940	145.38	1390	
	1040	155.19	1450	
	1140	171.75	1510	
	1240	178.08	1570	
	1340	182.87	1630	
	1440	185.00	1690	
	1540	187.01	1750	
	1640	187.48	1810	
	1740	189.58	1870	
	1840	191.80	1930	
	1940	193.45	1990	
	2000	193.75	2010	
	2015	222.20	2025	
	2040	236.65	2050	
	2140	253.95	2110	
	2240	263.17	2170	
	2340	268.55	2230	
06-02-89	0040	272.75	2290	50 gpm

TABLE
(continued)

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data
MH-3
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Time in minutes since start of test	Remarks
06-02-89	0140	275.76	2350	50 gpm
	0240	278.10	2410	
	0340	280.00	2470	
	0440	281.95	2530	
	0540	294.00	2590	
	0640	298.07	2650	
	0740	300.00	2710	
	0840	301.27	2770	
	0940	302.60	2830	
	1040	302.95	2890	
	1140	303.70	2950	
	1250	304.45	3010	
	1340	304.80	3070	
	1440	305.07	3130	
	1540	305.64	3190	
	1640	306.25	3250	
	1740	306.73	3310	
	1840	307.31	3370	
	1940	307.85	3430	
	2040	304.00	3490	
	2140	304.48	3550	
	2240	305.25	3610	
	2340	305.52	3670	
06-03-89	0040	306.40	3730	
	0140	309.17	3790	
	0240	314.15	3850	
	0340	314.90	3910	
	0440	315.10	3970	
	0540	315.50	4030	
06-03-89	0640	315.40	4090	50 gpm
	0740	315.50	4150	

TABLE
(continued)

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data
MH-3
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Time in minutes since start of test	Remarks
06-03-89	0840	315.50	4210	50 gpm
	0940	315.82	4270	
	1040	315.85	4330	Shut down
	1041	--	4331	Recovery
	1042	--	4332	
	1043	287.50	4333	
	1044	273.30	4334	
	1045	253.40	4335	
	1046	248.00	4336	
	1047	--	4337	
	1048	228.00	4338	
	1049	202.30	4339	
	1050	195.40	4340	
	1051	185.95	4341	
	1052	176.95	4342	
	1053	--	4343	
	1054	160.80	4344	
	1055	155.00	4345	
	1110	80.30	4360	
	1725	15.50	4735	
06-04-89	1615	14.50	6105	
06-05-89	0915	14.41	7125	

A P P E N D I X C

TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data
Harriman Heights Well 2
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Remarks
05-26-89	1210	185.21	non-pumping
05-31-89	1530	186.07	non-pumping
06-01-89	0755	186.05	non-pumping
06-02-89	0615	186.00	non-pumping
06-03-89	0950	186.75	non-pumping
06-03-89	1630	186.57	non-pumping

TABLE

**VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK**

**Water-Level Data
Freemont Well
(inactive)
72-Hour Pumping Test
May 31, to June 1, 1989**

Date	Hour	Depth to Water (feet)	Remarks
05-30-89	1500	14.65	
05-31-89	0840	15.00	
05-31-89	1445	15.00	
06-01-89	0705	15.57	
06-01-89	1920	16.60	
06-02-89	0610	16.54	
06-02-89	2000	17.50	
06-03-89	1000	18.00	
06-03-89	1645	20.41	

TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data
Layne Well 1
(inactive)
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Remarks
05-26-89	1625	5.42	
05-27-89	1507	5.50	
05-30-89	1445	5.83	
05-31-89	0837	5.87	
05-31-89	1420	7.06	
06-01-89	0650	7.61	
06-01-89	1905	7.45	
06-02-89	0530	7.90	
06-02-89	1910	7.93	
06-03-89	1025	7.83	
06-03-89	1720	6.75	

TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data
Mary Harriman Well 1
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Remarks
05-26-89	1315	16.25	pump on
05-27-89	1500	16.49	pump on
05-30-89	1413	17.03	pump on
05-31-89	0835	17.10	pump on
05-31-89	1424	19.35	pump on
06-01-89	0615	19.75	pump on
06-01-89	1900	19.81	pump on
06-02-89	0525	19.75	pump on
06-02-89	1905	20.00	pump on
06-03-89	1025	20.00	pump on
06-03-89	1655	18.52	pump on

TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data
Amato Well 1
(inactive)
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Remarks
05-26-89	--	11.50	
05-27-89	1450	11.75	
05-30-89	1420	12.42	
05-31-89	0850	12.67	
05-31-89	1450	12.58	
06-01-89	0655	12.70	
06-01-89	1915	12.56	
06-02-89	0553	12.67	
06-02-89	1920	12.59	
06-03-89	1015	12.95	
06-03-89	1640	12.86	

TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data
Amato Well 2
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Remarks
05-26-89	1305	6.35	
05-27-89	1440	6.73	
05-30-89	1430	6.95	
05-31-89	0900	9.35	
05-31-89	1455	6.99	
06-01-89	0700	7.41	
06-01-89	1925	13.95	
06-02-89	0555	9.68	
06-02-89	1935	7.07	
06-03-89	1010	9.33	
06-03-89	1655	7.35	

TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data
North Main Well
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Remarks
05-26-89	1235	303.80	pump on
05-27-89	1430	301.49	pump on
05-30-89	1445	296.81	pump on
05-31-89	0905	292.25	pump on
05-31-89	1540	296.81	pump on
06-01-89	0715	280.70	pump on
06-01-89	1920	294.56	pump on
06-02-89	0600	246.05	pump on
06-03-89	1005	280.70	pump on
06-03-89	1630	292.25	pump on

TABLE

VILLAGE OF HARRIMAN HARRIMAN, NEW YORK

Water-Level Data
Lizda Well
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Remarks
05-26-89	1245	126.87	pump on
05-27-89	1455	129.18	pump on
05-30-89	1417	129.18	pump on
05-31-89	0845	129.18	pump on
05-31-89	1450	129.18	pump on
06-01-89	0657	129.18	pump on
06-01-89	1920	129.18	pump on
06-02-89	0545	131.49	pump on
06-02-89	1920	131.49	pump on
06-03-89	1020	131.49	pump on
06-03-89	1645	131.49	pump on

TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data
MW 10
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Remarks
05-31-89	1015	2.12	
05-31-89	1605	2.15	
06-01-89	0930	2.15	
06-01-89	1715	2.15	
06-02-89	0730	2.14	
06-02-89	1615	2.14	
06-03-89	0705	2.15	
06-03-89	1130	2.15	
06-05-89	1240	2.14	

TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data
MW 6
72-Hour Pumping Test
May 31, to June 1, 1989

Date	Hour	Depth to Water (feet)	Remarks
05-31-89	1010	5.45	
05-31-89	0420	5.42	
06-01-89	0940	5.45	
06-01-89	1720	5.44	
06-02-89	0735	5.44	
06-02-89	1620	5.44	
06-03-89	0710	5.43	
06-03-89	1135	5.44	
06-05-89	1235	5.44	

**WELL REDEVELOPMENT REPORT
VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK**

Prepared For:

The Village of Harriman

January 1996

LEGGETTE, BRASHEARS & GRAHAM, INC.
Professional Ground-Water & Environmental Services
126 Monroe Turnpike
Trumbull, CT 06611

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FIGURE
(at end of report)

Figure

1

Well Location Map

**WELL REDEVELOPMENT REPORT
VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK**

SUMMARY

Leggette, Brashears & Graham, Inc. (LBG) has evaluated the potential to place the previously abandoned Mary Harriman Well 1 (MH-1A) back in service. The well was reported to yield about 350 gpm (gallons per minute) in 1947 prior to being placed in service. The well was abandoned in 1984 due to a significant loss in well yield and a replacement well (MH-1) was drilled.

Pumping test data for MH-1A indicates a maximum yield of 125 gpm or about 180,000 gpd (gallons per day) for the Village of Harriman's (Village) use, mainly during the peak demand season. The Village had to impose water-use restrictions in the summer of 1995 during drought conditions. The well will supply surplus water during peak season, drought and other emergency conditions.

The pumping of Well MH-1A, at a maximum rate of 125 gpm, would not significantly affect the water levels and yield of adjacent public supply wells for the Village. The evaluation conducted also indicates MH-1A can be pumped simultaneously with other existing public supply wells in service for the Village.

Water-quality data for MH-1A indicates all parameters are below the New York State Department of Health (NYSDOH) Maximum Concentration Level. The water-quality data report a concentration of 2.3 ug/l (micrograms per liter) of trichloroethene (TCE). The reported concentration of TCE does not exceed the NYSDOH drinking water standard of 5 ug/l. Well MH-1 is presently treated for similar concentrations of TCE, consequently, LBG recommends MH-1A be treated prior to use. The existing treatment facility, consisting of an airstripper, may require modification to be able to treat both MH-1A and MH-1. Additional evaluation of treatment capacity of the existing airstripper should be conducted.

A review of the geologic conditions, the temperature readings of the well water and Ramapo River and the microparticulate analysis results indicates there is no direct hydraulic connection between the adjacent Ramapo River and MH-1A, indicating that MH-1A is not under the direct influence of surface water, as defined by the United States Environmental Protection Agency Surface Water Treatment Rule.

INTRODUCTION

In September 1995, the Village of Harriman (Village) authorized Leggette, Brashears & Graham, Inc. (LBG) to further evaluate the potential to redevelop the abandoned Mary Harriman Well 1 (MH-1A) located in the pump house. The well was taken out of service in 1984 due to a substantial decrease in yield capacity. The Mary Harriman well field is shown on figure 1. The Mary Harriman well field includes Well MH-1A, MH-1 and MH-3. Well MH-1A and MH-1 are completed in a sand and gravel aquifer and MH-3 is completed in bedrock.

Original Mary Harriman Well 1 (inactive)

The inactive Mary Harriman Well 1 (MH-1A) was reported to be drilled in 1947. There is no documentation of who actually drilled MH-1A. The well was completed in the sand and gravel aquifer and supplied water to the Village until 1984. The original well was reported to be 34 feet in depth and yielded as high as 350 gpm (gallons per minute). The well was constructed of 12-inch diameter casing with the screen set from 24 to 34 feet. The pumping assembly was still in place and in good working condition until September 1995. The pump was a 40-hp (horsepower) 250-gpm vertical turbine pump. The pump discharged 250 gpm to the 200,000-gallon storage tank on Harriman Heights Road. An initial test on the well reported that, at a pumping rate of 250 gpm, the resultant water-level drawdown was only 13 feet. This would indicate a specific capacity of 19 gpm/foot at a pumping rate of 250 gpm.

In the early 1980's, the yield in MH-1A began to drop off. The Water Superintendent reported that the well was only yielding 80 gpm in 1981. Indications are that the well was never redeveloped since it was placed online in 1947. A letter to the Orange County Department of Health in January 1981 indicated that "the well's intake screen capacity is being reduced because of it becoming clogged or corroded". It was reported that the problem would be remedied with redevelopment of the well.

In 1984, the Village decided to abandon the well and drill a replacement well. Redevelopment of the well was not considered for several reasons; first, because of the age of the well; second, because the well was located in a pump house, not easily accessible; and

finally, the Village felt that it could not be without water from the well for any prolonged period of time, as necessary during a redevelopment program.

In 1984, a replacement well was completed in the sand and gravel aquifer. The replacement well was drilled approximately 10 feet outside the existing pump house from the original MH-1. The replacement well is presently yielding approximately 65 gpm.

On February 22, 1989, approximately five years since MH-1A was abandoned, a short pumping test was conducted on the well. Utilizing the existing 40-hp turbine pump for the well, which was found to be in excellent working condition, the discharge pipe was adapted to flow freely outside the pump house. No valve was installed to allow regulation of flow rate. When the pump was started, the well discharged extremely dark-colored water at a rate estimated between 150 to 180 gpm for approximately 24 seconds before breaking suction. The water level in the well was allowed to recover for 10 minutes at which time pumping was restarted. Again, the well yielded 150 to 180 gpm for approximately 24 seconds. This was repeated several times over the next hour. The discharge eventually became less turbid, appearing to clear. There was no evidence during the test of a collapse of the well screen. Due to the inability to decrease the pumping rate with a valve, LBG was not able to sustain a lower pumping rate for a longer pumping duration.

Present indications are that the well screen on the original MH-1 has not collapsed. The gradual decline in the yield of the well is likely a result of clogging of the water-bearing formation around the well, in the gravel pack and around the well, seriously reducing the capacity. This would result in gradual decline of well yield. If redevelopment is successful, the well could likely be placed back online at a pumping rate between 100 to 200 gpm.

In September 1995, a downhole television inspection of MH-1A indicated the abandoned well is 64 feet deep and constructed of 8-inch diameter casing and well screen. The 8-inch diameter well was installed throughout the 34 feet of 12-inch diameter outside casing. The well screen is approximately 25 feet in length and is in good condition. This is a significant contrast to the original well construction data on file at the Village. It is possible the 12-inch diameter well was drilled deeper and lined with the 8-inch diameter casing and well screen in the 1950's or 1960's, however, no records of this activity are on file. The inspection indicated a louvered bronze well screen. Everdur bronze well screens are resistant to unusually corrosive waters and

would likely last an additional 30 years. Everdur is known to be extremely resistant to acid treatment. A preliminary pump test recently conducted indicates a yield of about 30 gpm from the abandoned well. A copy of the well construction diagram is located in Appendix A.

In November 1995, Wm. Stothoff Company, Inc. redeveloped the well and increased the yield of the abandoned well from 30 gpm to a range estimated to be between 100 gpm and as high as 200 gpm.

November 16 to 17, 1995 - 24-Hour Pumping Test on MH-1A

In November 1995, following redevelopment of a well, Fred Lehman installed a 10-hp submersible pump in MH-1A at a depth of 39 feet. The test was conducted to confirm the safe yield of the well and water quality, in addition to evaluating the possible water-level interference effects from MH-1A on adjacent public supply wells, if any.

A pumping test was conducted from November 16 to 17, 1995. The test on MH-1A was started at 1045 hours on November 16, 1995. The initial pumping rate was 100 gpm for the first 115 minutes of the test. During the 100 gpm pumping rate, the water level declined from a pre-test static water level of 8.2 feet to 25.5 feet at 115 minutes into the test. At the 100 gpm pumping rate, the water level had generally stabilized at a depth of about 25.5 feet, and at this time, the pumping rate was increased to 125 gpm and maintained until 225 minutes into the test. At the 125-gpm pumping rate, the water level slightly declined and trended toward stabilization at a depth of 27.4 feet at 225 minutes into the test. At this time, the pumping rate was again increased to 150 gpm, however, the water level rapidly declined toward the pump intake set at 39 feet. At the 150-gpm pumping rate, the water level declined to a depth of 35.4 feet at 255 minutes into the test and, at this time, the rate was decreased to 125 gpm and maintained for the remainder of the test. At the final 125-gpm pumping rate interval, the water level rapidly rose to a depth of 29.45 feet (285 minutes) and eventually stabilized at 29.8 feet just prior to shutdown of the test. The yield and drawdown were stable for at least the last 20 hours of the test. The total drawdown at the final 125 gpm pumping interval was 21.6 feet. This would indicate a specific capacity of 5.8 gpm/foot at a rate of 125 gpm. The water-level plot and data are located in Appendix B.

Long-Term Yield of MH-1

The data from the November 1995 24-hour pumping test on MH-1A indicate the well is a reliable well and can easily be pumped at rates up to 125 gpm or about 180,000 gpd. At a pumping rate of 125 gpm, the water level would likely stabilize at about 30 feet, about 9 feet above the top of the well screen.

Short-Term Multiple Well Pumping Test of Wells MH-1 and MH-1A

On November 20, 1995, a short-term, 4.5-hour simultaneous multiple-well pumping test was conducted on Wells MH-1 and MH-1A. The test was conducted to confirm Wells MH-1 and MH-1A could be pumped simultaneously.

Well MH-1 was pumped at 65 gpm during the entire test and the water level declined from a pre-test static water level of 6.3 feet to stabilized level of 29.3 feet at the end of the test. Well MH-1A was pumped at 125 gpm during the entire test and the water level declined from a pre-test static water-level reading of 8.4 feet to a depth of 27.58 feet just prior to shutdown. The water-level plot and data are located in Appendix B.

The data indicate Wells MH-1 and MH-1A can be pumped simultaneous at rates up to 125 and 65 gpm, respectively, for a combined yield capacity of about 190 gpm.

WELL MONITORING PROGRAM

During the November 16 through 17, 1995 pumping test on Well MH-1A, an onsite and offsite well monitoring program was conducted. Water levels were measured in two of the closest onsite public supply wells for the Village; Well MH-1, an adjacent sand and gravel well and MH-3, a deep bedrock well. Wells MH-1 and MH-3 are located about 10 feet from Well MH-1A outside the pump house.

In addition, two of the closest offsite wells were monitored; the River Road well, a deep bedrock well which will be developed by the Village in the near future; and the Amato well, an

inactive sand and gravel well. The wells monitored are shown on figure 1. The water-level data from the monitoring wells are included in Appendix C.

The purpose of the well monitoring program was to determine if pumping of MH-1A at maximum pumping rate would significantly affect water levels and yield in adjacent wells.

Both offsite wells, the River Road well and Amato well and MH-3 located onsite, indicate no discernible decline in water levels resulting from pumping MH-1A. The data for MH-1 located approximately 10 feet outside the pump house from MH-1A indicated only 2 feet of drawdown during the test. The minimal drawdown in MH-1 during the individual 24-hour pumping on MH-1 and the data from the short-term multiple well pumping test on MH-1 and MH-1A indicate only minimal water-level interference effects between MH-1 and MH-1A and both wells can be pumped simultaneously without damaging water-level interference effects.

WATER QUALITY

Water samples were collected from MH-1A near the end of the test and analyzed for all parameters under New York State Department of Health (NYSDOH) Sanitary Code Subpart 5-1.1, including radon. In addition, microparticulate analysis (MPA) was conducted because of the close proximity of surface water (Ramapo River).

All constituents were found at levels below permissible limits. The laboratory report and field measurements are located in Appendix D. Chloride and sodium were reported at elevated levels of 214 mg/l (milligrams per liter) and 92.2 mg/l, respectively. The maximum concentration level (MCL) required by the NYSDOH for chloride is 250 mg/l. The maximum recommended concentration for sodium is 270 mg/l.

The water-quality data reports a concentration of 2.3 ug/l (micrograms per liter) of trichloroethene (TCE). The reported concentration of TCE does not exceed the NYSDOH drinking water standard of 5 ug/l. As you are aware, the water supply from MH-1, presently in service, is treated due to the similar concentrations of TCE. The well field is located adjacent to the Gaess site, a New York State Department of Environmental Conservation inactive hazardous waste site. Although the reported concentration of TCE is below the drinking water standard, if placed in service, MH-1A should also be treated considering, historically, the TCE

concentrations from MH-1 have fluctuated and have previously been reported to exceed the drinking water standard of 5 ug/l.

The reported concentration of radon in MH-1A is 526 pCi/l (picoCuries per liter). The United States Environmental Protection Agency (USEPA) may be setting the MCL for radon in the near future. It is expected that the MCL will be between 300 pCi/l and 1,000 pCi/l.

A review of the geologic conditions, the temperature reading of the well water and Ramapo River and the MPA results indicate there is no direct hydraulic connection between the adjacent Ramapo River and MH-1A, indicating that MH-1A is not under the direct influence of surface water as defined by the USEPA Surface Water Treatment Rule.

CONCLUSIONS AND RECOMMENDATIONS

Based on the results of the November 16 to 17, 1995 24-hour pumping test on Well MH-1A, the short-term multiple well test on MH-1 and MH-1A on November 20, 1995 and the interference study conducted during the test, LBG draws the following conclusions.

1. Pumping test data for MH-1A indicates a maximum yield of 125 gpm or about 180,000 gpd for the Village use mainly during the peak demand season. This well can supply surplus water during the peak season, drought and other emergency conditions.

2. The pumping of MH-1A at a maximum rate of 125 gpm would not significantly affect the water levels and yield of adjacent public supply wells for the Village.

3. The evaluation conducted indicates that MH-1A can be pumped simultaneously with the existing public supply wells online for the Village.

4. Water-quality data for MH-1 indicates all parameters are below the NYSDOH MCL. The water-quality data report a concentration of 2.3 ug/l of TCE. The reported concentration of TCE does not exceed the NYSDOH drinking water standard of 5 ug/l. Well MH-1 is presently treated for similar concentrations of TCE, consequently, LBG

recommends Well MH-1A be treated prior to use. The existing treatment facility, consisting of an airstripper, may require modification to be able to treat both Wells MH-1 and MH-1A. Additional evaluation of treatment capacity of the existing airstripper should be conducted.

5. A review of the geologic conditions, the temperature readings of the well water and Ramapo River and the MPA results indicates there is no direct hydraulic connected between the adjacent Ramapo River and MH-1A, indicating that MH-1A is not under the direct influence of surface water, as defined by the USEPA Surface Water Treatment Rule.

LEGGETTE, BRASHEARS & GRAHAM, INC.

Thomas P. Cusack

Thomas P. Cusack, C
Associate

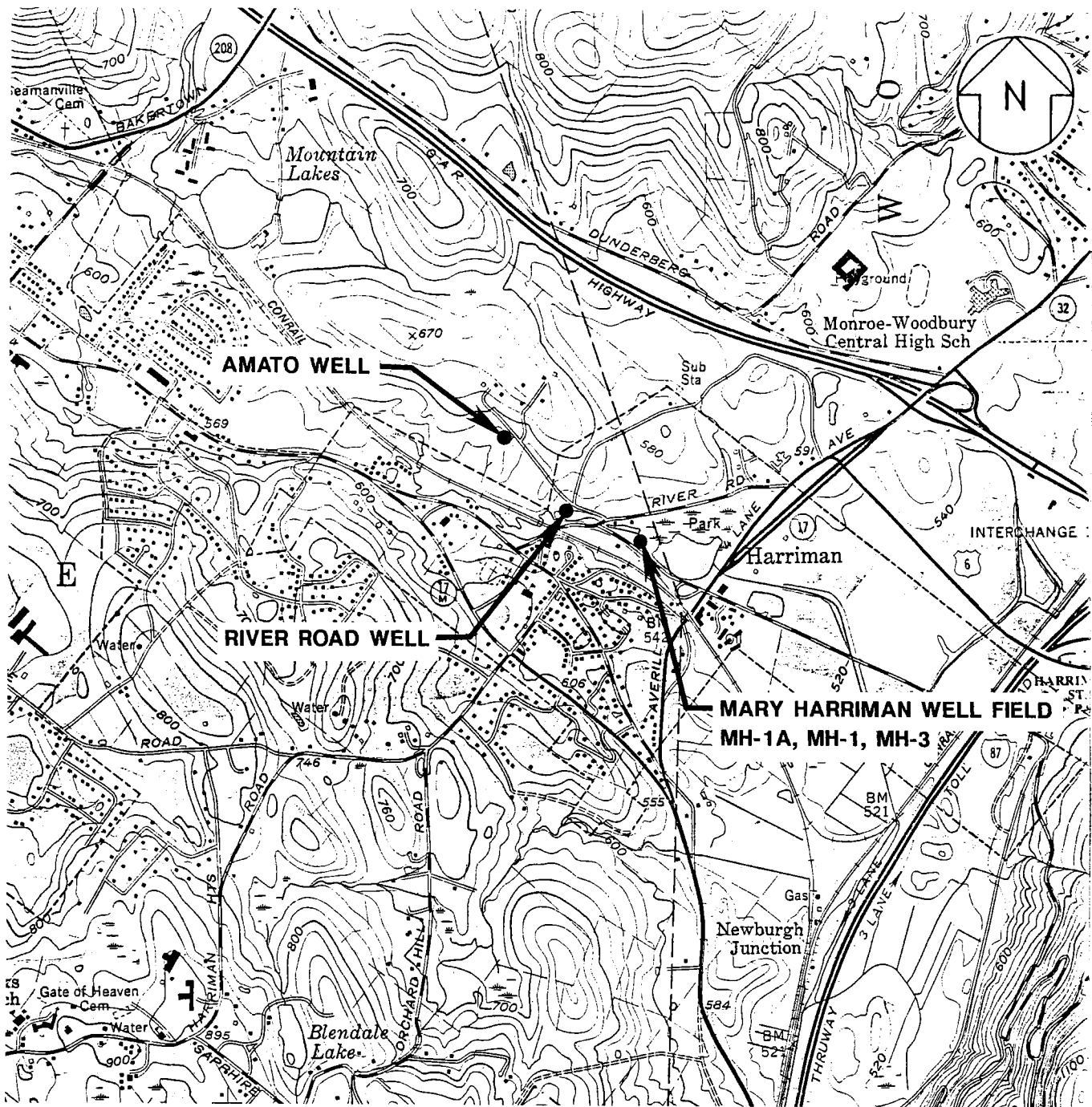


Reviewed by:

R. G. Slayback
R. G. Slayback, CPG
President

skd
January 22, 1996
harriwell.rpt/tpc

FIGURE



SOURCE: USGS TOPOGRAPHIC QUADRANGLE MONROE, NEW YORK.

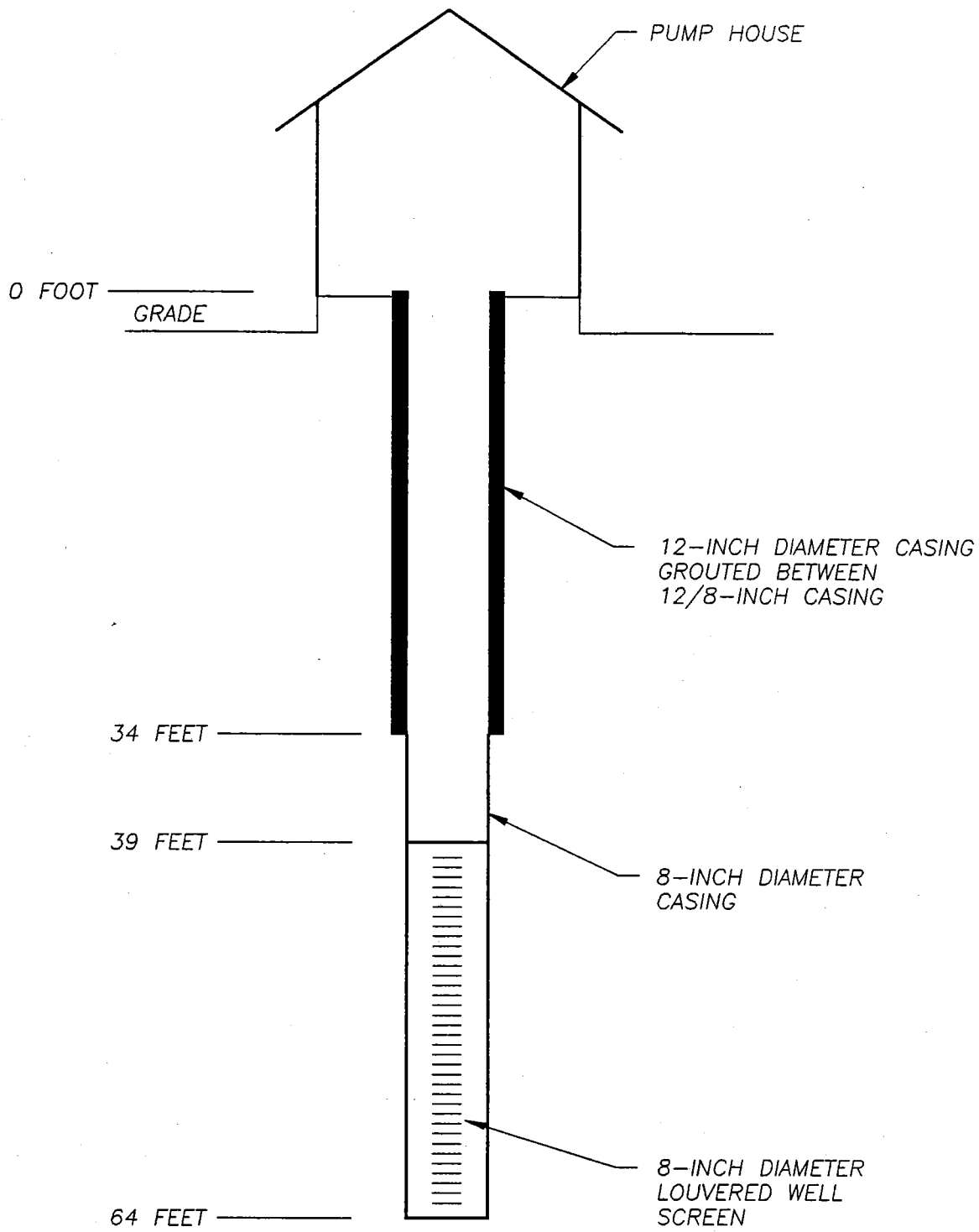
VILLAGE OF HARRIMAN HARRIMAN, NEW YORK

WELL LOCATION MAP

DATE	REVISED	PREPARED BY:
		LEGGETTE, BRASHEARS & GRAHAM, INC.
		Professional Ground-Water & Environmental Services
		126 Monroe Turnpike
		Trumbull, CT 06611
		(203) 452-3100
		DATE: 1/17/96
		FIGURE: 1

0 2000
SCALE IN FEET

APPENDIX A



VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

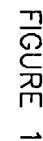
WELL COMPLETION DIAGRAM OF MH-1A

DATE	REVISED	PREPARED BY: LEGGETTE, BRASHEARS & GRAHAM, INC. Professional Ground-Water Consultants 126 Monroe Turnpike Trumbull, CT 06611 (203) 452-3100	
DATE: 1/17/96		MH-1A	

NOT TO SCALE

APPENDIX B

WATER-LEVEL DRAWDOWN AND PUMPING RATE
IN WELL MH-1A DURING THE
NOVEMBER 16-17, 1995 PUMPING TEST



LEGGETTE, BRASHEARS & GRAHAM, INC.

TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Reading During
November 16 through 17, 1995
Pumping Test on MH-1A

Time (military)	Depth to water (feet)	Time (minutes)	Comments
1040	8.22	0	November 16, 1995
1045	--	0	Start up
1046	21.50	1	100 gpm
1048	22.90	3	
1049	23.45	4	
1050	23.90	5	
1055	24.83	10	
1102	25.30	17	
1105	25.33	20	
1112	25.55	27	
1115	25.50	30	
1145	25.60	60	100 gpm
1240	25.52	115	Q increased to 125 gpm
1241	26.97	116	
1340	27.35	175	
1420	27.38	215	125 gpm
1430	27.37	225	Q increased to 150 gpm
1435	35.28	230	150 gpm
1500	35.43	255	Q decreased to 125 gpm
1322	--	277	
1530	29.48	285	
1630	29.48	345	
1730	29.48	405	
1830	29.52	465	
1930	29.52	525	125 gpm

TABLE
(continued)

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Reading During
November 16 through 17, 1995
Pumping Test on MH-1A

Time (military)	Depth to water (feet)	Time (minutes)	Comments
2030	29.51	585	125 gpm
2130	29.52	645	
2230	29.63	705	
2330	29.63	765	
2430	29.64	825	November 17, 1995
0100	29.70	855	
0200	29.71	915	
0300	29.72	975	
0400	29.72	1035	
0500	29.80	1095	
0600	29.81	1155	
0700	29.98	1215	
0800	29.99	1275	
0900	29.98	1335	
0930	--	1365	
1000	29.80	1395	125 gpm
1045	29.84	1440	Pump off
1046	19.41	1441	Recovery
1047	15.75	1442	
1048	13.37	1443	
1049	12.83	1444	
1050	11.30	1445	
1051	10.80	1446	
1052	10.52	1447	

TABLE
(continued)

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

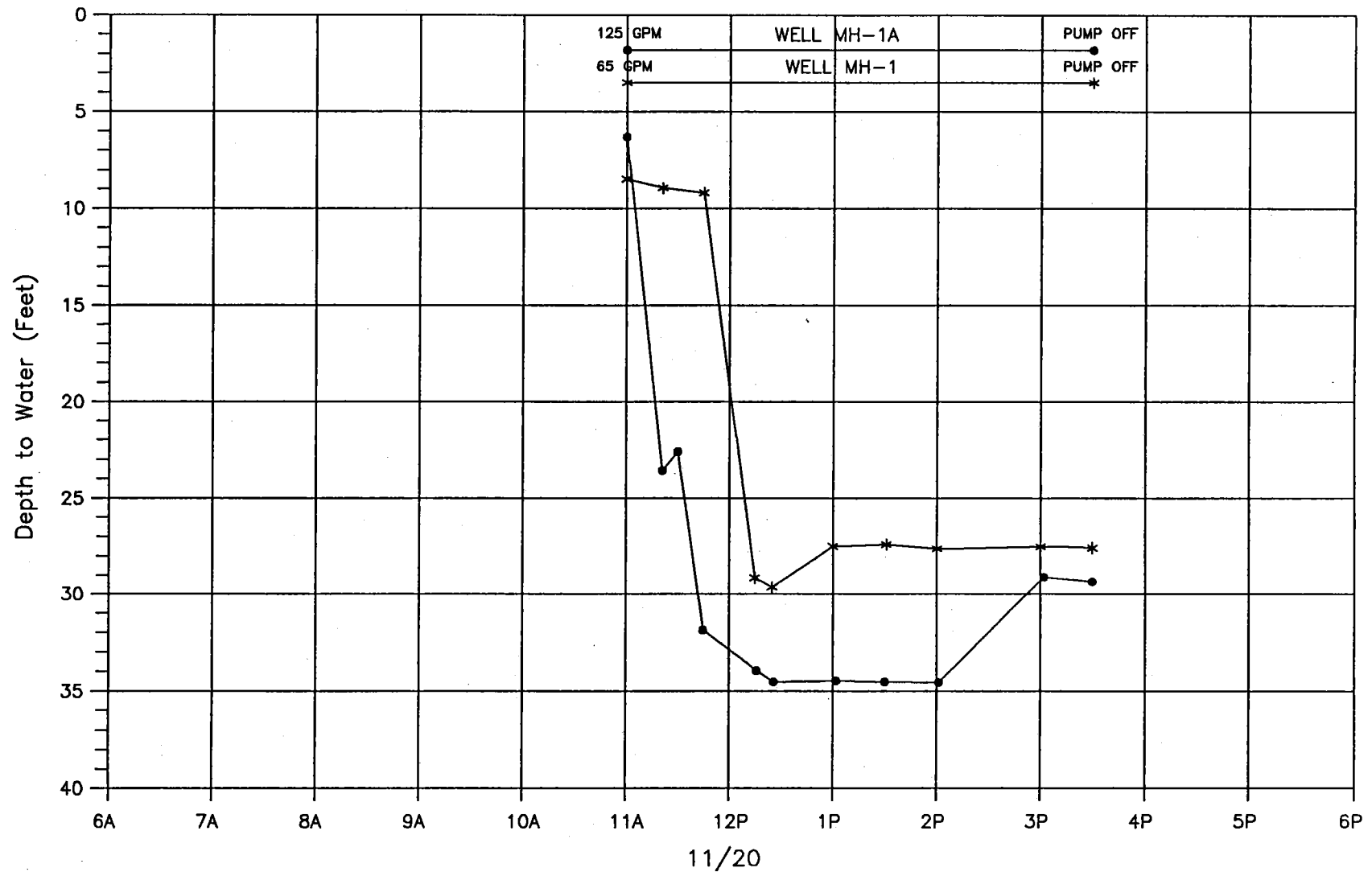
Water-Level Reading During
November 16 through 17, 1995
Pumping Test on MH-1A

Time (military)	Depth to water (feet)	Time (minutes)	Comments
1053	10.28	1448	November 17, 1995 Recovery
1055	10.15	1450	
1100	9.7	1455	
1115	9.15	1470	
1145	9.05	1500	
1245	8.52	1560	

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VILLAGE OF HARRIMAN HARRIMAN, NEW YORK

WATER-LEVEL DRAWDOWN AND PUMPING RATE
IN WELLS MH-1 AND MH-1A DURING THE
NOVEMBER 20, 1995 PUMPING TEST



TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Reading During
Simultaneous Pumping Test on Wells MH-1 and MH-1A
November 20, 1995

Time (military)	Depth to water (feet)		Time (minutes)	Comments
	MH-1*	MH-1A**		
1100	6.30	8.40	0	November 20, 1995 Pump on
1121	17.26 23.56	15.6 8.96	21	
1130	16.27 22.57	--	30	
1145	22.57 31.87	0.10 9.20	45	
1200				
1215	--	20.75 29.15	75	
1216	27.65 33.95	--	76	
1225	--	01.25 29.65	85	
1226	28.22 34.52	--	86	
1300	--	19.1 27.50	120	
1302	28.18 34.48	--	122	
1330	28.22 34.52	--	150	
1331	--	19 27.40	151	
1400	--	19.22 27.62	180	
1401	28.25 34.55	--	181	
1500	--	27.52	240	
1502	29.10	--	242	
1530	29.35	27.58	270	Pump off

* Pumped at 65 gpm during entire test.

** Pumped at 125 gpm during entire test.

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APPENDIX C

TABLE

**VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK**

**Water-Level Reading in Well MH-3
During the November 16 through 17, 1995
Pump Test on Well MH-1A**

Time (military)	Depth to water (feet)	Remarks
1010	13.80	November 16, 1995
1245	12.06	November 16, 1995
1341	11.35	November 16, 1995
1631	9.72	November 16, 1995
2200	6.26	November 16, 1995
0100	5.86	November 17, 1995
0530	5.02	November 17, 1995
0700	3.98	November 17, 1995
1020	2.30	November 17, 1995
1145	2.60	November 17, 1995
1245	2.52	November 17, 1995

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TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Reading in MH-1
During the November 16 through 17, 1995
Pump Test on Well MH-1A

Time (military)	Depth to water (feet)	Remarks
1040	5.86	November 16, 1995
1100	6.75	November 16, 1995
1140	6.85	November 16, 1995
1245	6.98	November 16, 1995
1345	7.07	November 16, 1995
1440	7.41	November 16, 1995
1625	7.38	November 16, 1995
1835	7.41	November 16, 1995
2245	8.31	November 16, 1995
0100	7.82	November 17, 1995
0500	7.90	November 17, 1995
0700	7.98	November 17, 1995
1025 1045	7.86	November 17, 1995
1052	7.06	November 17, 1995
1055	7.09	November 17, 1995
1145 1500	6.90	November 17, 1995
1245 1400	6.52	November 17, 1995

harriwell.tbl/tpc

TABLE

VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK

Water-Level Data During 24-Hour Pumping Test on MH-1A
on the River Road Well from
November 16 through 17, 1995

Date	Hour	Depth to water (feet)	Remarks
11/16/95	1030	15.56	
11/16/95	1420	15.52	
11/16/95	1630	15.95	
11/16/95	1830	15.52	
11/16/95	2100	16.00	
11/17/95	0930	15.59	
11/17/95	1250	15.55	

harriwell.tbl/tpc

TABLE

**VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK**

**Water-Level Data During 24-Hour Pumping Test on MH-1A
on the Amato Well from
November 16 through 17, 1995**

Date	Hour	Depth to water (feet)	Remarks
11/16/95	1032	12.82	
11/16/95	1420	12.71	
11/16/95	1830	12.73	
11/17/95	0810	12.50	
11/17/95	1300	12.51	

harriwell.tbl/tpc

APPENDIX D

TABLE

**VILLAGE OF HARRIMAN
HARRIMAN, NEW YORK**

**Temperature Measurements of Ground Water From
MH-1A and Ramapo River During the
November 16 through 17, 1995 Pumping Test on MH-1A**

Location	Temperature (°F)	Date/Time
Ramapo River	43.5	11/16/95 - 1215 hours
	43.0	11/16/95 - 1900 hours
	43.1	11/17/95 - 0700 hours
	43.3	11/17/95 - 955 hours
EW1	52.4	11/16/95 - 1210 hours
	52.4	11/16/95 - 1855 hours
	52.4	11/17/95 - 0705 hours
	52.4	11/17/95 - 1000 hours

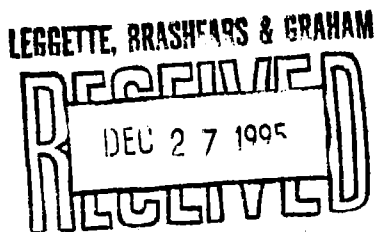
harriwell.tbl/tpc

ORANGE COUNTY LABORATORY
Goshen Turnpike
Walkill Park West
Bloomingburg, NY 12721

ELAP#10510

Friday, December 08, 1995

(914) 733-1557



Page Number : 1

Harriman Water Dept.
1 Church St.

Harriman NY 10926

Client Code : HARRWAT

OCL Sample No : 26172

System Name : Harriman Water Dept.

Date Collected : 11/17/95

Exact Location : AMH-1

Time Collected : 13:45

Submit By : J Brill

Date Received : 11/17/95

Type Descr : 022 SID : 000 Fed ID : 3503531

Analysis		Result	Units	MCL/DL		Method	Lab	Date	By
Total coliform		absence				9223B	10510	11/17/95	HH
Chloride	LT	214	mg/L	250	MCL	4500CL	10510	11/21/95	PC
Color		5.0				2120	10510	11/17/95	VG
Alkalinity		252	mg/L			2320B	10510	11/21/95	PC
pH		7.04				4500H	10510	11/17/95	PC
Corrosivity		-0.241				2330	10510	11/21/95	PC
Cyanide-Total	ND	<0.009	mg/L	0.009	DL	EPA 335.2	11300	11/30/95	
Fluoride		0.12	mg/L			340.2	10510	11/28/95	VG
Calcium hardness		257	mg/L			3500CaD	10510	11/17/95	VG
Nitrate		1.6	mg/L	10.0	MCL	4500NO3D	10510	11/20/95	VG
Odor		none				2150	10510	11/21/95	PC
TDS		645				2540C	10510	11/17/95	PC
Sulfate		45	mg/L	250	MCL	375.4	10510	11/21/95	PC
Turbidity		3.6	ntu			2130	10510	11/17/95	VG
EPA 502.2 - VOC's				0.009	DL		11216	0/0/0000	
Benzene	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
Bromobenzene	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
Bromochloromethane	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
Bromomethane	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
n-Butylbenzene	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
sec-Butylbenzene	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
tert-Butylbenzene	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
Carbon Tetrachloride	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
Chlorobenzene	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
Chloroethane	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
Chloromethane	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
2-Chlorotoluene	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
4-Chlorotoluene	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC
Dibromomethane	ND	<0.5	ug/L	5.0	MCL	EPA 502.2	11216	11/28/95	PC

GT = greater than
LT = less than
ND = not detected

MCL = maximum contaminant level
DL = detection level

David M. Kennedy - Director

Analysis		Result	Units	MCL/DL	Method	Lab	Date	By
1,2-Dichlorobenzene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,3-Dichlorobenzene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,4-Dichlorobenzene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
Dichlorodifluoromethane	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,1-Dichloroethane	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,2-Dichloroethane	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,1-Dichloroethene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
cis-1,2-Dichloroethene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
trans-1,2-Dichloroethene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,2-Dichloropropane	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,3-Dichloropropane	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
2,2-Dichloropropane	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,1-Dichloropropene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
cis-1,3-Dichloropropene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
trans-1,3-Dichloropropene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
Ethylbenzene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
Hexachlorobutadiene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
Isopropylbenzene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
p-Isopropyltoluene (p-cymene)	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
Methylene Chloride	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
n-Propylbenzene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
Styrene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,1,1,2-Tetrachloroethane	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,1,2,2-Tetrachloroethane	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
Tetrachloroethene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
Toluene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,2,3-Trichlorobenzene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,2,4-Trichlorobenzene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,1,1-Trichloroethane	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,1,2-Trichloroethane	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
Trichloroethene		2.3	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
Trichlorofluoromethane	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,2,3-Trichloropropane	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,2,4-Trimethylbenzene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
1,3,5-Trimethylbenzene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
p/m-Xylene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
o-Xylene	ND	<0.5	ug/L	5.0	MCL EPA 502.2	11216	11/28/95	PC
Vinyl Chloride	ND	<0.5	ug/L	2.0	MCL EPA 502.2	11216	11/28/95	PC
Drinking Water Primary Inorganic				2.0	MCL	11216	0/0/0000	
Arsenic	ND	<0.002	mg/L	0.05	MCL EPA 206.3	11216	12/1/95	CEH
Barium		0.025	mg/L	2.0	MCL EPA 200.7	11216	12/1/95	BRJ
Cadmium	ND	<0.002	mg/L	0.005	MCL EPA 200.7	11216	12/1/95	BRJ
Chromium	ND	<0.006	mg/L	0.10	MCL EPA 200.7	11216	12/1/95	BRJ
Lead		0.001	mg/L	0.015	MCL EPA 239.2	11216	11/30/95	BRJ
Mercury	ND	<0.0002	mg/L	0.002	MCL EPA 245.1	11216	11/29/95	CEH
Selenium	ND	<0.002	mg/L	0.01	MCL EPA 270.3	11216	12/6/95	CEH
Silver	ND	<0.010	mg/L	0.05	MCL EPA 200.7	11216	12/1/95	BRJ
Secondary Inorganics(NY)				0.05	MCL	11216	0/0/0000	
Copper		0.006	mg/l	1.0	MCL EPA 200.7	11216	12/1/95	BRJ

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David M. Kennedy - Director

Analysis		Result	Units	MCL/DL		Method	Lab	Date	By
Iron	ND	<0.050	mg/l	0.3	MCL	EPA 200.7	11216	12/1/95	BRJ
Manganese		0.103	mg/L	0.3	MCL	EPA 200.7	11216	12/1/95	BRJ
Sodium		92.2	mg/L	No Limit	MCL	EPA 200.7	11216	12/1/95	BRJ
Zinc		0.022	mg/L	5.0	MCL	EPA 200.7	11216	12/1/95	BRJ
EPA 531.1 - Methylcarbamate Pe				5.0	MCL		11216	0/0/0000	
Aldicarb	ND	<0.0009	mg/L	0.003	MCL	EPA 531.1	11216	11/21/95	IC
Aldicarb Sulfone	ND	<0.0006	mg/L	0.002	MCL	EPA 531.1	11216	11/21/95	IC
Aldicarb Sulfoxide	ND	<0.0004	mg/L	0.004	MCL	EPA 531.1	11216	11/21/95	IC
Carbofuran	ND	<0.0010	mg/L	0.04	MCL	EPA 531.1	11216	11/21/95	IC
Oxamyl (vydate)	ND	<0.0005	mg/L	0.05	MCL	EPA 531.1	11216	11/21/95	IC
Methomyl	ND	<0.0009	mg/L	0.05	MCL	EPA 531.1	11216	11/21/95	IC
3-Hydroxycarbofuran	ND	<0.0010	mg/L	0.05	MCL	EPA 531.1	11216	11/21/95	IC
Carbaryl	ND	<0.0010	mg/L	0.05	MCL	EPA 531.1	11216	11/21/95	IC
EPA 549 - Diquat				0.05	MCL		11216	0/0/0000	
Diquat	ND	<0.0002	mg/L	0.02	MCL	EPA 549	11216	11/30/95	IC
EPA 547 - Glyphosate				0.02	MCL		11216	0/0/0000	
Glyphosate	ND	<0.006	mg/L	0.05	MCL	EPA 547	11216	11/29/95	IC
EPA 548 - Endothall				0.05	MCL		11216	0/0/0000	
Endothall	ND	<5	ug/L	100.0	MCL	EPA 548	11216	11/22/95	
SOC's (EPA 504) - Microextractab				100.0	MCL		11216	0/0/0000	
Ethylene dibromide (1,2-Dibromoe	ND	<0.02	ug/L	0.05	MCL	EPA 504	11216	12/5/95	BL
1,2-Dibromo-3-chloropropane (DB	ND	<0.02	ug/L	0.20	MCL	EPA 504	11216	12/5/95	BL
SOC's(EPA 507)-Nitrogen/Phosp				0.20	MCL		10248	0/0/0000	
Metribuzin	ND	<0.01	mg/L	50.0	MCL	EPA 507	10248	12/1/95	CR
Butachlor	ND	<0.01	mg/L	50.0	MCL	EPA 507	10248	12/1/95	CR
Metolachlor	ND	<0.01	mg/L	50.0	MCL	EPA 507	10248	12/1/95	CR
SOC's (EPA 508) - Organohalide				50.0	MCL		11216	0/0/0000	
Endrin	ND	<0.002	ug/L	0.20	MCL	EPA 508	11216	11/28/95	BL
Propachlor	ND	<0.30	ug/L	50.0	MCL	EPA 508	11216	11/28/95	BL
Toxaphene	ND	<0.80	ug/L	3.00	MCL	EPA 508	11216	11/28/95	BL
PCB - aroclor 1016	ND	<0.20	ug/L			EPA 508	11216	11/28/95	BL
PCB - aroclor 1221	ND	<0.15	ug/L			EPA 508	11216	11/28/95	BL
PCB - aroclor 1232	ND	<0.20	ug/L			EPA 508	11216	11/28/95	BL
PCB - aroclor 1242	ND	<0.25	ug/L			EPA 508	11216	11/28/95	BL
PCB - aroclor 1248	ND	<0.25	ug/L			EPA 508	11216	11/28/95	BL
PCB - aroclor 1254	ND	<0.25	ug/L			EPA 508	11216	11/28/95	BL
PCB - aroclor 1260	ND	<0.35	ug/L			EPA 508	11216	11/28/95	BL
Dieldrin	ND	<0.001	ug/L	5.0	MCL	EPA 508	11216	11/28/95	BL
SOC's (EPA 515.1) - Chlorinated				5.0	MCL		11300	0/0/0000	
2,4-D	ND	<1.5	ug/L	50.0	MCL	EPA 515.1	11300	12/1/95	
Dalapon	ND	<0.5	ug/L	50.0	MCL	EPA 515.1	11300	12/1/95	
Dicamba	ND	<0.2	ug/L	50.0	MCL	EPA 515.1	11300	12/1/95	
Dinoseb	ND	<0.1	ug/L	7.0	MCL	EPA 515.1	11300	12/1/95	
Pentachlorophenol	ND	<0.2	ug/L	1.0	MCL	EPA 515.1	11300	12/1/95	
Pichloram	ND	<0.5	ug/L	1.0	MCL	EPA 515.1	11300	12/1/95	
2,4,5-TP (Silvex)	ND	<0.05	ug/L	10.0	MCL	EPA 515.1	11300	12/1/95	
SOC's (EPA 525.1) NY				10.0	MCL		11216	0/0/0000	
Alachlor	ND	<0.10	ug/L	50.0	MCL	EPA 525.1	11216	11/29/95	
Atrazine	ND	<0.10	ug/L	3.0	MCL	EPA 525.1	11216	11/29/95	

GT = greater than
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DL = detection level

David M. Kennedy - Director

ORANGE COUNTY LABORATORY
Goshen Turnpike
Wallkill Park West
Bloomingburg, NY 12721

ELAP#10510

Friday, December 08, 1995

(914) 733-1557

Page Number : 4

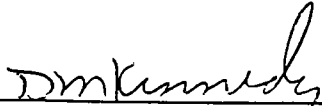
Analysis		Result	Units	MCL/DL		Method	Lab	Date	By
Simazine	ND	<0.10	ug/L	4.0	MCL	EPA 525.1	11216	11/29/95	
Benzo(a)pyrene	ND	<0.04	ug/L	0.2	MCL	EPA 525.1	11216	11/29/95	
Di(2-ethylhexyl) adipate	ND	<0.20	ug/L	50.0	MCL	EPA 525.1	11216	11/29/95	
Di(2-ethylhexyl) phthalate	ND	<0.20	ug/L	6.0	MCL	EPA 525.1	11216	11/29/95	
Hexachlorobenzene	ND	<0.10	ug/L	1.0	MCL	EPA 525.1	11216	11/29/95	
Hexachlorocyclopentadiene	ND	<0.10	ug/L	5.0	MCL	EPA 525.1	11216	11/29/95	
Aldrin	ND	<0.10	ug/L	5.0	MCL	EPA 525.1	11216	11/29/95	
Chlordane (Total)	ND	<0.10	ug/L	2.0	MCL	EPA 525.1	11216	11/29/95	
Heptachlor	ND	<0.05	ug/L	0.4	MCL	EPA 525.1	11216	11/29/95	
Methoxychlor	ND	<0.20	ug/L	10.0	MCL	EPA 525.1	11216	11/29/95	
Lindane	ND	<0.10	ug/L	0.2	MCL	EPA 525.1	11216	11/29/95	
Heptachlor Epoxide	ND	<0.10	ug/L	0.2	MCL	EPA 525.1	11216	11/29/95	

Remarks : Passes NYSDOH drinking water standard

Copies to:

GT = greater than
LT = less than
ND = not detected

MCL = maximum contaminant level
DL = detection level


David M. Kennedy - Director



Hazen Research, Inc.
4601 Indiana St. • Golden, Colo. 80403
Tel: (303) 279-4501 • Telex 45-860
FAX: (303) 278-1528

DATE December 15, 1995
HRI PROJECT 002-62F
HRI SERIES NO. K399/95
DATE RECD. 11/21/95
CUST P.O.# None Rec'd

Orange County Laboratory
Goshen Turnpike
Wallkill Park West
Bloomingburg, NY 12721


REPORT OF ANALYSIS

SAMPLE NO. K399/95-1

SAMPLE IDENTIFICATION: 26172 AMH-1
11/17/95 @ 0930

PARAMETER	RESULT	DETECTION LIMIT	METHOD	ANALYSIS DATE	ANALYST
Gross Alpha(\pm Precision*), pCi/l (T)	4.7(\pm 4.9)	1.6	EPA 900.0	12/12/95 @ 1445	LD
Gross Beta(\pm Precision*), pCi/l (T)	1.7(\pm 5.7)	7.9	EPA 900.0	12/12/95 @ 1445	LD
Radium 226(\pm Precision*), pCi/l (T)	0.6(\pm 0.6)	0.5	SM 705 Modified	11/30/95 @ 0815	RO
Radium 228(\pm Precision*), pCi/l (T)	0.0(\pm 0.8)	1.3	Ra-05	11/27/95 @ 1105	LD
Radon 222(\pm Precision*), pCi/l (T)	526(\pm 80)	127	EPA 600/2-87/082 App. B	11/22/95 @ 1120	EdF

By:


Robert Rostad
Laboratory Manager

CODES:

(T)=Total (D)=Dissolved
(S)=Suspended (R)=Recoverable
(PD)=Potentially Dissolved
<=Less Than

*Variability of the radioactive disintegration process (counting error) at the 95% confidence level, 1.96 x sigma.

Certification Authority Lab ID's:

US EPA Region VIII - CG: CT - PH-0152; KS - E-265; KY - 90076; NH - 232895-A; NY ELAP - 11417.

REPORT: PARTICULATES, GIARDIA, AND CRYPTOSPORIDIUM



ENVIRONMENTAL ASSOCIATES, LTD.
1185 E. Main St. Bradford, PA 16701
(814) 368-3990 Fax (814) 368-7915

Filter ID: 5227 Client: Village of Harriman

Station/Body of water: AMH-1 Harriman, NY

RECEIPT OF FILTER:

Date Received: 11/18/95 # of filters: 1 Type: _____ Carrier: Federal Express

COLLECTION:

Collector: TPC Date collected: 11/17/95
Temperature: °F Turbidity: _____
Water Type: Drilled Well

FILTER PROCESSING

Color of water around filter: tan Total volume of sediment: 0.35 ml
Filter color: tan Volume of sediment/100 gallons: 0.03 ml
Color of sediment: brown IFA equivalent gallon volume examined: _____
gallons filtered: 1041 Phase equivalent gallon volume examined: 57

GIARDIA/CRYPTOSPORIDIUM # Observed Calc. #/100 Gallons

Giardia cyst confirmed:	<u>0</u>	<u>0</u>
Giardia cyst presumptive:	<u>0</u>	<u>0</u>
Cryptosporidium oocyst confirmed:	<u>0</u>	<u>0</u>
Cryptosporidium oocyst presumptive:	<u>0</u>	<u>0</u>

ANALYSIS OF PARTICULATES:

key = (EH) - extremely heavy [$>20/\text{field}$ @ 100X]
(M) - moderate [$4-9/\text{field}$ @ 100X]

(H) - heavy [$10-20/\text{field}$ @ 100X]
(R) - rare [$<1-3/\text{field}$ @ 100X] (NF) - none found

PARTICULATE DEBRIS

	Quantity	Description
Large part. 5 μm & larger	<u>EH</u>	<u>fine silt & sand, clumped</u>
Small part. up to 5 μm	<u>EH</u>	<u>fine brown & amorphous</u>
Plant debris	<u>NF</u>	

PROTOZOANS

	Quantity	Description
Other Coccidia	<u>NF</u>	
Other protozoans	<u>NF</u>	

OTHER ORGANISMS

Nematodes	<u>NF</u>	
Nematode eggs	<u>NF</u>	
Rotifers	<u>NF</u>	
Crustaceans	<u>NF</u>	
Crustacean eggs	<u>NF</u>	
Insects	<u>NF</u>	
Other	<u>NF</u>	

ALGAE

Green Algae	<u>NF</u>	
Diatoms	<u>NF</u>	
Blue-Green Algae	<u>NF</u>	
Flagellated Algae	<u>NF</u>	

COMMENTS:

Due to the nature of the sediment the equivalent of 57 gal. was examined. No biological materials were observed. Based upon microscopic particulate analysis and the proposed EPA risk factors associated with bio-indicators there is a low risk of surface contamination (EPA risk factors= 0 low risk).

CALCULATED VALUES

Total algae	<u>----</u>	% Sediment Reduction	<u>----</u>
Log removal algae	<u>----</u>	Filtration performance	<u>----</u>

REPORT REVIEWED BY:

Jessica H. Bortis

DATE: December 5, 1995

EPA Relative Surface Water Risk Factors

Client: Village of Harriman
 Water Source: AMH-1 Harriman, NY
 Lab ID#: 5227
 Date: 11/17/95

Primary Particulates	#/100 gallon	Relative Frequency	Relative Risk Factor	Comments
Giardia (confirmed)	0	NF	0	
Coccidia (confirmed)	0	NF	0	
Diatoms (with chloroplasts)	0	NF	0	
Other Algae (with chloroplasts)	0	NF	0	
Insects/larvae	0	NF	0	
Rotifers	0	NF	0	
Plant Debris (with chlorophyll)	0	NF	0	
EPA Relative Risk = 0			Low Risk	

Secondary Particulates			
Nematodes	0	NF	
Crustaceans	0	NF	
Amoeba	0	NF	
Non-photo.flagellates & ciliates	0	NF	
Photosynthetic flagellates	0	NF	
Other:	0	NF	

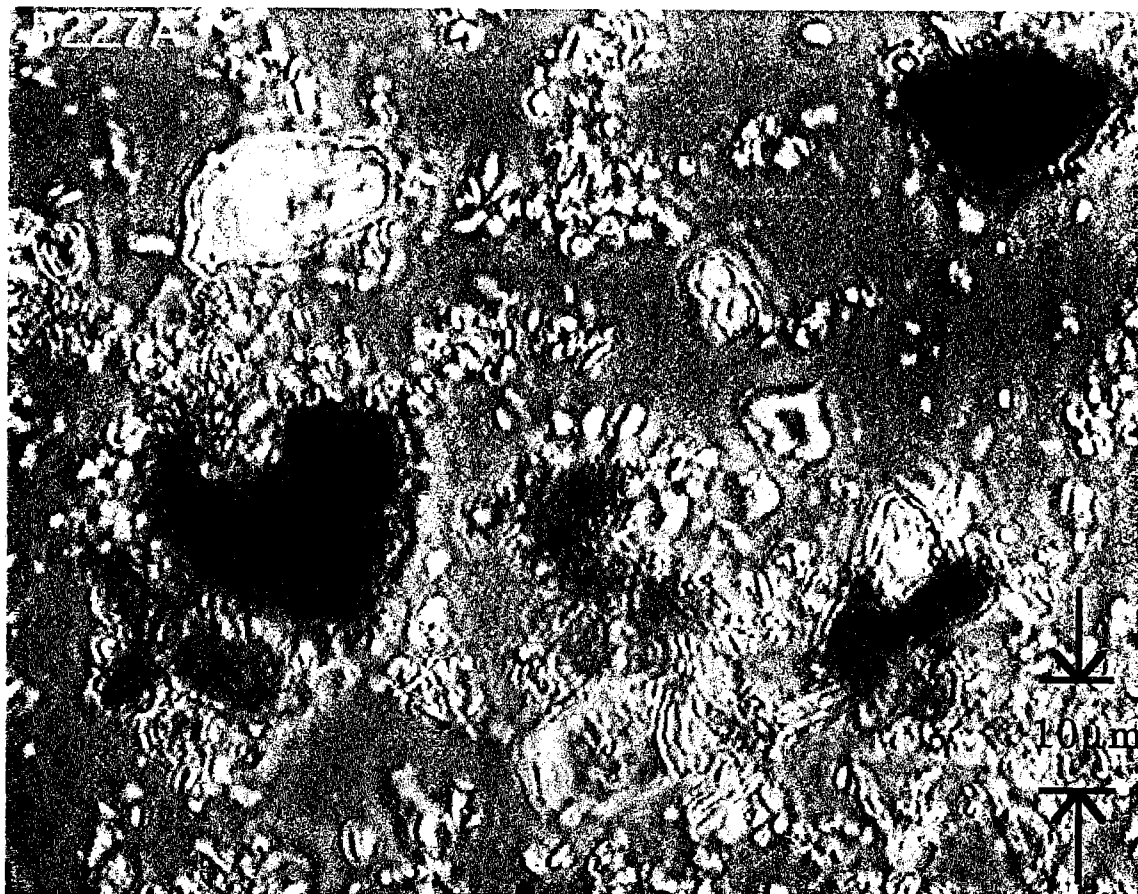
COMMENTS: Due to the nature of the sediment the equivalent of 57 gal. was examined. No biological materials were observed. Based upon microscopic particulate analysis and the proposed EPA risk factors associated with bio-indicators there is a low risk of surface contamination (EPA risk factors= 0 low risk).

REFERENCE: Consensus Method for Determining Groundwaters Under the Direct Influence of Surface Water Using Microscopic Particulate Analysis (MPA) USEPA Manchester Environmental Laboratory, EPA 910/9-92-029, October 1992.

Report reviewed: *Joselyn H. Bontros* Date: *December 5, 1995*

Environmental Associates, Ltd.

L072692



5227A Typical sediment

400x

LEGGETTE, BRASHEARS & GRAHAM, INC.

PROFESSIONAL GROUNDWATER AND ENVIRONMENTAL ENGINEERING SERVICES

4 RESEARCH DRIVE, SUITE 204
SHELTON, CT 06484
(203) 929-8555
FAX (203) 926-9140
www.lbgweb.com

February 14, 2017

Mr. Steven Welle
Mayor
Village of Harriman
1 Church Street
Harriman, NY 10926

RE: Mary Harriman Park Well Field
January 2017 Sodium and Chloride Sampling

Dear Mr. Welle:

Groundwater samples were collected by Leggette, Brashears & Graham, Inc. (LBG) from the Village of Harriman's Mary Harriman Park (MHP) monitoring wells and Production Wells MH-1A and MH-3R on January 6, 2017. This sampling event was completed as part of the groundwater sampling program that has been conducted at MHP over the last three years. No surface-water samples were collected from the Ramapo River as part of the January 6, 2017 sampling event.

Monitor Wells

Monitoring Wells MHP-MW-1S, 2S, 2D, 3S, 3D and 4S were installed at MHP in February 2007 in an effort to determine the source of the elevated sodium and chloride concentrations that had been detected in routine samples collected from MHP Production Wells MH-1, MH-1A and MH-3R. The monitoring well designations of "S" or "D" indicate whether the screen setting in the monitoring well is placed in the shallow or deeper portion of the stratified-drift aquifer.

Monitoring well MHP-MW-5 was installed in 2004 as part of a program to monitor the effects of de-watering taking place at the nearby wastewater treatment plant. Wells MW-6, 7, 8 and 9 are 2 ½-inch diameter test wells located behind the pump house fence in the park. The MHP monitoring well locations are shown on figure 1 and a summary of the available monitoring well construction information and groundwater elevation measurements collected during the January 2017 sampling event are included on table 1.

Sample Collection

Groundwater samples were collected from monitoring wells MW-1S, 2S, 2D, 3S, 3D, 4S and 5, as well as Production Wells MH-1A and MH-3R during the January 6, 2017 sampling event. No samples were collected from Production Well MH-1 during the sampling event because the well has been taken out of service.

Water samples were collected from the monitoring wells following the removal of a minimum of three volumes of water to ensure the samples were representative of the groundwater in the aquifer. The volumes of water were removed using a submersible pump and/or hand bailed using a disposable polyethylene bailer. The samples from the Production Wells were collected from sample taps inside the pump house with the assistance of a representative from the Village of Harriman's Water Department.

The water samples were submitted Envirotest Laboratories, Inc. for analysis for sodium and chloride. A copy of the laboratory report for the groundwater samples collected is included in Appendix I.

Groundwater Quality

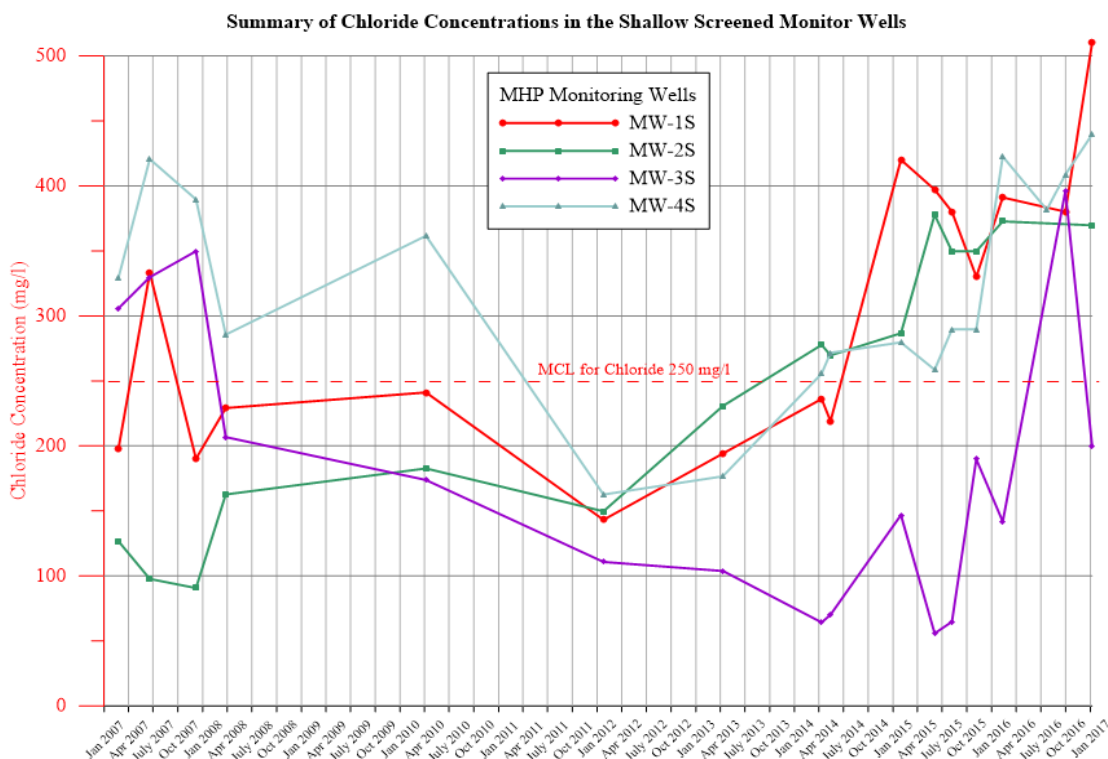
Table 2 contains a summary of the sodium and chloride water-quality results for the MHP monitoring wells and Production Wells from 2007 to the present. Individual graphs showing the sodium and chloride concentration changes over time for the monitoring wells and Production Wells are included in Appendix II and Appendix III, respectively.

Concentrations of chloride in the MHP monitoring wells during the January 2017 sampling event ranged from 200 mg/l (milligrams per liter) to 510 mg/l. The highest chloride concentration of 510 mg/l was detected in monitoring well MW-1S. Chloride concentrations in all of the monitoring wells except MW-3S and MW-5 exceeded the New York State Department of Health (NYSDOH) drinking water standard maximum contaminant level (MCL) for chloride of 250 mg/l.

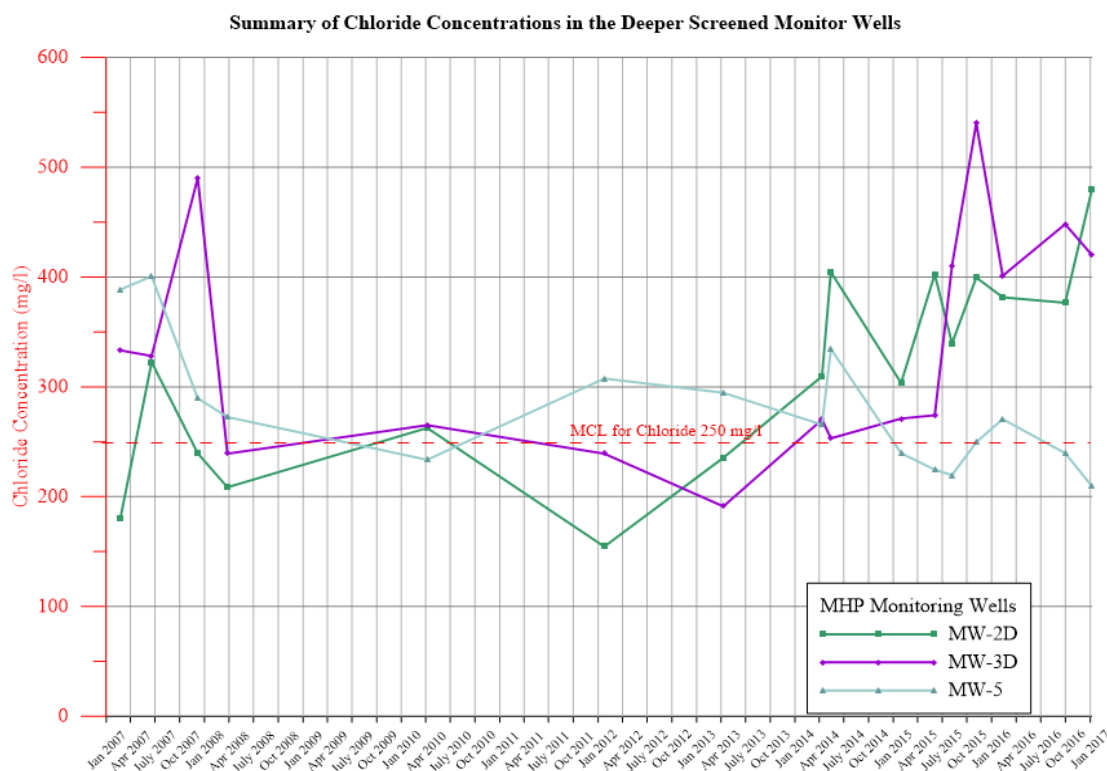
Concentrations of sodium in the MHP monitoring wells in January 2017 ranged from 121 mg/l to 263 mg/l. The highest reported sodium concentration of 263 mg/l occurred in monitoring well MW-4S. Currently, the NYSDOH does not have an MCL established for sodium; however, the maximum recommended concentration is 270 mg/l. None of the onsite wells exceeded the maximum recommended concentration for sodium during this sampling

event. However, water containing more than 20 mg/l of sodium is not recommended for drinking by people on severely sodium restricted diets and this threshold of 20 mg/l was exceeded in all of the monitoring wells. The distribution of sodium and chloride concentrations in the onsite wells during the January 2017 sampling event is shown on figure 1.

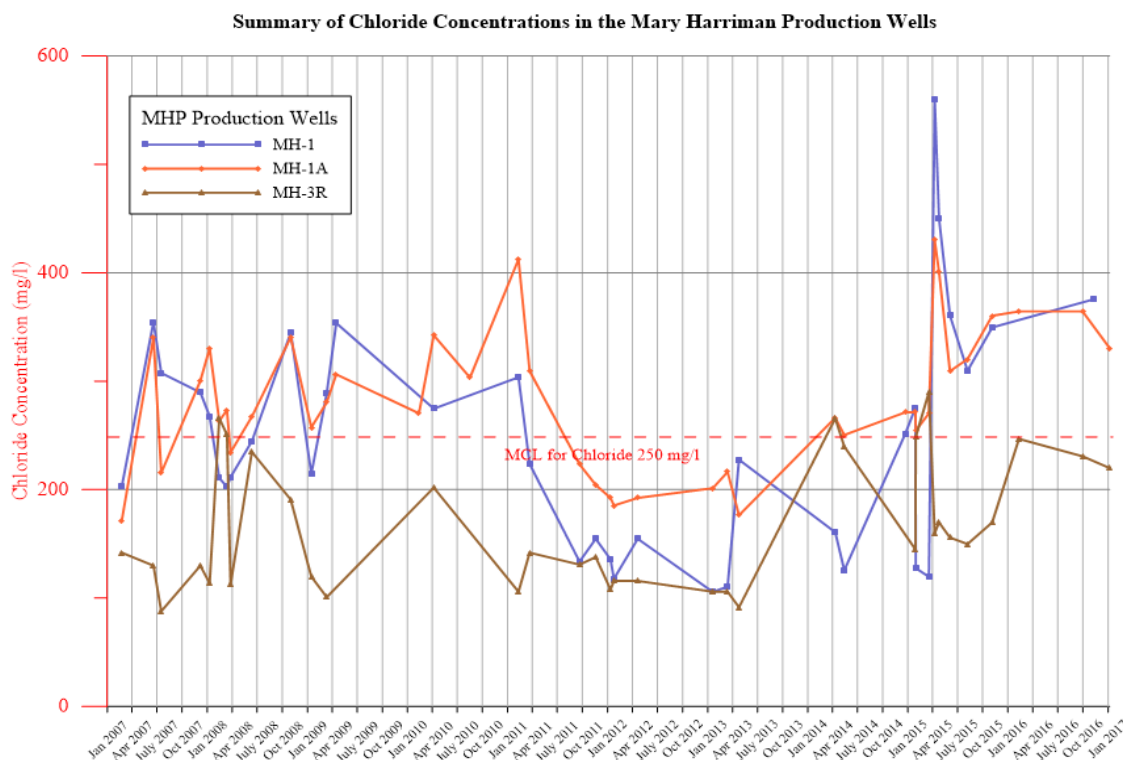
Below is a graph showing the chloride concentrations from all of the onsite monitoring wells screened in the shallow aquifer formation. The graph for the shallow screened monitoring wells shows an overall increase in concentrations of chloride in the shallow aquifer at the well field beginning in 2012.



The chloride concentrations from the monitoring wells screened in the deeper portion of the stratified-drift aquifer at the well field are provided in the graph below. The deeper screened monitoring wells also show an overall trend of increasing chloride concentrations in the groundwater at the well field beginning in 2012. The only monitoring well which has not shown a similar increasing trend is MW-5.

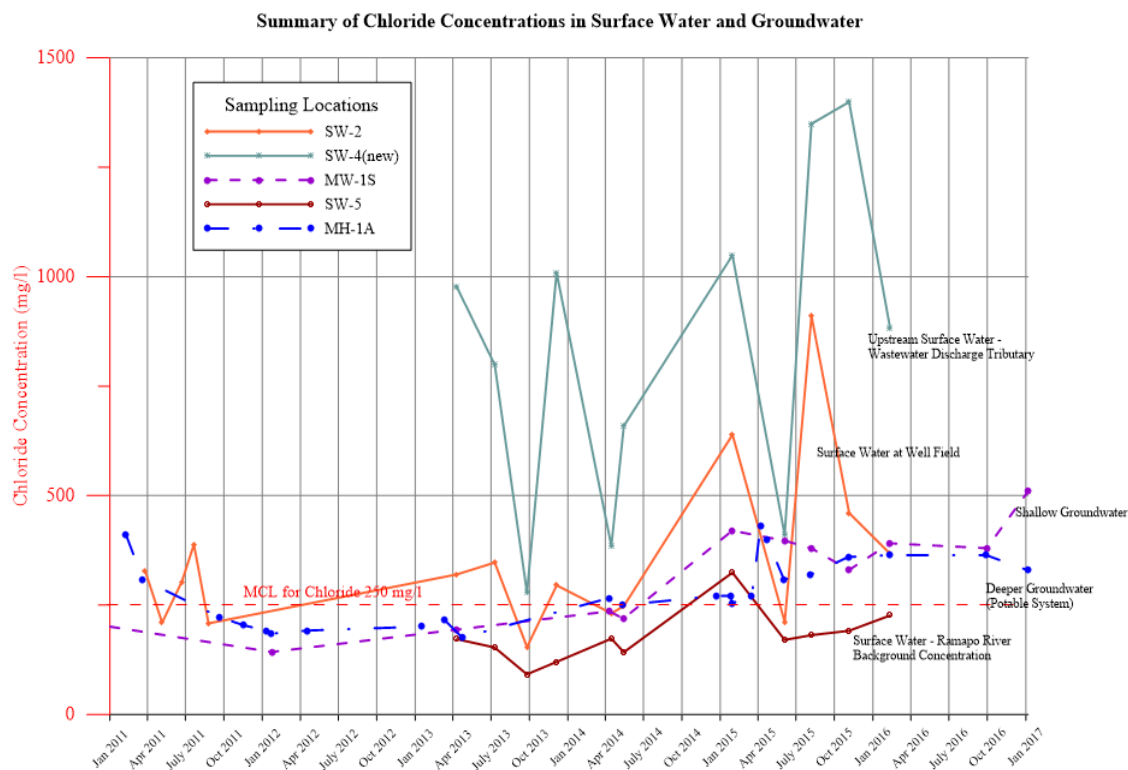


Individual graphs for the sodium and chloride concentrations in the Production Wells are included in Appendix III. In 2011, Wells MH-1, MH-1A and MH-3R reported a decrease in chloride concentrations as a result of dilution of the aquifer from significantly above-average rain events/precipitation received that year and implementation of engineering controls (i.e. curbing) at the well field. However, since 2013, concentrations in the Production Wells have again shown an overall increasing trend and chloride concentrations above the MCL have been reported. The chloride results from April 2015 in MH-1 and MH-1A showed a dramatic increase in concentration and concentrations in overburden Production Wells MH-1 and MH-1A have remained elevated. As a result of the increase in chloride concentration, MH-1 has been taken out of service by the Village and dilution of water from MH-1A and MH-3R in the distribution system with water from the nearby North Main bedrock production well has been implemented. A graph overlaying the chloride concentrations from all of the Production Wells at the MHP well field is provided below.



Discussion

Based on previous surface-water and groundwater sampling conducted at the MHP well field and from the Ramapo River between April 2013 and February 2016, the increase in chloride concentrations at the well field and in the MHP Production Wells are likely the result of the elevated chlorides in the surface water from the adjacent Ramapo River recharging the groundwater. The graph below shows an overlay of the chloride concentrations in the surface water from the upstream tributary receiving discharge from the upstream Village of Kiryas Joel Wastewater Treatment Plant (SW-4 (new)), surface water at the MHP well field (SW-2 in the Ramapo River), shallow groundwater (MW-1S) in the overburden aquifer at the well field, and deeper groundwater (MH-1A) in the overburden aquifer at the well field. The locations of the surface water sampling points are shown on figure 2. In general, the chloride concentration changes seen in the surface water and groundwater follow similar fluctuating patterns and the concentrations in the groundwater decrease from shallow to deep because of dilution in the aquifer. A slight delay in response to changing concentrations in the deeper aquifer is also noted compared to the surface water and shallow groundwater.



The chloride concentrations in the surface water at the upstream sampling location SW-5 are much lower than the tributary stream (SW-4 (new)) and the surface water in the Ramapo River at MHP (SW-2). If the chloride concentrations in the surface water at the well field could be reduced to the concentrations reported upstream at SW-5, the chloride in the shallow and deep groundwater at the well field would also likely be reduced. However, the decrease in chloride concentrations in the groundwater at the well field would take time. The chlorides would need a mechanism or path out of the aquifer either through pumping (the MHP production wells), through slow leakage back into the stream, or by dilution over time from uncontaminated groundwater flow and surface-water recharge. If chloride concentrations in the Ramapo River remain elevated and/or continue to rise, the chloride concentrations in the MHP Production Wells will also.

Localized road salt application to paved areas also likely contributes to elevated chloride concentrations in groundwater. Even in SW-5 (the upstream, background monitoring point), chloride has been reported as high as 323 mg/l (January 2015). Therefore, a reduction in all potential sources of chloride near the well field (Ramapo River and nearby road salt application) is desirable.

Based on previous recommendations from LBG, the Village removed the salt storage shed from the MHP well field that was located near MW-4S in July 2016. The chloride concentration in MW-4S has remained elevated, likely from residual salt in the soils near the former shed location. An uncharacteristic rise in the chloride concentration in MW-3S (396 mg/L) was also observed during the September 2016 sampling event. The cause of this increase may have been related to activities conducted as part of the removal of the salt storage shed and underlying soils at the well field in July 2016. The January 2017 chloride concentration in MW-3S has decreased to 200 mg/L which is more in line with previous concentrations observed in this well.

Conclusions/Recommendations

The analytical results from the groundwater sampling event completed in January 2017 show a continuation of the overall rise in sodium and chloride concentrations in both the shallow and deeper overburden groundwater at the MHP well field. The main contributing source of the sodium and chloride to the elevated concentrations reported in the Production Wells appears to be recharge from the nearby Ramapo River, although road salt application to paved areas near the well field is likely also contributing.

LBG recommends continuation of quarterly sampling of the monitoring well network at the well field and the resumption of surface-water sampling in the Ramapo River to assess the trends in sodium and chloride concentrations at the well field over time. The sampling will be used to more accurately track concentration changes resulting from seasonal variations and travel time of chloride through the aquifer from surface water to shallow groundwater to deeper groundwater. Additionally, continued sampling of MW-3S, 3D and 4S will also document the effects of the removal of the salt storage shed on the chloride concentrations in the groundwater.

The installation of piezometers in the Ramapo River and the pond at the MHP well field should also be considered to assess changes in recharge gradient throughout the year. Pressure transducers could be installed on the piezometers to measure water level and conductivity daily to track how surface-water recharge is affecting groundwater at the well field and also to measure the fluctuations in chloride concentrations via the conductivity.


The installation of additional monitoring well locations should also be considered to collect additional water-level information, conduct recharge gradient assessments, and track

chloride concentrations. Monitoring well locations to be considered would be a shallow screened well adjacent to MW-5 and deeper screened wells adjacent to MW-1S and MW-4S.

Should you have any questions, please do not hesitate to contact me.

Very truly yours,

LEGGETTE, BRASHEARS & GRAHAM, INC.



Stacy Stieber, CPG
Associate/Hydrogeologist

Reviewed by:



Thomas P. Cusack, CPG
Principal

SS:cmm

Enclosures

cc: Village of Harriman Board

H:\Harriman-Na-Cl\2017\MHP Sampling - January.doc

TABLES

TABLE 1

VILLAGE OF HARRIMAN
MARY HARRIAMN PARK WELL FIELD
HARRIMAN, NEW YORK

Summary of Monitoring Well Construction Information

Monitoring Well ID	Construction Date	Reported Screen Setting (ft bg)	Depth to Water January 6, 2017 (ft btoc)	Groundwater Elevation January 6, 2017 (feet)
MHP-MW-1S	2/2/2007	11-21	11.90*	524.05
MHP-MW-2S	2/2/2007	11-21	9.40	524.01
MHP-MW-2D	2/2/2007	28-38	9.43	524.07
MHP-MW-3S	2/13/2007	4-14	4.40	523.77
MHP-MW-3D	2/12/2007	25-35	3.78	523.67
MHP-MW-4S	2/1/2007	5-15	4.73	523.56
MHP-MW-5	6/14/2004	45-50	13.49	515.68
MW-6	UK	UK (total depth 44.0)	NM	NM
MW-7	UK	UK (total depth 44.1)	NM	NM
MW-8	UK	UK (total depth 22.2)	NM	NM
MW-9	UK	UK (total depth 24.3)	NM	NM

ft bg feet below grade

ft btoc feet below top of casing

UK unknown

* Well stick-up appears to have been hit by a vehicle.

TABLE 2

**VILLAGE OF HARRIMAN
MARY HARRIAMN PARK WELL FIELD
HARRIMAN, NEW YORK**

Summary of Sodium and Chloride Water-Quality Results

Well ID	Collection Date	Sodium (mg/l)	Chloride (mg/l)
MH-Well 1	10/18/06	94	153
	11/21/06	81	136
	2/22/07	99	203
	5/16/17	94	143
	6/18/07	110	355
	7/16/07	48	308
	11/5/07	--	289
	12/6/07	165	290
	1/9/08	151	268
	2/13/08	101	211
	3/12/08	104	203
	3/25/08	124	212
	6/11/08	135	245
	10/31/08	206	345
	1/14/09	137	215
	3/11/09	145	289
	4/15/09	154	354
	4/6/10	120	275
	2/9/11	178	304
	3/22/11	119	224
	9/20/11	102	134
	11/18/11	100	155
	1/11/12	99.7	136
	1/23/12	94.8	118
	4/19/12	91.8	155
	1/18/13	48.8	106
	3/13/13	59.2	111
	4/24/13	190	228
	4/10/14	55	161
	5/13/14	68	126
	12/22/14	140	252
	1/28/15	170	276
	1/29/15	56	128
	3/18/15	56.0	120
	4/8/15	190	560
	4/24/15	190	450
	6/3/15	165	361
	8/6/15	183	310
	11/4/15	186	350
	2/10/16	NS	NS
	9/29/16	NS	NS
	11/10/16	174	376
	1/6/17	NS	NS
MH-Well 1A	10/18/06	160	204
	11/21/06	130	200
	2/22/07	130	171
	5/16/07	130	181
	6/18/07	110	340
	7/16/07	74	215
	11/5/07	--	240
	12/6/07	157	300

TABLE 2

**VILLAGE OF HARRIMAN
MARY HARRIAMN PARK WELL FIELD
HARRIMAN, NEW YORK**

Summary of Sodium and Chloride Water-Quality Results

Well ID	Collection Date	Sodium (mg/l)	Chloride (mg/l)
MH-Well 1A (continued)	1/9/08	153	330
	2/13/08	140	263
	3/12/08	140	273
	3/25/08	133	234
	6/11/08	136	267
	10/31/08	183	340
	1/14/09	149	257
	3/11/09	144	280
	4/15/09	164	306
	2/11/10	148	270
	4/6/10	138	342
	7/28/10	NS	810**
	8/16/10	NS	303
	2/9/11	169	412
	3/22/11	165	309
	9/20/11	135	223
	11/18/11	131	204
	1/11/12	135	192
	1/23/12	128	185
	4/19/12	124	192
	1/18/13	141	201
	3/13/13	132	216
	4/24/13	113	176
	4/10/14	130	266
	5/13/14	130	250
	12/22/14	150	271
	1/28/15	160	271
	1/29/15	150	254
	3/18/15	170	270
	4/8/15	170	430
	4/24/15	180	400
	6/3/15	165	309
	8/6/15	176	320
	11/4/15	264	360
	2/10/16	193	364
	9/29/16	171	364
	1/6/17	183	330
MH-Well 3R	10/18/06	160	191
	11/21/06	52	103
	2/22/07	68	142
	5/16/07	54	88
	6/18/07	41	130
	7/16/07	41	88
	11/5/07	--	296
	12/6/07	53	130
	1/9/08	45.9	114
	2/13/08	129	266
	3/12/08	132	251
	3/25/08	55.9	113
	6/11/08	51.2	235
	10/31/08	104	191

TABLE 2

**VILLAGE OF HARRIMAN
MARY HARRIAMN PARK WELL FIELD
HARRIMAN, NEW YORK**

Summary of Sodium and Chloride Water-Quality Results

Well ID	Collection Date	Sodium (mg/l)	Chloride (mg/l)
MH-Well 3R (continued)	1/14/09	52.2	120
	3/11/09	44.5	101
	4/6/10	76.4	202
	2/9/11	48.4	106
	3/22/11	58.6	142
	9/20/11	96.3	131
	11/18/11	134	138
	1/11/12	46.2	108
	1/23/12	58.3	116
	4/19/12	44.6	116
	1/18/13	49.2	106
	3/13/13	125	106
	4/24/13	49.8	91.8
	4/10/14	120	266
	5/13/14	130	240
	1/28/15	54	145
	1/29/15	140	249
	3/18/15	149	290
	4/8/15	55	160
	4/24/15	60	170
	6/3/15	52.1	156
	8/6/15	66.6	150
	11/4/15	59.9	170
	2/10/16	71.4	247
	9/29/16	64.5	231
	1/6/17	78.9	220
MHP-MW-1S	2/22/07	100	198
	6/18/07	120	333
	12/6/07	129	190
	3/25/08	151	229
	4/6/10	125	241
	1/23/12	84.4	143
	4/9/13	110	194
	4/10/14	140	236
	5/13/14	120	219
	1/29/15	200	420
	6/3/15	232	397
	8/6/15	206	380
	11/4/15	169	330
	2/10/16	163	391
	9/29/16	190	380
	1/6/17	201	510
MHP-MW-2S	2/22/07	89	127
	6/18/07	45	98
	12/6/07	128	91
	3/25/08	102	163
	4/6/10	95.4	183
	1/23/12	99.1	150
	4/9/13	110	231
	4/10/14	120	278
	5/13/14	110	270

TABLE 2

**VILLAGE OF HARRIMAN
MARY HARRIAMN PARK WELL FIELD
HARRIMAN, NEW YORK**

Summary of Sodium and Chloride Water-Quality Results

Well ID	Collection Date	Sodium (mg/l)	Chloride (mg/l)
MHP-MW-2S (continued)	1/29/15	140	287
	6/3/15	184	378
	8/6/15	158	350
	11/4/15	186	350
	2/10/16	165	373
	9/29/16	NS	NS
	1/6/17	182	370
MHP-MW-2D	2/22/07	110	181
	6/18/07	110	323
	12/6/07	129	240
	3/25/08	121	209
	4/6/10	128	263
	1/23/12	99.3	155
	4/9/13	120	236
	4/10/14	140	310
	5/13/14	120	405
	1/29/15	160	304
	6/3/15	220	403
	8/6/15	196	340
	11/4/15	196	400
	2/10/16	168	382
	9/29/16	202	377
	1/6/17	189	480
MHP-MW-3S	2/22/07	190	306
	6/18/07	94	330
	12/6/07	175	350
	3/25/08	145	207
	4/6/10	123	174
	1/23/12	67.3	111
	4/10/13	77	104
	4/10/14	50	64.5
	5/13/14	49	70.4
	1/29/15	69	147
	6/3/15	38.3	56
	8/6/15	52.2	65.0
	11/4/15	75.4	190
	2/10/16	82.1	142
	9/29/16	158	396
	1/6/17	121	200
MHP-MW-3D	2/22/07	220	333
	6/18/07	120	328
	12/6/07	272*	490
	3/25/08	165	239
	4/6/10	165	265
	1/23/12	127	239
	4/9/13	130	191
	4/10/14	140	270
	5/13/14	140	253
	1/29/15	160	271
	6/3/15	219	274
	8/6/15	211	410

TABLE 2

**VILLAGE OF HARRIMAN
MARY HARRIAMN PARK WELL FIELD
HARRIMAN, NEW YORK**

Summary of Sodium and Chloride Water-Quality Results

Well ID	Collection Date	Sodium (mg/l)	Chloride (mg/l)
MHP-MW-3D (continued)	11/4/15	261	540
	2/10/16	201	443
	9/29/16	239	448
	1/6/17	245	420
MHP-MW-4S	2/22/07	320*	330
	6/18/07	240	421
	12/6/07	244	390
	3/25/08	192	286
	4/6/10	203	362
	1/23/12	131	163
	4/9/13	130	177
	4/10/14	140	256
	5/13/14	150	272
	1/29/15	170	280
	6/3/15	178	225
	8/6/15	184	290
	11/4/15	169	290
	2/10/16	197	423
	7/22/16	210	382
	9/29/16	141	409
	1/6/17	263	440
MHP-MW-5	2/22/07	170	389
	6/18/07	120	401
	12/6/07	154	290
	3/25/08	121	273
	4/6/10	114	234
	1/23/12	130	308
	4/9/13	150	295
	4/10/14	130	266
	5/13/14	130	313
	1/29/15	130	240
	6/3/15	135	225
	8/6/15	132	220
	11/4/15	136	250
	2/10/16	129	271
	9/29/16	126	240
	1/6/17	123	210
MW-7	5/13/14	130	279
MW-8	5/13/14	130	335
NYSDOH MCL (mg/l)		NE*	250

* No established MCL for sodium, recommended limit is 270 mg/l.

** Laboratory error suspected, well resampled.

Note: Bold denote criteria exceedance.

mg/l Milligrams per liter

NYSDOH New York State Department of Health

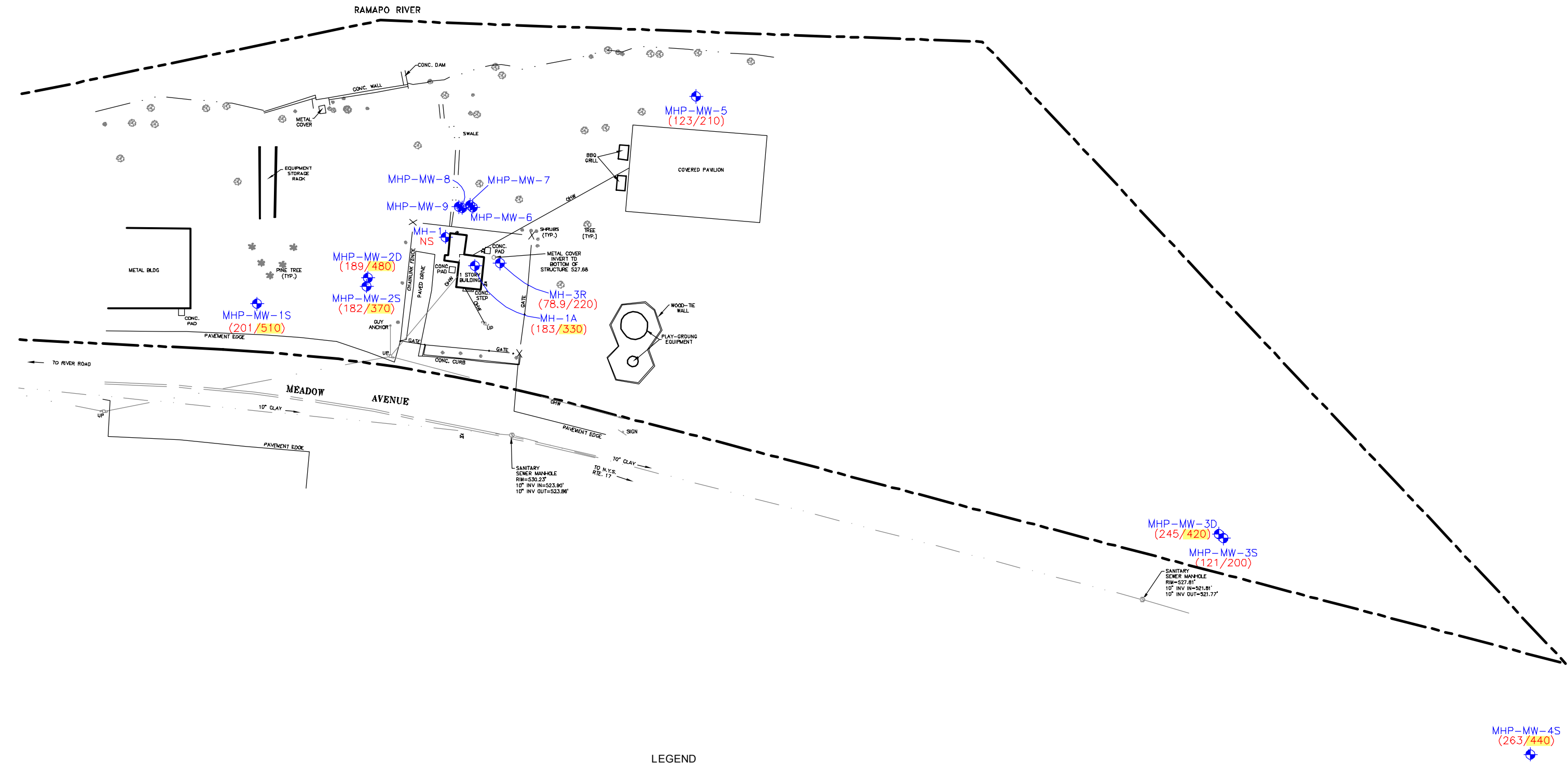
MCL Maximum Concentration Level

NS Not sampled

H:\Harriman-Na-Cl\2017\NaCl summary table MHP_Jan.doc



FIGURES

O:\DWG\ Village of Harriman\ Mary Harriman Well Field\2017\F1Jan2017.dwg, Layout1, 1/19/2017 3:45:40 PM, AcroPlot.pc3



SOURCE:
LANC & TULLY "MAP PREPARED FOR A PORTION OF MARY W HARRIMAN MEMORIAL PARK"
SHEET 1 OF 1, DATED NOVEMBER 12, 2010, REVISED SEPTEMBER 3, 2014.

LEGEND

- PROPERTY BOUNDARY
-  MHP-MW-5
(123/210)
SODIUM/CHLORIDE CONCENTRATION OF WELL
IN MILLIGRAMS PER LITER
- NS
NOT SAMPLED
-  HIGHLIGHTED NUMBER INDICATES
CONCENTRATION EXCEEDS NEW YORK STATE
DEPARTMENT OF HEALTH DRINKING WATER
STANDARD MAXIMUM CONTAMINANT LEVEL
FOR CHLORIDE



MARY HARRIMAN WELL FIELD
HARRIMAN, NEW YORK

SITE PLAN - SODIUM AND CHLORIDE CONCENTRATIONS
JANUARY 6, 2017

DATE	REVISED	PREPARED BY:
		LEGGETTE, BRASHEARS & GRAHAM, INC.
		Professional Groundwater and Environmental Engineering Services
		4 Research Drive Suite 204 Shelton, Connecticut 06484 (203) 929-8555
DRAWN:	RAC	CHECKED: SS
DATE:	01/19/17	FIGURE: 1

O:\DWG\Village of Harriman\Mary Harriman Well Field\2017\Figure2.dwg_Layout1_1/20/2017 3:18:58 PM_AcroPlt.pc3




LEGEND

● SW-3 SURFACE WATER SAMPLE LOCATION

MARY HARRIMAN WELL FIELD
HARRIMAN, NEW YORK

RAMAPO RIVER SURFACE WATER SAMPLING LOCATIONS

DATE	REVISED	PREPARED BY: LEGGETTE, BRASHEARS & GRAHAM, INC. Professional Groundwater and Environmental Engineering Services			
		 4 Research Drive Suite 204 Shelton, Connecticut 06484 (203) 929-8555			
DRAWN:	RAC	CHECKED:	SS	DATE:	01/20/17
				FIGURE:	2

APPENDIX I

ANALYTICAL REPORT

Job Number: 420-115349-1

SDG Number: Harriman NY Mary Harriman Park

Job Description: LBG, Inc.

For:

Leggette, Brashears & Graham, Inc.

4 Research Drive

Shelton, CT 06464

Attention: Stacy Stieber



Debra Bayer

Customer Service Manager

dbayer@envirotestlaboratories.com

01/18/2017

NYSDOH ELAP does not certify for all parameters. EnviroTest Laboratories does hold certification for all analytes where certification is offered by ELAP unless otherwise specified in the Certification Information section of this report. Pursuant to NELAP, this report may not be reproduced, except in full, without written approval of the laboratory. EnviroTest Laboratories Inc. certifies that the analytical results contained herein apply only to the samples tested as received by our laboratory. All questions regarding this report should be directed to the EnviroTest Customer Service Representative.

EnviroTest Laboratories, Inc. Certifications and Approvals: NYSDOH 10142, NJDEP NY015, CTDOPH PH-0554

Envirotest Laboratories, Inc.

315 Fullerton Avenue, Newburgh, NY 12550

Tel (845) 562-0890 Fax (845) 562-0841 www.envirotestlaboratories.com

METHOD SUMMARY

Client: Leggette, Brashears & Graham, Inc.

Job Number: 420-115349-1
SDG Number: Harriman NY Mary Harriman Park

Description	Lab Location	Method	Preparation Method
Matrix: Water			
ICP Metals by 200.7	EnvTest	EPA 200.7 Rev 4.4	
200 Series Drinking Water Prep Determination Step	EnvTest		EPA 200
Total Metals Digestion for 200.7	EnvTest		EPA 200.7
Chloride by Silver Nitrate Titration	EnvTest	SM21 SM4500CL-B-97,	

Lab References:

EnvTest = EnviroTest

Method References:

EPA = US Environmental Protection Agency

SM21 = "Standard Methods For The Examination Of Water And Wastewater", 21st Edition

METHOD / ANALYST SUMMARY

Client: Leggette, Brashears & Graham, Inc.

Job Number: 420-115349-1
SDG Number: Harriman NY Mary Harriman Park

Method	Analyst	Analyst ID
EPA 200.7 Rev 4.4	Sirico, Derek	DS
SM21 SM4500CL-B-97,	Tramantano, Matt	MT

SAMPLE SUMMARY

Client: Leggette, Brashears & Graham, Inc.

Job Number: 420-115349-1
SDG Number: Harriman NY Mary Harriman Park

Lab Sample ID	Client Sample ID	Client Matrix	Date/Time Sampled	Date/Time Received
420-115349-1	MHP-MW-1S	Water	01/06/2017 1152	01/06/2017 1450
420-115349-2	MHP-MW-2S	Water	01/06/2017 1127	01/06/2017 1450
420-115349-3	MHP-MW-2D	Water	01/06/2017 1133	01/06/2017 1450
420-115349-4	MHP-MW-3S	Water	01/06/2017 1038	01/06/2017 1450
420-115349-5	MHP-MW-3D	Water	01/06/2017 1030	01/06/2017 1450
420-115349-6	MHP-MW-4S	Water	01/06/2017 1055	01/06/2017 1450
420-115349-7	MHP-MW-5	Water	01/06/2017 1120	01/06/2017 1450
420-115349-8	MHP-1A	Drinking Water	01/06/2017 1240	01/06/2017 1450
420-115349-9	MHP-3R	Drinking Water	01/06/2017 1238	01/06/2017 1450
420-115349-10	MHP-1A/3R	Drinking Water	01/06/2017 1242	01/06/2017 1450

Stacy Stieber
Leggette, Brashears & Graham, Inc.
4 Research Drive
Shelton, CT 06464

Job Number: 420-115349-1
Sdg Number: Harriman NY Mary Harriman Park

Client Sample ID: MHP-MW-1S
Lab Sample ID: 420-115349-1

Date Sampled: 01/06/2017 1152
Date Received: 01/06/2017 1450
Client Matrix: Water

Analyte	Result/Qualifier	Unit	RL	Dilution
Method: 200.7 Rev 4.4 Prep Method: 200.7 Sodium	201000	ug/L	200	1.0
Method: SM4500CL-B-97, Chloride	510	mg/L	50.0	10

Stacy Stieber
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Job Number: 420-115349-1
Sdg Number: Harriman NY Mary Harriman Park

Client Sample ID: MHP-MW-2S
Lab Sample ID: 420-115349-2

Date Sampled: 01/06/2017 1127
Date Received: 01/06/2017 1450
Client Matrix: Water

Analyte	Result/Qualifier	Unit	RL	Dilution
Method: 200.7 Rev 4.4 Prep Method: 200.7 Sodium	182000	ug/L	200	1.0
Method: SM4500CL-B-97, Chloride	370	mg/L	50.0	10

Stacy Stieber
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Job Number: 420-115349-1
Sdg Number: Harriman NY Mary Harriman Park

Client Sample ID: MHP-MW-2D
Lab Sample ID: 420-115349-3

Date Sampled: 01/06/2017 1133
Date Received: 01/06/2017 1450
Client Matrix: Water

Analyte	Result/Qualifier	Unit	RL	Dilution
Method: 200.7 Rev 4.4 Prep Method: 200.7 Sodium	189000	ug/L	200	1.0
Method: SM4500CL-B-97, Chloride	480	mg/L	50.0	10

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Job Number: 420-115349-1
Sdg Number: Harriman NY Mary Harriman Park

Client Sample ID: MHP-MW-3S
Lab Sample ID: 420-115349-4

Date Sampled: 01/06/2017 1038
Date Received: 01/06/2017 1450
Client Matrix: Water

Analyte	Result/Qualifier	Unit	RL	Dilution
Method: 200.7 Rev 4.4 Prep Method: 200.7 Sodium	121000	ug/L	200	1.0
Method: SM4500CL-B-97, Chloride	200	mg/L	50.0	10

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Job Number: 420-115349-1
Sdg Number: Harriman NY Mary Harriman Park

Client Sample ID: MHP-MW-3D
Lab Sample ID: 420-115349-5

Date Sampled: 01/06/2017 1030
Date Received: 01/06/2017 1450
Client Matrix: Water

Analyte	Result/Qualifier	Unit	RL	Dilution
Method: 200.7 Rev 4.4 Prep Method: 200.7 Sodium	245000	ug/L	200	1.0
Method: SM4500CL-B-97, Chloride	420	mg/L	50.0	10

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Job Number: 420-115349-1
Sdg Number: Harriman NY Mary Harriman Park

Client Sample ID: MHP-MW-4S
Lab Sample ID: 420-115349-6

Date Sampled: 01/06/2017 1055
Date Received: 01/06/2017 1450
Client Matrix: Water

Analyte	Result/Qualifier	Unit	RL	Dilution
Method: 200.7 Rev 4.4 Prep Method: 200.7 Sodium	263000	ug/L	200	1.0
Method: SM4500CL-B-97, Chloride	440	mg/L	50.0	10

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Job Number: 420-115349-1
Sdg Number: Harriman NY Mary Harriman Park

Client Sample ID: MHP-MW-5
Lab Sample ID: 420-115349-7

Date Sampled: 01/06/2017 1120
Date Received: 01/06/2017 1450
Client Matrix: Water

Analyte	Result/Qualifier	Unit	RL	Dilution
Method: 200.7 Rev 4.4 Prep Method: 200.7 Sodium	123000	ug/L	200	1.0
Method: SM4500CL-B-97, Chloride	210	mg/L	50.0	10

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Shelton, CT 06464

Job Number: 420-115349-1
Sdg Number: Harriman NY Mary Harriman Park

Client Sample ID: MHP-1A
Lab Sample ID: 420-115349-8

Date Sampled: 01/06/2017 1240
Date Received: 01/06/2017 1450
Client Matrix: Drinking Water

Analyte	Result/Qualifier	Unit	RL	Dilution
Method: 200.7 Rev 4.4				
Prep Method: 200				
Sodium	183000	ug/L	200	1.0
Method: SM4500CL-B-97,				
Chloride	330	mg/L	50.0	10

Stacy Stieber
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Job Number: 420-115349-1
Sdg Number: Harriman NY Mary Harriman Park

Client Sample ID: MHP-3R
Lab Sample ID: 420-115349-9

Date Sampled: 01/06/2017 1238
Date Received: 01/06/2017 1450
Client Matrix: Drinking Water

Analyte	Result/Qualifier	Unit	RL	Dilution
Method: 200.7 Rev 4.4				
Prep Method: 200				
Sodium	78900	ug/L	200	1.0
Method: SM4500CL-B-97,				
Chloride	220	mg/L	50.0	10

Stacy Stieber
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Shelton, CT 06464

Job Number: 420-115349-1
Sdg Number: Harriman NY Mary Harriman Park

Client Sample ID: MHP-1A/3R
Lab Sample ID: 420-115349-10

Date Sampled: 01/06/2017 1242
Date Received: 01/06/2017 1450
Client Matrix: Drinking Water

Analyte	Result/Qualifier	Unit	RL	Dilution
Method: 200.7 Rev 4.4				
Prep Method: 200				
Sodium	145000	ug/L	200	1.0
Method: SM4500CL-B-97,				
Chloride	300	mg/L	50.0	10

DATA REPORTING QUALIFIERS

Lab Section	Qualifier	Description
-------------	-----------	-------------

Certification Information

The following analytes are Not Part of the ELAP scope of accreditation

Sulfur, Tungsten, Silicon, Bicarbonate Alkalinity, 7 Day BOD 5210C, 28 Day BOD, Soluble BOD, Carbon Dioxide, Carbonate Alkalinity, CBOD Soluble, Chlorine, Cyanide (WAD), Ferrous Iron, Ferric Iron, Total Nitrogen, Total Organic Nitrogen, Dissolved Oxygen, pH, Phenolphthalein Alkalinity, Solids (Fixed), Solids (Percent), Solids (Percent Moisture), Solids (Percent Volatile), Solids (Volatile Suspended), Temperature, TKN (Soluble), Total Inorganic Carbon, Volatile Acids as Acetic Acid, 2-Aminopyridine, 3-Picoline, 1-Methyl-2-pyrrilidinone, Aziridine, Dimethyl sulfoxide, 1-Chlorohexane, Iron Bacteria, Salmonella, & Sulfur Reducing Bacteria.

The following analytes are Not Part of ELAP Potable Water scope of accreditation

Cobalt (200.7, 200.8), Tin (200.7), Strontium (200.7), Gold (200.7), Platinum (200.7), Palladium (200.7), Titanium (200.7), Phosphorus (365.3), Nitrate-Nitrite (10-107-4-1C, 353.2), m-Xylene & p-Xylene (502.2, 524), Naphthalene (502.2), o-Xylene (502.2, 524), & Fecal Coliform (9222D).

The following analytes are Not Part of ELAP Solid and Hazardous Waste scope of accreditation

Ammonia (SM 4500NH3G), TKN (351.2), Phosphorus (365.3), 1,2-Dichloro-1,1,2-trifluoroethane (8260), & Chlorodifluoromethane (8260).

The following analytes are Not Part of ELAP Non Potable Water scope of accreditation

Dissolved Organic Carbon (5310C), Mecoprop (8151A), & MCPA (8151A).

Definitions and Glossary

Abbreviation	These commonly used abbreviations may or may not be present in this report.
%R	Percent Recovery
DL, RA, RE	Indicates a Dilution, Reanalysis or Reextraction.
EPA	United States Environmental Protection Agency
MDL	Method Detection Limit - an estimate of the minimum amount of a substance that an analytical process can reliably detect. A MDL is analyte- and matrix-specific and may be laboratory-dependent.
ND	Not detected at the reporting limit (or MDL if shown).
QC	Quality Control
RL	Reporting Limit - the minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.
RPD	Relative Percent Difference - a measure of the relative difference between two points

EnviroTest Laboratories Inc.

CHAIN OF CUSTODY

315 Fullerton Avenue
Newburgh, NY 12550
TEL (845) 562-0890
FAX (845) 562-0841

115349

CUSTOMER NAME LBG, Inc.	
ADDRESS 4 Reservoir Dr. Suite 4004	
CITY, STATE, ZIP Shelton, CT 06484	PHONE NO. 203-284-9555
NAME OF CONTACT Steve Steber	
PROJECT LOCATION Harmon, NY	
PROJECT NUMBER / PO NO. Mary Harmon State	

REPORT TYPE	TURNAROUND
STANDARD <input checked="" type="checkbox"/> ISRA <input type="checkbox"/>	<input checked="" type="checkbox"/> NORMAL
NJ REG <input type="checkbox"/>	<input type="checkbox"/> QUICK
NYASP A <input type="checkbox"/> B <input type="checkbox"/> CLP <input type="checkbox"/>	<input type="checkbox"/> VERBAL
OTHER _____	

REPORT # (Lab Use Only) R#3	
SAMPLE TEMP. 23	SAMPLE REC'D ON ICE <input checked="" type="checkbox"/> Y <input type="checkbox"/> N
ph CHECK <input type="checkbox"/> Y <input type="checkbox"/> N	CHLORINE (RESIDUAL) <input type="checkbox"/> Y <input type="checkbox"/> N
REVIEWED BY: _____	

Matrix
DW = DRINKING WATER S = SOIL O = OIL
WW = WASTE WATER SL = SLUDGE GW = GROUND WATER

**NOTE: SAMPLE TEMPERATURE UPON
RECEIPT MUST BE 4° ± 2°C.**

NOTE: SAMPLE TEMPERATURE UPON RECEIPT MUST BE 4° ± 2°C.																			
ETL #	SAMPLING DATE	TIME	COMP	MATRIX	CLIENT I.D.	Total Number of Containers	40ml Glass HCL	Liter Amber HCL	250ml Amber Sulfuric	Liter Amber Organic Washed	250ml Plastic Nitric Acid	250ml Plastic Sodium Hydroxide	Liter Plastic	250ml Plastic Sulfuric Acid	250ml Plastic Sterile	250ml Plastic NAOH/ZN ACC	40ml Glass Sulfuric	40ml Glass DO	ANALYSIS REQUESTED
	11/17	1157	✓	SGW	MHP MW-15	2													NaCl
		1137	✓		- 25	2													
		1133	✓		- 20	2													
		1038	✓		- 25	2													
		1030	✓		- 30	2													
		1033	✓		- 45	2													
		1120	✓		- 5	2													
		1210	✓	SW	MHP-1A	2													
		1238	✓	SW	MHP-3R	2													
		1212	✓	SW	MHP-1/3R	2													

SAMPLES SUBMITTED FOR ANALYSIS WILL BE SUBJECT TO THE ETL TERMS AND CONDITIONS OF SALE UNLESS ALTERNATE TERMS ARE AGREED IN WRITING.

RELINQUISHED BY SB	COMPANY LBG	DATE 11/17	TIME 1450	RECEIVED BY	COMPANY	DATE	TIME
SAMPLED BY SB	COMPANY LBG	DATE 11/17	TIME 1030	RECEIVED BY	COMPANY	DATE	TIME
RELINQUISHED BY SB	COMPANY LBG	DATE 11/17	TIME 1450	RECEIVED BY SB	COMPANY LBG	DATE 11/17	TIME 1450

COMMENTS: **a Bill to Village of Harmon, After John Molligan**

LOGIN SAMPLE RECEIPT CHECK LIST

Client: Leggette, Brashears & Graham, Inc.

Job Number: 420-115349-1

SDG Number: Harriman NY Mary Harriman Park

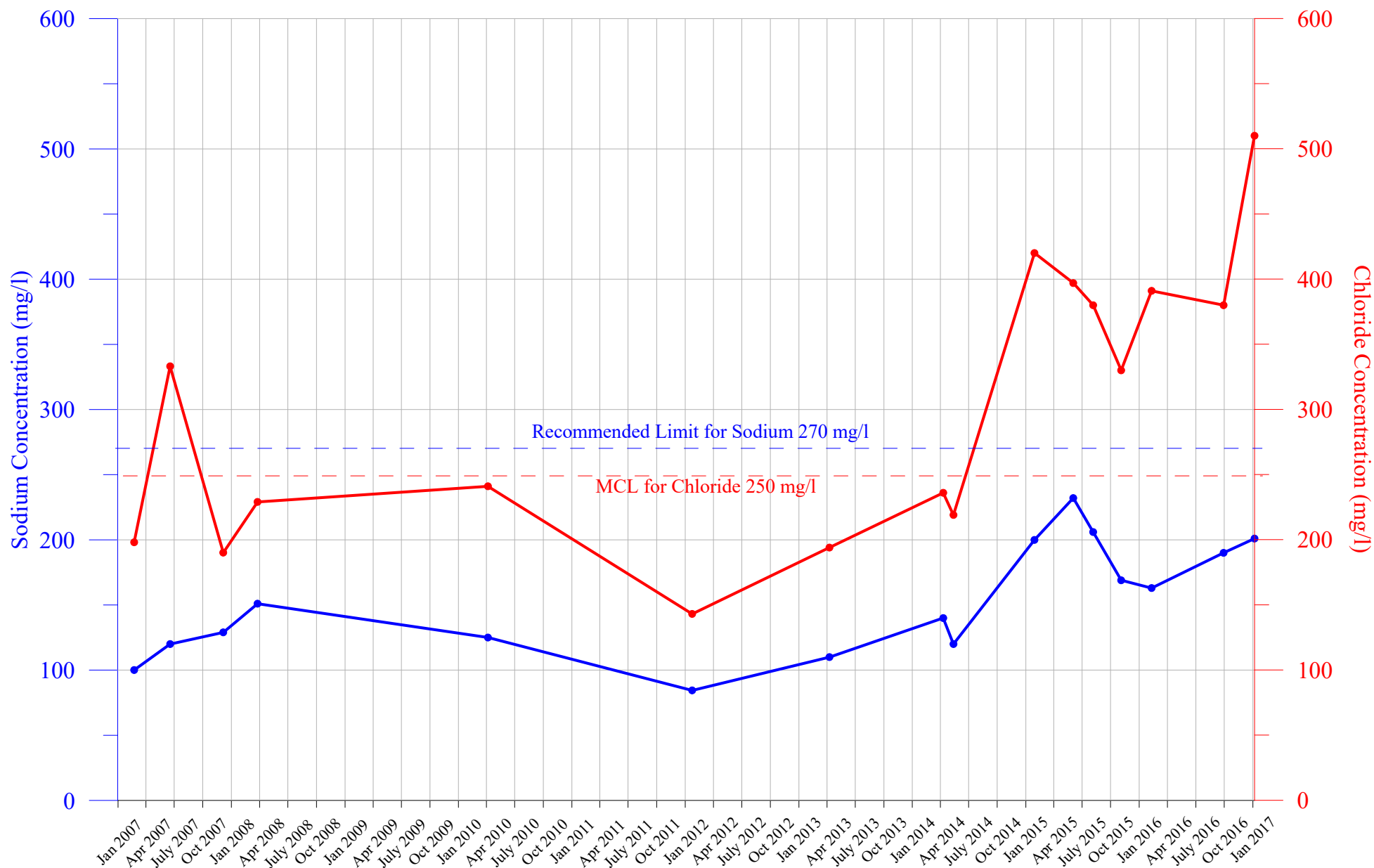
Login Number: 115349

Question	T/F/NA	Comment
Samples were collected by ETL employee as per SOP-SAM-1	NA	
The cooler's custody seal, if present, is intact.	NA	
The cooler or samples do not appear to have been compromised or tampered with.	True	
Samples were received on ice.	True	
Cooler Temperature is recorded.	True	2.3 C
Cooler Temp. is within method specified range.(0-6 C PW, 0-8 C NPW, or BAC <10 C	True	
If false, was sample received on ice within 6 hours of collection.	NA	
Based on above criteria cooler temperature is acceptable.	True	
COC is present.	True	
COC is filled out in ink and legible.	True	
COC is filled out with all pertinent information.	True	
There are no discrepancies between the sample IDs on the containers and the COC.	True	
Samples are received within Holding Time.	True	
Sample containers have legible labels.	True	
Containers are not broken or leaking.	True	
Sample collection date/times are provided.	True	
Appropriate sample containers are used.	True	
Sample bottles are completely filled.	True	
There is sufficient vol. for all requested analyses, incl. any requested MS/MSDs	True	
VOA sample vials do not have headspace or bubble is <6mm (1/4") in diameter.	NA	
If necessary, staff have been informed of any short hold time or quick TAT needs	True	
Multiphasic samples are not present.	True	
Samples do not require splitting or compositing.	True	

APPENDIX II

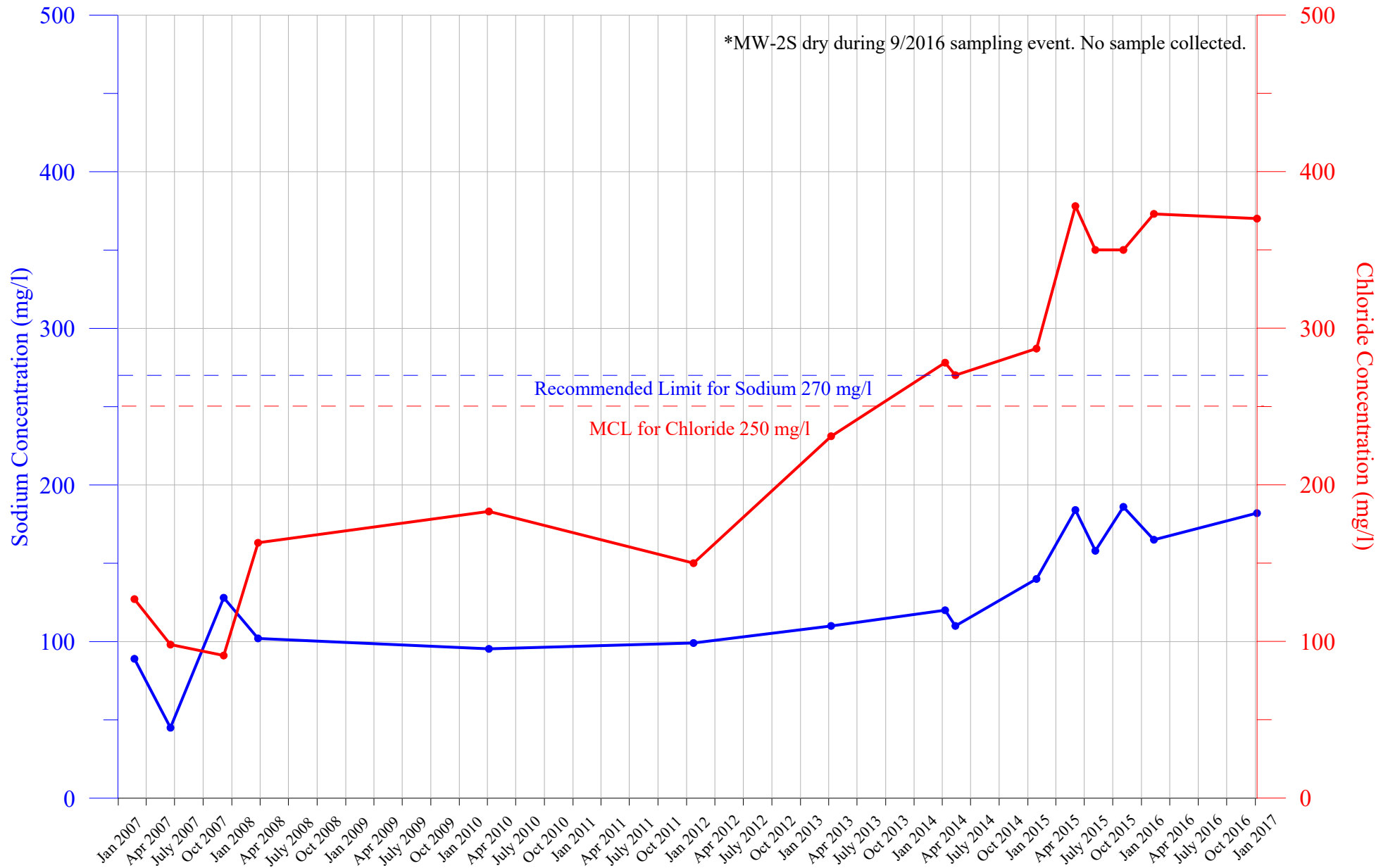
MARY HARRIMAN PARK WELL FIELD
HARRIMAN, NEW YORK

Summary of Sodium and Chloride Concentrations from Monitor Well MHP-MW-1S



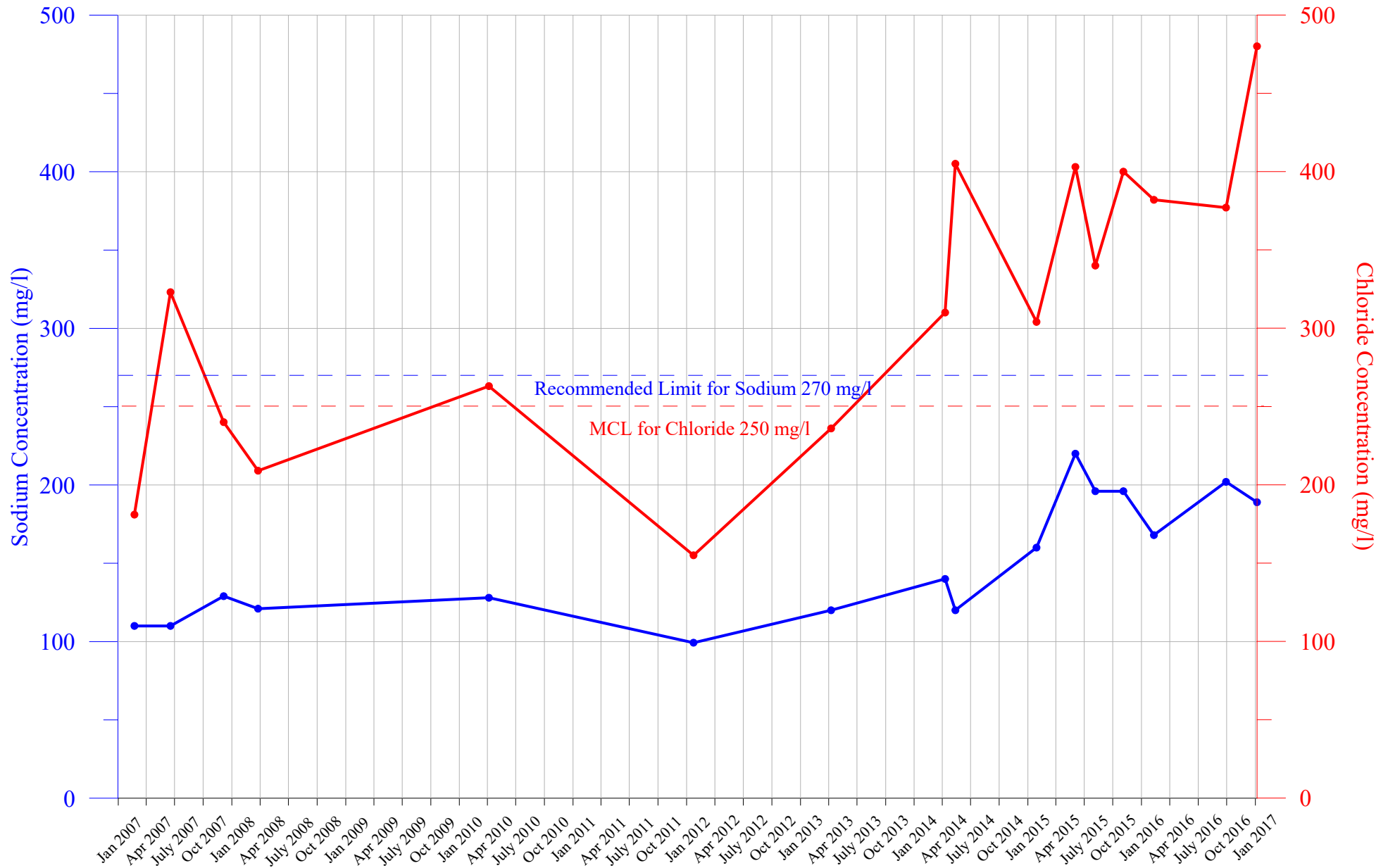
MARY HARRIMAN PARK WELL FIELD
HARRIMAN, NEW YORK

Summary of Sodium and Chloride Concentrations from Monitor Well MHP-MW-2S



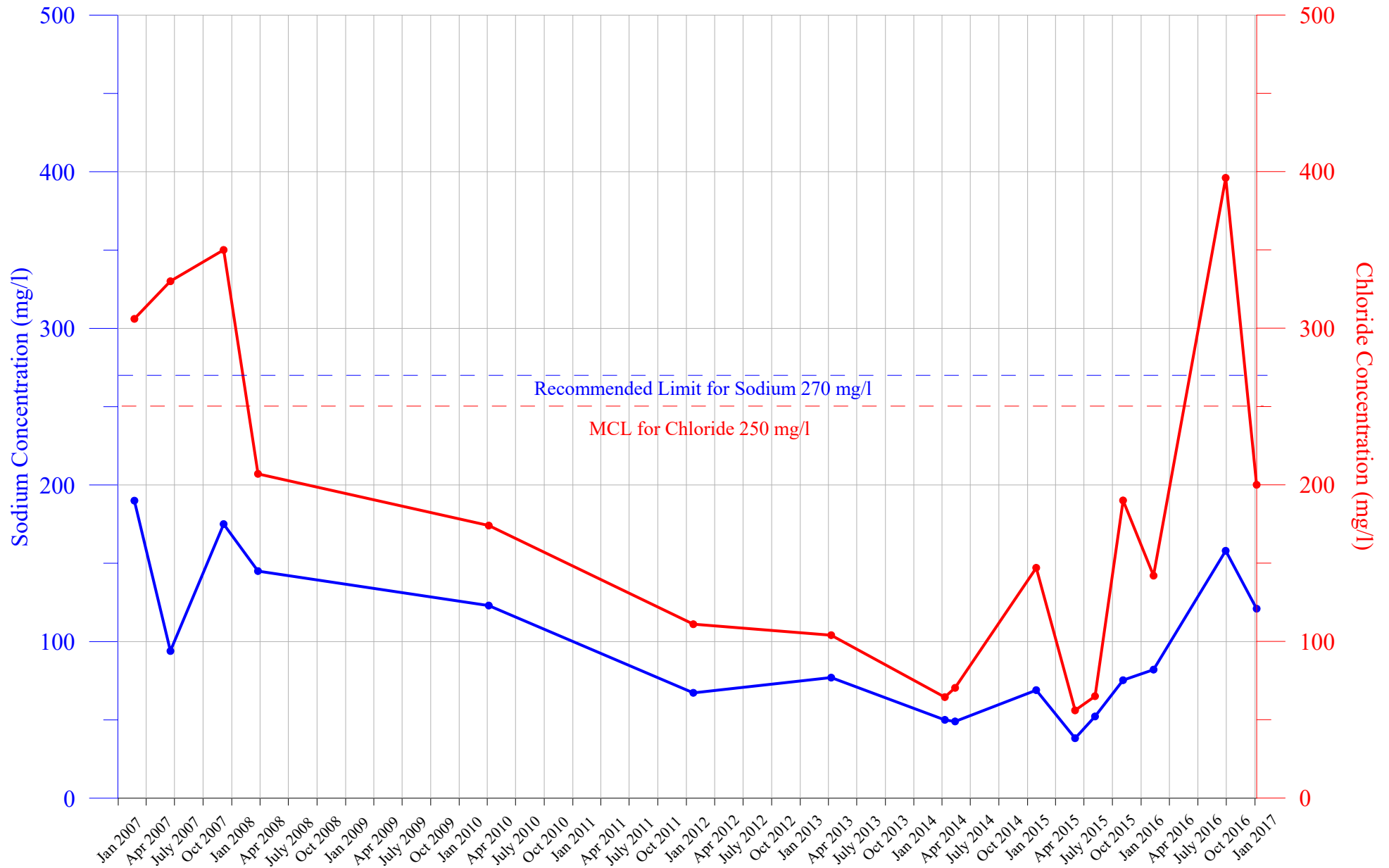
MARY HARRIMAN PARK WELL FIELD
HARRIMAN, NEW YORK

Summary of Sodium and Chloride Concentrations from Monitor Well MHP-MW-2D



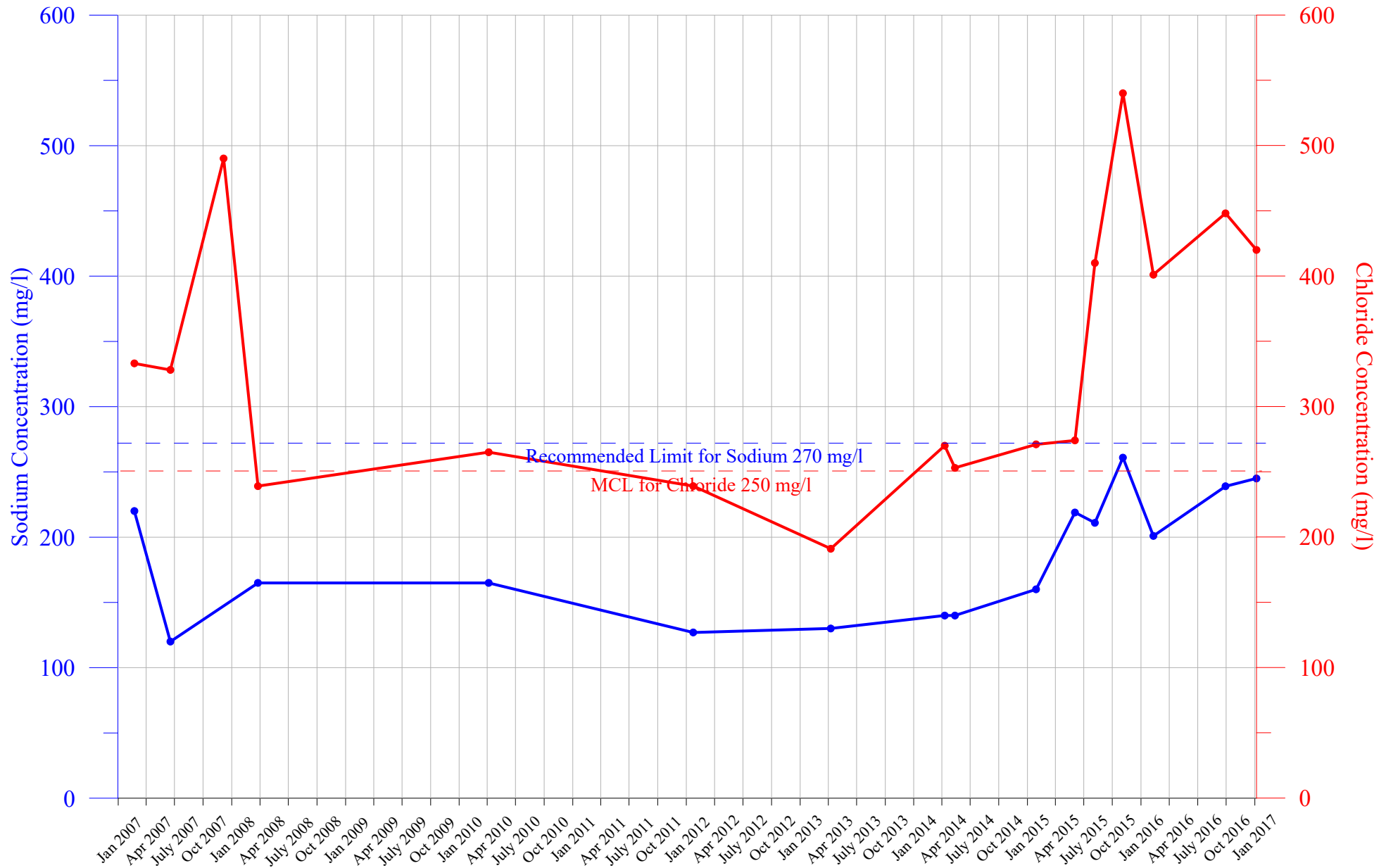
MARY HARRIMAN PARK WELL FIELD
HARRIMAN, NEW YORK

Summary of Sodium and Chloride Concentrations from Monitor Well MHP-MW-3S



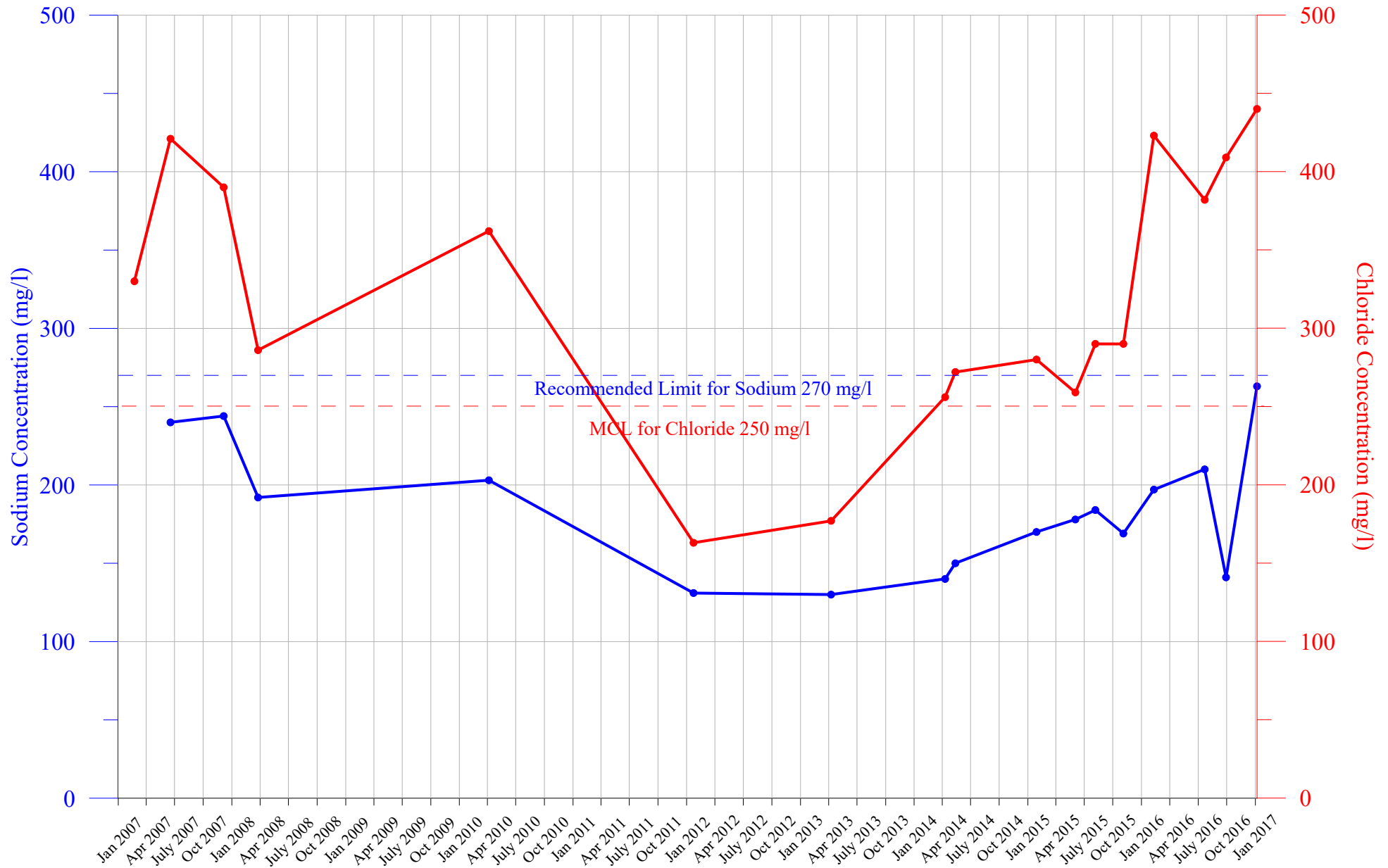
MARY HARRIMAN PARK WELL FIELD
HARRIMAN, NEW YORK

Summary of Sodium and Chloride Concentrations from Monitor Well MHP-MW-3D



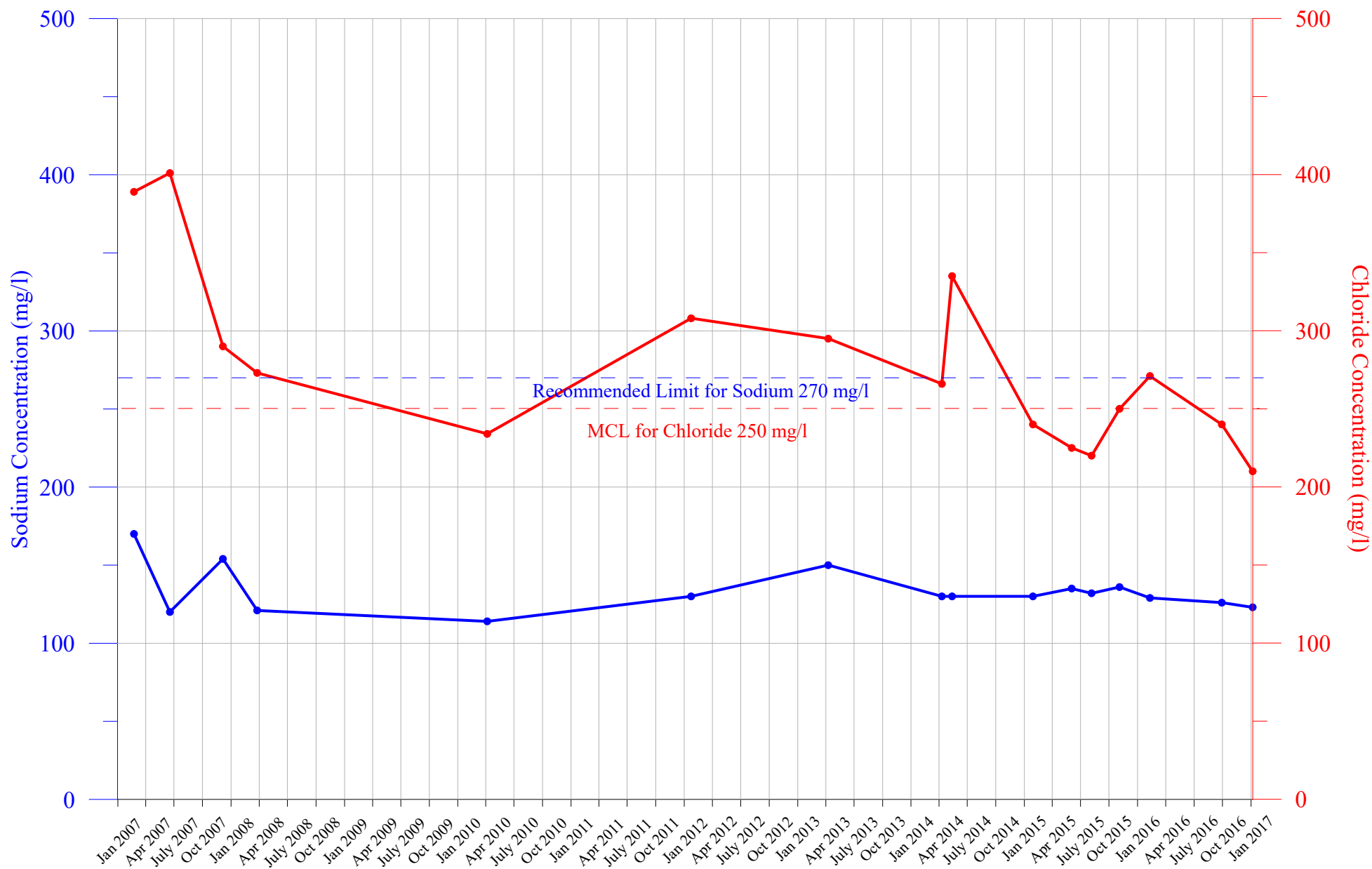
MARY HARRIMAN PARK WELL FIELD
HARRIMAN, NEW YORK

Summary of Sodium and Chloride Concentrations from Monitor Well MHP-MW-4S



MARY HARRIMAN PARK WELL FIELD
HARRIMAN, NEW YORK

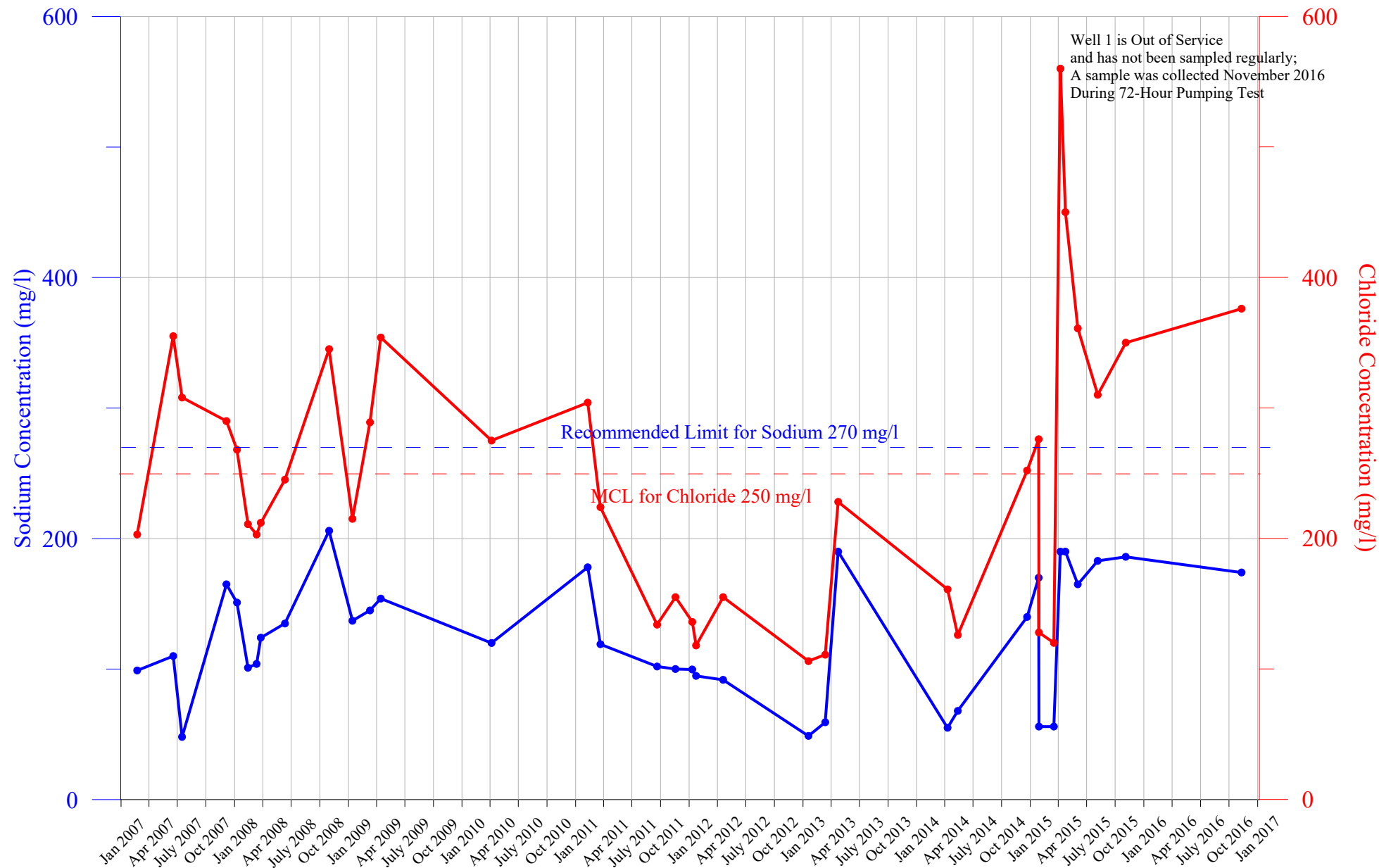
Summary of Sodium and Chloride Concentrations from Monitor Well MHP-MW-5



APPENDIX III

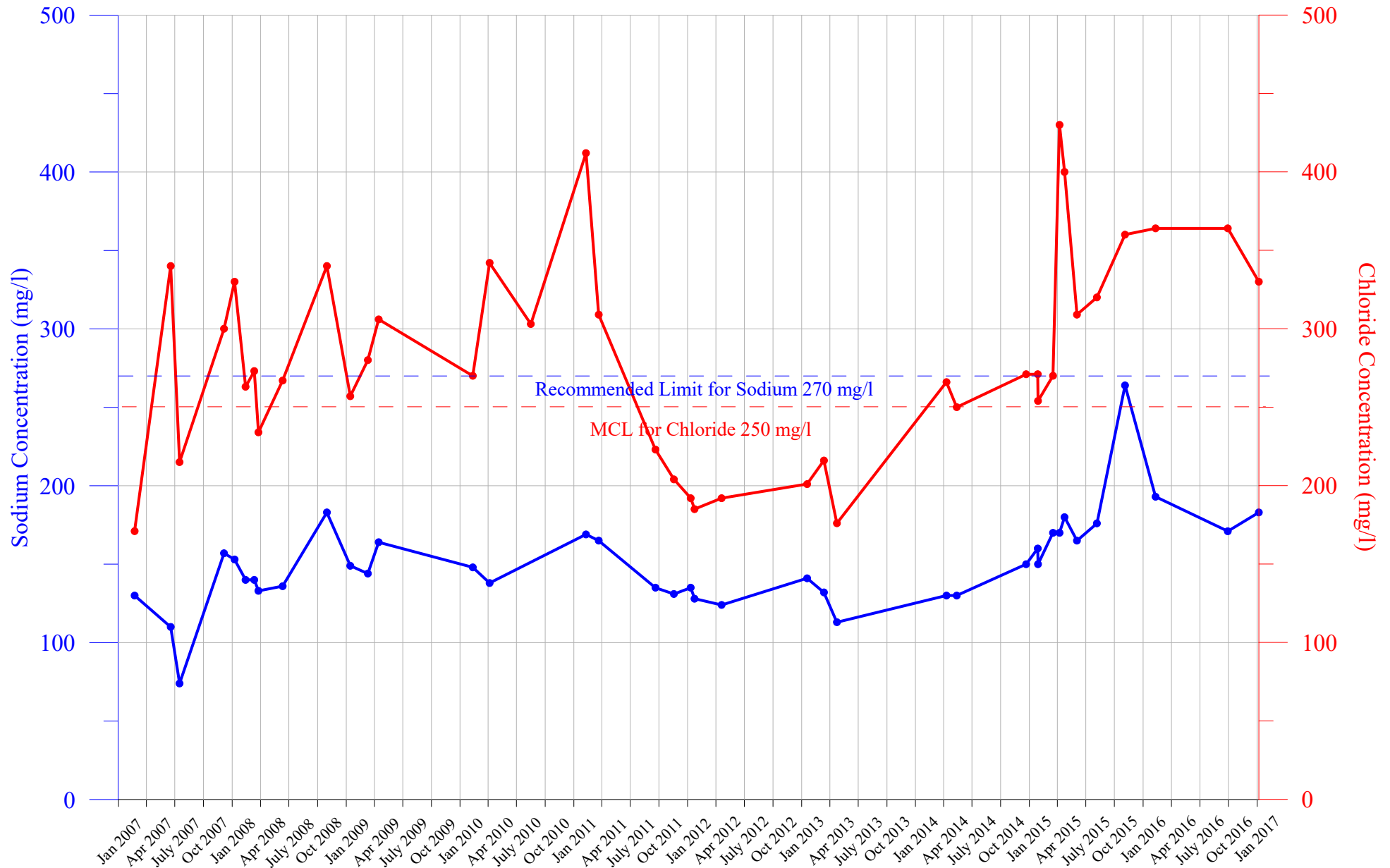
MARY HARRIMAN PARK WELL FIELD
HARRIMAN, NEW YORK

Summary of Sodium and Chloride Concentrations from Production Well MHP-Well 1



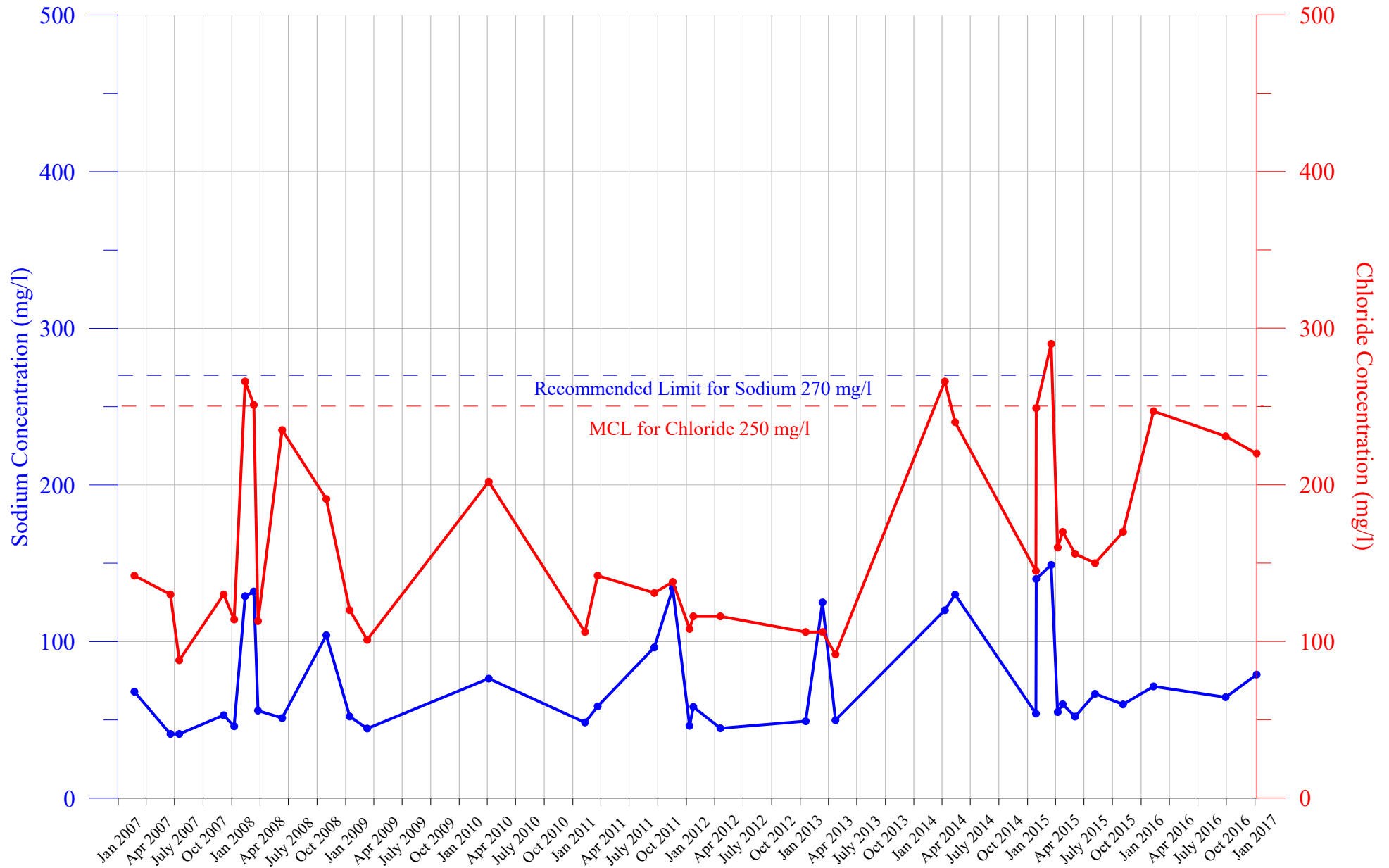
**MARY HARRIMAN PARK WELL FIELD
HARRIMAN, NEW YORK**

Summary of Sodium and Chloride Concentrations from Production Well MHP-Well 1A



MARY HARRIMAN PARK WELL FIELD
HARRIMAN, NEW YORK

Summary of Sodium and Chloride Concentrations from Production Well MHP-Well 3R



Appendix B: Standard Operating Procedures and Guidance

Sampling for 1,4-Dioxane and Per- and Polyfluoroalkyl Substances (PFAS) Under DEC's Part 375 Remedial Programs

Objective

The Department of Environmental Conservation (DEC) is requiring sampling of all environmental media and subsequent analysis for the emerging contaminants 1,4-Dioxane and PFAS as part of all remedial programs implemented under 6 NYCRR Part 375, as further described in the guidance below.

Sample Planning

The number of samples required for emerging contaminant analyses is to be the same number of samples where “full TAL/TCL sampling” would typically be required in an investigation or remedial action compliance program.

Sampling of all media for ECs is required at all sites coming into or already in an investigative phase of any DER program. In other words, if the sampling outlined in the guidance hasn't already been done or isn't part of an existing work plan to be sampled for in the future, it will be necessary to go back out and perform the sampling prior to approving a SC report or issuing a decision document.

PFAS and 1,4-dioxane shall be incorporated into the investigation of potentially affected media, including soil, groundwater, surface water, and sediment as an addition to the standard “full TAL/TCL sampling.” Biota sampling may be necessary based upon the potential for biota to be affected as determined pursuant to a Fish and Wildlife Impact analysis. Soil vapor sampling for PFAS and 1,4-dioxane is not required.

Upon an emerging contaminant being identified as a contaminant of concern (COC) for a site, those compounds must be assessed as part of the remedy selection process in accordance with Part 375 and DER-10 and included as part of the monitoring program upon entering the site management phase.

Special Testing Requirements for Import or Reuse of Soil: Soil imported to a site for use in a soil cap, soil cover, or as backfill must be tested for 1,4-dioxane and PFAS contamination in general conformance with DER-10, Section 5.4(e). Soil samples must be analyzed for 1,4-dioxane using EPA Method 8270, as well as the full list of PFAS compounds (currently 21) using EPA Method 537.1 (modified).

For 1,4-dioxane, soil exceeding 0.1 ppm must be rejected per DER 10: Appendix 5 - Allowable Constituent Levels for Imported Fill or Soil, Subdivision 5.4(e).

If PFOA or PFOS is detected in any sample at or above 1 ppb, then a soil sample must be tested by the Synthetic Precipitation Leaching Procedure (SPLP) and the leachate analyzed. If the SPLP results exceed 70 ppt combined PFOA/S, then the source of backfill must be rejected. Remedial parties have the option of analyzing samples concurrently for both PFAS in soil and in the SPLP leachate to minimize project delays.

The work plan should explicitly describe analysis and reporting requirements, including laboratory analytical procedures for modified methods discussed below.

Analysis and Reporting

Labs should provide a full category B deliverable, and a DUSR should be prepared by an independent 3rd party data validator. QA/QC samples should be collected as required in DER-10, Section 2.3(c). The electronic data submission should meet the requirements provided at:

<https://www.dec.ny.gov/chemical/62440.html>.

PFAS analysis and reporting: DEC has developed a *PFAS Analyte List* (below) for remedial programs. It is expected that reported results for PFAS will include, at a minimum, all the compounds listed. If lab and/or matrix specific issues are encountered for any compounds, the DEC project manager, in consultation with the DEC remedial program chemist, will make case-by-case decisions as to whether certain analytes may be temporarily or permanently discontinued from analysis at each site.

Currently, ELAP does not offer certification for PFAS compounds in matrices other than finished drinking water. However, laboratories analyzing environmental samples (e.g., soil, sediments, and groundwater) are required by DER to hold ELAP certification for PFOA and PFOS in drinking water by EPA Method 537 or ISO 25101. Labs must also adhere to the requirements and criteria set forth in the [Laboratory Guidance for Analysis of PFAS in Non-Potable Water and Solids](#).

Modified EPA Method 537 is the preferred method to use for environmental samples due to its ability to achieve very low detection limits. Reporting limits for PFAS in groundwater and soil are to be 2 ng/L (ppt) and 1 ug/kg (ppb), respectively. If contract labs or work plans submitted by responsible parties indicate that they are not able to achieve these reporting limits for the entire list of 21 PFAS, site-specific decisions will need to be made by the DEC project manager in consultation with the DEC remedial program chemist. Note: Reporting limits for PFOA and PFOS in groundwater should not exceed 2 ng/L.

Additional laboratory methods for analysis of PFAS may be warranted at a site. These methods include Synthetic Precipitation Leaching Procedure (SPLP) by EPA Method 1312 and Total Oxidizable Precursor Assay (TOP Assay).

SPLP is a technique for determining the potential for chemicals in soil to leach to groundwater and may be helpful in determining the need for addressing PFAS-containing soils or other solid material as part of the remedy. SPLP sampling need not be considered if there are no elevated PFAS levels in groundwater. If elevated levels of PFAS are detected in water, and PFAS are also seen in soil, then an SPLP test should be considered to better understand the relationship between the PFAS in the two media.

The TOP Assay can assist in determining the potential PFAS risk at a site. For example, some polyfluoroalkyl substances may transform to form perfluoroalkyl substances, resulting in an increase in perfluoroalkyl substance concentrations as contaminated groundwater moves away from the site. To conceptualize the amount and type of oxidizable perfluoroalkyl substances which could be liberated in the environment, a "TOP Assay" analysis can be performed, which approximates the maximum concentration of perfluoroalkyl substances that could be generated if all polyfluoroalkyl substances were oxidized.

PFAS-containing materials can be made up of per- and polyfluoroalkyl substances that are not analyzable by routine analytical methodology (LC-MS/MS). The TOP assay converts, through oxidation, polyfluoroalkyl substances (precursors) into perfluoroalkyl substances that can be detected by current

analytical methodology. Please note that analysis of highly contaminated samples, such as those from an AFFF site, can result in incomplete oxidation of the samples and an underestimation of the total perfluoroalkyl substances. Please consult with a DEC remedial program chemist for assistance interpreting the results.

1,4-Dioxane analysis and reporting: The reporting limit for 1,4-dioxane in groundwater should be no higher than 0.35 µg/L (ppb) and no higher than 0.1 mg/kg (ppm) in soil. Although ELAP offers certification for both EPA Method 8260 and EPA Method 8270 for 1,4-dioxane, DER is advising the use of Method 8270 SIM for water samples and EPA Method 8270 for soil samples. EPA Method 8270 SIM is not necessary for soils if the lab can achieve the required reporting limits without the use of SIM. Note: 1,4-dioxane is currently listed as a VOC in the Part 375 SCO tables but will be moved to the SVOC table with the next update to Part 375.

Refinement of sample analyses: As with other contaminants that are analyzed for at a site, the emerging contaminant analyte list may be refined for future sampling events based on investigative findings. Initially, however, sampling using this PFAS Analyte List and 1,4-dioxane is needed to understand the nature of contamination.

PFAS Analyte List

Group	Chemical Name	Abbreviation	CAS Number
Perfluoroalkyl sulfonates	Perfluorobutanesulfonic acid	PFBS	375-73-5
	Perfluorohexanesulfonic acid	PFHxS	355-46-4
	Perfluoroheptanesulfonic acid	PFHpS	375-92-8
	Perfluorooctanesulfonic acid	PFOS	1763-23-1
	Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluoroalkyl carboxylates	Perfluorobutanoic acid	PFBA	375-22-4
	Perfluoropentanoic acid	PFPeA	2706-90-3
	Perfluorohexanoic acid	PFHxA	307-24-4
	Perfluoroheptanoic acid	PFHpA	375-85-9
	Perfluorooctanoic acid	PFOA	335-67-1
	Perfluorononanoic acid	PFNA	375-95-1
	Perfluorodecanoic acid	PFDA	335-76-2
	Perfluoroundecanoic acid	PFUA/PFUdA	2058-94-8
	Perfluorododecanoic acid	PFDoA	307-55-1
	Perfluorotridecanoic acid	PFTriA/PFTTrDA	72629-94-8
	Perfluorotetradecanoic acid	PFTA/PFTeDA	376-06-7
Fluorinated Telomer Sulfonates	6:2 Fluorotelomer sulfonate	6:2 FTS	27619-97-2
	8:2 Fluorotelomer sulfonate	8:2 FTS	39108-34-4
Perfluorooctane-sulfonamides	Perfluorooctanesulfonamide	FOSA	754-91-6
Perfluorooctane-sulfonamidoacetic acids	N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9
	N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6



2828 Kraft Ave, Suite 141
Grand Rapids, Michigan 49512
T: 616.940.0600

Prepared for: Brown and Caldwell

Project Title: PFAS Sampling Standard Operating Procedures

Project No.: 082506.011

SOP Version 1.0

Subject: PFAS Sampling

Date: July 26, 2019

Prepared by:

A handwritten signature in blue ink, reading "Jennifer Overvoorde".

Jennifer Overvoorde, P.G.
Principle Geologist/Hydrogeologist

Reviewed by:

A handwritten signature in black ink, reading "Paul Dupre".

Paul Dupre, P.G.
Principle Geologist/Hydrogeologist

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List of Abbreviations

µg/L	micrograms per liter	QAPP	Quality Assurance Project Plan
4:2 FTS	Fluorotelomer sulphonic acid 4:2	RL	Reporting limit
6:2 FTS	Fluorotelomer sulphonic acid 6:2		
8:2 FTS	Fluorotelomer sulphonic acid 8:2		
BC	Brown and Caldwell		
EGLE	Michigan Department of Environment, Great Lakes and Energy		
EPA	United States Environmental Protection Agency		
ETFE	Ethylene-tetrafluoroethylene		
FEP	Fluorinated ethylene propylene		
HDPE	High-density polyethylene		
LDPE	Low-density polyethylene		
mL	milliliter		
N-EtFOSAA	N-ethyl perfluorooctane sulfonamidoacetic acid		
N-MeFOSAA	N-methyl perfluorooctane sulfonamidoacetic acid		
ng/L	nanograms per liter		
PCTFE	Polychlorotrifluoroethylene		
PFAS	per- and polyfluoroalkyl substances		
PFBA	Perfluorobutanoic acid		
PFBS	Perfluorobutanesulfonic acid		
PFDA	Perfluorodecanoic acid		
PFDoA	Perfluorododecanoic acid		
PFDS	Perfluorodecanesulfonic acid		
PFHpA	Perfluoroheptanoic acid		
PFHpS	Perfluoroheptanesulfonic acid		
PFHxA	Perfluorohexanoic acid		
PFHxS	Perfluorohexanesulfonic acid		
PFNA	Perfluorononanoic acid		
PFNS	Perfluorononanesulfonic acid		
PFOA	Perfluorooctanoic acid		
PFOS	Perfluorooctanesulfonic acid		
PFOSA	Perfluorooctanesulfonamide		
PFPeA	Perfluoropentanoic acid		
PFPeS	Perfluoropentanesulfonic acid		
PFTeDA	Perfluorotetradecanoic acid		
PFTrDA	Perfluorotridecanoic acid		
PFUnA	Perfluoroundecanoic acid		
PPE	Personal protective equipment		
PTFE	Polytetrafluoroethylene		
PVDF	Polyvinylidene fluoride		

Disclaimer:

The information contained in this SOP will be updated as new information becomes available. The user of this PFAS Sampling SOP is encouraged to visit the state-specific regulatory agency's website where the investigation will occur to access any current state-specific sampling and/or regulatory criteria or requirements.

In addition, before sampling is planned and/or conducted, the BC project manager and/or field sampler need to contact the BC PFAS CoP facilitator to verify the appropriateness and continued relevance of this SOP for their particular sampling of PFAS in the state they are doing it.

Section 1: Objectives

The objective of this standard operating procedure (SOP) is to provide methods for the planning and execution of per- and polyfluoroalkyl substances (PFAS) monitoring events and to provide standardized reporting formats for documentation of data. A further objective is to provide a technical resource that can be used for preparing field sampling plans and for training. Furthermore, these methods address drinking water, groundwater, surface water, leachate, soil, and sediment sample collection under a wide variety of physical and regulatory conditions. This SOP has been specifically developed with the objective of collecting samples for the quantitative analysis of PFAS compounds.

The procedures herein have been developed in conformance with the "Groundwater PFAS Sampling Guidance", (EGLE, 2018), various ITRC PFAS Fact Sheet publications, the National Groundwater Association's (NGWA) PFAS resource on sampling and analytical methods (NGWA, 2017), and USEPA Method 537.1.

Section 2: Applicability

This SOP is intended for use by Brown and Caldwell (BC) personnel for the documentation and sampling of residential wells, monitoring wells, surface water points, leachate, soil locations and sediment locations that may be part of environmental site assessments and/or investigations. Site specific sampling methods and procedures depend on current regulatory requirements, project specific objectives, and subsurface conditions and should be discussed in project specific planning documents and field readiness reviews. PFAS sample collection activities will be performed in accordance with current regulatory requirements and both those site-specific standard field sampling protocols and the additional procedures listed below in order to obtain representative samples and usable, valid data.

Laboratory method detection limits and reporting limits for PFAS samples are in the parts per trillion [nanogram per liter (ng/l)] range. Application of this SOP requires careful execution because PFAS compounds have been widely used in commerce and are present in some traditional sampling products (examples in the following sections). Thus, it is critically important to avoid potential sources of cross-contamination that can bias analytical results, which will maximize the potential for producing accurate data.

2.1 Health and Safety

This SOP does not address the safety concerns, if any, associated with the potential presence of PFAS during monitoring including potential physical and chemical hazards. The user must refer to and adhere to the site-specific Health and Safety Plan (HASP).

Section 3: Responsibilities

The BC project manager is responsible for properly planning and executing the project involving PFAS monitoring, including coordinating with the Regional Safety Unit Manager during the development of health and safety procedures specific to the chemical and physical hazards associated with PFAS monitoring.



The field staff are responsible for organizing and conducting the monitoring event, and for following project specifications defined in the project specific planning documents. In addition, they are responsible for recording pertinent field data on appropriate forms and in the field notebook.

The site safety officer, as defined in the site specific HASP, is responsible for overseeing the health and safety of BC personnel and for stopping work, if necessary, to mitigate any unforeseen safety hazards observed in the field.

Section 4: Potential Sources of PFAS Cross-Contamination

Potential sources of PFAS cross-contamination in the typical sampling environment include water used during drilling or decontamination, fluids and materials associated with drill rigs, materials used within the sampling environment, sampling equipment, field clothing and personal protective equipment (PPE), sun and biological protection products, personal hygiene and personal care products (PCPs), food packaging, and the environment itself.

The materials associated with sampling that have the potential for PFAS cross-contamination have been divided into three major groups (prohibited, allowable, or needs screening) and are summarized best in the MDEQ *PFAS Sampling Quick Reference Field Guide* (Quick Reference Guide) included as Appendix A.

Note that at this time no published research is available that documents the use of various materials and effect on sample results. Therefore, a conservative approach is recommended, and the guidance below is based on the collection of multiple environmental samples at various PFAS Sites.

4.1 PFAS-Free Water

The term PFAS-free water is defined here as water that does not contain significant concentrations of compounds in a specific PFAS analyte list that is being analyzed at a project-defined level. The significant concentrations depend on project data quality objectives and could, for instance, be less than the laboratory reporting limit, less than (<) one half of the limit of quantitation, or other defined criteria for the specific PFAS compound of interest (ITRC, 2017).

One important consideration for each project is to identify a PFAS-free water source to use for decontamination of sampling and drilling equipment when applicable. The decontamination of sampling tools or small equipment parts can be performed using laboratory-supplied verified PFAS-free water. Other water can only be used for decontamination purposes if it has been analyzed and shown to be PFAS-free as defined for the project. This applies to water brought on-site by drillers to use as charge water or equipment decontamination and/or the potable/non-potable water obtained directly from the site for decontamination purposes.

4.2 Sampling Equipment

The actual list of PFAS-containing materials potentially encountered onsite will change based on the specific sampled media and site-specific sampling conditions. Do not use equipment that contains known fluoropolymers. For example, the trademark Kynar® contains polyvinylidene fluoride (PVDF) (tubing, coatings on aluminum, galvanized or aluminized steel, etc.); the trademark Neoflon® contains polychlorotrifluoroethylene (PCTFE) (valves, seals, gaskets, food packaging, etc.); ethylene-tetrafluoroethylene (ETFE) including Tefzel® has been found in wire and cable insulation and covers, films for roofing and siding, liners in pipes, and some cable tie wraps.

Other precautions include:

- Do not use products containing the trademark Teflon® which contains polytetrafluoroethylene (PTFE) (drilling compounds, waterproofing, etc.) UNLESS an equipment blank has confirmed it to be PFAS-free.

- Many Teflon®-lined tubing suppliers have tested their tubing and are able to provide documentation that their tubing does not affect (leach or absorb) PFAS results.
- BC has conducted testing at sites with dedicated groundwater sampling pumps with Teflon® o-rings and Teflon®-lined low-density polyethylene (LDPE) tubing in monitoring wells have shown consistent <2.0 ng/L results when expected (i.e., background or side gradient of a known source).
- Sonic drilling joint compound contains Teflon®. There is a PFAS free joint compound that is a different color. Know the difference and verify with the driller what is being used before mobilization.
- Do not use (LDPE) for items that will come into direct contact with the sample media UNLESS an equipment blank has confirmed it to be PFAS-free.
 - LDPE does not contain PFAS in the raw material but may contain PFAS cross-contamination from the manufacturing process.
 - Materials that are either made of high-density polyethylene (HDPE), polypropylene, silicone, or acetate are preferred.
- LDPE bags (e.g., Ziploc®) that do not come into direct contact with the sample media and do not introduce cross-contamination with samples may be used.
- Glass bottles or containers may be used if they are known to be PFAS-free.
 - PFAS have been found to adsorb to glass, especially when the sample is in contact with the glass for a long period of time (e.g. being stored in a glass container).
- Aluminum foil may be used if the shiny side is placed away from the sample.
 - As a precaution, it is recommended that an equipment blank sample be collected on the aluminum foil to confirm it is PFAS-free.
- Proactive Pumps have begun manufacturing PFAS free pumps (i.e., the Mega Monsoon and most of their others as well have been certified PFAS free). The QED portable bladder pump is also PFAS free. Other companies are following suit so check with your pump rental supplier to make sure you are getting a PFAS free pump.

4.3 Field Clothing and Personal Protective Equipment (PPE)

Field planning and mobilizing efforts should address the physical, chemical, and biological hazards associated with each PFAS site. The mitigation of potential risks may be documented in a site-specific HASP or a QAPP. Due to the extensive use of PFAS in many industries and products, PPE may contain PFAS. During PFAS investigation, PPE containing PFAS should be avoided, whenever possible, to prevent cross-contamination. The development of the HASP or QAPP should consider these factors before mobilization in the field.

However, personal safety is paramount. The safety of staff should not be compromised by fear of PFAS containing materials without scientific basis. Deviation from this guidance, including those necessary to ensure the health and safety of sampling personnel (i.e., if flame-retardant suits must be worn per client site requirements), must be recorded in field notes.

Prohibited items include:

- Clothing that has been made or coated with water, dirt, and/or stain resistant chemicals or chemically treated for insect resistance and ultraviolet protection.
- Clothing that has been laundered with a fabric softener that contains PFAS.
- Sunscreens and insect repellents containing PFAS ingredients. Refer to Appendix A for a list of approved sunscreens and insect repellents.

Food must be consumed outside the Exclusion Zone identified in the HASP. Thoroughly wash hands with PFAS free water after consumption.

Personal hygiene and personal care products may only be used outside the Exclusion Zone. Do not handle these products when PPE is present that will be used during sampling. Thoroughly wash hands with PFAS free water after handling.

Section 5: Laboratories and Analytical Parameter Lists

Only a limited number of labs are currently certified to perform PFAS analysis. The following is a short list of qualified laboratories:

- Alpha Laboratory: Westborough, MA Mr. Jim Occhialini 1-800-624-9220
- Eurofins Eaton Analytical: South Bend, IN 574-233-4777
- Eurofins Lancaster Laboratory: Lancaster, PA 717-656-2300
- Eurofins Test America: West Sacramento, CA 916-373-5600
 - South Burlington, VT 802-660-1990
- Pace Analytical Services, LLC: Mr. Scott Martin 386-248-5195
 - Minneapolis, MN 612-607-1700
 - Ormond Beach, FL 386-672-5668
- SGS Accutest: Mr. Norm Farmer 407-425-6700 ext. 2602
- Vista Laboratory: El Dorado Hills, CA

Appendix B contains the list of PFAS parameters currently being analyzed at each laboratory, their reporting limits and analytical method(s) being used.

Section 6: General Preparation for All Sampling Events

6.1 Office

Physical aspects of the sampling program will be organized in the office prior to embarking on a field sampling project. The time spent in the field is very valuable and should be spent on sample collection, making field measurements and recording data and not on the organization of equipment and containers.

The sequence of sampling will be pre-determined on the basis of existing matrix-specific quality data, if available. Generally, the anticipated least contaminated sample locations will be sampled first, proceeding to the progressively more contaminated sample locations.

Update the PFAS sampling field checklist (Appendix C) per your specific Site and matrix (matrices) to be sampled. This checklist is to be included with your field note package to document correct PFAS sampling procedures are being followed.

6.2 Field

The following procedures will be conducted in the field prior to sampling.

- Tailgate Meeting and Rig Maintenance Check – The field team, including the drilling subcontractor if applicable, will go over the work plan and potential hazards that may be encountered to ensure that equipment/compounds being used are PFAS-free and work is performed to project specifications and in a safe manner. It is suggested that a discussion occurs with the driller during the RFP process regarding the use of PFAS-free equipment/compounds.

- Preparation of Work Area – A suitable work area will be established around the perimeter of the sample locations. This will provide a clean surface on which sampling equipment can be placed such that it will not become inadvertently contaminated leading to the potential cross-contamination of the sample(s).

Section 7: Residential Well (Drinking Water) Sampling

This guidance assumes staff have basic familiarity with and/or understanding of basic residential well sampling procedures.

7.1 Required Materials and Equipment

Many materials are required for successfully completing a drinking water sampling event. The field personnel should be aware of what is required to conduct the work in accordance with the project specific sampling plan and have required materials available and in working order prior to the beginning of the sampling. The following is a general list of materials that are needed for performing the tasks outlined in this SOP.

- Health and Safety supplies per the site-specific HASP
- Sample containers provided by the analytical laboratory
- pH/temperature measurement instrument
- Drinking water sampling data sheets
- Logbook, if required for the project
- General tools (e.g., clean 5-gallon bucket, adjustable wrench, etc.)

7.2 Field Procedures

7.2.1 Preparation

Before sampling, obtain the well construction record, if available. These can often be found through a state database or the local health department.

Contact the well owner to arrange a sample collection date.

7.2.2 Sample Collection

1. Discuss with the property owner water treatment devices/systems and identify an appropriate tap to sample. Inspect the tap for evidence of any Teflon tape or plumbers' putty. Remove the aerator from the sample point (if applicable). Note findings in the field book and/or on the sample form.
 - Sample locations should be upstream of the treatment device/system, if present.
 - Primary sample location should be an outside tap. Secondary sample location would be the kitchen sink. DO NOT collect a sample from a hose.
2. In accordance with USEPA Method 537.1, the tap must be flushed until the water temperature has stabilized based on field measurements (usually 3 to 5 minutes). Use the cold water tap only. Record the final pH and temperature reading prior to sampling.
 - If using an outside tap, collect the flushed water in a bucket and dispose of the water in the yard.
3. Samples will be collected in a 250-milliliter (mL) polypropylene bottle fitted with a polypropylene screw-cap. Teflon-lined caps are prohibited. Bottles may (laboratory dependent) contain Trizma®.
 - Unpowdered nitrile gloves should be changed frequently (i.e., between sampling intervals and/or if you believe they have become contaminated during the sampling process).
 - Never set the cap down, touch the part of the cap that contacts the bottle, or let anything touch the rim of the bottle or inside the cap.

- Fill the bottle to the neck only, taking care to not flush out the Trizma preservative (if present). Samples do not need to be collected headspace free.
- Cap the bottle, then gently agitate by hand until preservative is dissolved. Do not reopen the bottle.
- A field reagent blank (FB) will be submitted for each residential sample collected unless another governing document specifies a different frequency. Due to the elevated scrutiny with residential samples, a greater rate of field blanks ensures confidence in results.
 - The laboratory will fill the field blank sample bottle with PFAS-free water and preservatives, seal, and ship to the sampling site along with the sample bottles. For each FB shipped, an empty sample bottle (no preservatives) must also be shipped. At the sampling site, the sampler must open the shipped FB, pour the preserved PFAS-free water into the empty shipped sample bottle, and seal and label this bottle as the FB. The FB is shipped back to the laboratory along with the samples and analyzed to determine if PFAS were introduced into the sample during sample collection/handling
- Bag the sample away from the sample location using resealable LDPE bags (e.g., Ziploc®) and ship in a laboratory-provided cooler filled with wet ice. Samples must be chilled before and during shipment and must be confirmed to be at or below 4 °C when the samples are received at the laboratory. (USEPA Method 537.1)
- Chain of Custody (COC) should be single-bagged in resealable LDPE bags (e.g., Ziploc®) and taped to the inside of the cooler lid. The cooler should be taped closed with a custody seal and shipped by overnight courier or picked up by a laboratory courier.

7.3 Analytical Parameters

The current Unregulated Contaminant Monitoring Rule 3 (UCMR-3) Standard List (6 analytes – refer to the acronym list at the beginning of this document for full names): PFOS, PFOA, PFNA, PFHxS, PFHpA, PFBS

Expanded current UCMR-3 List (14 analytes): PFOS, PFOA, PFNA, PFHxS, PFHpA, PFBS, PFHxA, PFDA, PFUnA, PFTriA, PFDoA, PFTeA, NEtFOSAA, NMeFOSAA

These lists are subject to change so please check the regulations in the state where the project is in to verify the analyte list.

Section 8: Groundwater Sampling

This guidance assumes staff has familiarity with and/or understanding of basic groundwater sampling procedures.

8.1 Required Materials and Equipment

Many materials are required for successfully completing a groundwater sampling event. The field personnel should be aware of what is required to conduct the work in accordance with the project specific sampling plan and have the required materials available and in working order prior to the beginning of the sampling. The following is a general list of materials that are needed for performing the tasks outlined in this SOP.

- Health and Safety supplies as outlined in the HASP
- Groundwater sampling equipment such as pumps, bailers, etc., in accordance with the project specific goals and procedures.
- Sample containers provided by analytical laboratory
- Water quality measurement instrument (e.g., Multi-parameter Horiba U-22 or similar) as required
- Electric Water Level Meter

- PFAS-free Decontamination Supplies
- Groundwater sampling data sheets
- Logbook, if required for the project
- Site Map depicting the well locations
- General tools

8.2 Field Procedures

8.2.1 Water Level Measurement

The water level probe (i.e., the portion that comes into contact with the water in the well) will be decontaminated with an approved soap (i.e., Alconox® or Liquinox®) and rinsed with PFAS-free deionized water prior to and after each water level measurement. Disposable powderless nitrile gloves will be worn while determining the static water levels and the gloves should be changed between each well.

Observations and data will be recorded on the field data sheets and/or the logbook.

8.2.2 Well Purging

- If using a portable or dedicated bladder pump or some other submersible PFAS free pump, purge and stabilize the monitoring well using low-flow procedures described in the site's SAP or in accordance with the USEPA's *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures* (USEPA, 1996). Collect the PFC sample once the well parameters (pH, temp, etc.) have stabilized.
- If using a bailer, wells will either be purged of three volumes or purged to dryness using new HDPE bailers with a piece of new cotton-based twine.
 - For wells that purge dry, the wells will be purged completely and allowed to recover to within 90% of its original water level prior to sample collection.
- As a check on purging efficiency, the pH, conductivity, and temperature of the groundwater will be measured and noted on the field data sheets and/or the logbook. In wells where three or more well volumes are removed, if the variation between the last three measurements is greater than ± 0.2 S.U. for pH, $\pm 3\%$ for conductivity, and ± 0.5 degrees Celsius ($^{\circ}\text{C}$) for temperature after purging three well volumes, additional water will be purged until the measurements are within the variation.

8.2.3 Sample Collection

Wells will be sampled immediately or as soon as practicable after purging or within 24 hours for low yield (i.e. purged dry) wells.

If using a bailer, lower and raise it gently through the water column to minimize agitation and reduce aeration. The bailer should be lowered to the middle of the screened interval.

1. Samples will be collected in a 250-mL polypropylene bottle fitted with a polypropylene screw-cap. Teflon-lined caps are prohibited. Bottles may (laboratory dependent) contain Trizma®.
2. Fill sample bottles, taking care not to flush out the sample preservation reagent (if present). Samples do not need to be collected headspace free.
3. After collecting the sample, cap the bottle and agitate by hand until preservative is dissolved (if applicable). The sample will remain sealed from time of collection until extraction by the laboratory.
4. A FB will be submitted at a frequency specified in the site-specific QAPP/Work Plan or other governing document. If no document exists, a rate of 1 per 10 samples collected during each monitoring event or at least one FB per event is recommended.

- The laboratory will fill the field blank sample bottle with PFAS-free water and preservatives, seal, and ship to the sampling site along with the sample bottles. For each FB shipped, an empty sample bottle (no preservatives) must also be shipped. At the sampling site, the sampler must open the shipped FB, pour the preserved PFAS-free water into the empty shipped sample bottle, and seal and label this bottle as the FB. The FB is shipped back to the laboratory along with the samples and analyzed to determine if PFAS were introduced into the sample during sample collection/handling.
5. An equipment blank (EB) will be collected and submitted at a frequency specified in the site-specific QAPP/Work Plan or other governing document. If no document exists, a rate of 1 per 10 samples collected during each monitoring event or at least one EB per event is recommended.
 - Laboratory provided PFAS-free water will be poured over or through the sampling equipment, collected in an empty sample container, and sealed and labeled the bottle as the EB. The EB will be shipped back to the laboratory along with the samples and analyzed to determine if PFAS were introduced in the sample through use of the sampling equipment.
 6. Samples will be chilled from ambient temperature to at least 4 °C after collection and during shipment to the laboratory. In an effort for samples to not exceed this temperature, samples will remain in the laboratory provided sample cooler after collection at all times up until removal at the laboratory. The sample coolers will be refilled with ice regularly and meltwater removed as appropriate. Due to the potential for PFAS sample contamination, only “water ice” will be used (i.e., “blue ice” or a gel ice packet use is prohibited). Sample temperatures must be confirmed to be at or below 4 °C when the samples are received at the laboratory.
 7. Samples will be labeled with an adhesive label supplied by the laboratory. The label will contain the name of the laboratory, the name and affiliation of the sampler, the sample time and date, the intended analyte(s), the project name, and the well identification.
 8. Duplicate samples will be collected at a rate specified in the site-specific QAPP/Work Plan or other governing document. If no document exists, a rate of one per every ten samples collected (or at least one per event) is recommended and labeled (e.g., Dup 01, Dup 02, etc.) in a manner that will shield the sample identity from the laboratory. The sample point from which the duplicate will be collected will be recorded in the field notebook and/or on the field information sheet.

Field personnel will be aware of the holding times and will make arrangements to have the samples delivered to the laboratory to meet these holding times. Samples will be transported using either a lab courier or an overnight delivery service (preferably Federal Express), or by direct delivery to the laboratory.

Samples will be extracted as soon as possible but no later than 14 days from sample collection. The extracted sample will be analyzed within 28 days.

8.3 Analytical Parameters

There is no “standard” PFAS analytical parameter list for groundwater. Please refer to Appendix B for laboratory specific PFAS analyte lists.

Section 9: Surface Water Sampling

This guidance assumes staff has familiarity with and/or understanding of basic surface water sampling procedures.

9.1 Required Materials and Equipment

Many materials are required for successfully completing a surface water sampling event. The field personnel should be aware of what is required to conduct the work in accordance with the project specific sampling

plan and have all required materials available and in working order prior to the beginning of the sampling. The following is a general list of materials that are needed for performing the tasks outlined in this SOP.

- Health and Safety supplies per the HASP
- Surface water sampling equipment such as bailers, Kemmerer samplers, dipping cups, etc., in accordance with the project specific goals, sampling depths and procedures.
- Sample containers provided by the analytical laboratory
- Water quality measurement instrument (e.g., Multi-parameter Horiba U-22 or similar) as required
- Surface water sampling data sheets
- Logbook, as needed
- General tools (e.g., clean 5-gallon bucket, paper towels, etc.)

9.2 Field Procedures

9.2.1 Sample Collection

1. Rinse the sampler with water from just downstream of the surface water sample collection area in order to minimize the sediment disturbance at the surface water sample location.
2. Collect the PFAS sample and then collect a second surface water sample for field readings (temperature, pH, and specific conductance).
3. Samples will be collected in a 250-mL polypropylene bottle fitted with a polypropylene screw-cap. Teflon-lined caps are prohibited. Bottles may (laboratory dependent) contain Trizma®.
4. Fill sample bottles, taking care not to flush out the sample preservation reagent (if present). Samples do not need to be collected headspace free.
5. After collecting the sample, cap the bottle and agitate by hand until preservative is dissolved (if applicable). Samples do not need to be headspace free. The sample will remain sealed from time of collection until extraction by the laboratory.
6. A FB will be submitted at a frequency specified in the site-specific QAPP/Work Plan or other governing document. If no document exists, a rate of 1 per 10 samples collected during each monitoring event or at least one FB per event is recommended.
7. Duplicate samples will be collected at a rate specified in the site-specific QAPP/Work Plan or other governing document. If no document exists, a rate of one per every ten samples collected (or at least one per event) is recommended and labeled (e.g., Dup 01, Dup 02, etc.) in a manner that will shield the sample identity from the laboratory. The sample point from which the duplicate will be collected will be recorded in the field notebook and/or on the field information sheet
8. Sample preservation and shipment is similar to the methods provided in Section 8.2.3

9.3 Analytical Parameters

There is no “standard” PFAS analytical parameter list for surface water. Please refer to Appendix B for laboratory specific PFAS analyte lists.

Section 10: Leachate Sampling

This guidance assumes staff has familiarity with and/or understanding of basic leachate sampling procedures.

10.1 Required Materials and Equipment

Many materials are required for successfully completing a leachate sampling event. The field personnel should be aware of what is required to conduct the work in accordance with the project specific sampling plan and have all required materials available and in working order prior to the beginning of the sampling. The following is a general list of materials that are needed for performing the tasks outlined in this SOP.

- Health and Safety supplies per the site HASP
- Leachate sampling equipment such as pumps, bailers, etc., in accordance with the project specific goals and procedures
- Sample containers provided by the analytical laboratory
- pH/temperature measurement instrumentation
- Leachate sampling data sheets
- Logbook, if required.
- General tools (e.g., clean 5-gallon bucket, adjustable wrench, etc.)

10.2 Field Procedures

10.2.1 Vertical Sump/Manhole

1. Remove the individual sump/manhole cover.
2. Using a new disposable PVC or HDPE bottom-emptying bailer with a new piece of cotton-based twine, gently lower the sampling device to collect the leachate sample from the collection sump.
3. Raise the bailer gently through the water/leachate to reduce aeration. The sample will then be transferred from the bailer to the sample containers in a way which will minimize agitation and aeration.
4. Excess liquids obtained during sampling will be collected in a 5-gallon bucket and returned to the collection sump.

10.2.2 Side Slope Risers

1. Leachate will be collected from the sample port located on the discharge pipe.
2. Flush the tap until the water temperature has stabilized (approximately 3 to 5 minutes). Record the final pH and temperature reading prior to sampling.
3. Excess liquids obtained during sampling will be collected in a 5-gallon bucket and returned to the collection sump or to the primary sample collection point.

Duplicate samples will be collected at a rate specified in the site-specific QAPP/Work Plan or other governing document. If no document exists, a rate of one per every ten samples collected (or at least one per event) is recommended and labeled (e.g., Dup 01, Dup 02, etc.) in a manner that will shield the sample identity from the laboratory. The sample point from which the duplicate will be collected will be recorded in the field notebook and/or on the field information sheet.

Sample preservation and shipping will be similar to the procedures provided in Section 8.2.3.

10.3 Analytical Parameters

There is no “standard” PFAS analytical parameter list for leachate. Please refer to Appendix B for laboratory specific PFAS analyte lists.

Section 11: Soil Sampling

This guidance assumes staff has basic familiarity with and/or understanding of basic soil sampling procedures.

11.1 Required Materials and Equipment

- Health and Safety supplies per the project HASP
- Soil sampling equipment such as rulers, plastic bags, mason jars, aluminum foil, etc., in accordance with the project specific goals and procedures
- Soil screening equipment such as a Photo-ionization detector (PID) in accordance with the project specific goals and procedures
- Sample containers provided by analytical laboratory
- PFAS-free decontamination Supplies
- Boring log sheets
- Logbook, if required
- Site Map with proposed sample locations
- General tools

11.2 Field Procedures

11.2.1 Sample Collection

Sub-Surface Soil Samples from Soil Borings

Soil samples should be as undisturbed as possible, typically using a coring type of mechanism in a way that attempts to preserve the soil structure. Therefore, soil borings should be advanced using direct-push techniques or hollow-stem auger (HSA) drilling methods, depending on the site logistics and the sampling objectives at a given area of concern.

1. Soil samples will be collected from the borings using decontaminated split-barrel samplers (HSA) or macro-core samplers with dedicated acetate (or other PFAS-free) liners (direct-push rig).
2. Place a new clear plastic liner (use an acetate or other PFAS-free liner) into the steel core barrel of your direct push soil sampling device. Push or auger the sampling device into the subsurface at the desired sample location. Pull the core barrel out, place on a cutting board/surface, remove the liner and cut open. The sediment core is then sliced open to reveal a “clean face” for logging lithology and structure and for sampling.
 - Good housekeeping is paramount when collecting soil samples! The spreading of contaminated soil may result in cross contamination when analyzing at a ng/L range. Ensure that the cutting board is cleaned after each core is opened, logged and sampled.
3. Samples from each barrel/sampler will be screened in the field using a PID and readings for each sample interval will be recorded on the boring log and/or the field log book. Soil samples will be observed for physical properties such as color, sorting, grain size, etc.
 - **Shake Test:** While logging the sediment lithology, visual observations of any foam and/or staining will be noted and suspected contaminated media will be placed in a clear container and shaken for 10-20 seconds, looking for resulting foam. Foaming in the container would qualitatively indicate that the media in this area may contain residual levels of Aqueous Film-Forming Foam (AFFF) that may require further investigation, sampling and/or cleanup as discussed in Section 3.4 of the AFFF Interstate Technology Regulatory Council (ITRC) Fact Sheet published October 2018.

4. Soil to be tested will be removed from the split spoon or acetate liner and placed in a HDPE, glass, or polypropylene sample bottles with Teflon®-free caps, provided by the laboratory. Bottles should only be opened immediately prior to sampling. Fill each bottle to the neck of the container.
5. Samples will be chilled from ambient temperature to a minimum of 4 °C after collection and during shipment to the laboratory. In an effort for samples to not exceed this temperature, samples will remain in a sample cooler after collection at all times up until removal at the laboratory. The sample coolers will be refilled with ice regularly and meltwater removed as appropriate. Due to the potential for PFAS sample contamination, only “water ice” will be used (i.e., “blue ice” or a gel ice packet use is prohibited). Sample temperatures must be confirmed to be at or below 6 °C when the samples are received at the laboratory.
6. The soil sampling device will be decontaminated with an approved soap (i.e., Alconox® or Liquinox®) and rinsed with PFAS-free deionized water prior to and after each soil sample.
7. An equipment blank (EB) will be collected and submitted at a frequency specified in the site-specific QAPP/Work Plan or other governing document. If no document exists, a rate of 1 per 10 samples collected during each monitoring event or at least one EB per event is recommended.
 - Laboratory provided PFAS-free water will be poured over or through the sampling equipment, collected in an empty sample container, seal and label the bottle as the EB. The EB will be shipped back to the laboratory along with the samples and analyzed to determine if PFAS were introduced in the sample through use of the sampling equipment.
8. Duplicate samples will be collected at a rate specified in the site-specific QAPP/Work Plan or other governing document. If no document exists, a rate of one per every ten samples collected (or at least one per event) is recommended and labeled (e.g., Dup 01, Dup 02, etc.) in a manner that will shield the sample identity from the laboratory. The sample point from which the duplicate will be collected will be recorded in the field notebook and/or on the boring log.
9. Sample shipment will be similar to the procedures provided in Section 8.2.3.

Surficial Soil Samples

1. Before collecting a surficial soil sample (0-12 inches below the ground surface) the sample location will be carefully cleared by removing any vegetation layers, surface debris, or upper one centimeter of soil surface, as applicable.
2. The soil samples will be collected using a decontaminated stainless-steel hand auger, trowel, or equivalent tools.
3. Insert the sampling device into a freshly exposed soil surface (ground surface or soil core sampler).
4. Use HDPE, glass, or polypropylene sample bottles with Teflon®-free caps, provided by the laboratory. Bottles should only be opened immediately prior to sampling. Fill each bottle to the neck of the container.
5. Once collected, the samples will be stored and shipped consistent with the procedures outlined above for Sub-Surface Soil Samples.
6. The soil sampling device will be decontaminated with an approved soap (i.e., Alconox® or Liquinox®) and rinsed with PFAS-free deionized water prior to and after each sediment sample.
7. Equipment blanks and duplicate samples will be collected as described above.
8. A description of the soil data (e.g., soil description, location, time, etc.) will be recorded in the field sheets and/or project field book as described above.

11.3 Analytical Parameters

There is no “standard” PFAS analytical parameter list for soil samples. Please refer to Appendix B for laboratory specific PFAS analyte lists.

Section 12: Sediment Sampling

This guidance assumes staff has familiarity with and/or understanding of basic sediment sampling procedures.

12.1 Definitions

Surface Sediment = Generally considered to be the top 6 inches of a sediment layer (i.e., soil from 0-to-6-inches below sediment surface).

Shallow Aqueous Layer = is generally considered to range from 0 to 10 feet below water surface.

12.2 Required Materials and Equipment

- Maps/plot plan
- Safety equipment and personal protective equipment per the project HASP
- Tape measure
- Field Sheets
- Logbook, if required
- Sample containers, labels and Chain of Custody records
- Cooler(s) and wet ice
- PFAS free decontamination supplies
- Wading boots, hip waders
- Boat
- Marking stakes or flags
- Sampling tool (e.g. spade/shovel, scoop, trowel, corer, bucket auger, tube auger)
- “T” Handle with extension rods

Grease and/or tape used to assemble the sampling equipment could potentially contain PFAS. Please be aware and ensure all equipment being used is PFAS free.

12.3 Field Procedures

12.3.1 Preparation

- Preparation for the field collection of sediment samples will commence with an assessment of aqueous layer conditions. If an aqueous layer exists, (e.g., standing vs flowing water) and depth of the aqueous layer.
- If a point designated for sediment sample collection is located under a deep aqueous layer (i.e. too deep to wade in) a boat may be implemented to reach the collection location. It may also be necessary to clear the area of underwater plants or submerged branches and debris.

12.3.2 Sample Collection

1. Sediment samples should be as undisturbed as possible, typically using a coring type of mechanism in a way that preserves the sediment structure.

2. Place a new clear plastic liner (use an acetate or other PFAS-free liner) into the steel core barrel of your sediment sampling device. Push or auger the sampling device into the subsurface at the desired sample location. Pull the core barrel out, place on a cutting board, remove the liner and cut open. The sediment core is then sliced open to reveal a “clean face” for logging lithology and structure and for sampling.
 - **Shake Test:** While logging the sediment lithology, visual observations of any foam and/or staining will be noted and suspected contaminated media will be placed in a clear container and shaken for 10-20 seconds, looking for resulting foam. Foaming in the container would qualitatively indicate that the media in this area may contain residual levels of Aqueous Film-Forming Foam (AFFF) that may require further investigation, sampling and/or cleanup as discussed in Section 3.4 of the AFFF Interstate Technology Regulatory Council (ITRC) Fact Sheet published October 2018.
3. Use HDPE, glass, or polypropylene sample bottles with Teflon®-free caps, provided by the laboratory. Bottles should only be opened immediately prior to sampling. Fill each bottle to the neck of the container.
4. Samples will be chilled from ambient temperature to a minimum of 4 °C after collection and during shipment to the laboratory. In an effort for samples to not exceed this temperature, samples will remain in a sample cooler after collection at all times up until removal at the laboratory. The sample coolers will be refilled with ice regularly and meltwater removed as appropriate. Due to the potential for PFAS sample contamination, only “water ice” will be used (i.e., “blue ice” or a gel ice packet use is prohibited). Sample temperatures must be confirmed to be at or below 6 °C when the samples are received at the laboratory.
5. The sediment sampling device will be decontaminated with an approved soap (i.e., Alconox® or Liquinox®) and rinsed with PFAS-free deionized water prior to and after each sediment sample.
6. An equipment blank (EB) will be collected and submitted at a frequency specified in the site-specific QAPP/Work Plan or other governing document. If no document exists, a rate of 1 per 10 samples collected during each monitoring event or at least one EB per event is recommended.
 - Laboratory provided PFAS-free water will be poured over or through the sampling equipment, collected in an empty sample container, seal and label the bottle as the EB. The EB will be shipped back to the laboratory along with the samples and analyzed to determine if PFAS were introduced in the sample through use of the sampling equipment.
7. Duplicate samples will be collected at a rate specified in the site-specific QAPP/Work Plan or other governing document. If no document exists, a rate of one per every ten samples collected (or at least one per event) is recommended and labeled (e.g., Dup 01, Dup 02, etc.) in a manner that will shield the sample identity from the laboratory. The sample point from which the duplicate will be collected will be recorded in the field notebook and/or on the field information sheet.
8. Sample shipment procedures will be similar to those provided in Section 8.2.3.

12.4 Analytical Parameters

There is no “standard” PFAS analytical parameter list for sediment samples. Please refer to Appendix B for laboratory specific PFAS analyte lists.

Section 13: Quality Assurance/Quality Control

Field activities and sampling details will be documented in detail in the field. Field documentation will consist of a sampling chronology and notes in the site field book, residential/groundwater/soil/sediment sampling field data sheets, digital photography and laboratory chains-of-custody forms.

The field forms will be used to document specific field data such as instrument calibration, water level elevations, water quality sampling parameters, soil sample characteristics and other routine data collection activities. Ballpoint pens and fine or Ultra-Fine Point Sharpie® markers are allowable for record keeping. Rite in the Rain® notebooks are also allowable and can be used to document general activities and tasks including the dates, times, locations, and personnel involved in specific activities.

Deviations from project-specific planning documents will be documented and explained in the daily field notes. The project manager will be contacted to discuss project deviations. Field quality control can be maintained through 1) making sure employees are properly trained and/or have experience to conduct the work being implemented, and 2) performing routine field audits to evaluate how well employees are following procedures.

Section 14: Documentation and Recordkeeping

Field notes, Chains-of-Custody and Field Data Sheets will be submitted to the Project Manager or designate immediately following the field event for QA/QC. The Project Manager or designate will review and load the completed forms for incorporation into the project file.

References

- ASTM D4448-01 (2007) “Standard Guide for Sampling Ground-Water Monitoring Wells”
- ASTM D6452-99 (2005) “Guide for Purging Methods for Wells Used for Ground-Water Quality Investigations”
- EGLE, Groundwater Perfluoroalkyl and Polyfluoroalkyl (PFAS) Sampling Guidance, October 2018.
- EGLE, MDEQ PFAS Sampling Quick Reference Field Guide, October 2018.
- EGLE, Residential Well Perfluoroalkyl and Polyfluoroalkyl (PFAS) Sampling Guidance, October 2018
- Interstate Regulatory Technology Council (ITRC). “Aqueous Film-Forming Foam (AFFF).” (2018). ITRC Web. Web. October 2018. <https://pfas-1.itrcweb.org/wp-content/uploads/2019/03/pfas-fact-sheet-afft-10-3-18.pdf>
- Interstate Regulatory Technology Council (ITRC). “Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS).” (2018). ITRC Web. Web. 15 March 2018. https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_site_characterization_3_15_18.pdf
- National Groundwater Association (NGWA). 2017. “Groundwater and PFAS: State of Knowledge and Practice.” <http://www.ngwa.org/Professional-Resources/Pages/Groundwater-and-PFAS.aspx>. December.
- Puls, Robert W. and Michael Barcelona. 1996. Low-flow (minimal drawdown) sampling procedures. EPA Ground Water Issue. EPA/540/5 95/504. April 1996.
- USEPA (1998) Ground water sampling procedure: Low stress (low flow) purging and sampling. USEPA Region II.
- USEPA, Method 537 – Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Document Number: (EPA/600/R-08/092, Version 1.1, September 2009. https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NERL&dirEntryId=344038

Appendix A: MDEQ PFAS Sampling Quick Reference Field Guide



MDEQ PFAS SAMPLING QUICK REFERENCE FIELD GUIDE¹

All Items Used During Sampling Event

● Prohibited

- Items or materials that contain fluoropolymers such as
 - Polytetrafluoroethylene (PTFE), that includes the trademarks Teflon® and Hostaflon®
 - Polyvinylidene fluoride (PVDF), that includes the trademark Kynar®
 - Polychlorotrifluoroethylene (PCTFE), that includes the trademark Neoflon®
 - Ethylene-tetrafluoro-ethylene (ETFE), that includes the trademark Tefzel®
 - Fluorinated ethylene propylene (FEP), that includes the trademarks Teflon® FEP and Hostaflon® FEP
- Items or materials that contain any other fluoropolymer

Pumps, Tubing, and Sampling Equipment

● Prohibited

- Items or materials containing any fluoropolymer (potential items include tubing, valves, or pipe thread seal tape)

■ Allowable

- High-density polyethylene (HDPE)
- Low-density polyethylene (LDPE) tubing
- Polypropylene
- Silicone
- Stainless-steel
- Any items used to secure sampling bottles made from:
 - Natural rubber
 - Nylon (cable ties)
 - Uncoated metal springs
 - Polyethylene

▲ Needs Screening²

- Any items or materials that will come into direct contact with the sample that have **not** been verified to be PFAS-free
 - Do not assume that any sampling items or materials are PFAS-free based on composition alone

Sample Storage and Preservation

● Prohibited

- Polytetrafluoroethylene (PTFE): Teflon® lined bottles or caps

■ Allowable

- Glass jars⁴
- Laboratory-provided PFAS-Free bottles:
 - HDPE or polypropylene
- Regular wet ice
- Thin HDPE sheeting
- LDPE resealable storage bags (i.e. Ziploc®) that will not contact the sample media⁶

▲ Needs Screening²

- Aluminium foil⁴
- Chemical or blue ice⁵
- Plastic storage bags other than those listed as ■ Allowable
- Low-density polyethylene (LDPE) bottles

Field Documentation

● Prohibited

- Clipboards coated with PFAS
- Notebooks made with PFAS treated paper
- PFAS treated loose paper
- PFAS treated adhesive paper products

■ Allowable

- Loose paper (non-waterproof, non-recycled)
- Rite in the Rain® notebooks
- Aluminium, polypropylene, or Masonite field clipboards
- Ballpoint pens, pencils, and Fine or Ultra-Fine Point Sharpie® markers

▲ Needs Screening²

- Plastic clipboards, binders, or spiral hard cover notebooks
- All markers not listed as ■ Allowable
- Post-It® Notes or other adhesive paper products
- Waterproof field books

Decontamination

● Prohibited

- Decon 90®
- PFAS treated paper towel

■ Allowable

- Alconox®, Liquinox®, or Citranox®
- Triple rinse with PFAS-free deionized water
- Cotton cloth or untreated paper towel

▲ Needs Screening²

- Municipal water
- Recycled paper towels or chemically treated paper towels

Clothing, Boots, Rain Gear, and PPE

● Prohibited	■ Allowable	▲ Needs Screening ²
<ul style="list-style-type: none"> • New or unwashed clothing • Anything made of or with: <ul style="list-style-type: none"> ○ Gore-Tex™ or other water-resistant synthetics • Anything applied with or recently washed with: <ul style="list-style-type: none"> ○ Fabric softeners ○ Fabric protectors, including UV protection ○ Insect resistant chemicals ○ Water, dirt, and/or stain resistant chemicals 	<ul style="list-style-type: none"> • Powderless nitrile gloves • Well-laundered synthetic or 100% cotton clothing, with most recent launderings not using fabric softeners • Made of or with: <ul style="list-style-type: none"> ○ Polyurethane ○ Polyvinyl chloride (PVC) ○ Wax coated fabrics ○ Rubber / Neoprene ○ Uncoated Tyvek® 	<ul style="list-style-type: none"> • Latex gloves • Water and/or dirt resistant leather gloves • Any special gloves required by a HASP • Tyvek® suits, clothing that contains Tyvek®, or coated Tyvek®

Food and Beverages

● Prohibited	■ Allowable
<ul style="list-style-type: none"> • No food should be consumed in the staging or sampling areas, including pre-packaged food or snacks. <ul style="list-style-type: none"> ■ If consuming food on-site becomes necessary, move to the staging area and remove PPE. After eating, wash hands thoroughly and put on new PPE. 	<ul style="list-style-type: none"> • Brought and consumed only outside the vicinity of the sampling area: <ul style="list-style-type: none"> ○ Bottled water ○ Hydration drinks (i.e. Gatorade®, Powerade®)

Personal Care Products (PCPs) - for day of sample collection⁶

● Prohibited	■ Allowable	▲ Needs Screening ²
<ul style="list-style-type: none"> • Any PCPs⁶, sunscreen, and insect repellent applied in the sampling area. 	<p>PCPs⁶, sunscreens, and insect repellents applied in the staging area, away from sampling bottles and equipment followed by thoroughly washing hands:</p> <p>PCPs⁶:</p> <ul style="list-style-type: none"> • Cosmetics, deodorants/antiperspirants, moisturizers, hand creams, and other PCPs⁶ <p>Sunscreens:</p> <ul style="list-style-type: none"> • Banana Boat® for Men Triple Defense Continuous Spray Sunscreen SPF 30 • Banana Boat® Sport Performance Coolzone Broad Spectrum SPF 30 • Banana Boat® Sport Performance Sunscreen Lotion Broad Spectrum SPF 30 • Banana Boat® Sport Performance Sunscreen Stick SPF 50 • Coppertone® Sunscreen Lotion Ultra Guard Broad Spectrum SPF 50 • Coppertone® Sport High Performance AccuSpray Sunscreen SPF 30 • Coppertone® Sunscreen Stick Kids SPF 55 • L'Oréal® Silky Sheer Face Lotion 50 • Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 50 • Meijer® Sunscreen Continuous Spray Broad Spectrum SPF 30 • Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 15, 30 and 50 • Meijer® Wet Skin Kids Sunscreen Continuous Spray Broad Spectrum SPF 70 • Neutrogena® Beach Defense Water+Sun Barrier Lotion SPF 70 • Neutrogena® Beach Defense Water+Sun Barrier Spray Broad Spectrum SPF 30 • Neutrogena® Pure & Free Baby Sunscreen Broad Spectrum SPF 60+ • Neutrogena® UltraSheer Dry-Touch Sunscreen Broad Spectrum SPF 30 <p>Insect Repellents:</p> <ul style="list-style-type: none"> • OFF® Deep Woods • Sawyer® Permethrin 	<ul style="list-style-type: none"> • Products other than those listed as ■ Allowable

¹ This table is not considered to be a complete listing of prohibited or allowable materials. All materials should be evaluated prior to use during sampling. The manufacturers of various products should be contacted in order to determine if PFAS was used in the production of any particular product.

² Equipment blank samples should be taken to verify these products are PFAS-free prior to use during sampling.

³ **For surface water foam samples:** LDPE storage bags may be used in the sampling of foam on surface waters. In this instance, it is allowable for the LDPE bag to come into direct contact with the sample media.

⁴ **For fish and other wildlife samples:** Depending on the project objectives, glass jars and aluminum foil might be used for PFAS sampling. PFAS has been found to bind to glass and if the sample is stored in a glass jar, a rinse of the jar is required during the sample analysis. PFAS are sometimes used as a protective layer for some aluminum foils. An equipment blank sample should be collected prior to any aluminum foil use.

⁵ Regular ice is recommended as there are concerns that chemical and blue ice may not cool and maintain the sample at or below 42.8°F (6°C) (as determined by EPA 40 CFR 136 – NPDES) during collection and through transit to the laboratory.

⁶ Based on evidence, avoidance of PCPs is considered to be precautionary because none have been documented as having cross-contaminated samples due to their use. However, if used, application of PCPs must be done at the staging area and away from sampling bottles and equipment, and hands must be thoroughly washed after the use of any PCPs prior to sampling.

Appendix B: PFAS Analytical Laboratory

Eurofins Lancaster Laboratory



Per- and Polyfluorinated Alkyl Substances (PFAS)

Per- and Polyfluorinated Alkyl Substances (PFAS) or Perfluorinated Compounds (PFCs) are a large group of manufactured compounds that are widely used as surfactants in industrial applications and are also used heavily in Aqueous Film Forming Foams (AFFF) firefighting products. PFAS compounds demonstrate unique chemical characteristics that make them persistent in the environment and bioaccumulative in wildlife. Their water solubility enhances the presence of PFAS compounds in water.

Eurofins Environment Testing US has supported PFAS testing for more than 12 years and employs EPA Method 537 version 1.1 for the analysis of drinking water including the UCMR3 list of compounds. A modified 537 method, using isotope dilution, is used to report an expanded list of compounds for non-drinking water matrices. We utilize LC/MS/MS technology and isotopic dilution in order to detect and differentiate the compounds at the necessary reporting limits with the most accurate results.

Our Capabilities and Capacity

Eurofins Environment Testing US laboratories participated in the UCMR3 program, and hold certification with the

Department of Defense (DoD) ELAP program and state accreditations for per- and polyfluorinated chemical analysis that follow QSM 5.1 protocol. We were one of the first to have experience with Method 537 version 1.1 as we worked with EPA on the validation.

We perform analytical services on varied environmental matrices including drinking water, groundwater, soil, sediment, tissue, biosolids, and consumer products using LC/MS/MS and HRMS technologies in support of trace level reporting of emerging contaminants. Within our isolated PFAS laboratory, we run four dedicated systems over two shifts giving us unmatched capacity for any project size. Data can be provided in a Level II, III or IV Data Deliverable format to accommodate unique projects. We follow the EPA protocol to report branched and linear isomers.

Our depth of knowledge, redundancy of systems and state-of-the-art facilities are key to our success in supporting the PFAS market. Eurofins' reinvestment in the business ensures that we continue to offer highly sensitive methods, low reporting limits and compliance with method protocols meeting regulatory guidance.

TOP (Total Oxidizable Precursors) Analysis

TOP analysis is an analytical tool to determine the hidden or unknown mass of PFAS compounds in a sample. Water, soil, sediment and biota are treated with persulfate, hydroxide and heating to create a hydroxyl radical oxidation. This process converts polyfluorinated precursors to the more recalcitrant perfluorinated forms like PFOA and/or PFOS. When the oxidation is complete,

the PFAS compounds are extracted in the normal fashion and identified employing isotope dilution LC/MS/MS.

AFFF materials treated by the TOP assay have been shown to reveal additional PFAS compounds that can comprise of up to 70% of the fluorinated organics in the sample. The combination of the TOP analysis and the standard suite of PFAS compounds gives a more complete characterization of the PFAS compounds present in the sample.

Compound List

Acronym

10:2-fluorotelomersulfonate	10:2 FTS
4:2 fluorotelomersulfonate	4:2 FTS
6:2 fluorotelomersulfonate	6:2 FTS
8:2 fluorotelomersulfonate	8:2 FTS
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA
Perfluoro-octanesulfonate	PFOS
Perfluorobutanesulfonate	PFBS
Perfluorobutanoic acid	PFBA
Perfluorodecanesulfonate	PFDS
Perfluorodecanoic acid	PFDA
Perfluorododecanesulfonate	PFDoS
Perfluorododecanoic acid	PFDoA
Perfluoroheptanesulfonate	PFHpS
Perfluoroheptanoic acid	PFHpA
Perfluorohexadecanoic acid	PFHxDA
Perfluorohexanesulfonate	PFHxS
Perfluorohexanoic acid	PFHxA
Perfluorononanesulfonate	PFNS
Perfluorononanoic acid	PFNA
Perfluorooctadecanoic acid	PFOcDA
Perfluorooctanoic acid	PFOA
Perfluoropentanesulfonate	PFPeS
Perfluoropentanoic acid	PFPeA
Perfluorotetradecanoic acid	PFTeDA
Perfluorotridecanoic acid	PFTTrDA
Perfluoroundecanoic acid	PFUnA
Perfluorooctanesulfonamide	PFOSA
N-ethylperfluorooctane-1-sulfonamide	NEtPFOSA
N-ethyl-N-perfluorooctylsulfonylaminoethanol	NEtPFOSAE
N-methyl-perfluorooctane-1-sulfonamide	NMePFOSA
N-methylperfluorooctanesulfonamidoethanol	NMePFOSAE

Standard Services:

Volatiles
Semivolatiles
Metals
Pesticides/PCBs/Herbicides
Petroleum-Related Analysis
Waste Characterization
Water Quality

Drinking Water
Vapor & Air Analysis
Sediment & Tissue Testing
Method Development
Shale Oil & Gas Analysis

Specialty Services:

Dioxins/Furans
PCB Congeners
Hydrazines/NDMA
Explosives
Perchlorate
Alkyl PAHs, Alkanes, Biomarkers
PFC (PFOA)

Organic Acids
Aldehydes
1,4-Dioxane (low level)
Low-Level Mercury
PMI
Method 25D

Eurofins Lancaster
Laboratories Environmental, LLC
2425 New Holland Pike
Lancaster, PA 17601
717-656-2300

24/7 Emergency Response
717-556-7300

Appendix C: PFAS Sampling Field Checklist

PFCs Sampling Checklist

Date: _____

Weather (temp./precipitation): _____ Site Name: _____

Field Clothing and PPE:

- ☐ No clothing or boots containing Gore-Tex™
- ☐ All safety boots made from polyurethane and PVC
- ☐ No materials containing Tyvek®
- ☐ Field crew has not used fabric softener on clothing
- ☐ Field crew has not used cosmetics, moisturizers, hand cream, or other related products this morning
- ☐ Field crew has not applied unauthorized sunscreen or insect repellant

Field Equipment:

- ☐ No Teflon® or LDPE containing materials on-site
- ☐ All sample materials made from stainless steel, HDPE, acetate, silicon, or polypropylene
- ☐ No waterproof field books on-site
- ☐ No plastic clipboards, binders, or spiral hard cover notebooks on-site
- ☐ No adhesives (Post-It Notes) on-site

- ☐ Coolers filled with regular ice only. No chemical (blue) ice packs in possession

Sample Containers:

- ☐ All sample containers made of HDPE or polypropylene
- ☐ Caps are unlined and made of HDPE or polypropylene

Wet Weather (as applicable):

- ☐ Wet weather gear made of polyurethane and PVC only

Equipment Decontamination:

- ☐ "PFC-free" water on-site for decontamination of sample equipment. No other water sources to be used.
- ☐ Alconox and Liquinox to be used as decontamination materials

Food Considerations:

- ☐ No food or drink on-site with exception of bottled water and/or hydration drinks (i.e., Gatorade and Powerade) that is available for consumption only in the staging area

If any applicable boxes cannot be checked, the Field Lead shall describe the noncompliance issues below and work with field personnel to address noncompliance issues prior to commencement of that day's work. Corrective action shall include removal of noncompliance items from the site or removal of worker offsite until in compliance.

Describe the noncompliance issues (include personnel not in compliance) and action/outcome of noncompliance:

Field Lead Name: _____

Field Lead Signature: _____ Time: _____

PFC Sampling – Prohibited and Acceptable Items

Prohibited	Acceptable
Field Equipment	
Teflon® containing materials	High-density polyethylene (HDPE) materials
Low density polyethylene (LDPE) materials	Acetate Liners
	Silicon Tubing
Waterproof field books	Loose paper (non-waterproof)
Plastic clipboards, binders, or spiral hard cover notebooks	Aluminum field clipboards or with Masonite
	Sharpies®, pens
Post-It Notes®	
Chemical (blue) ice packs	Regular ice
Field Clothing and PPE	
New cotton clothing or synthetic water resistant, waterproof, or stain-treated clothing, clothing containing Gore-Tex™	Well-laundered clothing made of natural fibers (preferable cotton)
Clothing laundered using fabric softener	No fabric softener
Boots containing Gore-Tex™	Boots made with polyurethane and PVC
Tyvek®	Cotton clothing
No cosmetics, moisturizers, hand cream, or other related products as part of personal cleaning/showering routine on the morning of sampling	<p>Sunscreens - Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my face, Baby sunscreens that are “free” or “natural”</p> <p>Insect Repellents - Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellent, Herbal Armor, California Baby Natural Bug Spray, BabyGanics</p> <p>Sunscreen and insect repellent - Avon Skin So Soft Bug Guard Plus – SPF 30 Lotion</p>
Sample Containers	
LDPE or glass containers	HDPE or polypropylene
Teflon-lined caps	Unlined polypropylene caps
Rain Events	
Waterproof or resistant rain gear	Gazebo tent that is only touched or moved prior to and following sampling activities
Equipment Decontamination	
Decon 90®	Alconox® and/or Liquinox®
Water from an on-site well	Potable water from municipal drinking water supply
Food Considerations	
All food and drink, with exceptions noted on right	Bottled water and hydration fluids (i.e, Gatorade® and Powerade®) to be brought and consumed only in the staging areas

Appendix D: Federal and State Specific PFAS Website Hyperlinks

New York

General PFAS Information: <https://www.dec.ny.gov/chemical/108831.html>

USEPA

Method 537.1: https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=343042&Lab=NERL

General PFAS Information: <https://www.epa.gov/pfas>

Appendix E: Example Field Forms

Appendix F: ITRC PFAS Data Sheets

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS)

1 Introduction

The following topics are covered in this fact sheet:

- Polymer vs. Non-Polymer PFAS
- Perfluoroalkyl substances
- Polyfluoroalkyl substances
- PFAA Naming Conventions
- Long-Chain vs. Short-Chain
- Linear vs. Branched
- Acid vs. Anion
- Replacement Chemistry
- Physical and Chemical Properties

This fact sheet uses three conventions worth highlighting:

- **Anionic form of chemical names:** Many PFAS can exist in various ionic states (for example, acids, anions, cations), which has important implications for their chemical and physical properties. In most cases, this fact sheet uses the anionic form of a given PFAS name, as this is the state in which most PFAS exist in the environment.
- **“PFC” is not used:** The acronym “PFC” is poorly defined in the scientific literature, but typically refers to “perfluorinated compounds.” It does not include polyfluorinated substances which are increasingly recognized as important contaminants at many PFAS sites, while it does include unrelated chemicals that are not of concern at those sites.
- **“PFAS”, not “PFASs”:** The acronym “PFAS” stands for “poly- and perfluoroalkyl substances.” No single chemical within the PFAS class can be both polyfluorinated and perfluorinated, so by definition “PFAS” is plural and a small “s” is not needed. Some authors elect to add a small “s” to this acronym (PFASs) to emphasize the fact that it is plural, but it is not needed. When referring to a single chemical within the PFAS class, it is usually more accurate to simply name that specific chemical.

USEPA has compiled an online resource for PFAS information. The information includes topics such as Policy and Guidance, Chemistry and Behavior, Occurrence, Toxicology, Site Characterization and Remediation Technologies (USEPA 2017h).

1.1 Why do we need to understand PFAS Naming Conventions?

The number and complexity of environmentally-relevant PFAS and the exponential increase in related scientific publications have led to confusion in the environmental community and the public (Buck et al. 2011; Wang et al. 2017). The use of non-specific acronyms, such as perfluorinated compound (PFC), has hampered clarity of investigative results. Use of consistent naming conventions by researchers, practitioners, regulators, and stakeholders will reduce confusion and support clearer communication.

Proper naming also helps to distinguish PFAS from other organic compounds that contain fluorine. PFAS, which are fluorinated aliphatic (carbon chain) substances, do not include aromatic (carbon ring) substances that contain carbon-fluorine (C-F) bonds (for example, active pharmaceutical ingredients, crop protection) or chlorofluorocarbons (refrigerants). This is another reason to avoid the use of the more generic acronym, PFC, which can include these non-PFAS.

Chemical Abstract Service (CAS) numbers are another helpful tool for clearly identifying the chemical that is being referenced. However, even these have led to confusion when it comes to PFAS. Some PFAS may occur in various ionic states, such as acids, anions (negatively charged), cations (positively charged salts), and zwitterions (both positively and negatively charged dipolar molecules), each of which has its own CAS number (and some have no CAS number). The ionic state determines its electrical charge and its physical and chemical properties, which in turn controls its fate and transport in the environment and potential human health and ecological effects. Chemical and physical properties of the

ITRC has developed a series of six fact sheets to summarize the latest science and emerging technologies regarding PFAS. The purpose of this fact sheet is to:

- Provide an overview of terminology, names, and acronyms for PFAS, focusing on those most commonly reported in the environment. The fact sheet focuses on those PFAS most commonly tested for by current analytical methods, but also describes other important classes of PFAS.
- Summarize the common physical and chemical properties associated with PFAS, along with a discussion of those properties for which no data are currently available.

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

various states of a given per- or polyfluoroalkyl substance can be so different that they completely alter critical aspects of the substance, such as solubility, volatility, and bioaccumulative potential. As a result, care must be taken in selecting the correct CAS number to avoid confusion regarding the chemistry and behavior of the chemical being described.

2 PFAS Families

PFAS encompass a wide universe of substances with very different physical and chemical properties, including gases (for example, perfluorobutane), liquids (for example, fluorotelomer alcohols), surfactants (for example, perfluorooctane sulfonate), and solid material high-molecular weight polymers (for example, polytetrafluoroethylene [PTFE]). For this reason, it is helpful to arrange PFAS that share similar chemical and physical properties into families.

The PFAS families may be divided into two primary categories: polymer and non-polymer as shown in Figure 2-1. This fact sheet focuses primarily on non-polymer PFAS most commonly detected in the environment. The polymer family of PFAS is not addressed in detail in this fact sheet. Buck et al. (2011) is an open-access paper that provides a more detailed explanation of PFAS terminology, classification, and origins, and recommends specific and descriptive terminology, names, and acronyms for PFAS.

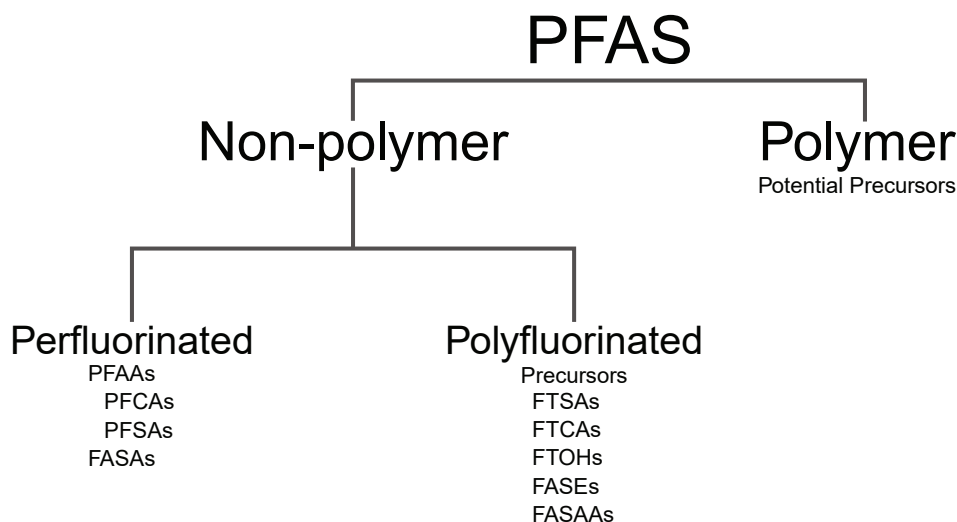


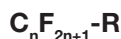
Figure 2-1. Summary of PFAS families

2.1 Non-Polymer PFAS

The family of non-polymeric PFAS encompasses two major classes: perfluoroalkyl substances and polyfluoroalkyl substances, which include many subgroups of chemicals, examples of which are shown in Figure 2-1. Table 2-1 provides general classification and chemical structures, examples of each class, and primary uses of the non-polymer PFAS highlighted in Figure 2-1. These compounds were selected as the focus of this fact sheet because they (1) are most commonly detected in humans, biota, and other environmental media; (2) appear to be relatively more abundant at PFAS investigation sites; (3) may have state or federal guidance values (see the *Regulations, Guidance, and Advisories Fact Sheet*); and/or (4) are included in most laboratory PFAS analyte lists.

2.1.1 Perfluoroalkyl Substances

Perfluoroalkyl substances are fully fluorinated (perfluoro-) alkane (carbon-chain) molecules. Their basic chemical structure is a chain (*or tail*) of two or more carbon atoms with a charged functional group *head* attached at one end. The functional groups commonly are carboxylic or sulfonic acids, but other forms are also detected in the environment. Fluorine atoms are attached to all possible bonding sites along the carbon chain of the tail, except for one bonding site on the last carbon where the functional group head is attached. This structure, which is illustrated in Figure 2-2 for perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), can be written as:



where “ $\text{C}_n\text{F}_{2n+1}$ ” defines the length of the perfluoroalkyl chain tail, “ n ” is >2 , and “ R ” represents the attached functional group head. Note that the functional group may contain 1 or more carbon atoms, which are included in the total number of carbons when naming the compound.

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

Perfluorooctane sulfonate (PFOS)



Perfluorooctane carboxylate (PFOA)



Figure 2-2. The tail and head structure of PFOS and PFOA molecules

Table 2-1. Major PFAS classes discussed in this fact sheet

Source: Adapted with permission from Buck, R.C., J. Franklin, U. Berger, J. M. Conder, I. T. Cousins, P. de Voogt, A. A. Jensen, K. Kannan, S. A. Mabury, and S. P. van Leeuwenet. 2011. "Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins." *Integrated Environmental Assessment and Management*, 7:513-541. Open access. Copyright 2011 SETAC. <http://dx.doi.org/10.1002/ieam.258>

Family	Class	Group	General Chemical Structure: C _n F _{2n+1} R, where R =	Examples	Uses
PERFLUORINATED	Perfluoroalkyl acids (PFAAs)	Perfluoroalkyl carboxylic acids (PFCAs)	-COOH	Perfluorooctanoic acid (PFOA), C ₇ F ₁₅ COOH	Surfactant
		Perfluoroalkyl carboxylates (PFCAs)	-COO ⁻	Perfluorooctanoate (PFOA), C ₇ F ₁₅ COO ⁻	
		Perfluoroalkane sulfonic acids (PFSAs)	-SO ₃ H	Perfluorooctane sulfonic acid (PFOS), C ₈ F ₁₇ SO ₃ H	Surfactant
		Perfluoroalkane sulfonates (PFSAs)	-SO ₃ ⁻	Perfluorooctane sulfonate, (PFOS), C ₈ F ₁₇ SO ₃ ⁻	
	Perfluoroalkane sulfonamides (FASAs)		-SO ₂ NH ₂	Perfluorooctane sulfonamide, C ₈ F ₁₇ SO ₂ NH ₂	Major raw material for surfactant and surface protection products
		N-Alkyl perfluoroalkane sulfonamides (MeFASAs, EtFASAs, BuFASAs)	-SO ₂ N(R')H where R' = C _m H _{2m+1} (m = 0, 1, 2, 4)	N-Ethyl perfluorooctane sulfonamide (EtFOSA), C ₈ F ₁₇ SO ₂ N(C ₂ H ₅)H N-Methyl perfluorooctane sulfonamide (MeFOSA), C ₈ F ₁₇ SO ₂ N(CH ₃)H	Intermediate environmental transformation products

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

Family	Class	Group	General Chemical Structure: $C_nF_{2n+1}R$, where R =	Examples	Uses
POLYFLUORINATED	Fluorotelomer substances	n:2 Fluorotelomer alcohols (n:2 FTOHs)	$-CH_2CH_2OH$	10:2 Fluorotelomer alcohol (10:2 FTOH), $C_{10}F_{21}CH_2CH_2OH$	Major raw material for surfactant and surface protection products
		n:2 Fluorotelomer sulfonic acids (n:2 FTSAAs)	$-CH_2CH_2SO_3H$	8:2 Fluorotelomer sulfonic acid (8:2 FTSA), $C_8F_{17}CH_2CH_2SO_3H$	Surfactant and environmental transformation products
		Fluorotelomer carboxylic acids (FTCAs)	$-CH_2COOH$	6:2 Fluorotelomer carboxylic acid (6:2 FTCA), $C_6F_{13}CH_2COOH$	Intermediate environmental transformation product
			$-CH_2CH_2COOH$	5:3 Fluorotelomer carboxylic acid (5:3 Acid), $C_5F_{11}(CH_2)_2COOH$	
	Perfluoroalkane sulfonamido substances	Perfluoroalkane sulfonamido ethanols (FASEs) and N-alkyl perfluoroalkane sulfonamido ethanols (MeFASEs, EtFASEs, BuFASEs)	$-SO_2N(R')CH_2CH_2OH$ where $R' = C_mH_{2m+1}$ (m = 0, 1, 2, 4)	N-Ethyl perfluorooctane sulfonamidoethanol (EtFOSE), $C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$	Major Raw Material for surfactant and surface protection products
				N-Methyl perfluorooctane sulfonamido ethanol (MeFOSE), $C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$	
		Perfluoroalkane sulfonamido acetic acids (FASAAs) and N-alkyl perfluoroalkane sulfonamido acetic acids (MeFASAAs, EtFASAAs, BuFASAAs)	$-SO_2N(R')CH_2COOH$ where $R' = C_mH_{2m+1}$ (m = 0, 1, 2, 4)	N-Ethyl perfluorooctane sulfonamido acetic acid (EtFOSAA), $C_8F_{17}SO_2N(C_2H_5)CH_2CO_2H$	Intermediate environmental transformation product
				N-Methyl perfluorooctane sulfonamido acetic acid (MeFOSAA), $C_8F_{17}SO_2N(CH_3)CH_2CO_2H$	

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

2.1.1.1 Perfluoroalkyl acids (PFAAs)

Perfluoroalkyl acids (PFAAs) are some of the most basic PFAS molecules. They are essentially non-degradable and currently are the class of PFAS most commonly tested for in the environment. Biotic and abiotic degradation of many polyfluoroalkyl substances may result in the formation of PFAAs. As a result, PFAAs are sometimes referred to as “terminal PFAS” or “terminal degradation products,” meaning no further degradation products will form from them under environmental conditions. Polyfluoroalkyl substances that degrade to create terminal PFAAs are referred to as “precursors.” The PFAA class is divided into two major groups (also shown in Table 2-1):

- *Perfluoroalkyl carboxylic acids* (PFCAs), or perfluoroalkyl carboxylates, are terminal degradation products of select precursor polyfluoroalkyl substances, such as fluorotelomer alcohols (FTOHs). The most frequently detected PFCA is PFOA.
- *Perfluoroalkane sulfonic acids* (PFSAs), or perfluoroalkyl sulfonates, are also terminal degradation products of select precursor polyfluoroalkyl substances, such as perfluoroalkylsulfonamidoethanols (PFOSEs). The most frequently detected PFSA is PFOS.

2.1.1.2 Perfluoroalkane sulfonamides (FASAs)

Perfluoroalkane sulfonamides (FASAs), such as perfluorooctane sulfonamide (FOSA), are used as raw material to make perfluoroalkyl sulfonamide substances that are used for surfactants and surface treatments. FASAs can degrade to form PFAAs such as PFOS. Examples include N-Methyl perfluorooctane sulfonamide (MeFOSA) and N-Ethyl perfluorooctane sulfonamide (EtFOSA).

2.1.2 Polyfluoroalkyl Substances

Polyfluoroalkyl substances and some side-chain fluorinated polymers are increasingly being identified as important to understanding the fate and transport of PFAS at release sites and in the environment (OECD 2013; Butt, Muir, and Mabury 2014; Liu and Mejia-Avendaño 2013; Wang et al. 2011; Mejia-Avendaño et al. 2016). Figure 2-1 highlights the polyfluoroalkyl substances that, to date, have most commonly been detected at PFAS sites (see Barzen-Hanson et al. 2017).

Polyfluoroalkyl substances are distinguished from perfluoroalkyl substances by not being fully fluorinated. Instead, they have a non-fluorine atom (typically hydrogen or oxygen) attached to at least one, but not all, carbon atoms, while at least two or more of the remaining carbon atoms in the carbon chain tail are fully fluorinated (Figure 2-3).

Fluorotelomer-based polyfluoroalkyl substances are named using an “n:x” prefix where “n” indicates the number of fully fluorinated carbon atoms ($n > 2$) and “x” indicates the number of carbon atoms that are not fully fluorinated ($x > 1$). An example of a polyfluoroalkyl substance is shown in Figure 2-3, which also illustrates the “n:x” naming convention.

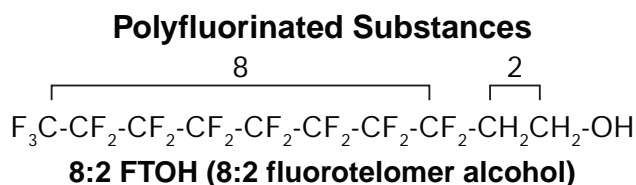


Figure 2-3. Example of a polyfluoroalkyl substance where two of the carbons in the tail (shaded blue) are not fully fluorinated, while the remaining carbons are. This also illustrates the “n:x” naming convention where “n” is the number of fully fluorinated carbons (in this case, 8) and “x” is the number of carbons that are not fully fluorinated (in this case, 2).

The carbon-hydrogen (or other non-fluorinated) bond in polyfluoroalkyl molecules creates a “weak” point in the carbon chain that is susceptible to biotic or abiotic degradation. As a result, many polyfluoroalkyl substances that contain a perfluoroalkyl $\text{C}_n\text{F}_{2n+1}$ group are potential precursor compounds that have the potential to be transformed into PFAAs.

Figures 2-4 and 2-5 provide some examples of degradation pathways for environmentally relevant polyfluoroalkyl precursors derived from two PFAS production methods, telomerization and electrochemical fluorination (ECF), respectively. Note that these figures include some PFAS not discussed in this fact sheet, but described in Buck et al. (2011).

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

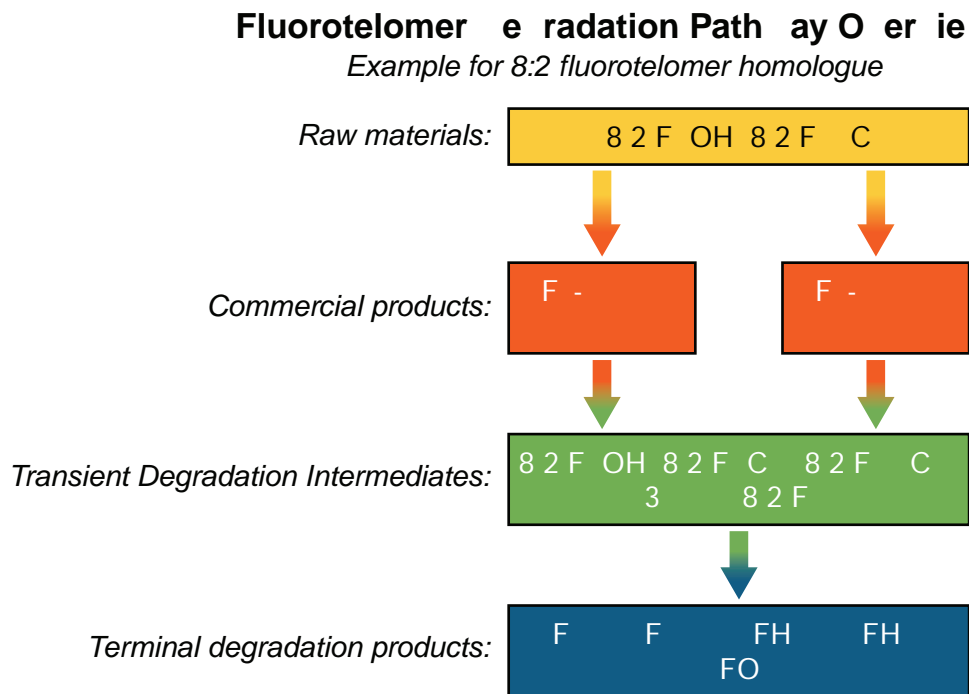


Figure 2-4. Fluorotelomer degradation pathway overview (*Example for 8:2 fluorotelomer homologue*)

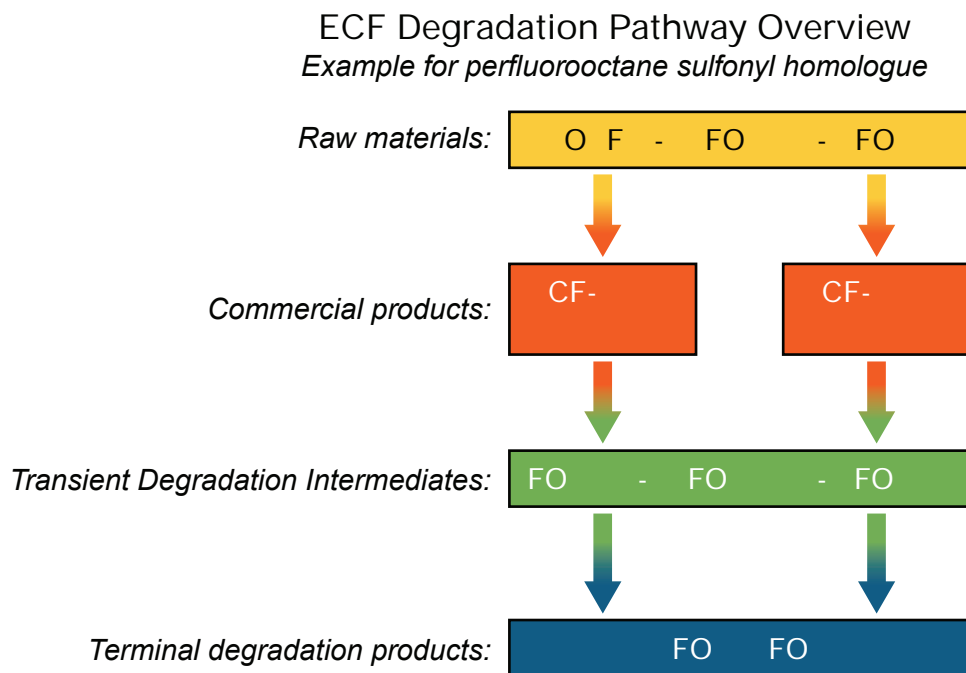


Figure 2-5. ECF degradation pathway overview (*Example for perfluorooctane sulfonyl homologue*).

2.1.2.1 Fluorotelomer Substances

Fluorotelomer substances are polyfluoroalkyl substances produced by the telomerization process. As shown in Figure 2-4, the degradation of fluorotelomer-based substances is a potential source of PFCAs in the environment (Buck et al. 2011). For many of these compounds, the naming convention identifies the number of perfluorinated and non-fluorinated carbons.

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

The following fluorotelomer substances (also shown in Table 2-1) are those most commonly detected in the environment to date:

- *Fluorotelomer alcohols* (FTOH): The n:2 fluorotelomer alcohols (n:2 FTOHs) are key raw materials in the production of n:2 fluorotelomer acrylates and n:2 fluorotelomer methacrylates (Buck et al. 2011).
- *Fluorotelomer sulfonic acids* (FTSA): The n:2 fluorotelomer sulfonic acids (n:2 FTSA) have been detected in environmental matrices at sites where aqueous film forming foam (AFFF) have been used, and also in wastewater treatment plant effluents and landfill leachate. FTSA are precursor compounds and can undergo aerobic biotransformation to form PFCAs (Buck et al. 2011).
- *Fluorotelomer carboxylic acids* (FTCA): These compounds form through the biodegradation of FTOHs (Figure 2-3; Buck et al. 2011; Liu and Avendaño 2013) and have been detected in landfill leachate. Note that the –COOH functional group on these fluorotelomer compounds mean they may have either an even or odd number of carbons, so they may have n:2 or n:3 prefixes.

2.1.2.2 Perfluoroalkane Sulfonamido Substances

All of the families of perfluoroalkane sulfonamido substances shown in Table 2-1 and discussed below have been detected in the environment and humans. *Perfluoroalkane* refers to the fully fluorinated carbon chain tail, but these compounds also contain one or more CH₂ groups in the head of the molecule attached to the sulfonamido spacer (see Figure 2-6). They are either used as raw materials for surfactant and surface treatment products, or they are present as intermediate transformation products of these raw materials. As shown in Figure 2-5, some perfluoroalkane sulfonamido substances have been found to degrade to PFOS (Mejia and Liu 2015). Environmentally relevant perfluoroalkane sulfonamido substances include:

- *Perfluoroalkane sulfonamido ethanols* (FASEs) and *N-alkyl perfluoroalkane sulfonamido ethanols* (MeFASEs, EtFASEs, BuFASEs) are raw materials for surfactant and surface treatment products (Buck et al. 2011). Figure 2-6 illustrates the structure of N-EtFOSE.
- *Perfluoroalkane sulfonamido acetic acids* (FASAA) and *N-alkyl perfluoroalkane sulfonamido acetic acids* (MeFASAA, EtFASAA, BuFASAA) are intermediate transformation products of FASEs, MeFASEs, EtFASEs, and BuFASEs (see Figure 2-5) (Buck et al. 2011).

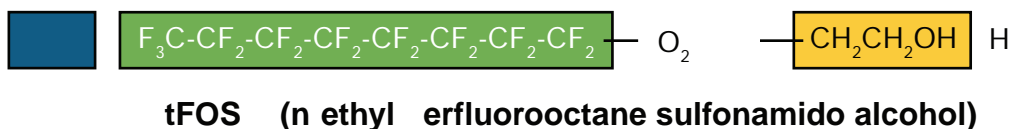


Figure 2-6. Example perfluoroalkane sulfonamido alcohol (FASE)

2.2 Polymeric PFAS

Polymers are large molecules formed by combining many identical smaller molecules (or monomers) in a repeating pattern. Polymeric substances in the PFAS family include fluoropolymers, polymeric perfluoropolyethers, and side-chain fluorinated polymers.

Side-chain fluorinated polymers contain a nonfluorinated polymer backbone from which fluorinated side chains branch off. Some may become precursors for PFAAs when the point of connection of a fluorinated side-chain on a polymer is broken to release a PFAA.

In general, polymeric PFAS are currently believed to pose less immediate human health and ecological risk relative to some non-polymer PFAS. As stated previously, most compounds of interest at environmental release sites are non-polymers.

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

3 PFAA Naming Conventions

PFAAs are the class of PFAS that make up the majority of PFAS typically included in commercial laboratory target analyte lists and are the primary PFAS for which federal or state health-based guidance values have been established. As a result, they tend to drive site investigation and remediation decisions, and so it is helpful to understand the naming conventions for this class. Many of the commonly detected PFAAs are denoted using the structural shorthand:

PFX_Y

where:

PF = perfluoroalkyl

X = the carbon chain length (using the same naming conventions as hydrocarbons based on the number of carbons ([for example, B for butane or 4 carbons, Pe for pentane or 5 carbons])

Y = the functional group

Table 3-1 illustrates how this naming structure works for the PFCAs and PFSA, which collectively are referred to as PFAAs.

Table 3-1. Basic naming structure and shorthand for perfluoroalkyl acids (PFAAs)

X	Y	Acronym	Name	Formula	CAS No.
B = buta (4 carbon)	A = Carboxylate or carboxylic acid	PFBA	Perfluorobutanoate	$C_3F_7CO_2^-$	45048-62-2
			Perfluorobutanoic acid	C_3F_7COOH	375-22-4
	S = Sulfonate or sulfonic acid	PFBS	Perfluorobutane sulfonate	$C_4F_9SO_3^-$	45187-15-3
			Perfluorobutane sulfonic acid	$C_4F_9SO_3H$	375-73-5
Pe = penta (5 carbon)	A = Carboxylate or carboxylic acid	PFPeA	Perfluoropentanoate	$C_4F_9CO_2^-$	45167-47-3
			Perfluoropentanoic acid	C_4F_9COOH	2706-90-3
	S = Sulfonate or sulfonic acid	PFPeS	Perfluoropentane sulfonate	$C_5F_{11}SO_3^-$	NA
			Perfluoropentane sulfonic acid	$C_5F_{11}SO_3H$	2706-91-4
Hx = hexa (6 carbon)	A = Carboxylate or carboxylic acid	PFHxA	Perfluorohexanoate	$C_5F_{11}CO_2^-$	92612-52-7
			Perfluorohexanoic acid	$C_5F_{11}COOH$	307-24-4
	S = Sulfonate or sulfonic acid	PFHxS	Perfluorohexane sulfonate	$C_6F_{13}SO_3^-$	108427-53-8
			Perfluorohexane sulfonic acid	$C_6F_{13}SO_3H$	355-46-4
Hp = hepta (7 carbon)	A = Carboxylate or carboxylic acid	PFHpA	Perfluoroheptanoate	$C_6F_{13}CO_2^-$	120885-29-2
			Perfluoroheptanoic acid	$C_6F_{13}COOH$	375-85-9
	S = Sulfonate or sulfonic acid	PFHpS	Perfluoroheptane sulfonate	$C_7F_{15}SO_3^-$	NA
			Perfluoroheptane sulfonic acid	$C_7F_{15}SO_3H$	375-92-8
O = octa (8 carbon)	A = Carboxylate or carboxylic acid	PFOA	Perfluorooctanoate	$C_7F_{15}CO_2^-$	45285-51-6
			Perfluorooctanoic acid	$C_7F_{15}COOH$	335-67-1
	S = Sulfonate or sulfonic acid	PFOS	Perfluorooctane sulfonate	$C_8F_{17}SO_3^-$	45298-90-6
			Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	1763-23-1
N = nona (9 carbon)	A = Carboxylate or carboxylic acid	PFNA	Perfluorononanoate	$C_8F_{17}CO_2^-$	72007-68-2
			Perfluorononanoic acid	$C_8F_{17}COOH$	375-95-1
	S = Sulfonate or sulfonic acid	PFNS	Perfluorononane sulfonate	$C_9F_{19}SO_3^-$	NA
			Perfluorononane sulfonic acid	$C_9F_{19}SO_3H$	474511-07-4
D = deca (10 carbon)	A = Carboxylate or carboxylic acid	PFDA	Perfluorodecanoate	$C_9F_{19}CO_2^-$	73829-36-4
			Perfluorodecanoic acid	$C_9F_{19}COOH$	335-76-2
	S = Sulfonate or sulfonic acid	PFDS	Perfluorodecane sulfonate	$C_{10}F_{21}SO_3^-$	126105-34-8
			Perfluorodecane sulfonic acid	$C_{10}F_{21}SO_3H$	335-77-3

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

X	Y	Acronym	Name	Formula	CAS No.
Un = undeca (11 carbon)	A = Carboxylate or carboxylic acid	PFUnA or PFUnDA	Perfluoroundecanoate	$C_{10}F_{21}CO_2^-$	196859-54-8
			Perfluoroundecanoic acid	$C_{10}F_{21}COOH$	2058-94-8
	S = Sulfonate or sulfonic acid	PFUnS or PFUnDS	Perfluoroundecane sulfonate	$C_{11}F_{23}SO_3^-$	NA
			Perfluoroundecane sulfonic acid	$C_{11}F_{23}SO_3H$	749786-16-1
DoD = dodeca (12 carbon)	A = Carboxylate or carboxylic acid	PFDoDA	Perfluorododecanoate	$C_{11}F_{23}CO_2^-$	171978-95-3
			Perfluorododecanoic acid	$C_{11}F_{23}COOH$	307-55-1
	S = Sulfonate or sulfonic acid	PFDoDS	Perfluorododecane sulfonate	$C_{12}F_{25}SO_3^-$	NA
			Perfluorododecane sulfonic acid	$C_{12}F_{25}SO_3H$	79780-39-5
TrD = trideca (13 carbon)	A = Carboxylate or carboxylic acid	PFTrDA	Perfluorotridecanoate	$C_{12}F_{25}CO_2^-$	862374-87-6
			Perfluorotridecanoic acid	$C_{12}F_{25}COOH$	72629-94-8
	S = Sulfonate or sulfonic acid	PFTrDS	Perfluorotridecane sulfonate	$C_{13}F_{27}SO_3^-$	NA
			Perfluorotridecane sulfonic acid	$C_{13}F_{27}SO_3H$	NA
TeD = tetradeca (14 carbon)	A = Carboxylate or carboxylic acid	PFTeDA	Perfluorotetradecanoate	$C_{13}F_{27}CO_2^-$	365971-87-5
			Perfluorotetradecanoic acid	$C_{13}F_{27}COOH$	376-06-7
	S = Sulfonate or sulfonic acid	PFTeDS	Perfluorotetradecane sulfonate	$C_{14}F_{29}SO_3^-$	NA
			Perfluorotetradecane sulfonic acid	$C_{14}F_{29}SO_3H$	NA

NA = not available

Note that for carboxylates, the total number of carbons used for naming the compound includes the carbon in the carboxylic acid functional group (COOH), and so although PFOA has seven carbons in its fluoroalkyl tail, all eight of the carbons in the molecule are used to name it, hence *perfluorooctanoate*. However, in terms of chemical behavior, PFOA would be more analogous to seven-carbon perfluoroheptane sulfonate, PFHpS, than to eight-carbon perfluorooctane sulfonate, PFOS.

Note that in Table 3-1, PFAA names and formulas are shown in both the anionic (also referred to as “deprotonated”) and acid (or neutral; also referred to as protonated) forms. The anionic form is the state that PFAAs are found in the environment, except in very rare situations (for example, extremely low pH). The anionic and acid forms of PFAA names are often incorrectly used interchangeably (for example, perfluorooctane sulfonate and perfluorooctane sulfonic acid), and the same acronym (in this case, PFOS) applies to both forms. However, as discussed in Sections 3.2 and 6.2.2, their physical and chemical properties are different and it is important to know which form is being described.

Until recently, carboxylates and sulfonates have been the classes most commonly tested for in the environment. However, a wide range of PFAS with other functional groups exist for which the same “PFXY” shorthand shown above may or may not apply. For naming conventions for these compounds, please refer to Buck et al. (2011).

A Note About PFAS Naming in Laboratory Reports

Even though PFAAs occur as anions in the environment, some laboratories report all of their results in the acidic form, while others may report PFCAs as acids (for example, perfluorooctanoic acid) and PFSAAs as anions (for example, perfluorooctane sulfonate). Different naming conventions in laboratory reports has led to confusion regarding exactly which form of the PFAA they are measuring. Although the lab is measuring the concentration of PFAA anions present in the sample, where the results are reported as an acid, the lab has adjusted for the H^+ cation (which has so little mass, this does not affect the resulting concentration).

It should be noted that the standards used by laboratories to perform analyses may be prepared from PFAA salts, as is often the case for sulfonate standards. If so, the lab must adjust the reported concentration to account for the mass of the counterion (typically Na^+ or K^+). The calculation to do this is described in Section 7.2.3 of EPA Method 537 (Shoemaker, Grimmer, and Boutin 2009).

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

3.1 Long Chain versus Short Chain Distinction

PFAAs are sometimes described as *long-chain* and *short-chain* as a shorthand way to group PFCAs and PFSAAs that may behave similarly in the environment. However, it is important not to make generalizations about PFAA behavior based only on chain length. As recent research suggests, other factors besides chain length may affect bioaccumulation potential of PFAS (Ng and Hungerbühler 2014).

According to the Organisation for Economic Co-operation and Development (OECD 2013):

- *Long-chain* refers to:
 - o perfluoroalkyl carboxylic acids, PFCAs, with eight or more carbons (seven or more carbons are perfluorinated)
 - o perfluoroalkane sulfonates, PFSAs, with six or more carbons (six or more carbons are perfluorinated)
- *Short-chain* refers to:
 - o perfluoroalkyl carboxylic acids with seven or fewer carbons (six or fewer carbons are perfluorinated)
 - o perfluoroalkane sulfonates with five or fewer carbons (five or fewer carbons are perfluorinated)

Table 3-2 illustrates the differences in the short-chain and long-chain PFCAs and PFSAs.

Table 3-2. Short-chain and long-chain PFCAs and PFSAs

Short-chain PFCAs				Long-chain PFCAs				
PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDaA
PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFUnS	PFDoS
Short-chain PFSAs				Long-chain PFSAs				

3.2 Anion versus Acid Form

As noted above, the names for the anionic and acid forms of PFAAs are often used interchangeably. However, it is critical to know which form is being discussed because of differences in their physical and chemical properties and behavior in the environment (see Section 6). Some important things to keep in mind regarding the anionic vs. acid forms are:

- Most PFAAs are present in environmental and human matrices in their anionic form. For example, PFOS is present in the environment in the anionic form, perfluorooctane sulfonate.
- Although laboratories may be reporting PFOA or PFOS using the acid form of their name, they are actually measuring the anionic form (for example, octanoate or sulfonate), as this is the form that exists in the environment.
- The acid form and their associated cationic salts have CAS numbers, while the anionic forms may not (see Table 3-1). For example, PFOS can exist as different salts (cationic), including sodium, lithium, potassium, or ammonium. Each of these salts will have a different CAS number:
 - o PFOS, acid form CAS No.: 1763-23-1
 - o PFOS, potassium salt CAS No.: 2795-39-3
 - o PFOS, ammonium salt CAS No.: 29081-56-9
- When the salt or acid exists in water or other liquids, it will dissociate and the salt or acid will break off and form the anion (COO⁻). Figure 3-1 illustrates the dissociation of perfluorobutanoic acid.
- It is most important to distinguish between the acid form and anionic form when reporting the physical and chemical properties. The discussion of PFAS properties in this fact sheet generally refers to the anionic form; it will be specifically called out if the acid form is being discussed.

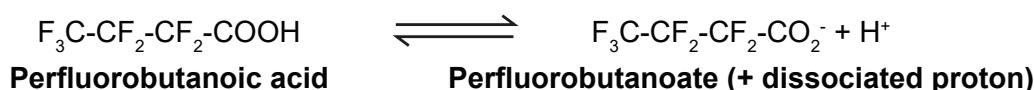


Figure 3-1. Dissociation of perfluorobutanoic acid

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

4 Linear and Branched Isomers of PFAS

Many PFAS may be present as mixtures of linear and branched isomers (chemicals with the same chemical formula, but different molecular structures) depending on the manufacturing process that was used. These structural differences are important because they may affect how the compounds behave in the environment and may provide an indicator of their source. Structural differences are described below:

- A *linear isomer* is composed of carbon atoms bonded to only one or two carbons, which form a straight carbon backbone. There can be only one linear isomer in a C_n homologue (compounds with the same number of carbons in their tail) group.
- In a *branched isomer*, at least one carbon atom is bonded to more than two carbon atoms, which forms a branching of the carbon backbone. There can be many isomers per C_n homologue group.

Figure 4-1 illustrates the structures of linear and branched PFOS.



Figure 4-1. Linear and one branched isomer of PFOS

The formula “ $C_nF_{2n+1}-$ ” (where n is greater than or equal to 3) includes linear and branched structures. For example, PFOS and PFHxS are routinely present in environmental samples as a mixture of linear and branched isomers.

Accurate quantification of PFAS that are mixtures of linear isomers and branched isomers in environmental matrices can be difficult (Riddell et al. 2009). However, they may be useful in understanding sources of PFAS and the age of the source, since the production of isomers varies by manufacturing processes. For example, the telomerization process produces only linear PFAAs, whereas the ECF process produces a mixture of linear and branched PFAA isomers (see Table 4-1 and the *History and Use Fact Sheet*). The presence of linear and branched isomers may also have implications for partitioning and transport.

Table 4-1. Manufacturing processes and potential PFAAs produced

Manufacturing Process	Commonly Found Polyfluorinated Substance (Precursors)	Potential PFAAs Produced
Telomerization	FTSA ¹	Linear PFCAs
	FTCA ²	Linear PFCAs
	FTOH	Linear PFCAs
Electrochemical Fluorination	FOSE	Branched and Linear PFCAs Branched and Linear PFSA
	FOSAA	Branched and Linear PFCAs Branched and Linear PFSA

¹Fluorotelomer sulfonate: found at AFFF sites
²Fluorotelomer carboxylic acids (for example, 5:3 Acid) found in landfill leachate

5 Replacement Chemistry

Concern regarding the persistence, bioaccumulation, and possible ecological and human health effects of long-chain PFAAs has led manufacturers to develop replacement short-chain PFAS chemistries that should not degrade to long-chain PFAAs (USEPA 2006a; OECD 2017). The short-chain alternatives include fluorotelomer-based products with a six-carbon perfluorohexyl chain and ECF-based products with a four-carbon perfluorobutyl chain. These products may degrade to form short-chain PFAAs, such as PFHxA and PFBS, respectively (Wang et al. 2013; Buck 2015). While a full discussion of such replacement chemistries is not possible here, it is important to be aware of this trend toward shorter-chain chemistries, as some of these PFAS increasingly may be detected in the environment.

Examples of this trend are replacement PFAS that have been developed for use as processing aids in the manufacturing of fluoropolymers. The replacements are generally fluorinated ether carboxylates. Two of these that have been detected

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

in the environment and generated public concern and regulatory actions are given here (their molecular structures are illustrated in Figure 5-1):

- GenX—trade name for ammonium, 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoate ($\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{COO}^- \text{NH}_4^+$; CAS No. 62037-80-3), a perfluoropolyether carboxylate surfactant (Wang et al. 2013; Buck 2015)
- ADONA—trade name for ammonium 4,8-dioxa-3H-perfluorononanoate ($\text{CF}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{-OCHFCF}_2\text{COO}^- \text{NH}_4^+$ (CAS No. 958445-44-8), a polyfluoropolyether carboxylate surfactant (Gordon 2011)

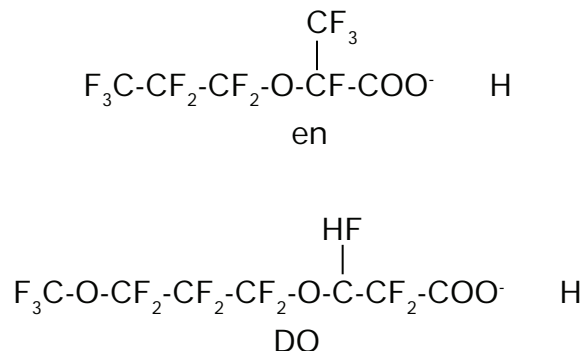


Figure 5-1. Example replacement chemistry structures

6 Physical and Chemical Properties

The physical and chemical properties of PFAS, in concert with the characteristics of the environmental system, determine the environmental behavior of organic contaminants, including the compound's state and partitioning behavior (Banks, Smart, and Tatlow 1994). Partitioning can occur between neutral and ionic molecular forms, solid and liquid states, and between different media and biota (aqueous, pure phase, soil/sediment, biota, and atmospheric). The environmental behavior of many PFAS is further complicated by their surfactant properties.

Figure 6-1 illustrates key chemical and physical properties and distribution coefficients. Comparing the chemical and physical properties of different PFAS provides insight into similarities and differences in their environmental behavior and can inform investigation design.

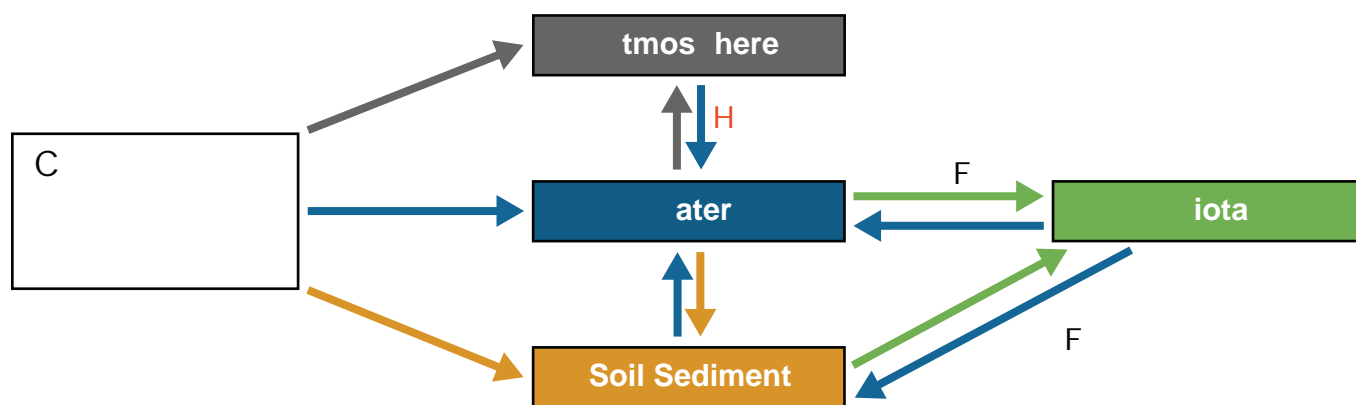


Figure 6-1. The role of key physical and chemical properties (shown in red) in influencing environmental compound behavior. Other key distribution coefficients (for example, K_d , K_{oc} shown in grey) are addressed in the *Environmental Fate and Transport Fact Sheet*. T_m = melting point; T_b = boiling point; pK_a = acid dissociation constant; p = vapor pressure; S = solubility; H = dimensionless Henry's law constant; K_d = soil and sediment partitioning coefficient; K_{oc} = organic carbon partitioning coefficient; BAF = bioaccumulation factor; and $BSAF$ = biota-sediment accumulation factor.

There is a large variation in published data on chemical and physical properties of PFAS. Reliable physical and chemical properties of PFAS are scarce (for example, vapor pressure and Henry's law constants), and some of the available values are modeled, as opposed to directly measured. With a few exceptions (K_{oc} and BCF or BAF values), many of the available properties are based on the acid form of the PFAA, which are not present in the environment, unless at $pH < 3$, which is not typical. Table 6-1 provides a general summary of the available chemical and physical property information

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

for PFCAs and the sensitivity of this information in relation to the acid vs. anionic form. For example, the anionic forms of PFOA and PFOS have documented bioconcentration factor and bioaccumulation factor properties (Martin et al. 2003a; 2003b) while other properties are not readily available.

Table 6-1. Available physical and chemical properties for PFCAs

Properties								Environmentally Relevant?
PFAA State	CAS No.	S_w	P°	K_h	K_{ow}	K_{oc}	BCF and/or BAF	
Acid	Y	Y	Y	E	E	E	N	No
Cation:								No
NH_4^+	Y	Y	N	N	N	N	N	
Li^+	Y	Y	N	N	N	N	N	
Na^+	Y	Y	N	N	N	N	N	
Anion	M	N	N	N	N	Y	Y	Yes

S_w = solubility in water

P° = vapor pressure

K_h = Henry's Law Constant

K_{ow} = octanol/water partition coefficient

K_{oc} = organic carbon partition coefficient

BAF = bioaccumulation factor

BCF = bioconcentration factor

Y = data available

N = no data available

M = data may be available for some

E = data estimated, not directly measured

6.1 Physical Properties

Many PFAS are in solid form at room temperature, often as a white powder or waxy substance, though some may be liquids. As mentioned before, data regarding physical properties of PFAS are scarce, and for PFAAs may relate to the acid form of the compound, which is not the most environmentally relevant form. Some melting point data are available for standards of PFCAs in the acid form. Measured vapor pressures for the acid form of PFOA, PFNA, PFDA, PFUnA, and PFDoA (Barton, Botelho, and Kaiser 2008; Kaiser et al. 2005) and fluorotelomer alcohols (Krusic et al. 2005) are also available. Similarly, Henry's Law constants are available for fluorotelomer alcohols (Goss et al. 2006). For PFAAs, the acid form is known to partition into air from aqueous solutions at very low pH (Kaiser et al. 2010). Care should be taken when reviewing available physical property information for PFAS to ensure that it applies to the form (for example, acid or anionic) of concern to the project or site in question.

6.2 Chemical Properties

6.2.1 Fluorine and the Carbon-fluorine (C-F) Bond

As previously mentioned, understanding PFAS chemical properties is key to understanding the diversity of uses and applications associated with this class of compounds, as well as their unique environmental behavior. Some key fluorine chemical properties and the characteristics they impart to PFAS are provided in Table 6-2.

Properties such as the high electronegativity and small size of fluorine lead to a strong C-F bond, the strongest covalent bond in organic chemistry (Kissa 2001; Banks, Smart, and Tatlow 1994). The low polarizability of fluorine further leads to weak intermolecular interactions, such as van der Waals interactions and hydrogen bonding (Kissa 2001; Banks, Smart, and Tatlow 1994). It is mainly the unique properties of fluorine that give many PFAS their mutually hydro- and lipophobic (stain-resistant) and surfactant properties and make them thermally and chemically stable. Not all of these characteristics (for example, surface activity) are universal to all PFAS.

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

Table 6-2. Fluorine characteristics, resulting characteristics and properties of PFAS

Fluorine Characteristic	Description	Result	Resulting Property of PFAS
High electronegativity	Tendency to attract shared electrons in a bond	Strong C-F bond	Thermal stability
			Chemical stability (low reactivity)
		Polar bond with partial negative charge towards F	Strong acidity (low pKa) ¹
Low polarizability	Electron cloud density not easily impacted by the electric fields of other molecules	Weak intermolecular interactions (for example, van der Waals, hydrogen bonds)	Hydrophobic and lipophobic surfactant properties ²
		Low surface energy	
Small size	Atomic radius of covalently bonded fluorine is 0.72 Å	Shields carbon	Chemical stability (low reactivity)
¹ When paired with an acid functional group such as a carboxylic or sulfonic acid ² When paired with a functional group that is hydrophilic (for example, a carboxylate) Å = Angstrom			

6.2.2 Acid Dissociation Constants

Knowing whether a chemical will dissociate in other liquids is important to understanding its fate and transport in the environment. The acid dissociation constant (K_a) is a quantitative measurement of the strength of an acid in solution, although it is usually presented in the form of the logarithmic constant (pK_a). The larger the value for pK_a , the smaller the extent to which the chemical will dissociate at a given pH. Chemicals with small pK_a values are called *strong acids* and those with large pK_a values are called *weak acids*.

Many PFAAs, such as PFCAs and PFSA, are strong acids due to the electron withdrawing effects of fluorine extending to their acid functional groups (Kissa 2001, Banks, Smart, and Tatlow 1994). As a result, most PFAAs readily dissociate in water and other environmental matrices. Therefore, at most environmentally relevant pHs, PFCAs and PFSA are present in the dissociated anionic form rather than the acid form.

The acid and anionic forms have very different physical and chemical properties. For example, perfluorooctanoate anion is highly water soluble and has negligible vapor pressure, whereas perfluorooctanoic acid has very low water solubility and sufficient vapor pressure to partition out of water into air. It is essential to distinguish between the acid form and the anionic form when looking at physical and chemical properties or fate and transport evaluations.

Specific pK_a values for PFAAs are generally not available. Limited model-predicted and experimental values are available for PFOA, and range from -0.5 to 3.8 (Burns et al. 2008; Kissa 2001; Barton, Kaiser, and Russell 2007; Goss 2008), suggesting that at nearly neutral pH (near pH = 7.0), PFOA will exist in the aqueous phase in anionic form and the amount of acid PFOA in most environmentally relevant systems will be negligible. A recent study estimates that the pK_a values of PFBA, PFHxA, PFHpA, PFOA, PFNA, PFDA, and PFUnA are all less than 1.6 and pK_a values of PFSA are expected to be even lower (Vierke, Berger, and Cousins 2013).

6.2.3 Thermal and Chemical Stability

Terminal PFAAs, such as PFOA and PFOS, are extremely stable, thermally and chemically, and resist degradation and oxidation. Thermal stability of PFAAs is primarily attributable to the strength of the C-F bond in the fluoroalkyl tail (Kissa 2001). The stability is determined by the specific functional group that is attached to the fluoroalkyl tail. PFCAs and PFSA are the most stable fluorinated surfactants. The acid forms of these PFAAs decompose at temperatures greater than 400°C, but complete mineralization occurs at temperatures greater than 1000°C. In a practical situation like a municipal incinerator, the mineralization temperature may be lower due to the presence of other substances that contain hydrogen. The thermal stability is lower for the salts of PFAA compounds and depends on which cation is the counter ion. For example, the 20% decomposition temperature of sodium perfluorooctanoate is 298°C, but is 341°C for lithium perfluorooctanoate (Kissa 2001). Additionally, salts of PFSA are more thermally stable than the corresponding salts of PFCAs (Kissa 2001).

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

The strength of the C-F bond, shielding of carbon by fluorine, and inductive effects (caused by fluorine electronegativity) also lead to PFAS chemical stability. For example, electron-rich chemical species called nucleophiles normally would be attracted to the partial positive charge of carbon. If they can get close enough to the carbon to bond with it, this would eliminate a fluorine from the molecule, making it vulnerable to degradation. However, the size of the fluorine atoms surrounding the carbon prevents this from happening (Banks, Smart, and Tatlow 1994; Schwarzenbach, Gschwend, and Imboden 2003). This is why processes such as hydrolysis, which involve eliminating one or more fluorines, are ineffective at degrading PFAS. Similarly, many PFAS are resistant to degradation by oxidative processes that rely on a loss of electrons (Kissa 2001). PFAS are also resistant to reductive processes, which involve gaining electrons. Despite having a high affinity for electrons, fluorine does not have vacant orbitals favorable for accepting additional electrons (Park et al. 2009).

6.2.4 Octanol/Water Partition Coefficient, K_{ow}

The octanol/water partition (K_{ow}) coefficient is sometimes used as a proxy for uptake in biological systems. The K_{ow} value is defined as “the ratio of a chemical’s concentration in the octanol phase to its concentration in the aqueous phase of a two-phase [octanol/water system]” (USEPA 2015d). The vapor pressure, melting point, and boiling point of neutral, volatile, non-polymeric PFAS (for example, FTOH) can be measured, and K_{ow} can be either estimated or measured. The K_{ow} values that are typically tabulated for the PFCAs and PFSA are for the acid form and are therefore not relevant because PFCAs and PFSAs are anionic at environmental pHs. Additionally, because many PFAS bind to proteins (proteinphiles), some PFAS may bioaccumulate by mechanisms other than those that drive more traditional hydrophobic contaminants (Ng and Hungerbühler 2013; 2014). Other PFAS may simply be detected in organisms due to ongoing exposures and their extended human half-lives (for example, concentrations in drinking water) (Wiesmueller 2012; Gyllenhammar et al. 2015). It should be noted that although the K_{ow} for some organic contaminants can be used for estimating K_{oc} , this cannot be performed for estimating values for PFAS.

7 Summary

This fact sheet addresses naming conventions and physical and chemical properties of some of the most commonly reported PFAS considering historical use, current state of science research related to environmental occurrence, and available commercial analyses. For naming conventions related to additional PFAS, refer to Buck et al. (2011). In general, values for physical and chemical properties of many non-polymeric PFAS are not available. With the 2015 major global manufacturer phase-out of long-chain PFAAs and their potential precursors, such as those based on C8 chemistry (see *History and Use Fact Sheet*), replacement PFAS (for example, short-chain alternatives and non-polymer perfluoropolyethers) have been commercially introduced (many following review by USEPA) and may continue to be developed. In the future, it may be necessary to expand the current naming conventions and acronym approaches to ensure that standardized naming is available for additional members of the PFAS class of compounds. Further, additional information on physical and chemical properties of these compounds may become available as increased numbers of PFAS are included in environmental and human health-related studies. Refer to the other PFAS fact sheets for further information on these properties and how they are practically applied.

8 References and Acronyms

The references cited in this fact sheet, and the other ITRC PFAS fact sheets, are included in one combined list that is available on the ITRC web site. The combined acronyms list is also available on the ITRC web site.



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ECOS

Regulations, Guidance, and Advisories for Per- and Polyfluoroalkyl Substances (PFAS)

1 Introduction

Per- and polyfluoroalkyl substances (PFAS) became contaminants of emerging concern in the early 2000s. In recent years federal, state, and international authorities have established a number of health-based regulatory values and evaluation criteria. The terms ‘regulatory’ or ‘regulation’ are used in this fact sheet to refer to requirements that have gone through a formal process to be promulgated and legally enforceable as identified under local, state, federal, or international programs. The terms ‘guidance’ and ‘advisories’ apply to all other values.

2 Regulation of PFAS

The scientific community is rapidly recognizing and evolving its understanding of PFAS in the environment, causing an increased pace of development of guidance values and regulations. A recent analysis of data acquired under the USEPA’s Unregulated Contaminant Monitoring Rule (UCMR) program found that approximately six million residents of the United States had drinking water with concentrations of perfluorooctanoic acid (PFOA) or perfluorooctane sulfonate (PFOS), or both, above the USEPA’s Lifetime Health Advisory (LHA) of 70 nanograms per liter (ng/L, equivalent to parts per trillion [ppt]) (Hu et al. 2016). Many of the public water systems with detections of PFOA or PFOS above the USEPA LHA have taken action to reduce these levels. However, most public water systems that supply fewer than 10,000 customers and private wells were not included in the third round of monitoring, or UCMR3 program, and remain untested.

Human health protection is the primary focus of the PFAS regulations, guidance, and advisories developed to date. The values for PFOS and PFOA can vary across programs, with differences due to the selection and interpretation of different key toxicity studies, choice of uncertainty factors, and approaches used for animal-to-human extrapolation. The choice of exposure assumptions, including the life stage and the percentage of exposure assumed to come from non-drinking water sources, may also differ (see Table 5-1).

In addition to values that specify health-based concentration limits, agencies have used various strategies to limit the use and release of PFAS. For example, the USEPA worked with 3M to achieve the company’s voluntary phase-out and elimination of PFOS (USEPA 2000), and with the eight primary U.S. PFOA manufacturers to eliminate or reduce PFOA and many PFOA precursors by 2015 (USEPA 2017a). Buck et al. (2011) define precursors as PFAS polymers or other functional derivatives that contain a perfluoroalkyl group and “degrade in the environment to form PFOS, PFOA, and similar substances.” Additionally, the Organisation for Economic Cooperation and Development OECD (2015a) has described various international policies, voluntary initiatives, biomonitoring, and environmental monitoring programs to control PFAS. More information is in the *History and Use Fact Sheet*.

3 Regulatory Programs

Authority for regulating PFAS is derived from a number of federal and state statutes, regulations, and policy initiatives. This section provides a brief overview of the major federal statutes and regulatory programs that govern PFAS, along with examples of representative state regulatory programs.

3.1 Federal PFAS Regulations

3.1.1 Toxic Substances Control Act (TSCA)

The TSCA authorizes the USEPA to require reporting, record-keeping, and testing of chemicals and chemical mixtures that may pose a risk to human health or the environment. Section 5 of TSCA allows the USEPA to issue Significant New Use Rules (SNURs) to limit the use of a chemical when it is newly identified, or a significant new use of an existing chemical is identified, before it is allowed into the marketplace (USEPA 2017a). The USEPA has applied a SNUR to PFOS in four separate actions and to 277 chemically-related PFAS (USEPA 2017i). Collectively, these SNURs placed significant restrictions on the use and import of PFAS, allowing only limited uses in select industries and for certain applications. In

ITRC has developed a series of six fact sheets to summarize the latest science and emerging technologies regarding PFAS. The purpose of this fact sheet is to:

- describe the primary state and U.S. federal programs that are being used to regulate PFAS
- summarize current regulatory and guidance values for PFAS in groundwater, drinking water, surface water/effluent, and soil (Tables 4-1 and 4-2)
- provide information (summarized in Tables 5-1 and 5-2) regarding the basis for differences between various drinking water criteria for perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS)

Regulations, Guidance, and Advisories for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

addition, one of the rules required companies to report all new uses in the manufacture, import, or processing of certain PFOA-related chemicals for use in carpets or for aftermarket treatment. A recently proposed SNUR (USEPA 2015c) would designate the manufacture, import, and processing of certain PFOA and PFOA-related chemicals (long-chain perfluoroalkyl carboxylates [PFCAs]) as a significant new use. The significant new use would apply to any use that is not ongoing after December 31, 2015, and for all other long-chain PFCAs for which there is currently no ongoing use (USEPA 2015a).

3.1.2 Safe Drinking Water Act (SDWA)

The SDWA is the federal law that protects public drinking water supplies throughout the nation (USEPA 1974). Under the SDWA, the USEPA has authority to set enforceable Maximum Contaminant Levels (MCLs) for specific chemicals and require testing of public water supplies. The SDWA applies to all public water systems in the United States but does not apply to private domestic drinking water wells nor to water not being used for drinking.

USEPA has not established MCLs for any PFAS. However, in May 2016, USEPA established an LHA for PFOA and PFOS in drinking water of 70 ng/L. This LHA is applicable to PFOA and PFOS individually, or in combination, if both chemicals are present at concentrations above the reporting limit (USEPA 2016b, c). The LHA supersedes USEPA's 2009 short-term (week to months) provisional Health Advisories of 200 ng/L for PFOS and 400 ng/L for PFOA (USEPA 2009c), which were intended for use as interim guidelines while USEPA developed the LHA. The LHA for PFOA and PFOS is advisory in nature; it is not a legally enforceable federal standard and is subject to change as new information becomes available (USEPA 2016b, c).

Much of the current data available regarding PFAS in public drinking water was generated by USEPA under UCMR3 (USEPA 2017f). USEPA uses the UCMR to collect data for chemicals that are suspected to be present in drinking water but do not have health-based standards set under the SDWA. The third round of this monitoring effort, or UCMR3, included six PFAS:

- perfluorooctanesulfonic acid (PFOS)
- perfluorooctanoic acid (PFOA)
- perfluorononanoic acid (PFNA)
- perfluorohexanesulfonic acid (PFHxS)
- perfluoroheptanoic acid (PFHpA)
- perfluorobutanesulfonic acid (PFBS)

Samples were collected during a consecutive 12-month monitoring period between 2013 and 2015 from large public water systems (PWS) serving more than 10,000 people, and a limited number of smaller systems determined by USEPA to be nationally representative. Some of the six PFAS mentioned above were detected in 194 out of 4,920 PWS tested (~4%), which serve about 16.5 million people in 36 states and territories (Hu et al. 2016). However, Hu et al. (2016) note that the UCMR3 data may under-report the actual presence of low-level PFAS due to the relatively high reporting limits for EPA method 537.

Table 3-1. UCMR3 occurrence data

Exceed LHA (70 ppt)	Number of PWS	Percent of PWS
PFOS	46	0.9 %
PFOA	13	0.3 %
Σ PFOA + PFOS ¹	63	1.3 %
Note 1: PWS that exceeded the combined PFOA and PFOS health advisory (USEPA 2016d; 2017o)		

Many of the public water systems where PFOA or PFOS were detected in UCMR3 above the USEPA LHA have taken action to reduce these levels. Occurrence data produced by the UCMR program are used by the USEPA, as well as some states, to help determine which substances to consider for regulation. All of the data from the UCMR program are published in the National Contaminant Occurrence Database (NCOD) and available for download from USEPA's website (USEPA 2017f).

Regulations, Guidance, and Advisories for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

When the USEPA determines there may be an imminent and substantial endangerment from a contaminant that is present in or likely to enter a public water supply, under Section 1431 of the SDWA USEPA may issue Emergency Administrative Orders (EAOs) to take any action necessary to protect human health if state and local authorities have not acted (42 U.S.C. §300i). USEPA has issued at least three such EAOs to protect public and private water supply wells contaminated with PFAS (USEPA 2009d; 2014b; 2015a).

3.1.3 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

PFAS, including PFOA and PFOS, are not listed as CERCLA hazardous substances but may be addressed as CERCLA pollutants or contaminants (40 CFR 300.5). CERCLA investigations are beginning to include PFAS when supported by the conceptual site models (for example, USEPA 2017c). PFAS have been reported for 14 CERCLA sites during 5-year reviews (USEPA 2014a).

CERCLA does not contain any chemical-specific cleanup standards. However, the CERCLA statute requires, among other things, that Superfund response actions ensure protectiveness of human health and the environment, and comply with federal laws and regulations that constitute “applicable or relevant and appropriate requirements” (ARARs); the statute also provides possible ARAR waivers in limited circumstances. The lead agency (as defined in 40 CFR 300.5) identifies potential ARARs and to-be-considered values (TBCs), based in part on the timely identification of potential ARARs by states. Risk-based goals may be calculated and used to determine cleanup levels when chemical-specific ARARs are not available or are determined not to be sufficiently protective (USEPA 1997).

3.1.3.1 CERCLA Protection of Human Health

The tables in Section 4 include current state regulatory and guidance values for PFAS. These values are not automatically recognized as ARARs. In the Superfund program, USEPA Regions evaluate potential ARARs, including state standards, on a site-specific basis to determine whether a specific standard or requirement is an ARAR for response decision and implementation purposes. Determining if a state requirement is promulgated, substantive, and enforceable are some of the factors in evaluating whether a specific standard may constitute an ARAR (40 CFR 300.5; 40 CFR 300.400(g); USEPA 1988; USEPA, 1991).

Risk-based cleanup goals are calculated when chemical-specific ARARs are not available or are determined not to be protective (USEPA 1997). The USEPA’s Regional Screening Level (RSLs) Generic Tables (USEPA 2017m) and the RSL online calculator (USEPA 2017l) provide screening levels and preliminary remedial goals. These goals are based on toxicity value calculations that have been selected in accordance with the USEPA’s published hierarchy (USEPA 2003a). Currently, PFBS is the only PFAS listed in the RSL generic tables. For PFBS, the generic tables provide a non-cancer reference dose, screening levels for soil and tap water, and soil screening levels for the protection of groundwater. The RSL calculator supports site-specific calculations for PFBS, PFOA, and PFOS in tap water and soil. Non-cancer reference doses are provided for PFOA and PFOS. A cancer ingestion slope factor is also provided for PFOA, but screening levels are based on the non-cancer endpoint. Although less frequently used, the USEPA also provides tables and a calculator for Removal Management Levels (RMLs). In general, RMLs are not final cleanup levels, but can provide a reference when considering the need for a removal action (for example, drinking water treatment or replacement) (USEPA 2016a).

Because RSLs and RMLs are periodically updated, they should be reviewed for revisions and additions before using them. RSLs and RMLs are not ARARs, but they may be evaluated as TBCs. The USEPA has emphasized that RSLs are not cleanup standards (USEPA 2016g) and suggests that final remedial goals be derived using the RSL calculator so that site-specific information can be incorporated.

3.1.3.2 CERCLA Protection of the Environment

CERCLA requires that remedies also be protective of the environment. Risk-based cleanup goals that are protective of the environment are site-specific and depend on the identification of the protected ecological receptors.

3.1.4 Other Federal Programs

PFAS are not currently regulated under the Resource Conservation and Recovery Act (RCRA), the Clean Water Act (CWA), nor the Clean Air Act (CAA).

Regulations, Guidance, and Advisories for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

3.2 State PFAS Regulations

Several states have been actively involved with addressing PFAS contamination across multiple regulatory programs. Examples of key state programs for water, soil, remediation, hazardous substances, and consumer products are described below, and information about regulatory, advisory and guidance values are discussed in Section 4 and presented in Tables 4-1 and 4-2. At the present time, no state requires monitoring of public water supplies for PFAS. The Texas Risk Reduction Program (TRRP) has derived risk-based inhalation exposure limits (RBELs) for select PFAS. These RBELs are applicable to PFAS that may volatilize from soil to air at remediation sites managed under the TRRP rule (Texas Commission on Environmental Quality [TCEQ], 2017).

3.2.1 Product Labeling and Consumer Products Laws

PFOS, PFOA, and their salts are under consideration for 'Listing' as potential Developmental Toxicants under California's Proposition 65 (Office of Environmental Health Hazard Assessment [CA OEHHA] 2016). If finalized, the listing will include labeling requirements for manufacturers, distributors, and retailers, and will prohibit companies from discharging these PFAS to sources of drinking water. Washington has required the reporting of PFOS in children's products since 2011 (Washington State 2008). Proposed rules would require reporting of PFOA in children's products starting in January 2019. Washington also tests products for chemicals to ensure manufacturers are reporting accurate information.

3.2.2 Chemical Action Plans

Washington prepares chemical action plans (CAPs) under an administrative rule that addresses persistent, bioaccumulative, and toxic (PBT) chemicals (Washington State 2006). These CAPs are used to identify, characterize, and evaluate uses and releases of specific PBTs or metals. Washington is currently preparing a PFAS CAP that is expected to be completed in 2018.

3.2.3 Designation as Hazardous Waste or Hazardous Substance

Regulations that target select PFAS as hazardous wastes or hazardous substances have been promulgated in Vermont and New York, and are under development in several other states. Vermont regulates PFOA and PFOS as hazardous wastes when present in a liquid at a concentration > 20 ppt, but allows exemptions for: (1) consumer products that were treated with PFOA and are not specialty products; (2) remediation wastes managed under an approved CAP or disposal plan; and (3) sludge from wastewater treatment facilities, residuals from drinking water supplies, or leachate from landfills when managed under an approved plan (VTDEC 2016).

In 2017, the New York State Department of Environmental Conservation (NYDEC) finalized regulations that identify PFOA, ammonium perfluorooctanoate, PFOS (the acid) and its salt, perfluorooctane sulfonate, as hazardous substances that may be found in Class B firefighting foams (NYDEC 2017). The regulations specify storage and registration requirements for Class B foams that contain at least 1% by volume of one or more of these four PFAS, and prohibit the release of one pound or more of each into the environment during use. If a release exceeds the one-pound threshold, it is considered a hazardous waste spill and must be reported; cleanup may be required under the State's Superfund or Brownfields programs (NYDEC 2017).

3.2.4 Drinking Water, Groundwater, Surface Water, Soil, and Remediation Programs

Several states have developed standards and guidance values for PFAS in drinking water and groundwater (see Section 4 tables). Many states have either adopted the USEPA LHAs for PFOA and PFOS or selected the same health-based values, choosing to use the concentrations as advisory, non-regulated levels to guide the interpretation of PFOA and PFOS detections. Other states, such as Vermont, Minnesota, and New Jersey, have developed health-based values based on their own analysis of the scientific data. Michigan is currently the only state that regulates certain PFAS in surface water, although Minnesota has enforceable discharge limits for specific waterbodies. New Jersey has adopted an Interim Ground Water Quality Standard for PFNA, and its drinking water advisory body has recommended proposed MCLs for PFOA and PFNA. While several states have adopted enforceable groundwater standards for PFOA and PFOS, no state other than New Jersey currently has MCLs (or proposed MCLs) for PFAS.

In California, when evaluating the discharge or cleanup of chemicals, the Regional Water Quality Control Boards (RWQCBs) are required to initially set the effluent limitation or cleanup standard at the background concentration of each chemical. This is done regardless of whether there is a drinking water standard or other health-based value available. For anthropogenic chemicals such as PFAS, the initial value is the analytical detection limit in water. Technical, economic, and health-based criteria are also considered (for example, CA RWQCB 2016).

Regulations, Guidance, and Advisories for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

Various states address the remediation of PFAS in groundwater and soil; guidance and advisory values may be used by state remediation programs to determine site-specific cleanup requirements (see Section 4 tables). Texas has developed toxicity criteria for 16 PFAS under the TRRP (TCEQ, 2017). These criteria are used to calculate risk-based soil and groundwater values and can also be used for other media such as sediment and fish tissue.

4 Available Regulations, Advisories, and Guidance

Regulatory, advisory, and guidance values have been established for PFOS, PFOA, and several other PFAS in environmental media as well as various terrestrial biota, fish, and finished products. Tables 4-1 and 4-2, provided as a separate Excel file, are intended to identify currently available U.S. and international standards and guidelines for groundwater, drinking water, surface water, and effluent or wastewater (Table 4-1), and soil (Table 4-2). The available standards list is changing rapidly. These tables are published separately so they can be updated periodically by ITRC. The fact sheet user should visit the ITRC web site (www.itrcweb.org) to access current versions of the tables.

Table 4-1 presents the available PFAS water values established by the USEPA, each pertinent state, or country (Australia, Canada and Western European countries). The specific agency or department is listed with the year it was published, the media type (groundwater, drinking water, surface water, or effluent), and whether it was published as guidance or as a promulgated rule.

Table 4-2 presents the available PFAS soil values established by the USEPA, each pertinent state, or country (Australia, Canada and Western European countries). Soil screening levels for both groundwater protection and human health are presented. The specific agency or department is listed with the year the value was published.

5 Basis of Standards and Guidance

Drinking contaminated water is a potential source of human exposure (see reviews in Lindstrom et al. 2011; NJ DWQI 2017a). As noted above, UCMR3 sampling detected PFOA or PFOS concentrations above the EPA Lifetime HA of 70 ng/L in the source water for municipal systems that supply approximately 6 million U.S. residents (Hu et al 2016). Although there are other potential sources that may lead to PFAS exposures (for example, consumer products), protection of the potable water supply is the primary driver behind most of the available state and federal regulations and guidance, due to the potential for exposure and the known or presumed toxicity of these compounds.

While numerous animal and human studies have evaluated both non-cancer and cancer health effects related to exposure to a limited number of PFAS, including PFOA and PFOS, little to no health-effects data are available for many PFAS. As a result, many of the available standards and guidance are for PFOA and PFOS. In animal studies, PFOA exposure has been associated with adverse effects on the developmental, reproductive, and immune systems and the liver (see summary of original research in USEPA 2016f). There is also evidence of both PFOA and PFOS affecting immune systems, including reduced disease resistance (National Toxicology Program [NTP] 2016) and tumors in rats (USEPA 2016e, f). These and other effects have also been found in human epidemiological studies (ATSDR 2016; C8SP 2017; USEPA 2016e, f; NTP 2016). The International Agency for Research on Cancer (IARC) concluded that PFOA is “possibly carcinogenic to humans (Group 2B)” (IARC 2016), and USEPA concluded that there is suggestive evidence of carcinogenic potential for both PFOA and PFOS in humans (USEPA 2016e, f).

Tables 5-1 and 5-2, provided as a separate Excel file, summarize the differences in the PFOA (Table 5-1) and PFOS (Table 5-2) values for drinking water in the United States, demonstrating that they are attributable to differences in the selection and interpretation of key toxicity data, choice of uncertainty factors, and the approach used for animal-to-human extrapolation. Differences in values are also due to the choice of exposure assumptions, including the life stage used, and the percentage of exposure assumed to come from non-drinking water sources. Only those agencies that have used science or policy decisions that are different from those of the USEPA LHAs are shown. The available information is increasing rapidly and these tables will be updated periodically by ITRC. The fact sheet user should visit the ITRC web site (www.itrcweb.org) to access the current version of the tables.

Some states have not yet developed values or adopted the USEPA LHA. It may be appropriate to consult with the lead regulatory authority (local or federal) to determine the appropriate values to use for site evaluation.

Regulations, Guidance, and Advisories for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

6 References and Acronyms

The references cited in this fact sheet, and the other ITRC PFAS fact sheets, are included in one combined list that is available on the ITRC web site. The combined acronyms list is also available on the ITRC web site.



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E C O S

History and Use of Per- and Polyfluoroalkyl Substances (PFAS)

1 Introduction

The unique physical and chemical properties of per- and polyfluoroalkyl substances (PFAS) impart oil and water repellency, temperature resistance, and friction reduction to a wide range of products used by consumers and industry. For example, PFAS, have been used in coatings for textiles, paper products, and cookware and to formulate some firefighting foams, and have a range of applications in the aerospace, photographic imaging, semiconductor, automotive, construction, electronics, and aviation industries (KEMI 2015; USEPA 2017b). USEPA has compiled a web-based resource for PFAS information. The information includes topics such as Policy and Guidance, Chemistry and Behavior, Occurrence, Toxicology, Site Characterization and Remediation Technologies (USEPA 2017h).

The scientific community is rapidly recognizing and evolving its understanding of the environmental and health impacts associated with the release of PFAS. Certain PFAS, most notably some of the perfluoroalkyl acids (PFAAs), such as perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), are mobile, persistent, and bioaccumulative, and are not known to degrade in the environment (USEPA 2003b; ATSDR 2015; NTP 2016; Concawe 2016).

Understanding the manufacturing history of PFAS, as well as past and current uses, allows for the identification of potential environmental sources of PFAS, possible release mechanisms, and associated pathway-receptor relationships.

ITRC has developed a series of six fact sheets to summarize the latest science and emerging technologies regarding PFAS. The purpose of this fact sheet is to:

- provide an overview of the discovery and development of PFAS and the subsequent detection of PFAS in the environment
- describe emerging concerns of potential adverse human health effects, and efforts to reduce use or replace with alternate formulations, or both
- identify the major sources of PFAS in the environment, as well as other sources of PFAS to the environment that may be of interest

2 Discovery and Manufacturing History

PFAS are a complex family of more than 3,000 manmade fluorinated organic chemicals (Wang et al. 2017) that have been produced since the mid-20th century, although not all of these may be currently in use or production. Table 2-1 provides a general timeline of initial synthesis and commercial production of some of the more well-known PFAS, along with some of the more frequently associated products.

PFAS are produced using several different processes. Two major processes have been used to manufacture fluorosurfactants (includes PFAAs) and side-chain fluorinated polymers: electrochemical fluorination (ECF) and telomerization (KEMI 2015). ECF was licensed by 3M in the 1940s (Banks, Smart, and Tatlow 1994), and used by 3M until 2001. ECF produces a mixture of even- and odd- numbered carbon chain lengths of approximately 70% linear and 30% branched substances (Concawe 2016). Telomerization was developed in the 1970s (Benskin 2011), and yields mainly even numbered, straight carbon chain isomers (Kissa 2001; Parsons et al. 2008).

Table 2-1. Discovery and manufacturing history of select PFAS

PFAS ¹	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS ²)
PFOA		Initial Production	Protective Coatings					
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		
Dominant Process ³		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		
Notes: 1. This table includes fluoropolymers, PFAAs, and fluorotelomers. PTFE (polytetrafluoroethylene) is a fluoropolymer. PFOS, PFOA, and PFNA (perfluorononanoic acid) are PFAAs. 2. Refer to Section 3.4. 3. The dominant manufacturing process is shown in the table; note, however, that ECF and fluorotelomerization have both been, and continue to be, used for the production of select PFAS.								
Sources: Prevedouros et al. 2006; Concawe 2016; Chemours 2017; Gore-Tex 2017; US Naval Research Academy 2017								

3 Health and Environmental Investigations

3.1 Initial Studies

Studies that found some PFAS in the blood of occupationally exposed workers in the 1970s and reported detections in the blood of the general human population in the 1990s (Buck et al. 2011) led to increased awareness of PFAAs in the environment, associated human exposure, and the potential for health effects. PFAAs (such as PFOS and PFOA) are found in the blood and serum of most people whether exposed in the workplace or not. This is attributed to widespread use, ability to bind to blood proteins and long half-lives in humans (Kannan et al. 2004; Karrman et al. 2006; Olsen et al. 2003). Laboratory studies using animals and epidemiological studies of human populations show that exposure to some PFAS may be associated with a wide range of adverse human health effects (USEPA 2016b, c; ATSDR 2017).

Although some PFAS have been manufactured for more than 50 years, PFAS were not widely documented in environmental samples until the early 2000s. Early detection at low reporting limits was hindered due to analytical capability challenges arising from the unique surface-active properties of PFAS (Giesy and Kannan 2001; 3M 2000). Many manuscripts have since been published showing widespread distribution of certain PFAS, such as PFAAs, in various matrices including sediments, surface and groundwater, wildlife, and human blood (whole, plasma, and serum) (Kannan et al. 2004; Yamashita et al. 2005; Higgins et al. 2005; Rankin et al. 2016). Some PFAS (such as PFAAs) are found in many places throughout the globe, even in areas well beyond where they were initially used or manufactured (Houde et al. 2011).

3.2 Emerging Awareness

The awareness and emphasis on various PFAS have evolved. Early focus was on the longer-chain (see Section 3.4), perfluoroalkyl acids (PFAAs). In 2016, USEPA issued a Lifetime Health Advisory (LHA) for two of the most widely detected PFAAs, PFOA and PFOS. Set at 70 nanograms per liter (ng/L, equivalent to parts per trillion [ppt]), the LHA applies for each PFAA, as well as in combination, in drinking water (USEPA 2016d).

History and Use of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

Six additional PFAAs have recently gained attention after their inclusion in the USEPA Unregulated Contaminant Monitoring Rule (UCMR). The third round of monitoring, or UCMR3, was promulgated in 2012 for tracking chemicals suspected to be present in drinking water, but do not have health-based standards set by the Safe Drinking Water Act. A summary of the occurrence data is included in the *Regulations, Guidance, and Advisories Fact Sheet*.

Many state regulatory agencies now request or require an expanded list of perfluoroalkyl substances (short and long chain), and fluorotelomers and polyfluoroalkyl substances are also receiving increased attention. This progression is illustrated in Figure 3-1.

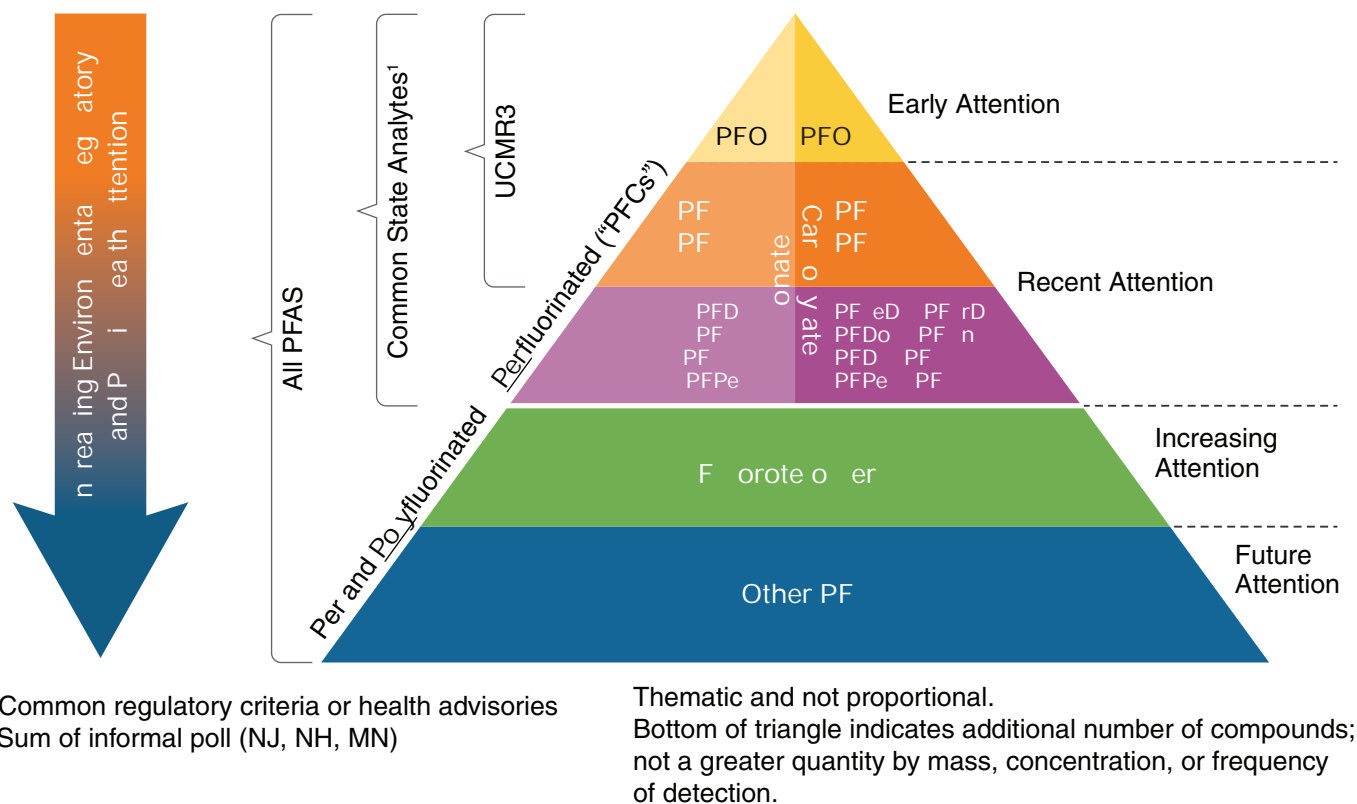


Figure 3-1. Emerging awareness and emphasis on PFAS occurrence in the environment
(Source: J. Hale, Kleinfelder, used with permission)

3.3 Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention on Persistent Organic Pollutants (POPs) is a United Nations treaty signed in 2001 aimed at reducing or eliminating the production, use, and release of key POPs. POPs are defined as synthetic, organic compounds that, to varying degrees, resist photolytic, biological, and chemical degradation (KEMI 2004 and 2005; USEPA 2017k).

In 2009, *Annex B of the Stockholm Convention* was amended to include PFOS, because it is persistent in the environment and is not known to degrade at any environmental condition. At this time, the U.S. has not ratified the amendment (KEMI 2017). According to the Stockholm Convention website, PFOA and PFHxS (perfluorohexane sulfonic acid) are currently proposed for listing.

3.4 Phase-out of Long-Chain PFAS

Due to industry and regulatory concerns about the potential health and environmental impacts, there has been a reduction in the manufacture and use of long-chain PFAAs. Long-chain PFAAs include perfluorinated carboxylates (PFCAs) with eight or more fully fluorinated carbons (for example, PFOA) and perfluorinated sulfonates (PFSA)s with six or more fully fluorinated carbons (for example, PFHxS and PFOS), their salts, and precursor compounds capable of forming long-chain PFAAs (USEPA 2009a; Buck et al. 2011; OECD 2013; Wang et al. 2015).

History and Use of Per- and Polyfluoroalkyl Substances (PFAS) *continued*

- In May 2000, 3M, the principal worldwide manufacturer and sole U.S. manufacturer of PFOS, announced a voluntary phase-out of perfluorooctanyl chemistries, which included PFOS, PFHxS, PFOA, and related precursors. 3M reportedly completed most of the phase-out by the end of 2002, with the remaining phase-out completed by 2008 (USEPA 2003b; USEPA 2017e; 3M 2017b).
- USEPA issued Significant New Use Rules (SNURs) under the Toxic Substances Control Act (TSCA) to restrict any future use or production of 183 PFAS, which include 88 of the PFOS-related chemicals phased-out by 3M. However, the SNURs allowed for continued, low-volume use of some of these PFAS in the photographic/imaging, semiconductor, etching, metal plating, and aviation industries. Also, due to the long shelf-life of PFOS-based fire-fighting foams, they may still be stored and in use at various facilities (see Section 4.2) (USEPA 2007). SNURs for some long-chain PFCAs and PFASs have been proposed (USEPA 2015b).
- In January 2006, USEPA initiated the PFOA Stewardship Program (USEPA 2006b). The eight major manufacturing companies committed to reducing PFOA, other longer-chain PFCAs (such as perfluorononanoic acid [PFNA] and perfluoroundecanoic acid [PFUnA]), and related precursors (for example, 8:2 fluorotelomer alcohol [FTOH]) that could be converted to these PFCAs from their global facility emissions and product content. USEPA indicates all eight companies successfully satisfied the program goals, meeting a 95% reduction by 2010, and elimination by 2015 (USEPA 2017e). Even though the program goals were met, materials imported to the United States may contain these PFCAs and related precursors.

PFAS are manufactured globally. Recently increased production of PFOA and related PFAS in China, India, and Russia have potentially offset the global reduction anticipated with the U.S. phase-out (OECD 2015b). PFAS manufacture began in China in the 1980s (World Bank 2017a, b), and PFOS production in China increased with the long-chain PFAA phase-out in the United States (Concawe 2016). In 2016, PFOS and its derivatives were still being produced in Germany, Italy, and China (Witteveen+Bos and TTE 2016), but by early 2017, China was the only known producer of PFOS. China has ratified the Stockholm Convention on POPs and a grant from Global Environment Facility (GEF) was approved in 2017 to support the reduction of PFOS in China (World Bank 2017a).

3.5 Replacement Chemistry

Manufacturers have been developing replacement technologies, including reformulating or substituting longer-chain substances with shorter-chain perfluoroalkyl or polyfluorinated substances that include, but are not limited to, compounds produced with ECF and fluorotelomerization, such as: FTOH, perfluorobutane sulfonyl fluoride (PBSF)-based derivatives (for example, perfluorobutane sulfonate [PFBS] in lieu of PFOS), polyfluoroethers (for example, GenX and ADONA used in the manufacture of fluoropolymers) and other types of PFAS (Hori et al. 2006; OECD 2007; Herzke, Olson, and Posner 2012; Wang et al. 2013; Wang et al. 2015; Holmquist et al. 2016).

Many long-chain PFAS alternatives are structurally similar to their predecessors and manufactured by the same companies (Concawe 2016; Wang et al. 2015). However, it is not yet clear if some of these chemicals can achieve the same performance effectiveness of some of their predecessors. For example, a 2015 study concluded that there are no non-fluorinated alternatives that provide equivalent technical performance in textiles (Danish EPA 2015).

Several studies suggest some of the replacement PFAS may or may not be less hazardous than the long-chain predecessors, although publicly available information on most replacement chemicals is limited (Wang et al. 2015; RIVM 2016). Documentation regarding the USEPA's review of hundreds of "shorter chain-length PFAS telomeric" substitutes for long-chain PFAS is available under the TSCA New Chemicals Program (OECD 2013; USEPA 2017g). Other documentation regarding replacement chemistries is available from the FluoroCouncil (2017).

Information on environmental contamination by replacement PFAS is limited, and most are not detected by standard analytical methods (Wang et al. 2013). Treatment processes used to remove these chemicals from waste streams may not be as effective as with longer-chain PFAS (Sun et al. 2016).

4 Major Sources of PFAS in the Environment

PFAS are used in many industrial and consumer applications. Major sources may have released PFAS into the environment and impacted drinking water supplies in many areas of the United States (Environmental Working Group and Northeastern University Social Science Environmental Health Research Institute 2017).

4.1 Production and Manufacturing Facilities

Both in the United States and abroad, primary manufacturing facilities produce PFAS and secondary manufacturing facilities use PFAS to produce goods. Due to the solubility and persistence of many PFAS, environmental release mechanisms associated with these facilities include air emission and dispersion, spills, and disposal of manufacturing wastes and wastewater. Potential impacts to air, soil, surface water, stormwater, and groundwater are present not only at release areas but potentially over the surrounding area (Shin et al. 2011). Table 4-1 summarizes potential major sources of PFAS releases to the environment based on the manufacturing sector. Manufacturing of commercial products and consumer goods summarized in Section 5 may also be environmental sources but are not included in this table.

Table 4-1. Potential major manufacturing sources of PFAS releases to the environment

Sector	Example Uses	References
Textiles & Leather	Factory- or consumer-applied coating to repel water, oil, and stains. Applications include protective clothing and outerwear, umbrellas, tents, sails, architectural materials, carpets, and upholstery.	Rao and Baker 1994; Hekster, Laane, and de Voogt 2003; Brooke, Footitt, and Nwaogu 2004; Poulsen et al. 2005; Prevedouros et al. 2006; Walters and Santillo 2006; Trudel et al. 2008; Guo et al. 2009; USEPA 2009a; Ahrens 2011; Buck et al. 2011; UNEP 2011; Herzke, Olsson, and Posner 2012; Patagonia 2015; Kotthoff et al. 2015; ATSDR 2015
Paper Products	Surface coatings to repel grease and moisture. Uses include non-food paper packaging (for example, cardboard, carbonless forms, masking papers) and food-contact materials (for example, pizza boxes, fast food wrappers, microwave popcorn bags, baking papers, pet food bags).	Rao and Baker 1994; Kissa 2001; Hekster, Laane, and de Voogt 2003; Poulsen et al. 2005; Trudel et al. 2008; Buck et al. 2011; UNEP 2011; Kotthoff et al. 2015; Schaidler et al. 2017
Metal Plating & Etching	Corrosion prevention, mechanical wear reduction, aesthetic enhancement, surfactant, wetting agent/fume suppressant for chrome, copper, nickel and tin electroplating, and post-plating cleaner.	USEPA 1996; USEPA 1998; Kissa 2001; Prevedouros et al. 2006; USEPA 2009b; UNEP 2011; OSHA 2013; KEMI 2015; Danish EPA 2015
Wire Manufacturing	Coating and insulation.	Kissa 2001; van der Putte et al. 2010; ASTSWMO 2015
Industrial Surfactants, Resins, Molds, Plastics	Manufacture of plastics and fluoropolymers, rubber, and compression mold release coatings; plumbing fluxing agents; fluoroplastic coatings, composite resins, and flame retardant for polycarbonate.	Kissa 2001; Renner 2001; Poulsen et al. 2005; Fricke and Lahl 2005; Prevedouros et al. 2006; Skutlarek, Exner, and Farber 2006; van der Putte et al. 2010; Buck et al. 2011; Herzke, Olsson, and Posner 2012; Kotthoff et al. 2015; Miteni 2016; Chemours 2017
Photolithography, Semiconductor Industry	Photoresists, top anti-reflective coatings, bottom anti-reflective coatings, and etchants, with other uses including surfactants, wetting agents, and photo-acid generation.	SIA 2008; Choi et al. 2005; Rolland et al. 2004; Brooke, Footitt, and Nwaogu 2004; van der Putte et al. 2010; UNEP 2011; Herzke, Olsson, and Posner 2012

4.2 Class B Fluorine-Containing Firefighting Foams

Class B fluorine-containing firefighting foams (firefighting foam) for extinguishing flammable liquid fires include aqueous film forming foam (AFFF), fluoroprotein (FP), and film forming fluoroprotein foam (FFFP) (Concawe 2016). These foams have been stored and used for fire suppression, fire training, and flammable vapor suppression at hundreds of military installations and civilian airports (Hu et al. 2016), as well as at petroleum refineries and storage facilities, and chemical manufacturing plants throughout the United States. Additionally, local fire departments in communities have used and maintained quantities of firefighting foam in their inventories. Despite the phase-out of longer-chain PFAAs, these products still have long-chain PFAA constituents in firefighting foam due to the long shelf-life of these products. Facilities that manufactured firefighting foams are also potential sources.

Firefighting foams are a complex mixture of both known and unidentified PFAS of differing molecular structures present in varying proportions. Foams were produced to meet firefighting specifications, rather than formulated to contain a specified mixture of PFAS. These types of firefighting foams have been in use since the 1960s. The United States Naval Research Laboratory began research on the development of firefighting foams in the 1960s, which led to advancements in performance and increased safety (U.S. Naval Research Laboratory 2017). Fluorotelomer foams have been in use since the 1970s and became the predominant foam after 2001 when long-chain ECF-based foams were discontinued.

Firefighting foams are released into the environment through a variety of practices and mechanisms (Anderson et al. 2016; Hale 2016):

- low volume releases of foam concentrate during storage, transfer or equipment calibration
- moderate volume discharge of foam solution for apparatus testing
- occasional, high-volume, broadcast discharge of foam solution for firefighting and fire suppression/prevention
- periodic, high volume, broadcast discharge for fire training
- leaks from foam distribution piping between storage and pumping locations

Firefighting foam is applied by mixing foam concentrate and water to make foam solution. When applied to a fire, the foam solution is aerated at the nozzle, yielding finished foam. Thousands of gallons of foam solution may be applied during a given event. Figure 4-1 illustrates the use of firefighting foam, how it may be released to the environment, and potentially affected media.

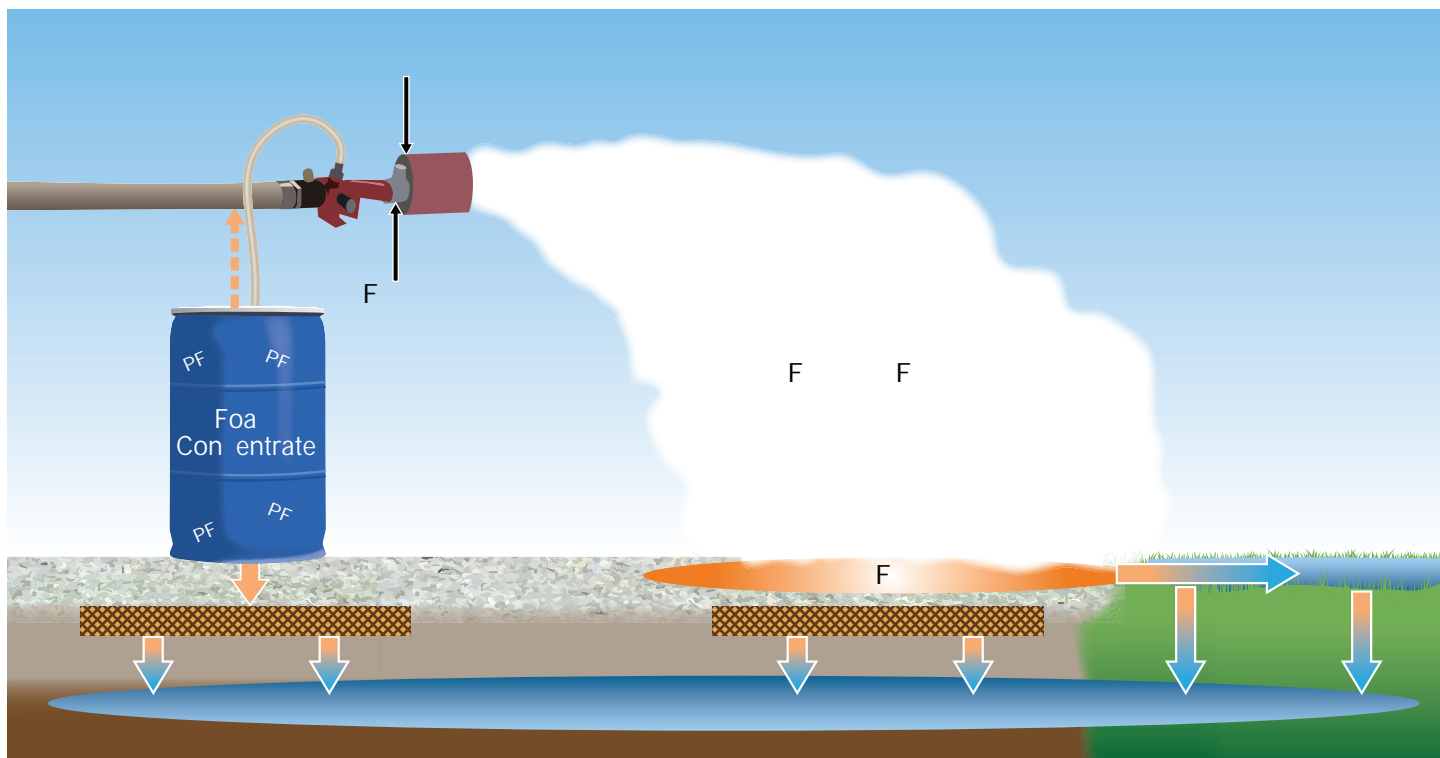


Figure 4-1. Release of firefighting foam

(Source: Adapted from figure by J. Hale, Kleinfelder, used with permission)

The U.S. Department of Defense (USDOD) has undertaken an evaluation of potential firefighting foam contamination at its facilities nationwide (Anderson et al. 2016). Similar efforts have been undertaken by some states. For example, the Minnesota Pollution Control Agency (MPCA) conducted a state-wide survey of firefighting foam use at training sites. Working with the State Fire Chief Association, the MPCA identified more than two dozen locations where Class B foams were likely used in firefighting training (Antea Group 2011).

4.3 Waste Disposal

Disposal of wastes generated during primary PFAS production and secondary manufacturing using PFAS can be sources of PFAS environmental contamination. As PFAS manufacturing processes change with time, the resulting type and composition of waste streams also change. Given that PFAS production and use began several decades before the enactment of federal and state regulations governing waste disposal (for example, Resource Conservation and Recovery Act [RCRA] in 1976 [USEPA 2017d]), environmental impacts, including impacted drinking water supplies, from disposal of legacy PFAS industrial waste have been documented (Shin et al. 2011; MPCA 2017).

Leachate from some municipal solid waste landfills has been shown to be a source of PFAS release to the environment, with the presence of some PFAS reportedly due to the disposal of consumer goods treated with hydrophobic, stain-resistant coatings (Busch et al. 2010; Eggen, Moeder, and Arukwe 2010). PFAS composition and concentration in leachates vary depending on waste age, climate, and waste composition (Allred et al. 2015; Lang et al. 2017).

The evolution of waste reduction and landfill technology has provided significant protection to human health and the environment (Hickman 1999). Leachate collection systems are essential to providing systematic transport of leachate to a central location for recirculation, treatment, or offsite treatment (Arabi and Lugowski 2015). Leachate treatment by wastewater treatment plants (WWTPs) is common prior to discharge to surface water, or distribution for agricultural or commercial use (Lang 2016). Standard WWTP technologies may do little to reduce or remove PFAS and discharge of landfill leachate treated at WWTPs represents a secondary source of certain PFAS release to the environment (Ahrens et al. 2015; CRC Care 2017).

4.4 Wastewater Treatment

Consumer and industrial use of PFAS-containing materials, including disposal of landfill leachate and firefighting foam, results in the discharge of PFAS to WWTPs. WWTPs, particularly those that receive industrial wastewater, are possible sources of PFAS release. (Lin, Panchangam, and Lo 2009; Ahrens et al. 2009).

4.4.1 WWTP Operations

Conventional sewage treatment methods do not efficiently remove PFAAs (Ahrens et al. 2011; Schultz et al. 2006). Evaluation of full-scale WWTPs has indicated that conventional primary (sedimentation and clarification) and secondary (aerobic biodegradation of organic matter) treatment processes, can result in changes in PFAS concentrations and classes (for example, an increase in the concentrations of PFAAs in effluent, presumably from degradation of precursor PFAS) (Schultz et al. 2006).

Some PFAS are frequently detected in WWTP effluent (for example, PFOA and PFBS), with concentrations of some PFAS ranging up to hundreds of ng/L; effluents are believed to be major point sources of these chemicals in surface water (Ahrens 2011). Hu et al. (2016) demonstrated that the presence of WWTPs in an area was predictive of the presence of PFOS and PFOA in drinking water. PFOS and PFOA are two of the most frequently detected PFAS in wastewater. (Hamid and Li 2016). Using WWTP effluent-impacted surface water as a source of tap water can, in turn, recycle the PFAS back to the WWTP, recirculating PFAS in the water cycle (Hamid and Li 2016).

At some WWTPs, studies have shown concentrations of PFAS in ambient air to be 1.5 to 15 times greater than reference sites (Ahrens et al. 2011). PFAS distribution (primarily PFAAs and FTOH, with higher concentrations of FTOH) changes based on the specific PFAS sources in the effluent and the type of treatment methods employed at the WWTP. Lagoon systems contain a greater fraction of PFAAs.

4.4.2 Biosolids

PFAS (measured as PFCAs and PFSAAs) have been found in domestic sewage sludge (Higgins et al. 2005). USEPA states that more than half of the sludge produced in the United States is applied to agricultural land as biosolids, therefore biosolids application can be a source of PFAS to the environment (USEPA 2017n). The most abundant PFAS found in biosolids (PFOS and PFOA) are the same as in WWTP effluent; however, biosolids may also contain other long-chain PFAS (Hamid and Li 2016). Application of biosolids as a soil amendment can result in a transfer of PFAS to soil

(Sepulvado et al. 2011). These PFAS can then be available for uptake by plants and soil organisms. There are indications that PFAAs can enter the food chain through the use of biosolids-amended soil (Lindstrom et al. 2011; Blaine et al. 2013; Blaine et al. 2014; Navarro et al. 2017). Further studies show that PFAS concentrations can be elevated in surface and groundwater in the vicinity of agricultural fields that received PFAS contaminated biosolids for an extended period of time (Washington et al. 2010).

5 Other Sources of PFAS—Use of Commercial and Consumer Products

PFAS are widely used in consumer products and household applications, with a diverse mixture of PFAS found in daily use in varying concentrations (Clara et al. 2008; Trier, Granby, and Christensen 2011; Fujii, Harada, and Koizumi 2013; OECD 2013; ATSDR 2015; Kotthoff et al. 2015; KEMI 2015; USEPA 2016b, c).

Environmental releases associated with the use of commercial and consumer products are primarily related to management of solid waste (for example, disposal of used items in a municipal solid waste [MSW] landfill), and wastewater disposal (for example, discharge to WWTPs, private septic systems, or other subsurface disposal systems).

As increased environmental sampling for PFAS occurs, it is likely that additional sources may emerge. Studies have shown that physical degradation of some consumer products (such as PFAS-treated paper, textiles, and carpets) may be a source of PFAS in house dust (Bjorklund, Thuresson, and de Wit 2009). Additionally, studies have also shown that professional ski wax technicians may have significant inhalation exposures to PFAS (Nilsson et al. 2013) and snowmelt and surface waters near ski areas may have measurable PFAS impacts (Kwok et al. 2013).

6 References and Acronyms

The references cited in this fact sheet, and the other ITRC PFAS fact sheets, are included in one combined list that is available on the ITRC web site. The combined acronyms list is also available on the ITRC web site.

Commercial and Consumer Products Containing PFAS:

- paper and packaging
- clothing and carpets
- outdoor textiles and sporting equipment
- ski and snowboard waxes
- non-stick cookware
- cleaning agents and fabric softeners
- polishes and waxes, and latex paints
- pesticides and herbicides
- hydraulic fluids
- windshield wipers
- paints, varnishes, dyes, and inks
- adhesives
- medical products
- personal care products (for example, shampoo, hair conditioners, sunscreen, cosmetics, toothpaste, dental floss)



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ECOS

1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large group of compounds used in non stick coatings, textiles, paper products, some firefighting foams, and many other products. These compounds have many manufacturing and product applications because they repel oil and water, resist temperature extremes, and reduce friction. PFAS include compounds that vary in molecular weight and can have multiple structures and functional groups. Over the years, manufacturing and use of these compounds has resulted in their presence in the environment. More information about the manufacturing history and use of PFAS, including the two major production processes, electrochemical fluorination (ECF) and telomerization, is included in the *History and Use* fact sheet.

The scientific community is rapidly recognizing the environmental and health effects of PFAS. Some of the perfluoroalkyl acids (PFAAs), such as perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), are mobile, persistent, and bioaccumulative, and are not known to degrade in the environment (USEPA 2003b; ATSDR 2015a; NTP 2016; Concawe 2016). USEPA has compiled an online resource for PFAS information that includes guidance on policy, chemistry and behavior, occurrence, toxicology, site characterization, and remediation technologies (USEPA 2017h). The National Groundwater Association (NGWA) has also published a resource on PFAS that includes information about fate and transport (NGWA 2017).

Understanding the fate and transport of a chemical in the environment is fundamental to the investigation and remediation of any contaminated site. This fact sheet focuses on how the unique chemical and physical properties of PFAS affect their behavior in the environment.

ITRC has developed a series of fact sheets that summarize the latest science and emerging technologies regarding PFAS. This fact sheet describes:

- four major sources of PFAS (fire training/fire response sites, industrial sites, landfills, and wastewater treatment plants/biosolids)
- processes that influence the fate and transport of PFAS from these sources in the environment (partitioning, transport, and abiotic and biotic transformation)
- processes that affect PFAS concentrations in air, surface water, groundwater, soil and sediment, and biota (plants, invertebrates, fish, and humans)

2 Major Sources of PFAS

There are four major sources of PFAS: fire training/fire response sites, industrial sites, landfills, and wastewater treatment plants/biosolids. Other point and diffuse sources of PFAS exist, and may be significant locally, but generally are expected to be small by comparison to these main four sources. This section provides a general discussion of the fate and transport processes associated with each source. Figures 1 through 3 illustrate conceptual site models (CSMs) for these four sources. Sections 3 and 4 provide specific details on the processes and media identified in the CSMs. See the *History and Use* fact sheet for information on PFAS uses, applications, and releases from each of these sources. Information about risk assessment, and human and ecological receptors is included in the *Site Characterization Considerations, Sampling Precautions and Laboratory Analytical Methods* fact sheet.

2.1 Fire Training/Fire Response Sites

Aqueous film-forming foams (AFFFs) are commercial surfactant solutions used for several decades by the U.S. military, civilian airports, and other facilities to extinguish hydrocarbon fires. In 1969, the U.S. Department of Defense (DOD) issued military specification Mil-F-24385, which dictates the performance of all AFFFs (with performance standards referred to as “Mil-Spec”). Once an AFFF was shown to perform to MIL-F-24385 requirements, the product was listed on the U.S. military’s AFFF Qualified Product Listing (QPL). Since July 1, 2006, the Federal Aviation Administration has required Part 139 certified airports purchase only AFFF that is Mil-Spec compliant (FAA 2006, 2016; 14 CFR 139.317).

Multiple AFFF formulations have been produced over the years, and the exact composition of any given AFFF used or manufactured in any given year is highly variable (Backe, Day, and Field 2013). The fluorosurfactants in AFFF formulations can either be produced using the electrochemical fluorination (ECF) process or the fluorotelomerization process. Both ECF-derived and telomer-derived AFFF contain highly diverse mixtures of PFAS (Barzen-Hanson et al. 2017). The ECF process results in a PFAS mixture dominated by perfluoroalkyl acids (PFAAs)—both perfluoroalkyl sulfonate (PFSA) and perfluoroalkyl carboxylate (PFCA) homologues, while the fluorotelomerization process produces AFFF formulations dominated by polyfluorinated compounds with lesser amounts of PFAAs (Houtz et al. 2013). ECF-based AFFF formulations were voluntarily phased out of production in the United States in 2002, but DOD reportedly has

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over a million gallons of ECF-based AFFF in their inventory as of 2011 (Darwin 2011). Studies to date show ECF-based AFFF is the dominant source of PFAS at AFFF-impacted sites, likely due to the longer period of ECF-based AFFF use and the relative coincidence of implementation of engineering controls for releases and wider use of telomerized AFFF (Pancras et al. 2016; Anderson et al. 2016). Fluorotelomerization-derived AFFFs are still manufactured and used in the United States but have been reformulated to limit, if not eliminate, long-chain PFAS.

2.1.1 AFFF releases

AFFF is released to the environment under various scenarios (see Figure 1). Although fire-training areas (FTAs) have received the most attention, AFFF use at military and civilian facilities is highly varied. In addition to FTAs, many other sites are also likely affected by AFFF due to past emergency response incidents, operational requirements that mandated periodic equipment calibrations on emergency vehicles, and episodic discharge of AFFF-containing fire suppression systems within large aircraft hangars and buildings (Anderson et al. 2016; Thalheimer et al. 2017). Accidental releases of AFFF from storage tanks, railcars, and piping during delivery or transfer have also occurred. Once released to the environment, AFFF can contaminate soil, surface water, and groundwater.

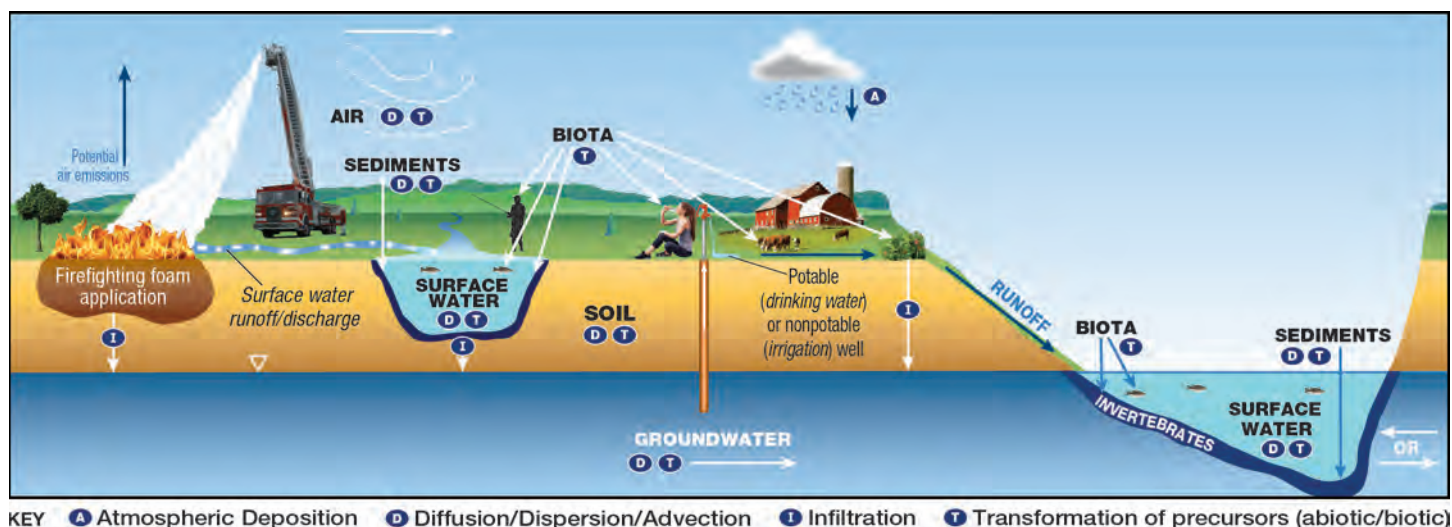


Figure 1. Conceptual site model for fire training areas.

(Source: Adapted from figure by L. Trozzolo, TRC, used with permission)

AFFF-impacted sites often are also contaminated with petroleum hydrocarbons from unburned fuel. PFAS and hydrocarbon plumes at these sites may follow the same flow paths, though the extent of contamination may be significantly different. These co-contaminants, particularly light nonaqueous phase liquids (LNAPLs), may affect the fate and transport of AFFF-derived PFAS (Guelfo and Higgins 2013; Lipson, Raine, and Webb 2013; McKenzie et al. 2016). Certain air-based or in situ oxidation remedial activities aimed at treating co-contaminants may affect PFAS composition, fate, and transport as well (McKenzie et al. 2015). Additionally, the altered soil and groundwater geochemistry and redox conditions may result in oxidation of some PFAS precursor compounds, degrading them to terminal PFAAs (Harding-Marjanovic et al. 2016; McKenzie et al. 2016; McGuire et al. 2014). In addition to AFFF, firefighting foams may also consist of fluoroprotein and film-forming fluoroprotein foam.

2.2 Industrial Sites

Industrial source sites include primary manufacturing facilities where PFAS-containing products are synthesized and made into products or chemical feedstocks, or where PFAS are used as processing aids in fluoropolymer production (where PFAS are not intended to be in the final product). Secondary manufacturing facilities may use these products or feedstocks as part of industrial processes, such as the coating application to finished products. In some industrial settings, PFAS may be used for worker safety purposes - such as using PFOS-based materials to suppress harmful mists. PFAS composition and release mechanisms will vary for each facility, but general pathways are illustrated in Figure 2.

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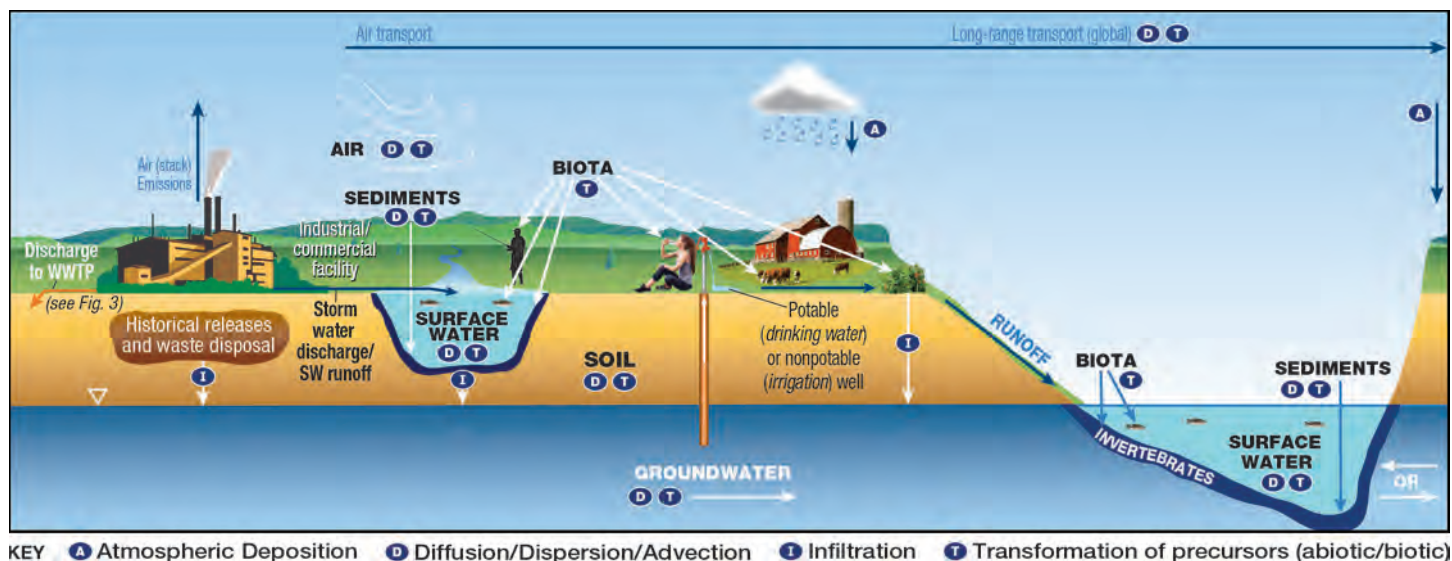


Figure 2. Conceptual site model for industrial sites.

(Source: Adapted from figure by L. Trozzolo, TRC, used with permission)

Manufacturing facilities that may be sources of PFAS releases to the environment include textile and leather processors, paper mills, metal finishers, wire manufacturers, plating facilities, manufacturers, as well as facilities using surfactants, resins, molds, plastics, photolithography, and semiconductors (see the *History and Use* fact sheet for more information).

Industrial facilities may release PFAS to the environment via wastewater discharges (see Section 2.4), on- and off-site disposal of wastes, accidental releases such as leaks and spills, and stack emissions. Stack emissions may result in aerial deposition of PFAS to soil and surface water (with subsequent infiltration to groundwater) within the airshed of the facility, as shown in Figure 2 (Davis et al. 2007; Shin et al. 2011). Stack emissions may result in short- and long-range air transport of PFAS. PFAS in aerosols and adsorbed on particles are more likely to be deposited near the source, while long-range transport typically involves PFAS vapors. Industrial facilities may also contain areas where fire training or fire response has occurred, AFFF storage areas, and AFFF fire suppression systems inside buildings.

The composition of PFAS released from industrial facilities depends on the type of PFAS produced or used by the facility. For example, textile coating operations may use water-emulsion or powdered feedstocks that contain greater proportions of PFCAs compared to PFSA (Lassen et al. 2015; Gremmel, Frömel, and Knepper 2016). In contrast to AFFF release sites, industrial sites may be less likely to co-release contaminants that affect redox or other subsurface fate and transport conditions (unless the site also includes AFFF releases from historical fire training or fire suppression activities).

2.3 Landfills

Landfills are sources of PFAS because they are the ultimate repositories not only for PFAS-contaminated industrial waste, sewage sludge, and waste from site mitigation, but also for PFAS-bearing consumer goods treated with hydrophobic, stain-resistant coatings (Busch et al. 2010; Eggen, Moeder, and Arukwe 2010). Given the production timeline of PFAS, consumer products landfilled since the 1950s are potential sources to the environment. Industrial waste can be a significant source of PFAS in landfills, particularly those that accept waste from the production or application of PFAS (Oliaei et al. 2013). In addition, many landfills accept sewage sludge from wastewater treatment facilities that may contain PFAS. Figure 3 includes illustrations of landfills and wastewater treatment plants (WWTPs) sources.

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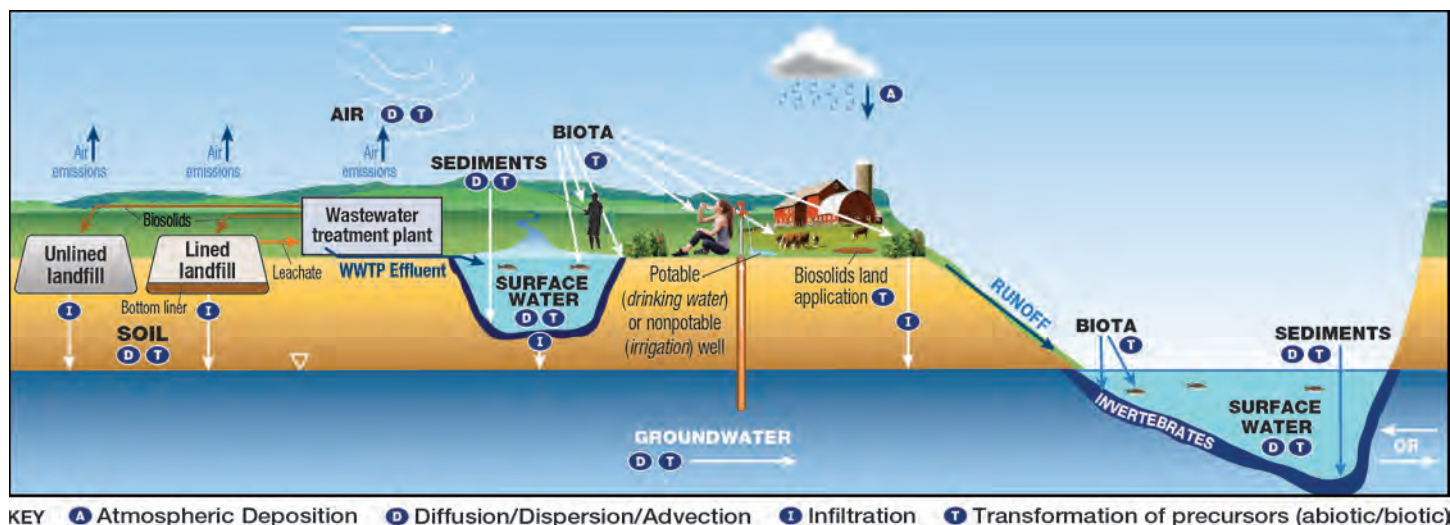


Figure 3. Conceptual site model for landfills and WWTPs.

(Source: Adapted from figure by L. Trozzolo, TRC, used with permission)

2.3.1 Landfill Construction

Landfills are either lined or unlined (Figure 3). Municipal solid waste, construction and demolition, and industrial landfills constructed since the 1990s are required by federal or state regulations to install a composite liner, a layer of compacted soil, and a leachate collection system (40 CFR 258.40). Leachate collected from landfills is typically treated on site or transported to either a nearby municipal WWTP or evaporation ponds. The processes for managing leachate have implications on the ultimate fate and transport of PFAS. If liners or leachate collection systems fail, PFAS may directly enter the environment. Landfills constructed before the 1990s are not required to have synthetic flexible membrane liners, compacted soil liners, or leachate collection systems, causing waste to be in direct contact with underlying soil or groundwater. Therefore, unlined landfills have a higher potential of contributing PFAS to groundwater (Oliaei et al. 2013). Landfill caps reduce infiltration of water to waste and may reduce the overall mass of PFAS entering the environment from a landfill, but more research on their effectiveness is needed (Hamid, Li, and Grace 2018).

2.3.2 Waste Age

Landfills containing sources of PFAS will continue to release PFAS at slow but relatively steady rates for decades following initial placement. In modeled anaerobic landfill reactors, most of the release is attributed to biological not physical mechanisms, indicating that the low solubility of the compounds is not solely responsible for slow release rates from landfills (Allred et al. 2015; Lang et al. 2016). While landfill leachate PFAS concentrations are relatively high, landfill leachate generally is considered only a minor source to the environment because the volume of leachate generated annually is low compared to the flow volume in most WWTPs (Busch et al. 2010). Legacy industrial waste landfills, however, may constitute a major source to the environment (ATSDR 2008, 2012).

2.3.3 PFAS Composition from Landfills

Relative concentrations of PFAS in leachate and groundwater from landfills are different than those at WWTPs and AFFF-contaminated sites. PFAS with fewer than eight carbons tend to dominate landfill leachate because they are less hydrophobic and therefore more likely to partition to the aqueous phase (Huset et al. 2011; Higgins and Luthy 2007). In particular, 5:3 fluorotelomer carboxylic acid (FTCA) is a common and often dominant constituent of PFAS found in landfills and is released from carpet in model anaerobic landfill reactors. This compound could prove to be an indicator of PFAS in the environment originating from landfills (Lang et al. 2017, 2016). PFAS may also be released to the air from landfills, predominantly as fluorotelomer alcohols (FTOHs) and perfluorobutanoate (PFBA) (Ahrens et al. 2011a). PFAS release rates vary with time for a given waste mass, with climate (for example, rainfall) as the apparent driving factor for the variations (Lang et al. 2017; Benskin et al. 2012).

2.4 Wastewater Treatment Plants

Municipal and industrial WWTPs can provide the following pathways for PFAS to the environment: point source discharges of effluent; leakage or unintended releases from surface impoundments; air emissions; or disposal of biosolids and other byproducts generated during the treatment process (see Figure 3). The composition of PFAS in these

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media is a function of the different sources and processes (Chen, Lo, and Lee 2012, Oliaei et al. 2006, Frömel et al. 2016, Schultz et al. 2006) including:

- type and concentration of PFAS received by the WWTP
- biological and chemical transformation of polyfluorinated substances to intermediate and terminal degradation products, such as perfluoroalkyl acids (PFAAs)
- physical or chemical partitioning, or both

At WWTPs, PFAAs may be created from the oxidation of polyfluorinated precursors during the treatment process (Oliaei, Kriens, and Kessler 2006; Frömel et al. 2016). Furthermore, PFAS could be concentrated in solid waste (for example, sewage sludge) throughout the treatment process (Schultz et al. 2006). Depending on waste management and disposal practices, this solid waste could contaminate groundwater, surface water, or both. PFAS may also be introduced to the environment through the land application of biosolids as a beneficial soil amendment, potentially allowing PFAS to enter surface water through runoff or infiltrate to groundwater (Lindstrom et al. 2011). The potential effects on groundwater or surface water depend on the amount and composition of PFAS present in biosolids, soil properties, infiltration rate, and land application practices. While further transformation of polyfluorinated substances in land-applied biosolids to PFAAs has been suggested (Sepulvado et al. 2011), other evidence suggests that some polyfluorinated substances remain in biosolids-amended soils for many years (Rich et al. 2015).

3 Fate and Transport Processes

Partitioning, transport, and transformation of PFAS occurs across multiple media types. While most research literature focuses on PFAAs (especially PFOS and PFOA), processes affecting precursor PFAS that can degrade to PFAAs over time are also important. Figures 1 through 3 illustrate these processes for the four main sources of PFAS. See Section 4 for media-specific discussions of fate and transport.

3.1 Partitioning

PFAS most commonly detected in the environment typically have a carbon-fluorine “tail” and a nonfluorinated “head” consisting of a polar functional group. The tail is hydrophobic and lipophobic, while the head groups are polar and hydrophilic. The competing tendencies of the head and the tail can lead to a wide distribution in the environment. The tail and head structure are illustrated for PFOS and PFOA in the following figure.

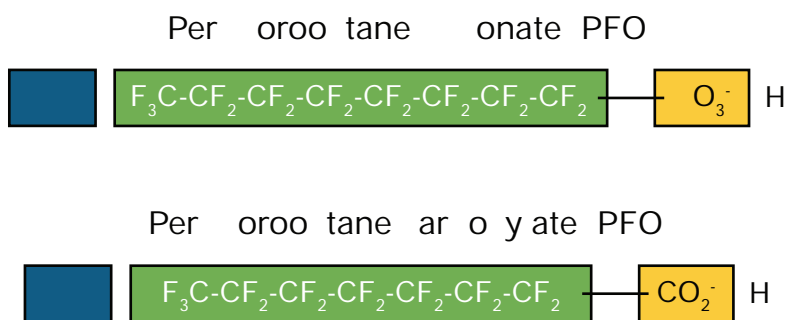


Figure 4. The tail and head structure of PFOS and PFOA molecules.

Given heterogeneous subsurface environments, multiple partitioning mechanisms should be considered when characterizing PFAS fate and transport.

Important PFAS partitioning mechanisms include hydrophobic and lipophobic effects, electrostatic interactions, and interfacial behaviors. The hydrophobic and lipophobic effects drive the association with organic carbon in soils, a process PFAS has in common with other organic contaminants (for example, chlorinated solvents). Electrostatic interactions are a function of the charge of the polar functional group at the head of the molecule. For instance, natural soils and aquifer materials often have a net negative surface charge that can repel the negatively charged heads

Partitioning Summary

- Multiple partitioning mechanisms affect PFAS: hydrophobic and lipophobic effects, electrostatic interactions, and interfacial behaviors.
- PFSAs are more strongly sorbed than their PFCA homologues.
- Longer chain PFAAs are more strongly sorbed than shorter chain PFAAs.
- PFAAs are:
 - o relatively mobile in groundwater but tend to associate with the organic carbon fraction of soil and sediment;
 - o less volatile than many other groundwater contaminants;
 - o sometimes transported on airborne particles; and
 - o generated by transformation of volatile precursors.

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of PFAAs. Because the head and the tail compete, partitioning to interfaces of environmental media such as soil/water, water/air, and water/NAPL co-contaminants can occur (Guelfo and Higgins 2013; McKenzie et al. 2016; Brusseau 2018).

The partitioning behavior of PFCAs and PFSAAs has been studied more in depth than that of other PFAS. At relevant environmental pH values, PFCAs and PFSAAs are present as organic anions and are therefore relatively mobile in groundwater (Xiao et al. 2015) but tend to associate with the organic carbon fraction that may be present in soil or sediment (Higgins and Luthy 2006; Guelfo and Higgins 2013). When sufficient organic carbon is present, organic carbon-normalized distribution coefficients (Koc values) can help in evaluating transport potential, though other geochemical factors (for example, pH and presence of polyvalent cations) may also affect PFAS sorption to solid phases. Table 3-1, provided as a separate Excel file, presents the available Koc values for commonly detected PFAAs and a several other PFAS often detected at release sites.

Sorption and retardation generally increase with increasing perfluoroalkyl tail length (Higgins and Luthy 2006; Guelfo and Higgins 2013; Sepulvado et al. 2011), indicating that the short-chain PFSAAs (for example, perfluorobutane sulfonic acid [PFBS]) and PFCAs (for example, perfluorohexanoic acid [PFHxA]) are retarded less than their long-chain counterparts (PFOS and PFOA, respectively). In addition, PFSAAs tend to sorb more strongly than PFCAs of equal chain length (Higgins and Luthy 2006), and branched isomers have less sorption than linear (Kärman et al. 2011). Sorption of PFCAs and PFSAAs is also affected by soil solution chemistry, with decreased pH and increased levels of polyvalent cations (for example, Ca^{2+}) leading to increased sorption and retardation (Higgins and Luthy 2006; McKenzie et al. 2015).

PFAAs are, in general, far less volatile than many other groundwater contaminants. Measured vapor pressures for some select PFAAs are available, including the acidic forms of PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), and perfluorododecanoic acid (PFDoA) (Barton, Botelho, and Kaiser 2008; Kaiser et al. 2005). Measured vapor pressures are also available for fluorotelomer alcohols (Krusic et al. 2005). Henry's Law constants are generally unavailable for PFAAs. Vapor pressures of these compounds are generally low and water solubilities are high, limiting partitioning from water to air (USEPA 2000b). However, under certain conditions, particularly within industrial stack emissions, PFAS can be transported through the atmosphere. Volatiles such as FTOHs may be present in the gas phase and anionic PFAS may be sorbed to particulates (Ahrens et al. 2012); see Section 4.1 for a more detailed discussion.

3.2 Transport

The resistance of most PFAS to biotic or abiotic degradation (except for precursor transformation discussed in Section 3.3) means that physical transport processes are critical for PFAS transport and potential for exposure.

3.2.1 Advection, Dispersion, Diffusion

Processes such as advection, dispersion, and diffusion can strongly influence the migration of PFAS within and between media. Advection (the flow-related transport of compounds within a fluid such as water or air) drives PFAS mobility in many cases, such as in an expanding groundwater plume. Advection, however, does not reduce concentration along the flow path. While advection is based solely on media properties and is independent of molecular, physical, or chemical properties of the contaminant, modeling the migration of PFAS due to fluid flow requires an understanding of how PFAS interact with the surrounding medium. This modeling should include the effect of sorption (see Section 3.1), which is often expressed in terms of how the contaminant velocity is reduced relative to advective velocity.

Small-scale changes in air and surface water velocities can disperse contaminants in multiple directions, contributing to rapid vertical mixing of PFAS and cross-media transport (for example, surface water to sediment and deposition from air to surface soil). In groundwater, dispersion is limited, meaning that plumes are relatively narrow as they move downgradient from a source (Payne, Quinnan, and Potter 2008). When PFAS plumes are wider than expected based on dispersion alone, the plume width may reflect the contribution of nonpoint sources (for example, air deposition) or comingled plumes (for example, some fire training areas).

In air and water, molecules moving in response to a concentration gradient is known as diffusion. In surface water and air, mixing caused by turbulence is also referred to as diffusion; for example, PFAS transport in oceans can be due to eddy diffusion (Lohmann et al. 2013). Diffusion in groundwater is often ignored because diffusion rates are slow relative to advection. However, diffusion of contaminant mass into lower permeability soils or site materials such as clays, bedrock, and concrete may enhance the long-term persistence of PFAS in groundwater. For instance, at one site PFAS penetrated 12 cm into a concrete pad at a fire training area, and diffusion was a contributing process (Baduel, Paxman, and Mueller 2015).

3.2.2 Deposition

While many PFAS exhibit relatively low volatility, airborne transport of some PFAS is a relevant migration pathway through industrial releases (for example, stack emissions). Once airborne, some PFAS are subject to photooxidation and transport, but they can eventually accumulate to measurable levels in soil and surface water through atmospheric deposition (Young and Mabury 2010; Ahrens and Bundschuh 2014; Rankin et al. 2016). Atmospheric deposition can occur as dry or wet deposition, both of which are relevant for PFAS (Barton, Kaiser, and Russell 2007; Barton, Zarzecki, and Russell 2010; Dreyer et al. 2010; Taniyasu et al. 2013). During dry deposition, PFAS that are preferentially associated with liquid or particle phases in air (aerosols) can be naturally deposited onto surfaces by sedimentation, diffusion, or other processes. When precipitation washes out these PFAS-containing aerosols, the process is known as wet deposition. Deposition is generally considered a removal process that reduces longer-range atmospheric transport. See Section 4.1 for further discussion of atmospheric deposition of PFAS.

3.2.3 Leaching

PFAS present in unsaturated soils are subject to downward leaching during precipitation or irrigation events that promote dissolution of soil-bound contaminant mass (Sepulvado et al. 2011; Ahrens and Bundschuh 2014). This process is a potential driver of PFAS transport from surface soils to groundwater and surface water, because releases often involve surface applications (for example, AFFF and biosolids) or atmospheric deposition. Leaching is also potentially relevant for plant uptake and transport of PFAS contained in landfill waste without adequate leachate control (Benskin et al. 2012; Yan et al. 2015; Lang et al. 2017). Leaching potential is a function of both media properties (for example, pH, redox conditions, and increased partitioning with organic-rich soil) and PFAS structural properties (for example, ionic charge, and chain length) (Gellrich, Stahl, and Knepper 2012). While some studies have reported PFAS transport by leaching (Lindstrom et al. 2011; Filipovic et al. 2015; Hellsing et al. 2016; Braunig et al. 2017), others have observed long-term retention of longer-chain PFAS on shallow soils after extended percolation (Sepulvado et al. 2011; Stahl et al. 2013; Anderson et al. 2016). This retention may reduce the potential for PFAS exposure by several pathways (for example, groundwater ingestion), but may increase the long-term persistence of the (soil-bound) source (Baduel, Paxman, and Mueller 2015).

3.2.4 Surfactant Properties and Micelle Formation

PFAS exhibit surfactant properties because they often contain hydrophobic and hydrophilic portions, which affect transport in ways that are complex and not well understood. By design, many PFAS preferentially form films at the air-water interface, with the hydrophobic carbon-fluorine (C-F) tail oriented towards the air and the hydrophilic head group dissolved in the water (Krafft and Riess 2015). This behavior influences aerosol-based transport and deposition and suggests that PFAS accumulates at water surfaces (Prevedouros et al. 2006).

This preference for the air-water interface may also influence vadose zone transport, where unsaturated conditions provide significant air-water interfacial area. Adsorption of PFOS and PFOA at the air-water interface can increase the retardation factor for aqueous-phase transport; this interfacial process accounted for approximately 50% of the total retention in a model system with 20% air saturation (Brusseau 2018). At higher concentrations, PFAAs can form aggregates in which the hydrophilic portions interact with the water phase and the hydrophobic portions interact with each other (for example, micelles or hemimicelles). For PFOS, the critical micelle concentrations (CMC) of 500 to 5,000 mg/L have been reported, but hemimicelles may form at concentrations as low as 0.001 times the CMC (Yu et al. 2009; Du et al. 2014; Brusseau 2018). This tendency to aggregate may cause PFAAs to act differently at high concentrations (for example, during release) and could enhance (or in some cases reduce) adsorption on carbon and minerals in the environment (Yu et al. 2009; Du et al. 2014).

Transport Summary

- Critical PFAS transport processes include: advection, dispersion, diffusion, atmospheric deposition, and leaching.
- Atmospheric transport and subsequent deposition can lead to measurable PFAS accumulation away from their point of release.
- Downward leaching of PFAS in unsaturated soils during precipitation or irrigation events is site specific and occurs as a function of media and PFAS structural properties.
- At high concentrations PFAAs can form micelles, which could enhance or reduce adsorption on carbon and minerals.

3.3 PFAS Transformation

Both biotic and abiotic transformations of some polyfluorinated substances (precursors) may form PFAAs. However, PFAAs likely do not degrade or otherwise transform under ambient environmental conditions. Unlike the fully fluorinated PFAAs, precursor PFAS contain carbon-hydrogen (C-H) and carbon-oxygen (C-O) bonds throughout the alkyl carbon chain. These C-H and C-O bonds are subject to a variety of biotic and abiotic reactions that ultimately form terminal end products. While available studies on both biotic and abiotic transformation of precursor PFAS primarily consist of controlled laboratory experiments (discussed below), an increasing number of field studies have demonstrated the importance of precursors at a variety of sites with different source scenarios (for example, Weber et al. 2017; Dassuncao et al. 2017).

Transformation Summary

- PFAS precursor chemicals can transform to PFAAs via biotic and abiotic processes.
- Transformation rates are highly variable and site specific.
- PFAAs are not known to transform under ambient environmental conditions.

3.3.1 Abiotic Transformation

Abiotic processes that can transform precursors under ambient environmental conditions include hydrolysis, photolysis, and oxidation. Hydrolysis of some precursors, followed by subsequent biotransformation, can produce PFSA. For example, PFOS is produced from perfluorooctane sulfonyl fluoride (POSF) (Martin et al. 2010). Other hydrolysis reactions produce PFCAs. The release of PFAAs by abiotic transformation may be slow. For instance, Washington and Jenkins (2015) report a half-life of over 50 years for the hydrolysis of fluorotelomer-derived precursors at neutral pH to form PFOA and other PFCAs. While direct photolysis of PFAS has not been observed, indirect photolysis of some precursors, notably FTOHs, does occur in the atmosphere, and can be a significant contributor to PFCA deposition (Armitage, MacLeod, and Cousins 2009; Yarwood et al. 2007). For example, 8:2 FTOH degrades to PFOA in the atmosphere through reactions with hydroxyl radicals and chlorine radicals, with similar reactions for 6:2 and 4:2 FTOHs (Ellis et al. 2004; Wallington et al. 2006).

Perfluoroalkanesulfonamides can also degrade abiotically through oxidation in the atmosphere to form PFCAs in yields that may be 10x greater than FTOHs (Martin et al. 2006). Also, oxidation of precursors by hydroxyl radicals can occur in natural waters, with the fluorotelomer-derived precursors being oxidized more rapidly than ECF-derived precursors (Gauthier and Mabury 2005; Plumlee, McNeill, and Reinhard 2009). Shorter-chain PFSA such as PFBS also can be produced by oxidation reactions between hydroxyl radicals and sulfonamido derivatives (D'Eon et al. 2006). Finally, in some cases, abiotic precursor transformations may not initially produce any PFAA (for example, the formation of various polyfluorinated sulfonamido intermediate compounds from ECF-derived precursors), though eventual formation of PFAAs may still be possible (Martin et al. 2010).

3.3.2 Biotic Transformation

While PFOA, PFOS, and all other PFAAs are resistant to microbial degradation, numerous studies have reported biotransformations of various precursors similar to the abiotic transformations discussed in Section 3.3.1. The current literature indicates:

- Numerous aerobic biotransformation pathways exist, with relatively rapid kinetics.
- All polyfluorinated precursors may have the potential to aerobically biotransform to PFAAs.
- Aerobic biotransformation of various fluorotelomer-derived precursors to PFCAs (including PFOA) occurs (for example, Harding-Marjanovic et al. 2015; D'Agostino and Mabury 2017).
- Aerobic biotransformation of various ECF-derived precursors to PFSA (including PFOS) occurs (Zhang et al. 2017; Mejia-Avendaño and Liu 2015; Mejia-Avendaño et al. 2016).

Fewer studies have been published regarding anaerobic biotransformation of PFAS. FTOHs have been observed to biotransform anaerobically, but appear to form stable polyfluorinated acids rather than PFCAs or PFSA (Zhang et al. 2013; Allred et al. 2015).

Note that fluorotelomer-derived precursors do not form PFSA, while degradation of ECF-derived precursors may form both PFSA and PFCAs. The extent to which ECF-derived precursors form PFCAs in situ is under study, along with other critical factors such as ambient biotransformation rates. In general, however, biotransformation rates are probably site specific and could be so slow as to be inconsequential at some sites.

4 PFAS Occurrence by Medium

PFAS occurrence in various environmental media is an active area of research. The material presented here is not the result of an exhaustive literature review but is included to provide a relative understanding of PFAS concentrations. As discussed in the *Site Characterization Considerations, Sampling Precautions and Laboratory Analytical Methods* fact sheet, analytical methods are still being optimized and standardized; thus, it is difficult to compare results between studies and conclusions may change over time. Media types presented here include air, soil and sediment, groundwater, surface water, and biota. The processes that influence media-specific PFAS concentrations are illustrated in Figures 1 through 3.

4.1 Air

Certain PFAS are found in ambient air, with elevated concentrations observed or expected in urban areas nearest to emission sources, such as manufacturing facilities, WWTPs, fire training facilities, and landfills (Barton et al. 2006; Ahrens et al. 2011a; Liu et al. 2015a). Table 4.1 includes summary information about occurrence of PFAS in outdoor air from selected studies.

Although outdoor air containing PFAS can enter buildings, the presence of indoor sources can cause indoor air concentrations of certain PFAS to be higher than outdoor air concentrations (Fromme et al. 2015; Shoeib et al. 2011). Examples of indoor sources of PFAS include many consumer products such as stain resistant coatings used on carpets and upholstery, water resistant clothing, grease-resistant paper, food packaging, nonstick cookware, cleaning products, personal care products, cosmetics, paints, varnishes, and sealants (ATSDR 2016; Liu et al. 2015; Liu et al. 2014; Gewurtz et al. 2009; Guo et al. 2009).

Once airborne, PFAS can occur in a gaseous state or be associated with particulate matter or other aerosols suspended within the air. Neutral volatile precursor compounds, such as FTOHs, are the dominant PFAS present in the gas phase and accounted for at least 80% of the total PFAS mass in ambient air in one urban area (Ahrens et al. 2012). Over the open oceans and in remote regions, FTOHs also dominate neutral PFAS and almost all are present in the gas phase (Bossi, Vorkamp, and Skov 2016; Lai et al. 2016; Wang et al. 2015; Dreyer et al. 2009). In contrast, ionic PFAS, such as PFOA and PFOS, characterized by low vapor pressure and high water solubility, tend to be the dominant species found in airborne particulate matter. PFOA is associated with smaller, ultrafine particles while PFOS is generally associated with larger, coarser fractions in both urban and semirural areas (Ge et al. 2017; Dreyer et al. 2015). Wet and dry deposition are the major mechanisms of removal of PFAS from the atmosphere and can occur from the scavenging of particle-bound PFAS or partitioning of gaseous PFAS to water droplets (Dreyer et al. 2010; Barton, Kaiser, and Russell 2007; Hurley et al. 2004). PFAS are commonly found in rain and snow, with wet and dry deposition estimated to occur on a time scale of a few days (Lin et al. 2014; Taniyasu et al. 2013; Dreyer et al. 2010; Kwok et al. 2010).

Short-range atmospheric transport and deposition may result in PFAS contamination in terrestrial and aquatic systems near points of significant emissions, contaminating soil, groundwater, and other media of concern (Davis et al. 2007), as well as several miles from industrial emission sources (Shin et al. 2011; Post, Cohn, and Cooper 2012; NYS DOH 2016; NH DES 2017; VT DEC 2016). Releases of ionic PFAS from factories are likely tied to particulate matter (Barton et al. 2006), which settle to the ground in dry weather and are also wet-scavenged by precipitation (Slinn 1984; Sehmel 1984). Models indicate that deposition depends on amount of PFAS emissions, local topography, particle size, weather patterns, and release characteristics such as smokestack height, effluent flowrate, and effluent temperature.

In addition to short-range transport and deposition, long-range transport processes are responsible for a wide distribution of PFAS across the earth, as evidenced by their occurrence in biota and environmental media in remote regions as far as the Arctic and Antarctic. Long-range transport processes and effects are similar to atmospheric transport of other recalcitrant compounds (Prevedouros et al. 2006; Benskin et al. 2012).

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Table 4.1. Observed PFAS concentrations in outdoor air

Location	Information	Concentrations (pg/m ³)
Japan, Hong Kong, and India (Ge et al. 2017)	Sampling and analysis of ambient particles at four sites. Ultrafine particles found to be largest contributor to mass fraction of PFCAs, while most PFOS mass was in the coarse-sized fractions. Seasonal differences in PFAS attributed largely to precipitation.	ΣPFAS (range) was about 5-15.
Shenzhen China (Liu et al. 2015a)	Air samples collected at 13 sites, including industrial areas with many industrial manufacturers, port districts, as well as less industrialized forested and tourist areas. Samples were analyzed for a range of PFCAs and PFSAs.	PFAS concentrations reported as mean ± SD (range): <ul style="list-style-type: none"> • PFHxS: 0.31 ± 0.39 (ND-1.2) • PFOS: 3.1 ± 1.2 (ND-4.3) • PFBA: 1.9 ± 1.8 (ND-5.0) • PFPeA: 1.9 ± 1.4 (ND-4.0) • PFHxA: 1.5 ± 1.5 (ND-3.6) • PFHpA: 0.042 ± 0.10 (ND-0.30) • PFOA: 5.4 ± 3.8 (1.5-15) • PFNA: 0.49 ± 0.33 (ND-1.0) • PFDA: 0.48 ± 0.38 (ND-1.2) • PFUdA: 0.018 ± 0.064 (ND-0.22) • PFDoA: 0.20 ± 0.19 (ND-0.54) • Overall ΣPFAS: 15 ± 8.8 (3.4-34)
Atlantic Ocean from North Atlantic to Antarctic (Wang et al. 2015a)	Measured neutral PFAS in the atmosphere across the Atlantic from the North Atlantic to the Antarctic, as well as snow from the Antarctic Peninsula.	Total ΣPFAS in air in the gas-phase mean (range): 23.5 (2.8 to 68.8).
Toronto, Canada (Ahrens et al. 2012)	Collected samples from a semi-urban location while investigating an improved technique for measuring the gas-particle partitioning of PFAS using an annular diffusion denuder sampler.	<ul style="list-style-type: none"> • ΣFTOHs (most abundant PFAS in the gas-phase): 39-153 • ΣFOSAs: 0.02-1.1 • ΣFOSEs: 0.33-0.79 • ΣFTACs: 0.87-5.9 • PFBA (dominant PFCA): 4.0-22.
Parkersburg, West Virginia USA (Barton, Kaiser, and Russell 2007)	Concurrent rain and air samples collected at nine locations at a manufacturing facility during a single precipitation event and analyzed for PFOA.	PFOA predominantly associated with particulates and detected as high as 1,100.
Albany, New York USA (Kim and Kannan 2007)	Measured PFCAs, PFSAs, and FTSAs in air, rain, snow, surface runoff water, and lake water in an urban area.	<ul style="list-style-type: none"> • ΣPFAS (gas-phase): 5.10-11.6 • ΣPFAS (particle-phase): 2.05-6.04
ND = Nondetect		

4.2 Soil and Sediment

PFAS are found in soil and sediment due to atmospheric deposition, exposure to impacted media (for example, landfill leachate or biosolids), and direct discharge. Soils and sediments may act as secondary sources of PFAS to groundwater and surface water through leaching and percolation processes, respectively. PFAS distribution in soils is complex, reflecting several site-specific factors such as total organic carbon (TOC), particle surface charges, and phase interfaces (see Section 3). Properties of individual PFAS, such as C-F chain length and ionic functional group, are also important factors. PFOS, PFOA, and other long-chain PFCAs are typically the predominant PFAS identified in surface sediments (Rankin et al. 2016; Strynar et al. 2012).

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Atmospheric transport and deposition of PFAS occur on regional and global scales (see Table 4.2 and Section 3.3 and Section 4.1). PFAA concentrations have been observed across a wide range of locations, which suggests that detection of a PFAA does not always imply a local source.

Other environmental sources of PFAS to soil include direct application (for example, AFFF and industrial discharge) or soil amended with PFAS-affected media, such as biosolids; see Table 4.2. Individual PFAS concentrations may be above 1,000 ng/g (1 mg/kg) at AFFF sites. In comparison to AFFF sites, published data on soil PFAS concentrations in industrial settings are limited (Table 4.2). PFAS soil concentrations at industrial sites and sites with applied biosolids or sludge may be highly variable, depending on the nature of PFAS release and proximity to the source.

PFAS discharge to surface waters has also affected sediments. Few studies have evaluated PFAS association with field-collected sediments (Table 4.2). Higher concentrations may be present in certain locations associated with direct PFAS discharge.

Table 4.2 Observed PFAS concentrations in soil and sediment

Location	Information	Concentrations (µg/kg)
Global Distribution (Rankin et al. 2016)	Worldwide survey of 62 soils samples, PFOA and PFHxA detected in all samples and PFOS detected in all but one sample; PFOS and PFOA the most frequently detected.	<ul style="list-style-type: none"> • ΣPFCAs: 0.029-14.3 • ΣPFASs: ND - 3.27 (only one sample was ND) Remote area (Lake Bonney, Antarctica): <ul style="list-style-type: none"> • PFOA = 0.048 • PFOS = 0.007
Global, locations not associated with known PFAS sources (Strynar et al. 2012)	Evaluated 60 soil samples from six countries and reported global median concentrations. PFOS detected in 48% and PFOA detected in 28% of the samples. Note that concentrations <LOQ (~0.5 µg/kg) were assigned a value of LOQ/√2 for the median calculations.	Global median concentrations: <ul style="list-style-type: none"> • PFOA: 0.124 • PFOS: 0.472
Location near industrial PFAS source (Davis et al. 2007)	Concentrations of ammonium perfluorooctanoate (APFO) in two soil borings located within an impacted well-field; concentrations decreased rapidly with depth.	APFO: 110-170
Fire Training/Fire Response (Houtz et al. 2013)	PFOS and PFOA in soils at an unlined fire training area	Median concentrations: <ul style="list-style-type: none"> • PFOS: 2,400 • PFOA: 21
Fire Training/Fire Response (Anderson et al. 2016)	In a survey of 40 sites impacted by PFAS, the most frequently detected compounds were PFOS (99% of surface samples), PFHxS (77%), and PFOA (79%). PFOS was detected at the highest concentrations.	PFOS: <ul style="list-style-type: none"> • Median: 53 • Max: 9,700
Industrial Areas (Zareitalabad et al. 2013)	PFOA and PFOS concentrations in soil were compiled.	Max: <ul style="list-style-type: none"> • PFOA: 48 • PFOS: 10
Municipal Biosolids (Sepulvado et al. 2011)	Six municipal biosolids and biosolid-amended surface soils	Biosolids: <ul style="list-style-type: none"> • PFOS: 80-219 • MeFOSAA: 63-143 • EtFOSAA: 42-72 • PFOA: 8-68 Biosolid-amended soil: <ul style="list-style-type: none"> • PFOS: 2-438
Sediments – Lake Ontario, Yangtze & Mississippi Rivers (Qi et al 2016; Yeung et al. 2013; Oliaei et al. 2013; Pan et al. 2014)	Maximum sediment concentrations of PFOA, PFOS, and other PFAAs	10's – 100's
ND = Nondetect LOQ = Limit of Quantitation		

4.3 Groundwater

Groundwater represents a potential PFAS exposure pathway by direct ingestion of contaminated drinking water or indirect ingestion of PFAS in crops irrigated with the contaminated water. Groundwater may also discharge to surface water, which can be another PFAS exposure pathway for human and ecological receptors. Due to the mobility and persistence of PFAA in soil and groundwater, PFAAs are expected to form larger plumes than other contaminants in the same hydrogeological setting. Sorption and partitioning, however, may restrict leaching rates from the vadose zone and reduce the advection-driven transport velocity of PFAS in groundwater, depending on specific properties of the compounds. These processes may help limit plume development and discharge to surface water and may also provide time for transformation of PFAA precursors. Groundwater geochemistry may dictate the extent of transformation since nearly all processes identified to date are aerobic (Liu and Mejia-Avendaño 2013). Groundwater extraction and treatment for containment or remediation of other contaminants can also influence plume development and distribution of PFAS in groundwater. At sites with remediation systems for other contaminants, PFAS-impacted water can be unknowingly reinjected into groundwater, as well as discharged to surface water or wastewater treatment plants and create secondary releases.

USEPA generated the most extensive PFAS groundwater occurrence dataset when it required approximately 4,900 public water systems (all large systems serving more than 10,000 people, plus a subset of smaller systems) to monitor six PFAAs in drinking water at points of entry to the drinking water distribution system. The study was conducted between 2013 and 2015 under the third Unregulated Contaminant Monitoring Rule (UCMR3) and included the results from treated water that largely originated from groundwater wells, but also included surface water and mixed sources. A summary of the UCMR3 occurrence data is included in the *Regulations, Guidance, and Advisories* fact sheet. One or more PFAS were detected in 4% of the reporting public water systems (USEPA 2017b); however, groundwater sources had approximately double the detection rate of surface water sources (Hu et al. 2016). Detections of longer-chain PFAAs were highly associated with groundwater, while shorter-chain PFAAs such as PFBS and perfluoroheptanoic acid (PFHpA) were more associated with surface water. Detections were geographically widespread but showed quantifiable associations with suspected sources including industrial sites, military fire training areas, AFFF-certified airports, and wastewater treatment facilities (Hu et al. 2016).

Groundwater occurrence data collected during several other key studies are summarized Table 4.3.

Table 4.3 Observed PFAS concentrations in groundwater

Location	Information	Concentrations (µg/L)
Various – New Jersey (NJ DEP 2014)	One or more PFAS detected in 19 of 21 untreated groundwater samples from drinking water treatment plants across the state; PFOA was detected in 7 and PFOS was detected in 5 of the 21 samples.	<ul style="list-style-type: none"> • PFOA: 0.009 – 0.057 • PFOS: 0.005 – 0.012
AFFF release sites other than fire training areas (Anderson et al. 2016)	Tested 149 groundwater samples; most commonly detected PFAAs: PFHxS (95%); PFHxA (94%), PFOA (90%), PFPeA (88%), PFBA and PFHpA (85%), PFOS (84%). The frequency of detections for PFASs in groundwater was generally higher than those of PFCAs which has been attributed to the use of specific AFFF formulations.	Median (Maximum): <ul style="list-style-type: none"> • PFHxS: 0.87 (290) • PFHxA: 0.82 (120) • PFOS: 4.22 (4,300) • PFOA: 0.405 (250) • PFPeA: 0.53 (66) • PFBA: 0.18 (64) • PFHpA: 0.235 (75)
Fire Training/Fire Response (Moody and Field 1999; Moody et al. 2003; Houtz et al. 2013)	Studies at U.S. military installations and other AFFF release areas have documented relatively high detection frequencies of PFAAs in underlying groundwater.	Maximum: <ul style="list-style-type: none"> • PFOA: 6,570 • PFOS: 2,300

4.4 Surface Water

Human exposure to PFAS from surface water can occur through direct ingestion or by consuming aquatic biota from contaminated waterbodies. Most PFAAs are acids with low pKa values, which means that in the environment they are most often present in their anionic form (deprotonated, see Section 6.2.2 of the *Naming Conventions and Physical and Chemical Properties* fact sheet). Due to the low volatility and low sorption coefficients of these anions, much of the PFAAs that reach surface water tend to remain in solution, although there is likely to be partitioning to sediment and uptake to biota. Once in surface water, PFAAs can contaminate groundwater through groundwater recharge (Liu et al. 2016; ATSDR 2008) or be transported to the oceans where they are then transported globally by ocean currents (Benskin et al. 2012). Upon reaching saline waters, however, the solubility of anionic PFAAs decreases and sorption increases, which likely results in a salting-out effect that scavenges some PFAAs, especially long-chain PFAAs, to the sediments of estuarine environments (Hong et al. 2013). Despite this, oceans are likely the main sink for PFAS, and have been estimated to contain the majority of PFCAs historically released into the environment (Armitage et al. 2006). In contrast to PFAAs, other PFAS (for example, FTOHs and some perfluoroalkyl sulfonamides) remain neutral at environmentally relevant pHs, have higher volatilities, and tend to partition into air. PFAS composition may also change within surface water because of biotic and abiotic degradation of PFAA precursors, as described in Section 3.3.

Freshwater, marine water, and stormwater PFAS concentrations usually depend on proximity to releases. In addition to releases associated with identified sources, stormwater runoff water from nonpoint sources may contribute significant loads of PFAS to surface water (Wilkinson et al. 2017; Zushi and Masunaga 2009). Table 4.4 shows some typical PFOS and PFOA environmental concentrations, organized by source type. In addition to PFOS and PFOA, many other PFAS have been observed in surface waters, including compounds other than PFAAs. For example, perfluoro-2-propoxypropanoic acid (PFPrOPrA) has been measured in the Cape Fear River in North Carolina at concentrations up to 4560 ng/L (Sun et al. 2016).

Table 4.4. Observed PFAS concentrations in surface water

Location	Information	Concentrations (ng/L)
Freshwater		
Remote Areas (Filipovic et al. 2015; Eriksson et al. 2013; Stock et al. 2007)	PFOS and PFOA concentrations in the Faroe Islands and remote areas of Sweden have been measured in the 100s of picograms per liter range, while concentrations in the Canadian Arctic have been measured in the single nanogram per liter range.	<ul style="list-style-type: none"> • 100s of pg/L • Single ng/ L
Industrial Areas, Japan, and Tennessee River, USA (Saito et al. 2004; Hansen et al. 2002)	PFOS concentrations can be as high as 144 ng/L; PFOA concentrations can be as high as 67,000 ng/L.	Maximums: <ul style="list-style-type: none"> • PFOS: 144 • PFOA: 67,000
Fire Training/Fire Response (Saito et al. 2004; Anderson et al. 2016)	AFFF-impacted surface water can have PFOS concentrations reaching 8970 ng/L and PFOA concentrations reaching 3750 ng/L.	Maximums: <ul style="list-style-type: none"> • PFOS: 8,970 • PFOA: 3,750
Municipal Wastewater Treatment Facilities (Becker, Gertsmann, and Frank 2008; Boulanger et al. 2005; Wilkinson et al. 2017; MDH 2008)	PFOS and PFOA reported in surface waters near municipal WWTP outfalls, with higher (4x) concentrations reported for surface water near outfalls of WWTP impacted by chrome plating wastewater.	Maximums (near typical WWTPs): <ul style="list-style-type: none"> • PFOS: 24 • PFOA: 25 Maximum (near WWTP affected by chrome plating waste): <ul style="list-style-type: none"> • PFOS: 100
Marine Water		
Open Water (Benskin et al. 2012; Cai et al. 2012a; Zhao et al. 2012)	PFAA concentrations in open waters tend to be on the order of picograms per liter.	pg/L
Coastal Areas (Benskin et al. 2012; Cai et al. 2012a; Zhao et al. 2012)	In heavily populated coastal areas, PFAA concentrations can be on the order of a few nanograms per liter.	ng/L

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Location	Information	Concentrations (ng/L)
Stormwater		
Residential/Undeveloped (Xiao, Simick, and Gulliver 2012; Wilkinson et al. 2016; Zhao et al. 2013b)	PFAS concentrations measured in residential, campus, and field settings in Minnesota, China, and England, respectively.	Maximums: <ul style="list-style-type: none"> • PFOS : 15.5 • PFOA : 19.1 • PFHxA : 4 • PFHpA : 22.5 • PFNA : 23
Commercial/heavy traffic – Minneapolis/St. Paul, MN; eastern and central China cities; and England (Xiao, Simick, and Gulliver 2012; Zhao et al. 2013b; Wilkinson et al. 2016)	PFOS and PFOA measured in storm water runoff from streets in areas not related to specific releases, but unidentified local or consumer sources may be responsible for higher concentrations detected.	Range: <ul style="list-style-type: none"> • PFOS : <LOQ - 590 • PFOA : 3.5 - 1,160 • PFHpA : ND – 6.8 • PFNA : ND – 648 • PFDA : ND – 10.6 • PFUnDA : ND – 2.9
Industrial Areas - Minneapolis and St. Paul, MN (Xiao, Simick, and Gulliver 2012)	PFOS measured in stormwater in an industrial area with suspected PFAS.	Range : <ul style="list-style-type: none"> • PFOS : 8.7-156
Airport Ditch, likely impacted by AFFF, Korea (Kim et al. 2014)	PFAAs measured, predominately PFHxS and PFOS.	<ul style="list-style-type: none"> • Total PFAAs: 6.42 - 804

4.5 Biota and Bioaccumulation

PFAS occur widely in biota, specifically in plants, invertebrates, fish, and humans, through bioaccumulation processes. PFAAs, particularly PFOS, are typically the dominant PFAS detected in biota (Houde et al. 2011). PFAA concentrations in biota are influenced by uptake and elimination of both PFAAs and their precursors, as well as biotransformation rates of PFAA precursors; see Section 3.3.2 (Asher et al. 2012; Gebbink, Bignert, and Berger 2016). Therefore, concentrations of PFAAs observed in biota at one location may not reflect concentrations in other environmental media.

4.5.1 Plants

Studies show evidence of uptake and accumulation PFAAs by plants in several settings and applications, including both controlled experiments and field investigations. Concerns about introducing PFAAs into livestock or crops have led to investigations of uptake and accumulation in plants. Uptake mechanisms and the extent to which native plant species remove and accumulate PFAS have not been as well studied.

PFAS may be introduced to plants from soil, water, or air by:

- irrigation water
- the application of biosolids- or sludge-amended soils
- soil and groundwater at PFAS sites or near releases of PFAS
- exposure through contact with rainwater and atmospheric deposition

Studies demonstrating plant uptake of PFAAs have focused on irrigated crops (Stahl et al. 2009; Scher et al. 2018), crops in biosolids-amended soil (Yoo et al. 2011, Blaine et al. 2013, 2014), and aquatic plants in constructed wetlands (Chen, Lo, and Lee 2012). Other investigations have focused on flora exposed to PFAAs in the natural environment (Zhang et al. 2015a) or near known PFAS sources (Shan et al. 2014). Plant uptake and bioaccumulation and partitioning within the plant appear to depend on PFAS chemical structure and the plant species. Most studies report partitioning of PFAAs within plants, with longer-chain PFAAs, especially PFSAs, partitioning to the roots and more soluble, shorter-chain PFAAs, especially PFCAs, partitioning to other parts of the plant (Lechner and Knapp 2011; Stahl et al. 2009; Blaine et al. 2013, 2014; Yoo et al. 2011; Scher et al. 2018; Gobelius, Lewis, and Ahrens 2017). The behavior of other PFAS such as PFAA precursors is currently the topic of ongoing research.

4.5.2 Invertebrates

Invertebrates act as the main component of the food web base and play a key role in the dynamics of biomagnification. Aquatic invertebrates can reside in the water column, as well as on (or in) the sediment substrate. In higher trophic level organisms, PFOS has been documented as the dominant PFAS, with concentrations increasing up the food chain, while PFOA has a lower bioaccumulation potential and concentrations are similar among species of different trophic level animals (Houde et al. 2011; Conder et al. 2008). In invertebrates, both PFOS and PFOA have maximum values within similar ranges (Ahrens and Bundschuh 2014). Studies present a PFAS range of approximately 0.1 to 10 µg/kg in invertebrate tissue, although their sources predominantly address marine organisms (Houde et al. 2011). Similar levels of PFOS have been found in freshwater invertebrates (< 2 to 4.3 µg/kg) and with a bioconcentration factor (BCF) (biota/water) estimated at 1,000 L/kg (Kannan et al. 2005). Concentrations of PFOS, PFCAs, and heptadecafluorooctane sulfonamide (PFOSA) have been observed in Lake Ontario invertebrates, ranging from < 0.5 to 280 µg/kg (Martin et al. 2004). The concentrations in invertebrates were higher than in fish from this lake.

In terrestrial systems, current research indicates bioaccumulation potential of PFOS is low, as is biomagnification (increasing concentrations in predators over their prey) from lower to higher trophic level organisms (CEPA 2017). In biosolid amended soils, PFAS bioaccumulation factors (BAFs) in earthworms have ranged from 2.2 to 198 g dw soil/g dw worm (Navarro et al. 2016). Maximum BAFs in earthworms for all PFAS types have been observed at < 45 g dw soil/g dw worm for biosolids amended soils and < 140 g dw soil/g dw worm for soils contaminated with AFFF (Rich et al. 2015).

4.5.3 Fish

Accumulation of PFAS in fish has been documented, particularly for PFOS, longer-chain PFCAs (with eight or more carbons), and perfluorodecane sulfonate (PFDS) (Houde et al. 2011; Martin et al. 2013; Conder et al. 2008). Of the PFAS, PFOS generally has the highest concentrations in fish due to the historically high use of this chemical and its bioaccumulation potential (Houde et al. 2011). PFDS, long-chain PFCAs, and other PFAS have also been measured in fish (Houde et al. 2011; Fakouri Baygi et al. 2016). Shorter-chain PFCAs and PFSA (less than eight and six carbons, respectively) are not readily bioconcentrated or accumulated (Conder et al. 2008; Martin et al. 2013; Houde et al. 2011), but as perfluoroalkyl chain length increases, PFSA are generally more bioaccumulative than PFCAs with the same number of carbons in the chain.

In fish, PFOS tends to partition to the tissue of highest protein density, including the liver, blood serum, and kidney (Falk et al. 2015; Ng and Hungerbühler 2013). This distribution pattern is contrary to other persistent chemicals, which tend to partition to adipose tissue.

Due to the difficulty of measuring octanol-water partitioning coefficients (K_{ow}) for PFAS, BAFs rely on calculations from empirical data instead of modeling (Haukås et al. 2007). For PFOS, bioconcentration from water is the predominant route of accumulation in fish (Martin et al. 2003a, b; Giesy et al. 2010), with dietary concentrations playing a reduced role in accumulation. In Michigan, concentrations of PFOS were found to be 10 to 20 times greater in predator fish than in their prey species (Kannan et al. 2005). PFOS appears to be the predominant PFAS concentrated from water, with BAFs in field-based studies ranging from approximately 550 to 26,000 L/kg (Naile et al. 2013; Lanza et al. 2017; Ahrens et al. 2015; Giesy et al. 2010) in whole fish.

Biomagnification and trophic transfer of PFAS in fish have been shown in some food webs (Franklin 2016; Fang et al. 2014). Because PFAS partition into proteins rather than lipids, however, the degree of observed biomagnification and trophic transfer in the field may be related to the quantity and composition of protein in the tissue measured, as well as the capability of the fish for metabolic biotransformation of PFAA precursors (Butt et al. 2010; Asher et al. 2012; Gebbink, Bignert, and Berger 2016).

Fish occurrence data collected during several other key studies are summarized in Table 4.5.

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Table 4.5 Observed PFAS concentrations in fish

Location	Information	Concentrations (µg/kg)
Industrial (Oliaei et al. 2013; Delinsky et al. 2010)	Near PFAS production plants, individual fish tissues such as liver, blood, and muscle have been reported to have elevated PFOS.	Maximum PFOS: • Liver: 6,350 • Blood: 29,600 • Muscle: 2,000
AFFF spill (Moody et al. 2002; Gewurtz et al. 2014; Lanza et al. 2017)	PFOS in fish liver, muscle, and whole fish samples were detected following an AFFF spill.	Maximum PFOS: • Liver: 72,900 • Muscle: 6,160 • Whole fish: 9,350
Wastewater treatment plant (Becker, Gerstmann, and Frank 2010; Li et al. 2008; Schuetze et al. 2010)	PFOS concentrations have been detected in fish collected near the outfall of wastewater treatment plants.	Maximum PFOS: Liver: 400 Serum: 84 Muscle tissue: 225

4.5.4 Humans

The accepted method for determining PFAS levels in humans is measurement in blood serum, because blood serum levels reflect cumulative exposure over several years (ATSDR 2015, 2015a; CDC 2017b). Biomonitoring studies indicate that some long-chain PFAAs are globally distributed in human sera (ATSDR 2015; Kato, Ye and Calafat 2015). The Center for Disease Control's National Health and Nutrition Examination Survey (NHANES) currently includes blood serum monitoring for twelve PFAAs. NHANES data indicate that monitored PFAAs concentrations have generally decreased since first collected from the U.S. population between 1999 and 2000. Serum PFOS and PFOA levels are generally higher in males, serum PFOS levels are generally higher than PFOA, and serum PFOS levels are higher in those 20 years and older than in those 12-19 years of age (CDC 2017a). Representative blood levels are provided in Table 4.6. Local exposures can lead to elevated PFAS concentrations in some populations, including (Olsen et al. 2017):

- proximity to industrial facilities using PFAS
- proximity to airports using AFFFs
- accidental industrial releases
- groundwater contamination-associated landfill leachates or biosolids application

Elevated PFAS serum concentrations may also result from ingestion of contaminated drinking water from surface water intakes at locations long distances (for example, hundreds of miles) downstream from an industrial source (Herrick et al. 2017). Long-term ingestion of low levels of PFAS (including those below health values) in drinking water may result in exposures substantially higher than in the general population not consuming contaminated drinking water (Post, Gleason and Cooper 2017; Bartell 2017).

The predominant route of exposure to most PFAS for the general public (as opposed to those living near a PFAS source or occupationally exposed) is typically the ingestion of PFAS in food (Gebbink, Berger, and Cousins 2015). Exposures are associated with contaminated foodstuffs, as well as the use of food-related consumer products such as grease-resistant paper or pizza boxes and nonstick cookware (ATSDR 2016). Hand-to-mouth transfer from treated textiles (for example, carpets and furniture) and indoor dust are also identified as significant sources of ingestion, particularly for children.

Proximity to atmospheric emission sources may also constitute a major source for the public through inhalation or depositional uptake routes (ATSDR 2015, 2016; USEPA 2016e, f). PFAS may be transferred from mother to fetus, and to breastfeeding infants. Both breastfed infants and infants ingesting formula prepared with PFAS-contaminated water may have higher exposure levels (Fromme et al. 2010; Mogensen et al. 2015). Occupational exposure to PFAS may be higher than the general exposures described above.

PFAS are not well adsorbed through the skin (ATSDR 2015a; USEPA 2016e, f), so dermal contact is not expected to be an important exposure route for the general public compared to other exposure pathways. However, dermal contact may pose a risk for people with high-level occupational exposures.

PFAAs are not metabolized, and long-chain PFAAs are excreted very slowly in humans, with half-lives of several years. Therefore, these compounds accumulate over time with continued exposure and remain in the body for many years after exposure ends (ATSDR 2015). Studies have reported both biotic and abiotic transformations of some polyfluorinated

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substances (precursors), which may form PFAAs (Buck et al. 2011), see also Section 3.3. Ingested precursors can be transformed in the body to PFAAs (USEPA 2016e, f). PFAS bioaccumulation potential generally increases with increasing chain-length. As with other organisms, PFAS in humans generally bind to proteins and accumulate in protein-rich tissues, including the blood, liver, and kidneys (ATSDR 2015). Because some PFAS biomagnify in food webs, the ingestion of contaminated biota, especially fish and apex predators, may be a major exposure route (ATSDR 2015; USEPA 2016e, f).

Table 4.6 Observed PFAS concentrations in humans¹

Location	Information	Concentrations (µg/L)
General U.S. population levels 1999-2000 (CDC 2017b)	1562 NHANES participants' serum collected in 1999-2000	Geometric mean in serum: <ul style="list-style-type: none"> • PFOA: 5.21 • PFNA: 0.551 • PFOS: 30.4 • PFHxS: 2.13
General U.S. population levels 1999-2000 (CDC 2017b)	2165 NHANES participants' serum collected in 2013-14	Geometric mean in serum: <ul style="list-style-type: none"> • PFOA: 1.94 • PFNA: 0.675 • PFDA: 0.185 • PFOS: 4.99 • PFHxS: 1.35
General U.S. population levels, 2000-2001 (Olsen et al. 2017)	645 blood donors' serum collected in 2000-2001	Geometric mean in serum: <ul style="list-style-type: none"> • PFOA: 4.7 • PFNA: 0.6 • PFDeA: 0.2 • PFOS: 35.1 • PFHxS: 2.3
General U.S. population levels, 2015 (Olsen et al. 2017)	616 blood donors' plasma collected in 2015	Geometric mean in plasma: <ul style="list-style-type: none"> • PFOA: 1.1 • PFNA: 0.4 • PFDA: 0.1 • PFOS: 4.3 • PFHxS: 0.9
General U.S. population levels, California (CA OEHHA 2013)	856 California teachers, serum collected in 2011-13	Geometric mean in serum: <ul style="list-style-type: none"> • PFOA: 2.5 • PFNA: 0.9 • PFDeA: 0.2 • PFUnA: 0.1 • PFOS: 6.9 • PFHxS: 1.6
Occupationally exposed U.S. population, California (Dobraca et al. 2015; CA OEHHA 2012)	101 firefighters, serum collected in 2010-11	Geometric mean in serum: <ul style="list-style-type: none"> • PFOA: 3.8 • PFNA: 1.1 • PFDeA: 0.9 • PFUnA: 0.2 • PFOS: 12.5 • PFHxS: 2.3
Residents near a PFOA production facility, U.S. (Emmett et al. 2006)	Serum collected 2004-2005	Mean in serum: <ul style="list-style-type: none"> • PFOA: 423

Note 1: Detection levels vary among studies. Data shown for select PFAS found in all or virtually all subjects. Other PFAS were analyzed and/or detected at some frequency in these studies.

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5 References and Acronyms

The references cited in this fact sheet, and the other ITRC PFAS fact sheets, are included in one combined list that is available on the ITRC web site. The combined acronyms list is also available on the ITRC web site.



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1 Introduction

PFAS contamination poses site characterization, sampling, and analytical challenges. PFAS have unique chemical and physical properties and they often occur in complex mixtures that can change over time. At environmental investigation sites, very low concentrations of several different PFAS must be sampled and analyzed. Many materials used in the course of environmental investigation can potentially contain PFAS. There is limited published research or guidance on how certain materials used by field staff affect sample results.

USEPA has compiled an online resource for PFAS that includes topics such as policy and guidance, chemistry and behavior, occurrence, toxicology, site characterization, and remediation technologies (USEPA 2017h). The National Groundwater Association (NGWA) has also published a resource on PFAS that includes information about sampling and analytical methods (NGWA 2017).

ITRC has developed a series of fact sheets that summarize the latest science and emerging technologies regarding PFAS. This fact sheet describes methods for evaluating PFAS in the environment, including:

- site characterization considerations
- sampling precautions
- laboratory analytical methods

2 Site Characterization Considerations

The purpose of site characterization is to understand the sources of contamination, site-specific contaminant fate and transport, and potential exposures and risks posed by a site. The site characterization techniques and study principles for PFAS-contaminated sites are generally the same as for any other site contaminated by hazardous substances. General site investigation principles and techniques will not be covered in this fact sheet, as these are well described in many existing guidance documents (for example, ASTM International 2011, 2013a, 2013b, 2014a, 2014b; Intergovernmental Data Quality Task Force (IDQTF) 2005; USEPA 1987, 1988a, 2000a, 2006c, 2013a, 2016i).

The unique chemical characteristics, uses, and transport mechanisms of PFAS should be accounted for when characterizing a contaminated site. PFAS sources (including ambient sources) pose many challenges, including their frequent occurrence as mixtures, the role of precursors, and the persistence and mobility of PFAS relative to other environmental contaminants.

2.1 Sources and Site Identification

The *Environmental Fate and Transport* fact sheet contains conceptual site models, including descriptions and figures, for four different common source scenarios. Phase 1 site characterization investigations (ASTM 2013c) may miss the potential for PFAS contamination at a site because these chemicals historically were not considered hazardous. Comparing timelines of site history (for example, processes, layout, chemical use, and release history) with the timeline of PFAS use and with existing drinking water data (for example, the UCMR3 data [USEPA 2017f]) can be helpful in determining source identification. A solid understanding of historical uses and the past presence of PFAS is critical to identifying PFAS that may have been released at a site. See the *History and Use* fact sheet for more information.

Another challenge is that commercial products and industrial releases may consist of complex PFAS mixtures that change over time through fate and transport mechanisms and may include unidentified PFAS. Changes in manufacturing practices as well as formula modifications also complicate the source identification. When characterizing source areas, there is often a focus on only perfluoroalkyl acids (PFAAs), particularly perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), which are the current chemicals of concern. These and other chemicals of concern were often released as part of original PFAS mixtures, but also may be transformation products of PFAA precursors. The focus on PFAAs means that significant portions of the total PFAS contamination might be missed, leading to underestimates of plume life expectancy for groundwater and mass flux as well as PFAS contaminant mass.

The variation in mixtures of PFAS, associated with different processes and products, may provide signatures that help identify source areas and distinguish between multiple sources. However, careful analysis is needed to distinguish between signatures associated with differing sources and those due to environmental partitioning or multiple releases over time.

Knowledge of PFAS fate, transport, and mode of release is essential to placing sampling locations. Some PFAS released at aqueous film-forming foam (AFFF) training or application sites or by industrial air emissions may result in large, diffuse areas of soil contamination (rather than point sources) that act as sources of groundwater contamination. Air emissions

Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

from industries using PFAS may result in releases to soil and surface water, with subsequent infiltration to groundwater (Davis et al. 2007; Shin et al. 2011).

2.2 Development of Initial Conceptual Site Model (CSM)

Conceptual site models for four different common source scenarios are included in the *Environmental Fate and Transport* fact sheet. These may be useful in developing a site-specific CSM. The CSM should include sources, site history, transport and exposure pathways, and receptor identification for a specific site. Any information pertaining to potential off-site PFAS contributors, such as landfills, wastewater treatment facilities, industrial sites, fire training areas and other sources, should be considered when determining possible secondary sources of PFAS.

2.2.1 Atmospheric, Geologic, and Hydrogeologic Framework

As with all contaminated sites, characterization relies upon an adequate understanding of the geology and hydrogeology of the site. Several PFAS, including the PFAAs of current regulatory concern, are relatively mobile in groundwater. Studies have reported both biotic and abiotic transformations of some polyfluorinated substances, referred to as precursors, which may form PFAAs. However, there is no evidence that PFAAs degrade or otherwise transform under ambient environmental conditions. Thus, PFAS plumes in groundwater may travel for several miles from the original source. At sites with highly permeable, low-organic matter soils, PFAS plumes can be extensive.

Partitioning behavior of perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFSAs) has been studied more than that of other PFAS. PFCAs and PFSAs are organic anions at all environmentally relevant pH values and tend to be mobile in groundwater (Xiao et al. 2015). However, these compounds, especially those with longer carbon chains, often associate with the organic carbon fraction of soil or sediment (Higgins and Luthy 2006; Guelfo and Higgins 2013) when present in the saturated zone. See the *Environmental Fate and Transport* fact sheet for more information.

At sites where PFAS are detected in surface water, the CSM should address the potential for PFAS transport by surface water and infiltration of the PFAS to groundwater in areas downstream of the site. Some PFAS are highly soluble and resistant to breakdown in the environment, which means they may be transported significant distances in surface water (Awad et al. 2011; Kwadijk, Kotterman, and Koelmans 2014). In Minnesota, PFAS-contaminated surface water moving through a natural and manmade drainage system was found to have infiltrated to groundwater in multiple locations (losing streams, lakes, ditches, and stormwater ponds) creating large, discrete areas of groundwater contamination several miles from the original source areas (ATSDR 2008; MDH 2017).

A thorough understanding of the geology and hydrogeology of a site (including groundwater-surface water interactions and air-surface water interactions) can make selection of sampling locations more efficient and reduce the number of required samples. Without careful preparation, multiple, and sometimes redundant, field efforts can make site characterization costly.

2.2.2 Investigation Strategies

Many PFAS sites consist of releases that occurred decades before PFAS were regulated. As a result, contaminant plumes have had years to develop, and in some cases, stabilize. Therefore, site characterization should not necessarily proceed the same way as for newer sites with more recent releases. At these sites, sampling begins near the source area and steps outward to determine extent. For PFAS releases, however, contamination may have occurred in areas upgradient of drinking water sources, thus drinking water supply sampling should be a top priority to ensure that human receptors are protected. Data from private drinking water supply wells may be useful in determining the extent of contaminant plumes, if the well construction and characteristics information are available.

After evaluating drinking water, soils should be characterized to determine the three-dimensional extent of soil and groundwater contamination. Soil and groundwater sampling locations should be informed by fate and transport characteristics of the site type and source (see *Environmental Fate and Transport* fact sheet). Tools for determining the extent of established plumes may include transect surveys using direct push technology, followed by installation of monitoring wells, or other appropriate techniques such as high-resolution site characterization (USEPA 2016i). Potential secondary sources should be identified, for example, from irrigation or biosolids application, and other anthropogenic factors affecting fate and transport of PFAS-contaminated media.

Certain PFAS are present in ambient air, and may be elevated near sources such as landfills, WWTFs, fire training facilities, and manufacturing plants. Typical air sampling methods for PFAS include either glass fiber or quartz fiber filters and a sorbent material such as polymeric resin or polyurethane foam to collect both the particle and gas phases. Most

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methodologies in the literature collect the particle phase and then the gas phase; however, some studies developed a method to collect the gas phase first followed by the particle phase in efforts to not overestimate the particle phase concentration (Barber et al. 2007; Jahnke 2007b, 2009; Ahrens et al. 2011a, 2012).

2.2.3 Risk Assessment

Site-specific risk assessment is informed by data and information iteratively collected in the site characterization. Of the many PFAS that may be found at contaminated sites, the toxicity of PFOA and PFOS has been studied the most thoroughly. A substantial database of toxicity information is also available for some other PFAS including PFBA, PFBS, PFHxA, PFNA, and GenX, while there is limited publicly available information on toxicity of other PFAS that may be present at PFAS-contaminated sites. USEPA has established a Health Advisory for protection from a lifetime exposure to PFOA and PFOS from drinking water of 70 ppt for each compound individually, or the total of both. While many states use these USEPA Health Advisories as guidance for PFOA and PFOS, several states have developed more stringent levels for these compounds; some states have also developed standards or guidance for other PFAS of local concern (see the *Regulations, Guidance, and Advisories* fact sheet). Given that PFAS typically occur in complex mixtures, and human and environmental receptors are exposed to some PFAS-forming complex mixtures, evaluating the true risks at a site can be particularly challenging. In the absence of risk-based values for some of the PFAS that are detected and because additional PFAS not detected by the analytical method may be present, the investigation team should identify data gaps and communicate the impact that these gaps have on risk analyses. Data gaps and scientific uncertainty must be documented so that as site cleanup progresses and more information becomes available, the project team can reassess potential risks from the site and better communicate to the public how site decisions are made.

2.2.3.1 Human Receptors

The presence of PFAS in the environment and consumer product has resulted in detectable levels (most frequently PFOA, PFNA, PFOS and PFHxS) in the blood serum of most of the U.S. population (CDC 2017b). The total body burden of these PFAS results from exposure to the PFAS themselves and formation from precursors through metabolism in the body (Olsen et al. 2017; D'eon and Mabury 2011). Blood serum levels of these PFAS in the general population have generally decreased over time (CDC 2017a). Risk assessment of PFAS exposure for humans near contaminated sites must include both exposures prevalent in the general population, such as from the food supply and consumer products, and exposures from the contaminated site, such as drinking water, house dust, ambient air, and locally caught fish. Exposures from even relatively low levels (for example, below 70 ng/L) of long-chain PFAS in drinking water are much higher than total exposures in the general population not impacted by a contaminated site (Bartell 2017).

The tendency of some PFAS to bioaccumulate (ATSDR 2015a) is also a critical component in evaluating potential health effects; food chain routes of exposure should be considered. For example, PFOS and longer-chain perfluorinated sulfonates, and PFNA and longer-chain perfluorinated carboxylates, are known to bioaccumulate in fish, including in species used for food (Conder et al. 2008). Also, as a result of chronic ingestion of water and exposure to other materials containing PFAS, women may carry PFAS in their blood and breast milk. These PFAS are transferred to their baby during pregnancy and through breast feeding. Serum levels of long-chain PFAS rapidly increase in breast fed infants due to the PFAS levels present in breast milk and the higher fluid consumption rates of infants (Mogensen et al. 2015; Winkens et al. 2017; Fromme et al. 2010; Verner et al. 2016a, b).

2.2.3.2 Ecological Receptors

PFAS present a potential hazard to wildlife by direct and dietary exposure on both individual and population levels (Environment Canada 2006, 2012). Numerous studies have shown PFAAs, particularly PFSAAs, are globally present in wildlife and may bioaccumulate in birds, fish, and mammals (including livestock); other animal classes are less studied (Houde et al. 2011; Lupton et al. 2014; OECD 2013). Biomagnification (in which concentrations increase with increasing trophic level) appears to be more complicated, occurring in some food webs but not others (Franklin 2016; Fang et al. 2014). Effects of PFAS exposure on wildlife vary widely by species and PFAS compound. Ecological toxicity information for many PFAS compounds is currently unavailable, while for others, data is limited and still evolving. Therefore, as site characterization activities for PFAS occur, the current state of the science should be reviewed before calculating ecological risk. More information is included in the *Environmental Fate and Transport* fact sheet.

3 Sampling

Sampling conducted to determine PFAS concentrations in water, soil, sediment, air, biota and other sources is similar to that for other chemical compounds, but with several additional specific considerations and protocols. If regulatory procedures, methods, or guidelines are inconsistent with the needs of a PFAS sampling program, then the governing

Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

agency should be contacted directly to determine an alternate approach or if an exception can be made. Other considerations for PFAS sampling include low laboratory detection limits, state and federal screening levels, and in some cases, cleanup criteria and potential for background concentrations of PFAS in the environment.

3.1 Equipment and Supplies

Many materials used in the course of environmental investigation can potentially contain PFAS. There is limited published research or guidance on how certain materials used by field staff affect sample results. Therefore, a conservative approach is recommended to exclude materials known to contain PFAS. Obtain and review all Safety Data Sheets (SDSs) before considering materials for use during PFAS sampling. Materials to avoid include:

- Teflon, polytetrafluoroethylene (PTFE)
- waterproof coatings containing PFAS
- food containers
- anything with fluoro in the name
- fluorinated ethylene propylene (FEP)
- ethylene tetrafluoroethylene (ETFE)
- low density polyethylene (LDPE), polyvinylidene fluoride (PVDF)

Many waterproof coatings contain PFAS, such as Gore-tex treated PPE or most waterproof papers, but some products are waterproofed with acceptable materials such as polyurethane, rubber, or PVC. Individual product specifications should be examined closely. In the case of Tyvek PPE, plain Tyvek does not contain PFAS while coated Tyvek does. In addition, materials incidentally transported to sites may contain PFAS. For example, fast food wrappers may contain PFAS. Due to the ubiquitous nature of PFAS, sampling crews must review all materials used to avoid contamination. Collection of quality assurance and quality control (QA/QC) samples is a useful tool to assess field contamination.

Two guidance documents identify materials and equipment that can be used in PFAS-focused investigations, as well as materials that should be avoided because they are known or suspected to be potential sources of PFAS:

- *Bottle Selection and other Sampling Considerations When Sampling for Per-and Poly-Fluoroalkyl Substances (PFAS)* (USDOD EDQW 2017b)
- *Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS), Contaminated Sites Guidelines*, (Government of Western Australia, Department of Environment Regulation 2016)

Sometimes it is impossible to eliminate materials that affect PFAS results in samples. For example, these materials might be needed at sites where hazards warrant the use of specific personal protective equipment (PPE), where PFAS are the secondary or co-contaminant and the primary contaminant requires specific materials for proper sampling, or where the opportunity to collect a sample occurs before a proper sampling program is developed. When PFAS-containing equipment and supplies cannot be eliminated, increasing the equipment rinse blank samples will more thoroughly document the PFAS concentrations. In these situations, a thorough QA/QC program becomes even more important.

Not all PFAS are hydrophilic, and some are volatile. As a result, these chemicals may sorb to sampling equipment and supplies or be lost from samples during sample collection. Preliminary data suggest that sorption may occur quickly. Additionally, volatile losses have not yet been characterized. Until they are better quantified, sampling efforts should consider whether these losses would affect project objectives and adjust accordingly.

3.2 Bottle Selection and Sample Amount

Containers should be specified in the analytical method, provided by the laboratory selected to perform the analyses, and should be certified by the laboratory to be PFAS-free. The term *PFAS-free* is a method or project-defined concentration level (for example, < 1/2 the limit of quantitation for the specific compound of interest). USEPA Method 537, Version 1.1 (September 2009) requires the use of 250 mL polypropylene containers and caps/lids for drinking water sampling (Shoemaker, Grimm, and Boutin 2009). Currently, USEPA has not issued guidance or analytical methods for any sample media other than drinking water. Depending on the analytical method used or program (for example state or DOD) requirements, polypropylene or high-density polyethylene (HDPE) bottles with unlined plastic caps are typically used (USDOD EDQW 2017b).

Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

Best practices in sample preparation must be used when selecting the size, volume, and representativeness of samples. To minimize effects from analyte sorption on sample containers, the laboratory must analyze the entire sample, including the sample container rinsate. The project screening or applicable regulatory levels, and the expected or potential concentration of the analytes, are also relevant. If the sample is known to contain high concentrations of PFAS (for example, AFFF formulations), loss is negligible and therefore the entire sample does not need to be used.

Because the concentration level of PFAS in aqueous samples determines whether the whole sample or an aliquot is used in the laboratory preparation, the sampler should collect an additional volume of each sample in a separate container. Then, the laboratory can screen the extra sample for high concentrations without affecting the final sample result. For soil or sediment, obtaining a representative subsample in the laboratory is critical, so the entire sample should be homogenized in the laboratory prior to subsampling. Coordinating with the laboratory is crucial to determine the appropriate sample container volumes for environmental media other than drinking water.

3.3 Sample Preservation, Shipping, Storage, and Hold Times

USEPA Method 537, Version 1.1 contains specific requirements for drinking water sample preservation, shipping, storage, and holding times (Shoemaker, Grimmer, and Boutin 2009). Currently, there is no USEPA guidance or requirement for other sample media. The chemical preservation required by Method 537, Trizma, is added for buffering and free chlorine removal and applicable to DW samples only. Until additional information is available, the thermal preservation, shipping, storage, and holding times contained in USEPA Method 537, Version 1.1 should be used for all other sample media except biota. For biota samples (for example, vegetation, fish), the samples should be frozen to limit microbial growth until sample preparation is performed at the laboratory. Microbial growth may result in PFAS values biased high due to biodegradation of precursor compounds; however, these effects have not been well studied.

3.4 Decontamination Procedures

Field sampling equipment, including oil/water interface meters, water level indicators, and other nondedicated equipment used at each sample location, require cleaning between use. The SDSs of detergents or soaps used in decontamination procedures should be reviewed to ensure fluoro-surfactants are not listed as ingredients. Use laboratory-certified PFAS-free water for the final rinse during decontamination of sampling equipment. Decontaminate larger equipment (for example, drill rigs and large downhole drilling and sampling equipment) with potable water using a high-pressure washer or steam. To the extent practical, rinse parts of equipment coming in direct contact with samples with PFAS-free water. Heavy equipment is best cleaned within a decontamination facility or other means of containment (for example, a bermed, lined pad and sump, or a portable, self-contained decontamination booth). Potable water sources should be analyzed in advance for PFAS. Wherever possible, rinse equipment with PFAS-free water immediately before use.

3.5 Field QC

Field quality control (QC) samples are a means of assessing quality from the point of collection. Such QC samples include, but are not limited to, field reagent blanks, equipment rinse blanks, and sample duplicates. USEPA Method 537, Version 1.1 contains specific requirements for the QC samples that must accompany drinking water samples. Collection and analysis of QC samples are important for PFAS analyses because of very low detection limits and widespread commercial use (historical and current) of PFAS containing products.

3.6 Sampling Precautions

Standard sampling procedures can be used at most PFAS sites. However, there may be some exceptions and additional considerations related to PFAS behavior, and issues associated with potential use of PFAS-containing or adsorbing sampling equipment and supplies.

3.6.1 Groundwater

The most inert material (for example, stainless steel, silicone, and HDPE), with respect to known or anticipated contaminants in wells should be used whenever possible. Dedicated sampling equipment installed in existing wells prior to investigation should be thoroughly checked to ensure that the equipment is PFAS-free. For long-term investigations, samples may be collected in duplicate with and without existing dedicated equipment. If PFAS analyses show that the equipment does not affect results, the equipment may be kept and used long term. This determination depends on project-specific requirements, however, and should only be used by a project team with full disclosure to all stakeholders.

Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

3.6.2 Surface Water

To avoid cross-contamination from sampling materials to sample media, the outside of all capped sample containers should be rinsed multiple times with the surface water being sampled before filling the containers. When site conditions require, remote sampling into sample containers can be accomplished by clamping the container onto the end of a clean extension rod. The extension rod must be made of PFAS-free material and have been decontaminated. Within the context of sample collection objectives, the sample location in the water column should consider the potential stratification of PFAS in solution and their tendency to accumulate at the air/water interface. For more information on stratification, see the *Environmental Fate and Transport* fact sheet.

3.6.3 Porewater

Peristaltic pumps with silicone and HDPE tubing are typically used for porewater sample collection, along with push point samplers, porewater observation devices (PODs), or drive point piezometers. Push point samples and drive point piezometers are made of stainless steel, while PODs consist of slotted PVC pipe and silicone tubing. These samplers should be dedicated and not reused across a site or multiple sites.

3.6.4 Soil/Sediment

Most core and grab sampling devices are constructed of stainless steel. Some core samplers include an HDPE sleeve inserted in the core barrel to retain the sample. PPE such as waders and personal flotation devices may be required. Ensure that materials that contact the media to be sampled do not have water-resistant coatings which contain PFAS.

3.6.5 Fish

The species of fish collected, as well as the portion of fish sampled (whole versus fillet), depends on the project goals (for example, ecological risk or human health). Studies have shown the majority of the PFAS in fish are stored in the organs, not the flesh (Martin et al. 2004; Yamada et al. 2014). Communicating project objectives to the laboratory is important prior to field work in order to determine the necessary quantity and quality of tissue, fish handling requirements, laboratory sample preparation (including single fish or composite fish samples, and whole or fillet preparation), and packing and shipping requirements.

3.6.6 Potential high concentration samples

The CSM or previous sampling may indicate areas of high concentrations of PFAS for which single-use, disposable equipment is recommended. If single-use is not possible, take additional precautions such as implementing a greater frequency of decontamination blanks and not reusing equipment to sample potentially low PFAS concentration samples. High concentration samples should be segregated during shipping to the laboratory.

Some projects may require the analysis of AFFF product that has been used at the site. All AFFF product samples must be considered high concentration samples. These samples should be segregated from other samples during sampling and shipping to avoid cross contamination. Samples that may contain high concentrations of PFAS should be clearly identified on the *Sample Chain of Custody* that is shipped with the samples. Field test kits are available for PFAS but have not been fully evaluated. While these kits cannot achieve low detection limits, they could be helpful in screening for potential high concentrations of PFAS in the field.

4 Quantitative Analysis

USEPA Method 537, Version 1.1 contains specific requirements for sample preparation and analysis of drinking water samples. Currently, there are no USEPA methods for the preparation and analysis of other sample media. However, other published methods may apply:

- ISO Method 25101 (ISO 2009)
- ASTM D7979 (ASTM 2017b)
- ASTM D7968 (ASTM 2017a)

To evaluate the laboratory's ability to meet the needs of a project, the laboratory's analytical procedure should be reviewed as part of the laboratory selection process. In addition, performance data such as concentrations observed in lab blanks and matrix spike recovery are necessary.

Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

4.1 Sample Preparation

The sample preparation procedure should be specified in the sample analysis procedure and should be included as part of the sample and analysis plan (SAP) or quality assurance project plan (QAPP). This procedure should demonstrate that extreme care is taken to prevent sample contamination during preparation and extraction. All supplies must be checked and confirmed as PFAS-free prior to sample preparation. Intermittent contamination can occur due to vendor supply or manufacturing changes; therefore, each lot of supplies should be verified and documented prior to use.

Because sample preparation may vary in different analytical procedures, the laboratory should document its preparation process for the samples. A critical step in the laboratory's preparation process is ensuring a representative sample or subsample is used for analysis. For all media, sample transfers should be minimized. Sample filtration to eliminate solid particulate from aqueous samples is not recommended because PFAS losses can occur due to adsorption of PFAS onto filters.

The entire aqueous sample received should be prepared and the sample container appropriately rinsed. Aqueous samples that are prepared using the whole sample must be extracted using SPE. The exception to this practice is samples containing high concentrations of PFAS, because each type of solid phase extraction cartridge has a defined capacity to retain PFAS analytes. Exceeding this capacity results in a low bias in PFAS results. In these instances, to prevent this bias, samples can be prepared using serial dilution techniques or analyzed using direct injection (for example, ASTM D7979). Most laboratories screen samples using a small volume sample to determine if it contains PFAS at concentrations too high for SPE sample preparation and analysis. For solid samples, the laboratory homogenizes the sample before subsampling and extraction.

To account for biases resulting from preparation steps, internal standards should be added to all samples (preferably extracted internal standards that are isotopically-labeled analogs of each analyte, if commercially available). The addition of internal standards to the sample should be clearly documented. Internal standards should be added to the sample at different steps in the process, depending on the sample preparation process used. Internal standards should also be added to whole field samples in the field container (SPE extraction samples) after subsampling, prior to addition of extraction solvent for soil or sediment samples, and after final dilution for serial dilution prepared samples (USDOD 2017a).

Depending on the analytical method used, cleanup procedures (for example, graphitized carbon) may be used on samples when matrix interferences (for example, bile salts and gasoline range organics) could be present. ENVI-Carb cleanup removes cholic acids, a known interference in fish tissue sample. The procedure should clearly state what type of cleanup process is used and in what instances.

The analytical procedure should describe what batch QC samples are prepared with each media type. Batch QC samples might include method blank (MB), laboratory control sample (LCS), laboratory control sample duplicate (LCSD), sample duplicate (SD), matrix spike (MS), and matrix spike duplicate (MSD). Additional QC may also be included. For samples with high concentrations of PFAS, in addition to an MS and an MSD, an LCSD and an SD may be warranted. The SD should be prepared using a different aliquot from the same sample bottle to create a second set of serial dilutions. Review of the laboratory's procedure should ensure that the laboratory is capable of using the batch QC needed for the project, including meeting the project's QC acceptance criteria.

4.2 Sample Analysis

Currently, the analytical detection method of choice for PFAS analysis is liquid chromatography-mass spectrometry-mass spectrometry (LC/MS/MS), which is especially suited for analysis of ionic compounds, such as the PFASs and PFCAs. Gas chromatography-mass spectrometry (GC/MS) can also be used for PFAS analysis, specifically the neutral and nonionic analytes, such as the fluorotelomer alcohols (FTOHs), perfluoroalkane sulfonamides, and perfluoroalkane sulfonamido ethanols. Currently, LC/MS/MS analysis of PFAS is widely available, whereas GC/MS analysis has limited commercial availability.

LC/MS/MS methods developed by laboratories may be based on USEPA Method 537, Version 1.1. The USEPA method does not contain steps to alleviate matrix interference issues potentially found in other sample media and does not contain steps to prepare solid sample media. Methods for other sample media may include extraction or sample preparation procedures for other matrices, use of isotope dilution, the addition of other PFAS analytes, and confirmation using confirmatory ions and ion ratios. Because these modifications are not standardized, analytical methods can result in greatly varied data, precision, and accuracy. Laboratories should provide performance data for the relevant media

Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

for each project. The USDOD EDQW has attempted to standardize many of these modifications through requirements contained in the USDOD Environmental Laboratory Accreditation Program (USDOD ELAP) document, the *DOD Quality Systems Manual for Environmental Laboratories* (DOD QSM), Version 5.1, Appendix B, Table B-15 (USDOD 2017a).

Certified analytical standards are available from several manufacturers. Products may have variable purity and isomer profiles, which may compromise the accuracy, precision, and reproducibility of data. Only certified standards of the highest purity available, for example, American Chemical Society grade, can be used for accurate quantitation. Standards containing linear and branched isomers are not commercially available for all applicable analytes. Currently, such standards are only available for PFOS and perfluorohexane sulfonic acid (PFHxS). Technical grades which contain branched and linear isomers are available for other PFAS, but these standards do not have the accuracy needed for quantitation purposes. These standards may, however, be qualitatively useful for verifying which peaks represent the branched isomers. Methods should specify the isomers quantified as well as the isomers included in standards used for quantitation purposes.

Isotope dilution is a quantitation technique that considers sample matrix effects on each individual PFAS quantitation in the most precise manner possible. This technique quantifies analytes of interest against the isotopically labeled analogs of the analytes, which are added to the sample prior to and after sample preparation. Addition prior to preparation helps account for loss of analyte during the preparation process, while addition after preparation to an aliquot of the sample extract accounts for the bias associated with the instrumentation. Methods using isotope dilution should include isotope recovery for each sample and analyte in data reports. Isotope analog recoveries should be reported, and minimum/maximum isotope recoveries may be required by specific analytical procedures. Low isotope recovery may indicate that quantitation was inadequate; the data are then reported as estimated values.

Mass calibration should occur at the frequency recommended by the instrument manufacturer and as needed based on QC indicators, such as calibration verifications. The instrument blanks, calibration curve, and initial and continual calibration verification requirements should be consistent with those published for other LC/MS/MS methods. The lowest calibration point should be a concentration at or below the limit of quantitation. A standard at the limit of quantitation concentration should be analyzed with each analytical batch to document the instrument's ability to accurately quantitate down to that concentration. Instrument blanks are critical in determining if the instrument is potentially affecting PFAS concentrations in samples.

Quantification by LC/MS/MS may be accomplished using a variety of techniques. For relatively simple matrices such as drinking water, Method 537 quantifies analytes by comparing the product ion of one precursor ion and retention time in samples to calibration standards. For more complex matrices, additional product ions and their ion ratios can be used to distinguish analytes from matrix interference. In an MS/MS system, an analyte can be fractured into more than one ion. By monitoring the area of each ion and comparing the ratio of those area counts, a more definitive identification can be made. This identification allows the analyst to distinguish true target analytes from false positives. This more detailed quantification is not required for drinking water matrices, but it is useful for more complex matrices.

As part of the laboratory selection process, the laboratory's analytical procedure should be evaluated to ensure these parameters are addressed in the documentation provided. In addition, the acceptance criteria for all the analytical QC elements should be evaluated to ensure that they are set at levels that meet the project's measurement quality objectives (MQOs). For DOD projects, these criteria can be found in the DOD QSM, Version 5.1, Appendix B, Table B-15 (USDOD 2017a).

4.3 Data Evaluation

Data evaluation is a critical step in any project; however, it becomes even more important when nonstandard methods are used, such as for PFAS. Without a standard method for media other than drinking water, laboratories' methods may vary greatly in their precision and accuracy. Over time, these methods become optimized based on new knowledge about sampling and analytical biases. Advances in instrumentation and analytical supplies (such as standards availability and improved analytical columns) often occur as well because of commercial demand. As a result, the precision and accuracy of the data generated by laboratories can change significantly over time, making it difficult to compare data generated over an extended time period. Thus, data evaluation should be performed using the most current knowledge on the state of science of PFAS.

Precision, accuracy, representativeness, comparability, completeness, and sensitivity (PARCCS) parameters should be assessed because they guide data evaluation (field collection and laboratory information). Data are reviewed in a

Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

systematic way by looking at the results of each QC indicator of the PARCCS parameters (for example, spike recoveries and method blanks) to obtain an understanding of the overall quality of the data. The most important goal of data evaluation is to ensure that any limitations to the PFAS data generated are understood, which establishes confidence that the data meet site-specific needs. More information is available in the IDQTF (2005) and USEPA (2000a) Quality Assurance Project Plan documents.

5 Qualitative Analysis

Several methods employing indirect measurement have been developed that more comprehensively assess the range of PFAS contamination at a site. Two techniques are available to measure organofluorine (Dauchy et al. 2017; Willach, Brauch, and Lange 2016; Ritter et al. 2017):

- Adsorbable organic fluorine (AOF) paired with combustion ion chromatography (CIC) measure the combusted organofluorine content of a sample as fluoride on an IC.
- Proton induced gamma-ray emission (PIGE) spectroscopy measures elemental fluorine isolated on a thin surface.

Both techniques isolate organofluorine material on a sorptive material such as activated carbon or an anion exchange cartridge prior to measurement; neither technique is currently commercially available. A third technique, total oxidizable precursor assay (TOP assay or TOPA) converts PFAA precursor compounds to PFAAs through an oxidative digestion. The increase in PFAAs measured after the TOP assay, relative to before, is a conservative estimate of the total concentration of PFAA precursors present in a sample, because not all PFAS present will be subject to quantitation or reaction, and will remain as undetected PFAS. The PFAAs generated have perfluoroalkyl chain lengths equal to, or shorter than, the perfluoroalkyl chain lengths present in the precursors (Houtz et al. 2013; Houtz and Sedlak 2012; Weber et al. 2017; Dauchy et al. 2017). Finally, quantitative time of flight mass spectrometry (QTOF-MS) can be used to determine both the chemical formula and structure of unknown PFAS in a sample, but analytical standards are required for unequivocal structural identification.

Library research, preliminary identification of potential PFAS sources, and information gathered from patents can assist in the identification of PFAS using QTOF-MS (Newton et al. 2017; Moschet et al. 2017; Barzen-Hanson et al. 2017). These methods are not standardized through a published USEPA method and range in commercial availability. To date, these methods have not undergone multilaboratory validation. As a result, TOP assay, the most widely commercially available of the techniques, is typically accepted as a means of determining PFAS load on remediation substances to estimate the replacement cycle, but not for site characterization.

6 References and Acronyms

The references cited in this fact sheet, and the other ITRC PFAS fact sheets, are included in one combined list that is available on the ITRC web site. The combined acronyms list is also available on the ITRC web site.



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ECOS

Remediation Technologies and Methods for Per- and Polyfluoroalkyl Substances (PFAS)

1 Introduction

Remediation technologies exploit chemical and physical properties to immobilize, remove, or destroy the targeted contaminants. Certain PFAS have recently been the subject of regulatory actions and attempted soil, sediment, and water remediation. These compounds have unique chemical properties that require new remediation technologies or innovative combinations of existing technologies. The decision to remediate PFAS should be driven by applicable regulations and an appropriate risk assessment.

USEPA has compiled an online resource for PFAS that includes topics such as policy and guidance, chemistry and behavior, occurrence, toxicology, site characterization, and remediation technologies (USEPA 2017h). The National Groundwater Association (NGWA) has also published a resource on PFAS that includes information about remediation technologies (NGWA 2017).

1.1 PFAS Remediation Technologies Overview

Currently, full-scale PFAS treatment in water is limited to sorption using carbon, mineral media (for example, clay), or a combination of these. Additional pilot and bench-scale technologies are currently being tested.

This fact sheet discusses the treatment technologies that have been successfully demonstrated through pilot testing at the field-scale. The accompanying tables summarize technologies that have only been tested in limited applications or in laboratory bench tests. Combining technologies may overcome limitations of any one given technology or expand the efficacy of each technology.

For each technology presented, this fact sheet discusses the following key elements:

- *Treatment Description* (according to each applicable media)
- *Treatment Mechanism* (for example, separation, sorption)
- *State of Development* – Is the technology at lab or bench-scale, field pilot-scale, or full-scale implementation? How many demonstration tests and what is the degree of commercialization for each technology?
- *Effectiveness* – Summary of demonstrated effectiveness on a broad range of PFAS (for example, Method 537 (Shoemaker, Grimmett and Boutin 2009) suite plus fluorotelomer sulfonates), a limited subset (for example, Third Unregulated Contaminant Monitoring Rule [UCMR3] list USEPA 2017f), or only perfluorooctane sulfonate (PFOS) and/or perfluorooctanoate (PFOA).
- *Sustainability Considerations* – Design considerations are evaluated including green remediation elements such as carbon footprint from energy usage, treatment media, and residual handling transport, as well as potential community impacts.

The current state of full-scale PFAS treatment in water is limited to sorption using carbon and/or mineral media (for instance, clay).

Two supporting tables comparing PFAS remediation technologies are available in a separate Excel file: Table 1, Solids Comparison, and Table 2, Liquids Comparison. The tables present all reported treatment technologies, including those tested only at the laboratory/bench scale. To be included in the tables, a technology must have been documented in a publicly available document. Some technologies, however, are only documented in literature supplied by the inventor/researcher/vendor of that technology, with no independent confirmation or peer-review process—be aware of possible biases. ITRC periodically updates the supporting tables and maintains the most current version on its website.

Air treatment is not included in this fact sheet because the current research is limited, and this topic is less applicable to site remediation projects.

ITRC has developed a series of fact sheets that summarize the latest science and emerging technologies related to PFAS. The purpose of this remediation fact sheet is to:

- provide an overview of remedial technologies and methods for treatment of solids (for instance, soil or sediment) and liquids (for instance, groundwater, leachate, or surface water);
- describe processes for the treatment of PFAS that are now in use or are under development; and
- describe the challenges and limitations for each treatment technology.

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1.2 Factors affecting remedy selection

Site characteristics that affect PFAS remedy selection include the nature of the source, release pathways, affected receptors, and fate and transport in the environment (see *Site Characterization Considerations*, *Sampling Precautions*, and *Laboratory Analytical Methods*; *Environmental Fate and Transport*; and *Naming Conventions and Physical and Chemical Properties* fact sheets). Other site characteristics relevant to remedy selection may be identified as remedial technologies advance. Strategies for remediation of the broader class of PFAS may require complementary technologies, several of which are still being developed, as described in Tables 1 and 2.

Other factors affecting PFAS remedy selection include:

- **Characteristics of PFAS.** The wide-ranging chemical and physical characteristics of PFAS affect the remedy effectiveness. Key factors include ionic state (anionic, cationic, and zwitterionic), types of ionic groups (sulfonate or carboxylate), lipo- and hydrophobicity, nature and reactivity of alkyl groups, chain length and branching, partitioning coefficients, volatility, solubility, and acidity.

- **Changes in PFAS properties.** Chemical and physical properties resulting from naturally occurring processes or due to remedial actions for other (comingled) contaminants, such as chlorinated solvents, and petroleum hydrocarbons, can affect PFAS distribution and mobility in groundwater (McGuire et al. 2014).

Example changes include:

- The alkyl functional group of some PFAS may be more readily subject to chemical or biological transformation than the fully fluorinated aliphatic chain. This is the basis, for example, for the total oxidizable precursor (TOP) assay to estimate concentrations of precursor compounds (Houtz and Sedlak 2012).
- Partial degradation of the carbon-carbon bonds in the aliphatic chain reported for some chemical remedies generates short-chain PFAS, which may be more mobile (Guelfo and Higgins 2013).
- Modifications in aquifer properties (for example, redox, pH, or other geochemical characteristics) during remediation of comingled contaminants results in a conversion of PFAS to the more stable and mobile perfluorocarboxylic acids (PFCAs) (McKenzie et al. 2015, 2016).

- **Community acceptance.** Communities are often faced with trade-offs in terms of cost, level of clean-up, and residual contamination as part of remediation efforts. Stakeholder engagement and effective risk communication strategies are an important aspect of the overall remedial technology selection process, especially where off-site receptors are identified.

Factors specifically challenging for PFAS remediation include:

- Multiple ionic states
- Variable isomers
- Differing alkyl groups
- Past remediation effects
- Common co-contaminants

1.3 Technical Maturity

The treatment technologies described here are organized by degree of current confidence in the technology. Three levels of confidence are defined as follows:

- **Demonstrated Technologies**—Technologies that have been demonstrated under pilot or full-scale conditions and are well documented for multiple applications in peer-reviewed literature. These technologies are discussed in greatest detail.
- **Partially Demonstrated Technologies**—Technologies that have been documented in peer-reviewed literature by multiple researchers or practitioners but have only been executed at the laboratory or bench scale. These technologies are briefly mentioned.
- **Promising Technologies**—Technologies that have been demonstrated at the laboratory or field pilot-scale, but the results have not been rigorously peer reviewed. Often, these results are only reported by one group (for example, one university, practitioner, or vendor) or lack detailed validation of the treatment or mechanisms. These technologies are omitted from the text and presented only in the technology comparison tables (Tables 1 and 2).

Experimental techniques to treat PFAS are under development, but only those technologies that have some level of publicly available documentation demonstrating effectiveness are included here.

2 Technologies for Treatment of Solids

Several technologies are currently available to remediate PFAS in solids. Most of these technologies have been demonstrated on soils only but may also apply to saturated sediments or sludge treatment.

Field-Demonstrated Treatment Technologies for PFAS in Solids

- Excavation and off-site landfilling or incineration
- Sorption/stabilization through ex situ soil mixing
- Ex situ thermal desorption and off-gas destruction

2.1 Capping

Technology Description: Capping places a cover over contaminated material such as landfill waste, contaminated soil, and sediments. Caps do not destroy or remove contaminants. The purpose of the cap is to prevent contact with the contamination and, depending on the design, to reduce or prevent further leaching of contaminants. For PFAS soil sites, the main purpose of a cap is to reduce or prevent further leaching of contaminants from soils to groundwater.

Treatment Mechanism: Caps isolate contaminants and prevent them from spreading and causing exposure by direct contact.

State of Development: Capping is a viable remediation method because it is simple technology that applies to most contaminants. Although capping has not been applied to a PFAS site, based on documented successes with other contaminants it offers promise for PFAS.

Effectiveness: Capping may prevent exposure and potentially reduce infiltration, but redevelopment options for the capped land surface may be limited. Caps are most effective when the seasonal high-water table is well separated vertically from the base of the contaminated solids. The PFAS contamination will remain at the site and therefore be a long-term liability. Contaminants could mobilize if site conditions change (for example, rising water table). Caps incur maintenance costs to maintain the integrity of the cap and require institutional controls to ensure the cap is not breached by future site uses or redevelopment.

Sustainability Considerations: The carbon footprint of capping includes earthwork equipment emissions and manufacturing and transporting capping material. Ecosystem restoration can be incorporated into the capping design (Lamb et al. 2014). Community impacts include truck hauling traffic and hindrance of redevelopment due to land use restrictions.

2.2 Excavation and Disposal

Technology Description: This remediation method includes removing contaminated soil and hauling it to a permitted landfill or incineration facility, then filling the excavated area with clean backfill.

Treatment Mechanism: This method isolates PFAS from receptors. Sometimes, PFAS-impacted soil is stabilized or solidified before disposal into a landfill. Disposal of PFAS-impacted soils or wastes into unlined landfills should be avoided. More studies are needed on interactions of PFAS with landfill linings.

Some states may require PFAS-contaminated solids to be treated at a Resource Conservation and Recovery Act (RCRA) permitted incinerator. The estimated temperature to destroy specific PFAS varies widely, from around 300° to greater than 1,000°C (Vecitis et al. 2008). Commercial incineration is often the only viable disposal option for media contaminated with PFAS.

State of Development: Solid wastes generated from environmental investigation and cleanup (for example, soil excavation, and investigation- and remediation-derived wastes) have been disposed at lined landfills, and therefore this is considered a well-demonstrated technology. PFAS have been reported in landfill leachate (Lang et al. 2017), although it is unlikely the source for these PFAS is investigation derived waste, as opposed to consumer product waste containing fluorochemicals. The combination of soil excavation and incineration is also considered to be a viable remedial option.

Remediation Technologies and Methods for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

Effectiveness: Excavation and disposal of PFAS-contaminated soil effectively removes a source area that may otherwise serve as a continuing source of groundwater contamination but does not result in destruction of the PFAS. Additionally, some nonhazardous waste landfills do not accept PFAS waste. Disposal of PFAS waste to landfills potentially adds to the PFAS contaminant load in the landfill leachate. In some states, the leachate is not analyzed or regulated for PFAS.

Sustainability Considerations: The carbon footprint for this approach includes earthwork equipment emissions, transporting contaminated soil and backfill, and manufacturing (such as resource extraction) of backfill material. Landfill incineration of the contaminated soil is energy intensive. Truck hauling traffic affects the local community. Guidance is available for performing a sustainability assessment for an excavation and disposal remedial design (Cappuyns and Kessen 2014; Goldenberg and Reddy 2014; Söderqvist et al. 2015; Song et al. 2018).

2.3 Sorption and Stabilization

Technology Description: Amendments added to the soil reduce or remove the potential for PFAS to mobilize from soil to groundwater.

Treatment Mechanism: Amendments adsorb or stabilize PFAS. These amendments include activated carbon and carbon nanotubes (CNTs), resins, minerals, biomaterials, and molecularly imprinted polymers. The amendments bind to PFAS and thus reduce their release from soil.

A few commercially available sorbents have been specifically developed to immobilize PFAS in soil.

State of Development: Sorption and stabilization techniques using carbon-based amendments are considered partially demonstrated technologies. Both granular activated carbon (GAC) and powdered activated carbon (PAC) rapidly remove PFAS from groundwater and surface water and can be applied to soil, but efficacy is reduced in the presence of organic co-contaminants (NGWA 2017). Performance also depends on PFAS chain length and functional group (Xiao et al. 2017). Laboratory tests should be conducted using site specific soils and the stabilizing amendment before field application to ensure success. Carbon amendments can be modified to enhance their sorption of PFAS. One patented amendment is carbon enhanced with aluminum hydroxide, kaolin clay, and other proprietary sorbents (USEPA 2017p).

Sorption and stabilization techniques using non-carbon-based sorbents, such as iron oxide minerals and modified organoclays (such as montmorillonite [Mt], hydrotalcite, and palygorskite) are promising, but only limited tests have been conducted. Minerals such as clays, silica, iron oxides, and zeolites have been used as sorbents for removing contaminants from groundwater and soil (Zhu et al. 2016; Rattanaoudom, Visvanathan, and Boontanon 2012; Zhou et al. 2010; Zhou, Pan, and Zhang 2013). The surface of organoclays can also be modified for enhanced PFOS and PFOA sorption (Zhou et al. 2010; Kambala and Maidu 2013; Zhu et al. 2016). Additionally, an amine-modified palygorskite clay sorbent has been patented for the treatment of PFOS and PFOA (Kambala and Maidu 2013).

Effectiveness: Carbon- and mineral-based sorption and stabilization techniques vary in their effectiveness according to site conditions and PFAS type. An example of a site condition that can affect sorption is high organic matter in soil, which can foul carbon sorbents with competing compounds. PFAS type affects sorption in that PFAS often occur as mixtures, including PFAS of different chain lengths with varying sorption characteristics. Sorption capacity was assessed in one study where CNTs were mixed with sediments at 4% weight per weight (w/w), and the sorption capacity of the sediment increased in comparison to untreated sediment (Kwadijk, Valzeboer, and Koelmans 2013).

Organoclays are used because they are environmentally benign, have a high sorption capacity, and can be easily modified to enhance their sorption capacity with mesopores. Organoclays have also been proven to work on several classes of contaminants (Zhu et al. 2016; Espana, Mallavarapu, and Naidu 2015; Zhou et al. 2008). The surface of organoclays are hydrophilic, and therefore ineffective for sorption of hydrophobic organic compounds like long-chain PFAS; however, modification with cations changes the surface to lipophilic. For example, Mt often exists as Na-Mt with a sodium cation on the surface, which is lipophilic and may be effective for long-chain PFAS.

Biomaterials such as chitosan, straw, and quarternized cotton do not perform as well as other sorbents, and the biomaterials may eventually degrade (Du et al. 2014).

Sorption and stabilization do not destroy PFAS, and information on the long-term stability of amendments for PFAS remediation is a data gap that currently limits their use. The amended soil can be mixed with concrete and other stabilizers to better trap the PFAS.

Remediation Technologies and Methods for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

Sustainability Considerations: The carbon footprint for sorption and stabilization includes emissions from earthwork equipment, manufacturing (for example, resource extraction), and transporting amendment material. Community impacts include hindrance of redevelopment due to land use restrictions. Resources are available for performing a sustainability assessment for sorption and stabilization remedial design (Goldenberg and Reddy 2014; Hou et al. 2016; Kuykendall and McMullan 2014).

2.4 Thermal

Technology Description: The mobilizing or destruction of chemicals using heat.

Treatment Mechanism: Heat is applied directly to the PFAS-contaminated soil. High temperatures can vaporize the chemicals or potentially destroy them. Vaporized chemicals can be captured and destroyed in off-gas treatment.

State of Development: Ex situ thermal treatment has been demonstrated at the field pilot-scale by a few technology vendors and is considered a partially demonstrated technology (Endpoint Consulting 2016; Enviropacific 2017). The use of this technology for PFAS-contaminated soil is still developing. Limited data sets are available, and several data gaps still exist. Additionally, no documented examples of in situ thermal treatment for PFAS-impacted soil have been identified.

Effectiveness: Results of one test indicated that the complete removal of a suite of nine PFAS was possible within 30 minutes but required temperatures over 900° C (Endpoint Consulting 2016). In another field pilot project, concentrations of 20 PFAS in soil were reduced to below reporting limits—greater than 99.9% reduction (Enviropacific 2017). At this time, it is unknown whether the pilot test resulted in volatilization or complete destruction. This test was performed at relatively lower temperatures (for example, approximately 450° C). There are still several data gaps related to thermal incineration of PFAS that should be considered when applying this technology. For example, the mass balance to assess whether PFAS are destroyed or simply mobilized is not completely understood.

Sustainability Considerations: Thermal treatment is an energy-intensive remediation method. Its carbon footprint includes the energy source and consumption during treatment system operation, as well as manufacturing and installation of heating system materials. Community impacts include managing the risks of potential vapor intrusion from volatile co-contaminants. Guidance is available for performing a sustainability assessment for thermal remedial design (Song et al. 2018; Vidonish et al. 2016).

3 Liquids Treatment

Several technologies are currently available for remediating PFAS in liquids. These technologies can be applied to drinking water supplies, groundwater, industrial wastewater, surface water, and other miscellaneous applications (such as landfill leachate). Influent concentrations of PFAS can vary by orders of magnitude for specific media or applications. These influent values, along with other general water quality parameters (for example, pH) can influence the performance and operating costs for the treatment technologies.

Field Demonstrated Treatment Technologies for Liquids

- Extraction and sorption with granular activated carbon or anion exchange resin
- Extraction and membrane filtration/reverse osmosis
- Extraction and precipitation/flocculation

3.1 Sorption

Many organic compounds can be treated by passing contaminated water through special granular media. The mechanism of this technology varies depending on the media, contaminant, and influent concentrations. There are two broad categories of PFAS sorption treatment: adsorption onto carbon media and ion exchange.

3.1.1 Granular Activated Carbon

Technology Description: Granular activated carbon (GAC) is made from organic materials, such as coal and coconut, which serve as effective adsorbent media because they are highly porous and provide a large surface area for contaminant contact. GAC treatment can be used for any aqueous-based treatment application (for example,

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municipal drinking water, groundwater, point-of-use residential, industrial wastewater, and landfill leachate). The GAC media is placed in packed-bed, flow-through vessels generally operated in series (lead-lag configuration). Either virgin or reactivated GAC can be used for most applications, but virgin GAC is the industry preference for more risk-averse drinking water applications. Commercial facilities in the United States conduct thermal reactivation of spent GAC, which can provide a more sustainable and less costly replacement option than virgin GAC and off-site disposal. To address concerns about using reactivated GAC, vendor bench-scale column studies can be performed prior to initial usage, and a quality control testing program can be implemented prior to delivery of each shipment.

Treatment Mechanism: Removal of PFAS from treated water by GAC is an adsorption process, as well as a physical mass transfer process from the aqueous phase onto solid media that does not involve any form of chemical degradation or transformation. Adsorption is a surface chemistry phenomenon by which an aqueous phase contaminant adheres to the surface of a granular media (via electrical, physical, or chemical processes), but does not penetrate it. The GAC adsorption capacity can vary considerably by media and contaminant. Adsorbent media must be removed and replaced when it becomes spent, meaning contaminants break through at concentrations above some established criteria. The spent media must be replaced and shipped off-site either for disposal (by landfilling or commercial incineration) or to be regenerated/reactivated for reuse consistent with applicable federal and state regulations.

State of Development: GAC is a demonstrated technology and is currently the most common water treatment method used for PFAS. Because of the limited treatment history and available technologies for PFAS, full-scale applications to date have mostly focused on higher priority private and public water supply and residential point-of-use treatment. Currently, only a few operating groundwater pump-and-treat applications use GAC treatment. Much of the published literature on GAC treatment of PFAS involves bench-scale and vendor column studies. Treatability data for full-scale operations involving different technologies, including GAC, have also been compiled and reported for several municipal wastewater treatment plants where PFAS have been detected in the influent.

Many sources in the literature support the use of GAC: Appleman et al. (2013); Szabo et al. (2017); and Woodard, Berry, and Newman (2017); and others cited in this section. These references also include more comprehensive bibliographies if further details are needed on specific topics or studies.

Effectiveness: GAC has been shown to reduce select PFAS to very low or nondetectable concentrations, on the order of nanograms per liter (equivalent to parts per trillion), with reported removal efficiencies in various references between 90% and >99%. The lower end of these reported GAC removal efficiencies may be the result of the faster breakthrough times for the short-chain PFAS (Xiao et al. 2017; Dickenson and Higgins 2016). Early municipal treatment plant sampling studies focused mostly on PFOA and PFOS, which are considered long-chain PFAS (defined as six carbon atoms or more) and currently drive most drinking water treatment decisions. Consequently, the shorter breakthrough times for PFAS with five carbon atoms or less were initially missed, and subsequently reported in the literature as lower GAC removal efficiencies.

Breakthrough and GAC usage should be checked for a variety of PFAS, not just PFOA or PFOS, including various chain-lengths.

Individual PFAS have different GAC usage capacities and corresponding breakthrough times. GAC removal capacity for PFOS is greater than PFOA, but both can be effectively captured. In general, PFAS containing five carbon atoms or less have higher GAC usage and much quicker breakthrough times than PFAS containing six carbon atoms or more with other factors being equal (such as influent concentration). Vendor column studies (Brewer 2017) with equivalent influent concentrations and empty contact bed times have shown that short-chain PFAS breakthrough times are approximately five times quicker than long-chain PFAS. Pilot and full-scale GAC treatment data show similar comparative breakthrough times (Brewer 2017).

In addition to usage capacity, several other factors affect GAC change-out frequency and cost for individual PFAS (for example, influent concentrations). Change-out frequency therefore cannot be predicted solely by the presence of specific short-chain PFAS. When concentrations of short-chain PFAS are much lower than concentrations of long-chain PFAS, GAC is still a cost-effective treatment for PFAS other than PFOA and PFOS. Because of the differences in GAC usage capacities between individual PFAS, treatability studies must evaluate the entire mixture of PFAS present in the influent to the extent practicable. Column studies are the best method to predict GAC performance and change-out frequency.

Column studies show that virgin GAC and thermally reactivated GAC have similar removal rates and breakthrough times (Brewer 2017). Based on vendor feedback (Mimna 2017), commercial thermal reactivation is performed at higher

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operating temperatures than steam or nitrogen regeneration systems and is capable of complete desorption and destruction of PFAS from spent GAC (Watanabe et al. 2016; Yamada et al. 2005). Also, vendor testing demonstrates that re-agglomerated bituminous coal provides better removal performance for PFAS than other types of GAC (Brewer 2017; Nowack 2017).

Sustainability Considerations: The carbon footprint for GAC includes energy source and consumption during treatment system operation, as well as manufacturing/disposal of treatment media. Spent single-use media requires incineration, which increase the carbon footprint. Regenerable media presents sustainability benefits because the media is reused; however, in drinking water applications, virgin material achieves greater confidence in treatment. Resources are available for performing a sustainability assessment for sorption remedial design (Amini et al. 2015; Choe et al. 2013, 2015; Dominguez-Ramos et al. 2014; Favara et al. 2016; Maul et al. 2014; Rahman et al. 2014; Ras and von Blottnitz 2012).

3.1.2 Biochar

Technical Description: *Biochar* is a hybrid word derived from *biomass* and *charcoal*. Biochar is a carbon-rich, porous solid synthesized from biomass, such as wood or manure, through a high-temperature low-oxygen process called “pyrolysis” (Ahmad et al. 2014). Key factors controlling the properties of biochar (for example, pore size, chemical composition, and hydrophobicity) include the temperature of pyrolysis and biomass feedstock.

Treatment Mechanism: The properties of biochar are comparable to those of GAC for sorptive purposes. Like GAC, biochar can adsorb organic contaminants.

State of Development: Biochar is considered a partially demonstrated technology. Various laboratory experiments have evaluated the efficacy of biochar compared to other media, but no full-scale treatment systems are in place for the removal of PFAS. This work demonstrates that biochar is potentially viable for treatment of PFAS, but additional research is needed to fully establish viability and costs.

Effectiveness: Xiao et al. (2017) compared one GAC and two commercially available biochars for treating an aqueous film-forming foam (AFFF)-impacted water supply. Based on batch studies, they concluded that biochars with large surface areas could be an alternative to GAC, although variability in biochar properties relative to GAC may affect reliability. While biochar removal is effective in ultrapure water, when used to treat river water (with more complicated water chemistry), biochar is ineffective compared to ion exchange and GAC and exhibited significantly slower adsorption kinetics (Rahman 2014).

Sustainability Considerations: The carbon footprint of this technology includes energy source and consumption during treatment system operation, as well as manufacturing/disposal of treatment media. The use of waste material as a starting feedstock results in a lower overall carbon footprint, though reactivation of biochar is not currently feasible and energy-intensive incineration or landfilling are required, which offsets some of the sustainability benefits.

3.1.3 Ion Exchange

Technology Description: Ion exchange (IX) uses synthetic, polymeric media to remove PFAS from water. IX media are employed similarly to GAC and can be used in combination with GAC.

Both regenerable and nonregenerable IX media are available. Nonregenerable IX is a single-use, disposable medium. Regenerable IX theoretically can be used indefinitely, however, insufficient operational data are available to understand its long-term durability. IX regeneration is a chemical process; the only demonstrated successful regeneration solution is a solvent-brine solution (Amec Foster Wheeler 2017). The regenerant solution can be distilled for reuse. The distillate residue is a concentrated PFAS waste that can be managed by off-site treatment (for example, incineration or possibly chemical oxidation).

Treatment Mechanism: IX is the process by which ions of one substance are replaced by similarly charged ions of another substance. The term denotes purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic ion exchangers. Many organic contaminants are ionic and can be removed through specialized ion exchange media. The media are often derived from organic polymers or plastic, and thus ion exchange media are referred to as “resins.” Regeneration of ion exchange resins is accomplished with a chemical flush, typically a highly acidic or basic solution, brine solution, or solvent-brine solution, rendering the resin reusable.

To date, IX has used positively charged, anion exchange media to remove negatively charged PFAS molecules, via binding of the carboxylic and sulfonic acid “heads” of perfluoroalkyl acids (PFAAs). Such IX media are manufactured to

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be more selective for PFAS than for typical competing mineral anions such as sulfate and nitrate. The fluorinated carbon chain of the PFAS molecule can also adsorb to IX media. This dual-mechanism, ion exchange plus adsorption, can result in higher removal compared to adsorption alone (Yu et al. 2009).

State of Development: IX is a fully demonstrated technology. Column tests comparing both regenerable and single-use ion exchange media have shown IX to be effective for the removal of several PFAS (Woodard, Berry, and Newman 2017; Conte et al. 2015). Full-scale IX systems are currently in operation in Australia at Australian Defense sites, and a full-scale system was installed in the United States in 2017. The U.S. Department of Defense (DOD) recently funded a SERDP project, ER18-C2-1306: “Combined In Situ/Ex Situ Treatment Train for Remediation of Per- and Polyfluoroalkyl Substance (PFAS) Contaminated Groundwater” to optimize regenerable IX and on-site destruction with plasma under a number of laboratory conditions (SERDP-ESTCP 2017).

Effectiveness: IX is a demonstrated effective technology for removal of anionic PFAS. It has higher adsorption capacity for some PFAS and significantly faster reaction kinetics compared to GAC (Conte et al. 2015). The combination of these properties means an equivalent treatment system for IX is smaller and thus uses less media. Like GAC, usage capacities and corresponding breakthrough times vary depending on PFAS functional groups and chain length. Short chain PFAS may break through faster under certain influent conditions. However, certain single-use IX media have been identified that may have higher usage capacities for short-chain PFAS. An IX treatment system can also include multiple vessels in a lead-lag configuration, consisting of both single-use and regenerable IX media. This design optimizes removal properties and operating costs for a mixture of short and long-chain length PFAS.

Sustainability Considerations: The carbon footprint for IX includes energy source and consumption during treatment system operation, as well as manufacturing/disposal of treatment media. Spent single-use IX media requires incineration or other treatment for disposal, resulting in an increased carbon footprint. Regenerable IX media offers sustainability benefits because the media can be reused, but the process for regenerating requires energy and creates a concentrated waste stream which must be managed. Disposal or treatment of the regenerant stream can be problematic and expensive. Regeneration solutions may present exchange system and treated water corrosion issues if media are not rinsed thoroughly prior to being placed back in service.

3.2 Precipitation/Flocculation/Coagulation

Technology Description: Coagulation–flocculation is a common pretreatment approach used in wastewater treatment plants for removing various particles and dissolved constituents. Coagulants, either commodity or proprietary chemicals, can be added to water (conventional technology) or generated by anode–cathode reactions of metals plates inserted into the water (electrocoagulation).

Technology Mechanism: Coagulants assist in forming solids. Flocculation is typically conducted by adding a soluble polymer and slowly mixing to allow the particles to agglomerate and grow. Upon solid formation, constituents such as PFAS can be physically incorporated into, or sorbed onto, the flocculated particulate (which is known as co-precipitation). The precipitated solids are then separated from the water by sedimentation, filtration, or a combination of both processes. The solid material containing the PFAS requires disposal.

State of Development: Current literature only documents bench-scale study results on treating PFAS via precipitation, flocculation, or coagulation and therefore this is considered a partially developed technology. Evaluations have focused on conventional commodity chemical coagulation (for example, aluminum or ferric salts) and nonconventional coagulation (for example, proprietary chemical coagulants or electrocoagulation). Pilot and full-scale applications have not been documented in the United States (Birk and Alden 2017).

Unconventional precipitation (for example, electrocoagulation or advanced chemical precipitants) has shown more potential for direct PFAS treatment, but little data is available.

Effectiveness: Electrocoagulation reactors, which range from basic to sophisticated designs, are highly efficient, compact, relatively low-cost, and completely automatable (Baudequin et al. 2011; Lin et al. 2015a). Recent studies have found that PFAAs, such as PFOA and PFOS, can be quickly sorbed on the surface of zinc hydroxide particulates generated by electrocoagulation (Lin et al. 2015a).

One commercially available proprietary chemical product has been shown in tests to reduce PFAS in groundwater containing AFFF (Birk and Alden 2017; CH2M 2017). This research also shows that conventional (ferric salt) and proprietary chemicals in combination are more effective than either alone. Current data have been developed at elevated

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concentrations, but removal for lower ($\mu\text{g/L}$) concentrations has also been shown (CH2M 2017; Birk 2015). No available data show precipitation effectiveness at very low (ng/L) concentration ranges.

Conventional PFAS precipitation induced by coagulation and flocculation has shown limited applicability for complete treatment of PFAS. Therefore, conventional chemical precipitation could be considered mainly as a pretreatment technology to sorb or precipitate PFAS prior to final filtration or destruction. Also, if used to remove conventional parameters such as solids or natural organic material (NOM), pretreatment would allow PFAS removal technologies to achieve the desired treatment goals in a more cost-effective and technically feasible manner.

Sustainability Considerations: The carbon footprint of this technology includes energy source and consumption during treatment system operation, as well as manufacturing of treatment media. Additionally, extracted solids containing PFAS require final disposal or destruction.

3.3 Redox Manipulation

Technology Description: Redox manipulation is the process of changing the oxidation-reduction potential of water through addition of oxidizing or reducing amendments, or by adding energy to a system to create oxidizing or reducing free radicals. These changes affect the mobility or structure (transformation or destruction) of the PFAS. PFCAs are generally more amenable to redox manipulation than perfluoroalkane sulfonic acids (PFSA). Redox manipulation may be effective at treating many co-contaminants and may also alter organic matter, which can affect PFAS mobility. These system changes may allow subsequent treatment steps to manage target PFAS more effectively.

Treatment Mechanisms: Redox manipulation mechanisms may include both redox transformation (oxidative, reductive, and nucleophilic processes) of PFAS and changes in redox conditions in the impacted media (for example, groundwater), resulting in changes in the mobility and sorption of PFAS (McKenzie et al. 2015; Arvaniti et al. 2015). Redox transformation involves the transfer of electrons between reactants. In oxidative processes, electrons are transferred to the reactive species (the oxidant) from the target (PFAS), whereas in reductive processes the opposite occurs. In nucleophilic processes, a reactant (the nucleophile) bonds with the PFAS compound and displaces an atom or group of atoms from the PFAS molecule.

Susceptibility to redox transformation depends on reaction conditions and the reactive species involved. For some specific technologies, more than one transformation mechanism or reactive species may be involved. For example, plasma, sonolytic, and photolytic technologies may combine physical (high-temperature pyrolysis) and free radical attack processes. PFAS carbon chains do not easily transform, because their carbon-carbon bonds are shielded in part by the tightly bound fluorine atoms that surround the carbon chain (Kissa 2001). The carboxylic or sulfonic group “heads” of PFAS are commonly more susceptible to redox transformation than carbon chain “tails,” resulting in partial transformation of the parent compound but not in cleavage of the aliphatic chain (Houtz and Sedlak 2012; Anumol et al. 2016). The tail and head structure are illustrated for PFOS and PFOA in the following figure.

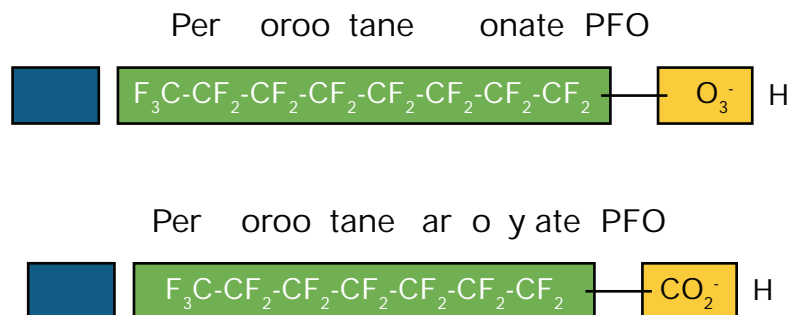


Figure 1. The tail and head structure of PFOS and PFOA molecules.

Reactions of zero valent metals with PFAS, generally considered a reductive process, may also affect mobility and sorption of PFAS in addition to (or rather than) PFAS transformation (Arvaniti et al. 2015). Complete mineralization/defluorination of PFAS via zero valent metal reactions has not been demonstrated to date; however, research in this area is ongoing.

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Combined redox and nucleophilic attack almost completely mineralize PFOA (Niu et al. 2012; Mitchell et al. 2014). A reactant formed in several redox manipulation approaches, the solvated electron (free electron in solution), shows promise for PFAS destruction (Park et al. 2009; Gu et al. 2016; Li et al. 2012; Stratton et al. 2017; Blotvogel, Giraud, and Borch 2018).

State of Development: Redox technologies have not been widely applied beyond laboratory bench-scale tests because of concerns that partial transformation (as opposed to complete destruction) will produce more mobile or toxic products. Therefore, redox technologies are considered a partially developed technology, with both successes and challenges. For example, chemical oxidation affects PFAA transport, but the direction (increased or decreased transport) and magnitude depend on reaction conditions (McKenzie et al. 2015). Apparent in situ destruction of PFAAs in groundwater at a fire training site has also been achieved using a combined ozone/persulfate approach (Eberle, Ball, and Boving 2017). The main difficulty in using redox-based technologies is achieving extremely low (ng/L) PFAS cleanup objectives, particularly for in situ remedies. Additionally, reactive species (for example, oxidizing radicals) interact with other compounds present in soil and groundwater that are more susceptible to oxidation and are at relatively higher concentrations than the target PFAS.

Despite these challenges, several options show promise for ex situ treatment, including electrochemical (Schaefer et al. 2015; Urtiaga et al. 2015), sonolytic (Vecitis et al. 2008; Rodriguez-Freire et al. 2015), plasma (Stratton et al. 2017), and reductive (Arvaniti et al. 2015) technologies. These approaches have successfully degraded an array of high-concentration PFAS at the laboratory scale. However, none of these technologies are sufficiently mature yet to assess PFAS treatment costs and overall effectiveness with confidence.

Effectiveness: A wide range of PFAS treatment methods based upon oxidation-reduction chemistries have been evaluated. These studies demonstrate the following:

- PFAS exhibit a wide range of reactivity toward destructive processes, based upon characteristics including chain length, nature of alkyl groups, and branched versus linear isomers.
- Treatment of PFAS at AFFF sites depends on the composition and production processes of the given AFFF formulation used at the site.
- Except for limited field pilot testing of one ozone and one persulfate-based chemical oxidation technology, none of the technologies summarized in Table 2 have matured beyond laboratory-scale studies.
- While promising, the relatively few field pilot applications have not yet been closely analyzed or duplicated in highly controlled and monitored studies.

Partial transformation can affect other physical and chemical characteristics of PFAS (see Section 1.2). For instance, persulfate-based transformation of PFAS may be incomplete (Houtz and Sedlak 2012) or negligible (McKenzie et al. 2015, 2016), whereas in other cases efficient transformation is reported (Hori et al. 2008; Lee et al. 2009; Liu et al. 2012; Park et al. 2016; Yin et al. 2016). Redox processes in the subsurface can generate unwanted byproducts (for instance, nitrate and bromate from chemical oxidation) depending on site and reaction conditions (Siegrist, Crimi, and Simpkin 2011). Site-specific treatability tests are recommended.

Sustainability Considerations: The carbon footprint for this technology includes energy source and consumption during treatment system operation, manufacturing of amendment materials, and manufacturing and installation of injection points (if implemented in situ). Electrochemical treatment options also require handling of hazardous investigation derived waste, which is a sustainability consideration.

3.4 Membrane Filtration

Membrane filtration refers to a variety of separation technologies based on the nominal size of the membrane pores. Types of membranes include reverse osmosis (RO), nanofiltration (NF), microfiltration (MF), and ultrafiltration (UF). Low pressure membranes such as MF and UF cannot reject PFAS since their pore sizes are larger than the effective diameter of the PFAS molecules (about 1 nm) (Tsai et al. 2010; Rahman et al. 2014). For that reason, MF and UF are not discussed here. Although bench-scale studies indicate that the membrane molecular weight cut-off (MWCO) of NF/RO is probably the most important factor for removal of PFAS for these technologies, other factors, such as ionic charge, may also influence performance.

Two terms, “salt passage” and “salt rejection,” generally describe how membrane systems perform. Salt passage is the percentage of dissolved constituents (contaminants) in the feedwater allowed to pass through the membrane. The opposite of salt passage, salt rejection, is the percentage of feed water that does not pass through the membrane. In

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general, NF membranes have lower rejection rates (95%) than RO (> 99%), because NF membranes have larger pores (Rahman et al. 2014 provides an excellent review of many of the relevant studies). As with all other treatment options, bench-scale and pilot-scale testing are required to understand the field applicability and establish essential detailed design criteria such as pretreatment needs and cost effectiveness.

3.4.1 Reverse Osmosis

Technology Description: RO membranes are effective in removing most organic and inorganic compounds from water solutions. In recent years, new polymer chemistry and manufacturing processes have improved efficiency, lowering operating pressures and reducing costs. As a result, RO membranes are increasingly used by industry to concentrate or remove chemicals. RO is commonly used around the world in household drinking water purification systems, the production of bottled mineral water, self-contained water purification units (for the U.S. military), and industrial applications (for example, water supply to cooling towers, boilers, and deionized water). The largest application of RO is in desalination.

Reverse osmosis is most useful as one element within a treatment train, where the reject water is further treated or captured.

Treatment Mechanism: RO separates compounds from water solutions by passing pressurized water across a semipermeable membrane. Treated water (permeate) passes through the membrane and the rejected water (concentrate) is collected for disposal or discharge, depending on the nature of the compounds and particles present.

State of Development: RO has been studied in bench-scale studies and pilot plants for wastewater and drinking water PFAS applications and is considered a partially developed technology. Conventional and advanced treatments have been studied in several pilot plants and drinking water treatment plants, demonstrating both treatments operating simultaneously as well as the effectiveness of traditional drinking and wastewater treatment methods alongside PFAS-specific technologies.

Effectiveness: Influent pretreatment is critical for RO membranes because of their spiral-wound design. Membranes are highly susceptible to fouling (loss of production capacity) because some accumulated material cannot be removed from the membrane surface.

RO removal of PFAS from various waters has been studied (for example, semiconductor wastewater, drinking water, surface water, and reclaimed water), combined with NF in some cases. PFOS removal > 99% was achieved using four different types of membranes over a wide range of feed concentrations, from 0.5 to 1500 mg/L (Tang et al. 2006). Another study tested five RO and three NF membranes at feed concentrations of 10 mg/L PFOS over four days (Tang et al. 2007). The PFOS rejection and permeate flux performances were > 99% for RO and 90 to 99% for NF. The use of RO and NF as advanced drinking water treatments is still limited, but both technologies have been shown to be successful for the removal of longer-chain (> C5) PFAAs (Loi-Brugger et al. 2008; Tang et al. 2006). Conventional and advanced treatment efficiencies to remove PFOA and PFOS from surface water of the Llobregat River in northeast Spain were also studied. Results were compared in several pilot plants, and in a drinking water treatment plant that operates with UF and RO treatment alongside traditional treatment processes (Flores et al. 2013).

Another study examined the fate of PFSA and PFCA in two water reclamation plants that further treat water from wastewater treatment plants in Australia (Thompson et al. 2011). Plant A used adsorption and filtration methods alongside ozonation, while Plant B used membrane processes and an advanced oxidation process, to produce purified recycled water. At both facilities, PFOS, perfluorohexane sulfonate (PFHxS), perfluorohexanoate (PFHxA), and PFOA were the most frequently detected PFAS. Comparing the two reclamation facilities, Plant A showed some removal during the adsorption/filtration stages. Overall, however, Plant A failed to completely remove PFOS and the PFCA shorter than perfluorononanoic acid (PFNA) in chain length. All PFAS present were removed by RO at Plant B from the finished water to concentrations below detection and reporting limits (0.4–1.5 ng/L).

Sustainability Considerations: The carbon footprint for this technology includes energy source and consumption during treatment system operation, as well as manufacturing/disposal of treatment media. RO requires power for high-pressure pumps and the management of concentrate, which can be energy intensive. The contaminant-rich brine rejected by RO must be disposed of appropriately. The removal of nontarget minerals from the treated water may increase its corrosivity, and posttreatment corrosion control measures are needed in most cases. Resources are available for performing a sustainability assessment for membrane filtration remedial design (Ras and von Blottnitz 2012).

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3.4.2 Nanofiltration

Technology Description: NF is a form of membrane technology that is pressure-driven and shown to be effective in the removal of PFAS (Tang et al. 2007). This method provides high water flux at low operating pressure (Izadpanah and Javidnia 2012). Like RO, NF is easy to operate and reliable for the removal of chemicals.

Technology Mechanism: Nanometer-sized membrane pores are used to separate compounds in a process similar to RO, but NF does not remove smaller ions such as chloride and sodium.

State of Development: NF is considered a partially developed technology because available data on the removal of PFAS are limited to laboratory-scale tests performed on flat sheet membrane coupons.

Effectiveness: No studies have reported either pilot or full-scale performance of NF membranes. Therefore, variations in performance due to fouling, flux, and concentration distributions in standard spiral-wound membrane configurations have not been characterized.

NF membranes tested include the Dow membranes NF-270, NF-200, and NF-90 and the SUEZ (formerly GE Water & Process Technologies) DK membrane. Reported rejections were generally > 95% for PFAS with molecular weights ranging from 214 g/mol to 713 g/mol (Steinle-Darling and Reinhard 2008; Appleman et al. 2013). However, lower rejections were observed for perfluoropentanoate (PFPeA) and perfluorooctane sulfonamide (FOSA)—about 70 and 90%, respectively (Steinle-Darling and Reinhard 2008). Recovery and salt passage information was not reported in these studies. Scaling up these results is challenging because rejection is affected by recovery, which can vary from one application to another.

Salt passage for PFOS was reported to range from < 1% for the tighter NF-90 membrane to about 6% for the looser NF-270 and DK membranes (Tang et al. 2007). PFOS salt passage also was correlated to sodium chloride salt passage, a common specification for membrane manufacturers (Tang et al. 2007). Salt passage incorporates both rejection and membrane recovery, therefore is a more useful parameter for predicting full-scale performance than rejection.

Pilot and full-scale testing of the selected NF membrane for PFAS removal is a crucial step when considering this treatment process. Choosing membranes with MWCO smaller than the targeted PFAS is also a key design consideration.

Appropriate disposal or treatment of the membrane concentrate stream is another design factor, especially when using high-pressure membranes for inland communities. Furthermore, NF membrane fouling mechanisms are poorly understood and further research is needed to develop cost-effective cleaning methods to restore membrane performance (Al-Amoudi and Lovitt 2007). As with other forms of filtration, pretreatment strategies to avoid fouling and membrane fabrication drive performance results.

Sustainability Considerations: The carbon footprint for this technology includes energy source and consumption during treatment system operation, as well as manufacturing/disposal of treatment media. NF requires power for pumps (generally less than RO), and the management of concentrate, which can be energy intensive.

4 References and Acronyms

The references cited in this fact sheet, and the other ITRC PFAS fact sheets, are included in one combined list that is available on the ITRC web site. The combined acronyms list is also available on the ITRC web site.



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ECOS

1 Introduction

1.1 What is AFFF?

Aqueous film-forming foam (AFFF) is highly effective foam intended for fighting high-hazard flammable liquid fires. AFFF products are typically formed by combining hydrocarbon foaming agents with fluorinated surfactants. When mixed with water, the resulting solution achieves the interfacial tension characteristics needed to produce an aqueous film that spreads across the surface of a hydrocarbon fuel to extinguish the flame and to form a vapor barrier between the fuel and atmospheric oxygen to prevent re-ignition. This film formation is the defining feature of AFFF.

There are two major classes of firefighting foams: Class A and Class B. Class A foams were developed in the 1980s for fighting wildfires. They are also used to fight structure fires. Class B foams are any firefighting foams that have been designed to effectively extinguish flammable and combustible liquids and gases; petroleum greases, tars, oils and gasoline; and solvents and alcohols. Class B foams can be synthetic foams, including aqueous film-forming foam (AFFF) or alcohol-resistant aqueous film-forming foam (AR-AFFF), or protein foams. This fact sheet focuses on AFFF as these foams contain fluorosurfactants and they are widely used. Per- and polyfluoroalkyl substances (PFAS) are the active ingredients in fluorosurfactants.

All Class B foams are not the same. Although not usually categorized this way from a fire protection viewpoint, they can be divided into two broad categories from a per- and polyfluoroalkyl substances (PFAS) perspective: Fluorinated foams that contain PFAS and fluorine-free foams that do not contain PFAS.

The vast majority of Class B firefighting foam that is currently in stock or service in the United States is AFFF or AR-AFFF. All AFFF products contain PFAS. This applies to foams used in the past and those being sold today. Foam currently in stock or new foam that is labeled as AFFF or AR-AFFF, contains perfluoroalkyl or polyfluoroalkyl substances, or both, as active ingredients (DOD 2018; Darwin 2004).

AFFF is used where there is a significant flammable liquid hazard present, including but not limited to the following locations:

- chemical plants
- flammable liquid storage and processing facilities
- merchant operations (oil tankers, offshore platforms)
- municipal services (fire departments, firefighting training centers)
- oil refineries, terminals, and bulk fuel storage farms
- aviation operations (aircraft rescue and firefighting, hangars)
- military facilities

Most AFFF products sold and currently stocked in the United States are either listed by Underwriters Laboratory (UL) based on conformance with UL Standard 162, “Foam Equipment and Liquid Concentrates” or have been tested by the U.S. Naval Research Laboratory (NRL) and qualified as meeting the requirements of the U.S. Department of Defense (DOD) Military Specification (MILSPEC), MIL-PRF-24385, “Fire Extinguishing Agent, Aqueous Film-Forming Foam” (DOD 2017). AFFF foams that meet the MILSPEC are required for use in military applications and at Federal Aviation Administration (FAA) regulated airports. All other AFFF foams are specified to UL Standard 162 (UL 2018) or other specifications for

ITRC has developed a series of fact sheets that summarize the latest science and emerging technologies regarding Per- and Polyfluoroalkyl Substances (PFAS) (ITRC 2018). This fact sheet is targeted to local, state, and federal regulators and tribes in environmental, health, and safety roles as well as AFFF users at municipalities, airports, and industrial facilities.

The purpose of this fact sheet is to outline how to properly identify, handle, store, capture, collect, manage, and dispose of AFFF.

The fact sheet is not intended to replace manufacturer specifications, or industry guidance for AFFF use, or discuss alternatives in detail. It is only intended to educate users on AFFF use to reduce and eliminate potential harm to human health and the environment.

Perfluoroalkyl substances are fully fluorinated (perfluoro-) alkane (carbon-chain) molecules. Their basic chemical structure is a chain of two or more carbon atoms with a charged functional group attached at one end.

Polyfluoroalkyl substances are not fully fluorinated. Instead, they have a non-fluorine atom (typically hydrogen or oxygen) attached to at least one, but not all, carbon atoms, while at least two or more of the remaining carbon atoms in the carbon chain are fully fluorinated.

More information is included in the ITRC *Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS)* fact sheet (ITRC 2018).

applications outside of military and FAA applications. DOD maintains an online qualified products database (QPD) that lists all the AFFF foams that have been qualified to meet the MILSPEC (DOD 2018).

1.2 Human Health and Environmental Concerns with AFFF Use

All Class B foams have the potential to create an adverse environmental impact if released uncontrolled to the environment, particularly if the foam solutions reach drinking water sources, groundwater, or surface waters. Discharge of foams to surface waters, including fluorine-free foams, may potentially harm aquatic life due to excessive biological and chemical oxygen demand and, in some cases, acute toxicity, and may increase nutrient loading.

AFFF products (as well as other fluorinated foams, see Figure 1) are of concern because they contain PFAS. Some PFAS pose a risk to groundwater and surface water quality, but they are also highly persistent, may be highly mobile, and some bioaccumulate in organisms. PFAS are also not removed or destroyed by conventional wastewater treatment processes unlike many other hazardous substances.

The health effects of PFOS, PFOA, PFHxS, and perfluorononanoate (PFNA) have been more widely studied than other PFAS. Numerous animal and human studies have evaluated both non-cancer and cancer health effects related to exposure to a limited number of PFAS, including PFOA and PFOS. Little to no health-effects data are available for many PFAS. See the *Regulations, Guidance, and Advisories for Per- and Polyfluoroalkyl Substances (PFAS)* fact sheet (ITRC 2018) for more detailed discussion of potential health effects related to PFAS.

To date there have been only limited studies of human health effects specifically related to use of AFFF. Glass et al. (2014) reported elevated rates of some cancers among more highly exposed firefighters, but their study was not designed to evaluate specific associations between these health effects and any particular chemical among the many chemicals to which firefighters may be exposed. Rotander et al. (2015) measured PFOA, PFOS, and PFHxS levels in firefighters' serum but did not observe any association with studied health effects. A limited study in Norway observed elevated PFOS and PFHxS serum levels in 10% of firefighters studied, (Kärman et al. 2016), and suggested that use of personal protective equipment (PPE) may account for why elevated levels were not seen in more of the firefighters. Studies suggest that perfluoroalkyl acids like PFOS and PFOA are not well absorbed through the skin (ATSDR 2018), which is the most likely exposure pathway for AFFF foams. However, should the PFAS in AFFF enter the body they could cause health problems, so appropriate PPE should be used to prevent or minimize direct contact, ingestion, or inhalation of AFFF.

PFAS encompass a wide range of fluorinated carbon-chain compounds of differing carbon chain lengths, physical and toxicological properties, and environmental impacts. Long-chain PFAS are of particular concern and include PFOS and PFOA, which are recognized as persistent, bioaccumulative and toxic (PBT). Depending on when it was manufactured, AFFF may also contain fluorinated precursors known as fluorotelomers, that can breakdown in the environment to PFOA or other PFCAs. See the *Naming Conventions and Physical and Chemical Properties and the History and Use of Per- and Polyfluoroalkyl Substances (PFAS)* fact sheets (ITRC 2018) for more information.

1.3 Determining the Type of PFAS in AFFF in Current Inventory

Within these broad categories of Class B foams there are different types of foams. Figure 1 illustrates the categories of Class B foams and AFFF specifically. There are three possible types of AFFF products including:

- legacy PFOS AFFF
- legacy fluorotelomer AFFF (contain some long-chain PFAS)
- modern fluorotelomer AFFF (contain almost exclusively short-chain PFAS)

- Long-chain PFAS are defined as perfluoroalkyl carboxylates (PFCAs) with eight or more carbons, including perfluorooctanoate (PFOA), and perfluoroalkane sulfonates (PFASs) with six or more carbons, including perfluorohexane sulfonate (PFHxS) and perfluorooctane sulfonate (PFOS).
- Short-chain PFAS are defined as PFCAs with seven or fewer carbons, such as perfluorohexanoate (PFHxA), and PFASs with five or fewer carbons, such as perfluorobutane sulfonate (PFBS),

Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS) fact sheet (ITRC 2018)

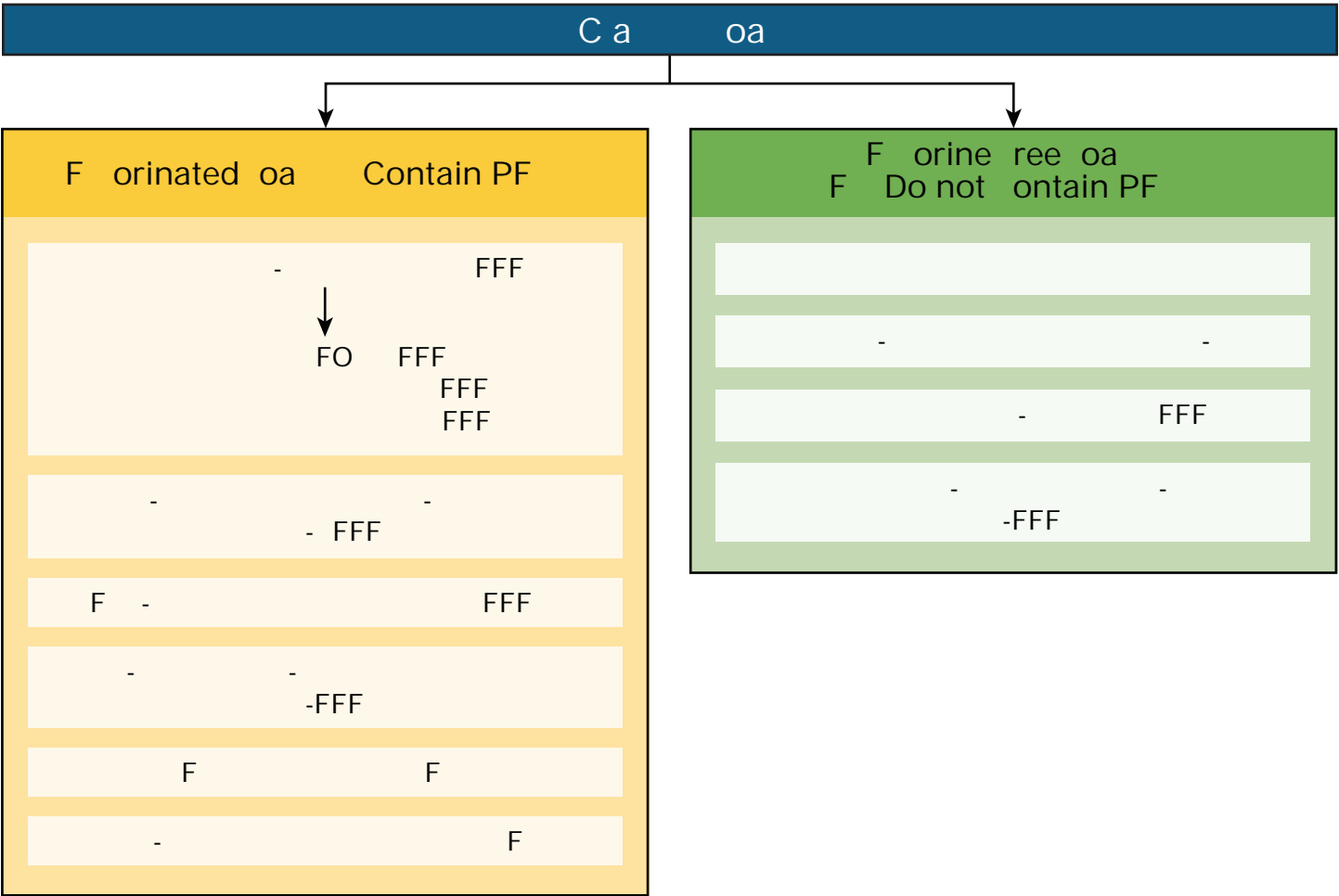


Figure 1. Types of Class B foams
(Source: S. Thomas, Wood plc, used with permission)

1.3.1 Legacy PFOS AFFF

These foams were manufactured in the United States from the late 1960s until 2002 exclusively by 3M and sold under the brand name “Lightwater” (DOD 2014). Lightwater AFFF contains PFOS and various precursors that could potentially break down in the environment to PFOS and shorter chain PFASs such as PFHxS. Some of these PFASs, including PFHxS, are also considered to be persistent. Older formulations may also contain PFOA as well as fluorinated precursors. The fluorinated precursors may also break down in the environment to PFOA and other perfluoroalkyl carboxylates (PFCAs) (Backe, Day, and Field 2013).

1.3.2 Legacy Fluorotelomer AFFF (contain some long-chain PFAS)

These foams were manufactured and sold in the United States from the 1970s until 2016 and encompass all other brands of AFFF besides 3M Lightwater (Schultz, Barofsky, and Field 2004). Although not made with PFOA, they contain polyfluorinated precursors (Backe, Day and Field 2013; Place and Field 2012) that are shown to degrade to PFOA and other PFCAs in the natural environment (Weiner et al. 2013; Harding-Majanovic et al. 2015). They may contain trace quantities of PFOA as an unavoidable byproduct of the manufacturing process. Legacy fluorotelomer-based AFFF foams have historically contained predominantly short-chain (C6) PFAS with formulations ranging from about 50–98% short-chains and the balance as long-chain PFAS. Importantly, the long-chain PFAS content of these foams has the potential to break down in the environment to PFOA and other PFCAs, but not to PFOS or other PFASs (Weiner et al. 2013).

1.3.3 Modern Fluorotelomer AFFF (contain almost exclusively short-chain PFAS)

In response to the U.S. Environmental Protection Agency (USEPA) 2010/2015 voluntary PFOA Stewardship Program (USEPA 2015), most foam manufacturers have now transitioned to the production of short-chain (C6) fluorotelomer-based PFAS. These foams are referred to as “modern” to distinguish them from the legacy foams manufactured before the phase-out. Short-chain (C6) PFAS do not contain or breakdown in the environment to PFOS and other long-chained

PFAS such as PFHxS and PFOA (see below) and are currently considered lower in toxicity and have significantly reduced bioaccumulation potential compared to long-chain PFAS (USEPA 2018). However, foams made with only short-chain (C6) PFAS may still contain trace quantities (parts per billion [ppb] levels) of PFOA and PFOA precursors as byproducts of the manufacturing process. As documented in the Helsingør Statement: “although some of the long-chain PFAS are being regulated or phased out, the most common replacements are short-chain PFAS with similar structures, or compounds with fluorinated segments joined by ether linkages. While some shorter-chain fluorinated alternatives seem to be less bioaccumulative, they are still as environmentally persistent as long-chain substances or have persistent degradation products” (Scheringer et al. 2014). Concerns have been raised that “little information is publicly available on [the] chemical structures, properties, uses, and toxicological profiles” of these shorter-chain formulations and that “increasing use of fluorinated alternatives will lead to increasing levels of stable perfluorinated degradation products in the environment, and possibly also in biota and humans” (Blum et al. 2015). Under the recently published European Union Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation on PFOA and PFOA-related substances, foams based on short-chain PFAS can contain no more than 25 ppb PFOA and 1,000 ppb total PFOA-related substances to be sold in the European Union (EU) after July 4, 2020 (Commission Regulation (EU) 2017).

1.4 When to Use Legacy AFFF

The decision about whether to use legacy AFFF should be considered in the development of Best Management Practices (BMPs; see Section 3) and in fire response plans. The decision should be based on a site-specific evaluation that considers likely fire hazards and potential risks associated with use of legacy AFFF. These decisions should be made prior to an emergency where Class B AFFF would be used so that BMP equipment, procedures, and training are already in place. During an actual response to a fire, the final decision on whether to use any Class B AFFF should be made by the emergency manager (for example, fire chief, incident commander or terminal manager) based on federal, state and local laws and the nature of the emergency. Decisions regarding the use of any type of foam should consider the nature of the firefighting properties of the foam and the benefits they provide for preservation of life, public safety, and property protection versus the potential environmental, public health, and financial risks the use of such foam could pose.

Decisions about when and how to use PFAS-containing foams should be made before, not during, an emergency. The team should consider key factors such as these:

- The nature of the firefighting properties of the foam
- The nature of the emergency
- The risk to life, public safety, and property
- Potential environmental, public health, and financial liabilities of using the foam

Currently, federal law does not prohibit the use of legacy AFFF remaining in existing stocks, whether containing PFOS or other long-chain PFAS. However, any discharge to a stormwater system, including AFFF containing long-chain PFAS, could be considered a pollutant and is regulated by the Clean Water Act. If long-chain PFAS from an AFFF release enters a drinking water source, it may impact entire communities. Depending on the size of the release and available dilution, the release could contaminate the source above USEPA drinking water health advisory levels or more stringent state and local regulatory criteria. These are potential liabilities that should be weighed against the cost of legacy AFFF disposal and replacement of a current inventory of AFFF during emergency response planning (DOD 2014).

While the disposal cost of legacy PFOS AFFF or certain formulations of legacy fluorotelomer (polyfluoroalkyl compounds produced by the telomerization process) AFFF solutions may be much greater than the cost of purchasing modern, shorter-chain replacement foam, the potential risks of keeping and using this legacy foam may be even greater. Also, replacement of legacy AFFF with short-chain AFFF or other foams may require thorough flushing and possible modification of existing systems that could produce significant amounts of flush water containing PFAS that would require proper disposal. Despite these issues, serious consideration should be given to the continued use, storage, and disposal of legacy AFFF. Organizations that are considering replacing their legacy AFFF stocks should focus first on removing from service legacy PFOS AFFF. A release of legacy PFOS AFFF to the environment, that is not mitigated, is likely to result in PFOS impacts to soils and possibly groundwater and surface water.

Legacy AFFF should only be used for emergency purposes in cases where insufficient amounts of short-chain AFFF or other foams are available and where there is a risk to human life, public safety or property. Where no regulation exists to the contrary, use of legacy AFFF containing PFAS remaining in inventory may depend on whether the facility can contain, collect, and treat the wastewater generated fighting the fire, and on the sensitivity of the surrounding environment. Use of alternative firefighting materials (for example, Class B fluorine-free foams) or Class A foams for smaller fires should be strongly considered whenever possible (FFFC 2016).

Firefighting industry best practice for Class B foams calls for the use of fluorine-free foam (FFF) for testing and training (FFFC 2016; Lastfire 2016). If the authority having jurisdiction requires testing of foam equipment or training of firefighters with AFFF, then only modern fluorotelomer AFFF should be considered for this purpose and any foam discharge should be collected and disposed of properly (see Table 1, Disposal).

1.5 Regulations Affecting the Sale and Use of AFFF

In the United States, 3M voluntarily ended production of PFOS-based AFFF in 2002. The USEPA subsequently restricted the future manufacture and import of most PFOS-based products, including firefighting foams, through two Significant New Use Rules (SNURs) (40 CFR 721.9582, Final Rules published 03-11-02 [13 PFAS] and 12-9-02 [75 PFAS]). In 2006, USEPA instituted the 2010/2015 voluntary PFOA Stewardship Program that resulted in the elimination of PFOA and other long-chain PFAS production by eight major fluorochemical manufacturers by 95% by 2010 and entirely by 2015. As a result, foam manufacturers have transitioned to the production of modern fluorotelomer AFFF (containing only short-chain [C6] PFAS) and other fluorinated Class B foams. In 2007, USEPA issued amendment to 40 CFR 721.9582 regulating another 183 PFAS (SNUR on 10-09-07). In 2015, USEPA proposed a SNUR for PFOA and other long-chain PFAS as a regulatory follow-up to the voluntary PFOA Stewardship Program (USEPA 2015); the SNUR has not been finalized. The SNURs subject specific PFAS chemicals to reporting requirements, but do not restrict the use of existing stocks of legacy AFFF containing those PFAS chemicals.

Currently, the DOD and FAA-regulated airports must meet the requirements established in the military specification MIL-PRF-24385 for AFFF formulations (DOD 2017; FAA 2004). Only AFFF formulations containing fluorosurfactants currently meet the MILSPEC, but the DOD is actively evaluating fluorine-free foams to determine if any can meet the MILSPEC performance requirements (SERDP-ESTCP 2017).

In addition to federal efforts for managing AFFF, several state governments have regulations or other programs that address the use of PFAS-containing foams. Organizations should check with their state and local government for regulations or policies that could impact their use and disposal of AFFF and other Class B foams. Examples of state regulations and policies are included in the following sections.

1.5.1 New York

State regulation 6 NYCRR Part 597 identifies PFOS and PFOA as hazardous substances. The release of more than 1 pound of PFOS and/or PFOA must be reported to the state. (For legacy fluorotelomer AFFF, it would normally require a release of thousands of gallons of foam concentrate to result in release of 1 pound of PFOA.) (New York State 2017).

1.5.2 Washington

In March 2018, the state of Washington passed a new law (Washington State 2018) that restricts the sale and use of Class B foams that contain PFAS. As of July 1, 2018, PFAS-containing foams may not be discharged or otherwise used in the state of Washington for training purposes. Beginning on July 1, 2020, PFAS-containing foams may be sold or distributed in the state only for the following specific uses:

- applications where federal law requires the use of a PFAS-containing firefighting foam, including but not limited to the requirements of 14 CFR 139.317 (such as military and FAA-regulated airports)
- petroleum terminals (as defined in RCW 82.23A.010)
- oil refineries
- chemical plants (WAC 296-24-33001)

1.6 Legacy Foam Replacements

Several states have implemented take-back programs for AFFF products. For example, in May 2018, the Massachusetts Department of Environmental Protection, in partnership with the Massachusetts Department of Fire Services, implemented a take-back program to assist fire departments in the proper disposal of legacy firefighting foams that could impact water resources (MA DEP 2018). Vermont has also announced a take-back program (VT 2018). Users should contact their state regulatory agency for information on available take-back programs.

1.6.1 Synthetic Fluorine-free Foam

Organizations should determine whether a Class B fluorine-free foam (FFF) can achieve the required performance specifications for specific hazards as part of their pre-planning for replacement materials (FFFC 2016). Most foam manufacturers now produce Class B FFF. The performance of these foams has improved significantly over the last

decade and is expected to continue to improve in the future. Purchasers of Class B foams, especially those not required to use MILSPEC AFFF, should investigate whether a Class B FFF will meet the site-specific requirements and should continue to review the performance specifications of FFF products as they make future purchasing decisions.

1.6.2 Modern Fluorotelomer AFFF

If it is determined that the performance of a fluorinated Class B foam is required for a specific hazard, or where federal regulations require AFFF use (for example, military applications and FAA-regulated airports), then organizations should purchase foams that consist of short-chain (C6) PFAS, modern fluorotelomer AFFF. U.S. foam manufacturers have switched over to using short-chain (C6) PFAS so it is likely that any AFFF bought today would meet that requirement (Tyco 2016). Users should confirm with their supplier. There is likely to be some designation on the label and the Safety Data Sheet that the foam contains short-chain (C6) PFAS, but even then, there will be a small amount of longer-chain (C8) impurities as stated in Section 1.3.3.

2 Best Management Practices (BMPs) For Class B AFFF Use

Firefighting foams are an important tool to protect human health and property from flammable liquid fire threats. Proper management and usage strategies combined with the current refinement of environmental regulations will allow an informed selection of the viable options to sustainably use firefighting foams.

BMPs should be established for the use of any firefighting foam to prevent possible releases to the environment that can lead to soil, groundwater, surface water, and potentially drinking water contamination. The discharge of firefighting foam to the environment is of concern because of the potential negative impacts it can have on ecosystems and biota due to the presence of chemicals such as PFAS. For example, for AFFF, the amount of PFAS from foam that may enter groundwater depends on information such as the type and amount of foam used, when and where it was used, the type of soil, and the depth to groundwater. AFFF is typically discharged on land but can run off into surface water or stormwater or infiltrate to groundwater. A more detailed description of the fate and transport of PFAS is included in the ITRC PFAS *Environmental Fate and Transport for Per- and Polyfluoroalkyl Substances (PFAS)* fact sheet (ITRC 2018).

BMPs are particularly important when Class B foams are used near sensitive environmental areas where impacts from chemicals present in foams have potential for lasting damage. Example sensitive areas:

- wetlands
- surface water bodies (particularly those used for water supplies like reservoirs or rivers with municipal water supply intakes)
- sensitive or endangered species habitat
- areas close to public and private drinking water supply wells
- sole source aquifers
- groundwater recharge areas

BMPs are key to fostering the safest use of AFFF in an environmentally responsible manner with the goal of minimizing risk from its use. It is important to establish BMPs before an emergency where AFFF would be used so that BMP equipment, procedures, and training are already in place. Although firefighting personnel may be aware that the foams they are using contain chemicals, they may not be aware of the potential environmental effects of AFFF use. Training of firefighting personnel is important to ensure BMPs are discussed and employed consistently and effectively.

Table 1 gives a summary of example BMPs. Users should follow BMPs to protect themselves, others, and the environment when using AFFF. Further BMP guidance can be found in other documents, such as the *Best Practice Guidance* developed by the Fire Fighting Foam Coalition (FFFC 2016), the US National Fire Protection Association's NFPA 11 (2016), and the Airport Cooperative Research Program's *Use and Potential Impacts of AFFF Containing PFASs at Airports* (ACRP 2017). Users at DOD facilities have other BMPs to follow and other requirements to meet MILSPEC, which would be followed in those circumstances.

BMPs start with pre-planning and deciding which foam to keep in stock. The team should consider key factors such as these:

- Whether fluorine-free foams can meet site-specific performance requirements
- Site-specific evaluation of likely fire hazards and potential risks for life, public safety, and property
- Potential environmental, human health, and financial liabilities associated with AFFF releases
- Site constraints, including existing equipment retrofit requirements to adapt to alternate foams

Table 1. BMPs for Foam Selection, Storage, Use, Planning, Mitigation, and Disposal

Foam Selection
Evaluate whether a Class B fluorine-free foam (FFF) can provide the required performance for the specific hazard. “Alternative techniques and agents must be evaluated well in advance of an emergency situation” (FFFC 2016).
Use AFFF and other fluorinated Class B foams only in situations of significant flammable liquid hazard with risk for public safety or significant property loss, where the performance of other foams has not been demonstrated to date.
Consider adopting a two-foam approach with FFF used to respond to small incidents and AFFF kept as emergency backup for major incidents. Ensure that proper labeling is in place and personnel are trained when multiple inventories exist at one facility to avoid comingling of foams.
Storage
Develop a foam inventory and stock tracking system documenting the foam composition, brand, and manufacturer.
“Obtain and follow manufacturers’ recommendations for foam concentrate and equipment” (FFFC 2016). The amount of foam in the system should be at least sufficient for the group of hazards that simultaneously need to be protected against.
Designate transfer areas and store fluorinated Class B foam concentrate in a covered area with secondary containment.
Design storage tanks to minimize evaporation of concentrate, label clearly to identify the type of concentrate and its intended concentration in solution. Keep foam within the temperature limitations provided by the manufacturer.
Properly maintain foam systems to ensure minimal accidental discharges. It is important to recognize the nature of the foam concentrates; small leaks of concentrate can create environmental impacts. Conduct regular inspections of tanks, storage containers, and any associated piping and machinery. Ensure that leaks are addressed promptly.
Consider the materials used for storage and handling. Corrosion is generally not an issue with foam concentrates, but some exceptions do exist. Manufacturers recommend stainless steel, high-density polyethylene (HDPE), or polypropylene containers for AFFF storage. Avoid using aluminum, galvanized metal, and zinc in storage tanks, piping, and handling equipment for foam concentrates (Angus 2017).
Ensure compatibility of foams before change-outs. Do not mix different types or brands of foam concentrates.
Use
Eliminate the use of AFFF products and other fluorinated “Class B foams for training and testing of foam systems and equipment” whenever possible (FFFC 2016). Instead, use specially designed non-fluorinated, PFAS-free training foams and surrogate liquid test methods available from most foam manufacturers.
If the authority having jurisdiction requires testing of foam equipment or training of firefighters with AFFF, then avoid the use of legacy AFFF and instead use modern AFFF that contains only short-chain (C6) PFAS whenever possible.
Evaluate if Class B foam is needed to fight a fire or if a Class A foam or just water can succeed in fighting the fire.
Provide containment, treatment, and proper disposal of foam solution. Avoid direct release to the environment to the greatest possible extent.
Collect, treat, and properly dispose of runoff/wastewater from training events or live fire events to the greatest extent possible.
Use appropriate personal protective equipment (PPE) when handling and using AFFF, and identify how to decontaminate materials and gear that comes into contact with foam.
“Follow applicable industry standards for design, installation, maintenance, and testing of foam systems” (FFFC 2016).
Keep records of when and where foam is used to respond to incidents, including foam type, manufacturer and brand, and amount used.
Make note of sensitive receptors (for example, streams, lakes, homes, areas served by wells) identified in the vicinity of foam use and report to environmental agencies as required.
Consider firefighter and public safety first.

Planning and Mitigation
Develop and communicate documented processes for a facility or installation with the stakeholders and regulatory agencies before a release occurs.
Develop runoff collection plans, equipment, and training processes specific to fluorinated Class B foam use.
Develop mitigation plans for uncontrolled releases of foam concentrate or foam solution to minimize environmental impacts.
Quickly and thoroughly clean up contaminated materials after an AFFF release.
Design new firefighting systems, when needed, to accommodate FFF products, considering their different properties, mode of action, and effectiveness.
Prioritize proper education, training, preplanning, and actions at an incident to ensure the most efficient use of the foam and equipment.
Disposal
Dispose of expired or unneeded Class B fluorinated foam concentrate at a Resource Conservation and Recovery Act (RCRA) permitted incinerator or another alternative incinerator that can ensure complete destruction of the PFAS. See <i>Remediation Technologies and Methods for Per- and Polyfluoroalkyl Substances (PFAS)</i> fact sheet for details on thermal destruction of PFAS (ITRC 2018).
Monitor developments in new disposal technologies.
Discontinue expired or unneeded AFFF concentrate donation programs (for example, donation to fire training school).

The ACRP developed a macros-enabled Microsoft Excel™ workbook screening tool that allows users to “better integrate BMPs into the AFFF life cycle at their facilities, identify and manage potential risks associated with historical or current AFFF use at their site, and prioritize where resources need to be allocated to address concerns regarding AFFF and PFAS” (ACRP 2017). Owners of AFFF stocks should consider evaluating this tool to see if it can assist them in implementing BMPs for their specific situation.

3 AFFF Releases and Recommended Investigative Actions

After a release of AFFF and firewater containing AFFF, immediate cleanup of AFFF followed by an environmental investigation may be needed to determine the type and extent of environmental impacts and whether additional response actions are needed. Users should identify if there are state or local environmental agency requirements for notification that apply to their site and circumstances.

3.1 Immediate Cleanup of Standing Foam and Foam-Impacted Materials

One of the most effective and least expensive methods of minimizing human health or environmental impacts of an AFFF release is to quickly and thoroughly clean up contaminated materials. Cleanup may include recovering standing flammable liquids, foam or capturing water used during firefighting operations with a vacuum truck, pumps, or hand-held equipment (for example, shovels, mops, other absorbent materials). Once cleanup is completed, if a large amount of foam soaked into the ground, removal of soils saturated with the foam should be considered. In all of these initial cleanup efforts, response personnel should use proper PPE (for example, turnout gear, Tyvek, gloves, boots) during handling of contaminated media. This task may require temporary stockpiling of these soils (on a liner with a cover) before final disposal or treatment can be arranged. For more information, see the *Remediation Technologies and Methods for Per- and Polyfluoroalkyl Substances (PFAS)* fact sheet (ITRC 2018).

3.2 Information Gathering After a Release of AFFF

For new releases, it is important to start the information gathering process as soon as possible after a discharge has occurred to maximize the quality of the information gathered and to be protective of human health and the environment. Questions to ask first responders or others with information related to the released AFFF include:

1. Based on readily available information (for example, Safety Data Sheets [formerly MSDSs], applicable MILSPECs), what are the active ingredients (name, concentration, proportions), brand, and manufacturer of the released foam? What volume was discharged?
2. What areas of the site were affected and are there drains, ditches, stormwater drainage systems, or other structures that could cause off-site migration of the foam?

3. Did the release occur inside a building (such as an airport hangar)? If so, it may be beneficial for the personnel to leave the structure until the AFFF has been removed from the building. The owner of the building may consider having the indoor air tested before the building is reoccupied. For more information, see the *Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS)* fact sheet (ITRC, 2018).

3.3 Surface Delineation (Visual) After New Releases

Site delineation can be performed immediately after a discharge occurs by using visual observations of foam and standing water, as a guide. Site delineation becomes harder to conduct as time passes, so it is important to conduct an initial site evaluation and delineation effort as soon as it can be safely performed. Photographic documentation of the affected areas and the use of markers (for example, survey tape, lath, pin flags) to identify the location of where AFFF was released can help to ensure that the continued characterization effort will provide accurate results and fewer resources will be spent assessing unaffected areas.

3.4 Field-Screening for First Responders After Releases

Currently, field-screening methods are limited to visual observation as described above as well as placing AFFF-contaminated media (add a little water if medium is solid) in a clear container and shaking the container, looking for resulting foam. Foaming in the container would qualitatively indicate that the media in this area may contain residual levels of AFFF that may require cleanup. Screening for released AFFF in the field using mobile instrumentation may soon be a practical alternative and could provide a way to quickly delineate affected surface soils and groundwater. Sensor-based technologies are under development (Chen et al. 2013), as well as inexpensive high-throughput screening tools such as particle-induced gamma emission that quantifies total fluorine on surfaces (Shaider et al. 2017; Ritter et al. 2017) and is being modified for quantifying total fluorine in groundwater.

If field screening during the initial delineation indicates significant surficial and near-surface contamination is present, removing and stockpiling soils should be considered, in consultation with environmental professionals and consistent with regulatory requirements, to minimize potential leaching to groundwater or runoff to nearby surface water. Confirmatory sampling may be needed after removal of contaminated material or after screening if no contaminated material is observable. If concentrations are less than applicable actions levels (check with the individual state authorities to determine the site-specific action levels), then no additional remedial activities may be necessary. Knowledge regarding the volume released, the concentration of PFAS in the released product, whether it was a mixture or concentrate, and the area affected is important. If only a small volume of AFFF concentrate is released in combination with a large amount of fresh water and is dispersed over a large area, the concentration in soil may not warrant cleanup. The initial cleanup actions (capture of AFFF and standing water) and collection of confirmation samples may be all that is needed for site closure. The *Regulations, Guidance, and Advisories for Per- and Polyfluoroalkyl Substances (PFAS)* fact sheet (ITRC 2018) includes more information.

3.5 Determining the Need for Further Actions

It is important to establish a working relationship with relevant stakeholders, including local or state regulatory agencies, preferably before, but at least immediately after a release of AFFF to determine the need for investigation and remedial activities. Developing and communicating documented processes for a facility with the stakeholders and regulatory agencies before a release occurs should be considered a best practice. The environmental media (for example, surface soil, subsurface soil, surface water, groundwater, sediment, biota) to be sampled are determined by identifying the potential media affected and in consultation with environmental professionals and consistent with regulatory requirements. The required site characterization effort will often become more involved and expensive as the time between release, discovery, and potential remedial actions increases. If a release is discovered immediately and remedial actions are taken promptly, the need for sampling activities is often reduced because fewer environmental media will be affected and potential impacts are more limited and easier to identify. Additional information about sampling and site characterization are included in the *Site Characterization Considerations, Sampling Precautions and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS)* fact sheet (ITRC 2018). Additional information about remediation methods is included in the *Remediation Technologies and Methods for Per- and Polyfluoroalkyl Substances (PFAS)* fact sheet (ITRC 2018).

3.6 Sampling After Discovery of a Historical Discharge

The sampling methods used, and locations investigated after an AFFF discharge, will depend on both the amount and type of foam released, as well as site-specific characteristics such as topography, affected media, land use, potential

infrastructure, and presence or absence of environmentally sensitive areas. Information about sampling, precautions, equipment, and laboratory analysis methods, are included in the *Site Characterization Considerations, Sampling Precautions and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS)* fact sheet (ITRC 2018). PFAS migration within and between different environmental media is influenced by many processes. The *Environmental Fate and Transport for Per- and Polyfluoroalkyl Substances (PFAS)* fact sheet (ITRC, 2018) includes more information on these processes. Except for conducting an initial sampling effort to confirm or refute a release of AFFF, entities collecting samples to delineate the degree and extent of PFAS should prepare and follow a detailed site sampling plan.

If a historical release of AFFF is suspected, it may be difficult to use visual observations to determine where to begin the delineation or characterization effort. Environmental professionals and state or local regulatory agencies should be consulted to determine investigation strategies and relevant regulatory requirements. For example, if a release occurred from a permanent structure (such as a tank or hangar fire-suppression system), the topography of the adjacent landscape, potential drainages or preferential pathways, or surface depressions may indicate where to begin a sampling effort. Gathering information from historical records (for example, internal incident reports or summaries, historic aerial photos, various documents available through a local regulatory agency) or interviewing individuals with knowledge of AFFF use and events at a facility may aid location of potential source areas.

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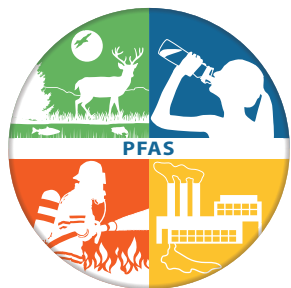
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