



Watervliet Arsenal

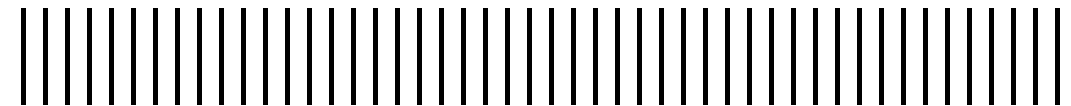
Watervliet, New York

Corrective Measures Performance Evaluation Report

**Building 40 Bedrock Groundwater Corrective Measures
Main Manufacturing Area**

Watervliet Arsenal, Watervliet New York

December 2008



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of Engineers**

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PIRNIE**

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Executive Summary

The Watervliet Arsenal (WVA) is conducting a Corrective Measures (CM) program for the bedrock groundwater at Building 40 of the WVA, which is located in the City of Watervliet, New York. The CM program is being conducted under contract with the U.S. Army Corps of Engineers (USACE), Baltimore District in accordance with a Resource Conservation and Recovery Act (RCRA) Administrative Order on Consent between the WVA, the New York State Department of Environmental Conservation (NYSDEC), and the United States Environmental Protection Agency (USEPA). The goal of the CM program is to treat the volatile organic compounds (VOCs), composed primarily of tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cDCE), and, to a lesser extent, vinyl chloride (VC), that are present in the bedrock groundwater and shale bedrock matrix at Building 40. The treatment program includes injections of sodium permanganate (herein referred to as “permanganate”) and groundwater sampling at the WVA property line compliance boundary.

In accordance with the approved CM Work Plan, the Corrective Action Objective (CAO) for the CM Program is to reduce the concentration of hazardous constituents in groundwater migrating from the site to New York State and Federal groundwater standards, or approved alternate concentration limits (ACLs) developed for the site. However, given the likely presence of dense non-aqueous phase liquids (DNAPL) in the fractured rock at the site, it was recognized by all parties that the achievement of the CAO may require an extensive time period and may not be achievable using currently available technologies. Accordingly, the CM program is subject to the following Performance Criteria, through which the CAO may be achieved over the long-term as a result of source reduction:

1. **Permanganate Distribution:** The permanganate must be well distributed to and within the boundary monitoring wells within one year after the initiation of full scale injections.
2. **Permanganate Residence Time:** The permanganate must persist for at least 30 days after injection in the boundary monitoring wells within two years after the initiation of full scale injections.

If these performance criteria are not met, the WVA is required to perform an evaluation as to whether the permanganate corrective measures, or any other potential corrective measures, are feasible for the site.

The corrective measures were initiated in September 2004 with injections on the west side (upgradient) of Building 40. Full scale injections into all five injection wells were



initiated in August 2005. The maximum permanganate distribution in the compliance boundary monitoring wells was achieved during the first full-scale injection event in August 2005 when permanganate was delivered to nine of the 18 compliance monitoring zones. Beginning with the November 2005 injection event, and in subsequent injection events, injection well clogging limited the amount and/or rate of oxidant that could be delivered to injection wells IW-2 and IW-3. Clogging in these wells, which are located in the central portion of the treatment area, was accompanied by a decrease in permanganate distribution in the compliance monitoring zones. As of the last injection event in September 2006, permanganate residence time was less than 30 days in 16 of the 18 monitoring zones.

Injection well IW-3 was reamed with a roller bit in August 2006 to clear the remains of a partially disintegrated FLUTE™ liner and to attempt to redevelop the well. In September 2006, well IW-2 was mechanically cleaned using a drilling rig equipped with a wire brushing device, and redeveloped using a combination of surging and pumping. Specific capacity testing performed before and after the redevelopment/cleaning indicated that the flow conditions in these wells had not improved significantly. A subsequent injection event in September 2006 confirmed this finding as injections into well IW-2 and IW-3 were limited due to lack of flow and the resulting permanganate distribution was the lowest since full-scale injections were initiated. Temperature and pressure data collected during the injection indicated that the permanganate injections were not influencing all portions of the treatment area. Further attempts to rehabilitate injection well IW-2 in March 2007 using AirBurst® technology did not result in significant increases in specific capacity.

Total VOC mass discharge through the compliance boundary during the baseline sampling was approximately 10 pounds per year (lb/yr). As of the last two sampling events conducted in September 2006 and September 2007, the mass discharge through the compliance boundary was approximately 18 lb/yr and 13 lb/yr, respectively. The minimum mass discharge measured during the monitoring period was 6.6 lb/yr during the November 2006 pre-injection sampling. This sampling event followed the first full scale permanganate injection event in August 2005. The apparent increases in the calculated mass discharge are likely due to a combination of reduced hydraulic conductivity (a component of the mass discharge calculation) and changes in the groundwater VOC concentrations. As of September 2007, total VOC concentrations in groundwater increased in seven of the 18 compliance monitoring zones and decreased in 11 of the 18 compliance monitoring zones.

Two bedrock core holes (CH-91 and CH-92) were drilled in December 2006 to evaluate bedrock fracture conditions and matrix contaminant concentrations. Evidence of permanganate staining was observed in five fractures in the upper 50 feet of CH-92 and at 122 feet below ground surface (bgs) in CH-91. However, estimated rock matrix pore

water VOC concentrations in CH-91 were consistent in both depth profile and concentrations with those of MW-87 (located ~15 feet south of CH-91), which was drilled and sampled prior to the initiation of injections in September 2004.

The results of the testing and monitoring conducted to date support the following conclusions:

1. The permanganate injections conducted to date have not decreased groundwater VOC concentrations at the compliance boundary or the mass flux at the compliance boundary, and rock core VOC pore water concentrations have not decreased after two years of injections. In addition, based on the increases in VOC concentrations in many of the compliance monitoring zones, the CM program may have increased the VOC mass discharge across the compliance boundary.
2. The persistent clogging problems indicate that a large portion of the injected permanganate mass is being oxidized to insoluble precipitates through interaction with the rock matrix, specifically the reduced sulfur (i.e., pyrite), present in the rock. This interaction with the rock is greatly limiting the effectiveness of the permanganate injections. Rock core, water level, pressure, and temperature monitoring has shown that the injections are influencing only a portion of the treatment area.
3. The CM program has failed to achieve the CM Performance Criteria and, therefore, cannot achieve the overall CAO of reduction of VOC concentrations in groundwater to state or federal standards.

Based on these data, and the lack of any other potentially effective remedial technology, achievement of the CAO is not technically feasible using currently available technologies. In accordance with Section 9.2.4.2 of the CM Work Plan, it is therefore recommended that the CM Program be discontinued and that selected Building 40 monitoring wells be included in the overall WVA Long Term Monitoring Program for future monitoring.

1. Introduction

On behalf of the Watervliet Arsenal (WVA), Malcolm Pirnie, Inc. (Malcolm Pirnie) is conducting a Corrective Measures (CM) program for the bedrock groundwater at Building 40 of the WVA, which is located in the City of Watervliet, New York (Figures 1-1 and 1-2). The CM program is being conducted under contract with the U.S. Army Corps of Engineers (USACE), Baltimore District in accordance with a Resource Conservation and Recovery Act (RCRA) Administrative Order on Consent between the WVA, the New York State Department of Environmental Conservation (NYSDEC), and the United States Environmental Protection Agency (USEPA). Details for the CM program are presented in the *Corrective Measures Work Plan, Building 40 Bedrock Groundwater, Main Manufacturing Area, Watervliet Arsenal, Watervliet, New York* (Malcolm Pirnie, 2004) (CM Work Plan) and the *Corrective Measures Monitoring Program, Building 40 Bedrock Groundwater, Main Manufacturing Area, Watervliet Arsenal, Watervliet, New York* (Malcolm Pirnie, 2004a) (CMMP).

The CM program is designed to treat the volatile organic compounds (VOCs), composed primarily of tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cDCE), and, to a lesser extent, vinyl chloride (VC), that are present in the bedrock groundwater and shale bedrock matrix at Building 40. This treatment is being accomplished using injections of sodium permanganate (herein collectively referred to as “permanganate”) in the treatment area/locations specified in the CM Work Plan. The locations of the monitoring and injection wells utilized for the CM program are shown on Figure 1-3.

1.1. Purpose

The purpose of this Corrective Measures Performance Evaluation Report (CM Performance Report) is to present the results of the injection, sampling, and maintenance activities that were performed as part of the CM program through 2007; evaluate the progress of the corrective measures in meeting the Corrective Action Objectives (CAOs); and recommend a future course of action based on the evaluation of the corrective measures. This report augments the information provided in the *Corrective Measures Installation and Startup Report, Building 40 Bedrock Groundwater, Main Manufacturing Area, Watervliet Arsenal, Watervliet, New York* (Malcolm Pirnie, 2006) (CM Startup Report), which was previously submitted to the NYSDEC and USEPA.



2. Well Rehabilitation

Beginning with the November 2005 injection event, and in subsequent injection events, injection well clogging limited the amount and/or rate of oxidant that could be delivered to injection wells IW-2 and IW-3 (Figure 1-3). Clogging in these wells, which are located in the central portion of the treatment area, was accompanied by a decrease in permanganate distribution in the compliance monitoring zones.

2.1. Injection Well IW-3

Injection well IW-3 was reamed in August 2006 to clear any remains of a partially disintegrated FLUTe™ liner. The reaming was conducted using a truck-mounted drilling rig equipped with a 5 7/8-inch roller bit. Upon the conclusion of reaming, the well was redeveloped to the extent possible by air lift methods. Approximately 100 gallons of a water/black solid precipitate slurry was removed from the well during redevelopment. However, flow from the well did not increase substantially as a result of the reaming and redevelopment.

2.2. Injection Well IW-2

Injection well IW-2 was mechanically brushed, surged, and pumped immediately prior to the September 2006 injection in an attempt to clear the well of precipitates. Approximately 40 gallons of a water/black solid slurry was removed from IW-2 during the cleaning. However, this activity did not significantly increase the conductivity of the well. In March 2007, an additional attempt was made to redevelop IW-2 using AirBurst® redevelopment techniques. AirBurst® is a patented technology that uses a high-pressure Bolt Air Gun that delivers a small volume of inert gas (nitrogen) to generate high intensity “pressure pulses” in the well to break up and remove mineral scales and biofilms from the borehole wall. Three AirBurst® passes of the entire 150 foot borehole were conducted at one foot spacing, offsetting the passes each time such that every six inches of borehole received the AirBurst® application. Each of these applications was conducted using 500 pounds per square inch (psi) of air pressure. The well was surged and pumped after the first three AirBurst® applications. A fourth pass using 1,200 psi of air pressure was conducted in the interval from 80 feet to 120 feet below ground surface (bgs), which, based on the geophysical profiling conducted after the well was installed, contained the most transmissive fractures. The well was then surged and pumped a second time. Specific capacity testing before and after the mechanical brushing and AirBurst® applications indicated no significant increase in the conductivity of the well from either of the rehabilitation attempts. Specific capacity test results are summarized in Table 2-1.

3. Supplemental Characterization Activities

Additional rock core testing and multi-level monitoring well installation/sampling were conducted in 2006. The purpose of the testing was to evaluate the progress of the corrective measures and to further aid in the assessment of permanganate distribution.

3.1. Rock Core Testing

Two bedrock core holes were drilled in December 2006 to evaluate whether manganese dioxide precipitation was occurring in the bedrock aquifer outside of the injection wells and to assess the degree to which the bedrock matrix had been treated by the first two years of permanganate injections. The locations of these core holes are shown on Figure 1-3. The first core hole (CH-91) was drilled adjacent to existing core hole MW-87 to a depth of 150 feet bgs. This core hole was used to collect rock core samples for rock matrix pore water VOC analysis by the University of Waterloo using the same methods and procedures as those utilized for previous studies at the WVA. The second core hole (CH-92) was drilled adjacent to injection well IW-2 to a depth of 80 feet, which is the approximate depth of the major transmissive fracture in IW-2. The purpose of CH-92 was to evaluate whether visually-evident fracture clogging was occurring outside of the injection well boreholes. The presence of solid precipitates was assessed visually in the field, through analysis of thin sections, and by observation of magnified core surfaces at the University of Waterloo.

Consistent with previous rock coring events, fracture orientation was generally parallel to the steep bedding of the shale bedrock. While fracture angles ranged from nearly horizontal to nearly vertical, the majority of the fracture angles were in the range of 60 degrees to 70 degrees from horizontal. Numerous calcite veins were noted, as well as pyrite in some of the fractures. Additionally, permanganate staining and/or solid precipitates were observed in several fractures. Coring logs from CH-91 and CH-92 are provided in Appendix A. Table 3-1 summarizes the permanganate staining and/or solid precipitates observed in the two core holes. Examples of the permanganate staining and solid precipitates are shown on Figure 3-1, which shows the fractures at 35 ft bgs and 56 feet bgs in CH-92.

Table 3-1
Permanganate Staining and/or Precipitates Observed in CH-91 and CH-92

Core Hole 91		Core Hole 92	
Run #	Depth (ft bgs)	Run #	Depth (ft bgs)
16	122.6	1	21
		3	31.4
		3	35
		3	38.2
		5	56.2

3.2. Monitoring Well Installation and Construction

To further enhance the analysis of the permanganate injections to the west of Building 40, MW-87 was outfitted with a Zone Isolation Sampling Technology (ZIST) in-line well system in March 2006. These systems, which are manufactured by BESST, Inc. Global Subsurface Technologies, consist of standard PVC well construction with a docking receptacle directly above the well screen into which a pump and sensor/data logger seat, thereby sealing off the screened interval for monitoring and sampling. Three one-inch wells were installed inside the MW-87 borehole, with screened intervals from 40 to 50 feet bgs, 90 to 100 feet bgs, and 140 to 150 feet bgs. The well construction log for the ZIST well system is included in Appendix A. During sampling, water in the sampling tube is pushed to the surface using compressed air or nitrogen. Because the water in the sample tube flows directly from the formation around the screened interval under natural hydrostatic pressure, it is only necessary to purge the small volume of water in the sampling tube before sampling. As each zone is self-contained with its own pump and tubing, all sampling zones can be purged simultaneously. The tubing, pump, and sensor/data logger can be removed from each well with relative ease in order to download data and maintain system components. The sensor and data logger are set up to record temperature, and pressure (water level), and were programmed to record data both during permanganate injections and during the post-injection monitoring periods. These data are presented in Section 5.

4. Permanganate Injections and Monitoring

Additional permanganate injections were performed in the corrective measures area as follows:

- Injection 6: April 3 – April 7, 2006
- Injection 7: September 25 – September 29, 2006

Pre-injection monitoring was conducted prior to each monitoring event in accordance with the CM Work Plan and CMMP. Permanganate distribution monitoring was conducted during and after each injection event, including the boundary monitoring wells and the newly installed multi-level ZIST system in MW-87. Details for each injection and monitoring event are summarized in Table 4-1 and discussed below.

4.1. Permanganate Injection No. 6

4.1.1. Pre-Injection Monitoring

Pre-injection monitoring was conducted from March 27-April 3, 2006. The results of the April 2006 pre-injection monitoring are shown in Appendix B (Tables B-1 through B-12 and Figures B-1 through B-12). VOC data from the April 2006 monitoring event were validated in accordance with the CMMP. The DUSR for the April 2006 VOC data is presented in Appendix C. Note that this DUSR includes samples collected during the October 2006 Long-Term Monitoring sampling event, which are discussed under separate cover.

4.1.2. Injection Parameters

Approximately 4,600 gallons of a five percent sodium permanganate solution were injected into injection wells MW-79, IW-1, IW-2, IW-3, and IW-4 during Injection No. 6. Due to the remaining partially disintegrated FLUTe™ liner and presumed clogging of fractures in injection well IW-3, the permanganate was not distributed evenly across the injection wells. Generally, the volume of permanganate that could not be injected into IW-3 was injected into IW-1, resulting in the injection of at least 900 gallons of the permanganate solution into each injection well, with the exception of IW-1 which received approximately 1,700 gallons. The injections were conducted using the entire open interval of the injection wells. Permanganate solution injection methods and rates are summarized in Table 4-2 below.

Table 4-2.
Injection No. 6 (April 2006) Parameters

Injection Well	Injection Method	Injection Pressure (psi)	Injection Rate (gpm)
MW-79	Pressurized	35	5.6 - 6
IW-1	Pressurized	30-35	3.9 - 6.1
IW-2	Pressurized	35-55	0.2 - 1.2
IW-3	Pressurized	Gravity-35	0.04 - 0.2
IW-4	Pressurized	35	8.0 - 8.6

Notes:

Gravity feed often performed overnight by draining remaining permanganate solution in mixing tank through tube connected to the well head.

gpm – gallons per minute

psi – pounds per square inch

4.1.3. Distribution Monitoring

Distribution monitoring was conducted during and after Injection No. 6 primarily using the compliance boundary wells MW-81 through MW-86R, and the newly installed multi-level ZIST system in MW-87. Monitoring was conducted in all three monitoring zones (designated 1, 2, and 3 for the shallow, middle, and deep zones, respectively) in each well. Periodic monitoring of the remaining wells included in the Building 40 groundwater monitoring program was also conducted. The wells were monitored for the presence of permanganate (both visual presence and concentration).

4.1.4. Injection Results

As shown in Table 4-1 and Figures 4-1 through 4-6, permanganate was observed in one zone in each of compliance boundary monitoring wells, except MW-84R, and in a total of five of the 18 compliance boundary monitoring zones following the April 2006 injection. Compliance monitoring zones where permanganate was observed were:

- MW-81-2
- MW-82R-2
- MW-83-3
- MW-85R-2
- MW-86R-2

Permanganate concentrations in these monitoring zones ranged from 11 milligrams per liter (mg/l) (MW-81-2) to approximately 16,567 mg/l (MW-86R-2). The highest permanganate concentrations were observed in monitoring zones MW-86R-2-, MW-83-3, and MW-82R-2-. The permanganate concentration of 16,567 mg/l in monitoring zone MW-86R-2 was equivalent to approximately 33 percent of the injected permanganate concentration. Permanganate concentrations in the remaining compliance monitoring

zones were generally less than 50 mg/l. As shown on Figures 4-1 through 4-6, permanganate residence times in the compliance monitoring zones following Injection No. 6 ranged from less than one week (MW-81-2 and MW-85R-2) to approximately five months (MW-83-3).

4.2. Permanganate Injection No. 7

4.2.1. Pre-Injection Monitoring

Pre-injection monitoring was conducted from September 11-22, 2006. The results of the September 2006 pre-injection monitoring are shown in Appendix B (Tables B-1 through B-12 and Figures B-1 through B-12). VOC data from the September 2006 monitoring event were validated in accordance with the CMMP. The DUSR for the September 2006 VOC data is presented in Appendix C. Note that this DUSR includes samples collected during the October 2006 Long-Term Monitoring sampling event, which are presented under separate cover.

4.2.2. Injection Parameters

Approximately 4,663 gallons of a five percent sodium permanganate solution were injected into injection wells MW-79, IW-1, IW-2, IW-3, and IW-4 during Injection No. 7. Permanganate could not be injected into IW-3 during the September 2006 injection as the borehole would not accept the injection fluids under both pressurized and gravity-drain injection conditions. Therefore, approximately half of the total injection volume was delivered through MW-79, with additional volume also delivered into IW-4. The injections were conducted using the entire open interval of the injection wells.

Permanganate solution injection methods and rates are summarized in Table 4-3 below. As shown in the table, injection rates in September 2006 declined from those achieved in the April 2006 injection.

Table 4-3.
Injection No. 7 (September 2006) Parameters

Injection Well	Injection Method	Injection Pressure (psi)	Injection Rate (gpm)
MW-79	Pressurized	25-30	3.6 - 5.6
IW-1	Pressurized	Gravity-40	1.0 - 3.3
IW-2	Pressurized	Gravity-35	0.1 - 1.5
IW-3	Pressurized	Gravity	N/A*
IW-4	Pressurized	Gravity-35	1.3 - 7.5

Notes:

Gravity feed often performed overnight by draining remaining permanganate solution in mixing tank through tube connected to the well head.

* Injection well would not accept injection fluids.

gpm – gallons per minute

psi – pounds per square inch

4.2.3. Distribution Monitoring

Distribution monitoring was conducted during and after Injection No. 7 primarily using the compliance boundary wells MW-81 through MW-86R, and the newly installed multi-level ZIST system in MW-87. Monitoring was conducted in all three monitoring zones in each well. Periodic monitoring of the remaining wells included in the Building 40 groundwater monitoring program was also conducted. The wells were monitored for the presence of permanganate (both visual presence and concentration).

4.2.4. Injection Results

As shown in Table 4-1 and Figures 4-1 through 4-6, permanganate was observed in one zone in three of the compliance boundary monitoring wells and in three of the 18 compliance boundary monitoring zones. Compliance monitoring zones where permanganate was observed were:

- MW-83-3
- MW-85R-2
- MW-86R-2

Permanganate concentrations in these monitoring zones ranged from 1 mg/l (MW-85R-2) to approximately 24,148 mg/l (MW-86R-2). The highest permanganate concentrations were observed in monitoring zone MW-86R-2. The permanganate concentration of 24,148 mg/l in monitoring zone MW-86R-2 was equivalent to approximately 48 percent of the injected permanganate concentration. Permanganate concentrations in the remaining compliance monitoring zones were generally less than 500 mg/l. As shown on Figures 4-1 through 4-6, permanganate residence times in the compliance monitoring zones following Injection No. 7 ranged from approximately one week (MW-85R-2) to over one month (MW-83-3 and MW-86R-2).

4.3. September 2007 Groundwater Sampling

A supplemental groundwater monitoring event was conducted from September 9-13, 2007 to evaluate groundwater conditions after the permanganate had dissipated. The results of the September 2007 monitoring are shown in Appendix B (Tables B-1 through B-12 and Figures B-1 through B-12) and are included in the discussions presented in Section 5.

4.4. MW-87 In-Situ Data Loggers

As discussed in Section 3, the three ZIST monitoring zones in monitoring well MW-87 were equipped with data loggers that are capable of recording water level, pressure, and temperature at variable frequencies. These data loggers were set to record before, during, and after the April and September 2006 permanganate injections. Figures 4-8 and 4-9 show water level variations (measured by changes in water pressure) for the April and

September 2006 injection events, respectively. Injection and sampling events are often clearly evident in the sensor data as spikes in pressure. The larger spikes with positive pressure anomalies generally correspond to injection events, while the smaller spikes with negative pressure anomalies generally correspond to groundwater sampling events. Monitoring zone MW-87-2 showed the greatest response to the injection events and was the only zone in monitoring well MW-87 that received permanganate during the two injections (April 2006 injection only). Additionally, as shown on Figure 4-7, examination of the recorded parameters from MW-87 and Hudson River tidal data from Albany, New York confirms a tidal influence on the water levels in the middle zone of MW-87.

5. Performance Evaluation

5.1. Permanganate Injections

In accordance with the approved CM Work Plan, the Corrective Action Objective (CAO) for the CM Program is to reduce the concentration of hazardous constituents in groundwater migrating from the site to New York State and Federal groundwater standards, or approved alternate concentration limits (ACLs) developed for the site. However, given the likely presence of dense non-aqueous phase liquids (DNAPL) in the fractured rock at the site, it was recognized by all parties that the achievement of the CAO may require an extensive time period and may not be achievable using currently available technologies. Accordingly, the CM program is subject to the following Performance Criteria:

1. **Permanganate Distribution:** The permanganate must be well distributed to and within the boundary monitoring wells within one year after the initiation of full scale injections.
2. **Permanganate Residence Time:** The permanganate must persist for at least 30 days after injection in the boundary monitoring wells within two years after the initiation of full scale injections.

5.1.1. Distribution

Permanganate distribution in the Building 40 groundwater is affected by three primary factors:

1. The rate at which the permanganate is consumed by the contaminant load and/or the natural oxidant demand of the groundwater and rock (rock oxidant demand);
2. The degree to which the fractures in the compliance monitoring zones are connected to the injection wells where the permanganate is introduced (i.e., direct connection through one fracture or indirect connection through two or more fractures); and
3. The amount of flow transmitted by the fractures that intersect the compliance zone, which is measured as fracture transmissivity, and which is a function of fracture aperture, fracture extent/size, and hydraulic head.

Table 5-1 and Figures 5-1 and 5-2 present a summary of permanganate distribution in the compliance boundary monitoring wells from the beginning of the CM injection program on September 30, 2004 through the last injection on September 29, 2006. As shown on Figures 5-1 and 5-2, the number of compliance zones that received permanganate peaked at a maximum of nine of the 18 compliance zones following the first full-scale injection in August 2005 and declined steadily during the following three injections to seven, five, and three zones, respectively. This decline occurred despite the continued injection of

equivalent volumes of permanganate and corresponds with the occurrence of the well injection well clogging described in Section 2.0. The permanganate distribution resulting from the last injection event in September 2006 was the lowest since full scale injections were initiated in August 2005. Based on these data, it is concluded that the corrective measures have failed to meet the Permanganate Distribution Performance Criteria.

5.1.1.1. Evaluation

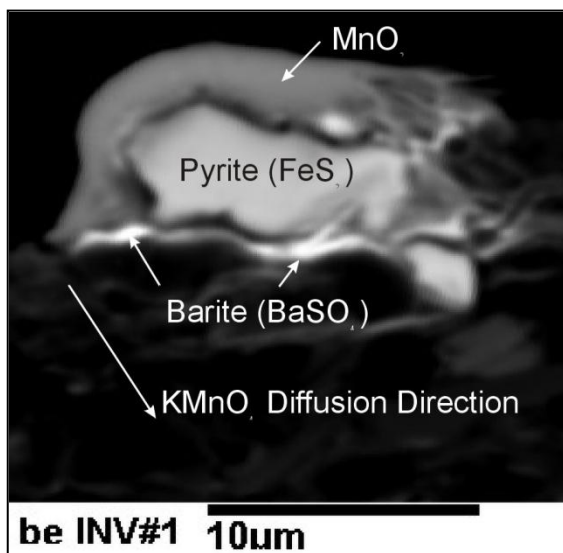
If permanganate clogging were the primary cause of the decrease in permanganate distribution, it would be expected that the lower transmissivity zones would be impacted before the higher transmissivity zones. As shown in Table 5-1, the monitoring data supports this expectation since the decline in permanganate distribution generally correlated with the relative transmissivity (as calculated through geophysical testing prior to the injections) of the individual compliance monitoring zones.

During the first two full-scale injections in August and December 2005, the transmissivity of the compliance monitoring zones receiving permanganate ranged from 0.1 square feet per day (ft^2/d) to $157.6 \text{ ft}^2/\text{d}$, with an average of $51.4 \text{ ft}^2/\text{d}$ and $51.8 \text{ ft}^2/\text{d}$, respectively. In both events, two monitoring zones with transmissivities less than $2.0 \text{ ft}^2/\text{d}$ received permanganate. During the April 2006 and September 2006 injections, the transmissivity of the compliance monitoring zones receiving permanganate ranged from $7.8 \text{ ft}^2/\text{d}$ (the transmissivity of zone MW-83-3) to $157.6 \text{ ft}^2/\text{d}$ and averaged $78.6 \text{ ft}^2/\text{d}$ and $97.6 \text{ ft}^2/\text{d}$, respectively. With the exception of zone MW-83-3, which, based on the data, appears to have a direct connection to one or more of the injection wells, no monitoring zone with a transmissivity less than $25 \text{ ft}^2/\text{d}$ received permanganate during the April 2006 injection. During the September 2006 injection, only zones with transmissivities greater than $125 \text{ ft}^2/\text{d}$ received permanganate (excluding zone MW-83-3).

As discussed in the CM Work Plan and the *Building 40 Chemical Oxidation Pilot Study Summary Report, Watervliet Arsenal, Watervliet, New York* (Malcolm Pirnie, 2003) (Pilot Study Report), rock oxidant demand testing was conducted prior to the corrective measures to evaluate the degree to which the permanganate would be consumed by the natural oxidant demand of the groundwater system. The results of the testing, which were conducted on crushed samples of rock, indicated that the rock oxidant demand ranged from 15 to 70 milligrams of permanganate per gram of rock and increased with increasing concentration of permanganate. However, these results were deemed to be conservative since they were performed on crushed rock samples with much more available surface area than a fracture plane. The results also indicated that pyrite oxidation (oxidation of the sulfur in pyrite [FeS] to sulfate [SO_4]) accounted for 30 to 80 percent of the rock oxidant demand – producing both manganese oxide precipitates and elevated sulfate concentrations in the groundwater. This phenomenon was evidenced in laboratory testing through scanning electron microscope imaging of rock core samples

that had been exposed to permanganate (Figure 5-3, below) and in the field during the permanganate injections (Table 5-2).

Figure 5-3: Oxidation of Pyrite by Permanganate in Rock Core Samples



Courtesy: University of Waterloo/University of New Brunswick

Table 5-2 summarizes sulfate concentrations in groundwater samples collected from the compliance monitoring wells during the pre-injection sampling events conducted prior to the permanganate injections. As shown in this table, sulfate concentrations in samples collected from the compliance monitoring wells increased to greater than 100 percent of the baseline concentration in more than half [11 out of 18 (61 percent)] of the compliance monitoring zones; by more than 500 percent in eight (44 percent) of the 18 compliance monitoring zones; and by more than 1,000 percent in five (28 percent) of the 18 compliance monitoring zones. In addition, based on the results of the September 2007 sampling, sulfate concentrations remained elevated at concentrations greater than 100 percent of the baseline in 44 percent (eight out of 18) of compliance zones one year after the last injection event in September 2006.

5.1.1.2. Conclusion

Based on the permanganate distribution, the transmissivity analysis, and the increases in aqueous sulfate concentrations in the compliance monitoring zones, it is concluded that the failure to achieve the Permanganate Distribution Performance Criteria is primarily due to the loss of fracture transmissivity that resulted from the interaction (consumption) of the permanganate with the bedrock material. This interaction produced solid precipitates that clogged or reduced the hydraulic transmission capacity of the bedrock fractures (most likely those immediately adjacent to the injection well boreholes) and consistently reduced permanganate distribution with each subsequent injection event to

the point where further injections were not possible in two of the five injection wells. As discussed in Section 2, attempts to rehabilitate the clogged wells were not successful.

5.1.2. Residence Time

Permanganate residence time in the Building 40 groundwater is controlled by three primary factors:

1. The concentration of permanganate that is delivered to a particular fracture or compliance monitoring zone;
2. The rate at which the permanganate in the fracture or compliance monitoring zone is consumed by the contaminant load and/or the rock oxidant demand;
3. The amount of advective groundwater flow in the fractures or compliance monitoring zone to which the permanganate is delivered, which is a function of hydraulic gradient and fracture transmissivity.

Table 5-3 presents a summary of permanganate residence time in the compliance monitoring wells following each injection event. Figure 5-4 presents the maximum permanganate residence times achieved in the compliance boundary monitoring wells during the six permanganate injection events conducted from September 2004 through September 2006. As shown on Figure 5-4, permanganate residence time met or exceeded the Residence Time CAO of 30 days in only six of the 18 (33 percent) compliance monitoring zones during *all injection events*. However, as shown in Table 5-3, the maximum number of compliance zones with permanganate residence times greater than 30 days following *any single injection event* was four (22 percent), following the December 2005 injection event. As of the last injection in September 2006, only two (estimated based on previous events – see Table 5-3 notes) of the 18 compliance monitoring zones (11 percent) contained permanganate for 30 days or more.

5.1.2.1. Evaluation

Since it was not possible to measure the hydraulic gradient in individual fractures, zone transmissivity is the only potential indicator of the degree to which advective groundwater flow (i.e., flushing) may have affected permanganate residence time or concentration. Table 5-3 summarizes permanganate concentrations in the compliance monitoring zones as they relate to the concentration of the injected permanganate solution, the combined fracture transmissivity of each compliance monitoring zone, and permanganate residence time. As shown in the table, the data indicates that no single factor contributed to either the concentration of permanganate delivered to a particular monitoring zone or the residence time of the permanganate once it reached that monitoring zone. For example, compliance monitoring zones with both the lowest (MW-82R-3: 0.1 ft²/day) and highest (MW-86R-2: 157.6 ft²/day) transmissivity exhibited permanganate residence times greater than 30 days. Likewise, the permanganate concentration in zone MW-81-1 (504 mg/l @ 1.2 ft²/day) was approximately five times

greater than the permanganate concentration in zone MW-85R-2 (96 mg/l @ 127.4 ft²/day) after the August 2005 injection. The lack of relationship between zone transmissivity, permanganate residence time, and permanganate concentration are also shown on Figures 5-5 and 5-6, respectively. As shown on these figures, neither permanganate residence time ($r^2 = -0.88^1$) or permanganate concentration ($r^2 = 0.43$) correlates statistically with zone transmissivity.

5.1.2.2. Conclusion

Based on the apparent lack of correlation between groundwater flow potential (as measured through zone transmissivity) and both permanganate concentration and residence time, it is concluded that the failure to achieve Permanganate Residence Time CAO is likely also due to the consumption of the permanganate by the bedrock material, as discussed in Section 5.1.1. In addition, as expected and as evidenced by the near-injection-strength permanganate concentrations detected in compliance zone MW-86R-2, and the extended permanganate residence times in both zone MW-86R-2 and zone MW-83-3, the degree of connection to the injection wells also likely influenced the permanganate residence time. This would be due to the assumption that a more direct connection provides less fracture surface area with which the permanganate can react prior to reaching the monitoring zone, which, in the absence of flushing, should also result in longer fracture residence time.

5.2. Bedrock Matrix Pore Water

Figures 5-7 and 5-8 present the estimated associated matrix pore water TCE and PCE concentrations, respectively, in the rock core samples collected from core hole CH-91 in December 2006 and from the monitoring well MW-87 borehole (approximately 15 feet south of CH-91) in December 2003. As shown in these figures, and consistent with previous rock core VOC profiles, elevated concentrations of TCE and PCE (defined herein as greater than 100 micrograms per liter [ug/l]) were generally detected in the rock matrix pore water in the interval from 20 feet bgs to approximately 110 feet bgs. These figures also show that the majority of TCE and PCE detections in the rock matrix were not associated with advective fracture pathways identified through geophysical testing.

Figures 5-7 and 5-8 show that estimated rock matrix pore water VOC concentrations in CH-91 were consistent in both depth profile and concentrations with those of MW-87 (located ~15 feet south of CH-91), which was drilled and sampled prior to the initiation of injections in September 2004. Table 5-5 (below) presents a comparison of the TCE and PCE concentrations in the samples collected from the two cores. As shown in the table, the statistical characteristics of the samples collected from the two cores were similar.

¹ A negative r^2 (adjusted for a y-axis intercept of 0) is indicative of random data without correlation.

Table 5-5
Summary of TCE and PCE Pore Water Concentrations in MW-87 and CH-91

	TCE Pore Water Concentration (ug/l)		PCE Pore Water Concentration (ug/l)	
	MW-87 Oct-03	CH-91 Dec-06	MW-87 Oct-03	CH-91 Dec-06
Mean	2,625	1,022	4,715	2,358
Median	3.01	4.93	5.51	29.07
Standard Deviation	10,189	6,547	19,639	12,791
Range	68,285	76,661	133,434	135,387
Minimum	ND	ND	ND	ND
Maximum	68,285	76,661	133,434	135,387
Count	152	166	152	166

These data indicate that the corrective measures have not had a discernable impact on rock matrix pore water concentrations in the treatment area. As stated previously, the rock matrix pore water contains the majority of the contaminant mass and, as such, is the main source for VOCs in the groundwater. Given the lack of source area (i.e., the bedrock matrix) treatment, the corrective measures cannot achieve the overall CAO of reducing the concentration of hazardous constituents in groundwater migrating from the site to New York State and Federal groundwater standards.

5.3. Aqueous Mass Discharge

Compliance boundary VOC mass discharge estimates were calculated for each compliance monitoring zone using the transmissivity values calculated for fractures that had detectable flow during the July 2004 geophysical testing (reported in the CMMP). As discussed in the CM Startup Report, the transmissivity values presented in this report are the sum of the individual transmissivities for fractures with detectable flow that intersect each compliance monitoring zone at the time of the geophysical testing. Mass discharge estimates were calculated using the following assumptions:

- **Discharge Zone Thickness:** Set as the thickness of the screened interval in each compliance monitoring zone.
- **Hydraulic Gradient:** Set at 0.003 ft/ft based on the hydraulic gradient in the Building 40 area calculated from WVA-wide water table groundwater elevations.
- **Horizontal Length of Discharge Zone:** Set as the distance between compliance monitoring wells.
- **VOC Concentration:** Set at the total VOC concentration in each compliance monitoring zone during each pre-injection monitoring event (average of two baseline events used for baseline estimates).

Compliance boundary VOC mass discharge estimates for the baseline and pre-injection monitoring events are presented in Table 5-6. Table 5-7 (below) presents changes from baseline in the estimated compliance boundary VOC mass discharge after each injection

event. As shown in Table 5-7, the estimated compliance boundary VOC mass discharge was similar to the baseline following the first three injection events. The estimated compliance boundary VOC mass discharge measured in November 2005 was approximately 34 percent less than the baseline, indicating that the permanganate injections on the east side of Building 40 in August 2005 resulted in the reduction of VOC concentrations in the area upgradient of the compliance boundary. As shown in Table 5-6, this treatment was most pronounced in the northern portion of the compliance boundary, as reflected by the changes in VOC mass discharge in monitoring wells MW-84R, MW-85R, and MW-86R.

Table 5-7
Summary of Changes in Compliance Boundary VOC Mass Discharge

	Compliance Boundary VOC Mass Discharge							
	Baseline	Jan. 2005	May 2005	Aug. 2005	Nov. 2005	Mar. 2006	Sept. 2006	Sept. 2007
Total VOC Mass Discharge (lb/yr)	10.0	10.0	11.5	10.0	6.6	10.6	18.0	13.1
% of Baseline VOC Mass Discharge	---	100%	115%	100%	66%	106%	180%	131%

However, beginning with the March 2006 pre-injection sampling (i.e., post-December 2005 injection event), VOC mass discharge along the compliance boundary increased such that, as of the last two sampling events conducted in September 2006 and September 2007, the mass discharge through the compliance boundary was approximately 180 percent and 131 percent of the baseline mass discharge, respectively. These apparent increases in the calculated mass discharge are likely due to a combination of factors, including:

1. Increases in the groundwater VOC concentrations in several of the compliance monitoring wells;
2. Redistribution of dissolved contaminant mass resulting from the injection of the permanganate solution; and
3. Reduced contaminant retardation potential due to the oxidation of adsorption sites on the fracture surfaces.

It should be noted that the VOC mass discharge calculation utilizes the hydraulic conductivities calculated prior to the initiation of permanganate injections. As discussed previously, it is likely that the hydraulic conductivity of several fractures/zones decreased due to clogging. Thus, the calculated increases in VOC mass discharge shown above are likely conservative. However, since the hydraulic conductivity of the monitoring zones cannot be re-measured due to the presence of the multi-level monitoring wells in the

boreholes, the degree to which the clogging impacted the VOC mass discharge calculation cannot be evaluated.

As shown in Table 5-8, as of the September 2007 sampling event, total VOC concentrations in groundwater increased from baseline concentrations in seven of the 18 compliance monitoring zones and decreased in 11 of the 18 compliance monitoring zones. However, the magnitude of the increases, which ranged from 116 percent of baseline to 700 percent of baseline, was far greater than the magnitude of the decreases relative to the total VOC concentrations across the compliance boundary.

In general, the greatest contributions to the baseline compliance boundary VOC mass discharge throughout the CM programs were from the compliance monitoring zones in the center and northern sections of the compliance boundary. The wells/zones are:

- MW-83 (Zone 1)
- MW-84R (Zone 1,2,3)
- MW-85R (Zone 2)
- MW-86R (Zone 2)

Together, these six zones comprised approximately 85 percent of the compliance boundary mass discharge at the time of the baseline sampling in August 2004, and approximately 86 percent of the compliance boundary mass discharge as of the September 2007 sampling.

The percentage of the total estimated compliance boundary VOC mass discharge contributed by these zones is shown in Table 5-9, below. Monitoring zones in which permanganate was observed during at least one monitoring event following the previous injection event are shaded in purple.

Table 5-9
Contribution to Total Compliance Boundary VOC Mass Discharge

Well (Zone)	Percentage of Total Estimated Compliance Boundary VOC Mass Discharge							
	Baseline	Jan. 2005	May 2005	Aug. 2005	Nov. 2005	Mar. 2006	Sept. 2006	Sept. 2007
MW-83-1	6%	23%	25%	30%	35%	27%	45%	32%
MW-84R-1	13%	10%	10%	8%	10%	5%	10%	9%
MW-84R-2	6%	5%	7%	7%	8%	6%	4%	5%
MW-84R-3	9%	7%	8%	8%	12%	15%	6%	6%
MW-85R-2	25%	22%	18%	26%	1%	23%	17%	30%
MW-86R-2	26%	20%	13%	4%	13%	7%	3%	4%
Total	85%	87%	81%	84%	79%	83%	84%	86%

As shown in Table 5-9, the total percentage of the compliance boundary VOC mass discharge contributed by the six zones remained relatively constant throughout the period of permanganate injections, despite the arrival of permanganate in four of the six compliance zones. The VOC mass discharge in four of these zones (MW-84R-1, MW-84R-2, MW-84R-3, and MW-85R-2) were generally unchanged from baseline conditions. The VOC mass discharge at zone MW-86R-2 decreased by 82 percent. Based on the arrival and residence time of the permanganate in this zone, this decrease was likely the result of the permanganate treatment. However, this decrease was offset by the increase in mass discharge at zone MW-83-1, which increased by more than 750 percent from baseline conditions.

Based on the analysis of VOC mass discharge, it is evident that the permanganate injections performed as part of the CM program have failed to reduce the VOC mass discharge from the Building 40 area. In addition, based on the increases in VOC concentrations in many of the compliance monitoring zones, the CM program may have increased the VOC mass discharge across the compliance boundary.

6. Conclusions and Recommendations

The results of the testing and monitoring conducted to date support the following conclusions:

1. The permanganate injections conducted to date have not decreased groundwater VOC concentrations at the compliance boundary or the mass flux at the compliance boundary, and rock core VOC pore water concentrations have not decreased after two years of injections.
2. The persistent clogging problems indicate that a large portion of the injected permanganate mass is being oxidized to insoluble precipitates through interaction with the rock matrix, specifically the reduced sulfur (i.e., pyrite), present in the rock. This interaction with the rock is greatly limiting the effectiveness of the permanganate injections. Rock core, water level, pressure, and temperature monitoring has shown that the injections are influencing only a portion of the treatment area.
3. The CM program has failed to achieve the Permanganate Distribution and Permanganate Residence Time CM performance criteria and, therefore, cannot achieve the overall CAO of reduction of VOC concentrations in groundwater to state or federal standards.

Based on these data, and the lack of any other potentially effective remedial technology for treatment of the VOC source mass in the bedrock matrix (as presented in Section 5.0 of the CM Work Plan), achievement of the CAOs is not technically feasible using currently available technologies. In accordance with Section 9.2.4.2 of the CM Work Plan, it is therefore recommended that the CM Program be discontinued and that the following actions be implemented.

1. Incorporate the results, conclusions, and recommendations presented herein into the Statement of Basis for the Main Manufacturing Area and submit the Draft Statement of Basis for the Main Manufacturing Area for public comment and subsequent regulatory approval.
2. Incorporate the following monitoring wells into the overall WVA Long Term Monitoring Program to be sampled annually in the spring (i.e., May or June). These wells are shown on Figure 6-1.

■ MW-79

■ MW-82R (Zones 1,2,3)

■ MW-83 (Zones 1,2,3)

■ MW-84R (Zones 1,2,3)

■ MW-85R (Zones 1,2,3)

■ MW-86R (Zones 1,2,3)



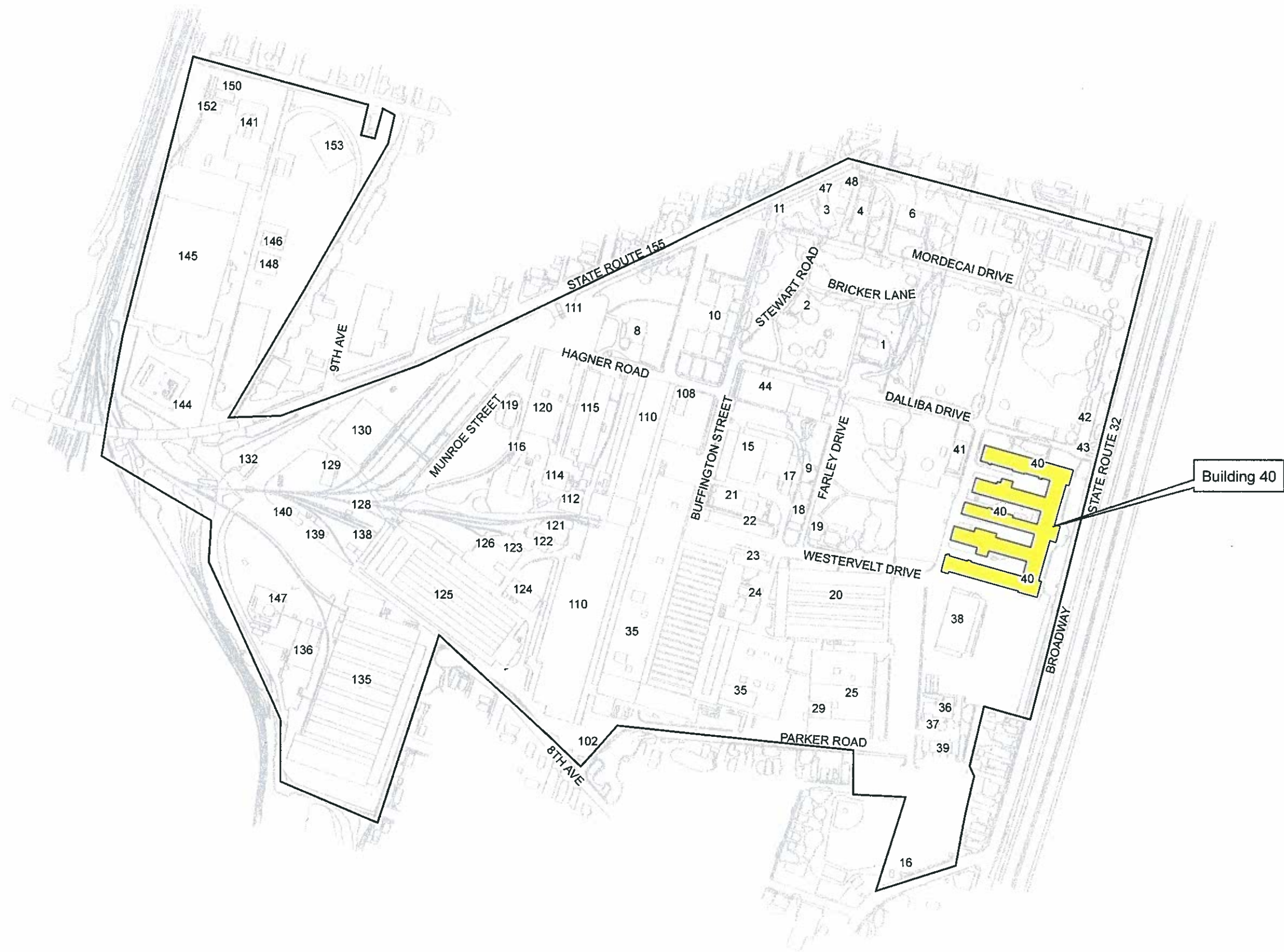
3. Permanently abandon the following monitoring and injection wells to eliminate potential future direct pathways for groundwater contamination. These wells are also shown on Figure 7-1.

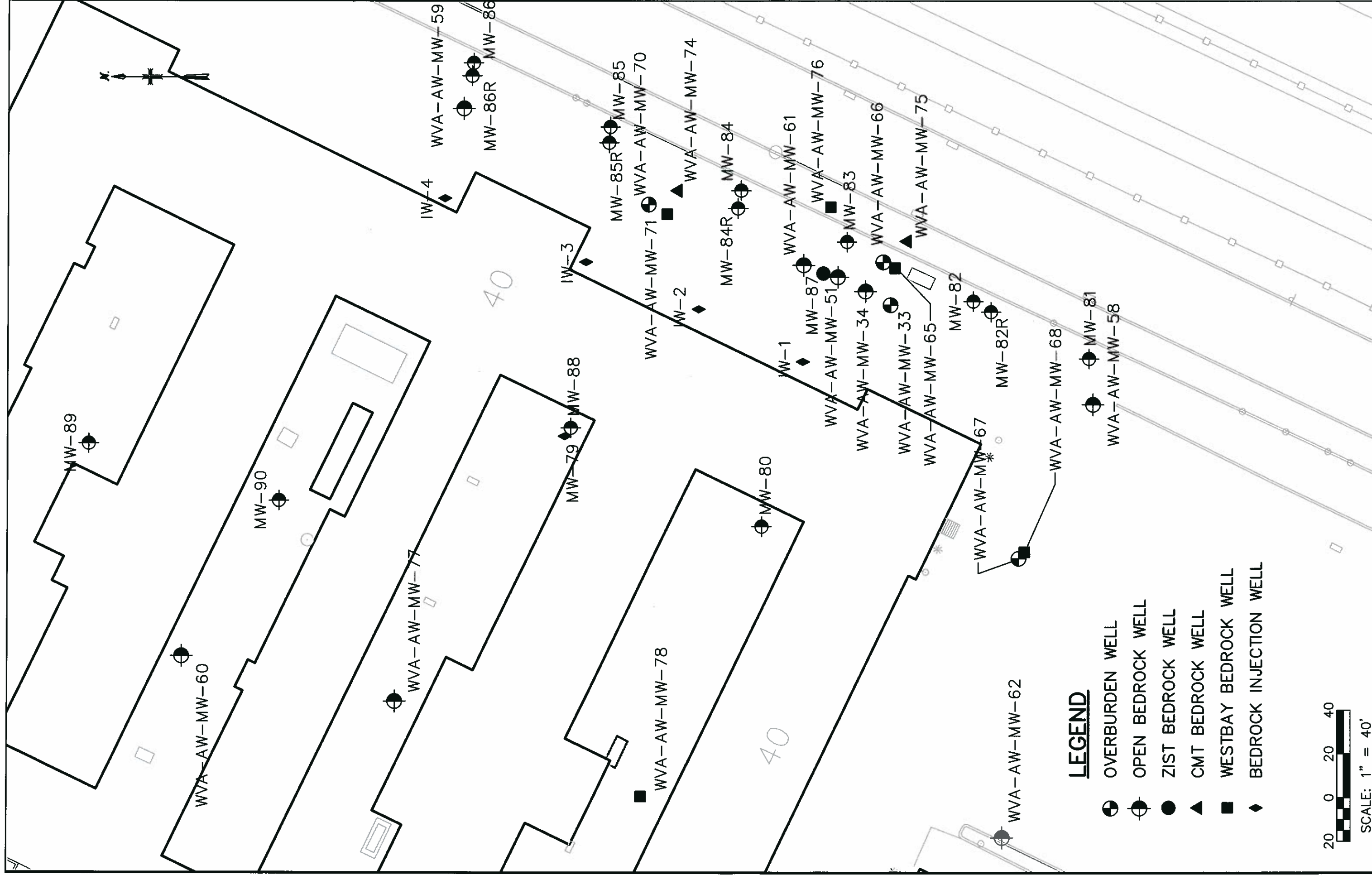
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|----------------|------------------------------|
| ■ WVA-AW-MW-33 | ■ WVA-AW-MW-76 |
| ■ WVA-AW-MW-34 | ■ WVA-AW-MW-77 |
| ■ WVA-AW-MW-51 | ■ WVA-AW-MW-78 |
| ■ WVA-AW-MW-58 | ■ WVA-AW-MW-80 |
| ■ WVA-AW-MW-59 | ■ MW-81 (Zones 1,2,3) |
| ■ WVA-AW-MW-60 | ■ MW-82 (replaced by MW-82R) |
| ■ WVA-AW-MW-61 | ■ MW-84 (replaced by MW-84R) |
| ■ WVA-AW-MW-62 | ■ MW-85(replaced by MW-85R) |
| ■ WVA-AW-MW-65 | ■ MW-86(replaced by MW-86R) |
| ■ WVA-AW-MW-66 | ■ MW-89 |
| ■ WVA-AW-MW-67 | ■ MW-90 |
| ■ WVA-AW-MW-68 | ■ IW-1 |
| ■ WVA-AW-MW-70 | ■ IW-2 |
| ■ WVA-AW-MW-71 | ■ IW-3 |
| ■ WVA-AW-MW-74 | ■ IW-4 |
| ■ WVA-AW-MW-75 | |

7. References

- Malcolm Pirnie, Inc., 2003. *Building 40 Chemical Oxidation Pilot Study Summary Report, Watervliet Arsenal, Watervliet, New York*. 2003.
- Malcolm Pirnie, Inc., 2004. *Corrective Measures Work Plan, Building 40 Bedrock Groundwater, Main Manufacturing Area, Watervliet Arsenal, Watervliet, New York*. July 2004 (finalized by letter August 2004).
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- Malcolm Pirnie, Inc., 2006. *Corrective Measures Installation and Startup Report, Building 40 Bedrock Groundwater, Main Manufacturing Area, Watervliet Arsenal, Watervliet, New York*. August 2006.







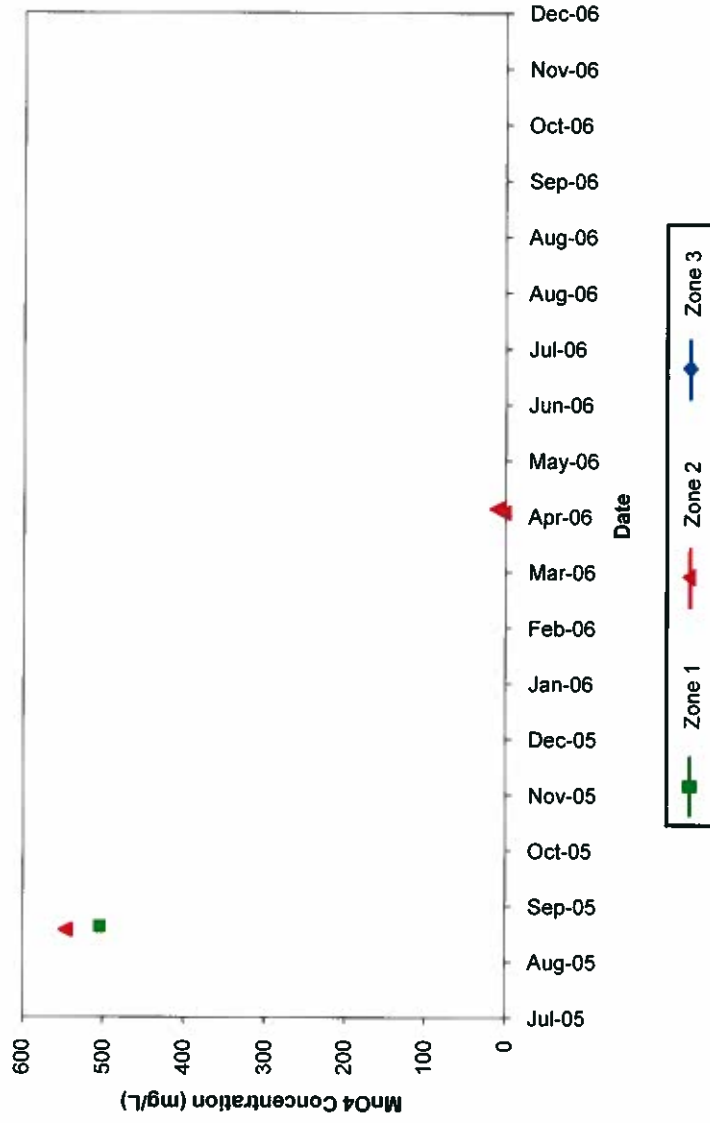
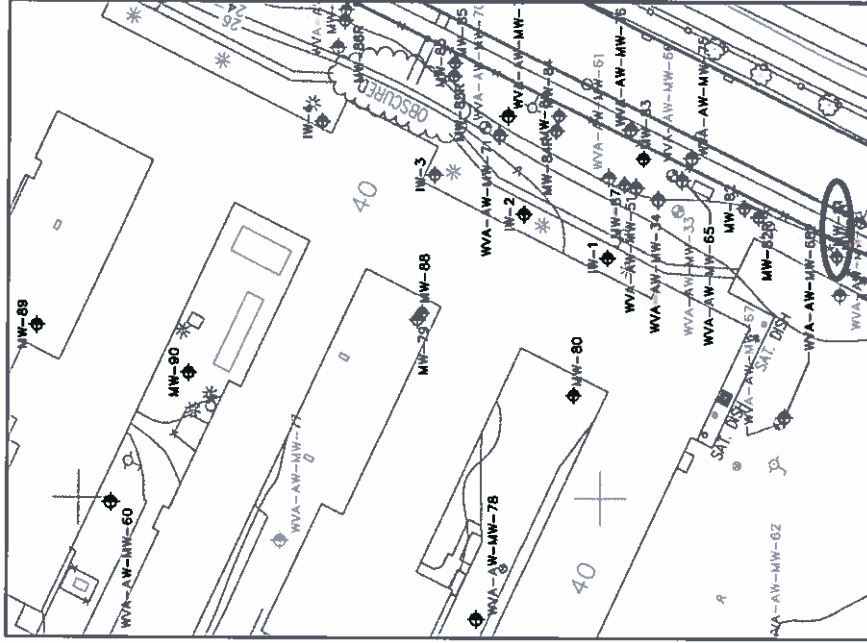
35 feet bgs



56 feet bgs



MW-81 MnO4⁻



GROUNDWATER CORRECTIVE MEASURES
BUILDING 40, WATERVLIET ARSENAL, WATERVLIET, NEW YORK

PERMANGANATE CONCENTRATIONS IN MONITORING WELL MW-81



GROUNDWATER CORRECTIVE MEASURES
BUILDING 40, WATERVLIET ARSENAL, WATERVLIET, NEW YORK

PERMANGANATE CONCENTRATIONS IN MONITORING WELL MW-82R

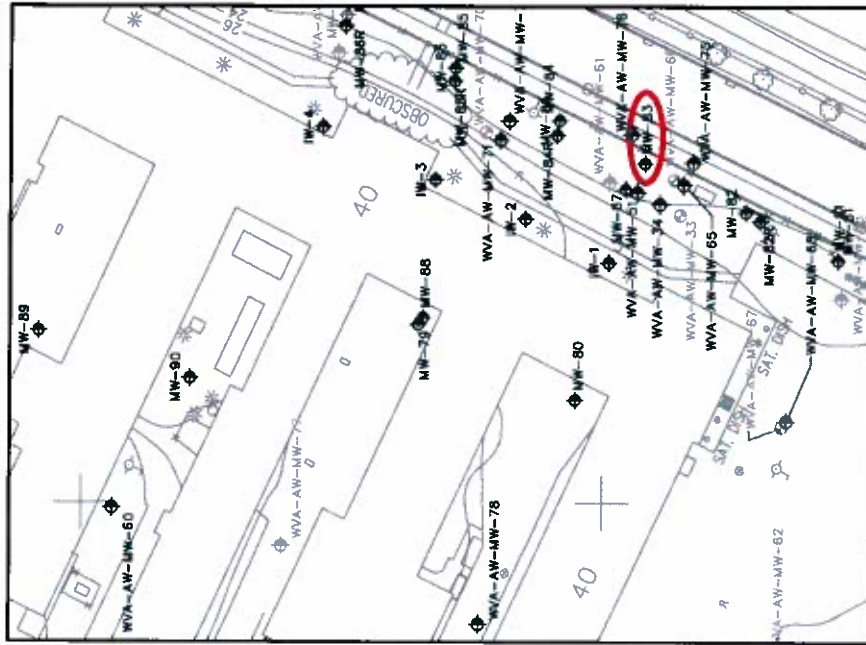
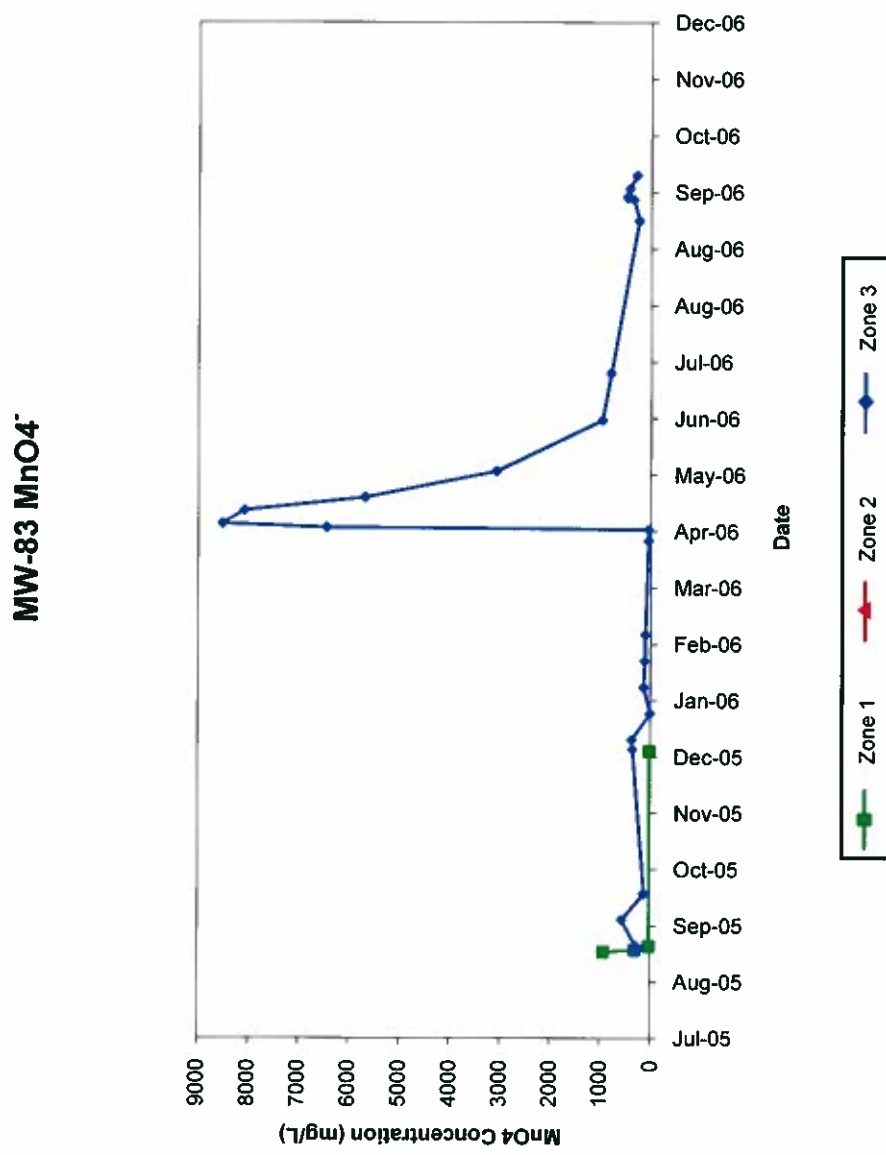
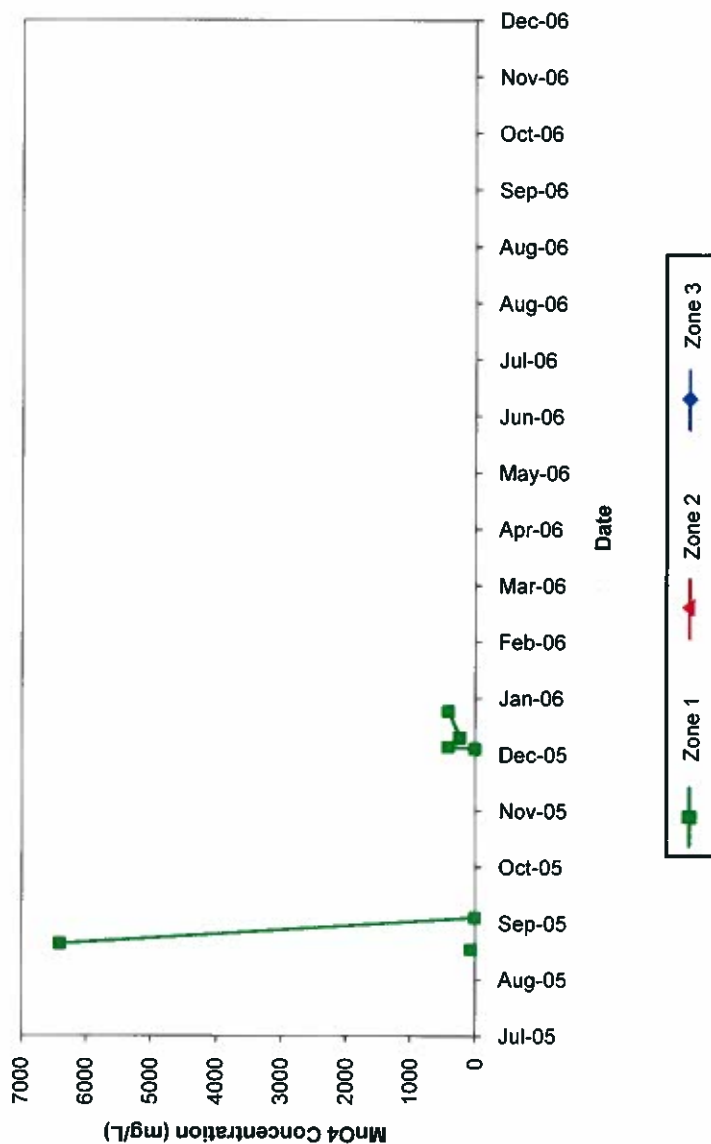
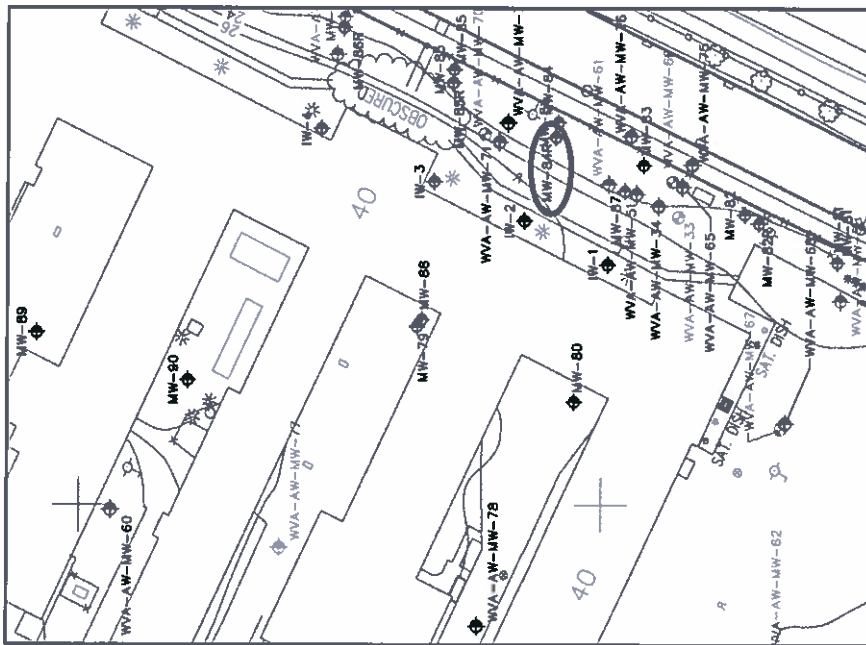


FIGURE 4-3

GROUNDWATER CORRECTIVE MEASURES
BUILDING 40, WATERVLIET ARSENAL, WATERVLIET, NEW YORK

PERMANGANATE CONCENTRATIONS IN MONITORING WELL MW-83

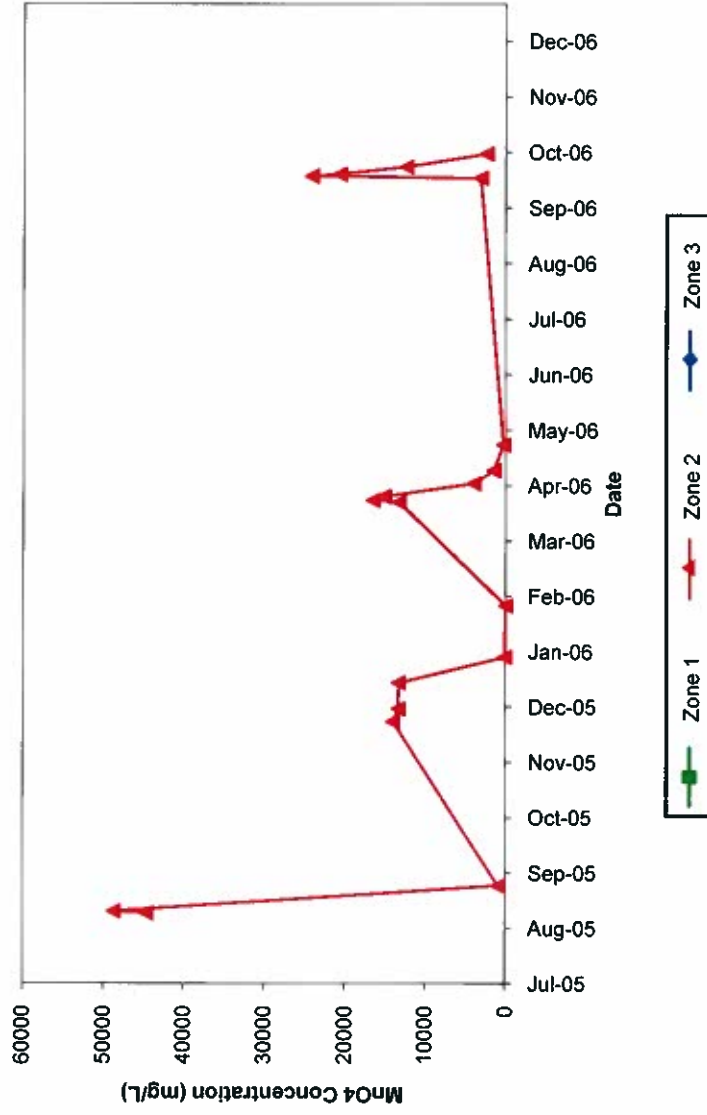
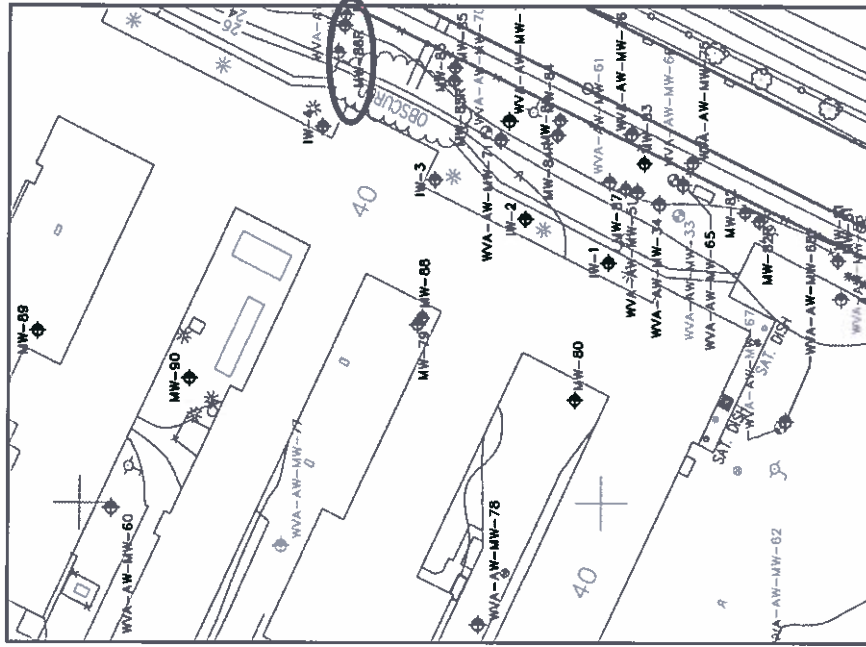
MW-84R MnO4⁻



GROUNDWATER CORRECTIVE MEASURES
BUILDING 40, WATERVLIET ARSENAL, WATERVLIET, NEW YORK

PERMANGANATE CONCENTRATIONS IN MONITORING WELL MW-84R

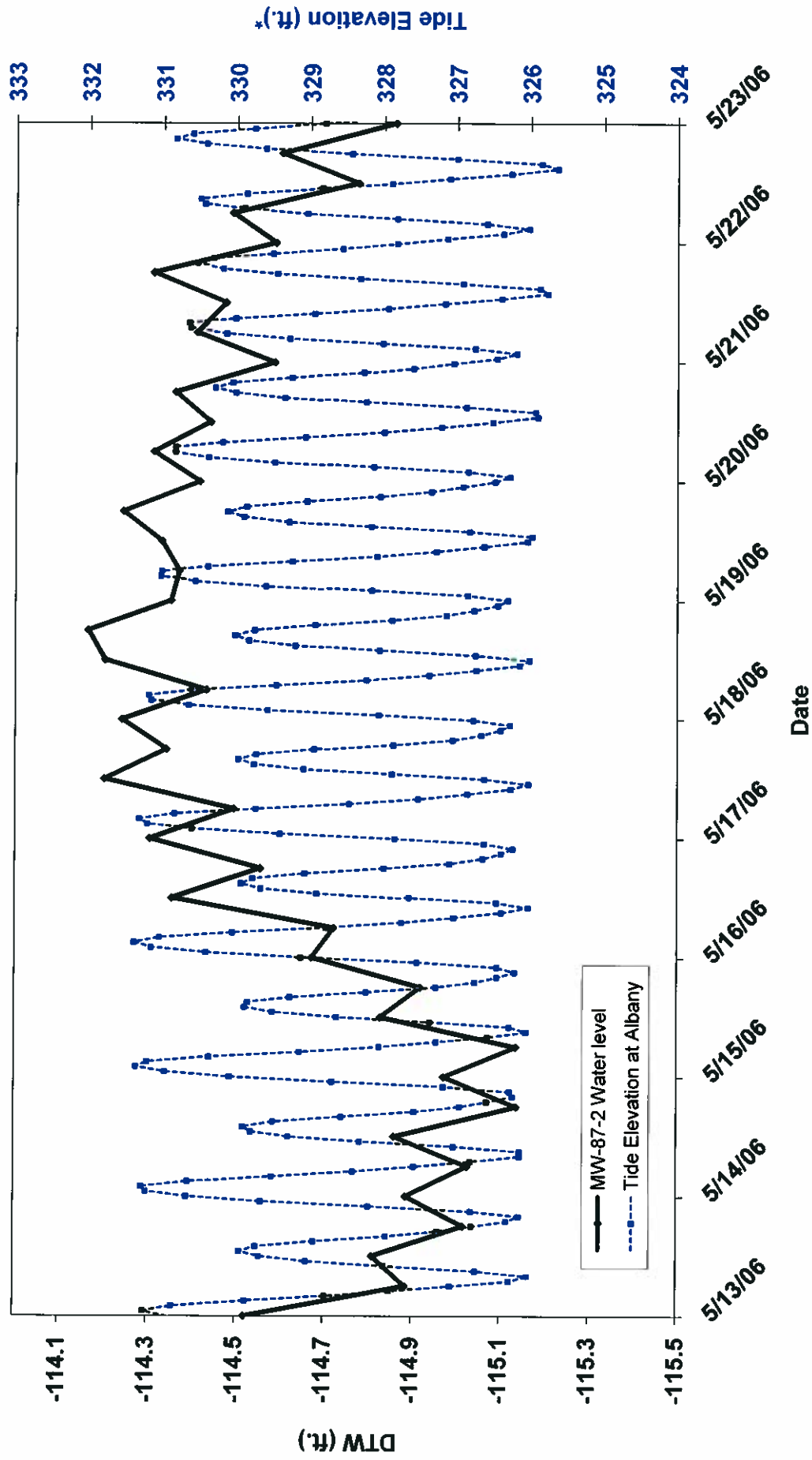
MW-86R MnO4⁻



GROUNDWATER CORRECTIVE MEASURES
BUILDING 40, WATERVLIET ARSENAL, WATERVLIET, NEW YORK

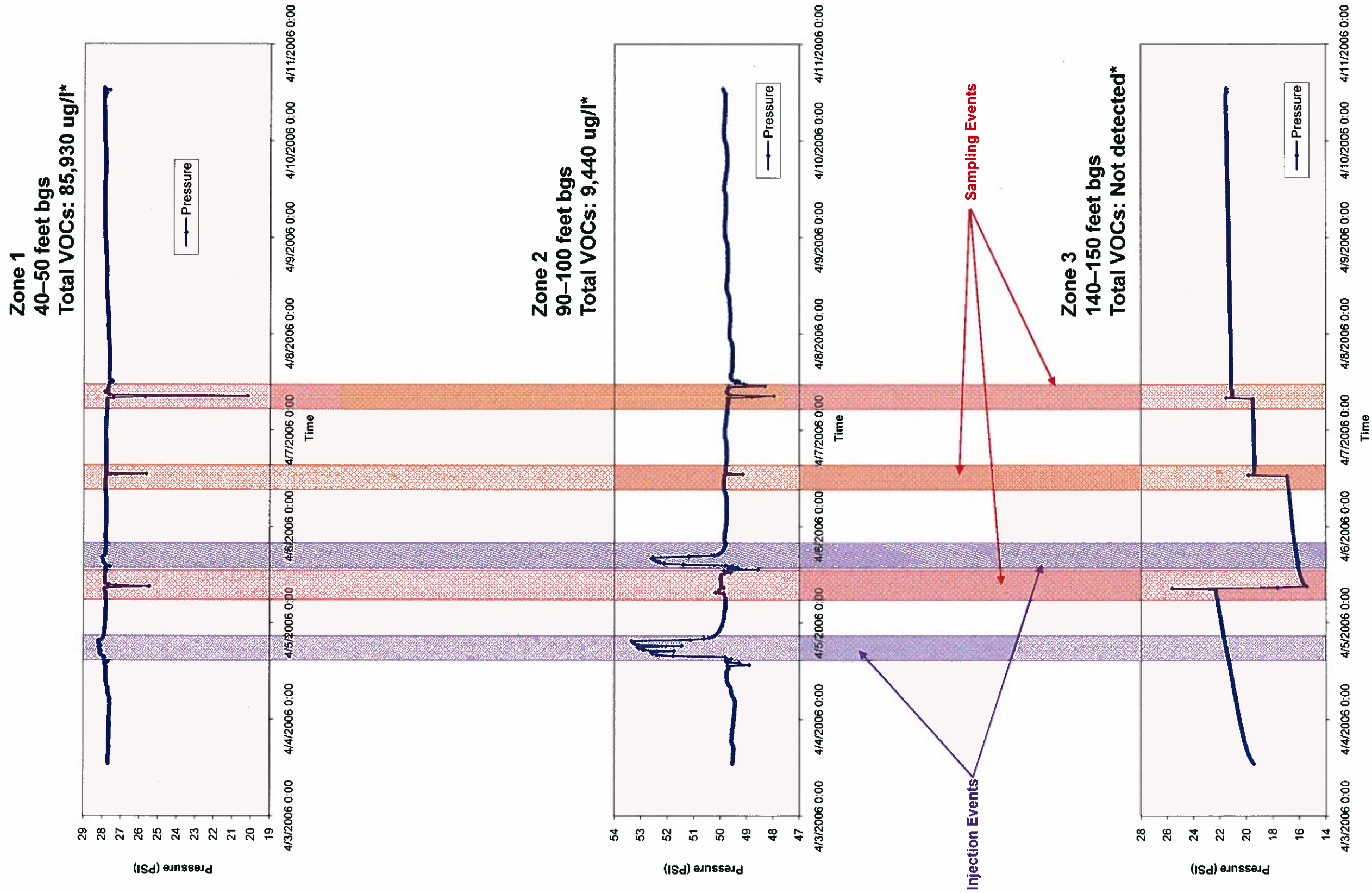
PERMANGANATE CONCENTRATIONS IN MONITORING WELL MW-86R

FIGURE 4-6

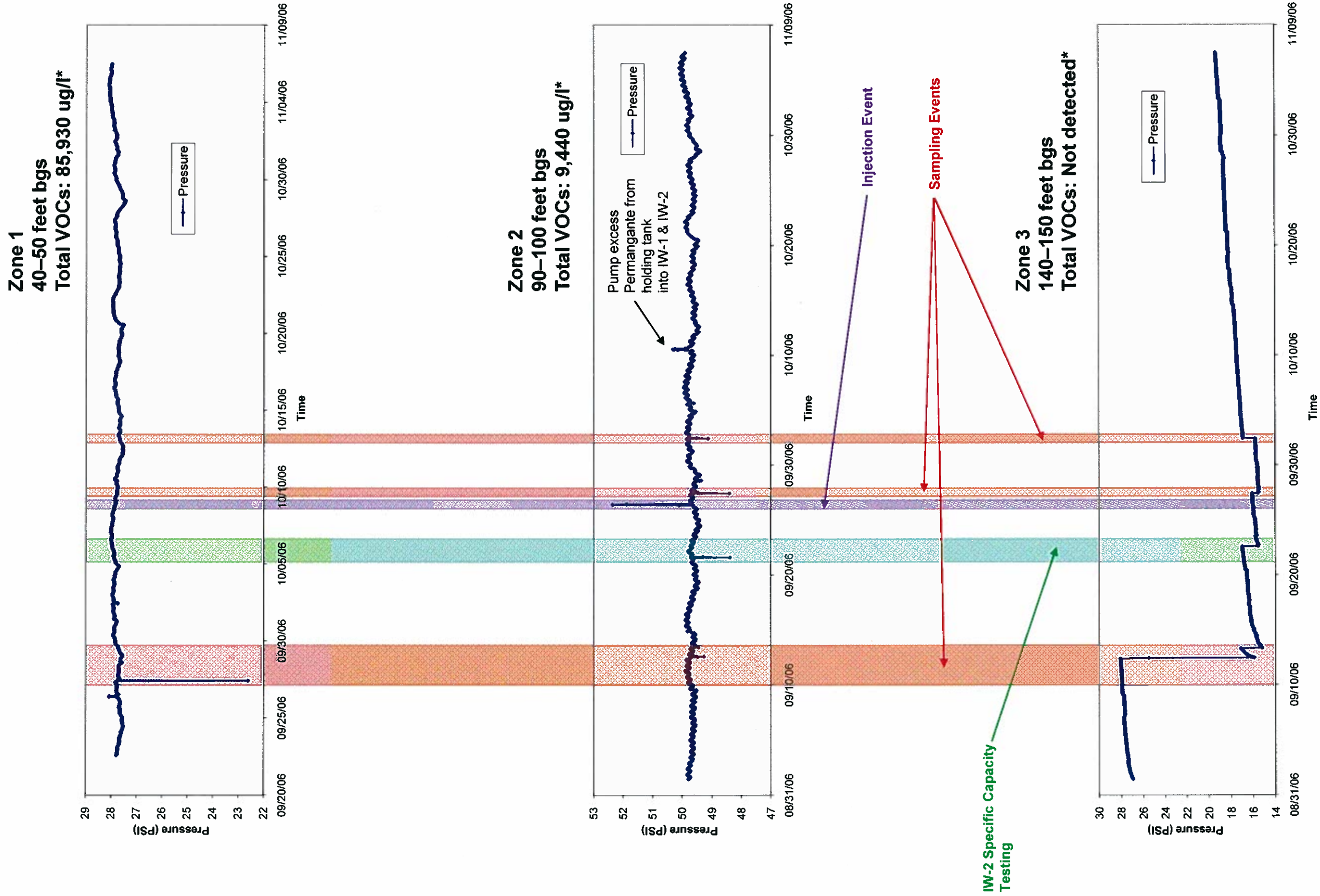


* Tide Elevation is based on arbitrary NOAA Station Datum for Station No. 8518995 (Albany, NY)

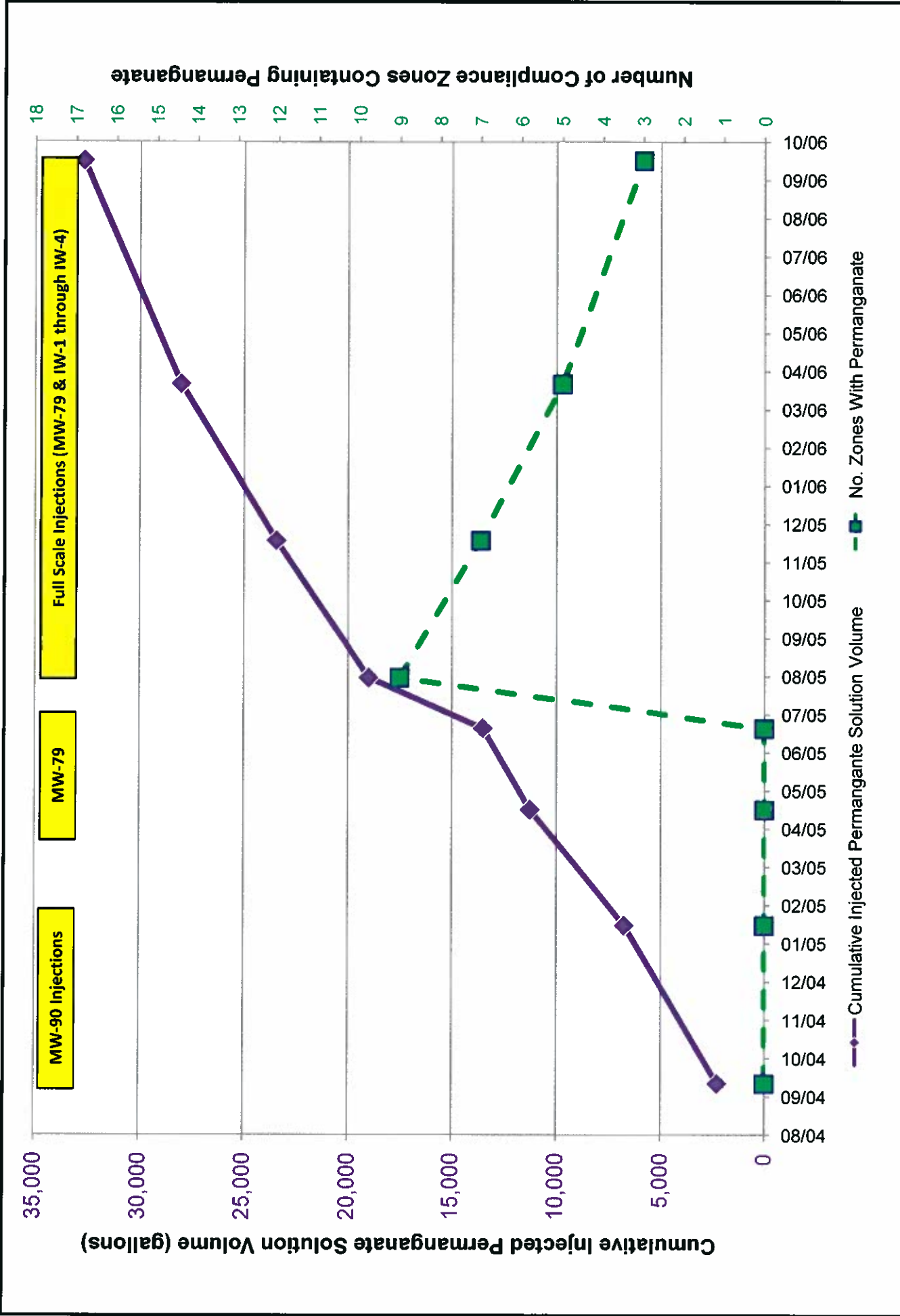
GROUNDWATER CORRECTIVE MEASURES STUDY
BUILDING 40, WATERVLIET ARSENAL, WATERVLIET, NEW YORK



* Data from September 2007

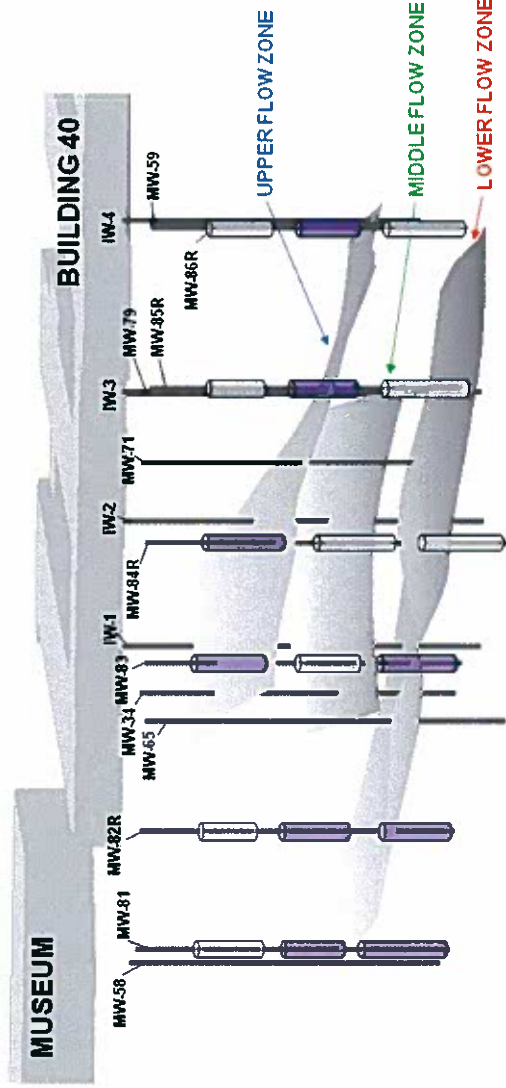


* Data from September 2007



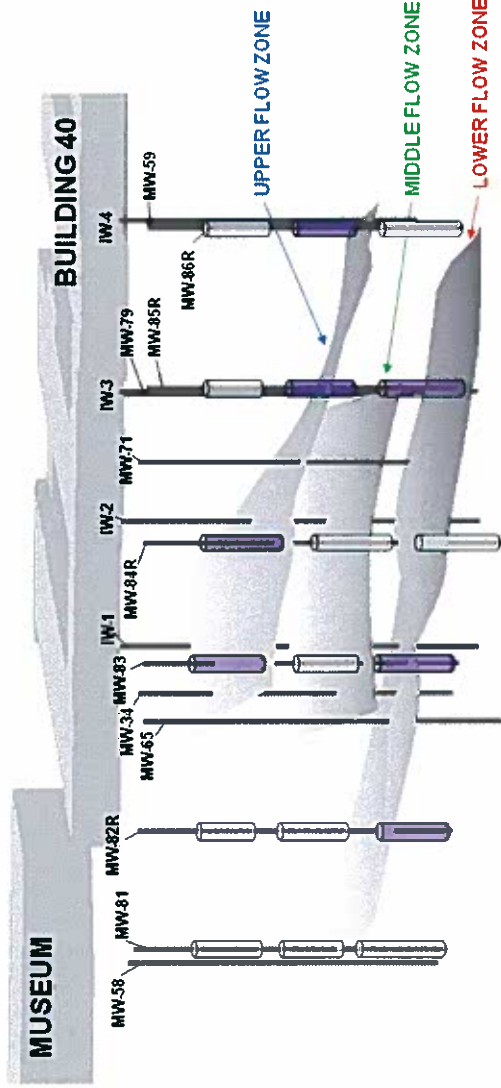
NORTH
→

AUGUST 2005



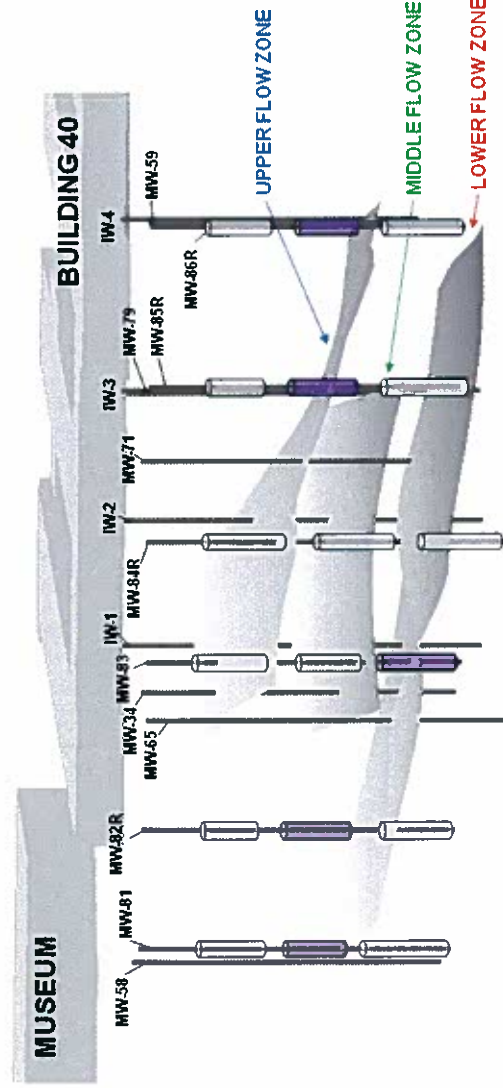
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NORTH
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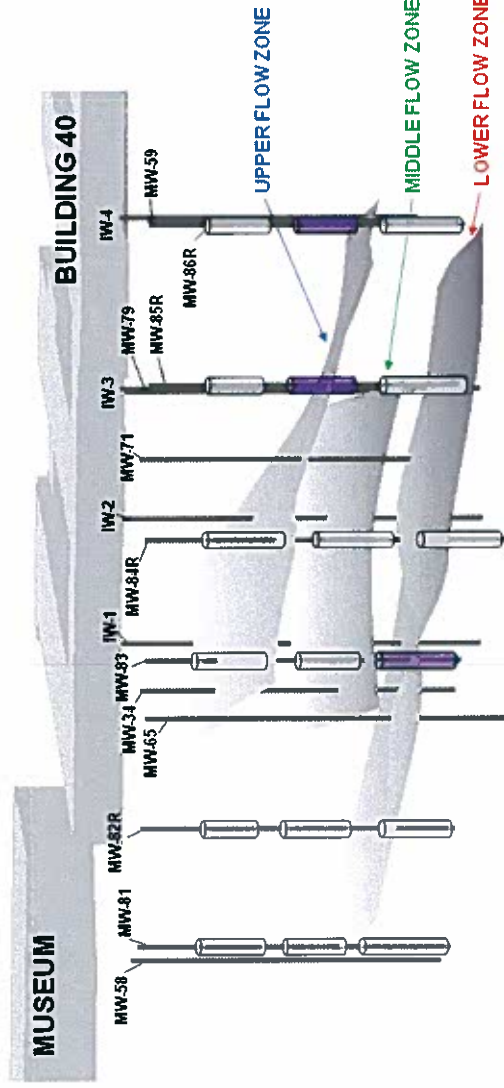
APRIL 2006

NORTH
→



SEPTEMBER 2006

NORTH
→



COMPLIANCE MONITORING ZONE
COMPLIANCE MONITORING ZONE WITH PERMANGANATE

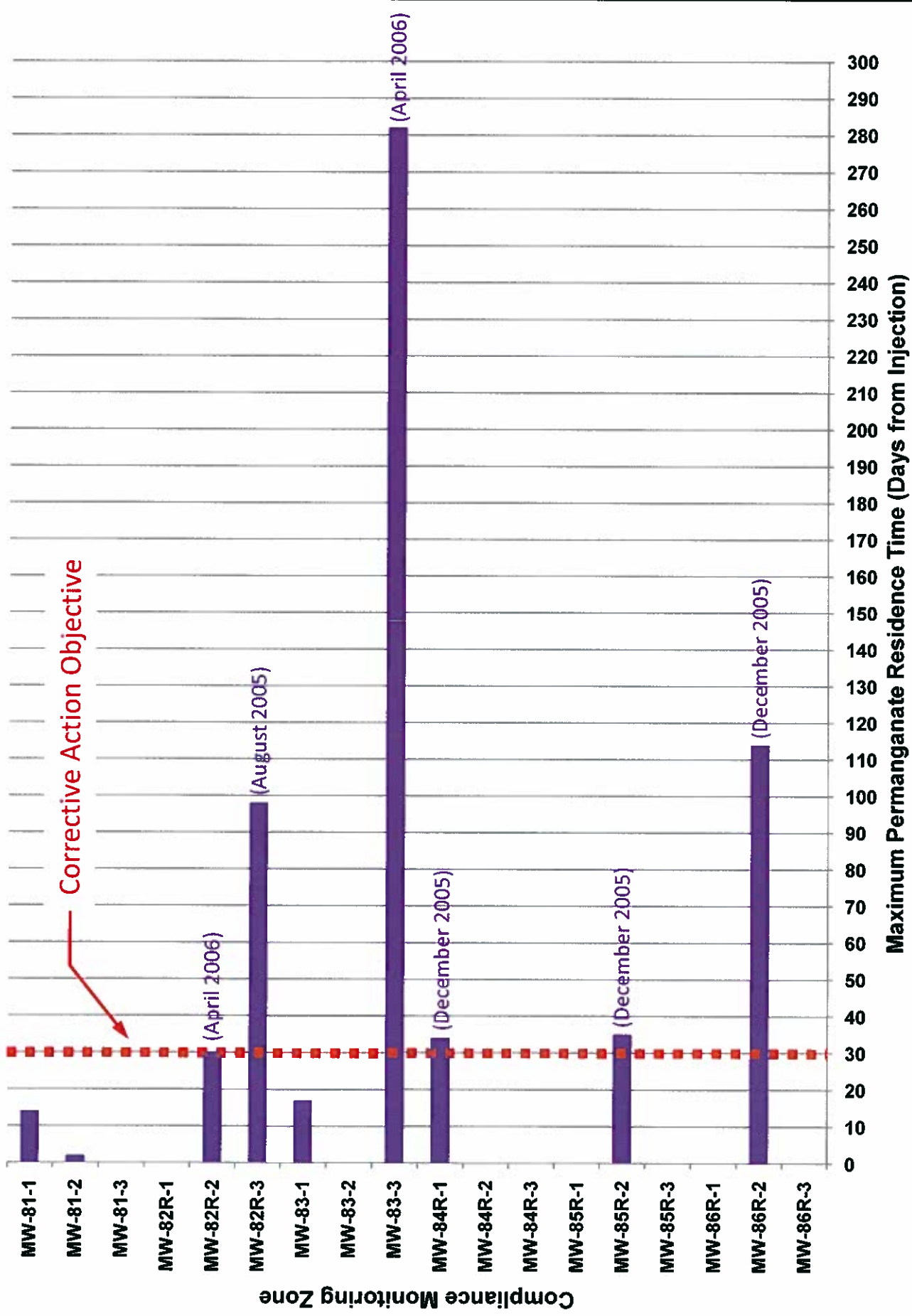
BUILDING 40 CORRECTIVE MEASURES
WATERVLIET ARSENAL, WATERVLIET, NEW YORK

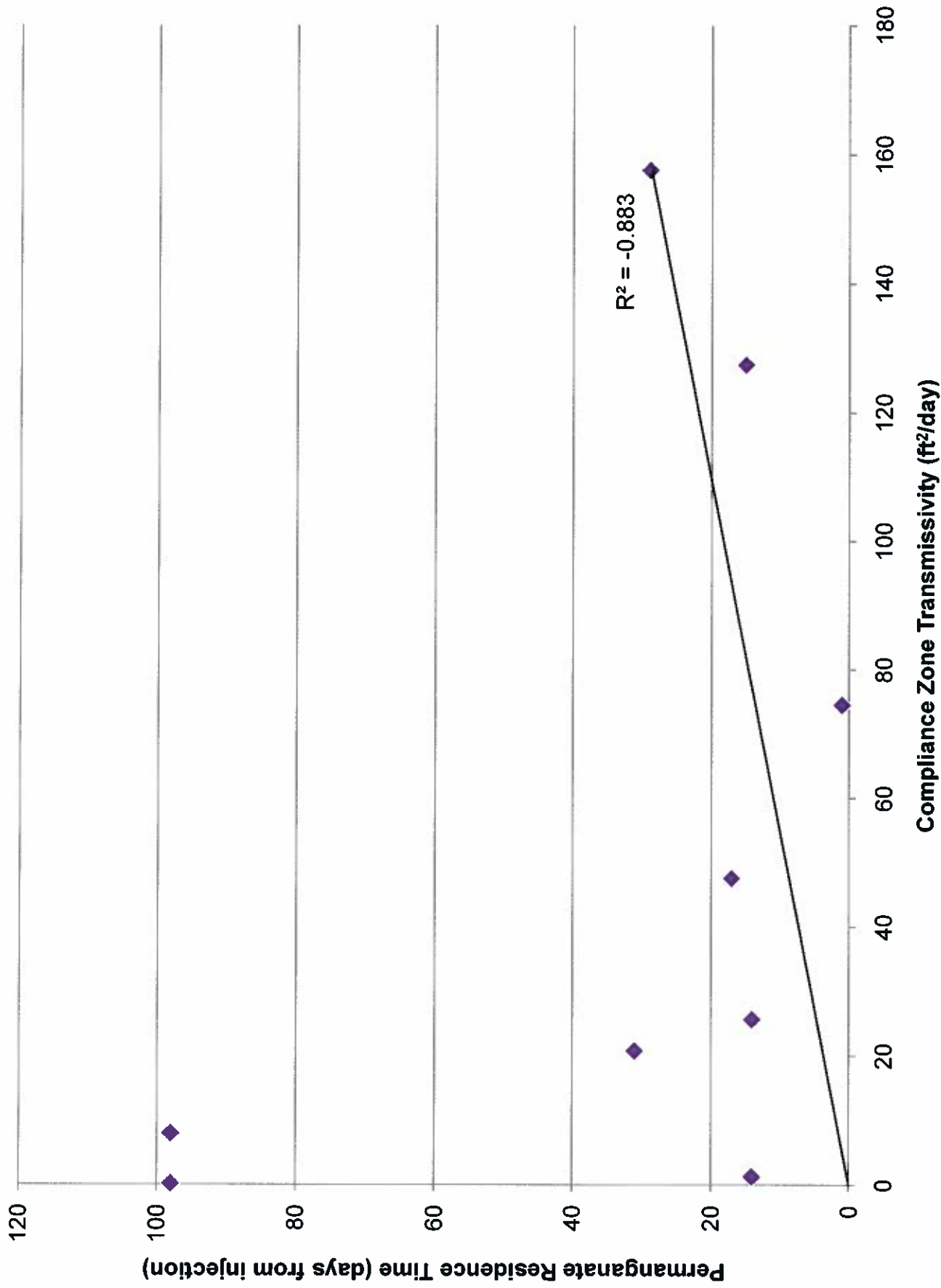
MALCOLM
PIRNIE

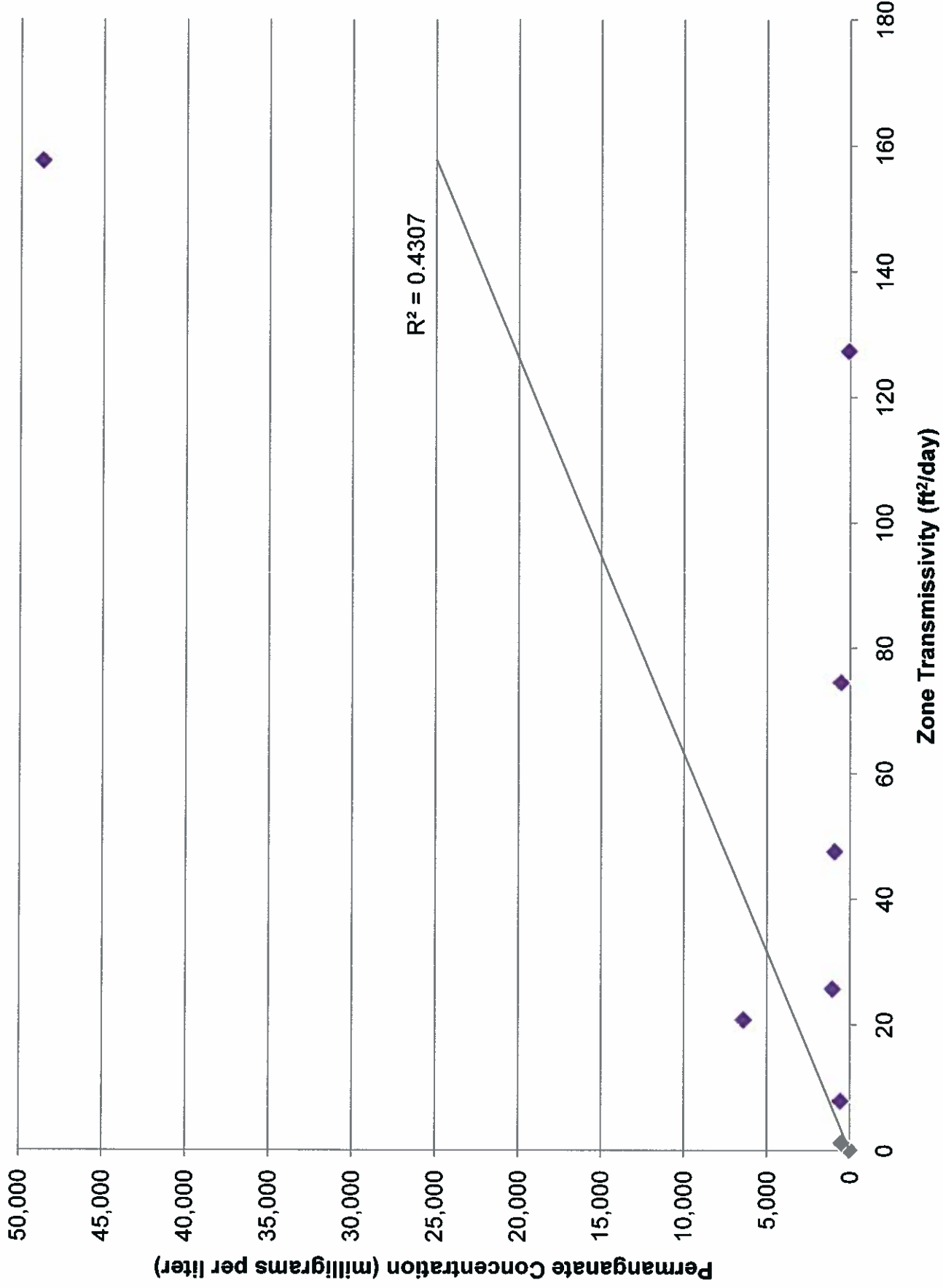
COMPLIANCE BOUNDARY PERMANGANATE DISTRIBUTION

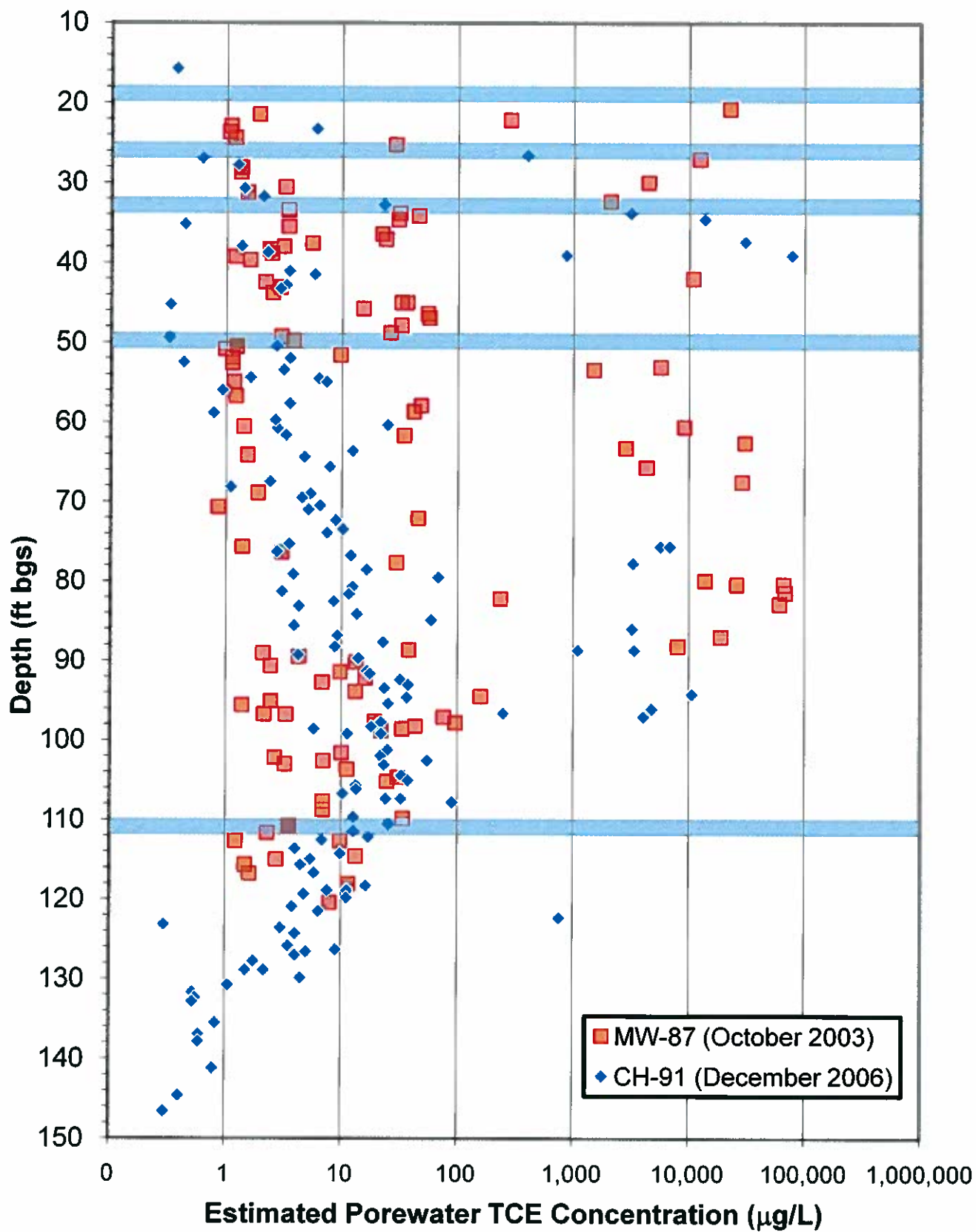
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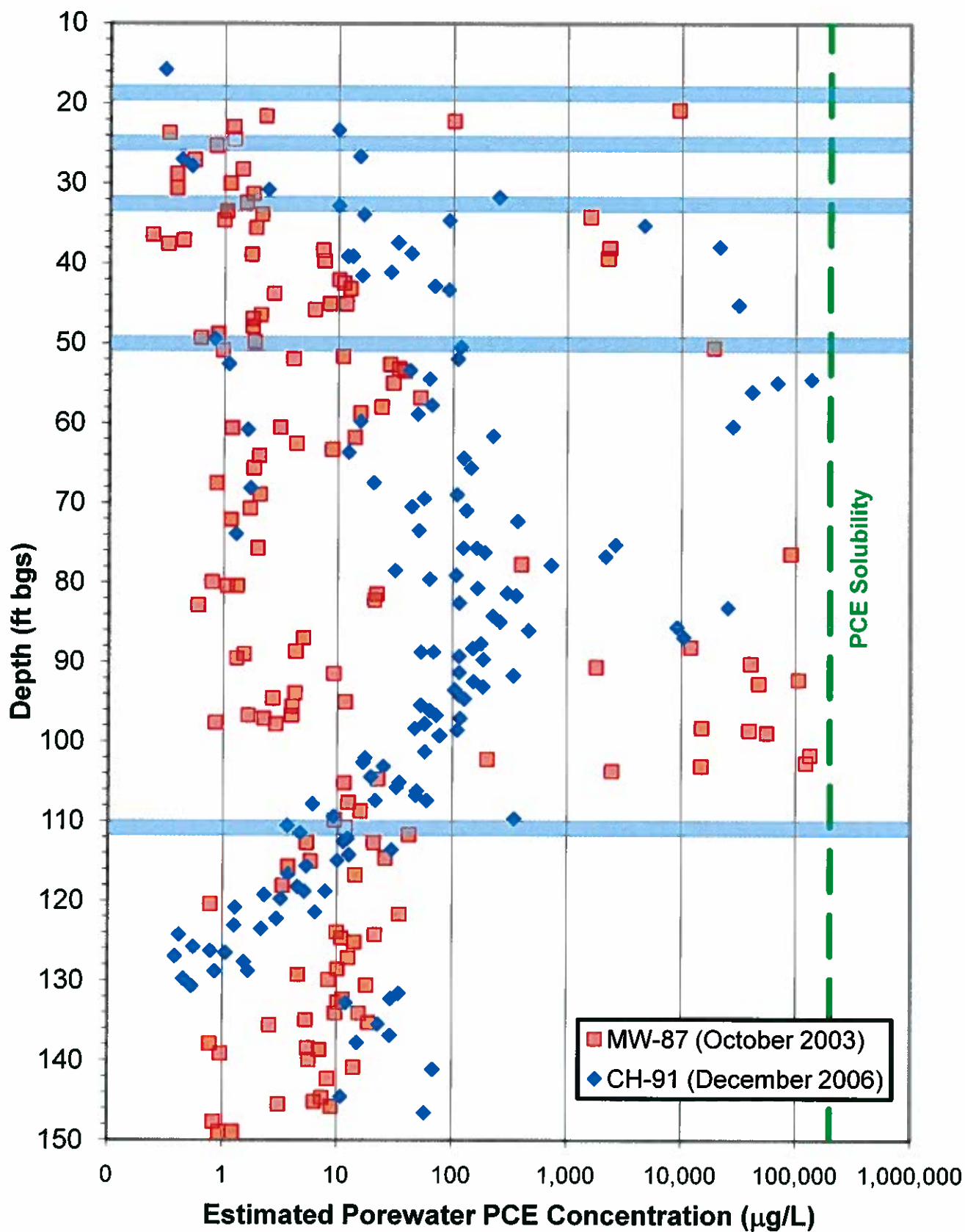
FIGURE 5-2











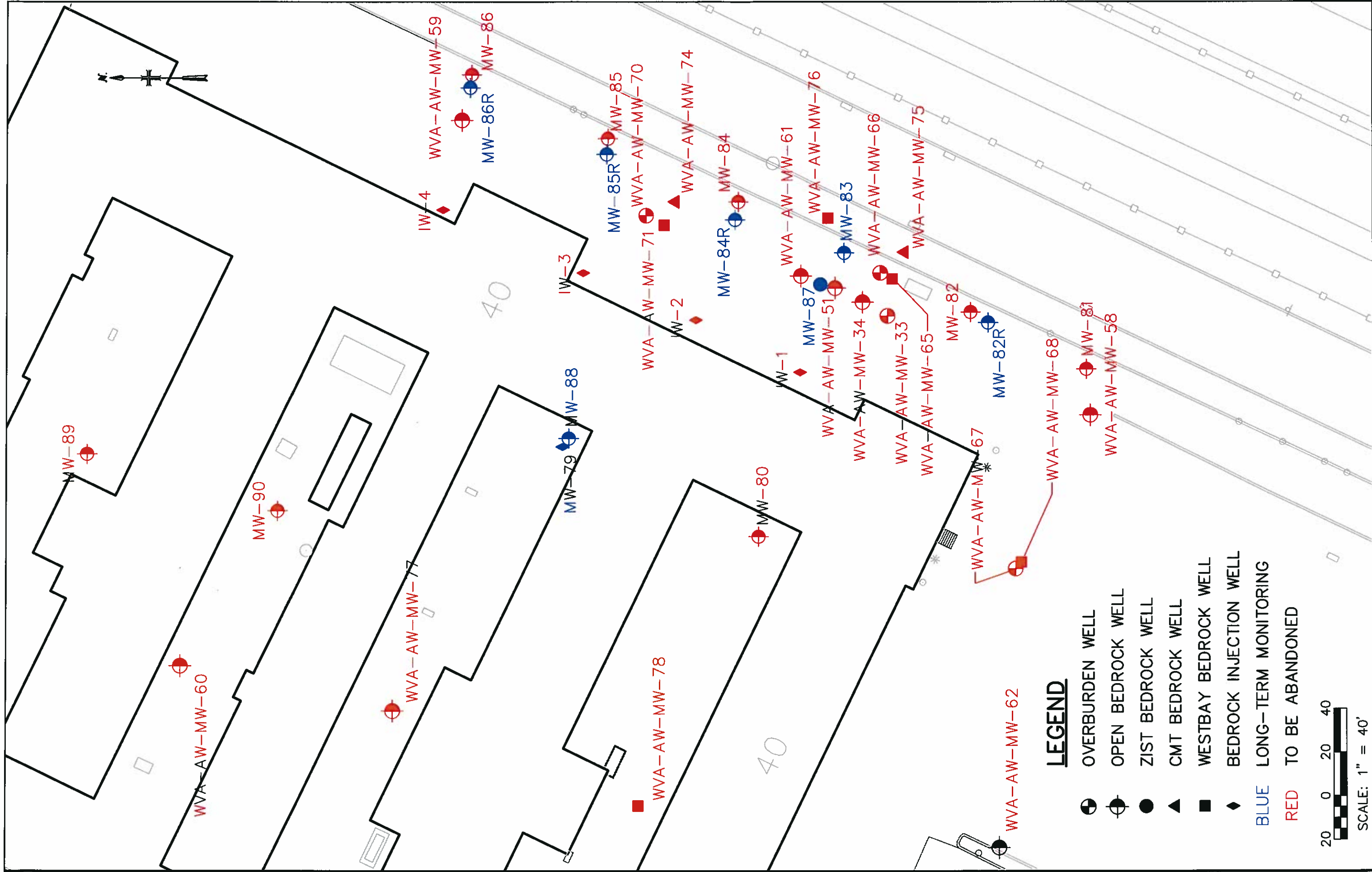


Table 2-1
Summary of Specific Capacity Test Results
Building 40 Groundwater Corrective Measures
Watervliet Arsenal, Watervliet, New York

Well ID	Test Date	Specific Capacity (gpm/ft)	Pumping Rate (gpm)	Pumping Duration	Notes
IW-2	9/22/04	0.080	0.45	54 min.	USGS
IW-2	9/15/06	0.075	1	3 hrs. 37 min.	Before brushing
IW-2	9/22/06	0.025	1	3 hrs. 50 min.	After brushing
IW-2	3/20/07	0.157	~4	45 min.	Before first airburst
IW-2	3/21/07	0.016	2	1 hr. 30 min.	After first airburst
IW-2	3/22/07	0.022	2	1 hr. 30 min.	After second airburst
IW-2	3/30/07	0.121	2	20 min.	
IW-2	3/30/07	0.043	4	45 min.	
MW-51	3/30/07	0.038	2	1 hr. 15 min.	
MW-34	3/30/07	0.134	~2	37 min.	

Notes:

Values in italics are estimated.

gpm/ft - gallons per minute per foot

min. - minutes

hr. - hours

Table 4-1
Permanganate Injection Summary
Building 40 Groundwater Corrective Measures
Watervliet Arsenal, Watervliet, New York

Injection No.	Date	Injection Location	Approximate NaMnO ₄ Solution Concentration	Amount Solution Injected (gallons)	Amount 40% NaMnO ₄ Injected (gallons)	Monitored Locations Where Permanganate Observed
1	9/30/05-10/1/05	MW-90	10%	2,250	550	Not observed
2	1/31/05 - 2/11/05	MW-90	10%	4,500	1,100	Not observed
3	5/3/05 - 5/5/05	MW-79 (lower)	5%	4,500	550	IW-1, IW-2, IW-3
3a	7/6/05 - 7/7/05	MW-79 (upper)	5%	2,250	275	MW-80
4	8/15/05 - 8/17/05	MW-79	4%	1,100		MW-80, 81-1, 81-2, 82R-2, 82R-3, 83-1, 83-3, 84-1
		IW-1	4%	1,100		85R-2, 86R-2
		IW-2	4%	1,100		
		IW-3	4%	1,100		
		IW-4	4%	1,100		
		Event Total		5,500	550	
5	11/29/05 - 12/1/05	MW-79	5%	900		MW-80, 82R-3, 83-1, 83-3
		IW-1	5%	895		84R-1, 85R-2, 85R-3, 86R-2
		IW-2	5%	1,080		
		IW-3	5%	655		
		IW-4	5%	900		
		Event Total		4,430	550	
6	4/3-06 - 4/7/06	MW-79	5%	900		MW-80, 81-2, 82R-2, 83-3
		IW-1	5%	1,730		85R-2, 86R-2
		IW-2	5%	930		
		IW-3	5%	70		
		IW-4	5%	970		
		Event Total		4,600	550	
7	9/25/06 - 9/29/06	MW-79	5%	2,250		MW-80, 83-3
		IW-1	5%	395		85R-2, 86R-2
		IW-2	5%	753		
		IW-3	5%	20		
		IW-4	5%	1,245		
		Event Total		4,663	550	
Totals				32,693	4,125	

Table 5-1

Summary of Permanganate Distribution in Compliance Monitoring Zones
 Building 40 Groundwater Corrective Measures
 Watervliet Arsenal, Watervliet, New York

Compliance Monitoring Zone	Transmissivity (ft ² /day)	September 2004	February 2005	May 2005	July 2005	August 2005	December 2005	April 2006	September 2006
MW-82R-3	0.1								
MW-83-2	0.1								
MW-81-1	1.2								
MW-84R-2	1.8								
MW-85R-3	1.89								
MW-84R-3	7.2								
MW-83-3	7.8								
MW-86R-3	16								
MW-81-3	20.6								
MW-84R-1	20.7								
MW-85R-1	25.2								
MW-82R-2	25.6								
MW-83-1	47.46								
MW-86R-1	49								
MW-81-2	74.5								
MW-85R-2	127.35								
MW-82R-1	132.8								
MW-86R-2	157.6								

Number of Monitoring Zones Receiving Permanganate	--	--	--	--	--	9	7	5	3
Average Transmissivity of Monitoring Zones Receiving Permanganate [square feet per day (ft ² /d)]	--	--	--	--	--	51.4	51.8	78.6	97.6

Table 5-2

Summary of Sulfate Concentrations in Compliance Monitoring Zones
Building 40 Groundwater Corrective Measures
Watervliet Arsenal, Watervliet, New York

Sample Date	Baseline (a)	1/25/2005	4/27/2005	8/15/2005	11/30/2005	3/30/2006	9/11/2006	9/10/2007
MW-81-1	33.2	25.4	20.6	20.3	14.8	11	13	14.9
MW-81-2	27.7	34	29.2	29.5	46.2	45.3	44.1	41.4
MW-81-3	19.1	31.9	37.1	18	24.7	4.95	21.2	8
MW-82R-1	51.3	28.3	25.3	64.1	144	112	191	57
MW-82R-2	18.8	13.8	15.3	27.7	41.2	39.2	73.9	40.9
MW-82R-3	50.1	55.5	55	58.6		86.4	92.1	61.4
MW-83-1	42.2	88.5	82.8	154	137	190	100	53.5
MW-83-2	86.1	64.6	72	58.3	44.2	40.7	352	71.6
MW-83-3	28.6	21	29.1	314	173			70.8
MW-84R-1	107.4	126	226	241	309	383	582	322
MW-84R-2	35.3	52.1	53.1	223	303	187	247	56.6
MW-84R-3	25.5	26.9	28.6	502	923	745	428	219
MW-85R-1	196.0	63	52.9	33.3	26.2	35.8	23.9	27.1
MW-85R-2	35.9	111	281	75.1	101	146	108	105
MW-85R-3	29.0	196	274	829	970	956	311	248
MW-86R-1	69.3	28.6	31.7	27.3	12.1	7.15	5.93	3.7
MW-86R-2	19.3	43.3	442	64	277	251	261	112
MW-86R-3	9.8	79.6	975	532	366	853	199	114

Notes:

All concentrations are milligrams per liter (mg/l)

(a) Baseline is the average of two sampling events conducted in August and September 2004

Concentration exceeds 100% of the baseline.

Concentration exceeds 500% of the baseline.

Concentration exceeds 1,000% of the baseline.

Table 5-3

Summary of Permanganate Residence Time in Compliance Monitoring Zones
Building 40 Groundwater Corrective Measures
Watervliet Arsenal, Watervliet, New York

Compliance Monitoring Zone	Permanganate Residence Time (days from injection)									
	September 2004	February 2005	May 2005	July 2005	August 2005	December 2005	April 2006	September 2006		
MW-81-1					14					
MW-81-2					1		2			
MW-81-3										
MW-82R-1										
MW-82R-2					14		30			
MW-82R-3					98	1				
MW-83-1					17	2				
MW-83-2										
MW-83-3					98	>112 (a)	282	>13 (b)		
MW-84R-1					31	34				
MW-84R-2										
MW-84R-3										
MW-85R-1										
MW-85R-2					15	35	2	8		
MW-85R-3										
MW-86R-1										
MW-86R-2					29	114	57	>13 (b)		
MW-86R-3										

No. Zones With Permanganate Residence Time >= 30 days	0	0	0	0	3	4	3	2		
---	---	---	---	---	---	---	---	---	--	--

Notes:

Blank Cells - Permanganate not detected

 Residence time meets or exceeds CAO of 30 days

(a) Permanganate still present at beginning of April 2006 injection event

(b) Actual residence time not known as groundwater conditions were altered by well redevelopment and coring activities.

Table 5-4

Summary of Permanganate Concentrations in Compliance Monitoring Zones
 Building 40 Groundwater Corrective Measures
 Watervliet Arsenal, Watervliet, New York

Compliance Monitoring Zone	Zone Transmissivity (ft ² /day)	August 2005 Injection		December 2005 Injection		April 2006 Injection		September 2006 Injection	
		Maximum Concentration (mg/l)	% Injected Concentration	Maximum Concentration (mg/l)	% Injected Concentration	Maximum Concentration (mg/l)	% Injected Concentration	Maximum Concentration (mg/l)	% Injected Concentration
MW-82R-3	0.1	27	0.1%	5	0.01%				
MW-83-2	0.1								
MW-81-1	1.2	504	1.0%						
MW-84R-2	1.8								
MW-85R-3	1.9								
MW-84R-3	7.2								
MW-83-3	7.8	562	1.1%	370	0.7%	8,517	17.0%	470	0.9%
MW-86R-3	16								
MW-81-3	20.6								
MW-84R-1	20.7	6,404	12.8%	421	0.8%				
MW-85R-1	25.2								
MW-82R-2	25.6	1,051	2.1%			1,221	2.4%		
MW-83-1	47.5	922	1.8%	22	0.04%				
MW-86R-1	49								
MW-81-2	74.5	547	1.1%			11	0.02%		
MW-85R-2	127.4	96	0.2%	1,279	2.6%	28	0.1%	12	0.02%
MW-82R-1	132.8								
MW-86R-2	157.6	48,700	97.4%	14,044	28.1%	16,567	33.1%	24,148	48.3%

Notes:

 Residence time meets or exceeds CAO of 30 days

mg/l - milligrams per liter

ft²/day - square feet per day

Blank cells - permanganate not detected in monitoring zone

Injected permanganate concentration ~ 50,000 mg/l

No permanganate present in compliance monitoring zones during injections prior to August 2005.

Table 5-6
Summary of Compliance Boundary VOC Mass Discharge
Building 40 Groundwater Corrective Measures
Watervliet Arsenal, Watervliet, New York

Zone ID	Estimated VOC Mass Discharge (pounds per year)									
	Baseline	January 2005	May 2005	August 2005	November 2005	March 2006	September 2006	September 2007		
MW-81-1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		0.000
MW-81-2	0.002	0.001	0.001	0.001	0.001	0.001	0.000	0.000		0.000
MW-81-3	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000		0.000
MW-82R-1	0.173	0.753	1.183	0.767	0.577	1.046	2.011	0.968		
MW-82R-2	0.028	0.033	0.028	0.051	0.038	0.025	0.019	0.032		
MW-82R-3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
MW-83-1	0.552	2.260	2.912	3.004	2.322	2.908	8.089	4.243		
MW-83-2	0.009	0.010	0.009	0.006	0.010	0.008	0.005	0.005		
MW-83-3	0.310	0.119	0.121	0.142	0.089	0.000	0.000	0.127		
MW-84R-1	1.323	1.026	1.158	0.832	0.676	0.573	1.738	1.189		
MW-84R-2	0.557	0.529	0.765	0.684	0.544	0.596	0.707	0.695		
MW-84R-3	0.913	0.740	0.883	0.843	0.780	1.541	1.076	0.786		
MW-85R-1	0.311	0.088	0.084	0.037	0.020	0.019	0.010	0.004		
MW-85R-2	2.518	2.189	2.129	2.590	0.089	2.410	3.155	3.932		
MW-85R-3	0.110	0.011	0.268	0.331	0.312	0.324	0.298	0.329		
MW-86R-1	0.223	0.101	0.056	0.058	0.046	0.035	0.010	0.014		
MW-86R-2	2.623	1.998	1.487	0.423	0.851	0.774	0.465	0.466		
MW-86R-3	0.375	0.165	0.479	0.260	0.272	0.341	0.499	0.335		
Total	10.028	10.023	11.564	10.031	6.627	10.602	18.076	13.126		

Legend

0 - 0.1	
0.1 - 1.0	
>1.0	

Table 5-8
Summary of Compliance Boundary VOC Concentrations
Building 40 Groundwater Corrective Measures
Watervliet Arsenal, Watervliet, New York

Zone ID	Total VOC Concentration (ug/l)							
	Baseline	January 2005	May 2005	August 2005	November 2005	March 2006	September 2006	September 2007
MW-81-2	14	7	9	9	6	6	3	3
MW-81-1	18	16	15	21	15	10	14	47
MW-81-3	19	18	26	22	19	19	10	8
MW-82R-3	165	80	118	18	18	20	12	7
MW-82R-2	263	315	264	482	363	240	181	304
MW-82R-1	318	1,382	2,171	1,407	1,059	1,920	3,690	1,776
MW-86R-1	2,026	913	507	523	418	302	81	118
MW-85R-1	2,648	748	714	319	171	161	88	33
MW-83-1	3,388	13,871	17,874	18,437	14,250	16,290	45,310	23,766
MW-85R-2	4,327	3,762	3,658	4,450	153	4,130	5,406	6,739
MW-86R-2	6,953	5,296	3,942	1,121	2,255	2,052	1,232	1,236
MW-86R-3	9,786	4,304	12,507	6,780	7,096	8,900	13,020	8,757
MW-83-3	10,573	4,060	4,133	4,852	3,027	0	0	4,336
MW-85R-3	12,675	1,300	31,000	38,270	36,000	37,430	34,420	37,950
MW-84R-1	16,400	12,713	14,345	10,312	8,383	7,100	21,473	14,731
MW-83-2	22,891	25,500	22,610	16,863	26,200	21,200	13,563	14,540
MW-84R-3	32,540	26,371	31,472	30,049	27,790	54,900	38,330	28,009
MW-84R-2	71,475	67,790	98,160	87,780	69,750	85,000	100,790	99,070

Notes:

Data in ascending order of Baseline VOC concentration.

ug/l - micrograms per liter

Permanganate detected in monitoring zone during subsequent injection event.

Attachment A

Corrective Measures Technology Screening Update

Building 40 Bedrock Groundwater

Watervliet Arsenal, Watervliet, New York

September 2009

This Corrective Measures Technology Screening Update has been prepared in accordance with the letter from the New York State Department of Environmental Conservation (NYSDEC), dated April 14, 2009, providing comments and conditional approval of the *Corrective Measures Performance Evaluation Report, Building 40 Bedrock Groundwater Corrective Measures, Main Manufacturing Area, Watervliet Arsenal, Watervliet, New York* (CM Performance Evaluation). The purpose of the update is to evaluate any new corrective measures technologies that have been become available since the initial screening documented in the *Corrective Measures Work Plan, Building 40 Bedrock Groundwater, Main Manufacturing Area, Watervliet Arsenal, Watervliet, New York*, dated July 2004 (Work Plan).

Background

The 2004 technology screening was based on the following assumptions, which were presented in Section 5.1 of the Work Plan.

1. The majority of the chlorinated volatile organic compound (CVOC) mass in the bedrock aquifer in the Building 40 area is present in the shale bedrock matrix. This bedrock CVOC mass is a continuing source for the CVOCs in the bedrock groundwater. There is no evidence of any active source of CVOCs in the unsaturated zone contributing to the bedrock groundwater.
2. It is unlikely that any of the currently available corrective measures technologies will result in the achievement of NYSDEC Class GA groundwater standards (equivalent to USEPA Maximum Contaminant Limits [MCLs]) in the bedrock groundwater.
3. Based on the data collected during the various investigations and studies, there are no identified risks to human health or the environment associated with the presence of the CVOCs in the bedrock groundwater in the Building 40 area via contact, ingestion, or discharge of the groundwater.

The corrective action objective (CAO) for the Building 40 bedrock groundwater was to reduce the concentration of hazardous constituents in groundwater migrating from the site to New York State and Federal groundwater standards or approved alternate concentration limits (ACLs) developed for this site. However, given the presence of DNAPL in the fractured rock at the site, it was recognized that the achievement of the CAO may take a very long time or may not be achievable using currently available

technologies (Work Plan Section 5.2). It was also recognized that any potential corrective measures technology must be capable of treating the ongoing source of the VOC contamination in the bedrock matrix.

Using these assumptions, the following corrective measures technologies were screened for their potential effectiveness at meeting the CAO (Work Plan Section 5.3).

1. Monitored Natural Attenuation (MNA)
2. Containment
3. In-situ Enhanced Bioremediation (ISB)
4. In-situ Chemical Oxidation (ISCO)
5. No Action

Of these, in-situ chemical oxidation (ISCO) using sodium permanganate was chosen as the only alternative that was potentially capable of meeting the CAO over the long term through source treatment of the bedrock matrix. As discussed in the CM Performance Evaluation, a permanganate ISCO corrective measures program was initiated in 2004 and was continued through 2006, after which time permanganate injections were discontinued due to clogging of the injection boreholes, reduced permanganate distribution, and apparent increases in the VOC mass discharge across the compliance boundary. Attempts to correct this situation in 2006 and 2007 through well cleaning/redevelopment were unsuccessful and it was determined that the ISCO corrective measures were not capable of meeting the corrective measures performance metrics and, therefore, the CAO.

Technology Screening Update

Information Sources

The following programs/information resources were utilized to identify and review new technologies for remediation of CVOCs in groundwater that may be potentially applicable to the Building 40 bedrock groundwater:

- United States Environmental Protection Agency (USEPA) Superfund Technology Innovation Program (TIP) (formerly the Technology Innovation Office (TIO));
- USEPA Cleanup Information (CLU-IN) Website (www.clu-in.org);
- Federal Remediation Technologies Roundtable;
- Environmental Security Technology Certification Program (ESTCP);
- Strategic Environmental Research and Development Program (SERDP);
- Interstate Technology and Regulatory Council (ITRC);
- Air Force Center for Engineering and the Environment (AFCEE);

- Naval Facilities Engineering Command (NAVFAC);
- National Groundwater Association – Groundwater On-line Database;
- University of New Hampshire Bedrock Bioremediation Center; and
- U.S. Geological Survey (USGS) Toxic Substances Hydrology Program.

In addition, the following publications were reviewed:

- Federal Remediation Technologies Roundtable. 2009. *Treatment Technologies Screening Matrix*.
- Geosyntec Consultants. 2007. *Final Report, Bioaugmentation Pilot Study, Former Naval Air Warfare Center, West Trenton, New Jersey*. June 2007.
- Interstate Technology Regulatory Council (ITRC). 2008. *In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones*. June 2008.
- LaChance, John (TerraTherm) and Pierre Lacombe (USGS). 2009. *Thermal Treatment of DNAPL in Fractured Bedrock Using Thermal Conduction Heating*. Presentation for 2009 Fractured Rock Technology Seminar and Guided Site Tour, Naval Air Warfare Center, West Trenton, New Jersey. June 2009.
- McDade, James M., Travis McGuire, Charles Newell. 2005. *Analysis of DNAPL Source-Depletion Costs at 36 Field Sites*. Spring 2005.
- National Groundwater Association. *Fractured Rock: State of the Science and Measuring Success in Remediation*. September 2005.
- National Research Council (NRC). 2005. *Contaminants in the Subsurface, Source Zone Assessment and Remediation*.
- Sale, Tom, Charles Newell, Hans Stroo, Robert Hinchee, and Paul Johnson (ESTCP). 2008. *Frequently Asked Questions Regarding Management of Chlorinated Solvents in Soils and Groundwater*. July 2008.
- Strategic Environmental Research and Development Program. 2007. *Project Fact Sheet: A Comparison of Pump-and-Treat Natural Attenuation, and Enhanced Biodegradation to Remediate Chlorinated Ethene-Contaminated Fractured Rock Aquifers*, Naval Air Warfare Center, West Trenton, New Jersey. October 2007.
- United States Environmental Protection Agency. 2005. *Steam Enhanced Remediation Research for DNAPL in Fractured Rock, Loring Air Force Base, Limestone, Maine*. National Risk Management Research Laboratory, Cincinnati, Ohio. August 2005.

Results

Remedial strategies presented in these information sources focused primarily on potential methods for in-situ source treatment. Source treatment technologies employed included:

- In-situ enhanced bioremediation (ISB);

- In-situ chemical oxidation (ISCO);
- Monitored natural attenuation (MNA); and
- In-situ thermal remediation (ISTR).

With the exception of ISTR, each of these technologies was previously evaluated in the Work Plan. Containment through groundwater extraction or barrier treatment (i.e., reactive walls) was also utilized in cases where a sensitive receptor (i.e., drinking water user) was, or could be, impacted by the CVOCs present in the groundwater. However, similar to the discussion presented in the Work Plan, it was recognized that containment technologies would not result in cleanup of the site and were solely implemented for the protection of downgradient receptors. There are no receptors at risk downgradient of the Watervliet Arsenal CVOC bedrock contamination.

Technologies reviewed and/or presented in the majority of the reviewed sources focused on source treatment as a means to reduce contaminant concentrations and shorten remedial timeframes. Much of the available literature focuses on treatment of CVOCs in unconsolidated media; however, some information pertaining to fractured bedrock sites was available. This information included compilations of work at several sites and two case studies. In general, these studies yielded the following information:

1. ISCO, primarily with permanganate, has been used most widely as the preferred source remediation technology at fractured bedrock sites where groundwater was contaminated with CVOCs.
2. Containment technologies were the most commonly used remedial technologies where prevention of exposure to potential human and/or ecological receptors was the primary remedial objective.
3. ISB and, more recently, ISTR, have been implemented as source treatment technologies at the pilot study level and/or at a much smaller scale than at the Watervliet Arsenal.
4. Delivery and distribution of injected materials, and treatment of contaminants in microfractures, low flow zones, and the rock matrix, presented the biggest obstacle to the success of source treatment technologies in fractured bedrock.
5. Release of contaminants stored in the matrix can sustain contaminant discharge for extended periods of time (i.e., decades), even where aqueous source treatment activities have been implemented.
6. In almost all cases, it was stipulated that achievement of groundwater standards (i.e., Maximum Contaminant Limits [MCLs]) was likely not possible within a reasonable timeframe at fractured bedrock sites – particularly those where matrix storage of contaminants was prevalent.

7. The cost of remediation at fractured bedrock sites is typically on the order of several million dollars and, as discussed above, generally does not result in the achievement of groundwater standards.

Information on the following two relevant case studies was also reviewed:

1. ISTR pilot at the former Loring Air Force Base (AFB) in Limestone, Maine; and
2. ISB and ISTR pilots at the former Naval Air Warfare Center (NAWC) in West Trenton, New Jersey.

The results of these case studies are summarized below:

Loring Air Force Base

Loring AFB was added to the Superfund National Priorities List in 1990. Subsequent investigations showed that chlorinated VOCs were present in the bedrock groundwater beneath a former quarry. The Record of Decision (ROD), signed in 1999, recognized that it was impractical to restore groundwater in fractured rock to drinking water standards. However, an agreement was made between the United States Air Force (USAF) and the USEPA Region 1 to use the quarry to conduct a research project to further the development of remediation technologies in fractured rock, and with the hope of recovering contaminant mass to reduce the timeframe for natural attenuation of the remaining contaminants. Steam enhanced remediation (SER) was chosen as the preferred remedial technology for the site.

The results of the study showed that the amount of energy that could be injected during the limited-time project was low and that the target zone for treatment could not be completely heated. Despite the limited heating that occurred, effluent vapor and water samples showed that some contaminants were removed, likely as a result of air stripping from fracture surfaces. However, the amount of contaminants removed was limited and had no discernable impact on groundwater concentrations. The study concluded that steam injection may not be the best method for remediation for highly complex low permeability fractured sites and that extremely long injection times would likely be necessary for any full scale operations. However, even with long injection times, heat losses would likely limit the ability to heat the entire target zone.

NAWC West Trenton

NAWC has been the subject of an active remediation program since 1993. Historical releases of chlorinated solvents at the site led to the presence of elevated concentrations of CVOCs in the bedrock groundwater. The current remedial system is based on pumping and treatment of impacted groundwater and has been operating since 1997. The primary purpose of the system was to contain the CVOC plume and prevent off-site migration. The concentrations of CVOC in groundwater at monitoring points have generally decreased in the period from 1997 to the present, but have remained greater

than groundwater quality standards. The sedimentary fractured bedrock at the site has been extensively characterized using similar methods to those used at the WVA, including rock matrix VOC characterization, borehole geophysical testing by the USGS, and multi-level groundwater monitoring well installation.

ISB PILOT

A bioaugmentation pilot study was conducted to evaluate whether source treatment through ISB could potentially accelerate the shut-down of the groundwater extraction system. The study included the injection of an electron donor (emulsified soybean oil) and a culture containing TCE-degrading bacteria (KB-1[®]) into two well pairs. The total size of the treatment area was approximately 9,000 square feet and extended 120 feet below ground surface. Extracted water from one well was dosed with the injection materials and injected into its paired well within the test plot area. The results of the pilot showed that TCE concentrations in the test area were reduced. However, back-diffusion from the matrix resulted in contaminant rebound, which necessitated additional donor injections. These data indicate that the treatment method did not address VOC contamination in the rock matrix, which will continue to act as a continuing source of aqueous groundwater contamination that will require long-term operation of the site-wide groundwater extraction remedy. The results of the pilot confirm the conclusion of the original screening conclusions presented in the Work Plan Section 5.3.

ISTR PILOT

An additional pilot study utilizing ISTR of the fractured bedrock by thermal conduction heating (TCH) is being conducted in a 36-foot by 36-foot test area in another portion of the NAWC plume. The depth of treatment is approximately 55 feet below ground surface (bgs). The pilot test area includes 15 heater wells, 3 groundwater sampling/temperature monitoring wells, and 5 additional temperature monitoring points. The heater wells also served as vapor recovery points and the entire test area was covered with a concrete pad to facilitate the collection of vapors. Based on discussions with NAVFAC personnel, the initial results of the pilot were promising. Target temperatures were reached in the majority of the treatment area within approximately 4 months, with the exception of some zones where fractures appeared to inhibit heating, and significant VOC mass was recovered through the vapor extraction wells. The total subcontractor cost for the pilot was \$500,000 and the approximate 4-month energy cost was \$85,000, which included a dedicated electricity supply connection. Based on PID readings in the vapor effluent, the pilot removed approximately 275 pounds of VOCs, which is equivalent to only approximately 3 percent of the total VOC mass at Building 40.

Conclusions

The results of the technology screening confirm that there are no new applicable corrective measures technologies that have become available since the initial screening

documented in the Work Plan. In-situ thermal remediation technologies, which had been developed at the time of the initial screening, but were not included in the Work Plan, are not applicable to the Building 40 site for the following reasons:

1. The applicability of ISTR in bedrock at the full-scale level is questionable due to the large heat loss potential resulting from the presence of both known and unknown fracture pathways. This was confirmed in the ISTR pilot conducted at Loring AFB.
2. ISTR, if successful, results in the volatilization of contaminants from the groundwater to the soil vapor. These vapors must be collected at the ground surface through a vapor extraction system. Since a significant portion of the Building 40 plume lies beneath Building 40 where the ability to collect vapors is inhibited by historic foundations and preferential flow pathways (i.e., canal tunnels and storm sewers), the use of ISTR would likely result in the release of CVOC vapors into the Building 40. The presence of the plume beneath Building 40 would also limit the ability to heat the bedrock beneath building, where much of the VOC mass resides.
3. Due to the intensive energy requirements and close heater-well spacing required, ISTR is prohibitively expensive in larger treatment areas such as that at Building 40. For example, the NAWC pilot treated a volume of approximately 71,000 cubic feet (ft³) at a cost of \$585,000. This equates to approximately \$2,100 per pound of VOC removed, or approximately \$225 per cubic yard treated. Given that the approximate total volume of the Building 40 treatment area is 5,800,000 ft³ (~215,000 cubic yards (yd³)) the resulting treatment cost would likely exceed \$45 million. Likewise, a study conducted by McDade et. al., found that the average cost of ISTR is approximately \$100 per yd³ in unconsolidated materials. As demonstrated by the NAWC pilot, these costs would likely be higher in bedrock due to the close heater well spacing that would be required.

This information supports the conclusion of the CM Performance Evaluation that achievement of the CAO for the Building 40 bedrock groundwater is not practicable using currently available technologies. Accordingly, it is recommended that the CM Program be discontinued and that the selected Building 40 monitoring wells listed in the CM Performance Evaluation be included in the overall WVA Long Term Monitoring Program for future monitoring.

Attachment B

VOC Mass Discharge Evaluation and LTM Work Plan

Building 40 Bedrock Groundwater

Watervliet Arsenal, Watervliet, New York

Final - August 2010

This VOC mass discharge evaluation and long term monitoring plan (LTM Plan) for the Building 40 bedrock groundwater has been prepared in accordance with the following documents.

- The New York State Department of Environmental Conservation (NYSDEC) letter, dated April 14, 2009, providing comments and conditional approval of the *Corrective Measures Performance Evaluation Report, Building 40 Bedrock Groundwater Corrective Measures, Main Manufacturing Area, Watervliet Arsenal, Watervliet, New York* (CM Performance Evaluation).
- The NYSDEC letter, dated January 29, 2010, providing final comments on the draft versions of this document and associated previous responses to comments dated, September 2, 2009 and January 21, 2010.

The purpose of the evaluation is to assess the changes in VOC mass discharge across the compliance boundary since the last sampling event in 2007 and the effect of new hydraulic conductivity estimates on the VOC mass discharge. As stated in the CM performance evaluation, it is likely that the hydraulic conductivity of several fractures/zones decreased due to clogging associated with the precipitation of manganese dioxide particulates from the injection solution.

Background

Compliance boundary VOC mass discharge estimates utilized during the corrective measures program and in the CM Performance Evaluation were estimated for each compliance monitoring zone using the hydraulic conductivity (K) values calculated for fractures that had detectable flow during the July 2004 geophysical testing. The K values utilized for the VOC mass discharge calculations were the sum of the individual K values for fractures with detectable flow that intersected each compliance monitoring zone at the time of the geophysical testing in 2004. Mass discharge estimates were calculated using the following assumptions:

- **Discharge Zone Thickness:** Set as the thickness of the screened interval in each compliance monitoring zone.
- **Hydraulic Gradient:** Set at 0.003 ft/ft based on the hydraulic gradient in the Building 40 area calculated from WVA-wide water table groundwater elevations.

- **Horizontal Length of Discharge Zone:** Set as the distance between compliance monitoring wells.
- **VOC Concentration:** Set at the total VOC concentration in each compliance monitoring zone during each monitoring event.

May 2009 Sampling

In accordance with the NYSDEC letter dated April 14, 2009, the compliance boundary wells were re-sampled in May 2009 to evaluate current VOC concentrations. All three monitoring zones in each well were sampled, with the exception of monitoring zone MW-82-3, which did not contain sufficient water for sampling. The results of the May 2009 sampling are summarized in the attached tables. In general, the May 2009 VOC concentrations in the samples collected from the compliance monitoring wells were less than those detected in the September 2006 and 2007 samples. Permanganate was not detected in any of the compliance monitoring zones during the May 2009 sampling.

VOC Mass Discharge Evaluation

2004 Hydraulic Conductivity Estimates

Compliance boundary VOC mass discharge estimates for the baseline and pre-injection monitoring events utilizing the 2004 (baseline) K estimates are presented in Table B-1. Table B-2 (below) presents changes from baseline in the estimated compliance boundary VOC mass discharge after each injection event. As shown in Table B-2, the estimated compliance boundary VOC mass discharge in May 2009 was approximately 85 percent of the baseline using the 2004 K estimates and the was the second lowest mass discharge estimate measured during the CM program.

Table B-2
Summary of Changes in Compliance Boundary VOC Mass Discharge

	Compliance Boundary VOC Mass Discharge								
	Baseline	Jan. 2005	May 2005	Aug. 2005	Nov. 2005	Mar. 2006	Sept. 2006	Sept. 2007	May 2009
Total VOC Mass Discharge (lb/yr)	10.0	10.0	11.5	10.0	6.6	10.6	18.0	13.1	8.5
% of Baseline VOC Mass Discharge	---	100%	115%	100%	66%	106%	180%	131%	85%

2009 Hydraulic Conductivity Estimates

It is not possible to re-evaluate fracture / monitoring zone K in the compliance monitoring wells using the geophysical methods employed in 2004 due to the presence of the multi-level monitoring wells in the boreholes. Accordingly, standard slug tests were performed in each monitoring zone in October 2007 to estimate the K after three years of permanganate injections. It is important to note that slug tests are not directly comparable to the geophysical testing and may not be appropriate for use in bedrock;

however, given the limitations imposed by the presence of the multi-level wells, slug tests were utilized to gain an understanding of the potential changes in K resulting from the generation of manganese dioxide precipitates.

Table B-3 compares K values calculated in 2004 with those calculated based on the 2007 slug tests. As shown in the table, the estimated K values in 2007 were generally less than 50 percent of the baseline values measured in 2004. However, several of the 2007 estimated K values were similar in magnitude to, or greater than, the 2004 estimates, which indicates that the slug test results were likely not biased low as compared to the 2004 estimates. These data, recognizing the potential limitations described above, support the conclusion that clogging due to manganese dioxide precipitation has reduced the capacity of the bedrock fractures to transport groundwater through the compliance boundary.

Compliance boundary VOC mass discharge estimates for the September 2007 and May 2009 monitoring events utilizing the K estimates calculated from the 2007 slug test are presented in Table B-4. As shown in the table, the estimated VOC mass discharge in September 2007 and May 2009 using the new K values was 5.5 pounds per year and 4.2 pounds per year, respectively. A comparison of the calculated VOC mass discharge for these sampling events using the different K values is shown in Table B-5 below.

Table B-5
Comparison of VOC Mass Discharge Estimates

	September 2007		May 2009	
	2004 K	2007 K	2004 K	2007 K
Total VOC Mass Discharge (lb/yr)	13.1	5.5	8.5	4.2

Conclusions

The results of the groundwater sampling and the K evaluation support the CM Performance Evaluation conclusion that groundwater transport through the bedrock fractures has been inhibited by the deposition of manganese dioxide precipitates. This has resulted in a decrease in the VOC mass discharge across the compliance boundary, which was evidenced by the May 2009 sampling results and both the 2004 and 2007 K estimates.

LTM Plan

Monitored Natural Attenuation Evaluation

Reductive dechlorination is the most important process in the natural biodegradation of chlorinated solvents (i.e., PCE and TCE)¹. For reductive dechlorination to completely

¹ United States Environmental Protection Agency. 1998. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*, EPA/600/R-98/128, September 1998. (USEPA NA Protocol)

degrade CVOCs, such as PCE and TCE to ethene, the geochemical conditions in the subsurface must be ideal and the availability of microorganisms that are responsible for degradation must be present. Electron acceptors (CVOCs), electron donors (sulfate, nitrate, ferric iron, and methane), a reducing environment (oxidation reduction potential [ORP] less than 50 millivolts [mV]), an anaerobic environment (dissolved oxygen [DO] less than 2.0 mg/L), carbon source, and microbes (reductive dechlorinators) are all needed for reductive dechlorination to occur. The most important of these prerequisites is the presence of microbes that utilize hydrogen to dechlorinate VOCs (reductive dechlorinators) to innocuous components in anaerobic environments. In particular, the microbe *Dehalococcoides ethenogenes* (DHC) is required to completely convert chlorinated VOCs to ethene in the absence of oxygen.

The USEPA NA Protocol Table 2.3 contains a screening process to evaluate the potential for reductive dechlorination based on site monitoring data. Using data from groundwater samples collected from monitoring well MW-51 (located in the center of the impacted area) during the RFI and LTM program through 2003 (before the initiation of the permanganate corrective measures) resulted in a screening score of 23, which, according to the protocol, is indicative of strong evidence for anaerobic biodegradation of the chlorinated solvents present in the bedrock groundwater. These data included:

- The presence of relatively high concentrations (greater than 0.1 milligrams per liter [mg/l]) of the dissolved gases ethene and ethane, which are the final end products of the complete degradation of PCE and TCE.
- Low dissolved oxygen levels (less than 1 mg/l) and reducing conditions (reduction-oxidation potential less than 0 mV).
- Low nitrate and sulfate concentrations, which are indicative of the use of the nitrogen and sulfur as electron donors and which are potentially competing electron acceptors at high concentrations.
- Detectable concentrations of ferrous iron, which is indicative of both reducing conditions and the use of ferric iron as an electron donor.

Last, a groundwater sample collected from MW-51 in November 2003 showed the presence of DHC, which, as discussed above, can complete the reductive dechlorination process by converting vinyl chloride to ethene. Based on this information, it is anticipated that concentrations of chlorinated VOCs in the bedrock groundwater will decrease over time through natural attenuation processes.

Monitoring Plan

It is proposed that all zones in compliance boundary monitoring wells MW-82R, MW-83, MW-84R, MW-85R, and MW-86R be sampled on an annual basis starting in May 2010. Each well will be sampled for analysis of VOCs in accordance with the methods and procedures outlined in the June 2008 WVA LTM Plan Update, and any future updates. Due to the presence of chlorinated VOCs (CVOCs) in the compliance boundary

monitoring wells in the Building 40 area, a contingency monitoring plan has been developed in the event that anomalous CVOC concentrations are detected in these wells in the future. The contaminants of concern (COCs) in the wells are as follows:

- Trichloroethene (TCE)
- Tetrachloroethene (PCE)
- Cis-1,2-dichloroethene (cDCE)
- Vinyl chloride (VC)

Statistical Trigger

The proposed contingency evaluation protocol utilizes a well and contaminant-specific statistical “trigger” concentration that initiates a contingency evaluation in the event groundwater monitoring data indicates a potential changes in site conditions. This method is currently utilized by the NYSDEC for solid waste landfill monitoring programs to evaluate if a statistically significant release from a landfill has occurred [6 NYCRR Part 360-2.11(c)(5)(i)]. The statistical trigger will be calculated as follows:

1. The results for the COCs in each of the wells from the period of the spring of 2004 through the spring of 2009 were averaged to determine the mean “background concentration”. The standard deviation of the “background” data set was also established. The “background” mean and standard deviation will be the basis for all future comparisons.
2. Trigger values were established for each COC in each well as the sum of the background mean plus three times the background standard deviation. This test is commonly used to identify outlying data that fall outside the expected range of values based on a given baseline data set.
3. Monitoring events during which permanganate was present in the Building 40 compliance boundary wells (i.e., assumed zero concentrations) were not included in the calculations.
4. Monitoring events during which the compound was not detected were included as one half of the laboratory reporting limit for that compound.

Table B-6 presents a summary of the minimum, maximum, average, and standard deviation for each compound in each well, and lists the statistical trigger concentrations calculated from the data.

Contingency Monitoring

Upon receipt of analytical data, the result for each of the COCs in the wells in Table B-6 will be compared against the statistical trigger concentration. If the data for the COCs in a given well exceed the statistical trigger concentrations the NYSDEC will be notified of the condition within 15 days and potential follow up actions will be determined in consultation with the NYSDEC. If samples from three or more of the Building 40 compliance boundary wells contain COCs at concentrations greater than the corresponding statistical trigger concentrations, verification sampling consisting of quarterly sampling for one year will be conducted, with sampling results provided to the NYSDEC each quarter. The objective of the verification sampling will be to evaluate the potential causes of the increase in COC concentrations; to assess whether changes to the monitoring program are required; and, if necessary, to perform a risk evaluation and technology screening to evaluate potential corrective measures technologies that may be applicable to the site. Based on the results of the verification sampling, potential follow up actions will be determined in consultation with the NYSDEC. Significant increases in the levels of COCs will be discussed in the annual monitoring report and recommendations made for further actions, if necessary.

Table B-1

Summary of Compliance Boundary VOC Mass Discharge Using Baseline Hydraulic Conductivity Values

Building 40 Groundwater Corrective Measures

Watervliet Arsenal, Watervliet, New York

Zone ID	Estimated VOC Mass Discharge (pounds per year)								
	Baseline	January 2005	May 2005	August 2005	November 2005	March 2006	September 2006	September 2007	May 2009
MW-81-1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
MW-81-2	0.002	0.001	0.001	0.001	0.001	0.001	0.000	0.000	0.000
MW-81-3	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000	0.000
MW-82R-1	0.173	0.753	1.183	0.767	0.577	1.046	2.011	0.968	0.152
MW-82R-2	0.028	0.033	0.028	0.051	0.038	0.025	0.019	0.032	0.047
MW-82R-3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
MW-83-1	0.552	2.260	2.912	3.004	2.322	2.908	8.089	4.243	2.636
MW-83-2	0.009	0.010	0.009	0.006	0.010	0.008	0.005	0.005	0.005
MW-83-3	0.310	0.119	0.121	0.142	0.089	0.000	0.000	0.127	0.058
MW-84R-1	1.323	1.026	1.158	0.832	0.676	0.573	1.733	1.189	0.727
MW-84R-2	0.557	0.529	0.765	0.684	0.544	0.596	0.707	0.695	0.537
MW-84R-3	0.913	0.740	0.883	0.843	0.780	1.541	1.076	0.786	0.509
MW-85R-1	0.311	0.088	0.084	0.037	0.020	0.019	0.010	0.004	0.001
MW-85R-2	2.518	2.189	2.129	2.590	0.089	2.410	3.155	3.932	2.338
MW-85R-3	0.110	0.011	0.268	0.331	0.312	0.324	0.298	0.329	0.260
MW-86R-1	0.223	0.101	0.056	0.058	0.046	0.035	0.010	0.014	0.006
MW-86R-2	2.623	1.998	1.487	0.423	0.851	0.774	0.465	0.466	0.891
MW-86R-3	0.375	0.165	0.479	0.260	0.272	0.341	0.499	0.335	0.393
Total	10.028	10.023	11.564	10.031	6.627	10.602	18.076	13.126	8.562

Legend

0 - 0.1	
0.1 - 1.0	
>1.0	

Table B-3
Summary of Calculated Hydraulic Conductivity Values
Building 40 Boundary Wells
Watervliet Arsenal, Watervliet New York

Well ID	Units	Hydraulic Conductivity		
		October 2007	Baseline (Aug. 04)	Percent of Baseline
MW-81-1	ft/yr	0.889	11.8	8%
MW-81-2	ft/yr	24.2	755	3%
MW-81-3	ft/yr	15.5	171	9%
MW-82R-1	ft/yr	146	1310	11%
MW-82R-2	ft/yr	127	234	55%
MW-82R-3	ft/yr	0.445	0.869	51%
MW-83-1	ft/yr	178	422	42%
MW-83-2	ft/yr	69.5	1.01	> 100%
MW-83-3	ft/yr	4.94	64.7	8%
MW-84R-1	ft/yr	15.1	199	8%
MW-84R-2	ft/yr	22.4	16.0	> 100%
MW-84R-3	ft/yr	8.17	67.4	12%
MW-85R-1	ft/yr	8.84	263	3%
MW-85R-2	ft/yr	4.16	1162	0%
MW-85R-3	ft/yr	77.1	16.4	> 100%
MW-86R-1	ft/yr	68.8	497	14%
MW-86R-2	ft/yr	42.7	1513	3%
MW-86R-3	ft/yr	213	139	> 100%

Notes:

October 2007 K-values calculated using Bouwer & Rice Method (falling head slug test) in multi-level well.

August 2004 K-values derived from open borehole geophysical testing of fractures zones.

Table B-4**Summary of Compliance Boundary VOC Mass Discharge Using Updated Hydraulic Conductivity Values*****Building 40 Groundwater Corrective Measures****Watervliet Arsenal, Watervliet, New York**

Zone ID	Estimated VOC Mass Discharge (pounds per year)	
	September 2007	May 2009
MW-81-1	0.000	0.000
MW-81-2	0.000	0.000
MW-81-3	0.000	0.000
MW-82R-1	0.108	0.017
MW-82R-2	0.017	0.026
MW-82R-3	0.000	0.000
MW-83-1	1.790	1.113
MW-83-2	0.375	0.333
MW-83-3	0.010	0.004
MW-84R-1	0.090	0.055
MW-84R-2	0.973	0.752
MW-84R-3	0.095	0.062
MW-85R-1	0.000	0.000
MW-85R-2	0.014	0.008
MW-85R-3	1.541	1.220
MW-86R-1	0.002	0.001
MW-86R-2	0.013	0.025
MW-86R-3	0.514	0.603
Total	5.543	4.219

Legend

0 - 0.1	
0.1 - 1.0	
>1.0	

Notes

* Hydraulic conductivity values calculated from slug tests performed in October 2007.

Table B-6
Summary of Baseline Groundwater Data and Trigger Values
Long-Term Monitoring Plan Update
Watervliet Arsenal, Watervliet, New York

Monitoring Well	Area Monitored	Contaminant	Baseline Data (a)				Trigger Concentration (b) (ug/l)
			Minimum Concentration (ug/l)	Maximum Concentration (ug/l)	Average Concentration (ug/l)	Standard Deviation (ug/l)	
MW-82R-1	Building 40	Vinyl chloride	45	250	88	73	307
		cis-1,2 DCE	170	940	526	261	1,310
		TCE	20	480	177	141	599
		PCE	41	2,200	746	650	2,696
MW-82R-2	Building 40	Vinyl chloride	48	160	89	42	214
		cis-1,2 DCE	110	350	224	77	454
		TCE	1	10	4.7	4	17
		PCE	1	10	4.6	3.7	16
MW-82R-3	Building 40	Vinyl chloride	4.2	76	22	25	97
		cis-1,2 DCE	1.1	65	35	46	174
		TCE	2.5	2.5	2.3	0.4	4
		PCE	0.6	2.5	2.2	0.8	4
MW-83-1	Building 40	Vinyl chloride	120	1,000	396	307	1,318
		cis-1,2 DCE	4,300	6,000	5,278	626	7,156
		TCE	2,400	10,000	4,022	2,313	10,963
		PCE	6,100	29,000	10,078	7,320	32,039
MW-83-2	Building 40	Vinyl chloride	320	980	550	197	1,141
		cis-1,2 DCE	5,900	11,000	8,344	1,671	13,358
		TCE	960	5,300	3,473	1,530	8,064
		PCE	250	12,000	7,283	4,369	20,391
MW-83-3	Building 40	Vinyl chloride	49	670	320	203	928
		cis-1,2 DCE	1,300	6,350	2,979	1,659	7,955
		TCE	190	915	361	260	1,141
		PCE	410	2,600	943	776	3,272

Table B-6
Summary of Baseline Groundwater Data and Trigger Values
Long-Term Monitoring Plan Update
Watervliet Arsenal, Watervliet, New York

Monitoring Well	Area Monitored	Contaminant	Baseline Data (a)				Trigger Concentration (b) (ug/l)
			Minimum Concentration (ug/l)	Maximum Concentration (ug/l)	Average Concentration (ug/l)	Standard Deviation (ug/l)	
MW-84R-1	Building 40	Vinyl chloride	125	1,200	436	365	1,530
		cis-1,2 DCE	3,300	9,200	6,810	1,962	12,696
		TCE	1,300	5,100	2,085	1,125	5,461
		PCE	940	6,900	2,834	1,974	8,756
MW-84R-2	Building 40	Vinyl chloride	440	5,000	1,560	1,527	6,141
		cis-1,2 DCE	5,100	11,000	8,550	2,217	15,202
		TCE	8,150	20,000	13,675	3,583	24,423
		PCE	47,000	75,000	59,000	9,006	86,019
MW-84R-3	Building 40	Vinyl chloride	380	1,900	872	480	2,311
		cis-1,2 DCE	6,600	21,000	10,717	4,240	23,438
		TCE	3,400	14,000	7,333	3,319	17,290
		PCE	3,800	20,500	12,967	5,334	28,968
MW-85R-1	Building 40	Vinyl chloride	4	130	53	41	175
		cis-1,2 DCE	2	1,400	346	466	1,743
		TCE	0.5	235	30	77	261
		PCE	0.5	950	109	315	1,055
MW-85R-2	Building 40	Vinyl chloride	3	230	125	92	399
		cis-1,2 DCE	88	3,500	2,261	1,025	5,335
		TCE	16	730	436	275	1,261
		PCE	43	2,600	1,451	979	4,388

Table B-6
Summary of Baseline Groundwater Data and Trigger Values
Long-Term Monitoring Plan Update
Watervliet Arsenal, Watervliet, New York

Monitoring Well	Area Monitored	Contaminant	Baseline Data (a)				Trigger Concentration (b) (ug/l)
			Minimum Concentration (ug/l)	Maximum Concentration (ug/l)	Average Concentration (ug/l)	Standard Deviation (ug/l)	
MW-85R-3	Building 40	Vinyl chloride	510	1,900	834	439	2,150
		cis-1,2 DCE	120	4,100	2,719	1,136	6,126
		TCE	255	3,400	1,346	928	4,130
		PCE	100	32,000	23,200	11,366	57,299
MW-86R-1	Building 40	Vinyl chloride	11	89	36	27	118
		cis-1,2 DCE	26	850	321	275	1,146
		TCE	1	305	45	99	342
		PCE	1.1	1,200	142	397	1,333
MW-86R-2	Building 40	Vinyl chloride	19	91	39	21	102
		cis-1,2 DCE	390	1,400	1,054	322	2,021
		TCE	92	440	240	128	625
		PCE	290	5,350	1,684	1,660	6,665
MW-86R-3	Building 40	Vinyl chloride	28	1,200	575	357	1,647
		cis-1,2 DCE	2,150	8,400	5,594	2,113	11,934
		TCE	240	1,800	753	564	2,445
		PCE	330	6,900	2,036	2,161	8,520

Notes:

(a) Building 40 Baseline data calculated from 10 monitoring events (August 2004 through May 2009).
Building 25 and 114 baseline data calculated from 10 monitoring events (May 2004 through June 2009).

(b) Proposed trigger set at the 99% confidence interval (average plus 3 times standard deviation).

ug/l - micrograms per liter

DCE - Dichloroethene

TCE - Trichloroethene

PCE - Tetrachloroethene