Sterling Environmental Engineering, P.C.

REMEDIAL ACTION WORK PLAN

FOR

53 PUTNAM STREET
SARATOGA SPRINGS, NEW YORK
BCP #C546057

Prepared for:

Putnam Resources, LLC
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Saratoga Springs, New York 12866

Prepared by:

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(revised December 4, 2020)

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CERTIFICATION

I, Andrew Millspaugh, certify that I am a New York State registered professional engineer and that this Remedial Action Work Plan was prepared in accordance with all applicable statutes and regulations and is in substantial conformance with the DER Technical Guidance for Site Investigation and Remediation (DER-10).

_____

Andrew M. Millspaugh, P.E.
NY PE 094708

Professional Seal:

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LIST OF ACRONYMS

Acronym	Definition
AAR	Alternatives Analysis Report
AOC	areas of concern
amsl	above mean sea level
AWQS	Ambient Water Quality Standards and Guidance
BCP	Brownfield Cleanup Program
CAMP	Community Air Monitoring Plan
CFR	Code of Federal Regulations
COC	contaminant of concern
cVOC	chlorinated volatile organic compounds
DER-10	Division of Environmental Remediation/Technical Guidance for Site Investigation and Remediation
DFR	Daily Field Report
FER	Final Engineering Report
HASP	Health and Safety Plan
IET	Innovative Environmental Technologies, Inc.
ISGS	In-Situ Geochemical Stabilization
NYCRR	New York Codes, Rules and Regulations
NYSDEC	New York State Department of Environmental Conservation
NYSDOH	New York State Department of Health
PCB	polychlorinated biphenyls
PFAS	per- and polyfluoroalkyl substances
PID	photoionization detector
PPE	personal protective equipment
QAPP	Quality Assurance Project Plan
QEP	Qualified Environmental Professional
RAO	remedial action objective
RAWP	Remedial Action Work Plan
RI	Remedial Investigation
RRUSCO	Restricted Residential Use Soil Cleanup Objectives
SCG	standards, criteria, and guidance
SMP	Site Management Plan
SPDES	State Pollutant Discharge Elimination System
SVOC	semi-volatile organic compound
TOGS	Technical and Operational Guidance Series
UIC	Underground Injection Control
USEPA	United States Environmental Protection Agency
VOC	volatile organic compound

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1.0 INTRODUCTION AND PURPOSE

Sterling Environmental Engineering, P.C. (STERLING) has prepared this Remedial Action Work Plan (RAWP) on behalf of Putnam Resources, LLC ("Putnam Resources") for the New York State Department of Environmental Conservation (NYSDEC) Brownfield Cleanup Program (BCP) Site #C546057 located at 53 Putnam Street, City of Saratoga Springs, Saratoga County, New York (hereinafter the "Site"). Engineering design drawings detailing the selected remedy are included herein such that this RAWP also serves as a remedial design document. A location map is presented on Figure 1 and a map of the Site and surrounding area is presented on Figure 2.

A Remedial Investigation (RI) was conducted in accordance with a NYSDEC-approved RI Work Plan and Amendments No. 1 and No. 2 to identify the nature and extent of contaminants in environmental media and to evaluate potential threat to the public and the environment. The NYSDEC approved the RI Report by letter dated January 22, 2020.

An Alternatives Analysis Report (AAR) dated May 14, 2020 was approved by NYSDEC on May 18, 2020 that documents the process for development and evaluation of remedial alternatives to select a remedy for the Site.

The applicable cleanup criteria are the Restricted Residential Use Soil Cleanup Objectives (RRUSCO) and the Protection of Groundwater SCO as specified in 6 NYCRR Part 375, Table 375-6.8(b) and the NYSDEC Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations (AWQS), as set forth in the NYSDEC Division of Water Technical and Operational Guidance Series (TOGS 1.1.1) to achieve a Track 4 BCP cleanup (6 NYCRR Part 375-3.8(e)(4)).

This RAWP was prepared in accordance with the provisions of Division of Environmental Remediation Technical Guidance for Site Investigation and Remediation (DER-10), Section 5.3, and provides the following elements:

- Detailed description of the remedial action and remedial technology to be implemented.
- Listing of applicable Standards, Criteria, and Guidance (SCG).
- Description of erosion and sediment controls, stormwater management and monitoring, and dust, odor, and organic vapor control procedures during remediation, as applicable.
- A Quality Assurance Project Plan (QAPP).
- A Health and Safety Plan (HASP).
- A Community Air Monitoring Plan (CAMP).
- Description of confirmation and/or documentation sampling.
- Description of site restoration plans.
- Description of Institutional Controls.
- A requirement to submit a Site Management Plan (SMP), including a schedule for the final plan.
- Supporting engineering design drawings and figures exhibiting the remedial action.

1.1 Project Description

Putnam Resources plans to redevelop the approximately 0.3-acre Site for mixed commercial/residential use. The specific plans for final redevelopment depend on a variety of factors, such as: subsurface geotechnical conditions, permits, City approvals, community needs, and project financing. A complete description of current Site conditions is provided below.

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2.0 SITE CONDITIONS

2.1 Site Description

The Site is located within the Business District of the City of Saratoga Springs along Putnam Street. A map of the parcel comprising the Site is provided as Figure 2. A single-story masonry building occupied most of the rectangular-shaped property until the aboveground portion of the building was removed in March 2019 to facilitate remediation. There is no building slab except for a broken and deteriorated concrete floor slab at the southwest corner of the building footprint with dimensions of approximately 12 feet x 32 feet. Subsurface portions of building foundation walls were not removed during demolition and remain in place coincident with the outline of the building. The Site is surrounded by security fencing to prevent unauthorized access. The broken area of flooring, remaining foundation walls, and existing security fence are identified on attached engineering design drawings (see Sheet 1).

2.1.1 Land Use

The Site is currently vacant, and the Site and surrounding parcels are zoned for commercial use and residential accessory use (i.e., Transect Zone 6 – Urban Core). The property to the north is primarily a parking lot. The property to the south is occupied by a parking lot and commercial building. Properties to the west are primarily occupied by commercial buildings. Immediately east of the Site is Putnam Street. The Saratoga Springs Public Library occupies the property immediately east of Putnam Street. The nearest residential neighborhood is approximately 400 feet east of the Site.

2.1.2 Topography

The Site is generally flat at an elevation of approximately 285 feet above mean sea level (amsl). The surrounding topography located within 0.5 mile of the Site is relatively flat and ranges between approximately 270 to 350 feet amsl. Surface water bodies are not located within the immediate vicinity of the Site. Loughberry Lake (waterbody ID 1101-0068) is located approximately 1 mile northeast of the Site.

2.1.3 Surface Water, Wetlands, and Floodplains

The Site is located in the Business District of Saratoga Springs and surrounded by several buildings and parking lots. No surface water or wetlands are present at the Site, and the Site is not situated on a floodplain according to the City of Saratoga Springs geographic information system database. The Site is not located in a designated floodway or within a 100-year floodplain.

2.1.4 Primary Contaminants of Concern

Primary contaminants of concern (COC) are those compounds that will be addressed either through active remedial measures and/or engineering and institutional controls because they were detected during the RI and previous investigations at concentrations greater than the NYSDEC RRUSCOs, the Protection of Groundwater SCO, and/or NYSDEC AWQSs. Based upon a review of the documented history, previous investigations conducted at the Site, and data obtained during the RI, COCs include petroleum-related volatile organic compounds (VOC) (benzene, ethylbenzene, toluene), chlorinated VOCs (cis-1,2-dichloroethene, tetrachloroethene, trans-12-dichloroethene, trichloroethene, and vinyl chloride), pesticide compounds (4,4-DDT and 4,4-DDE), metal compounds (mercury, arsenic, barium, copper, zinc, and lead), and per- and polyfluoroalkyl substances (PFAS).

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Other categories of contaminants that were analyzed, but are not considered COC, include semi-volatile organic compounds (SVOC), polychlorinated biphenyls (PCB), and the "emerging contaminant" 1,4-Dioxane, as required by 6 NYCRR Part 375 and NYSDEC DER-10.

2.1.5 Areas of Concern

The RI identified the nature and extent of contamination in the soil, groundwater, and soil vapor, and specifically identified areas where COC are greater than NYSDEC RRUSCOs or greater than the NYSDEC AWQS. The conclusions of the RI Report are the basis for the remedy selected in the AAR. The areas of concern (AOC) identified in by the RI and the AAR are shown on Figure 3.

3.0 PREVIOUS INVESTIGATIONS

A list of environmental reports pertaining to the Site include the following:

- Underground Storage Tank Removal Report, prepared by Passaretti Geological & Environmental Consultants, Inc., dated May 10, 2002.
- Phase I Environmental Site Assessment and Limited Subsurface Investigation Report, prepared by CASmith, dated December 8, 2006.
- Laboratory data package to Ms. Mary Passaretti, dated December 23, 2013.
- Site Investigation Report, prepared by STERLING, dated November 5, 2015.
- Supplemental Site Investigation Report, prepared by STERLING, dated March 14, 2016.
- Groundwater Monitoring Report, prepared by STERLING, dated September 21, 2016.
- Preliminary Geotechnical Evaluation Report, Proposed Building, 53 Putnam Street, Saratoga Springs, NY, prepared by Dente Engineering, P.C., dated September 2018.
- Remedial Investigation Report, prepared by STERLING, dated January 14, 2020.
- Alternatives Analysis Report prepared by STERLING, dated May 14, 2020.

Each of these reports are available at the Site's Document Repository, the Saratoga Springs Public Library, located at 49 Henry Street, Saratoga Springs, New York either as a stand-alone report, or as an attachment to one of the more comprehensive reports listed above.

4.0 REMEDIAL ACTION OBJECTIVES

Remedial Action Objectives (RAO) are specific objectives for the protection of public health and the environment. The RAOs are established to prevent and minimize contaminant exposure pathways and are developed based on specific Standards, Criteria, and Guidance (SCG) to address contamination identified at the Site. The NYSDEC generic RAOs are as follows:

Groundwater

RAOs for Public Health Protection

- Prevent ingestion of groundwater with contaminant levels exceeding drinking water standards.
- Prevent contact with, or inhalation of volatiles, from contaminated groundwater.

RAOs for Environmental Protection

- Restore groundwater aquifer to pre-disposal/pre-release conditions, to the extent practicable.
- Remove the source of groundwater contamination.

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Soil

RAOs for Public Health Protection

- Prevent ingestion/direct contact with contaminated soil.
- Prevent inhalation exposure to contaminants volatilizing from soil.

RAOs for Environmental Protection

- Prevent migration of contaminants that would result in groundwater contamination.
- Prevent impacts to biota from ingestion/direct contact with soil causing toxicity or impacts from bioaccumulation through the terrestrial food chain.

Soil Vapor

RAOs for Public Health Protection

- Mitigate impacts to public health resulting from existing, or the potential for, soil vapor intrusion into buildings at a site.

4.1 Standards, Criteria, and Guidance (SCG)

Table 1 summarizes SCGs for soil and groundwater that may be applicable or relevant and appropriate to the Site.

4.1.1 Chemical-Specific SCGs

Chemical-specific SCGs for soil include Soil Cleanup Objectives identified in 6 NYCRR 375-6.8 and further described in NYSDEC Soil Cleanup Guidance Policy (CP-51). Chemical-specific SCGs for groundwater include NYSDEC TOGS 1.1.1 AWQS and Guidance Values and Groundwater Effluent Limitations.

4.1.2 Location-Specific SCGs

In accordance with DER-10, the current, intended, and reasonably anticipated future use of the Site and surroundings were considered in choosing Site-specific cleanup levels. The Site and surrounding parcels are zoned T-6: Transect Zone 6, Urban Core for commercial use and residential accessory use with site plan approval by the City of Saratoga Springs. The anticipated future use of the Site is consistent with the existing zoning. The property to the north is primarily a parking lot. The property to the south is occupied by a parking lot and commercial building. Properties to the west are primarily occupied by commercial buildings. Accordingly, RRUSCOs are appropriate for the Site.

5.0 DESCRIPTION OF SELECTED REMEDY

The selected remedy is based on current and anticipated future use of the Site, and is consistent with local zoning and surrounding property use. The selected remedy identified in the AAR consists of the following, as shown on Figure 3:

- Demolition of the above-ground portion of the building.
- Excavation of surface soil (i.e., upper 2 feet) containing elevated metals to meet RRUSCOs.
- In-situ treatment of impacted soil and groundwater to reduce or eliminate petroleum-related and chlorinated VOCs.
- Installation of a vapor barrier/venting system beneath the new building.
- Placement of a protective cover.

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- Groundwater monitoring.
- Institutional controls.

The general sequence to implement the remedy is expected to include the following tasks as described further in subsequent sections:

- Above-ground building demolition (completed).
- Implement community air monitoring and fugitive emission management programs.
- Excavate and remove surface soil (i.e., upper 2 feet) from areas indicated in Figure 3.
- Backfill surface soil excavation areas.
- Implement in-situ remediation.
- Monitor groundwater concentrations in and adjacent to the in-situ treatment area.
- Place a protective cover of two (2) feet of clean material, or redevelop the Site per construction plans, including construction of a building with a vapor barrier/vapor venting system.
- Pave areas surrounding the building as a protective cover.
- Monitor vapor venting system emissions after system start up.

5.1 Building Demolition

Demolition of the above-ground portions of the building was necessary for accessibility to perform Site remediation. The NYSDEC was notified, and demolition was completed in March 2019 in recognition of the necessity and importance of removing the building for remediation. The remaining portions of the building are foundation walls that are estimated to extend approximately four (4) feet below grade, and the 12 feet x 32 feet broken and deteriorated concrete floor slab at the southwest corner of the building footprint noted in Section 2.1. Neither the foundation walls, nor the broken floor slab will interfere with the selected remedy.

5.2 Remedial Excavation

Site work preparation will consist of establishing security measures and installing perimeter erosion sediment controls, as necessary. The remedy is not subject to a State Pollutant Discharge Elimination System (SPDES) General Permit for Stormwater Associated with a Construction Activity due to soil disturbance being confined to less than 1 acre. Temporary fencing will be installed or modified surrounding the remediation area, as necessary, to restrict access to authorized personnel only.

The upper 2 feet of soil will be excavated from the areas shown on Figure 3 and Sheet 1. Existing monitoring wells are not in the areas of excavation. Care will be taken to preserve existing monitoring wells for possible future use. Monitoring wells may be decommissioned at a later date in accordance with NYSDEC policy CP-43, and with the approval of NYSDEC. A Qualified Environmental Professional (QEP) will observe excavation activities to ensure conformance with this RAWP, including implementing sediment and erosion control and controlled Site security/access via fencing.

The selected contractor will furnish all labor, materials, equipment, tools, and appurtenances required to complete the excavation and will locate all existing utilities in work areas and install necessary erosion controls prior to commencing excavation activities. The contractor will be required to conduct operations to prevent damage to existing structures, safeguard people and property, minimize traffic inconvenience, provide safe working conditions, and comply with all applicable local rules and regulations. The remedial excavation contractor will be required by contract to implement and comply with this RAWP and direction from the on-site QEP. These arrangements clearly define the scope of work to be completed, and a separate

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scope of work from the remedial excavation contractor is not required. The remedial excavation contractor will be required to follow the equipment decontamination procedures described in Section 8.0.

5.2.1 Soil Management and Transport

Soil will be either temporarily stockpiled or loaded directly into trucks for off-site disposal. If temporary stockpiling is used, excavated soil will be placed on polyethylene sheeting and covered to minimize precipitation infiltration and dust migration. Soil stockpiles will be continuously encircled with a berm and/or silt fence. Silt fences or equivalent erosion control measures will be placed as necessary to prevent run-off from the Site. Stockpiles will be kept covered at all times with appropriately anchored sheeting and will be routinely inspected. Damaged sheeting will be replaced, as necessary.

Transport of materials will be performed by licensed haulers in accordance with appropriate local, State, and Federal regulations, including 6 NYCRR Part 364. Trucks will be properly placarded and prohibited from stopping and idling outside the Site on public roads. Site access points for truck and equipment transport will be kept clean of dirt and other materials. Trucks removing soil and debris must be properly covered before exiting the Site. After being loaded and before leaving the Site, trucks will be visually inspected for any loose soil or debris on the vehicle tires or body. Trucks removing soil and debris will be decontaminated before leaving the Site if visual inspection identifies contaminated soil, as described in Section 8.0.

5.2.2 Soil Disposal

Soil excavated from the areas shown on Figure 3 and Sheet 1 will be disposed off-site at a permitted landfill. Soil samples will be collected for waste characterization analysis based on the requirements of the selected landfill. A waste profile will be completed to gain acceptance of the soil at the disposal facility.

5.2.3 Documentation Sampling

Soil samples will be collected from the identified excavation areas to document the soil quality remaining in place following excavation. One soil sample will be collected from the top of each sidewall for every 30 linear feet of excavation sidewall. One sample will be collected from the floor of the excavation for every 900 square feet of bottom area. The approximate locations of the documentation soil samples are shown on Sheet 1. The number and type of soil samples to be collected from each of the three excavation areas is as follows, based on the dimensions of each area:

Location	Length (ft.)	Width (ft.)	Sq. Ft.	Wall Samples	Floor Samples
West Excavation	65	40	2,600	7	3
North Excavation	30	20	600	4	1
East Excavation	35	40	1,400	5	2

Each wall and floor sample from the West Excavation and East Excavation will be analyzed for total Mercury by USEPA Method 7471B, which was the only compound detected in the upper 2 feet of soil in those areas at concentrations greater than the RRUSCO. Each wall and floor sample from the North Excavation will be analyzed for SVOCs by USEPA Method 8270, which was the only class of compounds detected in the upper 2 feet of soil in that area at concentrations greater than the RRUSCO.

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5.2.4 Backfilling

All materials proposed for import onto the Site will be reviewed by a QEP for compliance with DER-10, and an NYSDEC "Request to Import/Reuse Fill or Soil" form will be prepared and submitted to the NYSDEC for approval of the source before material is imported to the Site. Sources will be sampled in accordance with NYSDEC DER-10 Section 5.4(e) and Table 5.4(e)10 including PFAS as emerging contaminants unless the material is exempt from testing in accordance with the requirements of DER-10 Section 5.4(e)5. Soil imported to the Site for use as backfill or as a protective cover will comply with the requirements of 6 NYCRR Part 375-6.7 (d).

5.3 In-Situ Treatment

The Site environmental conditions were provided to three qualified in-situ remediation consultants/contractors to review and propose an effective in-situ treatment regimen based on site-specific conditions and contaminants. The proposal prepared by Innovative Environmental Technologies, Inc. (IET) was selected based on the technical merits, company experience and qualifications, and schedule for implementation and completion.

IET's approach is designed to stabilize residual petroleum using In-Situ Geochemical Stabilization (ISGS) in the west AOC, and to use accelerated reductive dechlorination via both abiotic and microbial processes in the east AOC. The technical details, logistics, and procedures regarding these processes are provided in detail in IET's proposal and are therefore not repeated in the text of this RAWP. The In-Situ Injection portion of the remedy is shown on Sheet 2. IET's proposal is provided as Appendix A.

A direct-push drill rig will advance injection screens to target depths. Five equally distributed injection points will be installed in both the west and east AOCs, referred to as Areas A and B in the IET proposal. The radius of influence is estimated to be 10 feet for each injection point based on the soil types identified in the RI Report. As stated in IET's proposal (page 6, Objectives), "no waste stream will be generated" during the in-situ injection remediation.

Initially, compressed air will be injected into the subsurface via IET's proprietary injection trailer system to confirm the presence of open delivery routes and to enhance horizontal injection pathways. The ISGS and reductive dechlorination solutions will be injected from approximately 12 and 29 feet below ground surface with four evenly spaced injection intervals. This zone corresponds to the vertical zone where elevated concentrations of residual petroleum and cVOCs were detected during the RI.

The ISGS injection in the west AOC is estimated to take approximately 2 days to complete, and injection of the reductive dechlorination slurry is estimated to take approximately 1 day to complete. As described in greater detail in Appendix A, IET's proposed remediation includes injecting 3,510 gallons (32,152 pounds) of ISGS amendment in Area A. In Area B, 4,766.13 grams of Vitamin B-2, 686.53 grams of Vitamin B-12, 7,116.28 grams of Red Yeast Rice Extract, 2,500 pounds of Provect-IR, 810 pounds of Zero Valent Iron, 100 pounds of Sodium Sulfite, 100 pounds of Nutrient, and 1,000 pounds of Calcium Propionate will be mixed with 2,000 gallons of water and evenly distributed through five injection borings.

Injection of air prior to injecting fluids is a critical step in understanding and controlling the injection process at each injection location. Injection will occur in a safe and controlled manner that is constantly monitored to ensure the process does not adversely affect areas beyond those intended for treatment (i.e. the radius of influence), and does not open new subsurface pathways. Compressed air is delivered to the injection zone to confirm open pathways exist, both for safety and to ensure injectate will penetrate the

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subsurface. The injection time for the compressed air is short, lasting only long enough to affect the target radius of influence (10 feet) and is monitored by observing a drop in the injection pressure.

Injectate will be introduced at low pressures and flow rates to reduce likelihood of displacing high volumes of groundwater during implementation. The injection is designed to target 5% of available pore volume to prevent displacement of NAPL, groundwater, and soil vapor. The ISGS will oxidize the lighter end of the NAPL (more mobile components) allowing the heavier chain material to be encrusted and stabilized. The ISGS treatment encapsulation process minimizes NAPL/groundwater contact, thereby reducing the mass flux of dissolved-phase constituents of interest in the groundwater. The ISGS Technology Section in Appendix A provides greater detail on how the process reduces the flux of dissolved-phase constituents into the groundwater.

The remediation injection program will be subject to USEPA's Underground Injection Control (UIC) regulations. The USEPA UIC program categorizes the injection points/wells as well type code 5B6, Beneficial Use – Subsurface Environmental Remediation. USEPA Form 7520-16 will be completed and submitted to the USEPA before injection is initiated and the USEPA will be notified after the work is completed (i.e. a change in well status).

5.4 Vapor Barrier/Venting System

Future building construction will include a sub-slab vapor barrier and active sub-slab vapor venting system. The vapor barrier will be placed directly beneath the building slab and the vapor venting system will be installed below the vapor barrier and above the underlying soil. An appropriately sized fan or fans will operate to evacuate soil vapor that may accumulate beneath the building. The details regarding the vapor barrier and venting system cannot be determined until the proposed building is designed. Monitoring of soil vapor and emissions from the vapor venting system are part of the approved remedy; however, the vapor monitoring will not occur until after the building is constructed.

Vapor monitoring will be performed as soon as practicable after the vapor venting system begins operation. The construction details of the vapor venting system will not be known until the building design is completed. A vapor monitoring plan will be prepared and submitted to NYSDEC for review and approval as soon as possible after the design of the vapor venting system is completed.

The vapor monitoring plan is expected to include measuring system operating parameters such as air flow rate and vacuum; photoionization detector (PID) measurements; and system emissions sampling from the system piping for analysis of VOCs by USEPA Method TO-15.

5.5 Protective Cover

The approved remedy includes a protective cover to provide a barrier between soil and future users of the Site. The protective cover will consist either of a two (2) foot cover of soil in accordance with DER-10, Section 5.4 (e) and 6 NYCRR 375-6.7(d), or a two (2) foot cover of material other than soil (i.e., gravel, rock or stone), per DER-10, 5.4 (e) 5. Alternatively, the protective cover may consist of a combination of the concrete slab of the proposed building, pavement immediately surrounding the building, and possibly limited areas of landscaping for aesthetics, depending on the timing of Site development. The anticipated building will occupy most of the Site with an expected concrete slab thickness of at least 6 inches. Asphalt pavement surrounding the building is expected to be at least 4 inches thick with at least 6 inches of compacted subbase. Landscaping, if any, will consist of a minimum thickness of 2 feet of clean, imported soil, consistent with the requirements of DER-10, Section 4.1(f). The exact dimensions and thickness of cover materials will be determined during final redevelopment plans.

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5.6 Effectiveness Monitoring

The effectiveness of the implemented remedial measures will be determined by collecting subsurface soil samples from the petroleum-impacted area and monitoring groundwater quality after remediation is completed. The plans for soil sampling, groundwater sampling, and soil vapor monitoring are described in the following sections.

5.6.1 Subsurface Soil Sampling and Analysis

Subsurface soil samples will be collected and analyzed to evaluate the effectiveness of ISGS injection in the petroleum-impacted area, as follows:

1. Collect a sufficient volume of soil from the target treatment zone from three (3) soil borings **before** injection and perform the following tests. The approximate location of the soil borings are shown on Sheet 2.

    - Visually inspect, describe, and document the physical appearance of the soil samples, particularly, the presence or absence of visual petroleum (free product, sheen, etc.).

    - Perform a "sheen test" on each soil sample by placing a small portion of each sample in a clear glass jar with distilled water, briefly shake the jar, and observe whether a petroleum sheen appears on the surface of the water or sides of the glass jar.

    - Submit each soil sample for analysis of VOCs and SVOCs using Leaching Environmental Assessment Framework (LEAF), USEPA Method 1315.

2. Collect a sufficient volume of soil from the target injection zone from three (3) soil borings approximately two (2) weeks **after** treatment and perform the same tests described above. These three soil borings will be located within a few feet of pre-injection soil borings.

Subsurface soil samples also will be collected and analyzed to evaluate the effectiveness of the injection of the reductive dechlorination solution in the cVOC-impacted area (Area B), as follows:

1. Collect a sufficient volume of soil from the target treatment zone from four (4) soil borings **before** injection. The approximate locations of the soil borings are shown on Sheet 2. Three (3) of the soil borings will be located near RI soil borings H-22, H-26, and H-28 where cVOCs were detected in soil samples at concentrations greater than the UUSCOs and the Protection of Groundwater SCOs.

    - Visually inspect, describe, and document the physical appearance of the soil samples.

    - Submit each soil sample for analysis of VOCs (USEPA Method 8260C) using Leaching Environmental Assessment Framework (LEAF), USEPA Method 1315.

2. Collect a sufficient volume of soil from the target injection zone from four (4) soil borings approximately two (2) weeks **after** treatment and perform the same tests described above. These four soil borings will be located within a few feet of pre-injection soil borings.

The results of the before and after-injection soil samples will be compared to assess the success of the treatment in stabilizing NAPL and degrading cVOCs to mitigate a contributing source to groundwater impacts. The results of the soil sample analyses will be evaluated in conjunction with groundwater samples from nearby wells.

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5.6.2 Groundwater Monitoring

Changes in groundwater quality due to the in-situ remediation are anticipated approximately two (2) to three (3) weeks after injection. Groundwater sampling will be performed approximately four (4) weeks after completion of the in-situ remediation from wells MW-6, MW-7, and MW-8 near the east AOC, and from three (3) newly installed wells (MW-18, MW-19, and MW-20) in the west AOC. Monitoring wells MW-18, MW-19, and MW-20 will be installed in the effectiveness soil borings described in Section 5.6.1 drilled to collect subsurface soil samples. The approximate locations of the new monitoring wells are shown on Sheet 2. Groundwater field readings will be measured and recorded for dissolved oxygen, oxidation/reduction potential, specific conductivity, pH, temperature, and groundwater elevation to evaluate local changes in groundwater conditions. Groundwater samples will be submitted for laboratory analysis of VOCs and SVOCs by USEPA Methods 8260 and 8270, respectively, PFAS-21 compounds (Method 537M), sulfate, and total and dissolved iron.

Historical groundwater analytical results serve as a baseline condition for groundwater quality for comparison and determining effectiveness of remediation. A second round of groundwater sampling/monitoring of the same wells identified above will be performed approximately four (4) weeks after the first round of sampling. The results of each groundwater monitoring event will be submitted to the NYSDEC in a separate groundwater monitoring report.

A groundwater monitoring program specifying which wells will be sampled, sampling frequency, analytical parameters, and reporting will be included as part of the SMP. The program will be based on the results of groundwater monitoring/sampling completed during the 8-week period following remediation and will include recommendations for long-term monitoring, if needed.

5.6.3 Soil Vapor Monitoring

The effectiveness monitoring for soil and groundwater is to evaluate the short-term (within one to two months) effects and success of remediation. Effectiveness monitoring beyond this initial assessment period will be included in an SMP, per DER-10, Section 6.2.2 as part of long-term Site monitoring. The selected remedy includes installing a soil gas venting system as an integral part of a new building. Effectiveness of the soil gas venting system can only be performed after the building is constructed and during the Site management phase. Details for soil vapor monitoring will be appropriately included in the SMP.

6.0 QUALITY ASSURANCE PROJECT PLAN

A Quality Assurance Project Plan (QAPP) provided in Appendix B documents the procedures and protocols to ensure data quality with respect to sampling and analysis of soil and groundwater samples collected in connection with this RAWP. The QAPP is prepared in accordance with NYSDEC DER-10 Section 2.4 and includes sections addressing project organization, sampling procedures, data quality usability objectives, analytical methods, and laboratory quality assurance measures.

7.0 HEALTH AND SAFETY

A HASP was prepared in accordance with 40 CFR 1910 and 1926. The Site HASP addresses general construction health and safety issues and potential health and safety concerns associated with exposure to airborne dust and site-specific COCs. The site-specific HASP is provided in Appendix C.

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8.0 EQUIPMENT DECONTAMINATION

Decontamination procedures will be implemented to prevent tracking or moving contaminated media off-site. To minimize the potential cross-contamination on-site and reduce the extent of decontamination required, the following work practices will be implemented:

1. The amount of equipment and machinery that contacts contaminated soils will be limited to the minimum possible to efficiently complete the work, to the extent practicable.

2. The remedial excavation contractor will limit the volume of excavated soil in the excavator bucket and/or shake the bucket prior to turning the machine to minimize spillage while transferring soil to stockpiles or trucks.

3. Trucks removing excavation soil and debris will not be allowed to enter delineated excavation areas and must remain on the decontamination pad or areas of non-impacted surface soil.

4. The trucks removing soil and debris will be visually inspected for any loose soil or debris on the vehicle tires or body. Dry decontamination methods will be used to remove any loose soil or debris before the vehicle can leave the Site.

5. Excavation equipment will be decontaminated on the decontamination pad before being removed from the Site.

A decontamination pad of sufficient size to accommodate equipment requiring decontamination will be constructed on-site near the exit/entrance to the Site as shown on Sheets 1 and 2. The pad will be constructed of a minimum of 20 mil (or two layers of 10 mil) polyethylene sheeting draped over a soil berm to capture decontamination liquids. The pad will be sloped to one corner to allow collection and removal of decontamination liquids. Water used for decontamination will be containerized in 55-gallon drums or removed directly by a liquid waste hauler for proper off-site disposal.

Equipment decontamination will be conducted using dry methods to the greatest extent possible. If wet methods are required, a power washer or steam cleaner will be used. Only those portions of equipment that contact contaminated media will require decontamination. Decontamination will be performed before the equipment is removed from the Site. The decontamination procedure is as follows:

1. Remove loose soil and debris with a brush or power washer within remedial excavation areas.

2. Move equipment onto the decontamination pad.

3. Wash with a power washer or steam cleaner, if necessary.

4. Proceed directly from the decontamination pad to the stabilized Site access and exit the Site.

Air monitoring will be performed upwind and downwind of the decontamination area during decontamination procedures, consistent with the CAMP (Section 9.0). Persons conducting decontamination activities will wear suitable personal protective equipment (PPE) to protect against skin contact and inhalation of potential contaminated material. Decontamination waste generated from cleanup activities will be disposed off-site in accordance with Federal, State, and local regulations.

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9.0 COMMUNITY AIR MONITORING

A community air monitoring program will be implemented based on New York State Department of Health (NYSDOH) guidelines provided in NYSDEC DER-10. The CAMP will provide for real-time air monitoring at upwind and downwind perimeter locations of the work area during all ground intrusive and soil handling activities, including soil stockpiling, loading trucks for off-site disposal, and equipment decontamination. The site-specific CAMP is provided in Appendix D.

10.0 IMPLEMENTATION SCHEDULE

Remediation will be implemented as soon as possible after receiving NYSDEC approval of this RAWP. The expected duration to perform the remedial action is approximately 3 to 4 weeks after contractor mobilization. The remedial excavation will be performed first and is expected to take up to 2 weeks to complete. The in-situ injection is also expected to take up to 2 weeks to complete.

11.0 REPORTING

Daily Field Reports (DFR) will be prepared for each day remedial activities occur at the Site. DFRs will be provided to the NYSDEC within two (2) business days of completion of each DFR. Written progress reports will continue to be submitted to the NYSDEC on the 10th day of each month as required by the Brownfield Cleanup Agreement. A Final Engineering Report (FER), including a SMP, will be prepared and submitted to the NYSDEC at the conclusion of all activities required by this RAWP. Addendums to the RAWP may be prepared and submitted to the NYSDEC to document any additional changes to this work plan, as necessary.

The FER and accompanying SMP will conform to the requirements set forth in NYSDEC DER-10 Sections 5.8 and 6.2, respectively. The purpose of the FER is to document the completion of the remedial program in accordance with the RAWP and provide the necessary certification, per DER-10, Section 1.5.

The SMP will be prepared in advance of, or in conjunction with the FER and must be approved prior to approval of the FER. The SMP will provide the institutional and engineering controls required for the Site and identify physical components required to be operated, maintained, and monitored to ensure continued effectiveness of the remedy. The SMP is anticipated to include the following elements, based on the scope of the selected remedy and need for continued Site management after completion of the remedy:

- Institutional and engineering controls and environmental easement in compliance with Part 375-1.8 (h).
- An Excavation Work Plan.
- A Monitoring Plan, including provisions for performance monitoring, effectiveness monitoring, procedures for corrective action/contingency measures, and monitoring closeout criteria; and
- A Health and Safety Plan.

NYSDEC DER-10 Section 6.3(a) 6 and 7 stipulate the procedures during the Site management phase of the project "in the event that a periodic certification cannot be provided due to a failure of one or more of the institutional and/or engineering controls" or if corrective measures are warranted based on monitoring performed under an approved SMP. A corrective measures work plan will be submitted for NYSDEC approval if SMP monitoring results indicate the remedy has not achieved the remedial action goals.

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TABLES

Table 1
Standards, Criteria and Guidance for Soil and Groundwater
53 Putnam Street, Saratoga Springs, NY
BCP #C546057

Contaminant of Concern (COC) Soil	Unrestricted Use Soil Cleanup Objectives [(1)] (ppm)	Restricted Residential Use Soil Cleanup Objectives [(1)] (ppm)	Commercial Use Soil Cleanup Objectives[(1)] (ppm)
Volatile Organic Compounds, VOCs			
Benzene	0.06	4.8	44
cis-1,2-Dichloroethene(cis-1,2-DCE)	0.25	100	500
trans-1,2-Dichloroethene	0.19	100	500
Ethylbenzene	1	41	390
Tetrachloroethene (PCE)	1.3	19	150
Toluene	0.7	100	500
Trichloroethene (TCE)	0.47	21	200
Vinyl chloride (VC)	0.02	0.9	13
Pesticides			
4,4,4-DDD	0.0033	2.6	92
4,4,4-DDE	0.0033	1.8	62
4,4,4-DDT	0.0033	1.7	47
Metals			
Arsenic	13	16	16
Barium	350	350	400
Copper	50	270	270
Lead	63	400	1,000
Mercury	0.18	0.81	2.8
Zinc	109	2,200	10,000
PFAS			
PFAS Compounds	[(2)]	[(2)]	[(2)]

Notes:
[(1)] = As provided in 6 NYCRR Part 375-6.8.
[(2)] = There currently are no Soil Cleanup Objectives established by NYSDEC for PFAS.

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Table 1
Standards, Criteria and Guidance for Soil and Groundwater
53 Putnam Street, Saratoga Springs, NY
BCP #C546057

Contaminant of Concern (COC) Groundwater	Class GA Groundwater Standard[(a)] (µg/L)
Volatile Organic Compounds, VOCs	
Benzene	1
cis-1,2-Dichloroethene(cis-1,2-DCE)	5
trans-1,2-Dichloroethene	5
Ethylbenzene	5
Tetrachloroethene (PCE)	5
Toluene	5
Trichloroethene (TCE)	5
Vinyl chloride (VC)	2
Pesticides	
4,4,4-DDD	0.3
4,4,4-DDE	0.2
4,4,4-DDT	0.2
Metals	
Arsenic	25
Barium	1,000
Copper	200
Lead	25
Mercury	0.7
Zinc	2,000
PFAS	
PFAS Compounds	[(b)]

Notes:

[(a)] = As provided in 6 NYCRR Part 703.5 and T.O.G.S. 1.1.1 Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations

[(b)] = There currently are no groundwater standards or guidance values for PFAS in New York, although a minimum contaminant levels of 10 ppt for individual PFAS has been proposed. The USEPA has established a health advisory for drinking water of 70 ppt.

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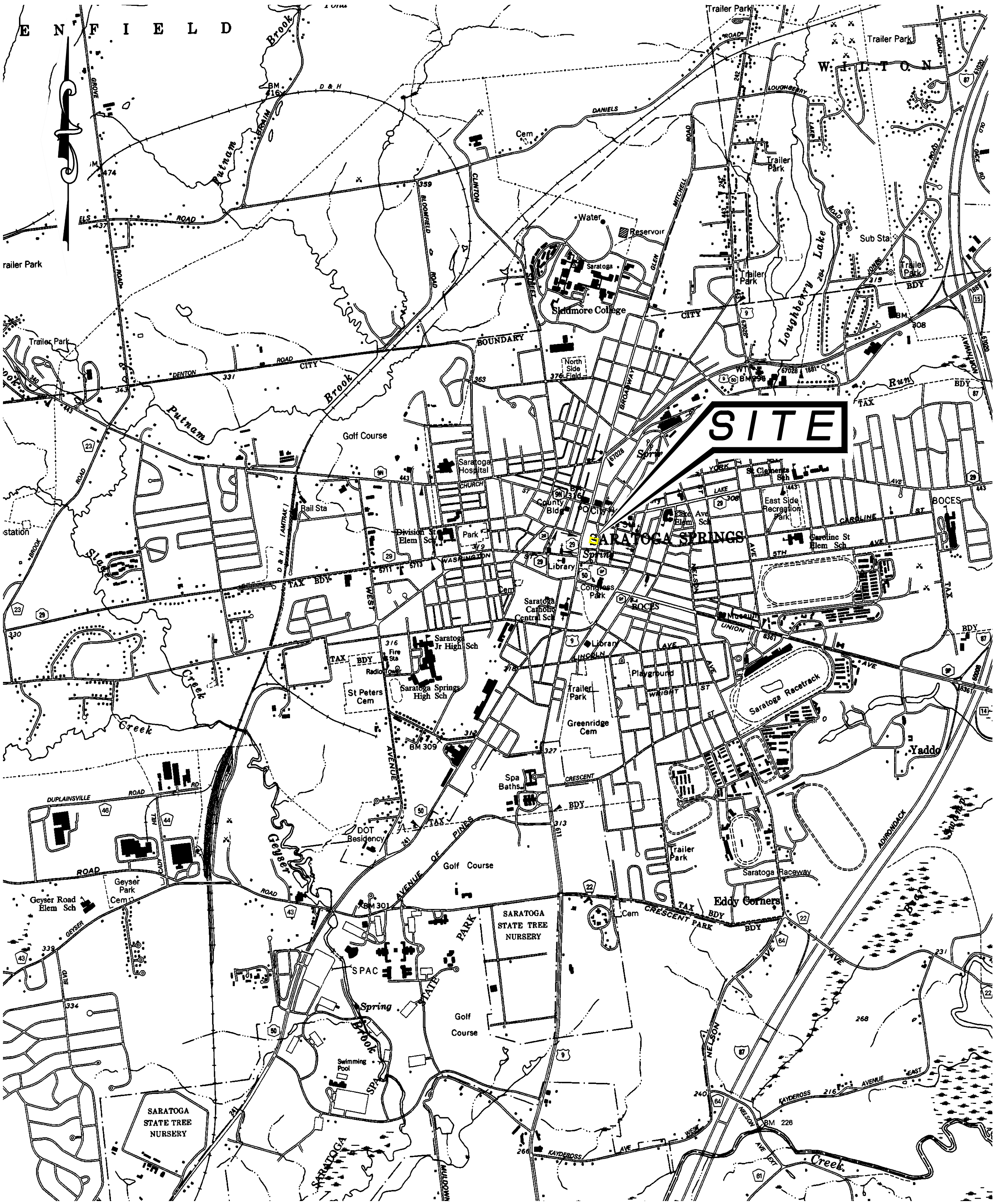
FIGURES



MAP REFERENCE: NYSDOT SARATOGA SPRINGS QUADRANGLE

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Sterling Environmental Engineering, P.C.
24 Wade Road ♦ Latham, New York 12110

SITE LOCATION MAP
PUTNAM RESOURCES, LLC
53 PUTNAM STREET

CITY OF SARATOGA SPRINGS | SARATOGA COUNTY, N.Y.

PROJ. No.: 2015-30	DATE: 2/13/2019	SCALE: 1" = 1000'	DWG. NO. 2015-30016	FIGURE 1

S:\Sterling\Projects\2015 Projects\Putnam Resources – 2015-30\ACAD\2015-30042_F-1 – Site Location Map 2019.dwg CAD 2/13/2019 3:32 PM

LEGEND:

MONITORING WELL LOCATION

0 20 40

SCALE: 1" = 20'

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24 Wade Road ♦ Latham, New York 12110

REMEDIAL ACTION WORK PLAN
SITE MAP – MONITORING WELL LOCATIONS
PUTNAM RESOURCES, LLC
53 PUTNAM STREET
CITY OF SARATOGA SPRINGS SARATOGA CO., N.Y.

PROJ. No.: 2015–30	DATE: 08/18/2020	SCALE: 1" = 20'	DWG. NO. 2015–30070	FIGURE 2

S:\Sterling\Projects\2015 Projects\Putnam Resources - 2015-30\ACAD\2015-30070_F-2 - Well Location Map.dwg TYLER.SWEET 8/18/2020 2:29 PM

APPROXIMATE PROPERTY LINE AND BCP SITE BOUNDARY

WEST AREA OF CONCERN*

EAST AREA OF CONCERN*

Concrete Block Building

Brick Building

gravel

gravel parking lot

retaining wall

foundation

wall

curb

Area = 0.310 ac.

S-106 (0-6")	
12/3/2018	
Mercury, Total	0.958

S-106 (6"-12")	
12/3/2018	
Mercury, Total	0.887

S-106 (12"-24")	
12/3/2018	
Mercury, Total	3.22

S-108 (12"-24")	
12/4/2018	
Benzo(a)anthracene	4.3
Benzo(a)pyrene	4.5
Benzo(b)fluoranthene	6.2
Chrysene	4.6
Dibenzo(a,h)anthracene	0.82
Indeno(1,2,3-cd)pyrene	3.4
Mercury, Total	1.88 J+

30'x20'x2'=1,200 cf
1,200 cf/27=45 CY
45 CYx1.6=72 Tons

65'x40'x2'=5,200 cf
5,200cf/27=193 CY
193 CYx1.6=309 Tons

S-105 (6"-12")	
12/3/2018	
Mercury, Total	1.53

S-105 (12"-24")	
12/3/2018	
Mercury, Total	2.22

S-101 (12"-24")	
11/30/2018	
Mercury, Total	1.27

35'x40'x2'=2,800 cf
2,800 cf/27=104 CY
104 CYx1.6=166 Tons

TOTAL EXCAVATED SOIL EXCEEDING RR SCO=309+72+166=547 Tons
ROUND UP TO 550 Tons (343 CY)

S-108 S-106 S-105 S-101

0 20 40

SCALE: 1" = 20'

LEGEND:

- APPROXIMATE AREA FOR IN-SITU TREATMENT
- AREA TO BE EXCAVATED AND REMOVED TO DEPTH OF 2 FEET
- EXCEEDS RESTRICTED RESIDENTIAL USE SOIL CLEANUP OBJECTIVES (SCOs) BUT IS LESS THAN COMMERCIAL USE SOIL CLEANUP OBJECTIVES (SCOs)
- EXCEEDS COMMERCIAL USE SOIL CLEANUP OBJECTIVES (SCOs) BUT IS LESS THAN INDUSTRIAL USE SOIL CLEANUP OBJECTIVES (SCOs)
- EXCEEDS INDUSTRIAL USE SOIL CLEANUP OBJECTIVES (SCOs)
- 1.88 J+ = CONCENTRATION (mg/kg)

* AREAS OF CONCERN ARE BASED ON PID MEASUREMENTS, VISUAL AND OLFACTORY OBSERVATIONS, AND THE RESULTS OF SOIL AND GROUNDWATER LABORATORY ANALYSIS

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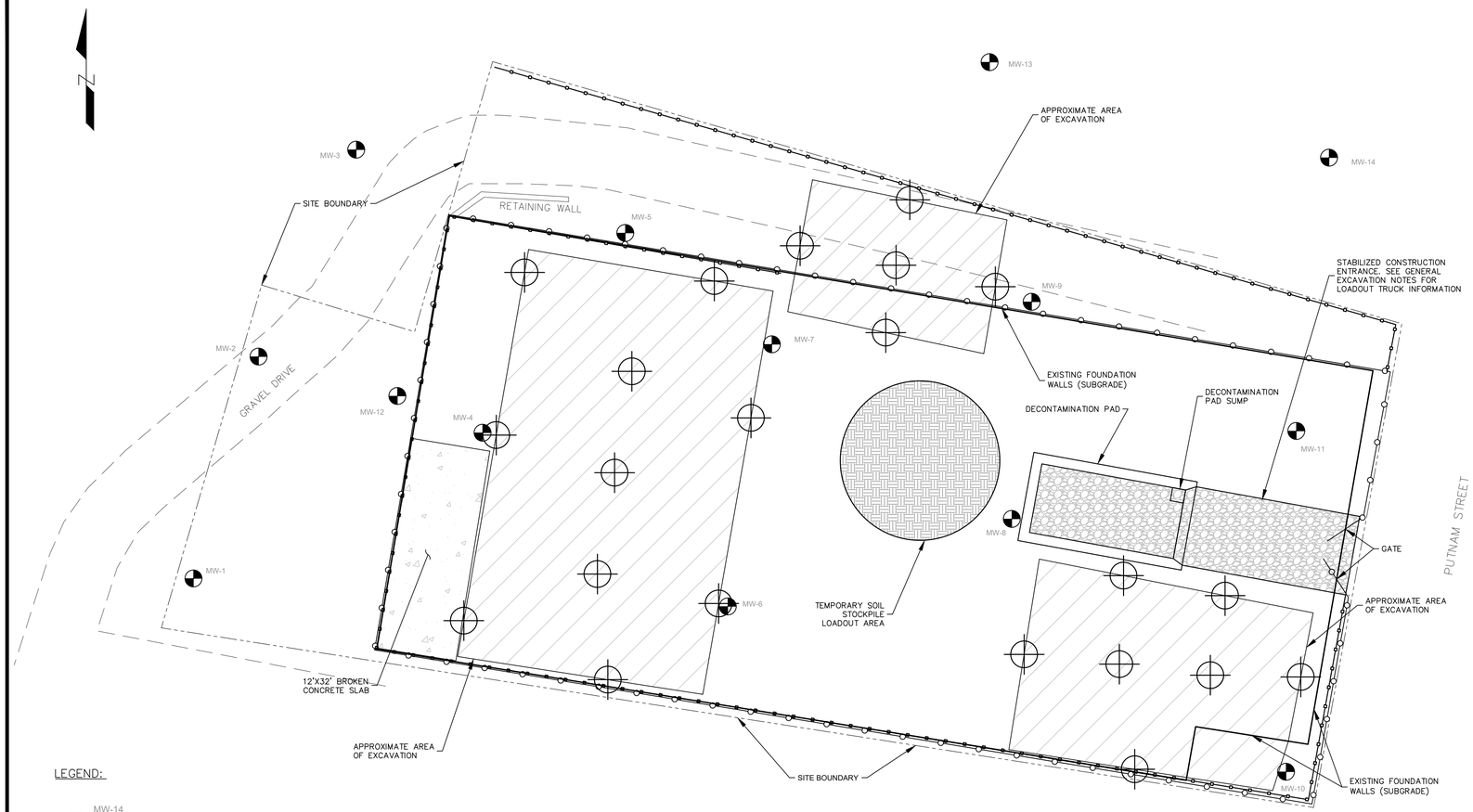
REMEDIAL ACTION WORK PLAN
PREFERRED ALTERNATIVE NO. 2
PUTNAM RESOURCES, LLC
53 PUTNAM STREET
CITY OF SARATOGA SPRINGS SARATOGA CO., N.Y.

PROJ. No.: 2015-30	DATE: 08/18/2020	SCALE: 1" = 20'	DWG. NO. 2015-30069	FIGURE 3

ENGINEERING DESIGN DRAWINGS



LEGEND:

- MW-14 — EXISTING MONITORING WELL
- SILT FENCE
- PROPERTY LINE
- SECURITY FENCE
- DOCUMENTATION SOIL SAMPLE

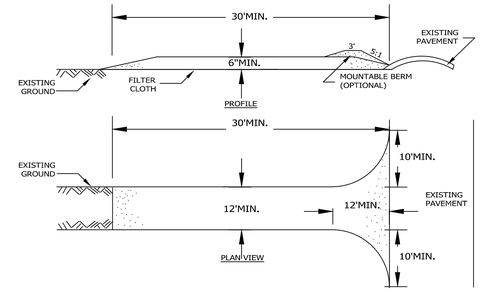
PERSPECTIVE VIEW

SECTION VIEW

SILT FENCE DETAIL
NOT TO SCALE

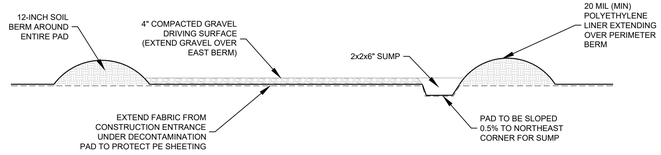
SILT FENCE NOTES:

1. PREFABRICATED UNITS SHALL BE GEOFAB, ENVIROFENCE, OR APPROVED EQUIVALENT.
2. WOVEN WIRE FENCE TO BE FASTENED SECURELY TO FENCE STAKES WITH WIRE TIES OR STAPLES.
3. FILTER FABRIC SHALL BE FASTENED SECURELY TO WOVEN WIRE FENCE WITH TIES SPACED EVERY 24" AT TOP AND MID SECTION.
4. WHEN TWO SECTIONS OF FILTER FABRIC ADJOIN EACH OTHER THEY SHALL BE OVERLAPPED BY 6" AND FOLDED.
5. MAINTENANCE SHALL BE PERFORMED AS NEEDED AND MATERIAL REMOVED WHEN "BULGES" DEVELOP IN THE SILT FENCE.



1. A STABILIZED CONSTRUCTION ENTRANCE IS TO BE INSTALLED IN ACCORDANCE WITH THE NEW YOUR STATE STANDARDS AND SPECIFICATIONS FOR EROSION AND SEDIMENT CONTROL.
2. STONE SIZE – USE 1–4 INCH STONE, OR RECLAIMED OR RECYCLED CONCRETE EQUIVALENT.
3. LENGTH – NOT LESS THAN 30 FEET.
4. THICKNESS – NOT LESS THAN SIX (6) INCHES.
5. WIDTH – TWELVE (12) FOOT MINIMUM, BUT NOT LESS THAN THE FULL WIDTH AT POINTS WHERE INGRESS OR EGRESS OCCURS.
6. GEOTEXTILE – WILL BE PLACED OVER THE ENTIRE AREA PRIOR TO PLACING OF STONE.
7. SURFACE WATER – ALL SURFACE WATER FLOWING OR DIVERTED TOWARD CONSTRUCTION ACCESS SHALL BE PIPED BENEATH THE ENTRANCE. IF PIPING IS IMPRACTICAL, A MOUNTABLE BERM WITH 5:1 SLOPES WILL BE PERMITTED.
8. MAINTENANCE – THE ENTRANCE SHALL BE MAINTAINED IN A CONDITION WHICH WILL PREVENT TRACKING OR FLOWING OF SEDIMENT ONTO PUBLIC RIGHTS–OF–WAY. ALL SEDIMENT SPILLED, DROPPED, WASHED OR TRACKED ONTO PUBLIC RIGHTS–OF–WAY MUST BE REMOVED IMMEDIATELY.
9. WHEN WASHING IS REQUIRED, IT SHALL BE DONE ON AN AREA STABILIZED WITH STONE AND WHICH DRAINS INTO AN APPROVED SEDIMENT TRAPPING DEVICE.
10. PERIODIC INSPECTION AND NEEDED MAINTENANCE SHALL BE PROVIDED AFTER EACH RAIN.

STABILIZED CONSTRUCTION ACCESS
(NOT TO SCALE)



DECONTAMINATION PAD CROSS SECTION
SCALE: N.T.S.

GENERAL NOTES

1. ALL TO BE PERFORMED AT THE DIRECTION OF, AND UNDER FULL TIME SUPERVISION BY THE PROJECT ENGINEER.
2. INSTALL EROSION AND SEDIMENT CONTROL MEASURES AND STABILIZED CONSTRUCTION ENTRANCE PRIOR TO ANY SITE DISTURBANCES.
3. EROSION AND SEDIMENT CONTROL MEASURES INSPECTIONS, MAINTENANCE AND REPAIR OR REPLACEMENT SHALL BE THE RESPONSIBILITY OF THE CONTRACTOR.
4. PRIOR TO REMOVAL OF EROSION AND SEDIMENT CONTROL MEASURES VEGETATION OR ALTERNATIVE STABILIZATION MUST BE ESTABLISHED AND THE PROPERTY OWNER AND PROJECT ENGINEER MUST BE NOTIFIED FOR INSPECTION AND FINAL APPROVAL OF THE WORK.
5. NO WORKER VEHICLES WILL BE ALLOWED ON THE SITE. ONLY REQUIRED EXCAVATION, GRADING, OR OTHER HEAVY EQUIPMENT WILL BE PERMITTED.
6. ALL EQUIPMENT DRIVEN ON SITE THAT DOES NOT REMAIN ON THE STABILIZED CONSTRUCTION ENTRANCE WILL REQUIRE DECONTAMINATION PRIOR TO LEAVING THE SITE.

STATE OF NEW YORK
ANDREW M. MILLSPAUGH
094708
LICENSED PROFESSIONAL ENGINEER

UNAUTHORIZED ALTERATION OR ADDITION TO THIS DRAWING IS A VIOLATION OF SECTION 7209, SUBDIVISION 2 OF THE NEW YORK STATE EDUCATION LAW.

NO.	DATE	RECORD OF WORK	DRN	CKD	APPR
1	02/10/21	LABEL SITE BOUNDARY	TMJ	TMJ	AMM

PROJECT	
PROJ. ENGR.:	AMM
PROJ. NO.:	2015–30
PREPARED BY:	TAS
DRAFTED BY:	TAS
CHECKED BY:	TMJ
APPROVED BY:	AMM
DATUM:	N/A
CONTOUR INTERVAL =	N/A FEET

0 5' 10' 20'
1" = 10'

REMEDIAL DESIGN DRAWING
SOIL EXCAVATION AND REMOVAL REMEDY
53 PUTNAM STREET
PUTNAM RESOURCES, LLC
CITY OF SARATOGA SPRINGS SARATOGA CO., NEW YORK

STERLING
Sterling Environmental Engineering, P.C.
24 Wade Road • Latham, New York 12110

DATE: 10/05/2020 | SCALE: 1" = 10' | DWG. NO. 2015–30071 | SHEET 1 OF 2

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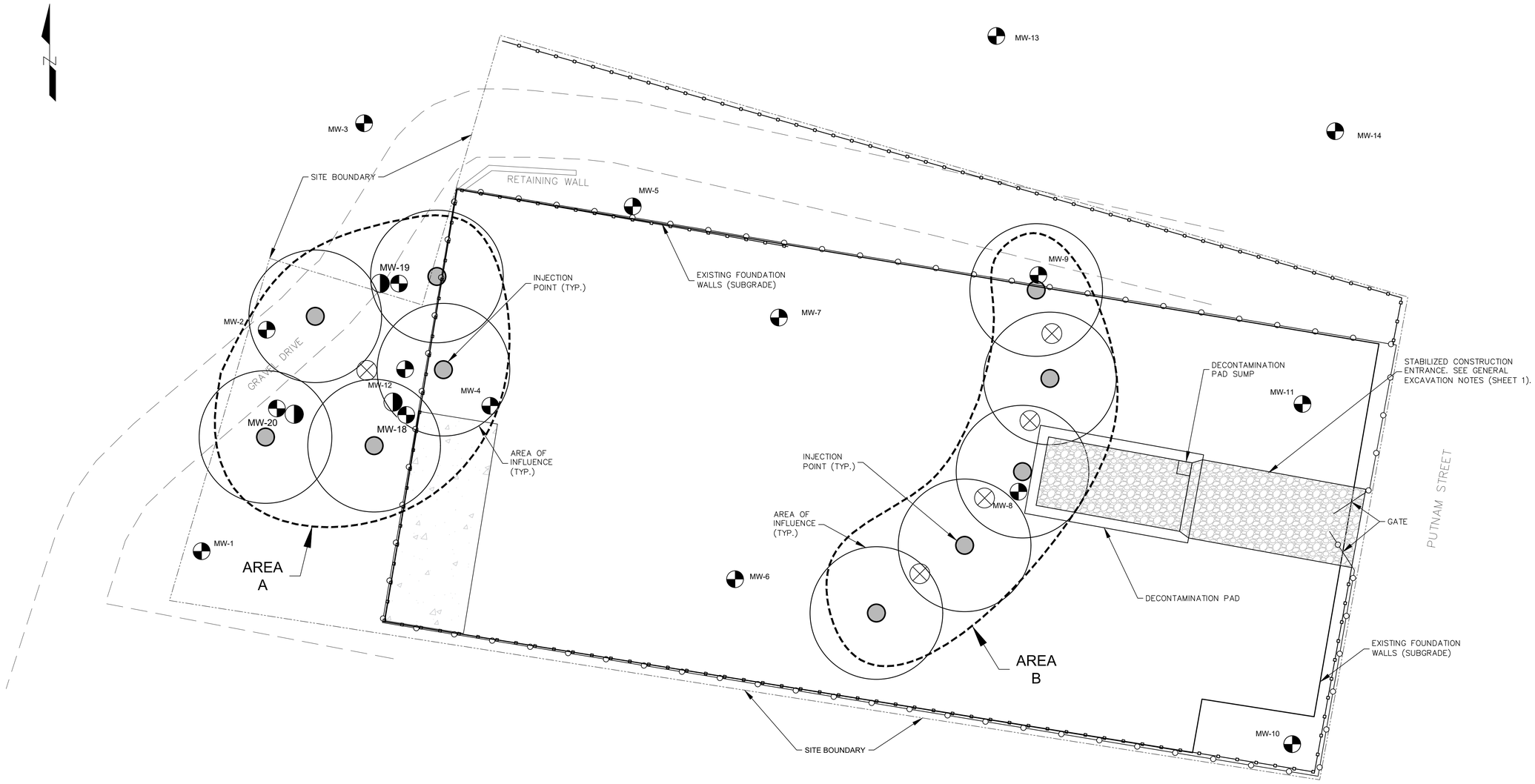


LEGEND:

- MW-14 — EXISTING MONITORING WELL
- MW-20 — EFFECTIVENESS MONITORING SOIL BORING/ MONITORING WELL
- IN–SITU INJECTION POINT
- PRE–INJECTION SOIL BORING
- EFFECTIVENESS SOIL BORING

IN–SITU INJECTION QUANTITIES

AREA A	
ISGS MIXTURE	3,510 GALLONS
AREA B	
VITAMIN B–2	4,766 GRAMS
VITAMIN B–12	686 GRAMS
RED YEAST RICE EXTRACT	116 GRAMS
PROVECT IR	2,500 POUNDS
ZERO VALENT IRON	810 POUNDS
SODIUM SULFITE	100 POUNDS
NUTRIENT	100 POUNDS
CALCIUM PROPIONATE	1,000 POUNDS
WATER	2,000 GALLONS

IN–SITU INJECTION NOTES

1. INJECTION LOCATIONS TO BE DETERMINED BY CONTRACTOR AND CONFIRMED BY PROJECT ENGINEER.
2. ISGS SOLUTION WILL BE THE APPROXIMATE QUANTITY LISTED ABOVE AND WILL TREAT BETWEEN 12 AND 29 FEET BELOW GROUND SURFACE (BGS) WITH FOUR EVENLY SPACED INJECTION INTERVALS.
3. A 10% ISGS SOLUTION WILL BE USED IN AREA A (3,600 GALLONS OF ISGS INJECTED AT RATES FROM 1–20 GPM AND PRESSURES RANGING FROM 10 TO 100 PSI).
4. THE REDUCTIVE DECHLORINATION SLURRY FOR AREA B WILL TREAT BETWEEN 12 AND 29 FEET BELOW GROUND SURFACE (BGS) WITH FOUR EVENLY SPACED INJECTION INTERVALS.
5. A SLURRY FOR AREA B WILL BE THE APPROXIMATE QUANTITIES LISTED ABOVE EVENLY DISTRIBUTED THROUGH INJECTION LOCATIONS AT RATES OF 1–20 GPM AND PRESSURES RANGING FROM 10 TO 100PSI.
6. THE ABOVE VOLUMES, FLOWRATES AND CONCENTRATIONS ARE ESTIMATES BASED ON CALCULATIONS AND KNOWN SITE CONDITIONS. ACTUAL QUANTITIES WILL BE DETERMINED BY CONTRACTOR, ADJUSTED AS NECESSARY BASED ON FIELD CONDITIONS, AND MONITORED DURING THE INJECTION PROCESS.

STATE OF NEW YORK · ANDREW M. MILLSPAUGH · LICENSED PROFESSIONAL ENGINEER · 094708

UNAUTHORIZED ALTERATION OR ADDITION TO THIS DRAWING IS A VIOLATION OF SECTION 7209, SUBDIVISION 2 OF THE NEW YORK STATE EDUCATION LAW.

NO.	DATE	RECORD OF WORK	DRN	CKD	APPR
1	12/03/20	ADDED EFFECTIVENESS SOIL BORING LOCATIONS	TAS	TMJ	AMM
2	04/01/21	MOVE EFFECTIVENESS SOIL BORING LOCATIONS	TAS	TMJ	AMM

PROJECT	
PROJ. ENGR.:	AMM
PROJ. NO.:	2015–30
PREPARED BY:	TAS
DRAFTED BY:	TAS
CHECKED BY:	TMJ
APPROVED BY:	AMM
DATUM:	N/A
CONTOUR INTERVAL =	N/A FEET

0 2' 4' 8' 16'
1" = 8'

REMEDIAL DESIGN DRAWING
IN–SITU INJECTION REMEDY
53 PUTNAM STREET
PUTNAM RESOURCES, LLC
CITY OF SARATOGA SPRINGS SARATOGA CO., NEW YORK

STERLING
Sterling Environmental Engineering, P.C.
24 Wade Road ● Latham, New York 12110

DATE: 10/13/2020 | SCALE: 1" = 8' | DWG. NO. 2015–30072 | SHEET 2 OF 2

S:\Sterling\Projects\2015 Projects\Putnam Resources - 2015-30\Drawings and Figures\ACAD\2015-30072_Sht-2_REDI-IN Plan_R2.dwg 4/7/2021 1:33 PM TYLER.SWEET

APPENDIX A

IET PROPOSAL FOR IN-SITU REMEDIATION

Innovative Environmental Technologies, Inc.

Proposal to Treat to Contaminated Soils and Groundwater using Multiple Technologies

To

Sterling Environmental Engineering, P.C.

For

53 Putnam Street
Saratoga Springs, NY

September 2020

Innovative Environmental Technologies, Inc.
3958 North State Route 3
Sunbury, OH 43074
(740) 965-6100
IET-INC.NET

September 23rd, 2020

Tom Johnson

Sterling Environmental Engineering, P.C.

Dear Mr. Johnson:

Innovative Environmental Technologies Inc. (IET) has completed a remedial design and cost estimate regarding the site located at 53 Putnam Street, Saratoga Springs, NY. The site has been identified as having soils and groundwater impacted by the historical release of semi volatile and volatile organic compounds and petroleum-related compounds. As a result of IET's evaluation of the provided data, a design which will stabilize the present NAPL via *In-Situ Geochemical Stabilization* (ISGS) in Area A and use reductive dechlorination in Area B is proposed. The proposed remedial program is designed to geochemically bind NAPL contamination in-situ and dechlorinate the CVOC's.

Further, the remedial approach presented herein is covered by four IET United States Patents and one IET United States Patent Application.

1) "Apparatus for In-Situ Remediation Using a Closed Delivery System", Patent Issue Date: May 16, 2006 Patent Number 7,044,152.

2) "Method for Accelerated Dechlorination of Matter", Patent Issue Date: October 31, 2006, Patent Number 7,129,388.

3) "Method for Accelerated Dechlorination of Matter", Patent Issue Date: May 12, 2009, Patent Number 7,531,709 (continuation of "388").

4) "Method for the Treatment of Groundwater and Soils Using Mixtures of Seaweed and Kelp", Patent Issue Date, April 3rd, 2012, Patent Number 8,147,694

5) "Inhibition of Methane Production during Anaerobic Reductive Dechlorination, by Restricting the Effectiveness of the Enzymes and Coenzymes that Catalyze Methanogenesis", Patent Issue Date: December 29, 2015, Patent Number 9,221,699.

The following estimate sets forth a lump sum price for the design, implementation and follow up of this process and is presented for budgetary consideration. All costs included in the lump sum price are listed below.

Included in the lump sum prices are:

- All chemicals and materials necessary to complete the proposed plan
- All equipment and personnel required to execute the proposed plan
- Handling and Management of materials on site
- Mobilization/Demobilization of the injection crews
- All per diem for the required crews
- Site Restoration
- Health and Safety Plan
- Final field injection report
- Final plot of injection points
- Six quarterly data analysis reports based on analytical data provided by Sterling Environmental Engineering, P.C.

Thank you for considering IET for your remediation needs. If you have any questions or concerns, please contact our office.

Best Regards,

Wade Meese, Vice President

Innovative Environmental Technologies, Inc.

740-965-6100

Table of Contents

OBJECTIVE

It shall be the objective of IET to utilize two distinct chemistries for the areas of concern at the 53 Putnam site located in Saratoga Springs, New York. An *in situ* stabilization of free product in the petroleum hydrocarbon impacted area will be utilized while the CVOC impacted area will treated using accelerated dechlorination via both abiotic and microbial processes.

In-Situ Geochemical Stabilization (ISGS) entails the use of modified permanganate solutions for the purposes of mass removal and flux reduction (i.e., NAPL stabilization). As the oxidant migrates through the treatment area, various (bio)geochemical reactions destroy the targeted compounds present in the dissolved phase. This causes a “hardening” or "chemical weathering” of the NAPL as it steadily loses its more labile components. This causes a net increase in viscosity of the organic material, which yields a more stable, recalcitrant residual mass. In addition, both the insoluble MnO_2 precipitate that results from permanganate oxidation and other mineral species included in the ISGS formulation accumulate along the NAPL interface, physically encapsulating the NAPL. This encapsulation minimizes NAPL/groundwater contact, thereby reducing the mass flux of dissolved-phase constituents of interest (COI) into the groundwater as below (Photograph 1).

Unlike the typical application of In Situ Chemical Oxidation (ISCO) reagents, ISGS is used to encapsulate NAPL, with chemical oxidation of COI’s being a secondary affect. As a result, the overall oxidant dosing is substantially less than with typical ISCO applications, resulting in rapid, highly effective treatment at a much lower cost.

Photograph 1: Untreated Soil Core and ISGS treated soil core

The chlorinated solvent remedial plan described herein is designed to treat source area and residual contamination through reductions of CVOCs in the saturated zones. It shall be the objective of IET to promote the conditions in-situ, necessary for accelerated dechlorination via both abiotic and microbial processes. Further, through the introduction of a micron zero valent iron colloidal suspension, reduction of the dissolved phased CVOCs will occur while initiating the production of hydrogen for microbial mineralization processes in order to mitigate off-site migration. No additional equipment or maintenance will be required and because no waste streams will be generated, no disposal permitting will be required during the remedial effort. IET proposes to implement a program, which shall:

- Supply all essential microbial elements necessary for dechlorination processes to occur.
- Introduce zero valent iron (ZVI) to further and quickly address dissolved phase compounds while acting synergistically with the anaerobic processes.

Anaerobic reductive dechlorination is a treatment process that has been successfully used to remediate soil and groundwater contaminated with chlorinated solvents. Reductive dechlorination only occurs in the absence of oxygen; and the chlorinated solvent actually substitutes for oxygen in the physiology of the microorganisms carrying out the process. The remedial treatment technology presented herein introduces sodium sulfite as an oxygen scavenger to the subsurface in order to ensure that this process would occur immediately.

In order to accelerate the natural processes, ZVI is proposed to be utilized at the site. ZVI is a reduced material that during the reduction process of the chlorinated compounds is oxidized. ZVI enhanced abiotic degradation of chlorinated volatile organic compounds (CVOCs) is essentially a reductive dechlorination process, which uses zero valent carbonyl iron as the reducing agent, and produces final reaction products such as ethane, ethene, and chloride ions in the degradation of CVOCs.

Anaerobic conditions occur when anaerobic bacteria use the chlorinated contaminant as the electron donor and, in most instances, allow the microorganism to derive useful amounts of energy from the reaction.

The proposed remedial plan for the site incorporates a variety of organic hydrogen donors; each of which has been selected and dosed based on the hydrogen release profile of the individual compounds. Slowly fermented substrates producing lower hydrogen (H_2) levels are more effective and persistent "selective" stimulators of dechlorination than rapidly fermented substrates producing higher H_2 levels. Maintaining and extending a low hydrogen release profile as a result of a single injection event is a focus of the remedial program. The mixed organic hydrogen donors used in this program promote this condition, utilizing varying concentrations of the substrates based on loading and the individual injection areas' long-term treatment objective. The organic hydrogen donors utilized in this program are: propionate, and Provect-IR. Hydrogen is also a substrate for methanogenic bacteria that convert H_2 to methane. By utilizing hydrogen, the methanogens compete with dechlorinating microbes. Therefore the remedial

design introduces the red yeast rice extract which will act as an inhibitor of the enzymes and co-enzymes that play a key role during methanogenesis.

Critical to the sustained microbial activity and general microbial health is sufficient bio available nutrient. The remedial program incorporates nitrogen and orthophosphate (o-PO_4) into the remedial program such that organelle and ATP-ADP formation is not limited throughout the microbial respiratory process. Cobalt-containing corrinoid cofactors such as vitamin B12 and also vitamin B2 are used to mediate the reductive dechlorination of the chlorinated compounds.

More detailed information regarding reductive dechlorination treatment and the materials used in the proposed design can be found in Appendix III.

It is imperative to the success of the proposed remedial technology that delivery of the various materials to the targeted groundwater and soils will be accomplished.

TREATMENT AREAS

AREA A

Area A (NAPL Area), will require 5 injection points based on a radius of influence of 10 feet. The ISGS solution will treat between 12 and 29 feet below ground surface (bgs) with four injection intervals evenly spaced within this zone. A direct push rig will be used to advance the injection screen to the target depths. A 10% ISGS solution is proposed for the area and the solution will target approximately 5% of the pore volume in the treatment area, assuming a 30% effective porosity. This equates to a total of 3,600 gallons of ISGS injected at rates from 1-20 gpm and pressures ranging from 10 to 100 psi. Area A is estimated to require 2 days to complete the implementation.

AREA B

Area B (CVOC area), will require 5 injection points based on a radius of influence of 10 feet. The reductive dechlorination slurry will treat between 12 and 29 feet below ground surface (bgs) with four injection intervals evenly spaced within this zone. A direct push rig will be used to advance the injection screen to the target depths. A total of 4,766.13 grams of Vitamin B-2, 686.53 grams of Vitamin B-12, 7,116.28 grams of Red Yeast Rice Extract, 2,500 pounds of Provect-IR, 810 pounds of Zero Valent Iron, 100 pounds of Sodium Sulfite, 100 pounds of Nutrient and 1,000 pounds of Calcium Propionate will be mixed with 2,000 of water and evenly distributed through injection locations at rates of 1-20 gpm and pressures ranging from 10 to 100psi.Area B is estimated to require 1 day to complete the implementation. A map illustrating the injection layout is presented below.

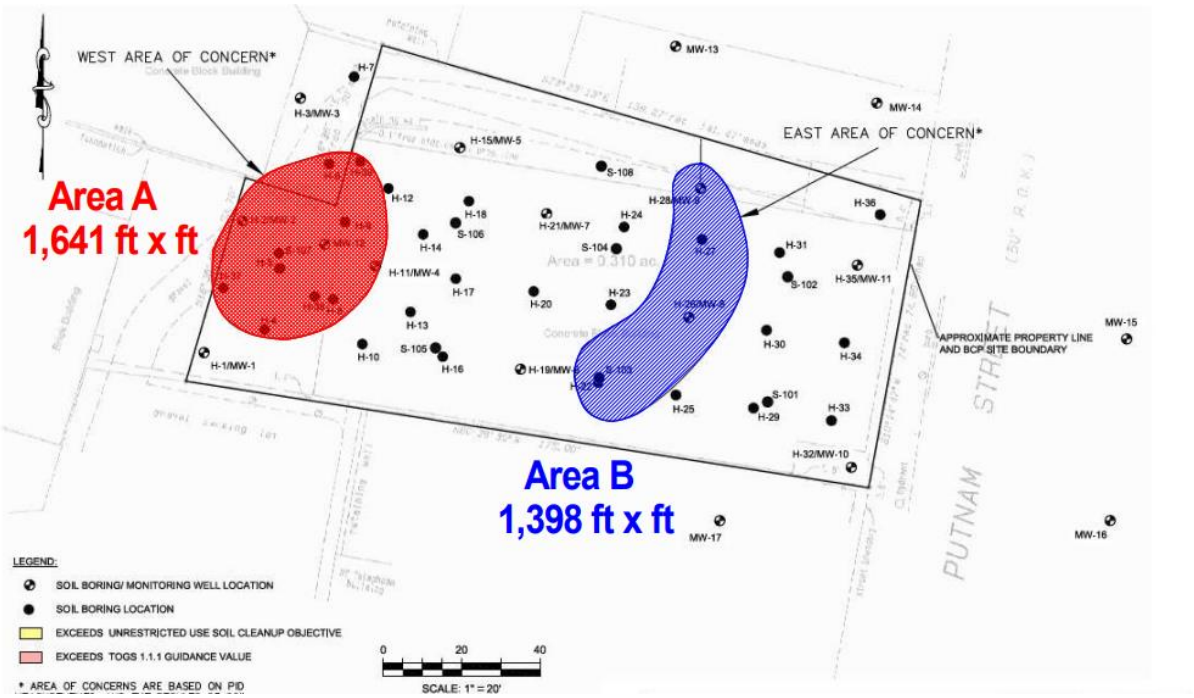


Figure 1. Site Map

SCOPE OF WORK

The injection events will require up to 10 injection points, which will encompass 3,039 square feet. IET estimates that this event will require a total of 3 days to complete all field activities associated with the implementation.

Subsurface Pathway Development

Initially, compressed air shall be delivered to the subsurface via IET proprietary injection trailer system. This process step allows for confirmation of open delivery routes while enhancing horizontal injection pathways. The confirmation of open and viable subsurface delivery pathways insures that upon introduction of the ISGS reagent, the injectate will flow freely thus minimizing health and safety risks associated with oxidant full injection lines and injection tooling when no subsurface delivery route has been established. Confirmation of open and free pathways is accomplished via observed pressure drops and free moving compressed gases to the subsurface.

Treatment area dependent steps

ISGS Emplacement

A 10% solution of In Situ Geochemical Stabilization will then be introduced at pressures between 10 and 100 psi and flow rates between 2-20 gpm. All pressures and flow rates will be monitored to prevent daylighting and mobilization of any NAPL. A small amount of water follows this step in order to rinse the injection equipment.

Reductive Dechlorination via Synergistic Technologies

Sodium Sulfite, Nutrient and Micro Nutrient Injection

A solution of sodium sulfite, calcium propionate, red yeast rice, nutrients and micro nutrients (riboflavin and vitamin B-12) are immediately injected into the subsurface fractures and voids that were developed during the gas injection step. Sodium sulfite acts as an oxygen scavenger, iron reducer and sulfate source. As an oxygen scavenger, the sodium sulfite prevents the oxidation of the ZVI by the dissolved oxygen while promoting anaerobic conditions that are favorable for the biodegradation of the CVOCs. Nutrients, injected as organic ammonia and ortho-phosphate, are required for the maintenance of the microbial metabolic pathways, ATP/ADP synthesis and organelle development. A ZVI and organic hydrogen donor solution is injected immediately following the sodium sulfite/bioslurry solution to reduce concentrations of dissolved-phase CVOCs while providing for rapidly generated hydrogen for the microbial stimulation.

Post Liquid Injection – Compressed Air Injection

Lastly, the injection lines are cleared of liquids and all injectants are forced into the created formation and upward into the vadose zone. This step ensures that all material is injected outward into the formation and minimizes any surface excursions of injectants following the release of the injection pressure. Once the injection cycle is complete, the injection point is temporarily capped to allow for the pressurized subsurface to accept the injectants.

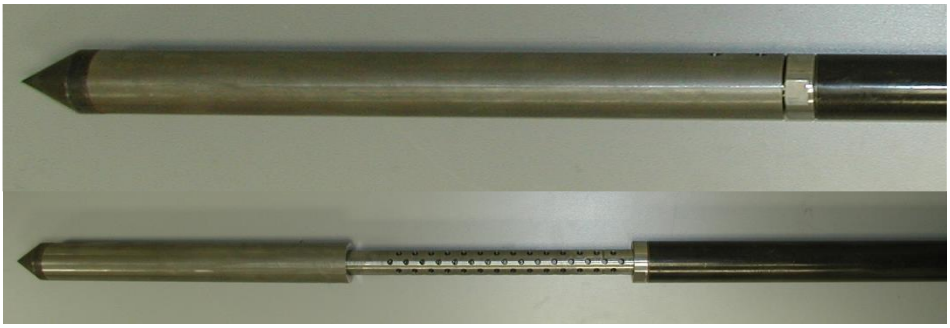
Equipment Description

The injections small occur via IET's mobile oxidation injection trailer and IET's direct-push equipment as described:

Injection Lines: High Pressure Stainless steel Braided Rubber one inch diameter hoses

Injection Trailer: IET Self-contained injection trailer, consisting of: two 220 gallon conical tanks capable of maintaining 30% solids as a suspension via lightning mixers; on-board generator, all stainless steel piping system, 2" pneumatic diaphragm pump with an operating pressure of 110 psi.; on-board 25 CFM/175 psig compressor with 240 gallons of air storage; and self-contained eye wash and safety shower.

Injection Rods: IET proprietary injection rods with retractable injection zones and backflow protection. Injection zones of 18 inches are to be used in combination with 24" injection AWJ-Rods where appropriate.



IET INJECTION SYSTEM
UNITED STATES PATENT 7,044,152

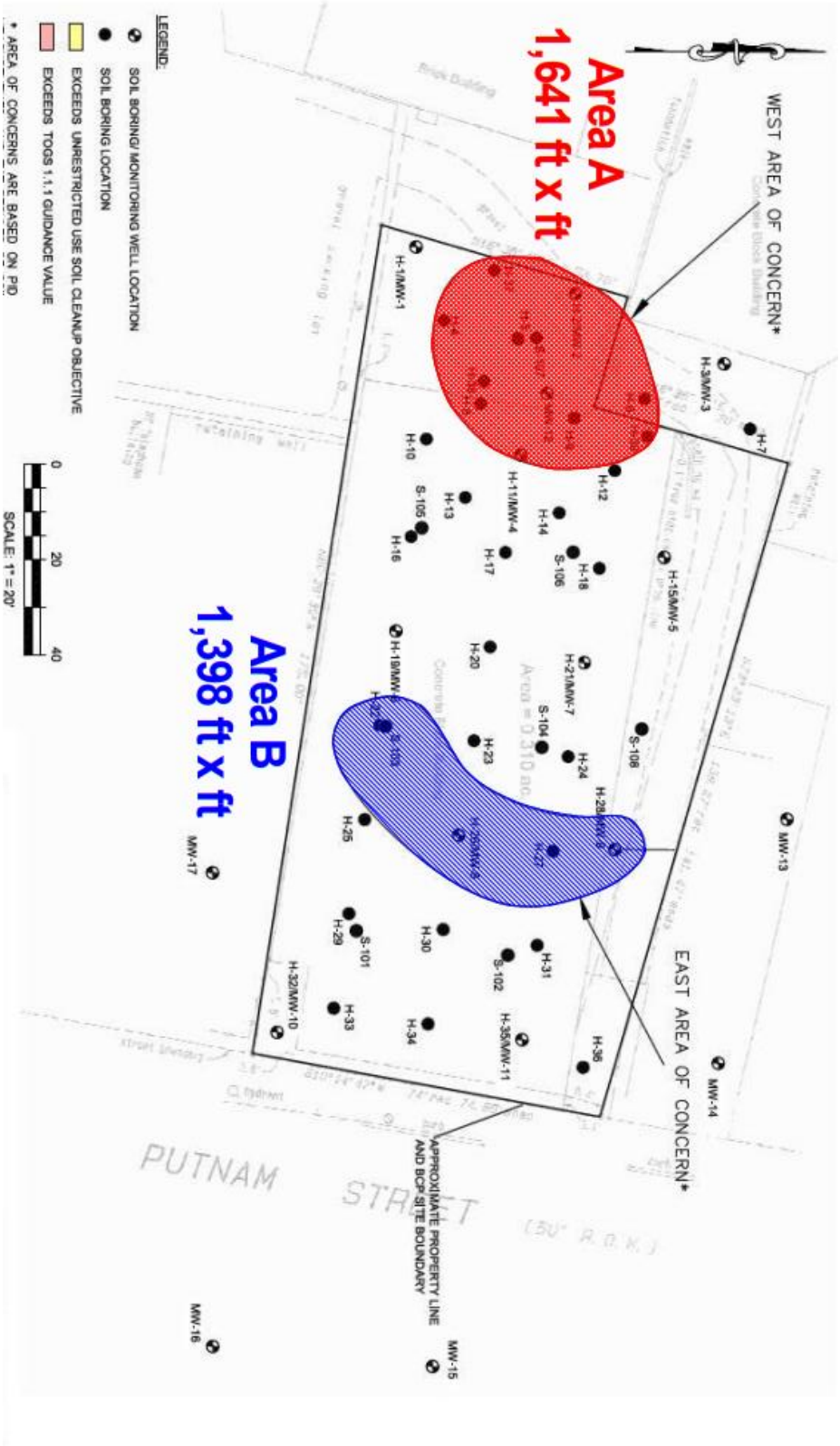
Injection Trailers Include: Multiple Liquid Feed Systems, Stainless Steel Piping, Isolated Compressed Gas Containment, Safety Shower, Eyewash Station, Onboard Generator, Chemical Resistant Construction, Mobile Office Space

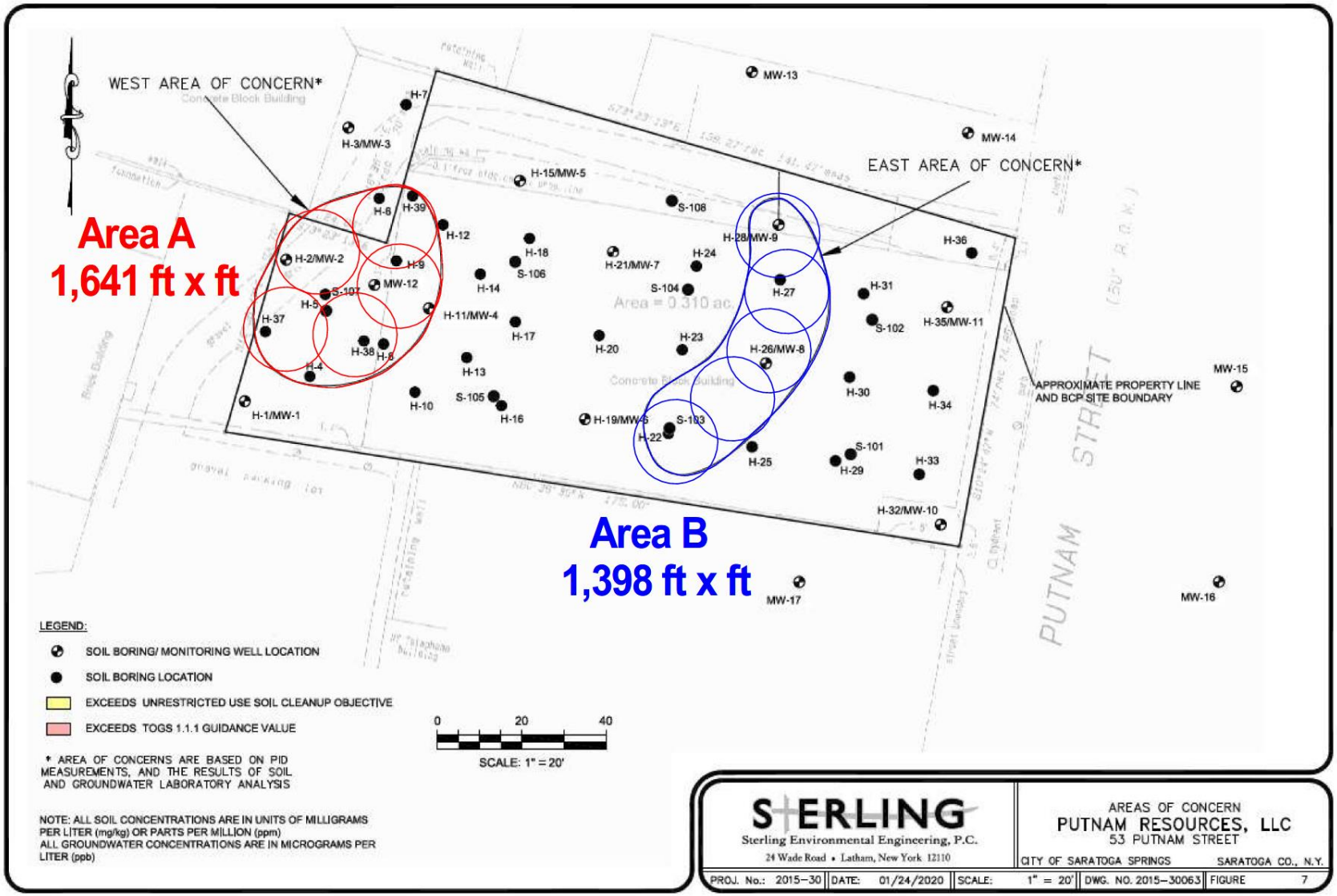
SUMMARY

Innovative Environmental Technologies, Inc. presents this design for the stabilization of NAPL and reductive dechlorination of CVOCs onsite for the defined treatment areas. IET has estimated that it will take **3** days to complete the remedial program with **0.5** day of site set-up and receiving materials.

APPENDICES:

APPENDIX 1 – SITE MAPS




WEST AREA OF CONCERN*
EAST AREA OF CONCERN*
Area A
1,641 ft x ft
Area B
1,398 ft x ft
MW-13
MW-14
MW-15
MW-16
MW-17
H-3/MW-3
H-15/MW-5
H-28/MW-9
H-2/MW-2
MW-12
H-11/MW-4
H-26/MW-8
H-35/MW-11
H-1/MW-1
H-19/MW-6
H-32/MW-10
APPROXIMATE PROPERTY LINE AND BCP SITE BOUNDARY
PUTNAM STREET
LEGEND:
SOIL BORING/ MONITORING WELL LOCATION
SOIL BORING LOCATION
EXCEEDS UNRESTRICTED USE SOIL CLEANUP OBJECTIVE
EXCEEDS TOGS 1.1.1 GUIDANCE VALUE
* AREA OF CONCERNS ARE BASED ON PID MEASUREMENTS, AND THE RESULTS OF SOIL AND GROUNDWATER LABORATORY ANALYSIS
NOTE: ALL SOIL CONCENTRATIONS ARE IN UNITS OF MILLIGRAMS PER LITER (mg/kg) OR PARTS PER MILLION (ppm)
ALL GROUNDWATER CONCENTRATIONS ARE IN MICROGRAMS PER LITER (ppb)
0 20 40
SCALE: 1" = 20'
STERLING
Sterling Environmental Engineering, P.C.
24 Wade Road • Latham, New York 12110
AREAS OF CONCERN
PUTNAM RESOURCES, LLC
53 PUTNAM STREET
CITY OF SARATOGA SPRINGS
SARATOGA CO., N.Y.
PROJ. No.: 2015-30
DATE: 01/24/2020
SCALE: 1" = 20'
DWG. NO. 2015-30063
FIGURE 7

APPENDIX 2 – DOSAGE CALCULATIONS

AREA A

Putnam Resources Area A	Saratoga Springs, NY		
Petroleum Impacted Area			
ISGS Injection			
Parameters	Units	Assumptions	
Target Area	Ft.X Ft.	1641	
Area of Influence of Remediation/Injection	Sq. Ft.	314	
Estimated Injection Points	# Injections	5	
Vertical Impacted Zone	Ft.	19	
Total Volume Targeted	Cu. Yd.	1155	
Porosity	%	30%	
Injection Parameters			
Anticipated ROI	Ft	10	
Pore Volume	Gal	70152.75	
ISGS Concentration in Pore Volume	%	5%	
Estimated Volume of ISGS (no factor of safety)	Gal	3510	
ISGS Concentration (1%, 4.5%, 7%, 10%+)	%	4.5%	
Pounds of ISGS	lbs.	32152	
Terminal Depth of Boring	ft	15'	
Treatment Zone	12-14', 17-19', 22-24, 27-29'		
Intervals Per Point	#	4	
Required Volume of ISGS/interval	gal	180	

AREA B

Putnam Resources Area B	Saratoga Springs, NY		
Chlorinated Solvent Impacted Area			
Parameters	**Units**	**Assumptions**	
Target Area	Ft.X Ft.	1398	
Soil Absorbsion Correction for GAC Constant	%	30	
Area of influence of Remediation Injection(s)	Sq. Ft.	314.159	
Estimated Number of Injections to Treat Area	# Injections	5	
vertical impacted zone	Ft.	19	
Total Volume Targeted	Cu. Yd.	983.7777778	
Porosity	%	30.00%	
Groundwater Flow Velocity	Ft/Yr	5.00	
Injection Depth	Ft - bgs	10-29'	
Volatile Organic Compounds in Water			
TCA	ppb	1	0.001 ppm
PCE	ppb	88	0.088 ppm
TCE	ppb	10	0.01 ppm
c-DCE	ppb	1000	1 ppm
t-DCE	ppb	100	0.1 ppm
1-1 DCA	ppb	1	0.001 ppm
1,1 DCE	ppb	1	0.001 ppm
VC	ppb	680	0.68 ppm
Injection Parameters			
Anticipated Radius of Influence	Ft	10	

Putnam Resources Area B	B2 Calculations		
Vitamin B2 Calculations			
	Number of Atoms/Molecule	Mol. Wt	
Carbon	17	12	204
Hydrogen	20	1	20
Cobalt	0	59	0
Nitrogen	4	14	56
Oxygen	6	16	96
Phosphorus	0	31	0
Grams/mole	376		
1 Molar solution =	376	g/liter	
Conversion molar to Micromolar	1.00E-06		
1 micromolar solution	3.76E-04	g/liter	
50 micromolar solution	1.88E-02	g/liter	
Anticipated radius of injection	10	feet	
Anticipated vertical impact	19	feet	
Estimated pore volume	30.00%	percent	
Calculated impacted liquid	13394.48312	gallons	
Calculated impacted liquid	50703.47642	liters	
B2 dosage/injection	953.2253567	grams	
Total Injections	5		
B2 Required for Project	4766.126783	grams	

Putnam Resources Area B	B12 Calculations		
Vitamin B12 Calculations			
	Number of Atoms/Molecule	Mol. Wt	
Carbon	63	12	756
Hydrogen	88	1	88
Cobalt	1	59	59
Nitrogen	14	14	196
Oxygen	14	16	224
Phosphorus	1	31	31
Grams/mole	1354		
1 Molar solution =	1354	g/liter	
Conversion molar to Micromolar	1.00E-06		
1 micromolar solution	1.35E-03	g/liter	
2 micromolar solution	2.71E-03	g/liter	
Anticipated radius of injection	10	feet	
Anticipated vertical impact	19	feet	
Estimated pore volume	30.00%	percent	
Calculated impacted liquid	13394.48312	gallons	
Calculated impacted liquid	50703.47642	liters	
B12 dosage/injection	137.3050141	grams	
Total Injections	5		
B12 Required for Project	686.5250707	grams	

Chlorinated Solvent Impacted Area				**Zonal Retention Rate**	**1095**	**Days**	**Percent Targeted by ZVI**	**75.00%**	
				ZVI Reaction Constant	**0.18**	**mXm/mL H2O**	**Dosage of IET-ZVI**	**73757.11**	**grams**
Units	**Assumptions**			**ZVI Parameters**	**Units**			**162**	**lbs**
Ft.	10			*ZVI Surface area*	*mXm/g*	*0.25*			
Sq. Ft.	314.159			***Specific Compound half Lives for IET ZVI***					
Ft.	19			PCE	min	14.40			
Cu. Yd.	221.0748519			TCE	min	79.20			
%	30.00%			1,1 DCE	min	468.00			
Gal.	13430.29725			t-DCE	min	4147.20			
mL	50363614.69			c-DCE	min	720.00			
				VC	min	597.60			
				TCA	min	108.00			
				DCA	min	396.00			
				Contaminant Conc. Aqueous			Targeted []		
Ft/Yr	5.00			PCE	ppb	88	66		
Days	1460			TCE	ppb	10	7.5		
Years	3			1,1 DCE	ppb	1	0.75		
Days	1095			t-DCE	ppb	100	75		
Percentage	0.750			c-DCE	ppb	1000	750		
Percentage	100.00%			VC	ppb	680	510		
				TCA	ppb	1	0.75		
				DCA	ppb	1	0.75		
				Clean-up Standard				**min for 1st order**	
				PCE	ppb	5		53.61	
				TCE	ppb	5			
				1,1 DCE	ppb	7			
				t-DCE	ppb	20		7909.94	
				c-DCE	ppb	20		3765.55	
				VC	ppb	1		5376.17	
				TCA	ppb	0.5			
				DCA	ppb	5			
							Total Mins	17105.26734	
							Hours	285.0877889	
							Days	11.87865787	

Organic Hydrogen Donor Calculations

Saratoga Springs, NY

Parameters	Units	Assumptions	
Target Area	Ft.X Ft.	1398	
Soil Absorbsion Correction for GAC Constant	%	30	
Targeted Radius of Influence per injection	Ft	10	
Area of influence of Remediation Injection(s)	Sq. Ft.	314.159	
Estimated Number of Injections to Treat Area	# Injections	5	
Vertical Impacted zone	Ft.	19	
Total Volume Targeted	Cu. Yd.	983.7777778	
Porosity	%	30.00%	
Mass of soil to be targeted	lbs	2065933.333	
Mass of soil to be targeted	grams	937933733.3	
Volume of Groundw ater targeted	gals	59764.5	
Contaminant Conc. - Tetrachloroethene in water	ppm	0.088	
Mass of Contaminant - Tetrachloroethene -w ater	lb.	0.043914955	**Calc Soil**
Mass of Contaminant - Tetrachloroethene-w ater	Grams	**19.93738939**	**ppm**
Mass of Contaminant - Tetrachloroethene-soil	lb.	25.28870871	12.24081547
Mass of Contaminant - Tetrachloroethene-soil	Grams	**11481.07375**	
Contaminant Conc. - Trichloroethene in water	ppm	0.01	
Mass of Contaminant - Trichloroethene in w ater	lb.	0.004990336	
Mass of Contaminant - Trichloroethene in w ater	Grams	**2.265612431**	
Mass of Contaminant - Trichloroethene in soils	lb.	3.770731289	1.83
Mass of Contaminant - Trichloroethene in soils	Grams	**1711.912005**	
Contaminant Conc. - Dichloroethene in water	ppm	1.101	
Mass of Contaminant - Dichloroethene in w ater	lb.	0.549435966	
Mass of Contaminant - Dichloroethene in w ater	Grams	**249.4439286**	
Mass of Contaminant - Dichloroethene in soils	lb.	7.869514863	3.81
Mass of Contaminant - Dichloroethene in soils	Grams	**3572.759748**	
Contaminant Conc. - Vinyl Chloride (V.C.) in water	ppm	0.68	
Mass of Contaminant - V.C in w ater	lb.	0.339342831	
Mass of Contaminant - V.C in w ater	Grams	**154.0616453**	
Mass of Contaminant - V.C. in soils	lb.	0.507939698	0.25
Mass of Contaminant - V.C in soils	Grams	**230.604623**	
H2 Demand outside of VOA	g/Kg	0.075	
H2 Demand outside VOA to maintain first order kinetics	Grams	70345.03	

Evaluated Substrates	Mol Weight	Moles of H2 produced per mole	Grams H+ produced/mole	Grams H+/gram material
Sodium Lactate	113.08	8	16	0.141492748
Sodium Acetate	67.08	4	8	0.119260584
Sodium Butyrate	111.08	8	16	0.144040331
Ethanol	46.1	2	4	0.086767896
Methanol	32	3	6	0.1875
Kelp	873	156	124.8	0.142955326
Provect -IR	180	19.2	38.4	0.213333333
PLE	956	212	424	0.443514644
Sodium Linolate	303.98	16	32	0.105270084
Calcium Propionate	113	12	24	0.212389381

Hydrogen Demand Moles - PCE	Moles PCE	69.45055038	277.8022015	277.8022015
Moles of PLE Required	Moles	1.310387743		
Moles Sodium Propionate Required	Moles	23.15018346		
Moles of Provect-IR Required	Moles	14.46886466		
Moles Kelp Required	Moles	1.780783343		
Hydrogen Demand Moles - TCE	Moles TCE	13.06537818	39.19613455	39.19613455
Moles of PLE Required	Moles	0.184887427		
Moles Sodium Propionate Required	Moles	3.266344546		
Moles of Provect-IR Required	Moles	2.041465341		
Moles Kelp Required	Moles	0.251257273		
Hydrogen Demand Moles - DCE	Moles DCE	39.48557517	78.97115034	78.97115034
Moles of PLE Required	Moles	0.372505426		
Moles Sodium Propionate Required	Moles	6.580929195		
Moles of Provect-IR Required	Moles	4.113080747		
Moles Kelp Required	Moles	0.506225323		
Hydrogen Demand Moles - VC	Moles VC	6.20429465	6.20429465	6.20429465
Moles of PLE Required	Moles	0.029265541		
Moles Sodium Propionate Required	Moles	0.517024554		
Moles of Provect-IR Required	Moles	0.323140346		
Moles Kelp Required	Moles	0.03977112		
Hydrogen Demand Moles - Outside VOA				
Moles of PLE Required	Moles	331.8161792		
Moles Sodium Propionate Required	Moles	5862.085833		
Moles of Provect-IR Required	Moles	3663.803646		
Moles Kelp Required	Moles	450.9296795		
			Total Organic H+ Demand	402.173781 Grams

		Propionate	Provect-IR	Kelp
Sw ag Factor	2			
Contaminant Hydrogen Demand + Background	Grams	666202.8356	663255.0354	406988.9315
Estimated Corrected Value - Organic Donor Demand	Grams	1332405.671	1326510.071	813977.8631
Estimated Corrected Value - Organic Donor Demand	lbs	2934.814254	2921.82835	1792.902782
Percent Allocation Organic Hydrogen Donors	%	34%	86%	0%
Dosage for Area		997.8368463	2498.163239	0
Dosage per point		**200**	**500**	**0**

PUTNAM RESOURCES AREA B

Chlorinated Solvent Impacted Area

	Point	Depth(s)	Location	Type	*B2 - Grams*	*RYR - Grams*	*Provect-IR*	*ZVI - lbs*	*Sulfite*	*Hydrolyzed Kelp*
Injection Point #		**10-29'**	outside		953.23	1423.26	500	162	20	0
Number of Pts		**5**	4	Totals	4766.13	7116.28	2500	810	100	0

Injection Points		
Materials		
4766.13	B2	
7116.28	RYR	
2500	Provect-IR	
810	ZVI	
100	Sulfite	
100	Nutrient	
1000	Propionate	
686.53	B12	

Point Summary	
Number of Points	5
Grams B2/pt	953.23
Grams RYR/pt	1423.26
Pounds Provect-IR	500
Pounds of ZVI/pt	162
Pounds of Sulfite/pt	20
Pounds of Nutrient/pt	20
Pounds of Propionate	200
Cost per Point	**$0.00**

Chlorinated Solvent Impacted Area

Injection Summary:	**Injection #1**	**Injection #2**	**Injection #3**	**Injection #4**
Depth of Injection	**12-14'**	**17-19'**	**22-24'**	**27-29'**
Grams B2/inj	238.31	238.31	238.31	238.31
Grams RYR/inj	355.81	355.81	355.81	355.81
Pounds of ZVI/inj	41	41	41	41
Pounds Provect-IR/inj	125	125	125	125
Pounds of Sulfite/inj	5	5	5	5
Pounds of Nutrient/inj	5	5	5	5
B12	34.33	34.33	34.33	34.33
Propionate	50	50	50	50
Gallons of Sulfite/Nutrient/zvi	100	100	100	100
Yeast/propionate Solution/inj				

APPENDIX 3 – TECHNOLOGY DISCUSSION

Innovative Environmental Technologies, Inc.

ISGS TECHNOLOGY DISCUSSION

In Situ Geochemical Stabilization (ISGS) entails the use of modified permanganate solutions for the purposes of mass removal and flux reduction (*i.e.,* NAPL stabilization). As the oxidant migrates through the treatment area, various geochemical reactions destroy the targeted compounds present in the dissolved phase. This causes a "hardening" or "chemical weathering" of the NAPL as it steadily loses its more labile components. This causes a net **increase in viscosity** of the organic material, which yields a more stable, recalcitrant residual mass. In addition, both the insoluble MnO_2 precipitate that results from permanganate oxidation and other mineral species included in the ISGS formulation accumulate along the NAPL interface, physically coating the NAPL and thereby reducing the flux of dissolved-phase constituents of interest (COI) into the groundwater as seen in the pictures below.

Summary – LNAPL Application: The primary objectives of the piloted technology are to demonstrate both mass removal and mass stabilization. To achieve these objectives the delivery of the ISGS material must effectively distribute the material to the targeted zone(s) and the formation of the Birnessite-like crust must be confirmed. Birnessite (**Photo 1**) is an oxide of Mn and Mg, along with Na, Ca and K with the composition:

$$(Na,Ca,K)(Mg,Mn)Mn_6O_{14} \cdot 5H_2O$$

Photo 1: Birnessite

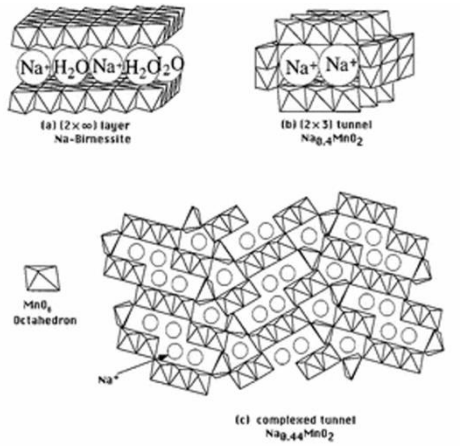
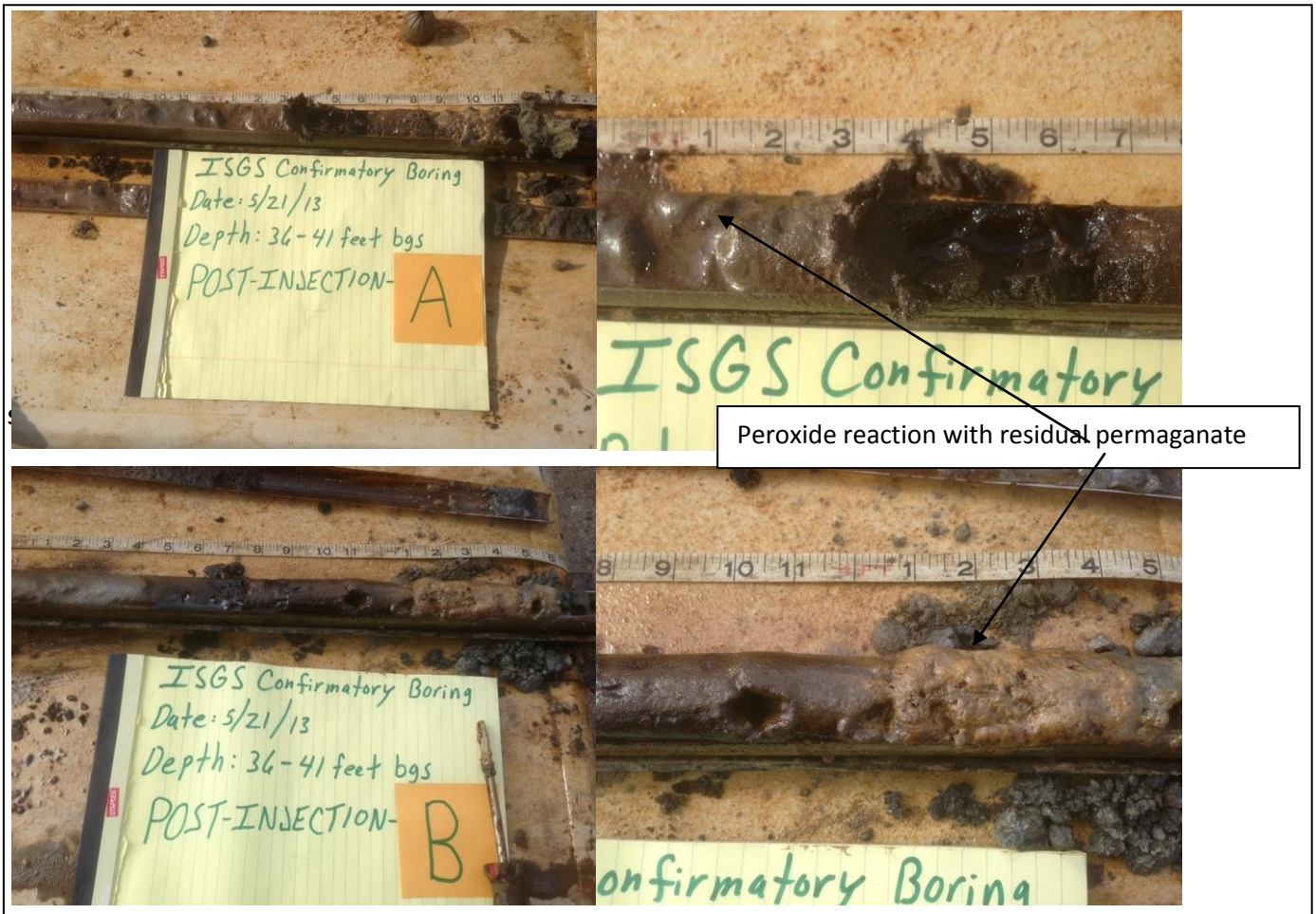


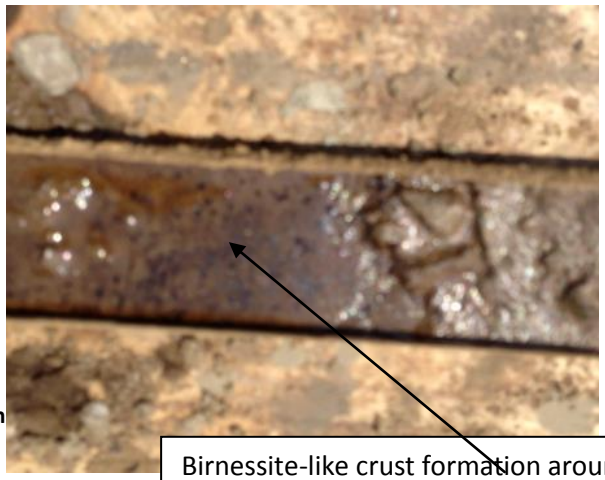
Figure 2 Schematic diagram of the structure of layered and tunnel manganese oxides.

The field sampling techniques one day following the injection event (traditional acetate liner advancement) proved ineffective in its ability to obtain characteristic samples below approximately 38' bgs. It was the opinion of IET that the residual hydrostatic pressure in the primary injection zone resulted in a "heaving" of the unconsolidated sands into the tooling. A consequence of this "heaving" was the inability of the acetate liner sampling tooling to overcome the hydrostatic head pressure. Samples down to 38' bgs were obtained and evaluated in the field. Photos of the day one sampling event are provided below in **Photo 2**. The day one sampling event provided evidence to support the 10' radius design basis of the pilot in the 35-38' injection zone, however without the benefit of the deeper injection zone samples a modification to the sampling technique was required. The day five sampling event utilized a discrete sampling method which allowed for the sampling of the entire injection profile (35-41' bgs). Photos of the day five sampling event are provided below in **Photo 3**.

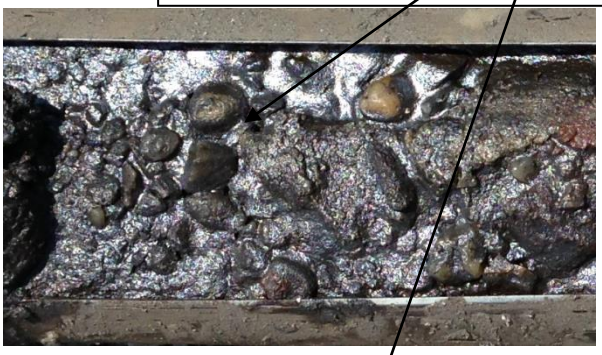


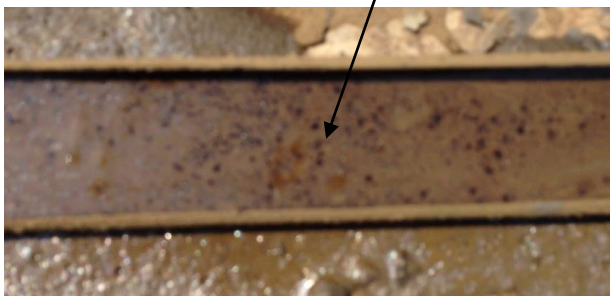
Sample "B" Location – Day 1

Day One sampling occurred so as to confirm delivery and the presence of the ISGS injectant. Day Five was used to evaluate the geotechnical formation.



Birnessite-like crust formation around "globels" of free-phase DNAPL and Saturated soil





In September 2013, a creosote site was injected by IET, prior to injection creosote was seen in samples and a strong odor was noted. Following injection the creosote that was observed above the peat layer was seen to have "solidified", with no associated odor (15 days following injection). In the picture below the peat layer is easily seen and the ISGS formation immediately above it.

The options available for a cost-effective and reliable technology to treat chlorinated hydrocarbon contaminants such as tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichlorethene (cis-1,2-DCE), and carbon tetrachloride in groundwater have in recent years moved away from traditional pump-and-treat processes, especially in cases where:

- NAPL, micro-emulsions or high concentration adsorbed materials are present leading to high dissolved phase concentrations.
- Access to groundwater is restricted by surface structures or uses.
- Local restrictions forbid the implementation of other available technologies such as air sparging or natural attenuation.
- Pump and Treat technologies have been applied, but have reached asymptotic removal rates.
- Contamination is extensive and concentrations are too high for risk based closure but otherwise relatively low (typically 100-7500 ppb).
- The migration of dissolved Chlorinated Aliphatic Compounds (CAHs) across property boundaries or into adjacent surface water presents a long-term remediation requirement.
- The vertical migration of free phase CAHs (DNAPL) into underlying drinking water aquifers is a concern.

The environmental chemistry of a site in part determines the rate of biodegradation of chlorinated solvents at that site. The initial metabolism of chlorinated solvents such as chloroethenes and chloroethanes in ground water usually involves a biochemical process described as sequential reductive dechlorination. The occurrence of different types and concentrations of electron donors such as native organic matter, and electron acceptors such as oxygen and chlorinated solvents, determines to a large degree the extent to which reductive dechlorination occurs during the natural attenuation of a site. To accelerate the natural processes, ZVI and enhanced microbial dechlorination processes are proposed to be utilized at the site. The utilization of coenzymes, oxygen scavengers and nutrients insures that little or no lag phase in the process is experienced and that the most efficient pathways may be utilized.

Program Elements

Oxygen Scavenger (sodium sulfite): Reductive dechlorination only occurs in the absence of oxygen; and, the chlorinated solvent actually substitutes for oxygen in the physiology of the microorganisms carrying out the process. As a result of the use of the chlorinated solvent during this physiological process it is at least in part dechlorinated. The site shall have introduced to the subsurface an oxygen scavenger to ensure that this process would occur immediately.

Zero Valent Iron (ZVI): ZVI may chemically be thought of having been the product of the positively charged metal ions receiving electrons to become the electrically neutral pure metal. The term "reduction" is applied to any chemical reaction that added electrons to an element. Thus ZVI is a reduced material. In a similar manner, the chemical term "oxidation" refers to any chemical reaction that removes electrons from a material. For a material to be reduced, some other material must be oxidized. In the reduction of a chlorinated compound the zero valent iron is oxidized. Zero valent iron enhanced abiotic degradation of chlorinated volatile organic compounds (CVOCs) is essentially a reductive dechlorination process, which uses granular cast iron as the reducing agent, and produces final reaction products such as ethane, ethene, and chloride ions in the degradation of TCE. During this treatment process, the corrosion of iron by water dominates the chemical processes. The corrosion of

iron by water results in ferrous ion generation, hydroxyl ion generation, and hydrogen gas generation. This results in a decrease in ORP (oxidation/reduction potential; that is, reducing conditions are produced) and an increase in pH. Accordingly, the end products of this reaction are ferrous iron, chloride ions, and the dehalogenated compound.

Frequently remedial sites show insignificant or incomplete dechlorination, especially those with high aquifer sulfate levels. It is generally overlooked that the rapid conversion of sulfate to toxic free sulfide during bacterial reductive dechlorination plays a significant role in the "stalling" of the biotic stalling frequently observed. Accumulation of free sulfide is especially important in sites that display both high sulfate and low available iron. Reductive dechlorination inhibition by free sulfide has been observed in microcosms conducted for high sulfate field sites. Free sulfide toxicity to microorganisms can be prevented if ferrous iron precipitates the free sulfide. Further, iron sulfide mineral precipitates have been shown to catalyze reductive dechlorination of chlorinated solvents at rates comparable to metallic iron, on a surface area normalized basis. Microcosms performed at high sulfate sites have been showed to both remove free sulfide toxicity to dehalogenating bacteria and to enhance catalytic reductive dechlorination when ferrous iron is added. Further, ferrous iron, itself, may act as an electron donor.

Injected, colloidal reactive iron is a promising technology, which may be applied, in a synergistic approach with compatible technologies. There are two primary reactions with CAHs that take place which will consume the iron and require stoichiometric consideration:

- the anaerobic iron corrosion reaction in which water is disassociated to form hydrogen gas; and
- the direct adsorption of a chlorinated hydrocarbon onto the surface of the iron, followed by reductive dehalogenation.

Recent research on elemental iron systems suggests that four mechanisms are at work during the reductive process:

- First, the Fe^0 acts as a reductant by supplying electrons directly from the metal surface to an adsorbed halogenated compound.
- Second, hydrogen gas is generated by the anaerobic corrosion of the metallic iron by water.
- Third, metallic iron may act as a catalyst for the reaction of hydrogen with the halogenated hydrocarbon using the hydrogen produced on the surface of the iron metal as the result of anaerobic corrosion with water. Theoretically, these reactions are not kinetically effective without a catalyst; thus, it is thought that impurities in the iron or surface defects act as that catalyst.
- Fourth, solubilized ferrous iron can also act as a reductant, albeit at a rate at least an order of magnitude slower.

Hydrogen gas can be used for reductive dehalogenation by the following reaction:

$$H_2 + X\text{-}Cl = X\text{-}H + H^+ + Cl^-$$

Organic Hydrogen Donors

General Discussion: The proposed remedial plan for the site incorporates a variety of organic hydrogen donors; each has been selected and dosed based on the hydrogen release profile of the individual compounds. Slowly fermented substrates producing lower H2 levels are more effective and persistent "selective" stimulators of dechlorination than rapidly fermented substrates producing higher

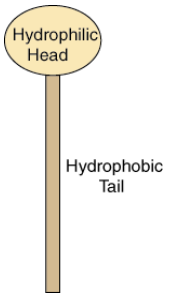
H2 levels. Maintaining and extended a low hydrogen release profile as a result of a single injection event is a focus of IET's program. The mixed organic hydrogen donor recommendations presented herein promotes this condition, utilizing varied concentration of the substrates based on loading and the individual injection areas long-term treatment objective. The general release profile of the organic hydrogen donors within the program are presented below:

Propionate:	Zero to 100 days,
Hydrolyzed Kelp:	60 to 500 days,
Yeast Extract:	150 to 365 days,
Provect-IR:	365 to 1500 days,

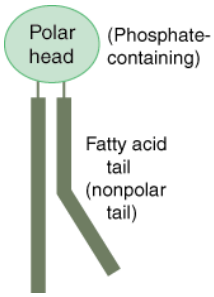
Propionate: Some electron donors are more efficient than others at producing the hydrogen necessary for dehalogenation, and a fundamental question is why this is the case. One very plausible explanation is that various groups of microorganisms compete for hydrogen, and that dehalogenating microorganisms can survive better than others at very low hydrogen concentrations (Fennel et al., 1995; Smatlak, et al., 1996; Yang and McCarty, 1998). On this basis, slug addition of a compound such as formate, ethanol, or glucose is not as effective for dehalogenation as propionate because the former compounds are converted rapidly to hydrogen and acetate, and the latter is not. The rapid conversion is a result of more favorable thermodynamics with respect to hydrogen formation. Such rapid conversion places hydrogen in a concentration range where methanogens and sulfate reducers can compete effectively with dehalogenators.

To further assist the efficacy of the propionate element, IET has proposed the use of a patent pending technology in which the propionate is encapsulated in a lipid bi-layer. A lipid bilayer is a thin polar membrane made of two layers of lipid molecules. This structure is called a "lipid bilayer" because it is composed of two layers of fatty acids organized in two sheets. The lipid bilayer is typically about five to ten nanometers thick and surrounds all cells providing the cell membrane structure. It forms a continuous barrier around cells and thus provides a semipermeable interface between the interior and exterior of a cell and between compartments within the cell. The cell membrane of almost every living organism is made of a lipid bilayer, as are the membranes surrounding the cell nucleus and other sub-cellular structures. The lipid bilayer is the barrier that sustains ions, proteins and other molecules and prevents them from diffusing into areas where they should not be. Lipid bilayers are ideally suited to this role because, even though they are only a few nanometers in width, they are impermeable to most water-soluble (hydrophilic) molecules. With the hydrophobic tails of each individual sheet interacting with one another, a hydrophobic interior is formed and this acts as a permeability barrier. The hydrophilic head groups interact with the aqueous medium on both sides of the bilayer. The two opposing sheets are also known as leaflets. Bilayer-forming lipids are amphipathic molecules (containing both hydrophilic and hydrophobic components). The hydrophilic fragment, typically termed the lipid head-group, is charged, or polar, whereas the hydrophobic section consists of a pair of alkyl chains (typically between 14 and 20 carbon atoms in length).

The structure of the lipid bilayer explains its function as a barrier. Lipids are fats, like oil, that are insoluble in water. There are two important regions of a lipid that provide the structure of the lipid bilayer. Each lipid molecule contains a hydrophilic region, also called a polar head region, and a hydrophobic, or nonpolar tail region (Figure 4). The phospholipid molecule's polar head group contains a phosphate group. It also sports two nonpolar fatty acid chain groups as its tail (Figure 5).

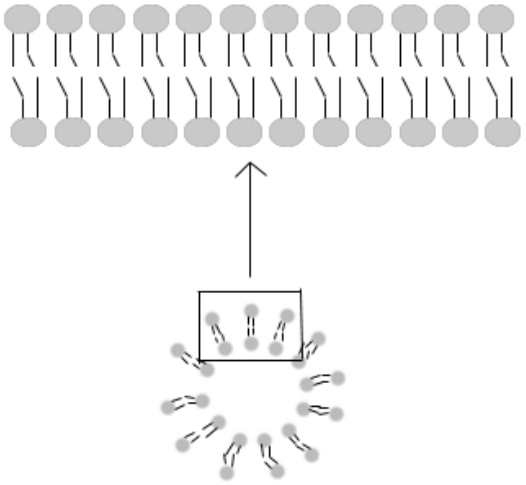


Basic Lipid Structure



Phospholipid Structure

The phospholipids organize themselves in a bilayer to hide their hydrophobic tail regions and expose the hydrophilic regions to water. This organization is spontaneous, meaning it is a natural process and does not require energy. This structure forms the layer that is the wall between the inside and outside of the cell.



Lipid Bilayer Structure

Natural bilayers are usually composed of phospholipids. The phospholipid bilayer is the two-layer membrane that surrounds many types of plant and animal cells. It's made up of molecules called phospholipids, which arrange themselves in two parallel layers, forming a membrane that can only be penetrated by certain types of substances. This gives the cell a clear boundary, and keeps unwanted substances out. Though the phospholipid bilayer works well most of the time, it can be damaged, and some types of unwanted substances can bypass it.

In an aqueous environment the lipids self-assemble into structures that minimize contact between water molecules and the hydrophobic components of the lipids by forming two leaflets (monolayers); this arrangement brings the hydrophobic tails of each leaflet in direct contact with each other, and leaves the head groups in contact with water (Figure 7).

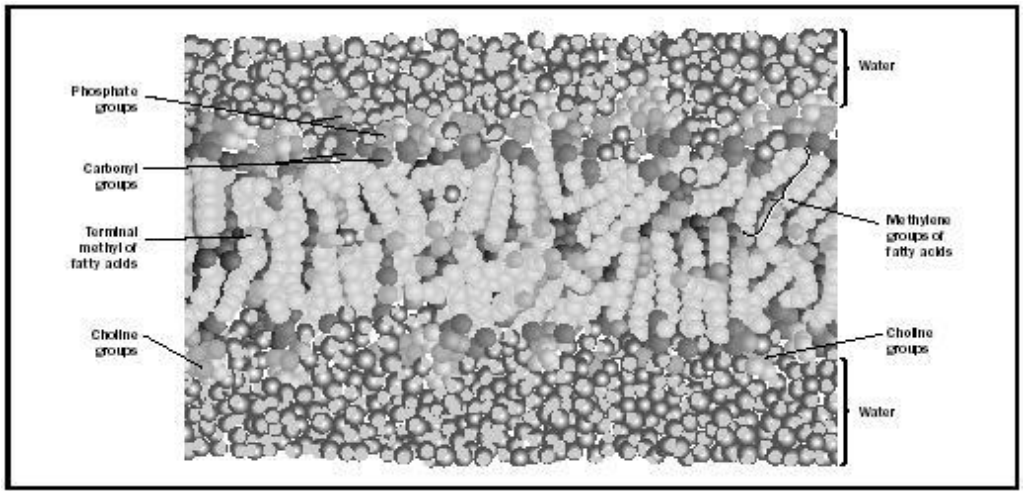


Image of a dipalmitolyphosphatidylcholine lipid bilayer

A potential major challenge in in-situ remediation is to engineer structures and materials that can efficiently encapsulate organic hydrogen donors at certain concentration, and controllably release their content at the target site over a specific period of time. Encapsulation prevents the species from direct biological interactions and from direct exposure to the environmental conditions that prevail on any given site. Moreover, encapsulating organic hydrogen donors can help control their efficiency by controlling their biodistribution and kinetics of release.

Among a wide variety of carriers, lipid-based systems present numerous advantages over other formulations. These carriers are biocompatible, biodegradable and can easily be produced by versatile and up-scalable processes. Lipid-based systems have been used for the encapsulation of a wide variety of various agents, while controlling their kinetics of release. The internal physical state of lipid core nanoparticles has been shown to dramatically affect the encapsulation, while maintaining significant prolonged release rates.

Based on all the above, it can be concluded, that due to the existence of the complicated structure of a potential lipid bi/multilayer electron donor, the release rates for the cations and anions in the solution will be significantly enhanced and will be much slower compared to single layer electron donors.

During in-situ reductive dechlorination the presence of a lipid multilayer compound will prove to be very effective since it will have the potential of lasting for a longer period of time in the environmental media under anaerobic conditions. At the same time the encapsulated material will also have the potential to decrease the amount of hydrogen provided during the process, which positively affects reductive dechlorination.

IET makes this recommendation based on a series of experimental procedures that were performed using encapsulated calcium propionate 80% in a distilled monoglyceride matrix. The results of the encapsulated material were compared with those of regular calcium propionate and the release rates of both materials in solution are presented below.

Monoglycerides are among the most promising polar lipid compounds able to bring new or improved functionality to food products since they can form self-assembly structures in both lipid and aqueous phases.

Two different dosages (0.5 g/L and 1 g/L) of both the regular calcium propionate (RCP) and the encapsulated 80% calcium propionate (ECP) were tested in order to compare the calcium release rates of

both materials. The materials were placed in capped 250-ml flasks and were mixed with the use of magnetic stirring plates. All the experiments were performed in duplicates. As the results on Table 1 show, ECP showed much slower release rates upon the completion of the 14-day experimental procedure. In fact the 0.5 g/L ECP did not show any release of calcium during the first 2 days of the mixing procedure, while the release was increased to 5.8% of total calcium content 14 days upon the start of the experiment. Similarly the 1 g/L ECP showed a 2-day calcium release of 11.7%, which increased to 17.5% during the 14-day sampling period. Conversely RCP showed much higher calcium release rates in the solution. For the 0.5 g/L RCP the amount of calcium released was at 37.4% after 2 days of mixing and 56.1% after 14 days. For the 1 g/L RCP calcium release was at 56.1% after 2 days and at 65.4% after 14 days.

2 DAYS - CAPPED				
Material	Dosage (g/L)	Available calcium (mg/L)	Calcium in Solution (mg/L)	% release in solution
ECP	0.5	86	0	0.0
RCP	0.5	107	40	37.4
ECP	1	171	20	11.7
RCP	1	214	120	56.1
14 DAYS - CAPPED				
Material	Dosage (g/L)	Available calcium (mg/L)	Calcium in Solution (mg/L)	% release in solution
ECP	0.5	86	5	5.8
RCP	0.5	107	60	56.1
ECP	1	171	30	17.5
RCP	1	214	140	65.4

Provect-IR: Provect-IR contains high quality ZVI to uniquely elicit ISCR reactions, and it is composed of a hydrophilic, solid and complex carbon source and hence it should generate little or no methane (< 5 mg/L). Provect-IR will last in the subsurface for at least 3 to 5 years, and there is some speculation that the pH buffering from iron on Provect-IR likely also decreases the probability of methane generation by suppressing the activity of methanogens that are perhaps more active at the more acidic pHs resulting from various fermentation processes.

The hydrophilic organic component of Provect-IR, which is composed of cellulose and hemicellulose, may be treated during the manufacturing process so that the components more easily undergo hydrolysis to glucose while maintaining an overall longevity of 3 to 5 years. Hydrogen gas is produced during glucose fermentation via several enzymatic pathways, depending on site conditions and microbial assemblages:

$$\text{Glucose} + 6H_2O \rightarrow 6CO_2 + 12H_2$$

$$Glucose + 2H_2O \rightarrow 2Acetate + 2CO_2 + 4H_2 + 2H^+$$

ZVI Component: Provect-IR also contains ZVI, which, as it corrodes, also serves as a source of hydrogen. Water corrosion of granular iron produces hydrogen and hydroxide resulting in an increase in pH and decline in redox potential (Eh):

$$Fe° + 2H_2O \rightarrow Fe^{2+} + H_2(aq) + 2OH^-$$

Nutrient: Critical to the sustained microbial activity and general microbial health is sufficient bio available nutrient. IET has incorporated nitrogen and o-PO_4 into the remedial program such that organelle and ATP-ADP formation is not limited throughout the microbial respiratory process.

Program Enhancements

Vitamins: Recent studies suggest that metal – containing coenzymes, found in certain types of anaerobic microorganisms, and can reductively dechlorinate one- and two-carbon solvents. Cobalt-containing corrinoid cofactors such as vitamin B12 mediate the reductive dechlorination of carbon tetrachloride and tetrachloroethene. In these biological systems the rate-limiting step to complete dechlorination to ethylene is the last stage conversion of vinyl chloride. The rate of that process has been found to be significantly enhanced by the presence of vitamin B12, which acts as an electron carrier. It is the core of B12, which contains cobalt, and the various oxidation states the cobalt obtains, which allows for the electron transfer intra-cellularly. The existence of the cobalt core has also been seen to catalyze the surface reaction of the iron lowering the necessary activation energy required for the electron transfer.

Red Yeast Rice: Researchers have found that red yeast rice, which is an Asian dietary staple made by fermenting yeast (*Monascus purpureus*) on rice, contains active ingredients of the statin drugs such as Lovastatin. Thus, studies have shown that red yeast rice can successfully inhibit the key enzyme hydroxymethylglutaryi-SCoA (HMG-CoA) reductase, resulting in the inhibition of methanogenic activity.

Miller and Wolin (2001) also used Lovastatin to inhibit the formation of the key precursor mevalonate. Mevalonate is formed by reduction of hydroxymethylglutaryi-SCoA (HMG-CoA). Based on their results they found that lovastatin inhibited the growth of *Methanobrevibacter* and CH_4 production. In fact 4 nmol/ml of culture medium resulted in 50% inhibition of growth and concentrations ≥10 nmol/ml of culture medium completely inhibited growth. Methane formation was also significantly inhibited. At the same time the populations of the nonmethanogens were not affected.

Coenzyme M (CoM; $HSCH_2CH_2SO_3^-$) is a cofactor which is found in all methanogens but not in other bacteria or archaea (Liu and Whitman 2008). CoM is involved in the terminal step of methane biosynthesis, where the methyl group carried by CoM is reduced to methane by methyl- CoM reductase. The methanogenic inhibitors involved in this group usually include 2-bromoethanesulfonate (BES), 2-chloroethanesulfonate (CES), 2-mercaptoethanesulfonate (MES), and lumazine (Liu et al. 2011). These inhibitors can competitively constrain the methyl transfer reaction at the terminal reductive step during methane formation in methanogens using H_2 and CO_2. Under normal circumstances, these compounds can inhibit all the groups of methanogens at relatively low concentrations. A traditional structural analog of CoM and BES has been widely used and considered as a methanogen-specific inhibitor in microbiological studies. Conrad et al. (2000) reported that 10 mM BES is the optimum concentration to inhibit the anaerobic methanogens in the rice roots systems. In the thermophilic environment of an

anaerobic digester, complete inhibition of the methanogenesis is achieved with the use of at least 50 mM BES. A higher BES concentration is needed for the inhibition of the hydrogenotrophic methanogens than the acetoclastic methanogens (Zinder et al. 1984); however, a similar system requires, only 10 mM of BES in order to inhibit the methanogenesis process (Siriwongrungson et al. 2007). Other studies show that concentrations of 5–20 mM in the soil (Wüst et al. 2009) are really effective in inhibiting methanogenesis. MES and CES also have similar inhibition effects and were used to decrease the methanogenic activity in the continuous-flow methanogenic fixed-film column (Bouwer and McCarty 1983). Various reports show that the pterin compound lumazine [2, 4-(1H, 3H)-pteridinedione] completely inhibited the growth of several methanogenic archaea at a concentration of 0.6 mM and was bactericidal for *M. thermoautotrophicum* strain Marburg (Nagar-Anthal et al. 1996).

Technology Summary: The application of these two synergist technologies: colloidal iron and microbial reductive dechlorination process may be further enhanced through microbial amendments and reducing agents. The proposed treatment technology presented herein applies these technologies.

Critical to the success of the proposed remedial technologies is the successful delivery of the various materials to the targeted groundwater and soils

IET PATENTS:

TITLE

Use of encapsulated substrates to control the release rates of organic hydrogen donors and accelerate the biotic process of anaerobic reductive dechlorination in soil and groundwater

Inventors: Michael Scalzi, Doylestown, PA
Antonis Karachalios, North Wales, PA

Assignee: Innovative Environmental Technologies, Inc.
Pipersville, PA (US)

FIELD OF THE INVENTION

The present invention relates to the mediation of subsurface soil and ground water contamination. More specifically, it relates to the introduction in the subsurface of encapsulated fermentable hydrogen donors, in order to control the release rates of hydrogen into the solution. The presence of the organic hydrogen donors, will allow for the anaerobic microorganisms present, to accelerate the reductive dechlorination of the organic compounds, resulting into the dehalogenation of soil and groundwater.

BACKGROUND OF THE INVENTION

Chlorinated solvents are one of the most frequently occurring types of contaminants in soil and groundwater at Superfund and other hazardous waste sites in the United States. They are organic compounds that contain chlorine atoms, and their properties make them ideal for many industrial-cleaning applications such as degreasing oils and fats. Common solvents include Tetrachloroethene (PCE) and Trichloroethene (TCE), used extensively in the dry-cleaning industry, and 1,1,1 - Trichloroethane (TCA) and Methylene Chloride used as industrial degreasers.

Chlorinated Solvents when released into the subsurface will tend to sink through the saturated zone as they are denser than water. As a result small droplets (ganglia) get trapped in the soil ‘pore-space’ as a Non-Aqueous Phase Liquid (NAPL), which can act as a long-term source of dissolved phase contamination. These NAPL source zones can hamper any site remediation effort, as they are difficult to treat and detect.

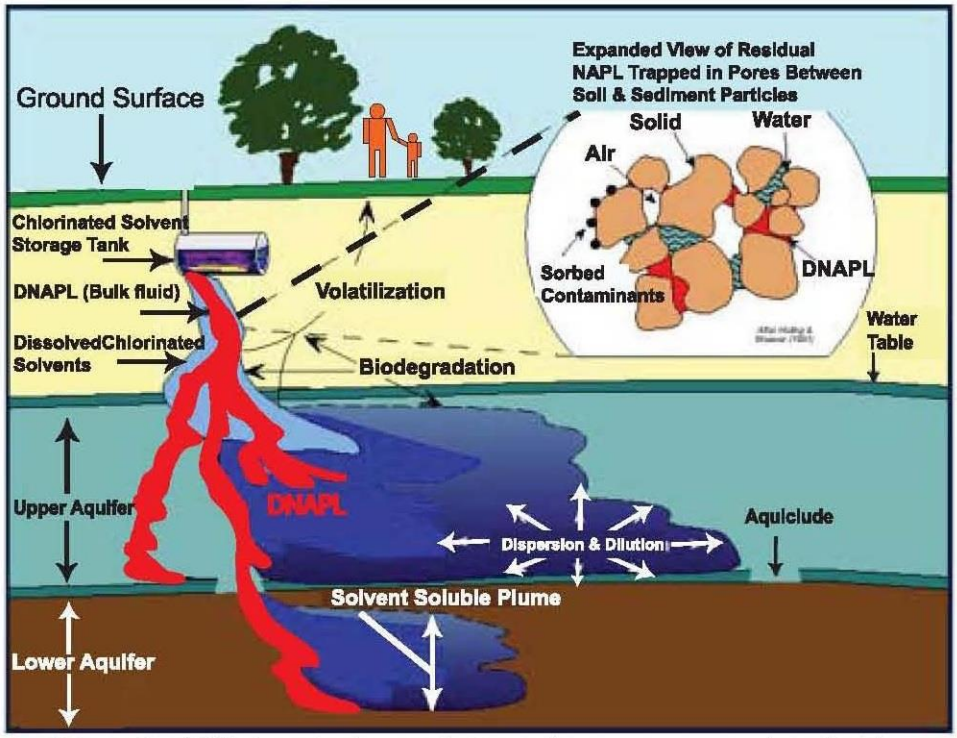


Figure 1. Chlorinated solvent pollution as dense NAPL migrate downward in an aquifer

Anaerobic reductive dechlorination is one treatment process that has been successfully used to remediate soil and groundwater contaminated with chlorinated solvents. The occurrence of different types and concentrations of electron donors such as native organic matter, and electron acceptors such as oxygen and chlorinated solvents, determines to a large degree the extent to which reductive dechlorination occurs during the natural attenuation of a site.

Reductive dechlorination only occurs in the absence of oxygen; and the chlorinated solvent actually substitutes for oxygen in the physiology of the microorganisms carrying out the process. Remedial treatment technologies usually introduce an oxygen scavenger to the subsurface in order to ensure that this process would occur immediately.

Anaerobic conditions occur when anaerobic bacteria use the chlorinated contaminant as the electron donor and, in most instances, allow the microorganism to derive useful amounts of energy from the reaction. It has been shown that vinyl chloride can be oxidized to carbon dioxide, water, and chloride ion via Fe (III) reduction. Significant anaerobic mineralization of DCE, VC, and methylene chloride also has been reported in the literature.

Halorespiration is a type of anaerobic respiration in which a chlorinated compound is used as a terminal electron acceptor. In this reductive dechlorination process, which enables the conservation of energy via electron transport phosphorylation, one or more chlorine atoms are removed and replaced by hydrogen. Halorespiration, also referred to as dehalorespiration, occurs when the organic compound acts as an electron acceptor (primary growth substrate) during reductive dechlorination. During dehalorespiration, the chlorinated organic compounds are used directly by microorganisms (termed dehalorespirators), such as an electron acceptor while dissolved hydrogen serves as an electron donor:

$$H_2 + C - Cl \rightarrow C - H + H^+ + Cl^-$$

where C – Cl represents the chlorine bond to the carbon in the chlorinated ethene molecule. Dehalorespiration requires not only the presence of competent microorganisms, but also the appropriate quantity and quality of electron donors, which serve as the driving force for dehalorespiration. A variety of electron donors have been shown to sustain reductive dechlorination, however only recently, it has been recognized that dissolved hydrogen is the actual electron donor in dehalorespiration (Wang, 2000).

Dehalorespiration occurs as a two-step process which results in the interspecies hydrogen transfer by two distinct strains of bacteria. In the first step, bacteria ferment organic compounds to produce hydrogen. During primary or secondary fermentation, the organic compounds are transformed to compounds such as acetate, water, carbon dioxide, and dissolved hydrogen. Fermentation substrates are either biodegradable nonchlorinated contaminants, or naturally occurring organic carbon. In the second step, the nonfermenting microbial consortia utilize the hydrogen produced by fermentation for dehalorespiration. Although compounds produced during fermentation have been demonstrated to drive dehalorespiration, hydrogen appears to be the most important electron donor for this process.

Dehalorespiration is targeting the addition of sufficient substrate in order to establish and maintain anaerobic conditions, conducive to reductive dechlorination for a period of time, and sufficient to degrade all constituents of concern and their daughter products. Common substrates used include acetate, propionate, butyrate, benzoate, glucose, lactate, formate, methanol, toluene, molasses, cheese whey, corn steep liquor, corn oil, hydrogenated cottonseed oil beads, solid food shortening, beef tallow, melted corn oil margarine, coconut oil, soybean oil, and hydrogenated soybean (Sieczkowski, 2012). These compounds serve as the precursors to dissolved hydrogen generation via fermentation. Obligate proton reducers are required to ferment organic substrate present in the subsurface environment to waste products of acetate, formate, dissolved hydrogen, and carbon dioxide (Zehnder, 1988). After fermentation, dissolved hydrogen becomes available for subsequent use by other microorganisms, such as methanogens and dehalorespirators. This syntrophic relationship of hydrogen producers and consumers is known as interspecies hydrogen transfer. Dehalorespiration relies on the presence of fermentable organic substrates that produce dissolved hydrogen. In addition to the quality of an electron donor, the quantity needs to be addressed as well. Since the dissolved hydrogen produced from the fermentation of organic substrates can be used by a variety of microorganisms (e.g. methanogens and dehalorespirators), it is important to consider the competition for dissolved hydrogen when assessing the potential for dehalorespiration (Gossett and Zinder, 1997). Researchers have used the Monod model to examine the uptake of dissolved hydrogen by competing bacteria groups. The Monod model is based on microbial growth under a limiting substrate (e.g. dissolved hydrogen) and is expressed as:

$$\mu = \mu_{max} \frac{S}{K_s + S}$$

where μ is the specific growth rate, μ_{max} is the maximum specific growth rate, S is the substrate concentration, and K_s is the half-saturation constant. The parameter K_s gives an indication of how rapidly μ approaches μ_{max}. A lower K_s suggests that a microorganism will reach its maximum specific growth rate at a lower substrate concentration than another microorganism with a higher K_s, and hence are better scavengers when competing for the same limiting substrate.

Smatlak and Gossett (1996) compared the kinetics of dissolved hydrogen use by methanogens and dehalorespirators and obtained Monod-half saturation constants, K_s, of approximately 1.0 and 0.1 mM H_2 for methanogens and dehalorespirators, respectively. Their results suggest that dehalorespirators are better scavengers for dissolved hydrogen than methanogens, and that the choice of an electron donor that ferments to release dissolved hydrogen at slow, steady, and low levels, such as propionate or butyrate, would favor dehalorespirators over methanogens in the competition for hydrogen (Wang, 2000).

In addition to electron donors, deficiencies of available vitamins and nutrients can also limit dehalorespiration; such nutrients may include organic carbon, nitrogen, phosphorous, amino acids, trace elements, and vitamin B_{12}. The complexity of undefined microbial communities makes the understanding of specific nutritional requirements difficult. Yeast extract, a complex substrate, has been shown to increase dechlorination rates to those greater than of simpler substrates. Nutrient amendments to a contaminated aquifer may also benefit reductive dechlorination by stimulating the activity of non-dehalorespirators, which for example, prevent the accumulation of an inhibitory product (Mohn and Tiedje, 1992). Maymo-Gatell et al. (1995) investigated the nutritional requirements of an anaerobic enrichment culture competent at transforming PCE to ethene. Their results suggested that the dehalorespiring culture was dependent on other microorganisms tosatisfy some nutritional requirements, and that yeast extract and vitamin B_{12} play roles in dechlorination activity. Vitamin B_{12} was also shown to be a factor in sustaining dehalorespiration by Dehalospirillum multivorans (Neumann et al, 1994).

Smatlak and Gossett (1996) measured K_s (H_2) values of 100 nM for dehalorespirators and 1,000 nM for methanogens, and suggested that dehalorespirators would out-compete methanogens for electron donors only at low dissolved hydrogen concentrations. This implies that reductive dechlorination by dehalorespirators will be optimal when the amount of available electron donor is low, in order to minimize the direction of electron donors to methanogenesis.

In natural systems, including contaminated aquifers, most H_2 becomes available to hydrogenotrophic microorganisms through the fermentation of more complex substrates by other members of the microbial consortium. The dechlorinators must then compete with other organisms, such as methanogens and sulfate-reducing bacteria, for the evolved H_2 (Figure 2). Figure 3 also describes the distribution of electrons during the microbial breakdown of organic electron donor substrates (Suthersan, 2001).

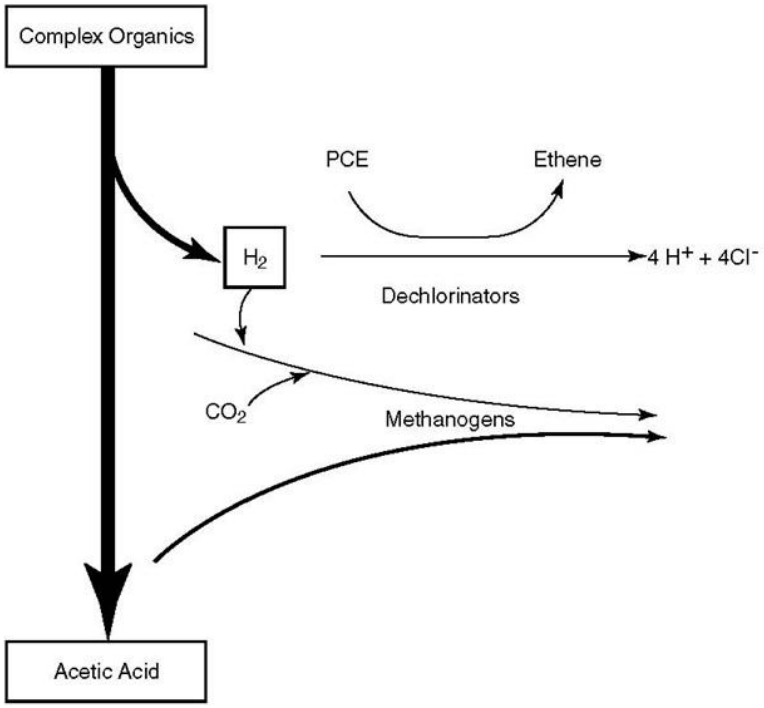


Figure 2. Energy diagram of microbial activity

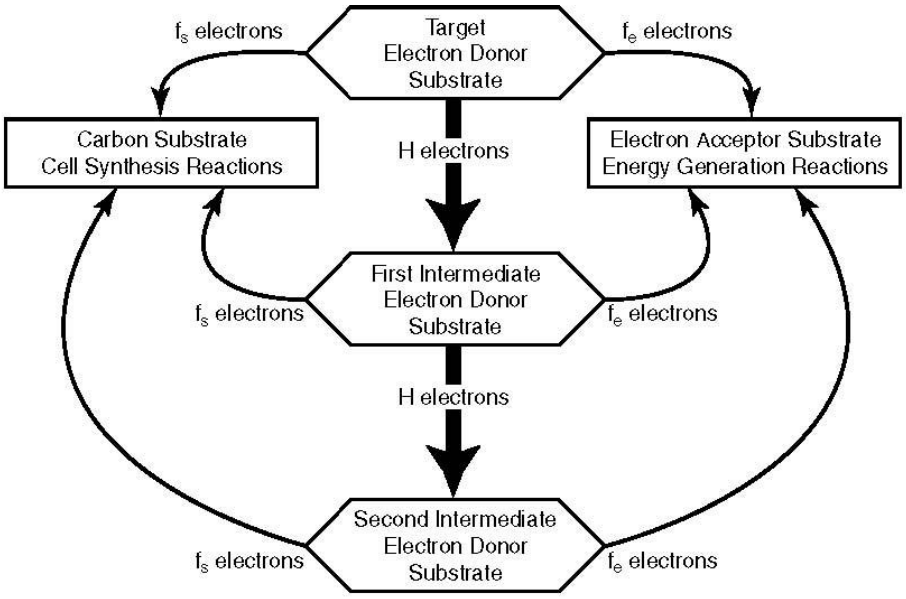


Figure 3. Distribution of electrons during the breakdown of organic electron donors

SUMMARY OF THE INVENTION

This invention provides an alternative method to control the release rate of the organic hydrogen donors in the solution during reductive dechlorination remedial process. The newly introduced organic substrates are encapsulated and that way have the potential to control the release of the organic hydrogen donors in the solution. Experimental results are also presented analytically below that show a significant difference in the release rate of calcium ions from the organic hydrogen donor calcium propionate in the solution.

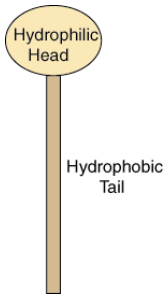
Organic and carbonyl salts have been effectively used as organic hydrogen donors during anaerobic dechlorination process. In fact calcium propionate has been found to be more effective than other electron donors that produce hydrogen necessary for dehalogenation, such as formate, ethanol, or glucose. The reason is that various groups of microorganisms compete for hydrogen, and that dehalogenating microorganisms can survive better than others at very low hydrogen concentrations. On this basis, slug addition of a compound such as formate, ethanol, or glucose is not as effective for dehalogenation as propionate, because the former compounds are converted rapidly to hydrogen and acetate, and the latter is not. The rapid conversion is a result of more favorable thermodynamics with respect to hydrogen formation. Such rapid conversion places hydrogen in a concentration range where methanogens and sulfate reducers can compete effectively with dehalogenators.

DETAILED DESCRPTION OF THE INVENTION

In one embodiment, a lipid bilayer is the effective encapsulating mechanisim. A lipid bilayer is a thin polar membrane made of two layers of lipid molecules. This structure is called a "lipid bilayer" because it is composed of two layers of fatty acids organized in two sheets. The lipid bilayer is typically about five to ten nanometers thick and surrounds all cells providing the cell membrane structure. It forms a continuous barrier around cells and thus provides a semipermeable interface between the interior and exterior of a cell and between compartments within the cell. The cell membrane of almost every living organism is made of a lipid bilayer,

as are the membranes surrounding the cell nucleus and other sub-cellular structures. The lipid bilayer is the barrier that sustains ions, proteins and other molecules and prevents them from diffusing into areas where they should not be. Lipid bilayers are ideally suited to this role because, even though they are only a few nanometers in width, they are impermeable to most water-soluble (hydrophilic) molecules. With the hydrophobic tails of each individual sheet interacting with one another, a hydrophobic interior is formed and this acts as a permeability barrier. The hydrophilic head groups interact with the aqueous medium on both sides of the bilayer. The two opposing sheets are also known as leaflets. Bilayer-forming lipids are amphipathic molecules (containing both hydrophilic and hydrophobic components). The hydrophilic fragment, typically termed the lipid head-group, is charged, or polar, whereas the hydrophobic section consists of a pair of alkyl chains (typically between 14 and 20 carbon atoms in length).

The structure of the lipid bilayer explains its function as a barrier. Lipids are fats, like oil, that are insoluble in water. There are two important regions of a lipid that provide the structure of the lipid bilayer. Each lipid molecule contains a hydrophilic region, also called a polar head region, and a hydrophobic, or nonpolar tail region (Figure 4). The phospholipid molecule's polar head group contains a phosphate group. It also sports two nonpolar fatty acid chain groups as its tail (Figure 5).



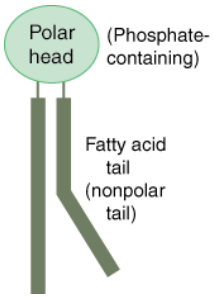


Figure 4. Basic Lipid Structure

Figure 5. Phospholipid Structure

The phospholipids organize themselves in a bilayer to hide their hydrophobic tail regions and expose the hydrophilic regions to water. This organization is spontaneous, meaning it is a natural process and does not require energy. This structure forms the layer that is the wall between the inside and outside of the cell.

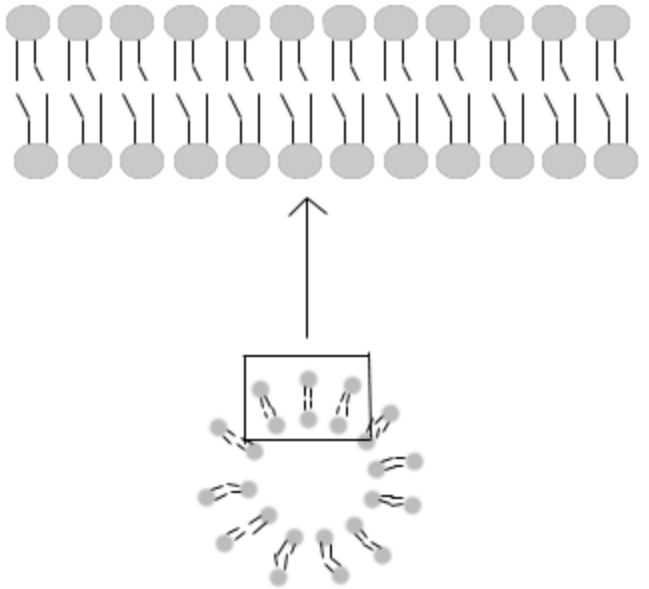


Figure 6. Lipid Bilayer Structure

Natural bilayers are usually composed of phospholipids. The phospholipid bilayer is the two-layer membrane that surrounds many types of plant and animal cells. It's made up of molecules called phospholipids, which arrange themselves in two parallel layers, forming a membrane that can only be penetrated by certain types of substances. This gives the cell a clear boundary, and keeps unwanted substances out. Though the phospholipid bilayer works well most of the time, it can be damaged, and some types of unwanted substances can bypass it.

In an aqueous environment the lipids self-assemble into structures that minimize contact between water molecules and the hydrophobic components of the lipids by forming two leaflets (monolayers); this arrangement brings the hydrophobic tails of each leaflet in direct contact with each other, and leaves the head groups in contact with water (Figure 7).

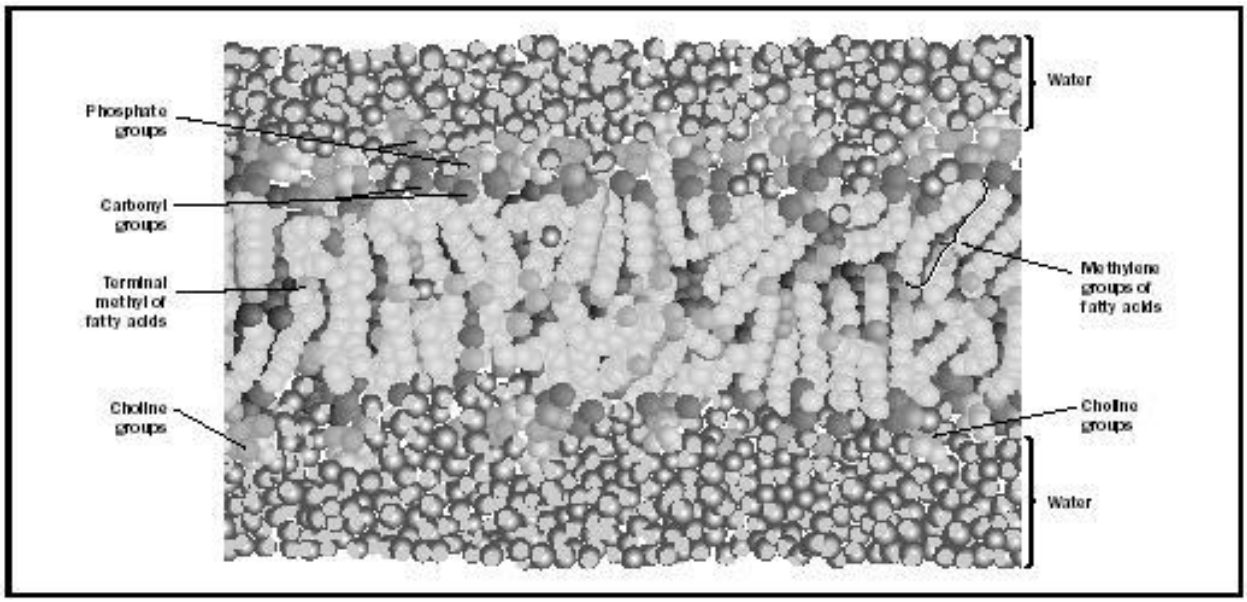


Figure 7. Image of a dipalmitolyphosphatidylcholine lipid bilayer

A potential major challenge in in-situ remediation is to engineer structures and materials that can efficiently encapsulate organic hydrogen donors at certain concentration, and controllably release their content at the target site over a specific period of time. Encapsulation prevents the species from direct biological interactions and from direct exposure to the environmental conditions that prevail on any given site. Moreover, encapsulating organic hydrogen donors can help control their efficiency by controlling their biodistribution and kinetics of release.

Among a wide variety of carriers, lipid-based systems present numerous advantages over other formulations. These carriers are biocompatible, biodegradable and can easily be produced by versatile and up-scalable processes. Lipid-based systems have been used for the encapsulation of a wide variety of various agents, while controlling their kinetics of release. The internal physical state of lipid core nanoparticles has been shown to dramatically affect the encapsulation, while maintaining significant prolonged release rates.

Based on all the above, it can be concluded, that due to the existence of the complicated structure of a potential lipid bi/multilayer electron donor, the release rates for the cations and anions in the solution will be significantly enhanced and will be much slower compared to single layer electron donors.

During in-situ reductive dechlorination the presence of a lipid multilayer compound will prove to be very effective since it will have the potential of lasting for a longer period of time in the environmental media under anaerobic conditions. At the same time the encapsulated material will also have the potential to decrease the amount of hydrogen provided during the process, which positively affects reductive dechlorination.

This invention presents the data received from a series of experimental procedures that were performed using encapsulated calcium propionate 80% in a distilled monoglyceride matrix. The results of the encapsulated material were compared with those of regular calcium propionate and the release rates of both materials in solution are presented below.

Monoglycerides are among the most promising polar lipid compounds able to bring new or improved functionality to food products since they can form self-assembly structures in both lipid and aqueous phases.

Two different dosages (0.5 g/L and 1 g/L) of both the regular calcium propionate (RCP) and the encapsulated 80% calcium propionate (ECP) were tested in order to compare the calcium release rates of both materials. The materials were placed in capped 250-ml flasks and were mixed with the use of magnetic stirring plates. All the experiments were performed in duplicates. As the results on Table 1 show, ECP showed much slower release rates upon the completion of the 14-day experimental procedure. In fact the 0.5 g/L ECP did not show any release of calcium during the first 2 days of the mixing procedure, while the release was increased to 5.8% of total calcium content 14 days upon the start of the experiment. Similarly the 1 g/L ECP showed a 2-day calcium release of 11.7%, which increased to 17.5% during the 14-day sampling period. Conversely RCP showed much higher calcium release rates in the solution. For the 0.5 g/L RCP the amount of calcium released was at 37.4% after 2 days of mixing and 56.1% after 14 days. For the 1 g/L RCP calcium release was at 56.1% after 2 days and at 65.4% after 14 days.

2 DAYS - CAPPED				
Material	Dosage (g/L)	Available calcium (mg/L)	Calcium in Solution (mg/L)	% release in solution
ECP	0.5	86	0	0.0
RCP	0.5	107	40	37.4
ECP	1	171	20	11.7
RCP	1	214	120	56.1
14 DAYS - CAPPED				
Material	Dosage (g/L)	Available calcium (mg/L)	Calcium in Solution (mg/L)	% release in solution
ECP	0.5	86	5	5.8
RCP	[illegible]	[illegible]	[illegible]	[illegible]
ECP	1	171	30	17.5
RCP	1	214	140	65.4

Table 1. Calcium release of ECP and RCP during a 2-day and a 14-day experiment

Claims

1. A method for accelerated biotic dechlorination of groundwater and soils, whereby reductive dechlorination processes are stimulated by-way of the introduction of a controlled release encapsulated fermentable organic hydrogen donor.
2. The method of claim 1 wherein the fermentable substrate consists of any one or a combination of materials, which when fermented result in dissolved volatile fatty acids (VFAs).
3. The method of claim 1 which may include, but are not limited to, organic salts of: *Acetate Butyrate*, Formate, Lactate, and Proprionate as well as carbohydrates.
4. The method of claim 1 in which the release of the organic salt is accomplished via an encapsulation of the salt.
5. The method of claim 4 in which the encapsulation of the salt is accomplished via liposomes, dendrimers or polymetric organic particles.
6. The method of claim 1 wherein the controlled release organic hydrogen donor is introduced into the targeted groundwater via temporary or permanent wells.

7. The method of claim 6 wherein the introduction of the controlled release organic hydrogen donor is accomplished via gravity feeding, induced gas stream and/or a pump.
8. The method of claim 6 wherein the remedial materials are delivered under pressure in either a gas or liquid stream.
9. The method of claim 1 wherein the controlled release organic hydrogen donor is introduced into the targeted area via mechanical mixing of the soils.
10. The method of claim 1 wherein the controlled release organic hydrogen donor is introduced into an open excavation prior to backfilling.
11. The method of claim 1 may be accompanied by additional materials known to further promote a suitable environment of reductive dechlorination.
12. The method of claim 11 wherein the additional materials assist in the control of pH control.
13. The method of claim 12 consists of hydroxides, carbonates and zero valent metals.
14. The method of claim 11 consists of biologically stimulating agents consisting of, but not limited to vitamins, yeast extract, biological cultures.

TITLE

Inhibition of methane production during anaerobic reductive dechlorination, by restricting the effectiveness of the enzymes and coenzymes that catalyze methanogenesis

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Antonis Karachalios, North Wales, PA

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Pipersville, PA (US)

FIELD OF THE INVENTION

The present invention relates to the use of various inhibitors of different enzymes and coenzymes systems that are responsible for the production of methane and therefore compete with halo-respiring bacteria during the anaerobic reductive dechlorination process. The present invention utilizes various compounds such as but not limited to red yeast rice, vitamin B10 derivatives, and ethanesulfonates to disrupt enzyme and coenzyme systems and limit the productivity of methanogens in producing methane. The inhibition of methanogenesis will result into lower methane production, which positively affects numerous environmental aspects of major concern, and will also help dehalogenating bacteria to more effectively utilize the environmental conditions that promote reductive dechlorination of chlorinated volatile organic compounds (CVOCs), in in-situ remediation processes.

BACKGROUND OF THE INVENTION

Halogenated volatile organic compounds (VOCs), including chlorinated aliphatic hydrocarbons (CAHs), are the most frequently occurring type of contaminant in soil and groundwater at Superfund and other hazardous waste sites in the United States. The U.S. Environmental Protection Agency (EPA) estimates that cleanup of these sites will cost more than $45 billion (1996) over the next several decades.

CAHs are manmade organic compounds. They typically are manufactured from naturally occurring hydrocarbon constituents (methane, ethane, and ethene) and chlorine through various processes that substitute one or more hydrogen atoms with a chlorine atom, or selectively dechlorinate chlorinated compounds to a less chlorinated state. CAHs are used in a wide variety of applications, including uses as solvents and degreasers and in the manufacturing of raw materials. CAHs include such solvents as tetrachloroethene (PCE), trichloroethene (TCE), carbon tetrachloride (CT), chloroform (CF), and methylene chloride (MC). Historical management of wastes containing CAHs has resulted in contamination of soil and groundwater, with CAHs present at many contaminated groundwater sites in the United States. TCE is the most prevalent of those contaminants. In addition, CAHs and their degradation products, including dichloroethane (DCA), dichloroethene (DCE), and vinyl chloride (VC), tend to persist in the subsurface creating a hazard to public health and the environment.

The options available for a cost-effective and reliable technology to treat chlorinated hydrocarbon contaminants such as PCE, TCE, cis-1,2-dichlorethene (cis-1,2-DCE), and VC in groundwater have in recent years moved away from traditional pump-and-treat processes, especially in cases where:

- NAPL, micro-emulsions or high concentration adsorbed materials are present leading to high dissolved phase concentrations.
- Access to groundwater is restricted by surface structures or uses.
- Local restrictions forbid the implementation of other available technologies such as air sparging or natural attenuation.
- Pump and Treat technologies have been applied, but have reached asymptotic removal rates.
- Contamination is extensive and concentrations are too high for risk based closure but otherwise relatively low (typically 100-7500 ppb).
- The migration of dissolved CAHs across property boundaries or into adjacent surface water presents a long-term remediation requirement.
- The vertical migration of free phase CAHs (DNAPL) into underlying drinking water aquifers is a concern.

The environmental chemistry of each site in part determines the rate of biodegradation of chlorinated solvents at that site. The initial metabolism of chlorinated solvents such as chloroethenes and chloroethanes in ground water usually involves a biochemical process described as sequential reductive dechlorination. The occurrence of different types and concentrations of electron donors such as native organic matter, and electron acceptors such as oxygen and chlorinated solvents, determines to a large degree the extent to which reductive dechlorination occurs during the natural attenuation of a site.

Laboratory studies have shown that a wide variety of organic substrates will stimulate reductive dechlorination including acetate, propionate, butyrate, benzoate, glucose, lactate, methanol, and toluene. Inexpensive, complex substrates such as molasses, cheese whey, corn steep liquor, corn oil, hydrogenated cottonseed oil beads, solid food shortening, beef tallow, melted corn oil margarine, coconut oil, soybean oil, and hydrogenated soybean oil have the potential to support complete reductive dechlorination.

Reductive dechlorination only occurs in the absence of oxygen; and, the chlorinated solvent actually substitutes for oxygen in the physiology of the microorganisms carrying out the process. As a result of the use of the chlorinated solvent during this physiological process, it is at least in part dechlorinated. Remedial treatment technologies usually introduce an oxygen scavenger to the subsurface in order to ensure that this process would occur immediately.

Heterotrophic bacteria are often used to consume dissolved oxygen, thereby reducing the redox potential in the ground water. In addition, as the bacteria grow on the organic particles, they ferment carbon and release a variety of volatile fatty acids (e.g., acetic, propionic, butyric), which diffuse from the site of fermentation into the ground water plume and serve as electron donors for other bacteria, including dehalogenators and halorespiring species. An iron source usually provides substantial reactive surface area that stimulates direct chemical dechlorination and an additional drop in the redox potential of the ground water via chemical oxygen scavenging.

Bacteria generally are categorized by: 1) the means by which they derive energy, 2) the type of electron donors they require, or 3) the source of carbon that they require. Typically, bacteria that are involved in the biodegradation of CAHs in the subsurface are chemotrophs (bacteria that

derive their energy from chemical redox reactions) and use organic compounds as electron donors and sources of organic carbon (organoheterotrophs). However, bacteria are classified further by the electron acceptor that they use, and therefore the type of zone that will dominate in the subsurface. A bacteria electron acceptor class causing a redox reaction generating relatively more energy, will dominate over a bacteria electron acceptor class causing a redox reaction generating relatively less energy.

Halophiles are salt-loving organisms that inhabit hypersaline environments. They include mainly prokaryotic and eukaryotic microorganisms with the capacity to balance the osmotic pressure of the environment and resist the denaturing effects of salts. Among halophilic microorganisms are a variety of heterotrophic and methanogenic archaea; photosynthetic, lithotrophic, and heterotrophic bacteria; and photosynthetic and heterotrophic eukaryotes.

One the other hand, methanogens, play a vital ecological role in anaerobic environments, since they remove excess hydrogen and fermentation products that have been produced by other forms of anaerobic respiration. Methanogens typically thrive in environments in which all electron acceptors other than CO_2 (such as oxygen, nitrate, trivalent iron, and sulfate) have been depleted.

Based on thermodynamic considerations, reductive dechlorination will occur only after both oxygen and nitrate have been depleted from the aquifer since oxygen and nitrate are more energetically favorable electron acceptors than chlorinated solvents. Almost any substrate that can be fermented to hydrogen and acetate can be used to enhance reductive dechlorination since these materials are used by dechlorinating microorganisms. However, hydrogen is also a substrate for methanogenic bacteria that convert it to methane. By utilizing hydrogen, the methanogens compete with dechlorinating microbes.

SUMMARY OF THE INVENTION

This invention provides different methods of inhibition of methane production from methanogenic bacteria by depressing the action of various enzymes and coenzymes that play a key role in the methane production. Various enzymes and coenzymes are targeted in the current invention. The inhibitors used, are found to be harmless for the rest of the bacteria that are present in the system.

The method of restricting methane production in methanogenic bacteria, by the use of the enzyme inhibitors, can be very useful during in-situ remediation of chlorinated solvents. This method is expected to positively affect the competition of the methanogen and halo bacteria for the organic hydrogen donors that are injected in the soil and groundwater system during the remediation process. The method also provides an alternative approach for the decrease of the emission levels of methane, which is considered a major greenhouse gas.

DETAILED DESCRPTION OF THE INVENTION

Biological methane formation is a microbial process catalyzed by methanogens. The methanogenic pathways of all species have in common the conversion of a methyl group to methane; however the origin of the methyl group varies. Most species are capable of reducing carbon dioxide (CO_2) to a methyl group with either a molecular hydrogen (H_2) or formate as the reductant. Methane production pathways in methanogens that utilize CO_2 and H_2, involve specific methanogen enzymes, which catalyze unique reactions using unique coenzymes.

Biosynthetic enzyme, 4-(β-D-ribofuranosyl)aminobenzene-5′-phosphate (β-RFA-P) synthase, is a key enzyme that catalyzes the first step of in methanopterin biosynthesis. This enzyme catalyzes the condensation between para-aminobenzoic acid (pABA) and 5-phospho-α-D-ribosyl-1-

pyrophosphate (PRPP) with concomitant formation of β-RFA-P, CO_2, and inorganic pyrophosphate (PPi). This enzyme is a phosphoribosyltransferase and a decarboxylase and forms a C-riboside, which is unique among phosphoribosyltransferases and pABA-dependent enzymes.

β-RFA-P synthase is an early step in the biosynthesis of tetrahydromethanopterin (H_4MPT), which is a modified folate that is of central importance in growth and energy metabolism of methanogens.

Methanofuran and H_4MPT, function as one-carbon carriers in the reversible reduction of CO_2 to a methyl group. H_4MPT is involved in multiple steps in methane formation, as in one carbon reactions involved in amino acid and nucleotide metabolism. Even though H_4MPT is found in *Archaea* and one class of Bacterium (e.g. *Methylobacterium extorquens*), the biosynthetic pathway for these two folates (folate and methanopterin) is different, suggesting that they play different functional roles in the physiology of the cell (Dumitru and Ragsdale, 2004).

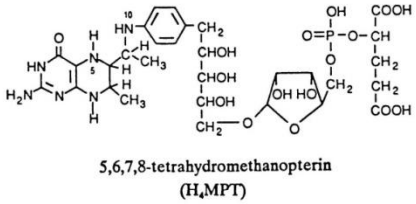


Figure 1. Structure of Tetrahydromethanopterin

Coenzyme F_{420} or 8-hydroxy-5-deazaflavin, is a two electron transfer coenzyme that is involved in redox reactions in methanogens in many Actinobacteria, and sporadically in other bacterial lineages. It occurs at varying levels in all methanogenic species and has also been identified in *Streptomyces griseus* and *Anacystis nidulans*. At least four different forms of the coenzyme have been described, all containing a deazariboflavin chromophore with an extended side-chain composed of two, three, four or five glutamic acid residues. Coenzyme F420-2 (i.e., with a side-chain consisting of two glutamic acid residues) appears to be the coenzyme form present in hydrogenotrophic methanogens, whereas methylotrophic species contain coenzymes F420-4 and F420-5 (Reynolds and Colleran, 1987).

One of the characteristics of F_{420} is that it acts as an electron donor for two steps in the reduction of CO_2 to a methyl group. The F_{420}-dependent NADP oxidoreductase enzyme from *Methanobrevibacter smithii* catalyzes the important electron transfer step during methanogenesis between NADP+ and F_{420}. During the reaction, NADP is reduced to NADPH by accepting one or more hydrides (H^-) from F_{420}. This is an important step of methane formation in methanogen bacteria such as *M. smithii*. Therefore, the NADP oxidoreductase enzyme plays a vital role in the formation of methane (Sharma et al. 2011).

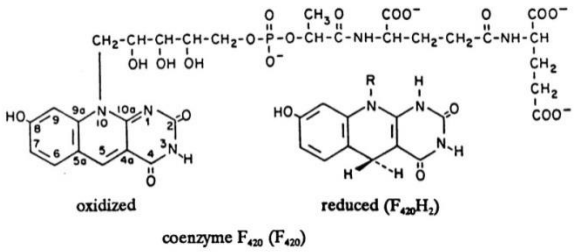
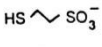


Figure 2. Structure of Coenzyme F_{420}

Coenzyme M (CoM) is the smallest cofactor known in nature. This cofactor is methylated on the sulfhydryl group, forming CH_3-S-CoM, the substrate for the methylreductase which catalyzes the terminal step in all methanogenic pathways. Coenzyme B is the second substrate for methyl-coenzyme M reductase, and as a consequence of the reaction, forms the heterodisulfide complex with CoM (CoB-S-S-CoM) (Ferry, 2002). 3-hydroxy-3-methylglutaryl coenzyme A (HMG-CoA) reductase, is also another enzyme that is very critical in methane production in *Methanobrevibactor* strains, since *Archaea* are the only bacteria known to possess biosynthetic HMG-CoA reductase (Miller and Wollin, 2001).



2-mercaptoethanesulfonic acid (coenzyme M, HS-CoM)

Figure 3. Structure of Coenzyme M (CoM)

The reduction of CO_2 to CH_4 with H_2 as the electron donor (Reaction 1) is the pathway of methanogenesis that this invention is focusied on.

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O, \qquad \Delta G^{o'} = -130.4 \text{ kJ/mol } CH_4 \quad (1)$$

The CO_2-reduction pathway (Figure 4) is observed in the presence of *Methanobacterium thermoautotrophicum* strains (Ferry, 2002).

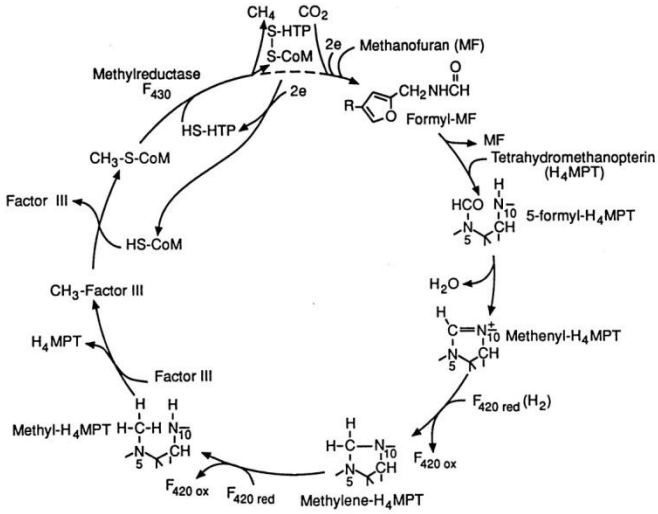


Figure 4. The pathway of CO_2-reduction to CH_4.

The steps are that are followed during the reduction of CO_2 to CH_4 are the following: first carbon dioxide is reduced to the formyl level, then the formyl group is reduced to the formaldehyde level, on the following step the methylene group is reduced to the methyl level and finally the methyl group is converted to methane. All four of the reductive steps are briefly described below (Ferry, 1992).

1. Reduction of Carbon Dioxide to the Formyl Level

The reduction of CO_2 to the formyl level is catalyzed by formyl-methanofuran dehydrogenase (FMF). FMF is the first stable intermediate in the pathway. Enzyme activity in the reverse direction is linked to the reduction of either methylviologen or coenzyme F_{420} in all extracts of *M. thermoautotrophicum* strain.

2. Reduction of the Formyl Level to the Formaldehyde Level

Prior to reduction, the formyl group is transferred to 5,6,7,8-tetrahydromethanopterin, as shown in Reaction 2, and then converted to the methenyl derivative by the dehydrating cyclization as shown in Reaction 3.

$$FMF + H_4MPT \rightarrow 5\text{-Formyl-}H_4MPT + 2MF, \qquad \Delta G^{o'} = -4.4 \text{ kJ/mol (2)}$$

$$5\text{-Formyl-}H_4MPT + H^+ \rightarrow 5,10\text{-methenyl-}H_4MPT^+ + H_2O, \qquad \Delta G^{o'} = -4.6 \text{ kJ/mol (3)}$$

The reduction of 5,10-methenyl-H_4MPT^+ to the formaldehyde level with reduced coenzyme F_{420} is shown in Reaction 4.

$$5,10\text{-methenyl-}H_4MPT^+ + F_{420}H_2 \rightarrow$$

$$5,10\text{-methylene-}H_4MPT + F_{420} + H^+, \qquad \Delta G^{o'} = +6.5 \text{ kJ/mol (4)}$$

Coenzyme F_{420} is an obligate two-electron carrier as mentioned above (redox potential ~ -350 mV) that donates or accepts a hydride ion. The disappearance of the 5,10-methenylene-H_4MPT dehydrogenase activity results into increasing dependence on F_{420} as an electron acceptor during the purification procedure or upon exposure to the air.

3. Reduction of the Methylene Group to the Methyl Level

The 5,10-methylene-H_4MPT reductase utilizes reduced F_{420} ($F_{420}H_2$) as the physiological electron donor for Reaction 5.

$$5,10\text{-methylene-}H_4MPT + F_{420}H_2 \rightarrow 5\text{-methyl-}H_4MPT + F_{420}, \qquad \Delta G^{o'} = -5.2 \text{ kJ/mol (5)}$$

This reaction proceeds in either direction; however the physiologically relevant methylene reduction is thermodynamically favored. Since H_2 is the source of electrons (Reaction 6), the reduction is exergonic and therefore could be associated with the generation of a primary electrochemical potential.

$$5,10\text{-methylene-}H_4MPT + H_2 \rightarrow 5\text{-methyl-}H_4MPT, \qquad \Delta G^{o'} = -14 \text{ kJ/mol (6)}$$

4. Conversion of the Methyl Group to Methane

a. Transfer of the Methyl Group to Coenzyme M

Prior to the reduction, the methyl group of 5-methyl-H_4MPT is transferred to Coenzyme M (HS-CoM), as shown in Reaction 7.

$$5\text{-methyl-}H_4MPT + HS\text{-CoM} \rightarrow CH_3\text{-S-CoM} + H_4MPT, \qquad \Delta G^{o'} = -29.7 \text{ kJ/mol (7)}$$

b. Reductive Demethylation of CH_3-S-CoM to Methane

The CH_3-S-CoM methylreductase catalyzes Raction 8. In the final reductive step of the pathway, CoM-S-S-HTP is reduced to the respective sulhydryl cofactors (Reaction 9).

$$CH_3\text{-S-CoM} + HS\text{-HTP} \rightarrow CH_4 + \text{CoM-S-S-HTP}, \qquad \Delta G^{o'} = -45 \text{ kJ/mol (8)}$$

$$\text{CoM-S-S-HTP} + H_2 \rightarrow HS\text{-CoM} + HS\text{-HTP}, \qquad \Delta G^{o'} = -40 \text{ kJ/mol (9)}$$

This invention provides various alternatives for the inhibition of the enzymes and coenzymes, which as mentioned above are integral parts of the methanogenesis process. The enzymes targeted in this patent are: methanopterin, coenzyme F_{420} and coenzymes A and M.

Biosynthetic enzyme, 4-(β-D-ribofuranosyl)aminobenzene-5′-phosphate (β-RFA-P) synthase, catalyzes the first step in methanopterin biosynthesis. The reduced form of methanopterin, H_4MPT, is involved in multiple steps in methanogenesis; it also replaces the functions of tetrahydrofolic acid, the predominant one-carbon carrier in eukaryotes and bacteria.

Given the importance of H_4MPT in growth and in energy production by methanogens, the inhibition of RFA-P synthase should specifically halt methanopterin biosynthesis and thereby preclude methanogenesis without adversely affecting the metabolism of other bacterial. Many researchers have performed studies that support the above hypothesis (Dumitru et al. 2003).

During the first step of methanopterin biosynthesis, RFA-P synthase catalyzes the conversion of phosphoribosylpyrophosphate (PRPP) and pABA to CO_2, inorganic pyrophosphate, and β-RFA-P (Figure 5).

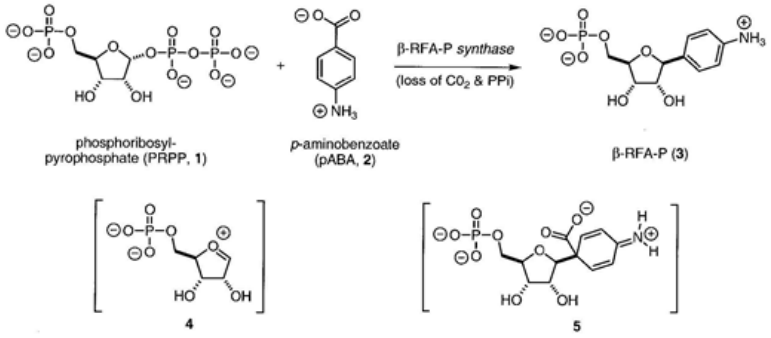


Figure 5. The reaction catalyzed by RFA-P synthase.

Some researchers partially purified and characterized the methanogenic RFA-P synthase, and the enzyme from *Archaeoglobus fulgidus* was purified to homogeneity, cloned and heterologously overexpressed. The reaction proceeds via the oxycarbenium intermediate and its adduct with pABA (Rasche and White, 1998). Most importantly though, other research groups (Dumitru et al. 2003) focused on designing competitive inhibitors that are structural analogs of pABA (Figure 6). Analogs of pABA that inhibit RFA-P synthase are highly selective because the amino group is the nucleophile in most pABA-dependent reactions, while the ring carbon 4 is the nucleophile in the RFA-P synthase-catalyzed reaction.

Figure 6. Analogs of pABA

The inhibitors presented by Dumitru et al. (2003) impair RFA-P synthase activity and arrest methanogenesis in pure cultures of methanogens. Supplying an excess of the natural substrate pABA to the culture relieves the inhibition, suggesting that RFA-P synthase is the cellular target. The inhibitors do not adversely affect the growth of acetogenic bacteria.

It has to be noted that pABA, is also more widely known as vitamin B10. Vitamin B10 is part of the vitamin B complex and is considered to be a water soluble vitamin. pABA is a component of pteroylglutamate; it was once considered a vitamin and named vitamin B-x because it serves as a provitamin for some bacteria.

Dumitru et al. (2003) synthesized various inhibitors, all of which were N-substituted derivatives of pABA, and determined their inhibition constants with PFA-P synthase. The results suggested that the pABA binding site in RFA-P synthase has a relatively large hydrophobic pocket near the amino group. Each of the pABA analogs was tested for their ability to inhibit methanogenesis and the growth of the methanogen *M. marburgensis* (formerly known as *M. thermoautotrophicum*). Insignificant amounts of methane were measured in the headspace of *M. marburgensis* cultures

whose growth was completely inhibited. At 100 nM, the most potent inhibitor currently, 4-[(2-pyridylmethyl)amino]benzoic acid, completely arrests the growth of methanogens and the formation of methane by *M. marburgensis*. Inhibition is fully reversed by supplementing the medium with pABA, indicating a competitive interaction between pABA and the inhibitor at the cellular target, which is most likely RFA-P synthase.

Acetogenesis is an anaerobic and hydrogenotrophic bacterial process that competes with methanogenesis in many anaerobic habitats. Each of the inhibitors was tested for its effect on the growth of the acetogenic bacterium *M. thermoacetica*. Methanopterin is not required for survival of bacteria; accordingly, none of the RFA-P synthase inhibitors described here affect the growth of *M. thermoacetica* at concentrations as high as 1 mM (Dumitru et al. 2003).

The effect of the inhibitors was tested on methane formation and volatile fatty acids (VFA) production. Methane production is completely inhibited by 5 mM 4-(ethylamino)benzoate or 9 mM 4-(isopropylamino)benzoate. 5 mM of 4-(2-hydroxyethylamino)benzoate inhibited methane production to 2.5% of the control level. As a control, 1 mM bromoethanesulfonate, an inhibitor of methyl-coenzyme M reductase, completely inhibited ($P<0.01$) methane production in all experiments (Dumitru et al. 2003).

The effect of some of the effective inhibitors on VFA production was also tested. VFA production was not depressed by adding an RFA-P synthase inhibitor at concentrations that completely block methanogenesis. For example, when 7 mM 4-ethylaminobenzoate was added to the artificial rumen system, acetate ($P<0.05$) and propionate ($P<0.10$) levels were elevated relative to the controls unexposed to the inhibitors. These results were consistent with the studies with pure cultures of acetogenic bacteria and indicate that the inhibitors do not adversely affect other bacteria (Dumitru et al. 2003).

Sharma et al. (2011) tested the potential inhibitory effect that Lovastatin and Compactin (Mevastatin) had on the F_{420}-dependent NADP oxidoreductase ezyme from *M. smithii*, during methanogenesis. Based on the results of their study it was found that both Lovastatin and Compactin (Mevastatin) compounds were effective as potential inhibitors of the F_{420}-dependent NADP oxidoreductase protein.

Lovastatin ($C_{24}H_{36}O_5$) is a secondary product of idiophase (secondary phase) of growth of fungi and is an inhibitor of enzyme 3-hydroxy-3-ethylglutaryl coenzyme A (HMG-CoA) reductase, a key enzyme in cholesterol production pathway in humans. There is a similarity between cholesterol formation in human and cell membrane formation in the *Archaea* as the lipid side of phospholipids in the cell membrane of *Archaea* is isoprenoid chains. Isoprenoid formation is an intermediate step of cholesterol production pathway (Mevalonate pathway) and HMG-CoA reductase is also a key enzyme for its production. Therefore, as an inhibitor of HMG-CoA reductase, lovastatin suppresses isoprenoid production and thus cholesterol synthesis and membrane formation in the *Archaea*. Wolin and Miller (2005) showed that lovastatin significantly reduced growth and activity of pure methanogenic bacteria without any negative effect on cellulolytic bacteria.

As mentioned above, $F_{420}H_2$-NADP is one of the coenzymes that act during the catalysis of the electron transfer step between $NADP^+$ and F_{420}, reducing NADP to NADPH with the acceptance of one or more hydrides (H^-) from F_{420}.

Sharma et al. (2011) determined a 3D model structure of the F_{420}-dependent NADP oxidoreductase from *M. smithii*. Based on their protein model of F_{420}-dependent NADP oxidoreductase enzyme, they detected that these residues are making a ligand binding site pocket, and after further studies they found that ligand F_{420} binds at the protein cavity. The inhibitor compounds Lovastatin and Compactin (Mevastatin) show more affinity for the model protein as compare to the natural ligand F_{420}. They share the same cavity as by F_{420} and surround by similar residues. In other words the inhibitor compounds Lovastatin and Compactin (Mevastatin) were very effective in blocking the activity site for methane production since the

enzyme was unable to bind with the substrate, resulting in decreased methane production. Lovastatin is a fungal metabolite isolated from cultures of Aspergillus terreus and Compactin (Mevastatin) is an antifungal metabolite from Penicillium brevicopactum. Sharma et al. (2011) establish that Lovastatin and Compactin (Mevastatin) may act as potent inhibitor for the F_{420}-dependent NADP oxidoreducatse protein in order to block its active site.

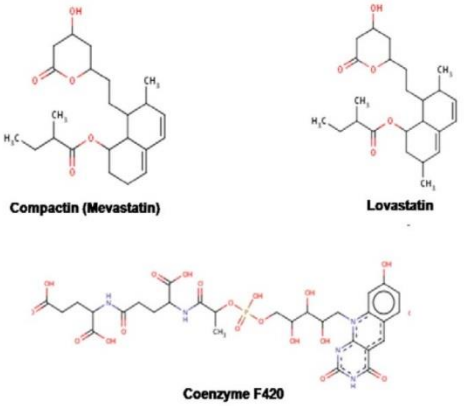


Figure 7. Structure of Compactin (Mevastatin), Lovastatin and F_{420}.

Researchers have found that red yeast rice, which is an Asian dietary staple made by fermenting yeast (*Monascus purpureus*) on rice, contains active ingredients of the statin drugs such as Lovastatin. Thus, studies have shown that red yeast rice can successfully inhibit the key enzyme hydroxymethylglutaryi-SCoA (HMG-CoA) reductase, resulting in the inhibition of methanogenic activity.

Miller and Wolin (2001) also used Lovastatin to inhibit the formation of the key precursor mevalonate. Mevalonate is formed by reduction of hydroxymethylglutaryi-SCoA (HMG-CoA). Based on their results they found that lovastatin inhibited the growth of *Methanobrevibacter* and CH_4 production. In fact 4 nmol/ml of culture medium resulted in 50% inhibition of growth and concentrations ≥10 nmol/ml of culture medium completely inhibited growth. Methane formation was also significantly inhibited. At the same time the populations of the nonmethanogens were not affected.

Coenzyme M (CoM; $HSCH_2CH_2SO_3^-$) is a cofactor which is found in all methanogens but not in other bacteria or archaea (Liu and Whitman 2008). CoM is involved in the terminal step of methane biosynthesis, where the methyl group carried by CoM is reduced to methane by methyl-CoM reductase. The methanogenic inhibitors involved in this group usually include 2-bromoethanesulfonate (BES), 2-chloroethanesulfonate (CES), 2-mercaptoethanesulfonate (MES), and lumazine (Liu et al. 2011). These inhibitors can competitively constrain the methyl transfer reaction at the terminal reductive step during methane formation in methanogens using H_2 and CO_2. Under normal circumstances, these compounds can inhibit all the groups of methanogens at relatively low concentrations. A traditional structural analog of CoM and BES has been widely used and considered as a methanogen-specific inhibitor in microbiological studies. Conrad et al. (2000) reported that 10 mM BES is the optimum concentration to inhibit the anaerobic methanogens in the rice roots systems. In the thermophilic environment of an anaerobic digester, complete inhibition of the methanogenesis is achieved with the use of at least 50 mM BES. A higher BES concentration is needed for the inhibition of the hydrogenotrophic methanogens than the acetoclastic methanogens (Zinder et al. 1984); however, a similar system requires, only 10 mM of BES in order to inhibit the methanogenesis process (Siriwongrungson et al. 2007). Other studies show that concentrations of 5–20 mM in the soil (Wüst et al. 2009) are really effective in inhibiting methanogenesis. MES and CES also have similar inhibition effects and were used to decrease the methanogenic activity in the continuous-flow methanogenic fixed-film column (Bouwer and McCarty 1983). Various reports show that the pterin

compound lumazine [2, 4-(1H, 3H)-pteridinedione] completely inhibited the growth of several methanogenic archaea at a concentration of 0.6 mM and was bactericidal for *M. thermoautotrophicum* strain Marburg (Nagar-Anthal et al. 1996).

Claims

What is claimed is:

1. A method for accelerating the biotic dehalogination of groundwater and soils affected by historic release of chlorinated aromatic and aliphatic compounds, by inhibiting the growth of methanogenic bacteria.

   Methane production inhibition is achieved by various inhibitory factors including, red yeast rice, vitamin B10 derivatives, and ethanesulfonates, to target enzyme and coenzyme systems that are responsible for the production of methane; therefore compete with halo-respiring bacteria during the anaerobic reductive dechlorination process in soil and groundwater media.
2. The method of claim 1 wherein the methane-producing bacteria to be inhibited are located in the soil and groundwater systems.
3. The method of claim 1 wherein the targeted enzyme of methane-producing bacteria to be inhibited is the biosynthetic enzyme, 4-(β-D-ribofuranosyl)aminobenzene-5′-phosphate (β-RFA-P) synthase.
4. The method of claim 1 wherein the targeted enzyme of methane-producing bacteria to be inhibited is 3-hydroxy-3-ethylglutaryl coenzyme A (HMG-CoA) reductase.
5. The method of claim 1 wherein the targeted coenzyme of methane-producing bacteria to be inhibited is Coenzyme M.
6. The method of claim 3 wherein the β-RFA-P synthase inhibitors are vitamin B10 derivatives.
7. The method of claim 4 wherein the HMG-CoA reductase inhibitor is Lovastatin, a secondary product of idiophase (secondary phase) of growth of fungi.
8. The method of claim 7 wherein red yeast rice is the Lovastatin source.
9. The method of claim 5 wherein the Coenzyme M inhibitors are 2-bromoethanesulfonate (BES), 2-chloroethanesulfonate (CES), 2-mercaptoethanesulfonate (MES), and lumazine.
10. The method of claim 1 wherein the inhibitory factors are introduced into the system.
11. The method of claim 1 wherein the step of injecting a predetermined amount of the inhibitory factors is in combination with fermentable substrates.
12. The method of claim 1 wherein inhibitory factors are proportionally mixed with oils and sugars.
13. The method of claim 12 wherein oils include vegetable, peanut, corn and fish oils.
14. The method of claim 12 wherein sugars include glucose and other fermentable materials that lead to glucose.

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(12) **United States Patent**
Scalzi et al.

(10) **Patent No.: US 7,531,709 B2**
(45) **Date of Patent: *May 12, 2009**

(54) **METHOD FOR ACCELERATED DECHLORINATION OF MATTER**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 241 days.

This patent is subject to a terminal disclaimer.

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(60) Provisional application No. 60/437,983, filed on Jan. 6, 2003.

(51) **Int. Cl.**
A62D 3/00 (2007.01)

(52) **U.S. Cl.** **588/316**; 588/406; 588/415

(58) **Field of Classification Search** ..... 588/313, 588/315, 316, 318, 319, 320, 402, 406, 415, 588/261; 423/240 R, 240 S
See application file for complete search history.

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(57) **ABSTRACT**

Accelerated dechlorination of soil and water contaminated with chlorinated solvents is achieved by stimulating anaerobic microorganisms and thus increasing the rate of biological mineralization of the solvents. This is accomplished by a treatment process consisting of colloidal suspension of metal powder, an organic hydrogen donor, chemical oxygen scavengers in solution with essential nutrients, and vitamin stimulants such as B2 and B12 delivered via compressed gases N or CO2 so as not to oxygenate an environment targeted for anaerobic processes. The treatment stimulates naturally occurring microorganisms while oxidizing dissolved phase target compounds via the surface action of the iron particles resulting in the breakdown of chlorinated solvents such as tetrachloroethene, trichloroethene, carbon tetrachloride and their daughter products.

16 Claims, 1 Drawing Sheet

METHOD FOR ACCELERATED DECHLORINATION OF MATTER

RELATED APPLICATION

This patent application is a continuation of co-pending patent application Ser. No. 10/610,558 filed Jul. 2, 2003 for "Method for Accelerated Dechlorination of Matter" which is related to provisional patent application Ser. No. 60/437,983 entitled "Method for Accelerated Dechlorination of Matter" filed on Jan. 6, 2003, priority from which is hereby claimed.

FIELD OF THE INVENTION

The present invention relates to the combined and synergistic utilization of chemicals in conjunction with the biomineralization processes of subsurface soil and groundwater pollutants. More specifically, it relates to an accelerated dechlorination of subsurface matter by anaerobic microorganisms in conjunction with oxygen scavengers, vitamins, nutrients, and zero valent metals.

BACKGROUND OF THE INVENTION

Through the years, chlorinated solvents have had a large impact on several industries, including pharmaceuticals, chemical processing, food extraction, dry cleaning, and metal cleaning. With wide spread use and improper handling and storage, extensive soil and water damage has occurred. Due to their toxicity, carcinogenicity, and persistence in the environment, chlorinated solvents are listed by the United States Environmental Protection Agency as high priority pollutants. If left untreated, chlorinated solvents may remain unchanged for a period of fifty years or more. The most common chlorinated solvents used are methylene chloride, tetrachloroethene, trichloroethene, carbon tetrachloride, chloroform, tetrachloroethane, dichloroethene and vinyl chloride. Carbon tetrachloride is a systematic poison of the nervous system, the intestinal tract, the liver, and the kidneys. Vinyl chloride and methylene chloride are known carcinogens, and could also affect the nervous system, the respiratory system, the liver, the blood, and the lymph system.

Chlorinated solvents are often found in separate phases mixtures commonly referred to as dense nonaqueous-phase liquids ("DNAPLs"). DNAPLs are visible, denser-than-water, separate oily phase materials in the subsurface whose migration is governed by gravity, buoyancy, and capillary forces. Chlorinated solvents partition into the water phase to create a dissolved contaminant plume when in contact with water, thus creating a long-term, continuing source of contamination as the soluble constituents slowly dissolve into moving groundwater.

One common technique for treating contaminated matter is the "pump-and-treat" method in which contaminated groundwater is pumped to the surface, cleaned chemically or by passing the groundwater through a bioreactor, and then reinjected into the groundwater. This process is carried out over a long period and various factors complicate the removal of these contaminants from the environment. Also, they are very volatile, highly mobile, denser than water, and generally found in the environment as mixtures of products with different degrees of chlorination. The "pump-and-treat" method is therefore problematic.

The problems with the "pump-and-treat" method can be overcome with the use of anaerobic microorganisms which have the capability to decompose a wide range of highly chlorinated compounds. However, anaerobic microorganisms are at a disadvantage in that their growth is slow when compared to that of aerobic organisms. In-situ they are at an even greater disadvantage due to the partitioning of the targeted substrates into the soil matrix. There is therefore a need in the art to utilize the ability of anaerobic microorganisms to decompose chlorinated compounds which can be achieved at a faster rate.

SUMMARY OF THE INVENTION

The present invention achieves accelerated dechlorination of soil and water contaminated with chlorinated solvents by stimulating anaerobic microorganisms and thus increasing the rate of biological mineralization of the solvents. This is accomplished by a treatment process consisting of a colloidal suspension of metal powder, organic hydrogen donor such as glucose, sucrose, alcohols, propionates, lactates, acetates, chitin, polylactate esters, glycerol tripolylactate, xylitol pentapolylactate, and sorbitol hexapolylactate, chemical oxygen scavengers in solution with essential nutrients, and vitamin stimulants such as B2 and B12 delivered via interconnected pneumatic pumps and pressurized vessels driven by compressed gases N or CO2 so as not to oxygenate an environment targeted for anaerobic processes. The treatment stimulates naturally occurring microorganisms while addressing dissolved phase target compounds via the surface action of the metal particles. The overall effect results in the breakdown of chlorinated solvents such as tetrachloroethene, trichloroethene, carbon tetrachloride and their daughter products. The incorporation of the B12 acts as both an enzymatic stimulus for the anaerobic action and a surface catalyst of the iron particle. Cobalt, the core element of the B12, enhances the surface oxidation of the metal further.

A closed delivery system is used to deliver the process utilizing a combination of gas and liquid delivery systems. All of the vessels are interconnected and valved, allowing for mixings, washings, filling, and discharge of materials via pressure vessels or mechanical pumping systems. The system utilized allows for a variety of dissimilar compounds to be delivered via a single injection line. Further, the switching between feed systems is accomplished without any loss of pressure to the delivery line eliminating the common problems experienced from the vacuum developed down-hole as pressure is released and reapplied. Lastly, the current system is fully self-contained requiring no electrical supply. The only site utility requirement is an available water source for slurry preparation.

One embodiment of the present invention is carried out in the following steps.

Step 1: Subsurface Pathway Development

Initially, a gas is delivered to the subsurface via the delivery system further described herein. The gas is used so as not to introduce oxygen into an environment targeted for anaerobic processes. Injection points are advanced via traditional direct push technology or may be permanently installed injection wells. The gas is introduced at a maximum pressure of approximately 175 psi such that delivery pathways and voids are established. Pathway development is verified by observing a substantial pressure drop at the surface monitoring point. Gas introduction is immediately halted once the pressure drop is observed.

Step 2: Sodium Sulfite Nutrient and Micro Nutrient Injection

A solution of sodium sulfite and nutrients (nitrogen and ortho-phosphate) is immediately injected into the subsurface pathways and voids that were developed during the gas injection step. Sodium sulfite acts as an oxygen scavenger, iron

reducer and sulfate source. As an oxygen scavenger, the sodium sulfite prevents the oxidation of the later-injected ZVI by the dissolved oxygen while promoting anaerobic conditions that are favorable for the biodegradation of the CVOCs. Nutrients, injected as organic ammonia and ortho-phosphate, are required for the maintenance of the microbial metabolic pathways, ATP/ADP synthesis and organelle development. Further, the incorporation of the ortho phosphate inhibits acetogenesis, a competing methanogenic reaction which consumes acetate and produces methane.

Step 3: Zero Valent Metal Injection

Immediately following the sodium sulfite/bioslurry solution injection, a colloidal suspension of a metal powder is added to an additional quantity of the bioslurry solution and the colloidal suspension is injected to reduce concentrations of dissolved-phase CVOCs while providing for rapidly generated hydrogen, the evolution of hydroxides and as a result overall microbial stimulation and biofilm formation.

Step 4: Anaerobic Hydrogen Source Injection

An anaerobic organic hydrogen source is injected immediately after the ZVI injection to provide a slow release hydrogen source for the anaerobic dechlorination of the CVOCs. Vitamin B12 and riboflavin B2 is mixed with the anaerobic stimulating hydrogen source to provide essential micro enzymes at the anaerobic sites.

Step 5: Sodium Sulfite/Nutrient Injection

A second injection of the sulfite/nutrient mixture is then performed to clear the injection lines and to provide for in-situ mixing and penetration of the anaerobic stimulating product.

Step 6: Post Liquid Injection—Gas Injection

Lastly, the injection lines are cleared of liquids by a second gas injection and all injectants are forced into the created formation and upward into the vadose zone. Once the injection cycle is complete, the injection point is temporarily capped to allow for the pressurized subsurface to accept the injectants. Once back-pressure diminishes, the injection rods are extracted. Injection boring locations are then sealed with bentonite or sand to prevent short-circuiting from adjacent injection locations.

Other objects and advantages of the present invention will be readily apparent to those of skill in the art from the following drawing and description of the preferred embodiment.

BRIEF DESCRIPTION OF THE DRAWINGS

The FIGURE is an apparatus and flow diagram which describes an in-situ delivery system of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

According to the preferred embodiment of the invention, the following process and delivery system apparatus is employed. In order to keep an anaerobic environment, nitrogen or carbon dioxide gas is used to propel all injectants into the subsurface. The gas is first injected into the subsurface at a maximum pressure of approximately 175 pounds per square inch until a significant pressure drop is observed at the injection pressure vessel. This process is referred to as delivery pathway development with the intent of opening pathways into the subsurface for the injections. These pathways are believed to be those more permeable pathways along which chlorinated solvents are more likely to have migrated, both in the vadose and saturated zones. Liquid and liquid-entrained injectants are then delivered with pressurized gas to the pathways that are produced during the pathway development.

Chemical oxygen scavengers, reducing agents such as sodium sulfite, are then injected to remove oxygen from groundwater and soil moisture immediately after pathway development in the subsurface, facilitating the anaerobic conditions that are preferred for the reductive dehalogenation of chlorinated solvents by indigenous bacteria. The resulting environment contains a wide spectrum of inorganic, biochemical, and enzymatic redox systems. Along with the reducing agents, nutrients such as organic ammonia and ortho-phosphate are added to the injectants in order to support microbial activity.

In an anaerobic environment, zero valent metal is then injected as an additive to the reducing agent bioslurry mixture. Zero valent metals have a moderately low toxicity and a good reducing power so that it can rapidly reduce higher concentrations of dissolved phase chlorinated solvents when injected via direct chemical reactions. Zero valent metals will continue to react with dissolved chlorinated solvents in groundwater until it is completely oxidized by chlorinated solvents, oxygen, or other oxidants that contact residual concentrations of zero valent iron. Under normal environmental conditions, zero valent metals are capable of being oxidized and reduced back and forth. The oxygen scavenger also promotes an anaerobic environment, stimulating the microorganisms.

With the addition of an electron donor source to provide hydrogen, the biodegradation process is initiated. An organic hydrogen donor such as a polylactate ester, glycerol tripolylactate, xylitol pentapolylactate, or sorbitol hexapolylactate, lactates, acetate, propionates, sugars, glucose, etc. is now injected with the intent of being cometabolized by indigenous anaerobic bacteria to produce dechlorinating conditions necessary for indigenous anaerobic bacteria to biodegrade residual concentrations of chlorinated solvents. This slow release process is controlled over time, maintaining a slow delivery of hydrogen at low concentrations which drives the anaerobic reductions. The volatile organic acid is then metabolized by indigenous bacteria to produce hydrogen, which can then be metabolized by chlorinated solvent degrading bacteria. Organic acids, hydrogen, nutrients, and bacteria then move with groundwater, enhancing the attenuation of chlorinated solvents as they move through the aquifer over a period of months.

The above-described process is preferably carried out by an apparatus such as shown in the diagram of the FIGURE. The direction of flow is indicated by arrows where appropriate. Not shown are conventional injection rods well-known in the art suitable for subsoil injections which are attached to an injection line in fluid communication with the discharge port **25**.

An embodiment of the inventive process begins by first filling the bioslurry tanks LT1 and LT2 and filling the feed tanks T1 and T2. A source of gas such as nitrogen or carbon dioxide is connected to inlet **21** and a water supply is connected to liquid inlet **23**. Valves V7 and V8 are opened which engage an electric actuator to fill bioslurry tanks LT1 and LT2. The micro-nutrients/sodium sulfate is then manually added to the bioslurry tanks LT1 and LT2 and allowed to mix. Valves V7 and V8 are closed along with disengaging the actuator when the bioslurry tanks are filled.

Next, a pre-mixed heated lactate including vitamins B2 and B12 is manually poured into feed tank T1. Valves V5, V6, V4, and V3 are then opened. Next, pump P2 is activated and tank T2 is filled with an appropriate volume of the bioslurry. All valves are closed when finished. The tops are then secured on

both feed tanks T1 and T2 and afterward valves V10 and V11 are opened to pressurize both feed tanks. After the injection rod has been properly placed at a selected location, the injection line is secured to discharge port **25** and valve V9 is opened.

The injection process begins when valve V1 is opened to create the injection pathways until a significant pressure drop is observed at the injection pressure vessel **31** which is filled with the source of compressed gas, preferably either nitrogen or carbon dioxide. Valve V1 is then closed and valve V3 opened to introduce the bioslurry mixture into the subsurface pathways from feed tank T2. Valve V3 is closed when feed tank T2 is empty.

Next, pump P2 is once again activated and tank T2 is filled with more of the bioslurry. Zero valent metal is then manually added and mixed with the bioslurry in tank T2. This mixture is then injected into the subsoil from tank T2 in the same way as the previous injection of the bioslurry mixture alone.

Now valve V2 is opened to introduce the lactate mixture into the subsurface from tank T1 and is closed after the tank is empty. Valves V4, V5, and V6 are then opened to directly deliver bioslurry from tanks LT1 and LT2 into the subsurface. All valves are closed when the desired amount of bioslurry has been injected. Finally, in order to cleanse the injection line of the viscous polylactate ester or other organic hydrogen donors, more reducing agent slurry is once again injected from tank T2 having been transferred there from tanks LT1 and LT2 as previously described. With the injections complete, a post injection line purge is performed by opening valves V9 and V1 and injecting gas to clear the lines of any remaining reducing agents. With the lines cleaned, the process is complete and the next injection location is prepared.

In accordance with the invention, a test was carried out and the following results observed. A site known to be contained with chlorinated solvents was geologically mapped. After determination of the subsurface contaminate concentrations, characteristics and the direction of flow of groundwater, a series of injection points were drilled. Contaminate concentrations of cis-1,2-DCE prior to the biodegradation process ranged from 6.6 ppb to 69 ppb. The initial concentration of VC ranged from 0.97 to 2 ppb. The initial concentration of TCE ranged from 0.23 to 12.0 ppb.

After determining the levels of the contaminants, biodegradation was initiated and maintained by the addition of iron powder, lactate, reducing agents, vitamin stimulants, and delivered by compressed gases and results were observed after four months. Iron powder was chosen for two primary reactions with chlorinated solvents, the first being the anaerobic iron corrosion reaction in which water is disassociated to form hydrogen gas, and the direct absorption of a chlorinated hydrocarbon onto the surface of the iron, followed by reductive dehalogenation. Four mechanisms are at work during the reductive process. First, the zero valent metals act as a reductant by supplying electrons directly from the metal surface to an absorbed halogenated compound. Next, hydrogen gas is generated by the anaerobic corrosion of the metallic iron by water. Third, metallic iron may act as a catalyst for the reaction of hydrogen with the halogenated hydrocarbon using the hydrogen produced on the surface of the iron metal as the result of anaerobic corrosion with water. Fourth, solubilized ferrous iron can also act as a reductant, albeit at a rate at least an order of magnitude slower.

At the end of the four month process, microbial processes are strongly active as demonstrated by the disappearance of tetrachloroethane, 1,1-TCA, and dichloromethane. The alkaline conditions over the four months would suggest that the chloride production observed is primarily due to the microbial dechlorination process. The 4,600 ppb increase in chlorides observed over the period suggest significant microbial activity. There appears to be no toxicity issues in any of the areas on site and there has not been any microbial accumulation of intermediates of the degradation pathways. As a by-product of the program, benzene has also been addressed in those areas where it has been found in the groundwater samples.

Therefore the foregoing description of the invention demonstrates that it provides a method for accelerated dechlorination of matter contaminated with chlorinated solvents utilizing mechanisms associated with zero valent metal oxidation. It shows that with the combination of organic acids, hydrogen donors, oxygen scavengers, nutrients and zero valent metal, when added to matter contaminated with chlorinated solvents, can provide a reducing environment. Thus, the compounds disclosed have shown great utility in aiding the destruction or inactivation of chlorinated solvents. The invention also confirms that zero valent metal, when added with other compounds which provide a source of electron donors, nutrients, and reducing agents, will stimulate naturally occurring microorganisms while oxidizing dissolved phase target compounds via the surface action of the iron particles resulting in the breakdown of chlorinated solvents.

It should be understood that there may be other modifications and changes to the present invention that will be obvious to those of skill in the art from the foregoing description, however, the present invention should be limited only by the following claims and their legal equivalents.

The invention claimed is:

1. A method for accelerated anaerobic dechlorination of subsoil matter, comprising the steps of:

supplying a mixture including a zero valent metal into soil pathways to biologically react with the dissolved chlorinated solvents in the groundwater; and

supplying an organic hydrogen donor into the soil pathways to produce dechlorinating conditions such that indigenous anaerobic bacteria biodegrade residual concentrations of chlorinated solvents.

2. The method of claim **1** further including the step of supplying a reducing agent into said soil pathways to remove oxygen from groundwater and soil moisture.

3. The method of claim **1** wherein the steps of supplying said mixture and said organic hydrogen donor are carried out by placing an injection rod into the soil and then injecting them under pressure through an injection rod.

4. The method of claim **3** further including the preliminary step of injecting a gas under pressure through said injection rod and into said soil to establish preferential delivery pathways therein.

5. The method of claim **2** wherein said reducing agent is sodium sulfite.

6. The method of claim **1** wherein said organic hydrogen donor further includes vitamins B2 and B12.

7. The method of claim **1** wherein the mixture further includes nutrients.

8. The method of claim **7** wherein said nutrients are organic ammonia and ortho-phosphate.

9. The method of claim **1** wherein said organic hydrogen donor is from the group consisting of lactate, propionate, chitin, butyrate, acetate, sugars, glycerol tripolylactate, xylitol pentapolylactate, and sorbitol hexapolylactate.

10. The method of claim **4** wherein said gas is from the group of nitrogen and carbon dioxide.

11. The method of claim **1** wherein said mixture including a zero valent metal is a colloidal suspension in a sodium sulfite solution.

12. The method of claim **3** further including, after the step of injecting the organic hydrogen donor, an additional step of

injecting into the soil a sodium sulfite and nutrient solution to provide for further in-situ mixing and penetration of anaerobic stimulating products.

13. The method of claim **4** further including a final step of gas injection to clear said injection rod and fluid conduit lines connected thereto.

14. The method of claim **1** wherein said metal is iron.

15. The method of claim **1** wherein said metal is in a colloidal suspension.

16. The method of claim **15** wherein the colloidal suspension includes a reducing agent.

* * * * *

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Scalzi et al.

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(54) **METHOD FOR ACCELERATED DECHLORINATION OF MATTER**

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See application file for complete search history.

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(57) **ABSTRACT**

Accelerated dechlorination of soil and water contaminated with chlorinated solvents is achieved by stimulating anaerobic microorganisms and thus increasing the rate of biological mineralization of the solvents. This is accomplished by a treatment process consisting of colloidal suspension of iron powder, polylactate ester such as glycerol tripolylactate, xylitol pentapolylactate, and sorbitol hexapolylactate, chemical oxygen scavengers in solution with essential nutrients, and vitamin stimulants such as B2 and B12 delivered via compressed gases N or C02 so as not to oxygenate an environment targeted for anaerobic processes. The treatment stimulates naturally occurring microorganisms while oxidizing dissolved phase target compounds via the surface action of the iron particles resulting in the breakdown of chlorinated solvents such as tetrachloroethene, trichloroethene, carbon tetrachloride and their daughter products.

10 Claims, 1 Drawing Sheet

METHOD FOR ACCELERATED DECHLORINATION OF MATTER

The present application is related to provisional patent application Ser. No. 60/437,983 entitled "Method for Accelerated Dechlorination of Matter" filed on Jan. 6, 2003, priority from which is hereby claimed.

FIELD OF THE INVENTION

The present invention relates to the combined and synergistic utilization of chemical oxidation and bio-mineralization of subsurface soil pollutants. More specifically, it relates to an accelerated dechlorination of subsurface matter by anaerobic microorganisms in conjunction with the oxidation of dissolved chlorinated compounds using zero valent iron.

BACKGROUND OF THE INVENTION

Through the years, chlorinated solvents have had a large impact on several industries, including pharmaceuticals, chemical processing, food extraction, dry cleaning, and metal cleaning. With wide spread use and improper handling and storage, extensive soil and water damage has occurred. Due to their toxicity, carcinogenicity, and persistence in the environment, chlorinated solvents are listed by the United States Environmental Protection Agency as high priority pollutants. If left untreated, chlorinated solvents may remain unchanged for a period of fifty years or more. The most common chlorinated solvents used are methylene chloride, tetrachloroethene, trichloroethene, carbon tetrachloride, chloroform, tetrachloroethane, dichloroethene and vinyl chloride. Carbon tetrachloride is a systematic poison of the nervous system, the intestinal tract, the liver, and the kidneys. Vinyl chloride and methylene chloride are known carcinogens, and could also affect the nervous system, the respiratory system, the liver, the blood, and the lymph system.

Chlorinated solvents are often found in separate phases mixtures commonly referred to as dense nonaqueous-phase liquids ("DNAPLs"). DNAPLs are visible, denser-than-water, separate oily phase materials in the subsurface whose migration is governed by gravity, buoyancy, and capillary forces. Chlorinated solvents partition into the water phase to create a dissolved contaminant plume when in contact with water, thus creating a long-term, continuing source of contamination as the soluble constituents slowly dissolve into moving groundwater.

One common technique for treating contaminated matter is the "pump-and-treat" method in which contaminated groundwater is pumped to the surface, cleaned chemically or by passing the groundwater through a bioreactor, and then reinjected into the groundwater. This process is carried out over a long period and various factors complicate the removal of these contaminants from the environment. Also, they are very volatile, highly mobile, denser than water, and generally found in the environment as mixtures of products with different degrees of chlorination. The "pump-and-treat" method is therefore problematic.

The problems with the "pump-and-treat" method can be overcome with the use of anaerobic microorganisms which have the capability to decompose a wide range of highly chlorinated compounds. However, anaerobic microorganisms are at a disadvantage in that their growth is slow when compared to that of aerobic organisms. In-situ they are at an even greater disadvantage due to the partitioning of the targeted substrates into the soil matrix. There is therefore a need in the art to utilize the ability of anaerobic microorganisms to decompose chlorinated compounds which can be achieved at a faster rate.

SUMMARY OF THE INVENTION

The present invention achieves accelerated dechlorination of soil and water contaminated with chlorinated solvents by stimulating anaerobic microorganisms and thus increasing the rate of biological mineralization of the solvents. This is accomplished by a treatment process consisting of a colloidal suspension of iron powder (ZVI), polylactate ester, such as glycerol tripolylactate, xylitol pentapolylactate, and sorbitol hexapolylactate, chemical oxygen scavengers in solution with essential nutrients, and vitamin stimulants such as B2 and B12 delivered via compressed gases N or CO2 so as not to oxygenate an environment targeted for anaerobic processes. The treatment stimulates naturally occurring microorganisms while oxidizing dissolved phase target compounds via the surface action of the iron particles resulting in the breakdown of chlorinated solvents such as tetrachloroethene, trichloroethene, carbon tetrachloride and their daughter products. The incorporation of the B12 acts as both an enzymatic stimulus for the anaerobic action and a surface catalyst of the iron particle. Cobalt, the core element of the B12, enhances the surface oxidation of the iron further.

A closed delivery system is used to deliver the process utilizing a combination of gas and liquid delivery systems. All of the vessels are interconnected and valved, allowing for mixings, washings, filling, and discharge of materials via pressure vessels or mechanical pumping systems. The system utilized allows for a variety of dissimilar compounds to be delivered via a single injection line. Further, the switching between feed systems is accomplished without any loss of pressure to the delivery line eliminating the common problems experienced from the vacuum developed downhole as pressure is released and reapplied. Lastly, the current system is fully self-contained requiring no electrical supply. The only site utility requirement is an available water source for slurry preparation.

One embodiment of the present invention is carried out in the following steps.

Step 1: Subsurface Pathway Development

Initially, a gas is delivered to the subsurface via the delivery system further described herein. The gas is used so as not to introduce oxygen into an environment targeted for anaerobic processes. Injection points are advanced via traditional direct push technology or may be permanently installed injection wells. The gas is introduced at approximately 175 psi such that delivery pathways and voids are established. Pathway development is verified by observing a substantial pressure drop at the surface monitoring point.

Step 2: Sodium Sulfate, Nutrient and Micro Nutrient Injection

A solution of sodium sulfite and nutrients (nitrogen and ortho-phosphate) is immediately injected into the subsurface fractures and voids that were developed during the gas injection step. Sodium sulfite acts as an oxygen scavenger, iron reducer and sulfate source. As an oxygen scavenger, the sodium sulfite prevents the oxidation of the later-injected ZVI by the dissolved oxygen while promoting anaerobic conditions that are favorable for the biodegradation of the CVOCs. Nutrients, injected as organic ammonia and ortho-phosphate, are required for the maintenance of the microbial metabolic pathways, ATP/ADP synthesis and organelle development.

Step 3: Zero Valent Iron (ZVI) Injection

Immediately following the sodium sulfite/bioslurry solution injection, ZVI is added to an additional quantity of the bioslurry solution and the colloidal suspension is injected to reduce concentrations of dissolved-phase CVOCs while providing for rapidly generated hydrogen for the microbial stimulation.

Step 4: Anaerobic Hydrogen Source Injection

An anaerobic organic hydrogen source is injected immediately after the ZVI injection to provide a slow release hydrogen source for the anaerobic dechlorination of the CVOCs. Vitamin B12 and riboflavin B2 is mixed with the anaerobic stimulating hydrogen source to provide essential micro enzymes at the anaerobic sites.

Step 5: Sodium Sulfite/Nutrient Injection

A second injection of the sulfite/nutrient mixture is then performed to clear the injection lines and to provide for in-situ mixing and penetration of the anaerobic stimulating product.

Step 6: Post Liquid Injection—Gas Injection

Lastly, the injection lines are cleared of liquids by a second gas injection and all injectants are forced into the created formation and upward into the vadose zone. Once the injection cycle is complete, the injection point is temporarily capped to allow for the pressurized subsurface to accept the injectants. Once back-pressure diminishes, the injection rods are extracted. Injection boring locations are then sealed with bentonite or sand to prevent short-circuiting from adjacent injection locations.

Other objects and advantages of the present invention will be readily apparent to those of skill in the art from the following drawing and description of the preferred embodiment.

BRIEF DESCRIPTION OF THE DRAWINGS

The FIGURE is an apparatus and flow diagram which describes an in-situ delivery system of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

According to the preferred embodiment of the invention, the following process and delivery system apparatus is employed. In order to keep an anaerobic environment, nitrogen or carbon dioxide gas is used to propel all injectants into the subsurface. The gas is first injected into the subsurface at approximately 175 pounds per square inch until a significant pressure drop is observed at the injection pressure vessel. This process is referred to as pre-injection fracturing with the intent of opening pathways into the subsurface for the injections. These pathways are believed to be those more permeable pathways along which chlorinated solvents are more likely to have migrated, both in the vadose and saturated zones. Liquid and liquid-entrained injectants are then delivered with pressurized gas to the pathways that are produced during the fracturization step.

Chemical oxygen scavengers, reducing agents such as sodium sulfite, are then injected to remove oxygen from groundwater and soil moisture immediately after fracturization of the subsurface, facilitating the anaerobic conditions that are preferred for the reductive dehalogenation of chlorinated solvents by indigenous bacteria. The resulting environment contains a wide spectrum of inorganic, biochemical, and enzymatic redox systems. Along with the reducing agents, nutrients such as organic ammonia and ortho-phosphate are added to the injectants in order to support microbial activity.

In an anaerobic environment, zero valent iron (ZVI) is then injected as an additive to the reducing agent bioslurry mixture. Zero valent iron has a moderately low toxicity and a good reducing power so that it can rapidly reduce higher concentrations of dissolved phase chlorinated solvents when injected via direct chemical reactions. Zero valent iron will continue to react with dissolved chlorinated solvents in groundwater until it is completely oxidized by chlorinated solvents, oxygen, or other oxidants that contact residual concentrations of zero valent iron. Under normal environmental conditions, zero valent iron is capable of being oxidized and reduced back and forth. The oxygen scavenger also promotes an anaerobic environment, stimulating the microorganisms.

With the addition of an electron donor source to provide hydrogen, the biodegradation process is initiated. A polylactate ester, such as glycerol tripolylactate, xylitol pentapolylactate, or sorbitol hexapolylactate, is now injected with the intent of being cometabolized by indigenous anaerobic bacteria to produce dechlorinating conditions necessary for indigenous anaerobic bacteria to biodegrade residual concentrations of chlorinated solvents. This slow release process is controlled over time, maintaining a slow delivery of hydrogen at low concentrations which drives the anaerobic reductions. The lactic acid is then metabolized by indigenous bacteria to produce hydrogen, which can then be metabolized by chlorinated solvent degrading bacteria. Lactic acid, hydrogen, nutrients, and bacteria then move with groundwater, enhancing the attenuation of chlorinated solvents as they move through the aquifer over a period of months.

The above-described process is preferably carried out by an apparatus such as shown in the diagram of the FIGURE. The conduit pathways for the fluids transported by this apparatus are shown in solid lines for the transfer of gases and dotted lines for the transport of fluids. The direction of flow is indicated by arrows where appropriate. Not shown are conventional injection rods well-known in the art suitable for subsoil injections which are attached to an injection line in fluid communication with the discharge port **25**.

An embodiment of the inventive process begins by first filling the bioslurry tanks LT**1** and LT**2** and filling the feed tanks T**1** and T**2**. A source of gas such as nitrogen or carbon dioxide is connected to inlet **21** and a water supply is connected to liquid inlet **23**. Valves V**7** and V**8** are opened which engage an electric actuator to fill bioslurry tanks LT**1** and LT**2**. The micro-nutrients/sodium sulfate is then manually added to the bioslurry tanks LT**1** and LT**2** and allowed to mix. Valves V**7** and V**8** are closed along with disengaging the actuator when the bioslurry tanks are filled.

Next, a pre-mixed heated lactate including vitamins B2 and B12 is manually poured into feed tank T**1**. Valves V**5**, V**6**, V**4**, and V**3** are then opened. Next, pump P**2** is activated and tank T**2** is filled with an appropriate volume of the bioslurry. All valves are closed when finished. The tops are then secured on both feed tanks T**1** and T**2** and afterward valves V**10** and V**11** are opened to pressurize both feed tanks. After the injection rod has been properly placed at a selected location, the injection line is secured to discharge port **25** and valve V**9** is opened.

The injection process begins when valve V**1** is opened to create the injection pathways until a significant pressure drop is observed at the injection pressure vessel **31** which is filled with the source of compressed gas, preferably either

nitrogen or carbon dioxide. Valve **V1** is then closed and valve **V3** opened to introduce the bioslurry mixture into the subsurface pathways from feed tank T2. Valve **V3** is closed when feed tank **T2** is empty.

Next, pump **P2** is once again activated and tank **T2** is filled with more of the bioslurry. Zero valent iron is then manually added and mixed with the bioslurry in tank **T2**. This mixture is then injected into the subsoil from tank **T2** in the same way as the previous injection of the bioslurry mixture alone.

Now valve **V2** is opened to introduce the lactate mixture into the subsurface from tank **T1** and is closed after the tank is empty. Valves **V4**, **V5**, and **V6** are then opened to directly deliver bioslurry from tanks LT**1** and LT**2** into the subsurface. All valves are closed when the desired amount of bioslurry has been injected. Finally, in order to cleanse the injection line of the viscous polylactate ester, more reducing agent slurry is once again injected from tank **T2** having been transferred there from tanks LT**1** and LT**2** as previously described. With the injections complete, a post injection line purge is performed by opening valves **V9** and **V1** and injecting gas to clear the lines of any remaining reducing agents. With the lines cleaned, the process is complete and the next injection location is prepared.

In accordance with the invention, a test was carried out and the following results observed. A site known to be contained with chlorinated solvents was geologically mapped. After determination of the subsurface contaminate concentrations, characteristics and the direction of flow of groundwater, a series of injection points were drilled. Contaminate concentrations of cis-1,2-DCE prior to the biodegradation process ranged from 6.6 ppb to 69 ppb. The initial concentration of VC ranged from 0.97 to 2 ppb. The initial concentration of TCE ranged from 0.23 to 12.0 ppb.

After determining the levels of the contaminants, biodegradation was initiated and maintained by the addition of iron powder, lactate, reducing agents, vitamin stimulants, and delivered by compressed gases and results were observed after four months. Iron powder was chosen for two primary reactions with chlorinated solvents, the first being the anaerobic iron corrosion reaction in which water is disassociated to form hydrogen gas, and the direct absorption of a chlorinated hydrocarbon onto the surface of the iron, followed by reductive dehalogenation. Four mechanisms are at work during the reductive process. First, the ZVI acts as a reductant by supplying electrons directly from the metal surface to an absorbed halogenated compound. Next, hydrogen gas is generated by the anaerobic corrosion of the metallic iron by water. Third, metallic iron may act as a catalyst for the reaction of hydrogen with the halogenated hydrocarbon using the hydrogen produced on the surface of the iron metal as the result of anaerobic corrosion with water. Fourth, solubilized ferrous iron can also act as a reductant, albeit at a rate at least an order of magnitude slower.

At the end of the four month process, microbial processes are strongly active as demonstrated by the disappearance of tetrachloroethane, 1, 1-TCA, and dichloromethane. The alkaline conditions over the four months would suggest that the chloride production observed is primarily due to the microbial dechlorination process. The 4,600 ppb increase in chlorides observed over the period suggest significant microbial activity. There appears to be no toxicity issues in any of the areas on site and there has not been any microbial accumulation of intermediates of the degradation pathways. As a by-product of the program, benzene has also been addressed in those areas where it has been found in the groundwater samples.

Therefore the foregoing description of the invention demonstrates that it provides a method for accelerated dechlorination of matter contaminated with chlorinated solvents utilizing mechanisms associated with zero valent iron oxidation. It shows that with the combination of lactic acid, oxygen scavengers, nutrients and zero valent iron, when added to matter contaminated with chlorinated solvents, can provide a reducing environment. Thus, the compounds disclosed have shown great utility in aiding the destruction or inactivation of chlorinated solvents. The invention also confirms that iron powder, when added with other compounds which provide a source of electron donors, nutrients, and reducing agents, will stimulate naturally occurring microorganisms while oxidizing dissolved phase target compounds via the surface action of the iron particles resulting in the breakdown of chlorinated solvents.

It should be understood that there may be other modifications and changes to the present invention that will be obvious to those of skill in the art from the foregoing description, however, the present invention should be limited only by the following claims and their legal equivalents.

The invention claimed is:

1. A method for accelerated anaerobic dechlorination of subsoil matter, comprising:

placing an injection rod into a soil to be treated to carry injectants under pressure to the soil;

injecting a soil fracturizing gas under pressure through said injection rod and into said soil to establish fluid pathways therein;

injecting a reducing agent under pressure through said rod and said soil pathways to remove oxygen from groundwater and soil moisture;

injecting a mixture under pressure including zero valent iron through said rod and into said soil pathways to react with the dissolved chlorinated solvents in the groundwater; and

injecting a polylactate ester mixture under pressure through said rod into the soil pathway to produce dechlorinating conditions such that indigenous anaerobic bacteria biodegrade residual concentrations of chlorinated solvents.

2. The method of claim **1** wherein said reducing agent is sodium sulfite.

3. The method of claim **2** wherein said polylactate mixture further includes vitamins B2 and B12.

4. The method of claim **1** wherein the mixture further includes nutrients.

5. The method of claim **4** wherein said nutrients are organic ammonia and ortho-phosphate.

6. The method of claim **5** wherein said polylactate ester is from the group consisting of glycerol tripolylactate, xylitol pentapolylactate, and sorbitol hexapolylactate.

7. The method of claim **6** wherein said fracturizing gas is from the group of nitrogen and carbon dioxide.

8. The method of claim **7** wherein said zero valent iron mixture is a colloidal suspension in a sodium sulfite solution.

9. The method of claim **8** further including, after the step of injecting the polylactate ester, an additional step of injecting into the soil a sodium sulfite and nutrient solution to provide for further in-situ mixing and penetration of anaerobic stimulating products.

10. The method of claim **9** further including a final step of gas injection to clear said injection rod and fluid conduit lines connected thereto.

* * * * *

METHOD FOR THE TREATMENT OF GROUND WATER AND SOILS USING MIXTURES OF SEAWEED AND KELP

FIELD OF THE INVENTION

The present invention relates to the mediation of subsurface soil and ground water contamination. Specifically, it relates to the injection of dried seaweed, kelp and or other mixtures for the dechlorination of soil and ground water contaminated with chlorinated solids.

BACKGROUND OF THE INVENTION

This invention aids in the remediation of environmental contaminants in subsurface soils and groundwater via the stimulation of anaerobic processes. Specifically, this invention relates to remediation processes involving the emplacement of solid-phase or aqueous-phase treatment agents. Emplacement of dried seaweed or kelp species as electron donors for microorganisms that carry out reductive dechlorination of chlorinated solvent source areas or plumes is illustrative of the invention.

Various species of Seaweed including Ascophyllum nodosum, Dulse, Nori, and Kelp contain substantial nutrients, beneficial to anaerobic processes. Seaweeds are available in a variety of forms including sheets, meals, flakes and powders that can either be hydrolyzed for solubility or remain insoluble as a slow release remedial product. In addition, dried seaweed can come in various sizes ranging from large granules characteristic of insoluble kelp meal to high mesh sizes of fine powder. The dynamic nature of seaweed has resulted in its wide use in varying commercial fields. Liquid seaweed extract as well as insoluble and (hydrolyzed) soluble dried seaweeds are commonly used as fertilizers to enhance the development and growth rate of plants. Seaweed is also used as a food additive for livestock to promote growth and health. Furthermore, seaweed has been an essential food source for years, used in sushi, chips, seasoning, and even as a dietary supplement for its high nutritional value.

The chemical composition of seaweeds allows for the contribution of stimulatingis comprised of fatty acids, carbohydrates, and proteins. Their concentrations of vitamins B2, and B12 in particular make seaweed an excellent alternative for environmental remediation. The species Ascophyllum nodosum contains high levels of enzymes, 17 amino acids, macro and micronutrients, plant hormones (auxins, cytokins, gibberillins), 25% alginic acid, and over 50% of carbohydrates and polysaccharides. Seaweeds also have over 72 minerals, and assorted vitamins (B2, B12, K) that encourage the vigorous and healthy growth of subsurface biological life. Seaweed and Kelp offer the necessary micronutrients and volatile fatty acid precursors that will provide long-term production of organic hydrogen necessary for reductive dechlorination of chlorinated

solvents in groundwater and soils. The high concentrations of many of these valuable nutrients provide optimal living conditions for the anaerobic processes responsible for the remediation of contaminated soil and groundwater sites.

Chlorinated solvents are the most common class of ground water contaminants at hazardous waste sites in the U.S. In a list of the top 25 most frequently detected contaminants at such sites, the Agency for Toxic Substances and Disease Registry (ATSDR) found that 10 of the top 20, including two of the top three, were chlorinated solvents or their degradation products. National Research Council, Alternatives for Ground Water Cleanup (National Academy Press, Washington, D.C. 1994). In fact, the same survey found that the most common contaminant, trichloroethylene (TCE), is present in more than 40% of National Priority List sites. The remediation of ground water contaminated by these compounds often presents unique obstacles related to their inherent characteristics, including hydrophobicity and high density. Many commercial process utilize raw vegetable oils and emulsions which co-elute the targeted solvents within the treatment liquid masking the presence of the compound targeted for treatment rather than stimulating the mineralization of said compound.

Natural attenuation of chlorinated solvents by reductive dechlorination often occurs at sites where an electron donor (food source or substrate for microbes) is present along with the chlorinated solvent contamination. As dissolved oxygen and other electron acceptors become depleted some microbes are capable of using the chlorinated solvents as electron acceptors. For selected compounds such as chlorinated ethylenes sequential dechlorination to a harmless byproduct ethylene can be achieved under favorable environmental conditions (EPA/600/R-10 98/128 September 1998).

In recent years efforts have been made to produce this anaerobic treatment effect by injection of electron donor into the subsurface. An overview of these technologies can be reviewed in the EPA document Engineered Approaches to In Situ Bioremediation of Chlorinated Solvents: Fundamentals and Field Applications (EPA 542-R-00-008 July 2000). Other inorganic and organic compounds can be degraded or immobilized under anaerobic conditions including selected toxic metals, nitrate, and MTBE. For sites that do not have sufficient amounts of natural electron donors to drive anaerobic natural attenuation, injection of microbial substrates has proven to be a cost-effective treatment or plume migration control measure. The microbial substrates can be injected into the contaminant source area where residual contamination is adsorbed onto soils or injected in a line across a ground water contaminant plume to form a permeable reactive wall to prevent further contaminant migration.

A wide variety of sugars, alcohols, organic acids, and even molecular hydrogen have been used successfully as electron donors to enhance anaerobic biotransformation processes. Most of these compounds are rapidly consumed after injection and must be replaced by either continuous low concentration delivery systems or with frequent batch additions of additive solution. Contaminant source areas can not be effectively removed or even precisely located for many ground water

contaminant plumes. The presence of residual chlorinated solvents adsorbed onto soils or present as dense non-aqueous phase product (DNAPL) serves as an example of persistent ground water plume source areas that can last for many decades. These persistent contaminant source areas continue to contaminate ground water for many years such that continuous operation of recirculation systems or frequent substrate injections can be very costly over the life of a project. Long-term injection of substrates into wells or infiltration galleries often leads to severe bacterial fouling problems adding to project operation and maintenance costs.

Recent interest has developed in the use of materials that slowly biodegrade or slowly release organic matter into ground water over time. A variety of vegetable oils have been demonstrated to be effective electron donors to stimulate anaerobic biodegradation. Although edible oils such as soybean oil have a much lower viscosity than a semisolid product, distribution in saturated soils is difficult. Soybean oil has a viscosity approximately times higher than water, which results in multiphase fluid flow and potential oil blockage of soil porosity. Injection of pure oil or large droplets of emulsified oil blocks soil pores producing treatment zones that are ineffective because they prevent free flow of ground water through the oil treated area. Injection of pure soybean oil into porous soil media has been shown to reduce water permeability by up to 100%.

In addition to slowly biodegradable hydrogen sources, soil and groundwater remediation process that utilize zero-valent metals have been applied with varying success. In the second embodiment of the invention, the addition of zero-valent metals to the micro dried seaweed or kelp allows for maintained reducing conditions resulting in greater longevity of the reactive metal surface. Zero-valent metal particles have been proven to effectively degrade halogenated solvents. For example, the mechanism and reaction rates of which iron reduces chlorinated aliphatics has been studied extensively due to iron's low cost and low toxicity. Additionally, the pathways of the dehalogenation of DNAPL's such as TCE have been proposed. TCE undergoes hydrogenolysis where the replacement of each of the three chlorines occurs sequentially. TCE reduces to cis-1 ,2-dichloroethene, trans-1 ,2-dichloroethene, and 1,1 - dichloroethene. These intermediates in turn reduce to ethene and ethane.

SUMMARY OF THE INVENTION

To overcome the foregoing problems, the present invention utilizes dried micro-seaweed species like nori, Ascophyllum nodosum, and dulse. Seaweed is brown algae that is widely available in both the wild and through cultivation all over the world. The best-known species of seaweed is Ascophyllum nodosum. Not only is Ascophyllum nodosum the most popular amongst researchers, but is also the most cultivated species of seaweed. Ascophyllum nodosum is native to the northern Atlantic and has wide variety of important nutrients beneficial to anaerobic processes. Ascophyllum nodosum has an

analyzed chemical composition of: 20 26% of sulphate uronic acids, 5 8% of Mannitol, 2 5% of Laminaran, 5 15% of fucoidin, 2500 2000mg/kg of Ascorbic acid, 150 300 mg/kg of Tocopherols, 30 60 mg/kg of Carotenes, 10 30 mg/kg of Niacin, 0.1 0.4 mg/kg of Biotin, 0.2 1 mg/kg of Folic acid, 5 10 mg/kg of Riboflavine, and 1 5 mg/kg of Thiamine. The species also has an assortment of elements including sulfur, potassium, chlorine, sodium, magnesium, calcium, phosphorous, bromine, cobalt, copper, iron, iodine, zinc, nickel and 0.004 mg/kg of Vitamin B12, and 10mg/kg of Vitamin K. Many of these organisms also are highly alkalizing, as a consequence their addition counter-acts the natural production of acids produced by-way of anaerobic dechlorinization. These organisms are commercially available dried, in multiple forms, and in large quantities. The dechlorination process may be further accelerated by the addition of a zero-valent metal powder to the dried seaweed. When emplaced in groundwater and soils impacted by chlorinated solvents the micro dried seaweed offer all the needed components for effective and rapid remediation of compounds such as tetrachloroethane, tetrachloroethene, trichloroethane, trichloroethene, carbon tetrachloride and their anaerobic daughter products.

The actions of seaweeds on the subsurface may be further enhanced with the inclusion of zero-valent metal particles. Alone, or in a mixture, the micro sized seaweed is particularly suited for dehalogenation of solvents including, but not limited to, tetrachloroethane, tetrachloroethene, trichloroethane, trichloroethene, carbon tetrachloride and their anaerobic daughter products. The present invention achieves accelerated dechlorination of soil and ground water contaminated with chlorinated solvents by stimulating anaerobic microorganisms and thus increasing the rate of biological mineralization of the solvents.

Overcoming these obstacles often demands innovation and an interdisciplinary approach that integrates hydrology, geology, chemistry, microbiology, and economics. In particular, an innovative approach has been conceived, and is described herein, to harness recent advances in the understanding of biodegradation processes involving chlorinated solvents for remediating residual source areas, or for cutting off dissolved plumes, by emplacing solid-phase or aqueous- phase treatment agents into a variety of soil types throughout much larger volumes of the subsurface than has been possible using conventional methods. By using micro dried seaweed or kelp, a variety of organic carbons, hydrogen sources, nutrients, and vitamins are delivered for anaerobic bacteria to digest and convert into gases like hydrogen. Specifically, the vitamins B2 and B12 from the seaweed help mediate the reductive dechlorination of PCE and TCE completely to ethane and ethane. The rate-limiting step from which vinyl chloride converts to ethylene has been found to be significantly enhanced by the presence of vitamin B12, which acts as an electron carrier. Using micro dried seaweed or kelp as an additive aids in the completion of the dechlorination as well as providing a supply of nutrients to prolong the remedial process.

One embodiment of this innovation involves delivering powdered dried seaweed or kelp as an electron donor, into induced fractures in low permeability soils to create and maintain nutrient-rich anaerobic conditions that will promote and

accelerate the long-term bioremediation of a chlorinated solvent or other dense nonaqueous phase liquid (DNAPL) sources. Individual use of hydrolyzed soluble seaweed or kelp has the ability to immediately dissolve into the ground and directly promote anaerobic processes responsible for the remediation of contaminated sites. The injection of powedered sized insoluble seaweed or kelp allows for a prolonged period of absorption that enhances and extends the anaerobic and remedial process. A second embodiment of this invention includes the addition of a zero-valent metal with the dried micro sized seaweed or kelp such that the dissolved chlorinated solvents are both biotically and abiotically degraded. Combined, these materials offer long term organic hydrogen sources, buffering capacity and essential nutrient for the sustained, biologically mediated anaerobic dechlorinization.

More specifically the invention comprises a method for accelerating biotic dechlorination of ground water and soils provided by the steps of first injecting into the ground water and soils by way of temporary rods or permanent wells a mixture containing a predetermined mass of micro dried powder seaweed or kelp put under pressure. Next, a mixture containing zero valent metal particles is injected to react with the dissolved chlorinated solvents. A second mixture containing zero valent metal particles is then injected so that the corrosion of the metal particles results in the elevation of the bulk PH of the surrounding ground water. Finally, the micro dried seaweed is again injected into the ground water and soils with an oxygen scavenger to remove oxygen and ensure that the subsurface environment is reductive. All injections of materials are done in such a matter as to ensure their dispersion into the subsurface. Alternately, a simple single step method of employing the invention is injecting a solution of zero valent iron, seaweed, and sodium sulfite into the subsurface using a pump.

In this respect, before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not limited in its application to the details of construction and to the arrangements of the components set forth in the following description or illustrated in the drawings. The invention is capable of other embodiments and of being practiced and carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein are for the purpose of description and should not be regarded as limiting.

As such, those skilled in the art will appreciate that the conception, upon which this disclosure is based, may readily be utilized as a basis for the designing of other structures, methods, and systems for carrying out the several purposes of the present invention. It is important, therefore, that the claims be regarded as including such equivalent constructions insofar as they do not depart from the spirit and scope of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

One embodiment of the present invention is carried out in the following steps:

Step 1: Subsurface Pathway Development

A gas is delivered to the subsurface as follows. Injection points are advanced via traditional direct push technology using injection rods or may be permanently installed injection wells. The gas is introduced at approximately 175 psi such that delivery pathways and voids are established. Pathway development is verified by observing a substantial pressure drop at the surface monitoring point. The gas is used so as not to introduce oxygen into an environment targeted for anaerobic processes.

Step 2: Sodium Sulfite and and Seaweed

Next a solution of sodium sulfite and micro-dried seaweed is immediately injected into the subsurface fractures and voids that were developed during the gas injection step. Sodium sulfite acts as an oxygen scavenger, iron reducer, and sulfate source. As an oxygen scavenger, the sodium sulfite prevents the oxidation of the later-injected ZVI (Zero Valent Iron) by the dissolved oxygen while promoting anaerobic conditions that are favorable for the biodegradation of the DVOCs. the components of seaweed make it an organic hydrogen donor, with necessary vitamins and minerals.

Step 3: Zero Valent Iron (ZVI) Injection

Immediately following the sodium sulfite/ seaweed solution injection, ZVI is added to an additional quantity of the micro seaweed solution and the colloidal suspension is injected to reduce concentrations of dissolved-phase CVOCs while providing for rapidly generated hydrogen for the microbial stimulation.

Step 4: Post Liquid Injection- Gas Injection

The injection lines are cleared of liquids by a second gas injection and all injectants are forced into the created formation and upward into the vadose zone. Once the injection cycle is complete, the injection point is temporarily capped to allow for the pressurized subsurface to accept the injectants. Once back-pressure diminishes, the injection rods are extracted. Injection boring locations are then sealed with bentonite or sand to prevent short-circuiting from adjacent injection locations.

The following table depicts an amount of injectants that could be used in this embodiment.

Component	Concentration
Iron	45% by wight
Blue Green Algae	5% by weight
Kelp	55% by weight

Another embodiment of the present invention is carried out in the following steps.

Step 1: Suspension injection

A solution of zero-valent iron, micro dried seaweed powder and sodium sulfite is injected into the subsurface using a pump. The following table depicts an amount of injectants that could be used in this embodiment.

Component	Concentration
Kelp	45% by weight
Iron	55% by weight

Therefore, the foregoing is considered as illustrative only of the principles of the invention. Further, since numerous modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and operation shown and described, and accordingly, all suitable modifications and equivalents may be resorted to, falling within the scope of the invention. What is claimed as being new and desired to be protected by Letters Patent of the United States is as follows:

CLAIMS

What is claimed is:

1. A method for accelerated biotic dechlorination of groundwater and soils, whereby anaerobic processes are stimulated comprising the following steps of:

Injecting into the groundwater and soils via temporary rods or permanent wells a mixture containing a predetermined mass of seaweed powder under pressure;

Injecting a mixture comprising zero valent metal particles to react with dissolved chlorinated solvents;

Injecting a mixture containing zero valent metal particles so that the corrosion of said metal particles results in the elevation of the bulk pH of the surrounding groundwater;

Injecting dried powdered seaweed or kelp in combination with an oxygen scavenger into the groundwater and soils to remove oxygen and ensure the subsurface environment is reductive.

2. The method of claim 1 wherein the pressure is achieved via compressed gas injection or a pumped liquid injection system.

3. The method of claim 1 wherein the delivered materials are educed into the compressed gas stream.

4. The method of claim 3 wherein the delivered materials are liquid and injected by pumping.

5. The method of claim 4 wherein when the materials are pumped, they are pumped as a suspension.

6. The method of claim 1 wherein the zero-valent metal particles is a powder consisting of particles between 100 nanometers and 500 micrometers in diameter.

7. The method of claim 3 wherein said gas is from the group consisting of air, nitrogen or carbon dioxide.

8. The method of claim 1 wherein the suspension of materials includes an oxygen scavenger such as a reducing agent.

9. The method of claim 8 wherein the reducing agent is sodium bisulfite.

10. The method of claim 1 wherein injecting the mixtures and materials is done in such a manner which ensures their dispersion into the subsurface.

11. A method for accelerated biotic dechlorination of groundwater and soils, whereby anaerobic processes are stimulated comprising the step of:

Injecting into groundwater and soils under pressure a mixture containing micro seaweed powder and zero-valant metal particles.

12. The method of claim 11wherein said metal is iron.

13. The method of claim 11 wherein the entireties of the materials are commingled immediately prior to emplacement into the subsurface.

14. The method of claim 13 wherein the entirety of the materials are packaged together as a mixture.

15. The method of claim 1 wherein said metal particles are iron particles.

16. The method of claim 1 wherein the step of injecting a predetermined mass of soluble micro seaweed is in conjunction with insoluble micro seaweed powder.

17. The method of claim 1 wherein the step of injecting a predetermined mass of soluble micro seaweed mixed with insoluble micro seaweed powder in addition to a mixture of zero valent iron.

ABSTRACT

The induction of reducing conditions and stimulating anaerobic process through the addition of species of seaweed (Dulse, Nori, Ascophyllum nodosum, and Kelp) to accomplish accelerated dechlorinization of soil and groundwater contaminated with chlorinated solvents and heavy metals.

APPENDIX 4 – CASE STUDY

Project Summary

In-Situ Geochemical Stabilization (ISGS) was utilized at a site located near Fanwood, New Jersey to remediate soils and groundwater impacted by the historical release of coal tars and heavy ended petroleum compounds. The compounds of concern included benzene, Benzo(a)anthracene, Benzo(a)pyrene, and multiple other VOC and SVOC contaminants. The in-situ program covered a total area of 8,955 square feet and treated soil and groundwater from 5-10 ft. below ground surface. The remedial liquids were injected into 44 points via direct push technologies (Fig.1). Two intervals between from 5-7 and 8-10 feet below ground surface (bgs) were used to inject the liquids into the targeted media affecting a radius of 7.5 feet for each point.

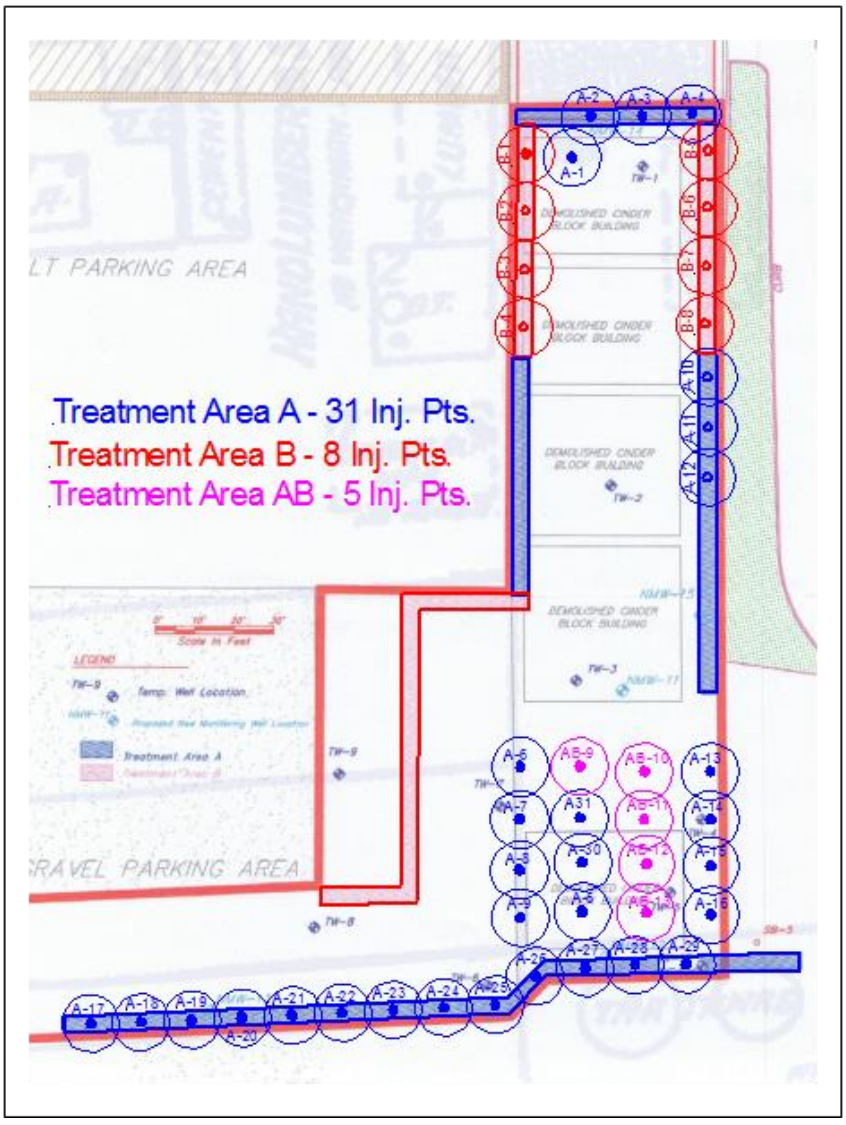


Figure 1. Site map showing the location of 44 in-situ injection points.

Innovative Environmental Technologies, Inc.

Remediation Plan

In-Situ Geochemical Stabilization (ISGS) entails the use of modified permanganate solutions for the purposes of mass removal and flux reduction (i.e., NAPL stabilization). As the oxidant migrates through the treatment area, various (bio)geochemical reactions destroy the targeted compounds present in the dissolved phase. This causes a “hardening” or "chemical weathering” of the NAPL as it steadily loses its more labile components. This causes a net increase in viscosity of the organic material, which yields a more stable, recalcitrant residual mass. In addition, both the insoluble MnO_2 precipitate that results from permanganate oxidation and other mineral species included in the ISGS formulation accumulate along the NAPL interface, physically coating the NAPL and thereby reducing the flux of dissolved-phase constituents of interest (COI) into the groundwater.

Unlike the typical application of In Situ Chemical Oxidation (ISCO) reagents, ISGS is used to encapsulate NAPL, with chemical oxidation of COIs being a secondary affect. As a result, the overall oxidant dosing is often substantially less than with typical ISCO applications, resulting in rapid, highly effective treatment at a much lower cost.

Results

Monitoring Wells

Five monitoring wells were sampled during the baseline sampling event of August 2013 and the first two post-injection sampling events. These wells are: MW-11, MW-12, MW-13, MW-14 and MW-15. The locations of the five monitoring wells are presented in the map below.

MW-11

Monitoring well MW-11 is located in the center of the main treatment area, where the demolition of the main building occurred. Based on the analytical data of the January 2014 sampling event, it appears that the remedial treatment event has dramatically impacted the concentrations of all targeted contaminants in the vicinity of monitoring well MW-11. The concentrations of almost all SVOC compounds have decreased to levels below the laboratory detection limits, while the total concentrations of the BTEX contaminants has decreased by 85%. The concentration of the total alkanes has also reached non-detect levels.

Table 1. CVOC Data for MW-11 (µg/L).

MW-11			
Sampling Date	**08/30/2013**	**10/16/2013**	**01/15/2014**
Acenaphtylene	0.461	0.312	ND 0.10
Benzo(a)anthracene	0.255	0.847	0.146
Benzo(a)pyrene	0.172	0.54	ND 0.10
Benzo(b)fluoranthene	0.218	0.76	ND 0.10
Chrysene	0.166	0.508	ND 0.10
Fluorene	0.791	0.314	0.239
Benzene	67.5	8.4	14.4
Ethylbenzene	6.6	ND 5.0	0.77 J
Toluene	46.5	ND 5.0	3.0
Total Xylenes	19.1	ND 5.0	2.7
Total Alkanes	63 J	ND	ND

ND: Not Detected

MW-12

Monitoring well MW-12 is located in the vicinity of injection points A-27 and A-28 in the southern part of the targeted treatment area. Based on the analytical groundwater data of the January 2014 sampling event, it appears that the remedial treatment event had a significant effect in the concentrations of the targeted SVOCs and VOCs. The concentrations of the SVOCs decreased significantly and reached levels below the laboratory detection in most occasions. Benzo(a)anthracene, Benzo(a)pyrene and Benzo(b)fluoranthene that recorded highly elevated concentrations during the August 2013 baseline sampling events have shown decreases of 93%, 96% and 95% respectively. Similarly the effect of the remedial injection was substantial for the concentrations of VOC compounds, with total alkanes decreasing below the laboratory detection limits and BTEX compounds overall decreasing by 68%.

Table 2. CVOC Data for MW-12 (µg/L).

MW-12			
Sampling Date	**08/30/2013**	**10/16/2013**	**01/15/2014**
Acenaphtylene	1.75	ND 0.10	0.151
Benzo(a)anthracene	5.13	0.44	0.385
Benzo(a)pyrene	6.31	0.162	0.248
Benzo(b)fluoranthene	6.30	0.222	0.292
Chrysene	5.15	0.224	0.261
Bis(2-Ethylhexyl)phthalate	5.80	ND 2.0	ND 2.0
Ideno(1,2,3-cd)pyrene	3.80	ND 0.10	0.105
Benzene	10.2	8.2	11.1
Ethylbenzene	3.8	1.6	0.51 J
Toluene	8.4	1.8	ND 2.0
Total Xylenes	22.4	7.3	2.8
Total Alkanes	412.4 J	ND	ND

ND: Not Detected

MW-13

Monitoring well MW-13 is located in the vicinity of injection points A-19 and A-20 in the southwestern part of the targeted treatment area. Based on the analytical data the injection event of September 2013 had a significant impact in the concentrations of all targeted SVOC compounds. Benzo(a)anthracene, Benzo(a)pyrene and Benzo(b)fluoranthene recorded decreases of 77%, 89% and 90% respectively compared to their August 2013 baseline sampling values, while naphthalene was the compound that was massively affected with the concentration decreasing from 1,920 µg/L in August 2013 to 1.18 µg/L in January 2014. BTEX concentrations appear to have slightly spiked during the January 2014 sampling event; however it is expected that they will decrease during the upcoming sampling event.

Table 3. CVOC Data for MW-13 (µg/L).

MW-13			
Sampling Date	**08/30/2013**	**10/16/2013**	**01/15/2014**
Acenaphtylene	81.3	11.6	0.64
Benzo(a)anthracene	2.92	0.435	0.684
Benzo(a)pyrene	1.75	ND 0.10	0.192
Benzo(b)fluoranthene	2.24	ND 0.10	0.233
Benzo(g,h,i)perylene	0.698	ND 0.10	ND 0.10
Benzo(k)fluoranthene	0.895	ND 0.10	0.121
Chrysene	2.02	0.235	0.409
Naphthalene	1,920	187	1.18
Benzene	100	48.7	175
Ethylbenzene	43.4	10.4	61.9
Toluene	160	24.4	161
Total Xylenes	179	41.6	171
Total Alkanes	3,625 J	ND	ND

ND: Not Detected

MW-14

Monitoring well MW-14 is located in the northern part of the targeted treatment area in the vicinity of injection points A-2 and A-3. Monitoring well MW-14 did not record elevated SVOC and VOC concentrations during the baseline sampling event with the exception of diethyl phthalate, benzene, ethylbenzene and toluene. During the 120-day post-injection sampling event the concentrations of the aforementioned compounds have all decreased to levels below the laboratory detection limits except for benzene that decreased by 43%.

Table 4. CVOC Data for MW-14 (µg/L).

MW-14			
Sampling Date	**08/30/2013**	**10/16/2013**	**01/15/2014**
Diethyl phthalate	7.2	-	ND 2.0
Benzene	8.1	7.1	4.6
Ethylbenzene	61.9	ND	ND 5.0
Toluene	2.0	ND 5.0	ND 1.0
Total Xylenes	ND	ND 5.0	ND 1.0
Total Alkanes	6.3 J	ND	ND

ND: Not Detected

MW-15

Monitoring well MW-15 is located in the center of the main treatment area, where the demolition of the main building occurred. Based on the analytical SVOC data of the January 2014 sampling event, it appears that the remedial treatment event has dramatically impacted the concentrations of all targeted contaminants in the vicinity of monitoring well MW-15. The concentrations of almost every SVOC compound have decreased to levels below the laboratory detection limits, while the concentrations of the BTEX contaminants that were significantly low during the baseline sampling event have also reached levels below the laboratory detection limits.

Table 5. CVOC Data for MW-15 (µg/L).

MW-15			
Sampling Date	**08/30/2013**	**10/16/2013**	**01/15/2014**
Acenaphtylene	0.197	ND 0.11	ND 0.10
Benzo(a)anthracene	0.459	ND 0.11	0.153
Benzo(a)pyrene	0.497	ND 0.11	ND 0.10
Benzo(b)fluoranthene	0.607	ND 0.11	ND 0.10
Chrysene	0.397	ND 0.11	ND 0.10
Naphthalene	0.453	0.541	ND 0.10
Benzene	0.31 J	0.52 J	ND 1.0
Ethylbenzene	ND	ND 1.0	ND 1.0
Toluene	0.58 J	ND 1.0	ND 1.0
Total Xylenes	0.62 J	ND 1.0	ND 1.0
Total Alkanes	5.4 J	ND 1.0	ND 1.0

ND: Not Detected

Free Product Data

Ten different wells were sampled before the implementation of the remedial injection event of September 2013 and the depth of the free product that was present in each well was measured. As Table 6 shows all ten wells appear to have elevated free product levels during the March 2013 baseline sampling event that ranged from 1.22 ft to 5.37 ft.

Table 6. Injection Thickness of Free Product (ft).

Well ID	Sampling Date					
	05/25/2012	06/07/2012	03/14/2013	10/16/13	10/18/13	1/15/14
TW-1/MW-14	4.16	3.90	4.24	**ND**	**ND**	**ND**
TW-2/MW-15	5.34	4.98	5.31	**ND**	**ND**	**ND**
TW-3/MW-11	5.26	5.12	5.37	**ND**	**ND**	**ND**
TW-4	5.35	5.02	5.11			
TW-5/MW-12	5.60	4.99	4.64	**ND**	**ND**	**ND**
TW-6	4.06	4.02	3.75			
TW-7	5.31	5.08	5.11			
TW-8/MW-13	3.43	3.07	3.26	**ND**	**ND**	**ND**
TW-9	1.15	1.14	1.22			
TW-10	5.02	5.09	4.16			

Five monitoring wells were sampled upon the completion of the injection event to address the effect of the remedial injection in the free product that was present in the subsurface. These wells are MW-11, MW-12, MW-13, MW-14 and MW-15.

Monitoring well MW-11 is closely located (within a few feet) from monitoring point TW-3 that recorded free product thickness of 5.37 ft in March 2013, in the area where the demolished Cinder Block Building is located. Based on the January 2014 sampling event no free product was detected in MW-11.

Monitoring well MW-12 is located in the vicinity of targeted treatment area A and more specifically close to injection points A-27 and A-28. Monitoring well TW-5 that recorded a free product thickness of 4.64 ft is also located in the same area. As the data from the last sampling event indicates the ISGS solution was very effective in treating the existing contamination since no free product was detected in MW-12.

Monitoring well MW-13 is also located in the vicinity of targeted treatment area A and more specifically close to injection points A-19 and A-20. Monitoring well TW-8 that recorded a free product thickness of 3.26 ft is located relatively close to MW-13. Based on the January 2014 data the ISGS solution was found effective in treating the targeted contamination since no free product was detected in MW-13.

Monitoring well MW-14 is located in the northern part of the targeted treatment area in the vicinity of injection points A-2 and A-3 very close to monitoring point TW-1. The thickness of free product in TW-1 was measured at 4.24 ft; however upon the completion of the remedial design no free product was detected in monitoring well MW-14.

Monitoring well MW-15 is located in the center of the main treatment area, where the demolition of the main building occurred, close to monitoring points MW-11, TW-2 and TW-3. Monitoring points TW-2 and TW-3 recorded free product thickness of 5.31 and 5.37 ft respectively. Monitoring well MW-15, similar to MW-11, did not show the presence of any free product during the January 2014 sampling event.

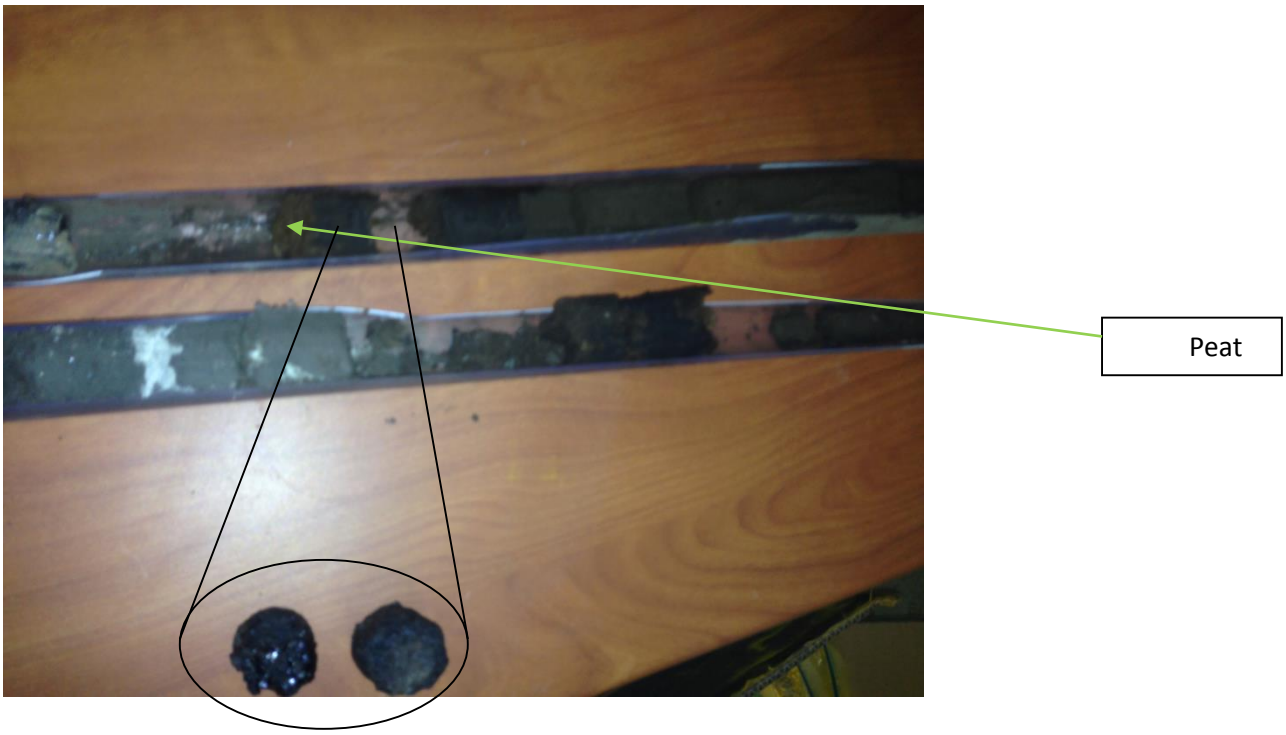
Conclusions and Recommendations

Based on the data provided, it appears that the injection of the In-Situ Geochemical Stabilization (ISGS) solution was very effective in addressing the contamination that was present on the site located in Fanwood, NJ.

The groundwater data is extremely encouraging with almost every VOC and SVOC compound either decreasing below the laboratory detection limits or recording significant concentration reductions compared to their baseline sampling values.

Furthermore the free product that was present in the ten wells that were sampled during the baseline sampling event disappeared within 30 days of the implementation of the injection event. All five monitoring wells that were sampled after the September 2013 injection event did not record any free product during the three post-injection sampling events of October 2013 (two events) and January 2014.

Two pictures of the received soil samples are presented below. It appears that following the ISGS solution injection the creosote with the strong odor that was observed above the peat layer was able to "solidify", with no associated odor (15 days following injection). In the picture below the peat layer is easily seen and the ISGS formation immediately above it.



Close-up of ISGS

APPENDIX B

QUALITY ASSURANCE PROJECT PLAN (QAPP)

Sterling Environmental Engineering, P.C.

QUALITY ASSURANCE PROJECT PLAN

53 PUTNAM STREET
SARATOGA SPRINGS, NEW YORK
BCP #C546057

Prepared for:

Putnam Resources, LLC
48 Union Avenue, Suite 1A
Saratoga Springs, New York 12866

Prepared by:

Sterling Environmental Engineering, P.C.
24 Wade Road
Latham, New York 12110

November 12, 2020

"Serving our clients and the environment since 1993"

QUALITY ASSURANCE PROJECT PLAN
(QAPP)

53 PUTNAM STREET
SARATOGA SPRINGS, NEW YORK
BCP #C546057

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1.0 INTRODUCTION

This Quality Assurance Project Plan (QAPP) was prepared by Sterling Environmental Engineering, P.C. on behalf of Putnam Resources, LLC ("Putnam Resources") for the New York State Department of Environmental Conservation (NYSDEC) Brownfield Cleanup Program (BCP) Site #C546057 located at 53 Putnam Street, City of Saratoga Springs, Saratoga County, New York (hereinafter the "Site"). This QAPP accompanies a Remedial Action Work Plan (RAWP) to establish processes and procedures necessary to ensure high quality, valid data are obtained that meet the remediation objectives.

Primary contaminants of concern (COC) are those compounds that will be addressed either through active remedial measures and/or engineering and institutional controls because they were detected during the RI and previous investigations at concentrations greater than NYSDEC Restricted Residential Use Soil Cleanup Objectives (RRUSCO), Protection of Groundwater SCOs specified in 6 NYCRR Part 375, Table 375-6.8(b), and NYSDEC Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations (AWQS), as set forth in the NYSDEC Division of Water Technical and Operational Guidance Series (TOGS 1.1.1).

The COCs identified in the Remedial Investigation (RI) include petroleum-related volatile organic compounds (VOC) (benzene, ethylbenzene, toluene), chlorinated VOCs (cis-1,2-dichloroethene, tetrachloroethene, trans-12-dichloroethene, trichloroethene, and vinyl chloride), pesticide compounds (4,4-DDT and 4,4-DDE), metal compounds (mercury, arsenic, barium, copper, zinc, and lead), and per- and polyfluoroalkyl substances (PFAS).

1.1 Purpose and Objectives

Analytical sampling of soil and groundwater will be performed in association with the selected remedy as described in the RAWP. Soil will be sampled and analyzed to document soil removal, evaluate the effectiveness of in-situ remediation, and to characterize soil imported for backfill, if any. Groundwater samples will be collected and analyzed to evaluate groundwater quality and effectiveness of in-situ remediation.

1.2 Key Project Personnel

Key project personnel are listed in Table 1.

Table 1 - Key Project Personnel

Project Personnel	Title	Organization	E-mail / Telephone
Samantha Salotto	Project Manager	NYSDEC Central Office	Samantha.Salotto@dec.ny.gov (518) 402-9903
Melissa Deyo	Project Manager	Alpha Analytical Laboratory	mdeyo@alphalab.com (508) 898-9220
Thomas M. Johnson, P.G.	Project Manager	Sterling Environmental Engineering, P.C.	Thomas.Johnson@sterlingenvironmental.com (518) 456-4900

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Andrew M. Millspaugh, P.E.	Quality Assurance Officer & Project Engineer	Sterling Environmental Engineering, P.C.	andrew.millspaugh@sterlingenvironmental.com (518) 456-4900
Paul Scholar	Field Team Leader	Sterling Environmental Engineering, P.C.	Paul.Scholar@sterlingenvironmental.com (518) 456-4900

2.0 SOIL AND GROUNDWATER SAMPLING

Analytical sampling of soil and groundwater will be performed in association with Site remediation to document completion and effectiveness of the selected remedy. A summary of the sampling and analysis of each media and applicable parameters is presented below. Tables 2 and 3 present the cleanup objectives and sampling methods, respectively.

2.1 Soil Sampling

Soil remaining after the remedial excavation is complete will be sampled and analyzed to document soil quality remaining in place and to characterize soil for disposal. All materials imported to the Site for purpose of backfill or grading, if any, will be sampled in accordance with NYSDEC DER-10 Section 5.4(e) and Table 4.4(e)10 including PFAS as emerging contaminants, unless the material is exempt from testing in accordance with the requirements of DER-10 Section 5.4(e)5. Soil imported to the Site for use as backfill or as a protective cover will comply with the requirements of 6 NYCRR Part 375-6.7 (d). The type of soil samples and parameters to be analyzed for are provided in Sections 2.1.1 through 2.1.3, and analytical methods are provided in Table 3.

2.1.1 Documentation Sampling

Documentation sampling will be performed to document the quality of the soil that is to remain in place within excavation areas after excavations are completed. These soil samples will be collected in accordance with the RAWP and analyzed for:

- Part 375 Mercury (Hg)
- Part 375 Semi-Volatile Organic Compounds (SVOC)

2.1.2 Imported Soil Sampling

Imported soil sampling will be performed to verify the quality of the soil brought onsite for use as backfill, if any, meets the soil cleanup objectives for the property in accordance with the RAWP. The number of samples will comply with DER-10, Table 4.4(e)10 and analyzed for the following parameters identified in DER-10, Appendix 5:

- Part 375 Volatile Organic Compounds (VOC)
- Part 375 Semi-Volatile Organic Compounds (SVOC)
- Part 375 Metals, Total

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- Part 375 Polychlorinated Biphenyls (PCB)
- Part 375 Pesticides
- Per/Polyfluoroalkyl Substances (PFAS) consisting of 21 compounds.

2.1.3 Subsurface Soil Sampling

Subsurface soil sampling will be performed before and after the in-situ treatment to determine the effectiveness of the treatment. Subsurface soil samples will be collected at the designated locations and analyzed for the following parameters in accordance with the RAWP:

- Part 375 Volatile Organic Compounds (VOC)
- Part 375 Semi-Volatile Organic Compounds (SVOC)

2.1.4 Waste Characterization Sampling

Waste characterization sampling will be performed for excavated soils that will be disposed offsite. Sample parameters and frequency will be in accordance with the disposal facility requirements.

2.2 Groundwater Sampling

Groundwater sampling will be performed to determine the effectiveness of the in-situ remediation and to monitor changes in the quality of the groundwater. Groundwater samples will be collected from onsite monitoring wells and analyzed for the following parameters in accordance with the RAWP:

- Volatile Organic Compounds (VOC) 8260
- Semi-Volatile Organic Compounds (SVOC) 8270
- Total and Dissolved Iron (Fe)
- Sulfate

2.3 Field Measurements

Field measurements will be monitored and recorded during groundwater sampling described in Section 2.2 to evaluate the local changes in groundwater from the in-situ treatment. The following parameters will be recorded from each monitoring well on the appropriate forms:

- Groundwater elevation
- Temperature
- Dissolved Oxygen
- Oxidation/Reduction Potential
- Specific Conductivity, and
- pH.

A water level meter will be used to measure the groundwater elevation. A multi-parameter water quality meter (i.e. ProDSS) will be used, calibrated, and maintained according to the manufacture's guidelines and recommendation. Onsite operation, calibration, and maintenance will be performed daily by trained personnel. Calibration of the instruments will be performed at the beginning and end of each sampling

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day and recorded on the appropriate form. If instruments appear to be reading incorrectly, additional calibration and/or maintenance will be performed to confirm proper operation of the instrument.

2.4 Reporting

The following sections provide the reporting requirements for soil and groundwater media.

2.4.1 Soil Sampling

Documentation soil samples will be collected from the footprint of the final excavation areas. Sidewall samples will be collected every 30 linear feet from the central section of the wall and floor samples will be collected for every 900 square feet of area. The number of each sample location type for each excavation is identified in the RAWP. These samples will be analyzed for the parameters identified in Section 2.1.1. Laboratory reporting limits for documentation soil samples will be below 6 NYCRR Part 375 Protection of Groundwater SCOs as outlined in Table 2.

Imported soil sampling will be performed prior to the soil being brought to the Site for use as backfill. The frequency of samples and parameters to be analyzed are identified in Section 2.1.2. Laboratory reporting limits for imported soil samples will be below 6 NYCRR Part 375 Protection of Groundwater SCOs as outlined in Table 2.

Subsurface soil sampling will be performed prior to and after in-situ treatment in the designated target treatment zones in accordance with the RAWP. The samples and parameters to be analyzed are identified in Section 2.1.3.

2.4.2 Groundwater Sampling

Groundwater samples will be collected, and field parameters will be measured and recorded in accordance with the RAWP. Laboratory reporting limits for aqueous samples will be below the water quality standards established by the New York State Division of Water - Technical Operation and Guidance Series (TOGS 1.1.1) and identified in Table 2.

2.5 Sampling Procedures

This section describes the sampling procedures to be implemented for the collection of soil and groundwater samples during the remediation process.

2.5.1 Soil Sampling

All soil samples will be collected using a stainless-steel trowel, specific for each sample, from the designated locations identified in the RAWP and Section 2.4 above. Volatile organic compound (VOC) samples will be grab samples from designated locations. The soil will be immediately placed in a laboratory-provided sampling jar. The remaining soil samples will be collected by placing the soil in a stainless-steel mixing bowl or sealable plastic bag to be blended into a composite sample and placed into laboratory provided sample jars. All soil samples will be handled, shipped, and tracked per Sections 2.6

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through 2.9. Sampling equipment will be appropriately disposed or decontaminated in accordance with the procedures described in the RAWP.

2.5.2 Groundwater Sampling

Groundwater samples will be collected using appropriate sampling equipment, specific for each sample location, from the designated locations identified in the RAWP. Wells will be purged a minimum of three (3) volumes of water prior to sample collection. Field parameters identified in Section 2.3 will be measured during purging and samples will be collected after field parameters stabilize. Groundwater will be collected in analyte-specific, laboratory-provided sampling containers, with appropriate preservatives if required by the analytical method. All samples will be handled, shipped, and tracked per Sections 2.6 through 2.9. Sampling equipment will be appropriately disposed or decontaminated in accordance with the procedures described in the RAWP.

2.5.3 PFAS Sampling

Sampling for PFAS compounds requires special consideration for use of field equipment, clothing, and supplies that may contain PFAS compounds resulting in unrepresentative samples. The Field Team must comply with the following table of prohibited and acceptable items for samples that will be analyzed for PFAS:

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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
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	**Sunscreens** - Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my face, Baby sunscreens that are "free" or "natural" **Insect Repellents** - Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellant, Herbal Armor, California Baby Natural Bug Spray, BabyGanics **Sunscreen and insect repellant -** Avon Skin So Soft Bug Guard Plus – SPF 30 Lotion
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

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Samples to be collected as part of the RAWP to confirm remediation cleanup objectives are achieved for soil and groundwater. Soil samples will be analyzed for VOCs, SVOCs, and Metals (Mercury). Groundwater samples will be analyzed for VOCs and SVOCs. The cleanup objective for these parameters are presented in Table 2.

Table 2 –Analytical Reporting Requirements

Analyte	Aqueous Sample Cleanup Objective	Soil Sample Cleanup Objective
VOCs	TOGS 1.1.1	6 NYCRR Part 375 Protection of Groundwater
SVOCs	TOGS 1.1.1	6 NYCRR Part 375 Protection of Groundwater
Metals	TOGS 1.1.1	6 NYCRR Part 375 Protection of Groundwater

Samples of imported soil will also be analyzed for PCBs and Pesticides and groundwater samples will also be analyzed for PFAS, Sulfate, and Iron as described in the RAWP; however, the remediation cleanup objectives do not apply to these parameters.

Sample media, analytical parameters, and reporting requirements are provided below in Table 3.

Table 3 –Sampling Requirements

Sample Media	Analytical Parameters	Holding Time (days)	Reporting	Laboratory
Soil	Part 375 VOCs via USEPA 8260C	14	Category B	Alpha Analytical Laboratories
Soil	Part 375 SVOCs via USEPA 8270D	14	Category B	Alpha Analytical Laboratories
Soil	Part 375 Pesticides USEPA 8081	14	Category B	Alpha Analytical Laboratories
Soil	Part 375 Metals via USEPA 6010	180	Category B	Alpha Analytical Laboratories
Soil	Part 375 Metals (Mercury) via USEPA 7471	28	Category B	Alpha Analytical Laboratories
Soil	Part 375 Metals (Hexavalent Chromium) via USEPA 7196	30	Category B	Alpha Analytical Laboratories

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Soil	Part 375 Metals (Cyanide) via USEPA 9012	14	Category B	Alpha Analytical Laboratories
Soil	Total PCBs via USEPA 8082	14	Category B	Alpha Analytical Laboratories
Soil	NY 21 PFAS via 537(M) Isotope Dilution	28	Category B	Alpha Analytical Laboratories
Groundwater	VOCs via USEPA 8260	14	Category B	Alpha Analytical Laboratories
Groundwater	SVOCs via USEPA 8270	7	Category B	Alpha Analytical Laboratories
Groundwater	Sulfate via USEPA 300.0	28	Category B	Alpha Analytical Laboratories

Note: Category A deliverables are required for samples analyzed for purposes of offsite disposal, unless otherwise required by the disposal facility. Category B laboratory deliverables are required for samples collected to confirm attainment of remediation cleanup objectives.

2.6 Laboratory Sample Custody Procedures

A New York State Department of Health (NYSDOH) Environmental Laboratory Accreditation Program (ELAP) certified laboratory will be used that meets the requirements for sample custody procedures and cleaning and handling sample containers and analytical equipment. A Chain of Custody (COC) form shall include the sampler(s) name, sample collection time, sample date, analysis type, container type, number of containers, type of preservatives, and reporting requirements. The COC shall accompany the samples from field collection, to analysis at the laboratory. Each recipient shall sign and date the COC form when the samples are received. A COC form is provided by the analytical laboratory.

2.7 Data Quality Requirements and Assessments

Data quality requirements and assessments are provided in the NYSDEC ASP, which includes the detection limit for each analyte and sample matrix. Analyte detection limits will be at least as low as the comparative regulatory standard. Note that the quantification limits, estimated accuracy, accuracy protocol, estimated precision, and precision protocol are determined by the laboratory and will be in conformance with the requirements of the NYSDEC ASP (latest revision).

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2.8 Sample Identification

Each sample container will have an affixed durable label that specifies the following sample information:

- Sample location.
- Sample type.
- Sample identification number.
- Date and time of sample collection.
- Laboratory analyte.
- Preservative type (if applicable).

2.9 Sample Preservation, Handling, and Shipment

All analytical samples will be placed in appropriate laboratory-provided sample containers as specified in the NYSDEC ASP. Holding time criteria identified for individual ASP methods will be followed.

Prior to transport to the laboratory, sample containers will be checked for proper identification and compared to the field logbook for accuracy. The samples will be wrapped with a cushioning material and will be placed in a cooler with ice immediately after sample collection and maintained at 4 degrees Celsius (4°C) throughout the duration of the sampling event and subsequent transport to and storage at the analytical laboratory until analysis.

Chain of Custody Forms will be placed in a sealed plastic bag and taped to the underside of the cooler lid. The cooler will be sealed with packaging tape and custody seals will be placed in such a manner that any opening of the cooler prior to arrival at the laboratory can be detected.

All samples will be transported to ensure laboratory receipt within 48 hours of sample collection in accordance with NYSDEC requirements. The laboratory will be notified prior to the shipment of the samples, or to arrange a courier pickup. Sample containers and preservation are listed in Table 4.

Table 4 – Sample Preservation Guidelines

Container Type	Container Size	Preservative	Matrix
Glass VOA Vial	40 mL	Hydrochloric Acid (HCL)	Groundwater (VOC)
Amber Glass Bottle	(2) 250 mL	Unpreserved	Groundwater (SVOC)
Plastic	250 mL	Unpreserved	Groundwater (Sulfate)
Glass Jar	4 oz. with septa	Unpreserved	Soil (VOC)
Glass Jar	8 oz	Unpreserved	Soil (SVOC)
Glass Jar	4 oz	Unpreserved	Soil (Pesticides)
Glass Jar	8 oz	Unpreserved	Soil (Metals – Cyanide)
Glass Jar	2 oz	Unpreserved	Soil (Metals – Mercury)
Glass Jar	4 oz	Unpreserved	Soil (Metals – Hexavalent Chromium)

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Glass Jar	2 oz	Unpreserved	Soil (Metals)
Glass Jar	8 oz	Unpreserved	Soil (PCB)
Plastic	8 oz	Unpreserved	Soil (PFAS)

3.0 DECONTAMINATION PROCEDURES

All field sampling equipment should be sterile and dedicated to a particular sampling location. In situations where this is not possible, decontamination procedures will be used to reduce cross-contamination between sample locations. A decontamination station will be established at an area located away from the suspected source of contamination and close enough to the sampling area to keep equipment handling to a minimum.

All non-disposable equipment will be decontaminated prior to initial use, prior to moving to a new sampling location, and prior to leaving the Site. Sampling should begin in the area of the Site with the lowest known contamination and proceed to the areas of highest suspected contamination.

3.1 Decontamination Procedures for Sampling Equipment

Teflon, PVC, polyethylene, polystyrene, and stainless-steel sampling equipment decontamination procedures will be as follows:

- Wash thoroughly with non-residual, non-ionic detergent (such as Alconox) and clean potable distilled water, using a brush to remove particulate matter or surface film.
- Rinse thoroughly with distilled water and air dry.

4.0 FIELD WORK DOCUMENTATION

Proper management and documentation of field work is essential to ensure all necessary work is conducted in accordance with the QAPP. Daily field reports, correspondence, and photo documentation should be collected, and submitted to the appropriate key project personnel (Table 1).

4.1 Daily Field Report

Pertinent information regarding the Site and sampling procedures must be documented. Notations should be made in a legible fashion, noting the time and date of all entries. Information recorded on task-specific field forms need not be duplicated in a log book. Information recorded in this field report should include, but not be limited to, the following:

- Project name and address.
- Name, address, and telephone number of field contact.
- Site address.
- Purpose of sampling.
- Location of sampling point(s).
- Number(s) and volume(s) of sample(s) taken.
- Description of sampling point and sampling methodology.
- Date and time of collection, arrival, and departure.

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- Sample distribution and method of storage and transportation.
- References, such as sketches of the sampling Site or photographs of sample collection.
- Field observations, including results of field analyses (e.g., pH, temperature, specific conductance), water levels, colors, odors, and sheens.
- Signature of personnel responsible for completing log entries.

4.2 Chain of Custody Forms

The Chain of Custody Form is initiated at the laboratory with bottle preparation and is shipped with the bottles. The Chain of Custody remains with the sample(s) at all times and lists the name of the person assuming responsibility for the samples. This person is tasked with ensuring secure and appropriate handling of the bottles and samples. The completed form should indicate that there were no lapses in sample accountability.

A sample is considered in an individual's custody if any of the following conditions are met:

- It is in the individual's physical possession,
- It is in the individual's view after being in his or her physical possession,
- It is secured by the individual so that no one can tamper with it, or
- The individual puts it in a designated and identified secure area.

At a minimum, the following information shall be provided on the Chain of Custody:

- Project name and address
- Project number
- Sample identification number
- Date
- Time
- Sample location
- Sample media
- Analysis requested
- Number and volume of containers
- Sampler(s) name(s) and signature(s)
- Spaces for relinquished by/received by signature and date/time.

The Chain of Custody Form is filled out and signed by the person performing the sampling. The original of the form travels with the sample(s) and is signed and dated each time the sample is relinquished to another party, until the samples reach the laboratory or analysis is complete. The field sampler keeps one copy, and a copy is retained for the project file. Each cooler will have a Chain of Custody that corresponds with the samples for that cooler.

5.0 FIELD CHANGES AND CORRECTIVE ACTION NOTIFICATION

Whenever there is a required or recommended investigation/sampling change or correction, the STERLING Project Manager must be notified for approval (Table 1 – Key Project Personnel).

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6.0 CALIBRATION PROCEDURES AND PREVENTATIVE MAINTENANCE

The following information regarding equipment will be maintained for the project:

1. Equipment calibration and operating procedures will include provisions for documentation of frequency, conditions, standards, and records reflecting the calibration procedures, methods of usage, and repair history of the monitoring unit. Calibration of field equipment will be performed in accordance with manufacturer recommendations.
2. Critical spare parts, necessary tools, and manuals will be available to facilitate equipment maintenance and repair.

7.0 SAMPLE WASTE DISPOSAL

Surplus soil and groundwater generated from sampling activities must be contained and managed through the Site construction activities. Soiled personal protective equipment (PPE) and disposable sampling equipment will be considered solid waste and contained for offsite disposal. If hazardous waste contamination of PPE or disposable equipment is suspected due to elevated measurements of screening instruments, visual observations, odors or other means, PPE and equipment will be drummed and secured onsite and an approved disposal method will be employed.

8.0 LABORATORY DATA DELIVERABLES, QUALITY ASSURANCE, AND QUALITY CONTROL

Laboratory analytical data require both Category A and Category B data deliverables as defined in the NYSDEC ASP, July 2005 (or latest available version). Quality Assurance/Quality Control (QA/QC) samples will be analyzed according to the frequency in Table 5.

Table 5 – Quality Assurance / Quality Control (QA/QC) Samples

QA/QC Sample Type	Frequency
Matrix Spike (MS)	1 per 20 samples
Matrix Spike Duplicate (MSD)	1 per 20 samples
Trip Blank (TB)	1 per 20 samples (or 1 per cooler)
Field Blank (FB)	1 per 20 samples
Duplicate (DUP)	1 per 20 samples

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8.1 Laboratory Trip Blanks

The laboratory supplies trip blank samples with sample containers when VOCs are analyzed. The purpose of trip blank is to detect additional sources of VOCs that might influence contaminant values reported in actual samples both quantitatively and qualitatively. The following are potential sources of contamination:

- Laboratory reagent water
- Sample containers
- Cross contamination in shipment
- Contact with analytical instrumentation during preparation of the sample containers and analysis of the samples at the laboratory
- Laboratory reagents used in analytical procedures

A trip blank consists of a set of 40 mL sample vials filled by the laboratory with demonstrated analyte-free water. Trip blanks should be handled, transported, and analyzed in the same manner as the samples acquired that day, except the trip blank samples are not opened in the field. Trip blanks must accompany samples at a rate of one set per shipment. The temperature of the trip blanks must be maintained at 4°C while onsite and during shipment. Trip blanks must be returned to the laboratory with the same set of bottles they accompanied in the field.

8.2 Duplicates and Matrix Spike/Matrix Spike Duplicates

The selected location for collecting Duplicate and matrix spike/matrix spike duplicates may be randomly chosen. Duplicate sample results are compared to the original sample to ensure proper sampling procedures.

Matrix spike samples are quality control procedures, consistent with NYSDEC ASP specifications, used by the laboratory for internal QA/QC. The matrix spike (MS) and matrix spike duplicates (MSD) are aliquots of a designated water sample which is spiked with known quantities of specified compounds. The matrix spike/matrix spike duplicates are used to evaluate the matrix effect of the sample upon the analytical methodology and to determine the precision of the applicable analytical method.

8.3 Field Blanks

Field Blanks are collected concurrent with PFAS sampling to test for cross contamination and interference form PFAS containing materials not associated with the sample media. A container of contaminant free water is provided by the laboratory and transferred to a second contaminant free sample container in the field at the location where a PFAS sample is collected. The transferred Field Blank is then handled as an analytical sample and analyzed for PFAS compounds to determine if outside sources are impacting the samples.

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APPENDIX C

HEALTH AND SAFETY PLAN
(HASP)

Sterling Environmental Engineering, P.C.

53 PUTNAM STREET
SARATOGA SPRINGS, NEW YORK

HEALTH AND SAFETY PLAN
(HASP)

Prepared for:

Putnam Resources, LLC
48 Union Avenue, Suite 1A
Saratoga Springs, New York 12866

Prepared by:

Sterling Environmental Engineering, P.C.
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November 12, 2020

"Serving our clients and the environment since 1993"

53 PUTNAM STREET
SARATOGA SPRINGS, NEW YORK

HEALTH AND SAFETY PLAN
(HASP)

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SITE SPECIFIC SUPPLEMENT

Project Information

Project Name:	53 Putnam St.
Site Address:	53 Putnam Street, Saratoga Springs, NY 12866
Sterling Project Manager:	Thomas M. Johnson Cell Phone: 518-441-4293 Email: Thomas.Johnson@sterlingenvironmental.com
Project Site Contact:	Same

Hazard Assessment

Scope of Work:	STERLING will provide environmental consulting and engineering consulting services to investigate and remediate the site in accordance with the New York State Department of Environmental Conservation (NYSDEC) Brownfield Cleanup Program.
Suspected Contaminants:	Contaminants known or suspected to be present for media to be contacted: • petroleum-related volatile organic compounds (VOCs) (Benzene, Ethylbenzene, Toluene), • chlorinated VOCs (cis-1,2-Dichloroethene, Tetrachloroethene, trans-1,2-dichloroethene, Trichloroethene, and Vinyl Chloride), • pesticide compounds 4,4-DDT and 4,4-DDE, • metal compounds (mercury, arsenic, barium, copper, zinc, and lead), and • PFAS. https://www.cdc.gov/niosh/npg/default.html
Contaminant Exposure Routes:	Skin: Prevent skin contact. Wear chemical resistant gloves when handling contaminated media. If skin becomes exposed, wash skin with soap immediately. Eyes: Prevent eye contact. Wear safety glasses at all times. If contaminants enter eyes, irrigate eyes immediately. Ingestion: Do not ingest contaminated media. Do not eat, drink, or smoke in exclusion zones. Wash hands thoroughly before eating. Seek medical attention if ingestion occurs. Inhalation: Do not inhale visible dust. Stand upwind of work zones. Seek medical attention for difficulty breathing.
Potential Hazards:	Strenuous activity: Warm up and stretch muscles prior to task. Plan the task to use the correct tool, have appropriate supplies, and coordinate tasks efficiently. Use proper lifting techniques (lift with your legs, not your back). Use a buddy or cart to lift or move items over 50 pounds. Handing contaminated media: Wear appropriate PPE and avoid contacting contaminated media with bare skin. Follow SOPs and site-specific work plans for collecting environmental samples. Work near or around heavy equipment: Be aware of work areas and equipment travel paths. Maintain clear line of site with operator and never enter travel path or swing radius without establishing visual contact. Wear high visibility clothing. Never work under an overhead load.

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	Work near roadway/traffic: Be aware of surroundings and proximity to traffic. Wear high-visibility reflective vest. Use vehicle hazard flashers and place traffic cones to designate work area. Slips, trips, and falls: Minimize distractions and stay alert when traversing uneven or unfamiliar terrain. Wear appropriate footwear for the conditions and avoid carrying bulky or awkward items. Use three points of contact when climbing or descending. Practice good housekeeping. Cold weather work: Know the effects of wind chill and be familiar with symptoms of frostbite and hypothermia. Wear multiple layers of loose fitting clothing (wool or synthetic material. NO COTTON). Wear an outer layer of wind/water proof material. Wear insulated hand and footwear. Schedule work for warmer time of day. Take breaks to warm up inside or in a vehicle. Warm weather work: Know the effects of the heat index and be familiar with symptoms of dehydration, heat stress, and heat stroke. Wear loose clothing and hat to block sun. Drink cool fluids regularly. Schedule work for cooler time of day. Take breaks to cool down in shaded area with air conditioning. Work near and around excavations: Be aware of utility markings. Stay at least 3 feet away from edge of excavation and do not enter any excavation deeper than 4 feet.

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Personal Protective Equipment / Monitoring Equipment / Safety Equipment

Item	Not Applicable	Required	Have Available
Personal Protective Equipment			
High-Visibility Shirt		**X**	
Reflective Vest			**X**
Hard Hat		**X**	
Safety Shoes		**X**	
Muck Boots (or equal)	**X**		
Hearing Protection			**X**
Safety Glasses		**X**	
Respirator	**X**		
Personal Floatation Device	**X**		
Coveralls (e.g., Tyvek)	**X**		
Rain Gear			**X**
Cold Weather Gear	**X**		
Monitoring Equipment			
Photoionization Detector			**X**
Dust Monitor			**X**
4-Gas Meter	**X**		
Safety Equipment			
First Aid Kit		**X**	
Cell Phone		**X**	
Fire Extinguisher (in vehicle)	**X**		
Flashlight	**X**		
Road Cones	**X**		

Emergency Services / Contacts

Saratoga Springs Fire Department	911 or (518) 587-3599
Saratoga Springs Police Department	911 or (518) 584-1800
Ambulance	911
Saratoga Hospital	(518) 587-3222
Poison Control Center	(800) 222-1222
NYSDEC Spills Emergency Response Program	(800) 457-7362

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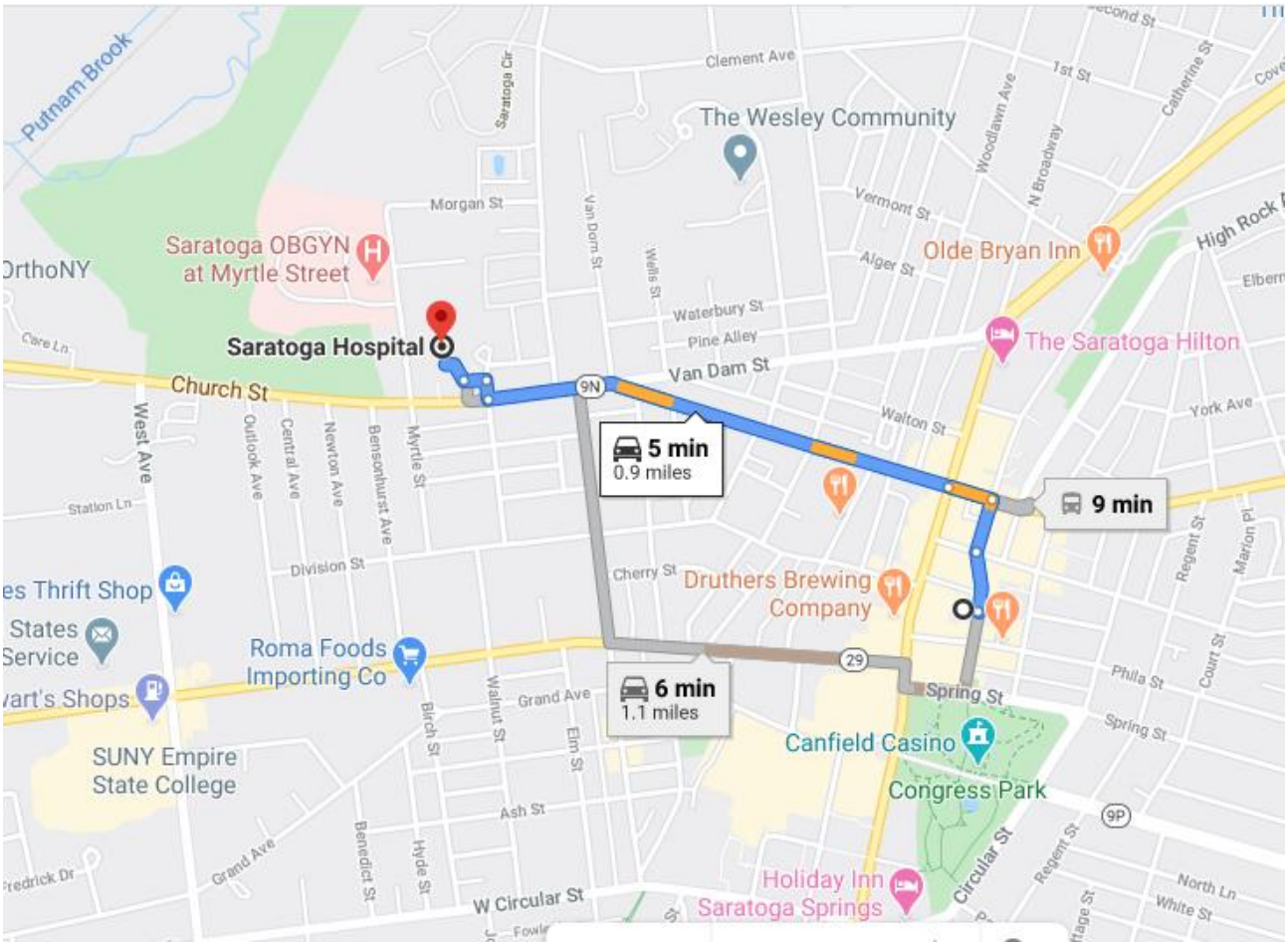
Emergency Room	Saratoga Hospital 211 Church Street Saratoga Springs, NY 12866
Directions	Turn by Turn Directions: Head **NORTH** on Putnam St. toward Gardner Lane (390 ft.) Continue onto Maple Ave. (360 ft.) Turn left onto Lake Ave. (295 ft.) Continue Straight onto Church St. (go 0.6 mi.) Turn right onto N. Van Rensselaer St. (130 ft.) Turn Left Turn Right

Emergency Room Map:



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HEALTH AND SAFETY PLAN

PERSONNEL ACCEPTANCE FORM

By signing below, I acknowledge that I have reviewed this Health and Safety Plan (HASP), am aware of site-specific hazards, and agree to comply with HASP.

NAME (PRINT)	SIGNATURE	DATE

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1.0 GENERAL INFORMATION

The Health and Safety Plan (HASP) identifies specific measures to ensure that hazardous substances or conditions do not adversely impact the health and safety of personnel and the general community (public) for site operations. The HASP is intended to identify potential hazards and appropriate precautions as defined by OSHA 29 CFR 1910.120 (Hazardous Waste Operations and Emergency Response).

All personnel working on this project must read this HASP, acknowledge understanding of this plan, and abide by its requirements.

In general, personnel are responsible for complying with all regulations and policies applicable to the work they are performing. The Project Manager is authorized to stop work if any personnel/subcontractor fails to adhere to the required health and safety procedures.

In addition to this HASP, each contractor must provide their own HASP that addresses minimum training requirements and potential hazards for activities specific to their scope of work.

2.0 DESIGNATION OF RESPONSIBILITIES

Implementing this HASP is the responsibility of all personnel. The Project Manager is responsible for overall project administration, including health and safety. The Field Team Leader is responsible for ensuring the HASP is implemented in the field and is the primary point of contact to the Project Manager. The Project Manager and Field Team Leader will be designated prior to any site activities.

The Project Manager is responsible for:

- Ensuring the availability, use, and proper maintenance of specified personal protective equipment (PPE), decontamination, and other health or safety equipment.
- Maintaining a high level of safety awareness among personnel/subcontractors and communicating pertinent matters to them promptly.
- Ensuring all field activities are performed in a manner consistent with this HASP.
- Monitoring for dangerous conditions during field activities.
- Ensuring proper decontamination of personnel and equipment.
- Coordinating with emergency response personnel and medical support facilities.
- Initiating immediate corrective actions in the event of an emergency or unsafe condition.
- Notifying the New York State Department of Environmental Conservation (NYSDEC) and project owner of any emergency, unsafe condition, problem encountered, or exception to the requirements of this HASP.
- Recommending improved health and safety measures.

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The Project Manager generally provides office support to the field team but may be present during field activities. The presence of the Project Manager shall in no way relieve any person or company of its obligations to comply with the requirements of the HASP and all applicable Federal, State and local laws and regulations.

The Field Team Leader is responsible for:

- Communicating with the Project Manager during field activities.
- Ensuring the HASP is implemented during field activities.
- Leading daily "tailgate" safety talks prior to beginning work.
- Monitoring for dangerous conditions during field activities.
- Ensuring proper decontamination of personnel and equipment.

All personnel involved in the project must be familiar with and conform to the safety protocols prescribed in this HASP, and communicate any relevant experience or observations to the Project Manager to ensure that these valuable inputs improve overall safety. Individual project members are the key elements in ensuring health and safety compliance. Every project member is considered responsible for implementing and following this HASP.

Requirements and guidelines in this HASP are subject to modification by the Project Manager in response to additional information obtained during field work regarding the potential for exposure to hazards. Updates will be communicated to field personnel as they are made.

2.1 Daily Tailgate Meeting

Each workday before beginning site activities, the Field Team Leader will lead a "tailgate" safety meeting with all personnel. On larger projects, daily safety meetings may be led by a dedicated safety officer for a general contractor. In these instances, STERLING personnel should attend and participate in the safety meeting. Safety meetings should review the day's work to be performed, anticipated hazards, and the weather forecast. An opportunity should be given to allow all workers to ask questions. If personnel arrive to the site after the safety meeting has ended, they should seek out the Field Team Leader to receive a summary of the meeting before beginning site work.

2.2 Stop Work Authority

All personnel have authority to stop work if or when they observe an unsafe act in progress or about to occur, or if a task is unclear and needs additional planning. Personnel will initiate a stop work order by notifying the Field Team Leader. If the Field Team Leader is in control of the task, work will be stopped immediately, the task will be reviewed, changes will be made to remedy the unsafe condition, and then work will resume if unsafe condition is corrected.

If the Field Team Leader is not in control of the task (e.g., unsafe act by a contractor), the Field Team Leader will immediately direct STERLING personnel to stop work and move to a safe location. If it is safe to do so, the Field Team Leader will notify those involved in the unsafe task to stop work to review the task. If it is unsafe, the Field Team Leader will notify a project representative in accordance with the chain of command (e.g., site superintendent). The Field Team Leader will then notify the STERLING Project Manager. Following notification, the Field Team Leader, Project Manager, and other project personnel will review the task, implement necessary corrections, and then resume work.

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3.0 SITE-SPECIFIC HEALTH AND SAFETY CONCERNS

3.1 Suspected Contaminant Hazards

Elevated concentrations of contaminants are present above the soil cleanup objectives (SCOs). Documented reports of a leaking underground storage tank (UST) and historical use of the property as a dry cleaners has resulted in the residual soil and groundwater contamination. The following is a list of the contaminants of concern identified during the Remedial Investigation (RI).

- petroleum-related volatile organic compounds (VOCs) (Benzene, Ethylbenzene, Toluene),
- chlorinated VOCs (cis-1,2-Dichloroethene, Tetrachloroethene, trans-1,2-dichloroethene, Trichloroethene, and Vinyl Chloride),
- pesticide compounds 4,4-DDT and 4,4-DDE,
- metal compounds (mercury, arsenic, barium, copper, zinc, and lead), and
- PFAS.

Although unlikely, unknown or unexpected materials of a hazardous nature may be encountered during ground intrusive activities. No work will be conducted if field observations or field measurements indicate that there is potential uncontrolled exposure to undefined hazards, or that exposures may exceed protection afforded by the requirements in this HASP.

3.2 Airborne Exposure Limits

Work zone air monitoring will be performed during intrusive activities if suspected contaminants include VOCs or metals. VOCs will be monitored with a photoionization detector calibrated with isobutylene to report total VOCs over a range of 0 to 100 ppm and a precision of 0.1 ppm. Metals will be monitored using particulate dust as a surrogate. Air monitoring will be performed in the work zone at a respirable height. Action levels for implementing engineering controls, administrative controls, or upgrading to Level C PPE are indicated in the table below.

Parameter	Permissible Exposure Limit (PEL)
Benzene	1 ppm
Toluene	200 ppm
Ethylbenzene	100 ppm
Xylenes	100 ppm
Naphthalene	10 ppm
Total VOCs	1.0 ppm
Particulate Dust (PM-10)	150 $\mu g/m^3$

3.3 Personal Protective Equipment (PPE)

The following table provides a summary of action levels for airborne hazards that may be encountered by workers during ground intrusive and construction activities, corresponding required actions, and the PPE level required for workers.

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AIR MONITORING METHODS, ACTION LEVELS, AND PROTECTIVE LEVELS FOR PERSONNEL

Hazard	Monitoring Unit	Action Level	Protective Levels/Action	Monitoring Schedule
Dust	Particulate Monitor Mini-ram or Equivalent	<5 mg/m^3 above background in the breathing zone.	Level D-Continue Work	Continuous for ground intrusive activities.
		<5 mg/m^3 above background in the breathing zone.	Level D-Continue Work	
		>10 mg/m^3 above background in the breathing zone.	STOP WORK EVACUATE AREA(1) Implement dust suppression measures	

(1) For all circumstances where work is stopped, the NYSDEC must be notified.

Word at the site will require Level D protection including the following PPE: hard hat, steel-toed boots, high visibility shirts, and safety glasses. Handling contaminated media will require use of nitrile gloves. Depending on suspected contaminants, air monitoring may be performed to determine when to evacuate a work area or when to upgrade to Level C PPE.

No work is anticipated requiring Levels B or A PPE and very limited or no work in Level C. If air monitoring results require PPE upgrades from Level D, then only medically qualified, trained personnel experienced in the use and limitations of air purifying or supplied air respirators will be used. Air purifying respirators with High-Efficiency Particulate Air (HEPA) filters, capable of removing particles of 0.3 micron or larger from air at 99.97% or greater efficiency, should be used when exposure to dust is a potential risk.

Unless the Project Manager directs otherwise, respirators used for organic vapors or particulates should have cartridges changed after eight (8) hours of use, or at the end of each shift, or when any indication of breakthrough or excessive resistance to breathing is detected. OSHA regulations require a Respiratory Protection Program for companies that require employees to enter areas where respirators are required and such Respiratory Protection Programs must address the requirements for replacement of cartridges.

3.4 Suspected Safety Hazards

Strenuous Activity

Field activities often involve strenuous activity such as traversing uneven terrain to reach sampling locations and lifting supplies and equipment. It is important to warm up and stretch muscles prior to beginning field tasks. Simple stretching should be performed to loosen muscles in the legs and back. Field tasks should be planned in advanced to ensure correct tools and supplies are available. Tasks should be coordinated efficiently to minimize strenuous activity to the greatest extent possible.

Work Near or Around Heavy Equipment

Typical hazards encountered include those inherent with proximity to heavy equipment operation such as being struck by, run over, or caught between. Heavy equipment accidents can cause serious injury and death. Site workers should be aware of all heavy equipment work areas, their travel path, and swing radius. If personnel on the ground need to approach or cross the path of a heavy machine, a clear line of

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visual contact should be established and maintained with the equipment operator until clear of the area. If you cannot see the equipment operator, they cannot see you.

Overhead Electric Lines

Heavy equipment must not operate closer than thirty (30) feet to any overhead lines, measured directly between any part of the equipment and the lines themselves except where electrical distribution and transmission lines have been de-energized and visibly grounded at the point of work, or where insulating barriers have been erected to prevent physical contact with the lines. If drilling or excavating is required within thirty (30) feet of any overhead lines, a written work plan must be provided by the contractor or other equipment operator that includes special measures designed to mitigate the risks and is in accordance with 29 CFR 1926.550(a)(15).

Slips, Trips, and Falls

There may be slip or trip hazards associated with uneven, slippery, or elevated work surfaces. Personnel should minimize distractions and stay alert when traversing unfamiliar terrain. Appropriate footwear should be worn for the conditions, such as traction devices for icy surfaces. Avoid carrying bulky or awkward items that alter your balance or obstruct your vision. Use three points of contact when using stairs or ladders.

Excavations

All excavations will be maintained to prevent access by unauthorized persons and will be filled or fenced off by the end of the workday. Absolutely no one will be permitted in the excavations, except the operator of equipment where the operator is always located above ground level. If equipment breaks down within the excavation, the equipment will have to be towed out of the excavation for repair. All subsurface samples will be obtained by operation of the excavating equipment and will be collected from the excavator bucket.

3.5 Excavator and Drill Rig Operations

Excavation will be performed with a track-mounted excavator or backhoe. To conduct soil borings, a hollow-stem auger or direct push drilling rig will be used. Working with or near this equipment poses potential hazards, including being struck by or pinched/caught by equipment, potentially resulting in serious physical bodily harm or inhaling dust.

In particular, the following precautions will be used to reduce the potential for injuries and accidents:

- The inspection of excavator and drill rig brakes, hydraulic lines, light signals, fire extinguishers, fluid levels, steering, tires, horn, and other safety devices will be conducted prior to the initial mobilization and checked routinely throughout the project.

- Excavator and drill rig cabs will be kept free of all non-essential items and all loose items will be secured.

- Excavators and drill rigs will be provided with necessary safety equipment, including seat belts.

- Drill rig cables and auger flight connections will be checked for evidence of wear. Frayed or broken cables or defective connections will be replaced immediately.

- Parking brakes will be set before shutting off any heavy equipment or vehicle.

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- All employees will be briefed on the potential hazards prior to the start of each excavation or drilling project.

3.6 Adverse Weather

Outdoor work can be affected by adverse weather, including electrical storms, extreme heat or cold, or extreme weather events (e.g., tornado, hurricane, blizzard). Prior to initiating field work, the field team will review the weather forecast for the duration of planned field work. The daily weather forecast will be reviewed during the daily tailgate meeting. If the forecast includes potentially adverse weather, an action plan will be reviewed, and the weather will be monitored throughout the day.

If lightning is encountered, all field activity must terminate, and personnel should seek shelter indoors or in a vehicle. Work can resume 30 minutes after the last lightning strike. Extreme heat and cold, ice and heavy rain can produce unsafe conditions. Such conditions, when present, will be evaluated on a case-by-case basis to determine if work shall terminate.

3.7 Fire and Explosion

Use of gasoline or diesel powered equipment increases the risk of fire and explosion hazards. Contractors will be required to store diesel fuel and gasoline in metal cans with self-closing lids and flash arrestors.

3.8 Requirement to Conduct Utility Mark Out

Prior to the start of any subsurface work, underground utilities and piping that may pose a potential hazard will be identified and located. "DigSafely.NewYork" or equivalent service will be called to locate and mark underground utilities. It is the responsibility of the entity performing the intrusive work to place a utility locate request. Generally, the utility locate is the responsibility of a general contractor or subcontractor. Note that state utility marking services generally only mark public utilities; private utilities must be located with a private locating service. Prior to field mobilization, site plans and other documents should be reviewed for documentation of subsurface utilities.

In the field, the field team should confirm with the responsible contractor that a utility locate request has been made and that utilities have been marked. Look around the work area for visual evidence that the locate request has been filled (e.g., utility flags and paint). If there is any question that utilities have not been marked, stop work and review with the contractor and Project Manager.

During intrusive work, ensure that markings are maintained and proper offsets are observed. Intrusive work should never occur within the Tolerance Zone without notifying the utility owner for specific requirements. The Tolerance Zone is generally defined as one half of the utility diameter plus 24 inches on both sides of the marked centerline.

In the event a utility is struck, work will stop and the Emergency Action Plan (Section 6.0) will be implemented.

3.9 Confined Space Entry

Confined space entry is not anticipated for excavating and sampling activities. If a project requires confined space entry, a specific HASP will be implemented.

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"Confined Space" is defined as a space that:

1. *"is large enough and so configured that an employee can bodily enter and perform assigned work;*
2. *has limited or restricted means for entry or exit (for example, tanks, vessels, silos, storage bins, hoppers, vaults, and pits are spaces that may have limited means of entry); and*
3. *is not designed for continuous employee occupancy."*

3.10 Site Work Zones

One of the basic elements of an effective HASP is the delineation of work zones for each ground intrusive location. The purpose of establishing work zones is to:

- Reduce the accidental spread of hazardous substances by workers or equipment from the contaminated areas to the clean areas;
- Confine work activities to the appropriate areas, thereby minimizing the likelihood of accidental exposures;
- Facilitate the location and evacuation of personnel in case of an emergency; and
- Prevent unauthorized personnel from entering controlled areas.

Although a work site may be divided into as many zones as necessary to ensure minimal employee exposure to hazardous substances, this HASP uses the three (3) most frequently identified zones: the Exclusion Zone, Decontamination Zone, and Support Zone. Movement of personnel and equipment between these zones should be minimized and restricted to specific access control points to minimize the spreading of contamination.

- Exclusion Zone

  During investigative work, the Exclusion Zone is the immediate excavation, test pit, borehole, or other area where contamination is either known or expected to occur and where the greatest potential for exposure exists. The following protective measures will be taken in the Exclusion Zone.

  Unprotected onlookers will be restricted from the excavation location so that they are at least twenty-five (25) feet upwind or fifty (50) feet downwind of excavation or drilling activities.

  Workers conducting activities and sampling in the Exclusion Zone will wear the applicable PPE. The actions to be taken and PPE to be worn in the Exclusion Zone if VOCs are above background levels are described in Section 3.3.

- Decontamination Zone

  The Decontamination Zone is located at entry/exit points to the Exclusion Zone and is where workers leaving the Exclusion Zone can properly decontaminate themselves and equipment. Depending on the scope of work and site layout, the Decontamination Zone may be a fixed location or a general process. For site investigations, a Decontamination Zone will be established at the upwind perimeter of the Exclusion Zone and will move as the exclusion zone moves with

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the investigative work. For larger scopes of work, the Decontamination Zone will be a semi-permanent location. The Decontamination Zone will include necessary personnel, equipment, and supplies. The size and configuration of the Decontamination Zone will be selected by the Project Manager. Personnel and equipment in the Exclusion Zone must pass through this zone before leaving or entering the Support Zone.

- Support Zone

  The Support Zone includes all areas located beyond the Exclusion and Decontamination Zones. Break areas, operational direction and support facilities will be located in this area. Eating and drinking will be allowed only in the Support Zone.

3.11 Natural Hazards

Work that takes place in the natural environment may be affected by plants and animals that are known to be hazardous to humans. Spiders, bees, wasps, hornets, ticks, poison oak and poison ivy are only some of the hazards that may be encountered. Individuals who may potentially be exposed to these hazards should be made aware of their existence and instructed in their identification. Emergencies resulting from contact with a natural hazard should be handled through the normal medical emergency channels. Individuals who are sensitive or allergic to these types of natural hazards should indicate their susceptibility to the Project Manager.

3.12 Heat and Cold Stress Hazards

If work is to be conducted during the winter, cold stress is a concern to the health and safety of personnel. Because disposable clothing such as Tyvek does not "breathe", perspiration does not evaporate and the suits can become wet. Wet clothes combined with cold temperatures can lead to hypothermia. If the air temperature is less than 40 degrees Fahrenheit (°F) and a worker's clothes become wet due to perspiration, the worker must change to dry clothes.

3.13 Signs and Symptoms of Cold Stress

- **Incipient frostbite**: is a mild form of cold stress characterized by sudden blanching or whitening of the skin.

- **Chilblain:** is an inflammation of the hands and feet caused by exposure to cold moisture. It is characterized by a recurrent localized itching, swelling, and painful inflammation of the fingers, toes, or ears. Such a sequence produces severe spasms, accompanied by pain.

- **Second-degree frostbite** is manifested by skin which has a white, waxy appearance and is firm to the touch. Individuals with this condition are generally not aware of its seriousness, because the underlying nerves are frozen and unable to transmit signals to warm the body. Immediate first aid and medical treatment are required.

- **Third-degree frostbite** will appear as blue, blotchy skin. This tissue is cold, pale and solid. Immediate medical attention is required.

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- **Hypothermia** develops when body temperature falls below a critical level. In extreme cases, cardiac failure and death may occur. Immediate medical attention is warranted when the following symptoms are observed:

    - Involuntary shivering;
    - Irrational behavior;
    - Slurred speech;
    - Sluggishness; and
    - Loss of consciousness.

3.14 Preventing Cold Related Illness/Injury

- Train personnel to identify the signs and symptoms of cold stress. Require field personnel to wear proper clothing for cold, wet and windy conditions, including layers that can be adjusted to changing weather conditions. It is important to keep hands and feet dry.

- Field personnel working in extremely cold conditions must take frequent short breaks in warm, dry shelters to allow their body temperature to increase. If possible, field work should be scheduled during the warmest part of the day. The buddy system should be used so that personnel can assist each other in recognizing signs of cold stress.

- Drink warm, sweet beverages and avoid drinks with caffeine and alcohol. Eat warm, high-calorie foods.

- Personnel with medical conditions such as diabetes, hypertension or cardiovascular disease or who take certain medications, may be at increased risk for cold stress.

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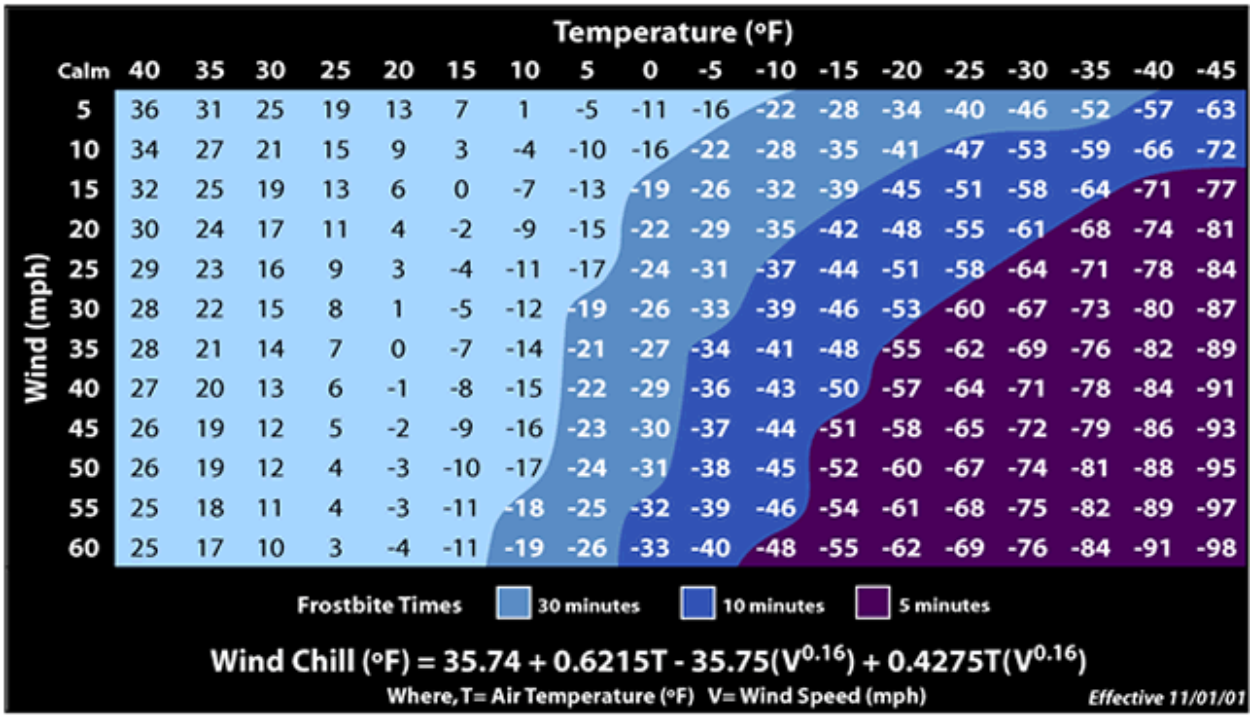
Wind Chill Chart



3.15 Treatment of Cold Related Injuries

If cold stress symptoms are evident, the affected person must move into a warm, dry sheltered area and all wet clothing should be removed and replaced with dry clothing. If frostbite is suspected, the affected person should be treated by trained medical personnel.

3.16 Signs and Symptoms of Heat Stress

Wearing PPE also puts a worker at a considerable risk for developing heat stress. This can result in health effects ranging from heat fatigue to serious illness or death. Consequently, regular monitoring, remaining hydrated and other precautions are vital.

- **Heat Rash** may result from continuous exposure to heat and humid air.

- **Heat Cramps** are caused by heavy sweating with inadequate electrolyte replacement. Signs and symptoms include:

    - Muscle spasms; and
    - Pain in the hands, feet and abdomen.

- **Heat Exhaustion** occurs from increased stress on various body organs, including inadequate blood circulation due to cardiovascular insufficiency or dehydration. Signs and symptoms include:

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- Pale, cool, and moist skin;
- Heavy sweating; and
- Dizziness, fainting, and nausea.

- **Heat Stroke** is the most serious form of heat stress. Temperature regulation fails, and the body temperature rises to critical levels. Immediate action must be taken to cool the body before serious injury or death occurs. Competent medical help must be obtained. Signs and symptoms are:

    - Red, hot, and unusually dry skin;
    - Lack of or reduced perspiration;
    - Dizziness and confusion;
    - Strong, rapid pulse; and
    - Loss of consciousness.

3.17 Preventing Heat Related Illness/Injury

Proper training and preventive measures will help avert serious illness and loss of work productivity. Preventing heat stress is particularly important because once someone suffers from heat stroke or heat exhaustion that person may be predisposed to additional heat injuries. To avoid heat stress, the following steps should be taken:

- Have workers drink sixteen (16) oz. (0.5 liter) of fluid (preferably water or diluted drinks) before beginning work. Urge workers to drink a cup or two every fifteen (15) to twenty (20) minutes, or at each monitoring break. A total of 1 to 1.6 gallons (four (4) to six (6) liters) of fluid per day are recommended, but more may be necessary to maintain body weight.

- If possible, adjust work schedules to avoid the hottest parts of the day.

- Encourage workers to maintain an optimal level of physical fitness.

- Shelter (air-conditioned, if possible) or shaded areas should be provided to protect personnel during rest periods.

- Train workers to recognize, identify, and treat heat stress.

For workers wearing standard work clothes, recommendations for monitoring and work/rest schedules are those approved by American Conference of Governmental Industrial Hygienists (ACGIH) and National Institute of Occupational Safety and Health (NIOSH). Workers wearing semi-permeable PPE or impermeable PPE should be monitored when the temperature in the work area is above 70°F.

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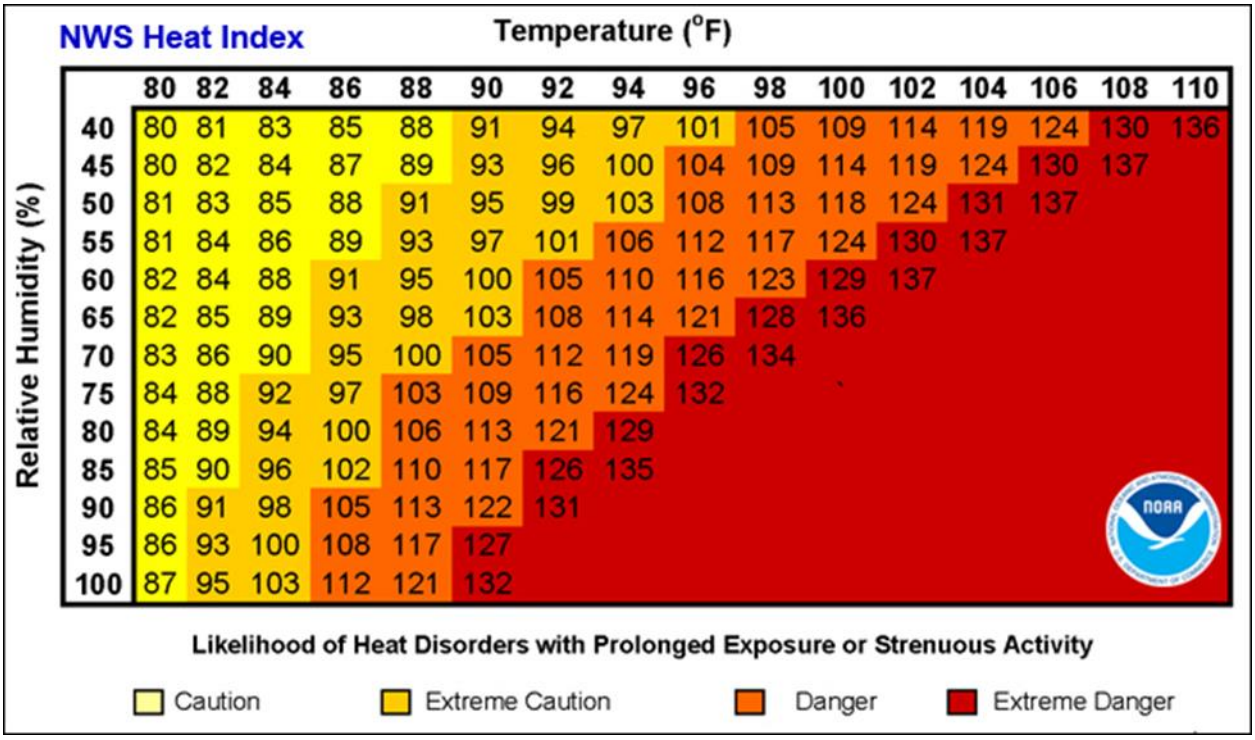
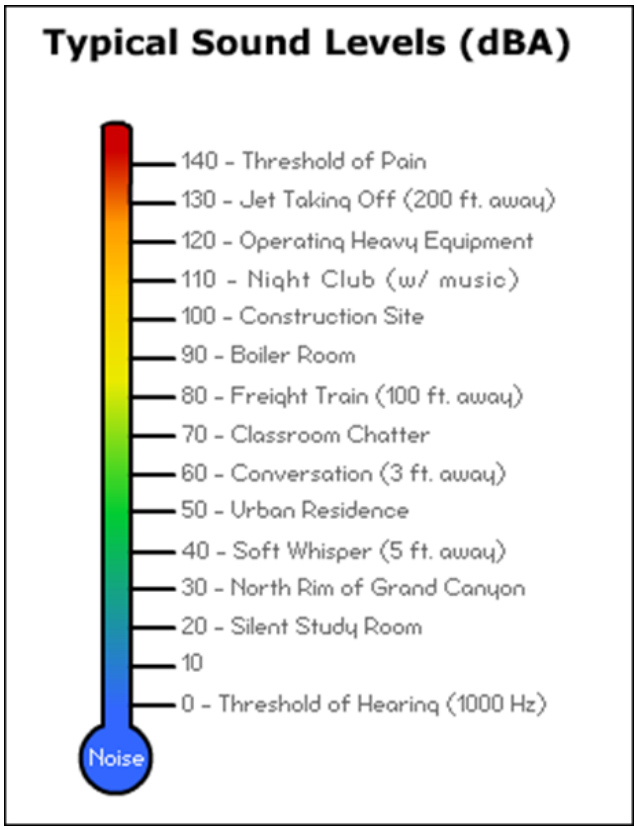


3.18 Noise Hazards

Work that involves the use of heavy equipment can expose workers to noise during field activities that can result in noise-induced hearing loss. Field personnel will have access to appropriate hearing protection such as ear muffs or disposable foam earplugs. The NIOSH recommended exposure limit for sound level exposure is 85 decibels (8-hour time weighted average). A general rule of thumb is to wear hearing protection whenever you need to raise your voice due to surrounding noise to be heard by someone standing next to you. The adjacent chart shows general noise levels.



3.19 Slip, Trip and Fall Hazards

Ground intrusive locations can contain a number of slip, trip and fall hazards for workers, such as:

- Holes, pits, or ditches
- Excavation faces
- Slippery surfaces
- Steep grades
- Uneven grades
- Snow and ice
- Sharp objects

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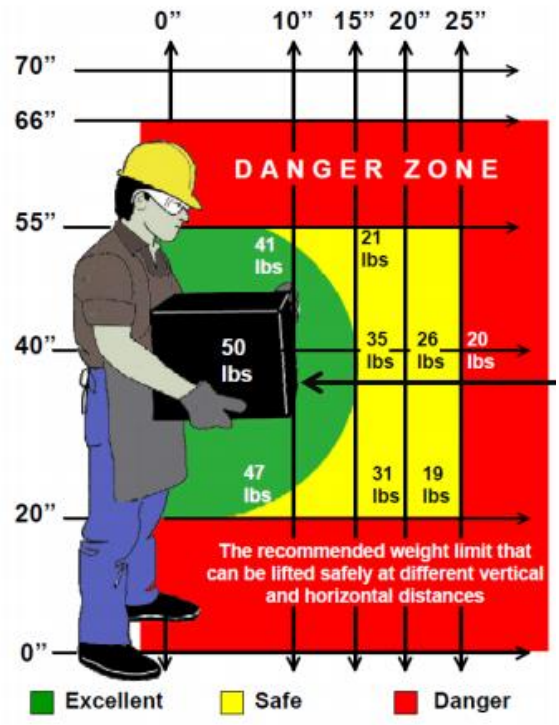
All workers must be instructed to keep back three (3) feet from the top edge of excavation faces.

Workers will be instructed to look for potential safety hazards and immediately inform the Project Manager regarding any new hazards. If the hazard cannot be immediately removed, actions must be taken to warn workers about the hazard.

3.20 Lifting Heavy Objects

Personnel often carry equipment and supplies to and around the work site. Proper planning, lifting technique, and use of assisting equipment are essential for injury prevention. Prior to initiating field activities, know the items to be used, their size and weight, and how far they need to be moved. The use of a vehicle, cart, or sled is preferred over carrying by hand.

If items must be lifted, workers should warm up muscles and stretch before lifting objects. Make sure the travel path is clear of obstructions and tripping hazards. Use proper lifting technique by keeping a wide stance, keeping your back straight, grasping the item firmly, keeping the item close to your body, and pushing with your legs to lift up. Never lift more than 50 pounds without assistance. The figure below shows recommended safe weight limits for lifting. Note that the recommended weight decreases as the load is moved away from the body. Regardless of any weight recommendation, know when to ask for help since each person has a different ability.



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3.21 Modifications to this Plan

Requirements and guidelines in this HASP are subject to modification by the Project Manager in response to additional information obtained during field work regarding the potential for exposure to hazards.

4.0 DECONTAMINATION METHODS

4.1 Contamination Prevention Methods

The Project Manager will make all workers aware of the potential for contamination. The following procedures will be established to minimize contact with contaminants:

- Workers will not walk through areas obvious of contamination;
- Workers will not directly touch potentially hazardous substances;
- Workers will wear gloves when touching soil or waste;
- Workers will wear disposable outer garments where appropriate; and
- Excavated soils will be placed on plastic sheeting and covered with plastic sheeting at the end of the workday.

4.2 Decontamination Methods

All workers, clothing, and equipment leaving designated contaminated areas must be decontaminated.

5.0 MEDICAL SURVEILLANCE PROGRAM

5.1 General

Workers who participate in field activities that meet the following criteria will be included in the Medical Surveillance Program:

- All who may be exposed to hazardous substances or health hazards at or above permissible exposure limits, without regard to the use of respirators, for thirty (30) days or more per year, as required by 1926.65(f)(2)(i-iv).

- All who wear a respirator for thirty (30) days or more every year as required by 1926.62(f)(2)(i-iv).

- All who are injured because of overexposure from an incident involving hazardous substances or health hazards.

5.2 Frequency of Medical Exams

Medical examinations and consultations will be provided on the following schedule to the workers who meet the above listed general qualifications:

- Prior to assignment to a work site, if any of the criteria noted above are anticipated.

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- At least once every twelve (12) months, unless the physician believes a longer interval (not greater than two (2) years) is appropriate.

- As soon as possible upon notification that a worker has developed signs or symptoms indicating possible overexposure to hazardous materials.

6.0 EMERGENCY ACTION PLAN

Workers will use the following standard emergency procedures. The Project Manager will be notified of any emergency and be responsible for ensuring that the appropriate procedures are followed and that the Project Manager is notified. A first aid kit, an eye wash unit that can provide a minimum flow rate of 0.4 GPM for fifteen (15) minutes, and a fire extinguisher rated 20A-B-C (or higher) will be readily available to workers. All workers will be trained in use of emergency supplies. Questions regarding procedures and practices described in the HASP should be directed to the Project Manager.

6.1 Notification

Any symptoms of adverse health, regardless of the suspected cause, are to be immediately reported to the Project Manager.

Upon the occurrence of an emergency, including an unplanned chemical release, fire or explosion, workers will be alerted and the area evacuated immediately. The Project Manager will notify the ambulance service, fire department and/or police department, as required. Emergency contact telephone numbers are provided below. Re-entry to the work area will be limited to those required to assist injured workers or for firefighting or spill control. Anyone entering the work area following an emergency incident must wear appropriate protective equipment.

6.2 Emergency Services

Emergency Services	Telephone Number
Saratoga Springs Fire Department	911 or (518) 587-3599
Saratoga Springs Police Department	911 or (518) 584-1800
Ambulance	911
Saratoga Hospital	(518) 587-3222
Poison Control Center	(800) 222-1222
NYSDEC Spills Emergency Response Program	(800) 457-7362

A map showing the preferred route to the hospital with written directions is presented in the Site Specific Supplement at the beginning of this HASP.

The following alarm systems will be utilized to alert workers to evacuate the restricted area:

- Direct Verbal Communication
- Radio Communication or Equivalent
- Portable or Fixed Telephone

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The following standard hand signals will also be used as necessary:

Hand Signal	Message
Hand gripping throat	Can't breathe/out of air
Grip co-worker's wrist	Leave area immediately, no debate!
Hands on top of head	Need assistance
Thumbs up	Yes/O.K.
Thumbs down	No/Problem

Upon activation of an alarm, workers will proceed to a designated assembly area. The designated assembly area will be determined on a daily basis by the Project Manager and updated as necessary depending upon work conditions, weather, air monitoring, etc. The location of the designated assembly area will be clearly marked and communicated to employees daily or upon relocation of the area. Workers gathered in the designated assembly area will remain there until their presence has been noted. A tally of workers on the daily restricted area access roster will be made as necessary to ensure all workers have been properly evacuated and accounted for.

Workers may return to the designated work area following authorization by the Project Manager.

6.3 Personal Injury

If anyone within a work area is injured and cannot leave the restricted area without assistance, emergency medical services will be notified (see Section 6.2) and appropriate first aid will be administered by certified Emergency Medical Technicians (EMTs).

6.4 Fire/Explosion

Upon the occurrence of a fire beyond the incipient stage or an explosion anywhere on the worksite property, the fire department will be alerted and all personnel moved to a safe distance from the involved area.

6.5 Equipment Failure

If any equipment fails to operate properly, the Project Manager will determine the effect of this failure on continuing operations. If the failure affects the safety of workers (e.g., failure of monitoring equipment) or prevents completion of the planned tasks, all workers will leave the work area until appropriate corrective actions have been taken.

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6.6 Record Keeping

Personnel must notify the Project Manager of the following incidents by the end of the work day the incident occurs, and provide a written account within 24 hours:

- **Near Miss**: This is an unplanned event that did not result in injury, or damage, but had the potential to do so. Near misses are opportunities to learn and improve tasks and safety measures.
- **Accident**: This is an unplanned event that causes personal injury or property damage.

The Field Team Leader must notify the Project Manager as soon as possible by phone and provide a written account via email describing the incident, who was involved, and how the incident could have been prevented. The Project Manager will maintain records of reports concerning occupational injuries and illnesses in accordance with 29 CFR 1904.

7.0 COVID-19 RESPONSE PLAN

A response plan has been prepared to address risks presented by the Severe Acute Respiratory Syndrome Coronavirus 2 (SARS-CoV-2) virus, which causes the Novel Coronavirus Disease 2019 (Covid-19). The plan is current at the time this HASP was prepared; however, it is subject to change according to the dynamic and evolving policies, guidelines, recommendations, executive orders, etc. associated with controlling Covid-19. The plan will be periodically updated and revised to reflect changing health and safety practices and procedures.

S:\Sterling\Projects\2015 Projects\Putnam Resources - 2015-30\Reports and Work Plans\HASP\2020-11-12 Putnam St. HASP.docx

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TABLE

Table A-1
Published Airborne Exposure Limits or Odor Thresholds in Parts Per Million (PPM) in Air for Substances that Exceed Applicable Standards in Soil and Groundwater

Substance	OSHA PEL/STEL/C	NIOSH REL/STEL	ACGIH TLV/STEL	IDLH	Cancer Causing	Range of Odor Thresholds
Groundwater - VOCs:						
Benzene	10/5/25	0.1/1	0.5/2.5	500	Y	1.5
n-Butylbenzene	NA	NA	NA	NA	NA	NA
sec- Butylbenzene	NA	NA	NA	NA	NA	NA
Cis-1,2-Dichloroethene (cis-1,2-DCE)	200/-/-	200/-	200/-	1000	N	19.1
1,1 Dichloroethane	100/-/-	100/-	100/-	3000	N	120
1,2 Dichloroethane	50/-/100	1/2	10/-	50	Y	6-10
Trans 1,2 Dichloroethene	200					
Ethylbenzene	100/-/-	100/125	100/125	800	N	2.3
Isopropylbenzene	50/-/-	50/-	50/-	900	N	
Naphthalene	10/-/-	10/15	10/15	250	N	0.084
N-Propylbenzene	NA	NA	NA	NA	NA	NA
Tetrachloroethene	100/-/200	NA	25/100	150	Y	1
Trichloroethene	100/-/200	25/-	50/100	1000	Y	28
Vinyl Chloride	1/-/5	NA	1/-		Y	3,000

NA = Not Available

Definitions of PEL, REL, STEL, TLV, C and IDLH are provided below:

PEL The Occupational Safety and Health Administration's (OSHA) Permissible Exposure Limit for airborne contaminants as a time-weighted average for an eight (8) hour work shift, as listed in 29 CFR 1910.1000.

REL The National Institute for Occupational Safety and Health's (NIOSH) Recommended Exposure Level for a work shift.

STEL A Short Term Exposure Limit as a 15-minute time-weighted average (No more than four (4) exposures per shift).

TLV The American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Value for airborne concentrations to which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effects.

C Ceiling Concentration – The concentration that should not be exceeded during any part of the working exposure.

IDLH The Immediately Dangerous to Life and Health maximum concentration from which one could escape within 30 minutes without experiencing any escape–impairing or irreversible health effects. (Note: Level C air-purifying respirators do not adequately protect an individual exposed to these concentrations.) These IDLH values were established by NIOSH and have not been peer reviewed. Caution is recommended with their application.

APPENDIX A:

COVID-19 RESPONSE PLAN

Sterling Environmental Engineering, P.C.

COVID-19 RESPONSE PLAN

53 PUTNAM STREET
SARATOGA SPRINGS, NEW YORK

Prepared for:

Putnam Resources, LLC
48 Union Avenue, Suite 1A
Saratoga Springs, New York 12866

Prepared by:

Sterling Environmental Engineering, P.C.
24 Wade Road
Latham, New York 12110

November 12, 2020

"Serving our clients and the environment since 1993"

COVID-19 RESPONSE PLAN

53 PUTNAM STREET
SARATOGA SPRINGS, NEW YORK

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Appendices

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1.0 GENERAL INFORMATION

Sterling Environmental Engineering, P.C. (STERLING) has issued extensive communications to all our staff in line with World Health Organization, Center for Disease Control (CDC), New York State Executive Orders, and the New York State Department of Health (NYSDOH) guidance on how to minimize the risk of viral infection to themselves and others by taking effective hygiene measures and avoiding situations where the risk of infection could be heightened. STERLING's first priority is always the health, safety, and security of our project team, clients, subcontractors and visitors. STERLING has implemented a specific Covid-19 health and safety policy at the outset of the virus and has updated that policy as the situation develops and changes, ensuring that STERLING has protections in place for its employees.

Key aspects of this policy include:

- Implementation of a Corporate Infectious Disease Control Policy and a Covid-19 Prevention Plan.
- Site mobilization is not to include greater than one person per vehicle.
- Personnel are required to maintain a minimum social distance of at least six (6) feet (or greater, if required by local law) at all times, unless not possible to complete a necessary task.
- Personnel are required to wear face masks whenever a social distance of at least six (6) feet cannot be maintained.
- Personnel are required to become familiar with and adhere to the most current guidelines contained in the New York Forward Reopening Guidelines for Construction.

The Covid-19 Response Plan, referred to as Addendum #1 to the existing Health and Safety Plan (HASP), identifies specific measures to help eliminate the potential for transmission of Covid-19 to STERLING personnel and minimize the potential to adversely impact the health and safety of authorized personnel, visitors, and the public. All STERLING personnel working on this project must read this addendum, acknowledge understanding of this plan, and abide by its requirements.

Requirements in this addendum are subject to modification by the Project Manager in response to additional information obtained from federal, state or local regulators and health officials, or as updates to the NYSDEC's Covid-19 Management Specifications (Appendix A) and guidance documents (Appendix B). Updates will be communicated to field personnel as they evolve. Work associated with the remediation activities at the 53 Putnam Street Site may continue to be performed after federal, state, and local regulations no longer require Covid-19 protocols, in which case, this addendum will no longer be in effect.

2.0 JOB SITE PROTECTIVE MEASURES

2.1 Entry/Exit Log and Acknowledgement Form for Covid-19

All workers and visitors will be required to read and acknowledge this plan and confirm that their health and travel history is NOT in one of the prohibited access groups identified in Appendix B and, to the best of their knowledge, do not pose an elevated risk of transmitting Covid-19 to others. Each person will be required to sign in and sign out each day they are onsite.

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2.2 Social Distancing

Onsite personnel should practice social distancing as much as possible. This includes the elimination of shaking hands and in-person meetings. Workers should maintain a minimum of 6-feet between themselves and others, per CDC guidelines and New York State executive orders, as much as possible. If close working quarters are required, workers must wear acceptable face coverings.

2.3 Work Prevention and Practice Controls

Onsite personnel should consistently practice good hygiene. Cloth face coverings should be washed and changed when soiled on a regular basis. Common areas, bathrooms, work trailers, vehicles, field equipment, and other items should be cleaned and sanitized regularly. Personnel protective equipment, including nitrile, vinyl or latex gloves are recommended to be worn during cleaning procedures.

3.0 COVID-19 EXPOSURE AND RECORDKEEPING

3.1 Covid-19 Exposure Situations

Onsite personnel who exhibit Covid-19 symptoms will not be allowed to enter the site and must remain at home until they are no longer showing symptoms and fulfill the latest CDC guidelines or protocols enforced by NYS Executive Orders, or are tested and are confirmed to not have the Covid-19 virus.

Onsite personnel who test positive for Covid-19 will be required to self-quarantine away from work and other personnel, remain in quarantine until symptoms are no longer present, and are cleared to return to work by health professionals. The local health department will be notified, and any co-workers, contractors, or suppliers who may have come into contact with the confirmed Covid-19 individual must be notified. Personnel will be allowed to re-enter a project site when they are no longer showing symptoms and have been cleared to return to work by health professionals.

3.2 Recordkeeping

Records for daily site entry, as well as workers testing positive for Covid-19, will be maintained for review upon request by the state or local health department.

S:\Sterling\Projects\2015 Projects\Putnam Resources - 2015-30\Reports and Work Plans\HASP\2020-10-02 Covid-19 Addendum\2020-11-12 - Covid-19 Response Plan_Redline.docx

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APPENDIX A

NYSDEC COVID-19 MANAGEMENT SPECIFICATIONS, APRIL 7, 2020

SECTION 01 35 33 – COVID-19 RISK MANAGEMENT

PART 1 – GENERAL

1.1 SUMMARY

A. This Section includes requirements for managing and minimizing the potential for transmission of the Severe Acute Respiratory Syndrome Coronavirus 2 (SARS-CoV-2) virus, which causes the Novel Coronavirus Disease 2019 (COVID-19). COVID-19 typically causes respiratory illness in people.

B. Transmission: SARS-CoV-2 is currently known to spread via respiratory droplets produced when a person infected with the virus coughs or sneezes, the same way flu and other respiratory illnesses spread. SARS-CoV-2 can also be transmitted if people touch surfaces and objects with the virus on it.

C. Symptoms: COVID-19 can cause mild to severe respiratory illness with symptoms of fever, cough, and difficulty breathing. Preliminary information suggests older adults and people with underlying health conditions or compromised immune systems may be at higher risk of severe illness from this virus. Center for Disease Control (CDC) believes that symptoms of COVID-19 begin between 2 and 14 days after exposure.

D. Best Practices to Prevent Infection: Currently the best way identified to prevent infection is to minimize the potential of exposure to SARS-CoV-2. CDC recommends everyday actions to help prevent the spread of any respiratory viruses

- Wash your hands often with soap and water for at least 20 seconds. If soap and water are not available, use an alcohol-based hand sanitizer, containing at least 60% alcohol.
- Avoid touching your eyes, nose, and mouth with unwashed hands.
- Avoid close contact with people who are sick.
- Stay home when you are sick.
- Cover your cough or sneeze with a tissue, then throw the tissue in the trash can and wash hands or use hand sanitizer.
- Clean and disinfect frequently touched objects and surfaces.
- Wear face masks
- Safe social distancing (e.g., maintain a distance of 6 feet between people, limited group meetings)

1.2 OBJECTIVE

A. The objective of this specification is to minimize transmission and subsequent infections of COVID-19 in project staff that may arise as a result of exposure to SARS-CoV-2 released into the environment during construction and renovation activities. Controlling the dispersal of airborne infectious agents is critical to achieving this objective.

1.3 PERFORMANCE REQUIREMENTS AND RESPONSIBILITIES

A. The intent of this Section is to document and formalize the Contractor's requirements for minimizing the risk of transmission of COVID-19 among site workers, project staff, and

the surrounding community during construction per the latest recommendations of federal, state and local health agencies. This includes developing a COVID-19 Management Plan, establishing procedures for conducting onsite work activities to prevent virus transmission, monitoring staff health, and reporting requirements.

B. The Contractor is expected to communicate the requirements described in this section to all site workers, subcontractors, and visitors to the site daily, during daily Health and Safety meetings as well as through site postings (see attachment).

C. Contractors and their subcontractors are required at all times to guard the safety and health of all persons on and in the vicinity of the work site.

D. Contractors and their subcontractors are required to comply with all applicable rules, regulations, codes, and bulletins of the New York State Department of Labor and the standards imposed under the Federal Occupational Safety and Health Act of 1970, as amended ("OSHA").

E. Contractors and their subcontractors must comply with all City or State of New York safety requirements for projects within the City or State of New York constructed in accordance with the applicable building code.

F. Contractors and their subcontractors shall stay current and immediately implement the most up-to-date government issued practices to protect the safety and health of your employees, clients, and the general public.

1.4 RELATED SECTIONS

A. None

1.5 REFERENCES

A. Occupational Safety and Health Administration (OSHA) Guidance on Preparing Workplaces for COVID-19

B. New York State Department of Health

C. Centers for Disease Control and Prevention (CDC)

D. National Institute for Occupational Safety and Health (NIOSH)

E. Health Insurance Portability and Accountability Act (HIPAA)

1.6 SUBMITTALS

A. The Contractor shall prepare a COVID-19 Management Plan which can be a Supplement, or Addendum, to the Contractor' Health and Safety Plan

B. The CONTRACTOR shall develop a one-page summary of site-specific practices for COVID-19 management and clearly display on site. Operating hours, delivery times, and extra considerations for works involving a high volume of personnel or potential for interaction with community members could also be included in the summary.

C. The Contractor's Daily Field Report shall include a Daily Health Checklist, with the following questions at a minimum:

DAILY HEALTH CHECKLIST

Is social distancing being practiced?	Yes ☐	No ☐
Is the tail gate safety meeting held outdoors?	Yes ☐	No ☐
Are remote/call-in job meetings being held in lieu of meeting in person where possible?	Yes ☐	No ☐
Were personal protective gloves, masks, and eye protection being used?	Yes ☐	No ☐
Are sanitizing wipes, wash stations or spray available?	Yes ☐	No ☐
Have any workers/visitors been excluded based on close contact with individuals diagnosed with COVID-19, have recently traveled to restricted areas or countries, or are symptomatic (fever, chills, cough/shortness of breath)?	Yes ☐	No ☐
Comments:		

1.7 COVID-19 MANAGEMENT PLAN

A. At a minimum, the COVID-19 Management Plan shall include:
   1. Identification of potential exposure pathways and exposure risks associated with work tasks, e.g. activity hazard analysis (AHA).
   2. Identification of local health department contact information and COVID-19 testing sites and procedures.
   3. Detailed written description of the onsite personnel protection measures that will be utilized and a detailed explanation of how they will be implemented, monitored, and communicated.
   4. Detailed written description of measures that will be taken to prevent transmission to or from the surrounding community and how they will be implemented and communicated.
   5. Procedures to be followed in the event a site worker is diagnosed with or is suspected of having COVID-19, including identification of all personnel potentially exposed and isolation requirements.
   6. Daily cleaning schedules and disinfection procedures per the most recent CDC guidelines.
   7. Cleaning and disinfection procedures in the event there is/are suspected COVID-19 case(s) among site personnel.
   8. Site access controls and entry/exit procedures.
   9. Plan view of points of egress and delivery locations.

B. The COVID-19 Management Plan must be updated following any issued change(s) in federal, state, or local health agency guidance.

1.8 PRECONSTRUCTION CONFERENCE

A. Pre-Construction Conference shall include a review of methods and procedures related to COVID-19 risk management including, but not limited to the following:
   1. Review of COVID-19 Management Plan

2. Review infection control procedures
3. Review staff monitoring and reporting requirements.

PART 2 - PRODUCTS - Not Used

PART 3 - EXECUTION

3.1 RISK IDENTIFICATION

A. COVID-19 is a new disease; scientists and health agencies are continuously learning about how it spreads. The Contractor shall adjust site policies based on the most up to date government issued guidance regarding transmission.

B. Contractor shall confirm staff that have worked in locations where quarantine orders are in place, have met the minimum quarantine guidance and do not have symptoms prior to mobilizing to site.

C. Contractor shall monitor staff daily, including checking, and documenting, temperature with no contact infrared thermometer, to confirm onsite staff do not exhibit COVID-19 symptoms. Contractor shall provide daily reports of those tests upon NYSDEC's request.

3.2 RISK MINIMIZATION

A. Engineering Controls
   1. Increasing ventilation rates of interior workspaces.
   2. Access controls, including fences and locking gates.
   3. Maintain 6 feet distances, using distance markers where appropriate in the field.

B. Administrative Controls
   1. Continuous and effective communication of administrative controls/requirements to all site personnel and visitors, through the posting of site signage, preparation and distribution of site plans, presented during site meetings, and verbal warnings if necessary.
   2. Require that all employees exhibiting any COVID-19 symptom do not enter the site and provide sick leave policies to support this requirement.
   3. To minimize face-to-face interaction, the Site's Health & Safety Officer's (or other designated employee) phone number shall be prominently posted and disseminated to project staff to be called for the purpose of site sign in and sign out by all visitors to the site upon arrival and exit. The designated employee will receive entry and exit calls each day and will fill out the site entry/exit log for each site visitor to reduce traffic in site trailer and/or the number of individuals contacting the site access tracking log.
   4. Staffing: only those employees necessary to complete critical path task(s) shall be present on-site at any given time. Work shall be scheduled to minimize the density of personnel in any given area at any given time.
   5. Working Remotely; employees shall be encouraged to complete work remotely if possible.
   6. Face-to-face meetings shall be replaced with video or phone conferences when practicable.

7. Social distancing shall be exercised for face-to-face meetings e.g. daily Health and Safety tailgate meeting. In addition, the Contractor shall plan to have multiple meetings (if necessary) to keep the number of participants to a threshold that allows for the practice of social distancing protocol. The Health and Safety officer will keep a record of all present for each meeting on the Health and Safety log.
8. Quarantine staff that have been in contact with a anyone that tested positive and notify NYSDEC immediately.

C. Safe Work Practices
1. The Contractor shall employ social distancing protocol for all onsite activities when able.
2. The Contractor provide PPE and adequate hand washing stations and hand sanitizer (containing a minimum of 60% alcohol) to allow site personnel and visitors to practice good personal hygiene.
3. The Contractor shall provide tissues, paper towels, no-touch trash cans, and disinfectants to maintain site cleanliness.
4. Sharing of tools and heavy equipment shall be limited to the extent practicable; handles of shared tools and equipment shall be sanitized regularly.

D. Personal Protective Equipment
1. Employees shall be provided disposable personal protective equipment (PPE), including gloves, goggles, face shields, face masks, and respiratory protection, as appropriate based on work environment and current recommendations by OSHA and CDC.
2. All PPE must be selected based on hazard to the worker, properly fitted and periodically refitted, consistently and properly worn when required, regularly inspected, maintained, and replaced, as necessary, and properly removed, cleaned, and stored or disposed of, to avoid contamination of self, others, or the environment.
3. PPE worn to prevent transmission of COVID-19 is not to be confused with PPE for protection against site contaminants.
4. PPE must be worn, removed, and disposed of correctly in order to remain effective.
    a. Face masks should fit snugly but comfortable against the side of the face and over the nose and be secured with ties or ear loops; cloth masks must include multiple layers of fabric, allow for breathing without restriction, and be able to be laundered and machine dried without damage.
    b. Face masks should be worn consistently and removed without touching eyes, nose, and mouth. An individual should wash their hands after handling a used face mask.
    c. Cloth face coverings should be sterilized by machine washing between use; disposable face masks shall be disposed of properly after using.
    d. Gloves are only effective if changed and disposed of frequently, to avoid cross-contamination.

3.3 NOTIFICATION OF POTENTIAL OR CONFIRMED INFECTION

A. The Contractor shall notify the Department immediately upon identification of a suspected or confirmed infection of COVID-19. This notification shall comply with HIPAA regulations.

B. The Contractor shall remove an individual suspected to have COVID-19 from the site immediately (to the individuals' hotel or local place of residence if transport home is not immediately feasible), as well as those who have worked in close contact with that individual for extended periods of time (an hour at a time or more) over the previous week. The individual with suspected infection shall contact their health care provider and/or follow local health department testing procedures and protocol.

C. While in the process of removing an employee exhibiting symptoms, steps should be taken to isolate the individual, place a surgical mask on the individual and inform the local health department and the NYSDEC.

D. In the event the individual with suspected infection cannot get home right away, they shall isolate in their hotel room (notifying hotel management of their symptoms), contact their health care provider, and/or follow local health department testing procedures and protocol.

E. In the absence of local health department information, the individual may call the New York State Hotline at 1-888-364-3065.

F. The Contractor shall maintain communication with potentially infected individual(s) and notify the Engineer upon receipt of COVID-19 test results.

G. Positively infected individuals may return to work at the site after 72 hours of being symptom-free and 7 days of isolation after the first symptoms appeared, or in accordance with the current federal, state, and local guidelines

H. OSHA recordkeeping requirements at 29 CFR Part 1904 mandate covered employers record certain work-related injuries and illnesses on their OSHA 300 log. COVID-19 can be a recordable illness if a worker is infected as a result of performing their work-related duties. However, employers are only responsible for recording cases of COVID-19 if all the following are met:

1. The case is a confirmed case of COVID-19 (see CDC information on persons under investigation and presumptive positive and laboratory-confirmed cases of COVID-19).

2. The case is work-related, as defined by 29 CFR 1904.5; and

3. The case involves one or more of the general recording criteria set forth in 29 CFR 1904.7 (e.g. medical treatment beyond first-aid, days away from work).

END OF SECTION

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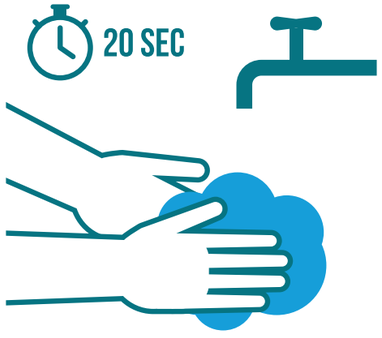
APPENDIX B

NYSDEC COVID-19 GUIDANCE DOCUMENTS

PREVENT INFECTION



Wash your hands and use hand sanitizer

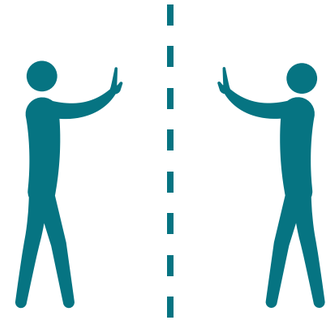
Wash your hands frequently and thoroughly, for a minimum of 20 seconds.

Use hand sanitizer, containing at least 60% alcohol when you are unable to wash you hands with soap and water.

Cover your cough or sneeze

Cover your mouth and nose when coughing or sneezing. Turn your head away from others, if possible, when sneezing.

Use a paper tissue or your sleeve and not your hand. Dispose of used tissues immediately.



Limit physical contact

Avoid handshakes, kisses and hugs.

Maintain at least 6 feet from all others persons when possible.

Keep clean

Regularly sanitize frequently touched and shared surfaces at home as well as at work.

Be considerate

Stay home whenever possible especially if you are experiencing symptoms.

NEW YORK STATE OF OPPORTUNITY | Department of Environmental Conservation

SITE ACCESS RESTRICTIONS

SITE ACCESS IS PROHIBITED FOR THE FOLLOWING PERSONS DUE TO COVID-19 RISK

- **You are experiencing flu-like symptoms including but not limited to:**

  Fever or feeling feverish/chills, cough, sore throat, diarrhea, vomiting, runny or stuffy nose, muscle or body aches, headaches, fatigue (tiredness)

- **You have traveled to CDC-restricted destinations during the last 2 weeks:**

  China, South Korea, Iran, United Kingdom & Ireland, all European Union countries, Switzerland and regions within the U.S. for which public health agencies have prohibited travel

- **You had direct contact with a person diagnosed with COVID-19 or suspected of having COVID-19 during the last 2 weeks**

  Immediately notify NYSDEC site management.

NEW YORK STATE OF OPPORTUNITY | Department of Environmental Conservation

APPENDIX C

ENTRY/EXIT LOG AND ACKNOWLEDGEMENT FORM

COVID-19 RESPONSE PLAN

ENTRY/EXIT LOG AND ACKNOWLEDGEMENT FORM

Project Name:_____
Project Number:_____
Date:_____

By signing below, I acknowledge that I have reviewed this Covid-19 Response Plan, and do not meet any of the prohibited access groups or pose an elevated risk of transmitting Covid-19 to others, in accordance to this addendum.

- You are not or have not experienced any flu-like symptoms, including but not limited to fever, chills, sore throat, vomiting, runny nose, muscle or body aches or fatigue.
- You have not travelled to any CDC restricted designations during the last two weeks.
- You have not had direct contact with a person diagnosed with Covid-19 or suspected of having Covid-19 during the last two weeks.

Name	Initials	Company	Time In	Time Out	Reason

APPENDIX D

COMMUNITY AIR MONITORING PLAN (CAMP)

NEW YORK STATE BROWNFIELD CLEANUP PROGRAM

53 PUTNAM STREET
SARATOGA SPRINGS, NY
BCP #C546057

COMMUNITY AIR MONITORING PLAN (CAMP)

1.0 INTRODUCTION

This Community Air Monitoring Plan (CAMP) has been prepared for 53 Putnam Street, Saratoga Springs, NY ("the Site"). The Site is currently in the New York State (NYS) Brownfield Cleanup Program (Site #C546057) which is administered by New York State Department of Environmental Conservation (NYSDEC). This CAMP provides the methods and procedures for real-time air monitoring to be implemented during the disturbance of Site soils relating to construction or remedial activities. This CAMP is to be utilized in coordination with the Health and Safety Plan (HASP) established for the project. Actions and requirements to protect the health and safety of onsite workers from airborne contaminants are addressed in the HASP.

This CAMP provides for real-time air monitoring of particulates at upwind and downwind perimeter locations of each designated work area for all ground-intrusive activities, such as excavation or drilling, soil stockpiling, loading trucks for off-site disposal, and equipment decontamination implemented at the Site. The CAMP was developed from the New York State Department of Health (NYSDOH) Generic CAMP provided in the DER-10 Technical Guidance for Site Investigation and Remediation. This CAMP provides a measure of protection for the downwind community (potential receptors include residences, businesses, and personnel not directly involved with work activities) from potential airborne contaminant releases as a direct result of investigative and remedial work activities. Contractors should employ Best Management Practices (BMPs) and common sense measures to minimize dust and odors around work areas.

2.0 VOC MONITORING

Volatile organic compounds (VOCs) will be monitored at the downwind perimeter of the immediate work area (i.e., the exclusion zone) on a continuous basis or as otherwise specified with a photoionization detector (PID). Upwind concentrations will be measured at the start of each workday and periodically thereafter to establish background conditions, particularly if wind direction changes. The monitoring work will be performed using equipment appropriate to measure the types of contaminants known or suspected to be present. The equipment will be calibrated at least daily for the contaminant(s) of concern or for an appropriate surrogate, in accordance with the manufacturer's requirements. The equipment will be capable of calculating 15-minute running average concentrations, which will be compared to the levels specified below.

- If the ambient air concentration of total organic vapors at the downwind perimeter of the work area or exclusion zone exceeds five (5) parts per million (ppm) above background for the 15-minute average, work activities must be temporarily halted and monitoring continued. If the total organic vapor level readily decreases (per instantaneous readings) below 5 ppm over background, work activities can resume with continued monitoring.

- If total organic vapor levels at the downwind perimeter of the work area or exclusion zone persist at levels in excess of five (5) ppm over background but less than 25 ppm, work activities must be

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halted, the source of vapors identified, corrective actions taken to abate emissions, and monitoring continued. After these steps, work activities can resume provided that the total organic vapor level 200 feet downwind of the exclusion zone or half the distance to the nearest potential receptor or residential/commercial structure, whichever is less - but in no case less than 20 feet, is below five (5) ppm over background for the 15-minute average.

- If the organic vapor level is above 25 ppm at the perimeter of the work area, activities must be shutdown.

- All 15-minute readings must be recorded and be available for State (NYSDEC and NYSDOH) personnel to review. Instantaneous readings, if any, used for decision purposes should also be recorded.

3.0 PARTICULATE MONITORING

Monitoring for particulates will be required during remediation-related ground intrusive activities and will include monitoring the upwind and downwind perimeters of the exclusion zone or work area, at a minimum. The particulate monitoring must use real-time monitoring equipment capable of measuring particulate matter less than ten (10) micrometers in size (PM-10) and capable of integrating over a period of 15 minutes (or less) for comparison to the airborne particulate action level.

As outlined in NYSDEC DER-10 Appendix 1B: Fugitive Dust & Particulate Monitoring, the monitoring equipment must meet, at a minimum, the following performance standards:

(a) Objects to be measured: Dust, mists or aerosols;
(b) Measurement Ranges: 0.001 to 400 mg/m^3 (1 to 400,000 ug/m^3);
(c) Precision (2-sigma) at constant temperature: +/- 10 g/m^3 for one second averaging; and +/- 1.5 g/m^3 for sixty second averaging;
(d) Accuracy: +/- 5% of reading +/- precision (Referred to gravimetric calibration with SAE fine test dust (mmd= 2 to 3 m, g= 2.5, as aerosolized);
(e) Resolution: 0.1% of reading or $1g/m^3$, whichever is larger;
(f) Particle Size Range of Maximum Response: 0.1-10;
(g) Total Number of Data Points in Memory: 10,000;
(h) Logged Data: Each data point with average concentration, time/date and data point number
(i) Run Summary: overall average, maximum concentrations, time/date of maximum, total number of logged points, start time/date, total elapsed time (run duration), STEL concentration and time/date occurrence, averaging (logging) period, calibration factor, and tag number;
(j) Alarm Averaging Time (user selectable): real-time (1-60 seconds) or STEL (15 minutes), alarms required;
(k) Operating Time: 48 hours (fully charged NiCd battery); continuously with charger;
(l) Operating Temperature: -10 to 50 °C (14 to 122 °F); and
(m) Particulate levels will be monitored upwind and immediately downwind at the working site and integrated over a period not to exceed 15 minutes.

The equipment will be equipped with an audible alarm to indicate exceedance of the action level. The action level is 150 micrograms per cubic meter (ug/m^3) measured as a 15 minutes average. In addition, fugitive dust migration will be visually assessed during all work activities. Calibration will be in accordance with the HASP and the instrument manufacturer's recommendations.

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The upwind sampling station will be situated upwind of the largest dust producing activity occurring at the Site at the boundary of the work zone. Similarly, the downwind sampling station will be directly downwind of the largest dust producing activity at the boundary of the work zone.

If the downwind PM-10 particulate level is 100 ug/m^3 greater than background (upwind perimeter) for the 15-minute period or if airborne dust is observed leaving the work area, then dust suppression techniques must be employed. Work may continue with dust suppression techniques provided that downwind PM-10 particulate levels do not exceed 150 ug/m^3 above the upwind level and provided that no visible dust is migrating from the work area.

If, after implementation of dust suppression techniques, downwind PM-10 particulate levels are greater than 150 ug/m^3 above the upwind level, work must be stopped and a re-evaluation of activities initiated. Work can resume provided that dust suppression measures and other controls are successful in reducing the downwind PM-10 particulate concentration to within 150 ug/m^3 of the upwind level and in preventing visible dust migration.

Should the action level of 150 ug/m^3 continue to be exceeded work must stop and DER must be notified. The notification shall include a description of the control measures implemented to prevent further exceedances. All readings must be recorded and be available for review by the NYSDOH, NYSDEC and Saratoga County Health Department, if requested.

The sampling locations will be periodically adjusted to account for observed changes in wind direction.

4.0 CAMP SPECIAL REQUIREMENTS

4.1 Special Requirements for Work Within 20 Feet of Potentially Exposed Individuals or Structures

When work areas are within 20 feet of potentially exposed populations or occupied structures, the continuous monitoring locations for VOCs and particulates must reflect the nearest potentially exposed individuals and the location of ventilation system intakes for nearby structures. The use of engineering controls such as vapor/dust barriers, temporary negative- pressure enclosures, or special ventilation devices should be considered to prevent exposures related to the work activities and to control dust and odors. Consideration should be given to implementing the planned activities when potentially exposed populations are at a minimum, such as during weekends or evening hours in non-residential settings.

- If total VOC concentrations opposite the walls of occupied structures or next to intake vents exceed 1 ppm, monitoring should occur within the occupied structure(s). Background readings in the occupied spaces must be taken prior to commencement of the planned work. Any unusual background readings should be discussed with NYSDOH prior to commencement of the work.

- If total particulate concentrations opposite the walls of occupied structures or next to intake vents exceed 150 mcg/m3, work activities should be suspended until controls are implemented and are successful in reducing the total particulate concentration to 150 mcg/m3 or less at the monitoring point.

- Depending upon the nature of contamination and remedial activities, other parameters (e.g., explosivity, oxygen, hydrogen sulfide, carbon monoxide) may also need to be monitored. Response levels and actions should be pre-determined, as necessary, for each site.

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4.2 Special Requirements for Indoor Work with Co-Located Residences or Facilities

Unless a self-contained, negative-pressure enclosure with proper emission controls will encompass the work area, all individuals not directly involved with the planned work must be absent from the room in which the work will occur. Monitoring requirements shall be as stated above under "Special Requirements for Work Within 20 Feet of Potentially Exposed Individuals or Structures" except that in this instance "nearby/occupied structures" would be adjacent occupied rooms. Additionally, the location of all exhaust vents in the room and their discharge points, as well as potential vapor pathways (openings, conduits, etc.) relative to adjoining rooms, should be understood and the monitoring locations established accordingly. In these situations, it is strongly recommended that exhaust fans or other engineering controls be used to create negative air pressure within the work area during remedial activities. Additionally, it is strongly recommended that the planned work be implemented during hours (e.g. weekends or evenings) when building occupancy is at a minimum.

5.0 FORMS FOR MONITORING AND RESPONSE

Air monitoring of particulate concentrations will be documented using the air monitoring form provided in Appendix 1. This form is to be completed on a daily basis and records of this form must be made available for NYSDEC and NYSDOH review upon request.

Response action to observed exceedances will be documented using the form provided in Appendix 2. This form must also be made available for NYSDEC and NYSDOH review upon request.

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APPENDIX 1

AIR MONITORING FORM

53 PUTNAM STREET
CITY OF SARATOGA SPRINGS, NEW YORK
BCP #C546057

Air Monitoring Form

Name ____________________________ **Weather Conditions** ____________________
Date ____________________________ **Wind Direction** ________________________

	UPWIND		**WORK AREA**		**DOWNWIND**	
Time	**PID** (ppm)	**DUSTTRAK** (mg/m^3)	**PID** (ppm)	**DUSTTRAK** (mg/m^3)	**PID** (ppm)	**DUSTTRAK** (mg/m^3)

APPENDIX 2

EXCEEDANCES AND ACTIONS TAKEN

53 PUTNAM STREET
CITY OF SARATOGA SPRINGS, NEW YORK
BCP #C546057

Exceedances and Actions Taken

Name _____ **Date** _____

Time _____ **Weather Conditions** _____

Location of Exceedance _____ **Wind Direction** _____

Type of Exceedance:

_____

_____

_____

_____

_____

_____

_____

Action Taken:

_____

_____

_____

_____

_____

_____