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## Chapter 18

# IN SITU STABILIZATION OF ZINC IN SOIL AND GROUNDWATER

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### ABSTRACT

A 21-acre parcel in the east coast region of the United States hosted several industrial operations from 1907 to 1982. Groundwater at a pH of 5 SU and containing as much as 30 mg/L of zinc discharges to a small stream on one edge of the facility. The site surface was remediated and redeveloped into an apartment complex. Groundwater remediation was not a requirement at the time that the apartment complex was built. Subsequent ecological studies indicated that surface water impacts were occurring from zinc discharging from groundwater, and therefore remediation was required. *In situ* stabilization technologies that could be applied to groundwater with minimal interference with site use were evaluated in bench-scale and in-field pilot tests. The bench scale testing using site soil and groundwater samples determined that a 4 weight percent (wt. %) slurry of magnesium hydroxide [Mg(OH)<sub>2</sub>] reduced zinc concentrations from 14.7 to 0.013 mg/L. Multiple extractions found a pH of 8.5 SU and a zinc concentration of 0.088 mg/L of zinc following about 1,200 aquifer pore volumes of leaching, equivalent to 400 years at the site groundwater flow rate. Pilot testing was completed with direct-push injection methods. Approximately 7.3 tons of reagent slurried in 4,205 gallons of water was injected at six points. Temporary well samples within the injection zone had post-injection zinc concentrations of <0.020 mg/L. A monitoring well downgradient of the injection zone yielded 21 mg/L of zinc prior to the injection. Within two weeks the concentration had decreased to 10 mg/L and at 8 months following injection the zinc concentration was 0.99 mg/L and the pH was 9.3 SU. The proposed remedial design took the form of a reactive zone at the edge of the facility, which treats groundwater prior to its discharge to surface water. Regulatory approval for the full-scale implementation was received in July 2007 and injection was begun in August 2007.

**Key words:** zinc, soil, groundwater, remediation, injection, stabilization

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## 1. INTRODUCTION

A 21-acre parcel in the east coast region of the United States hosted a number of industrial operations from 1907 to 1982. In the 1990's, interest in developing the site as residential housing lead to brownfield investigations, which identified petroleum hydrocarbon, chlorinated solvent, and zinc contamination in soil and groundwater. Soil removals from the site resulted in a recommendation for no further action with respect to surface soil by the regulatory agency. The site was redeveloped into 12 apartment buildings, recreational facilities, parking areas, and a stormwater basin. However, the regulatory agency required continued monitoring of groundwater and surface water after the development was completed. Upon review of surface water impacts from zinc, remediation of groundwater that discharges to surface water was required. This paper describes the remediation of zinc in the saturated soil and groundwater beneath the site in order to protect aquatic organisms in the surface water that receives the discharge of the zinc-bearing groundwater.

## 2. SITE CHARACTERIZATION

The shallowest soil beneath the site includes heterogeneous fill material consisting of clay to sand to gravel with varying amounts of debris. The fill overlies heterogeneous alluvium that grades downward into saprolite. The alluvium consists of layers and lenses ranging from silty and sandy clay to silty fine sand to gravelly sand with pebbles. Most of the soil is micaceous. The layers and lenses are typically less than two feet in thickness, with some sand units as thick as five feet. There is little lateral continuity evident in borings with spacings as little as 100 feet. At many locations there was a pattern of fining upwards (i.e., the gravelly sands were typically found at the base of the alluvium). The saprolite is typically clayey sand with gravel.

The water table is on the order of six feet below ground surface. Groundwater flow in the alluvium is generally from north to south. Groundwater discharges into two perpendicular culverts that bound the southern and southeastern edges of the former industrial parcel. The north-south culvert and the west-east culvert join to form a southward flowing stream at the southeastern corner of the site (see Figure 1). The hydraulic conductivity of the alluvium as measured in monitoring wells is on the order of 14 ft/d, yielding flow rates on the order of 100 ft/yr.

Zinc concentrations in soil are highly variable over short horizontal distances. However, there appear to be three general areas where concentrations of zinc greater than >750 mg/kg are found in soil. These are as follows: south of and beneath Building A, to the north-south culvert (range of 1,300 to 18,200 mg/kg; average of 5,420 mg/kg; n=8); beneath the north wing of Building A (range of 1,600 to 5,780 mg/kg; average of 3,020 mg/kg; n=5); and beneath the south wing of Building B (range of 890 to 3,000 mg/kg; average of 1,640 mg/kg; n=13). Other samples exceeding 750 mg/kg zinc were collected from west of the north-south culvert but do not generally form spatially contiguous or extensive "hotspots". The zinc in the soil forms a continuing source of dissolved zinc in the groundwater.

The groundwater has a low dissolved solids content (<500 mg/L). There are no dominant cations or anions in the groundwater, with the groundwater classified as a Ca+Mg, Na+K :: Cl+SO<sub>4</sub>, HCO<sub>3</sub> geochemical facies. The groundwater contains 1 to 2 mg/L of dissolved oxygen and is acidic, with an average pH of 5.6 SU. Zinc concentrations in groundwater samples collected in January 2006 were as high as 25.6 mg/L at MW-3A (see Figure 1). Zinc concentrations in the southern portion of the site are typically greater than 1 mg/L. Concentrations have been relatively unchanged over the last ten years of monitoring.

Groundwater discharges to the culverts crossing the site. Zinc concentrations in the surface water collected at and immediately down stream of the culvert confluence ranged from 1.44 to 2.35 mg/L in January 2006. The zinc concentration in the stream decreased to 0.819 mg/L as the stream left the site.

### **3. REMEDIAL OBJECTIVES AND APPROACH**

The regulatory agency required that groundwater remediation be undertaken to reduce the zinc concentrations in groundwater to the extent feasible in order to reduce the flux of zinc from groundwater to surface water. Although a regulatory groundwater standard of 2.0 mg/L exists, the lack of nearby groundwater wells precluded a need for groundwater remediation for the drinking water receptor pathway. The objective of the remediation is to reduce the zinc concentrations in the stream to approach the surface water quality standards for the protection of aquatic organisms, which incorporate hardness and range between 0.1 and 0.2 mg/L.

Groundwater remediation was deferred until after the apartment complex was built. The remedy, therefore, had to be implementable within the constraints posed by the existing facilities. These facilities precluded direct access to the zinc-bearing soils beneath the site. An injection treatment barrier (ITB) was selected as the most feasible approach for reducing the zinc flux from the groundwater to the surface water.

### **4. BENCH-SCALE TESTING**

Bench-scale treatment trials were completed using soil and groundwater samples collected by Environmental Alliance (Alliance) on 17 January 2006. The soil sample was collected from between depths of 12 to 20 feet below ground surface (bgs) near a location where previous sampling had found 18,200 mg/kg of zinc in the soil. The soil sample was homogenized and used in the treatability studies with its as received wet weight (moisture content) of 23 percent. The soil was a yellow-brown fine to medium sand with some silt and clay and occasional coarse gravel. Sieving of a representative sample found 6 percent coarse sand and fine gravel, 84 percent fine and medium sand, and 10 percent silt and clay.

The groundwater was collected from monitoring wells MW-3A and MW-12. Approximately 12 litres of groundwater were collected from each well. Equal volumes of water from the two wells were mixed to form the leaching solution (the extractant) in the treatment studies. The

groundwater chemistry from the two wells sampled in October 2004 is summarized in Table 1. The mixed groundwater pH was 6.4 SU.

The treatment procedure placed 10.0 g of as received soil in a container with 200 mL of blended groundwater to achieve a nominal liquid to solid ratio of 20 to 1<sup>2</sup>. The samples were not dried prior to use to minimize potential geochemical changes drying may cause. The samples were then tumbled for approximately 16 to 18 hours, filtered at 0.7  $\mu\text{m}$  and acidified prior to analysis by USEPA Method 6010B at CT Laboratories, Baraboo, Wisconsin.

The remediation had to reduce aqueous zinc concentrations using reagents that were amenable to injection. Two approaches were considered:

- Zinc sequestration as a hydroxide [ $\text{Zn}(\text{OH})_2$ ] can achieve the necessary concentration reductions with an increase of pH from the acidic site conditions to pH values in the range of 8 to 10 SU (Cortina et al., 2003). AquaMag<sup>®</sup>, a commercial magnesium hydroxide [ $\text{Mg}(\text{OH})_2$ ] slurry, was selected as a pH buffer for zinc stabilization. A comparable approach was evaluated by Cortina and others (2003) in column experiments using granular magnesium oxide [ $\text{MgO}$ ] that formed a layer of  $\text{Mg}(\text{OH})_2$  on the  $\text{MgO}$  when placed in the column. They found that reagent would maintain a pH on the order of 8.5 to 10.0 SU and zinc concentrations would be reduced from 75 mg/L to less than 0.04 mg/L for 100's of pore volumes.
- Zinc can also be sequestered as a zinc sulfide mineral [ $\text{ZnS}$ ] to low aqueous concentrations (Ayres, et al., 1994; Langmuir et al., 2003). Sulfide application is commonly used in waste water treatment systems as calcium polysulfides [ $\text{CaS}_x$ ]. The material has a very high pH and has the potential to create hydrogen sulfide odors. A slurry consisting of native sulfur and a pH buffer would produce polysulfides after injection (and thereby mitigate potential odor issues) was also evaluated.

The results of the treatment trials are presented in Table 2. The untreated soil leached with groundwater produced 14,700  $\mu\text{g/L}$  of zinc. Addition of all three reagents produced comparable results, with leachable zinc concentrations reduced by more than 99.9 percent. The sulfur-based reagents both increased the pH of the leachate to levels that could have formed  $\text{Zn}(\text{OH})_2$ , therefore we cannot be certain as to the degree to which the zinc was sequestered as hydroxide or sulfide minerals.

Following a review of the data presented above, a consensus was reached between Environmental Alliance and ReSolution Partners that AquaMag should be carried forward into a multiple groundwater leaching test to evaluate the long-term stability of the treatment when exposed to site groundwater.

A sample of soil treated with a 2 weight percent (wt %) dose of AquaMag was exposed to a 200 to 1 liquid to solid ratio applied in a single step. The pH of the extracted liquid was 7.5, and the zinc concentration was 8.1 mg/L. This result was well above a concentration in groundwater that was felt to be protective of the surface water quality standard between 0.1 and 0.2 mg/L. The multiple extractions were therefore carried out at a 4 wt % dose of AquaMag to improve upon the longevity of the buffering capacity. A 20 to 1 groundwater to solids ratio was used

<sup>2</sup> Based on the one sample of soil tested for moisture content, the liquid to solid ratio based on dry soil weight was on the order of 27 to 1 for the treatment trials.

Table 1. Groundwater chemistry.

Total Analytes (mg/L unless noted otherwise)	MW-3A	MW-12	Average
pH (SU)	5.35	5.35	5.35
Calcium	18.8	50.5	34.7
Magnesium	10.3	17.2	13.8
Sodium	25.6	29.1	27.4
Potassium	2.45	2.29	2.37
Iron	4.82	1.01	2.92
Manganese	2.66	3.36	3.01
<b>Zinc</b>	<b>29.0</b>	<b>7.37</b>	<b>18.2</b>
Alkalinity, as CaCO <sub>3</sub>	37.4	47.2	42.3
Sulfate	71.9	97.8	84.9
Chloride	67.7	93.7	78.7
Nitrate	2.5	1.5	2.0

Table 2. Bench-scale reagent evaluation.

Reagent Dose	Leached Zinc (µg/L)	Final pH (SU)
0	14,700	7.4
2 wt % Mg(OH) <sub>2</sub>	12.3	10.2
2 wt% CaS <sub>x</sub>	39.2	9.1
4 wt% buffered S	9.5	11.1

for each of 10 sequential extractions in which the initial treated aquifer mass was retained and leached repeatedly. The results are summarized in Table 3. Repeated leaching of 10 g of treated aquifer material with a cumulative 2,000 g of groundwater slowly reduced the pH of the resulting solution from 9.7 to 8.6 SU. The zinc concentrations were not detectable in the first extraction, a reduction of greater than 99.97 percent. Zinc concentrations rose to 0.088 mg/L as the pH slightly declined to 8.6 SU. The final zinc concentration still represented a 99.40 percent decrease over the initial concentrations and is still well below the 2.0 mg/L goal. The sequential extractions were estimated to be equivalent to about 400 years of leaching at the site groundwater flow rate.

Treated groundwater will discharge to the stream that leaves the site. The initial pH of the treated aquifer and groundwater is above the 8.5 pH surface water quality criterion. The stream contains a mixture of groundwater and surface water. The titration of a surface water sample collected from location SG-3 (pH of 6.9 SU) using treated groundwater (pH of 9.8 SU) demonstrated that the surface water pH criterion was not exceeded until about equal volumes of groundwater and surface water were mixed. The discharge of the groundwater would have to more than double the stream flow across the site before the pH criterion is exceeded.

## 5. PILOT-SCALE TESTING

ReResolution Partners and Redox Tech mobilized to the site in September 2006 to perform a pilot test designed to determine the feasibility of injecting AquaMag to create an in situ treatment barrier. The test was conducted on the south side of the site in the immediate vicinity of monitoring well MW-3A (Figure 1). This location was selected due to the relatively high zinc concentrations previously identified in the groundwater in MW-3A and its accessibility.

Soil borings and temporary 1-inch diameter PVC wells advanced by direct push techniques were installed and sampled prior to slurry injection (Figure 2). Filtered groundwater samples were collected MW-3A and the temporary wells using a peristaltic pump. The temporary wells were removed and all boreholes were plugged with bentonite to minimize potential short circuiting through the boreholes during slurry injection. Following the completion of the injection, five additional borings and two temporary monitoring wells were advanced to evaluate the effects of the reagent injection (Figure 2). Well MW-3A was also re-sampled 8 months following the injection. As a planned precautionary measure, the surface water in the unnamed tributary flowing through the culvert along the south edge of the site was sampled at the point the water leaves the culvert. No evidence of direct AquaMag discharge or pH increase in the stream was observed.

Approximately 7.3 tons (1,100 gallons) of AquaMag as a 61 weight percent aqueous suspension of magnesium hydroxide  $Mg(OH)_2$ , was delivered in drums and staged in the parking lot near the test site. Potable water used to make up the injection solution to yield the equivalent of a 2 wt % dose was obtained from the site maintenance facility. Injections were completed through 1.5-inch direct-push tooling advanced with a truck-mounted Geoprobe 6600. A 1.5-inch drive tool was advanced to 20 feet and pulled back to 19, 16, 13, and 11 feet for injections in the same borehole. A support trailer with a 550-gallon tank and two air-driven diaphragm pumps

was used to mix the AquaMag with potable water and inject the solution through the downhole tooling.

Table 3. Multiple groundwater extraction results.

Extraction Number	Post-Extraction pH (SU)	Zinc Concentration ( $\mu\text{g/L}$ )
Untreated	7.4	14,700
1	9.7	<4.00
2	9.7	5.70
3	9.2	5.90
4	8.8	12.0
5	8.6	17.2
6	8.6	9.4
7	8.6	13.8
8	8.6	23.9
9	8.5	46.8
10	8.6	88.4

In general, the pilot test area was underlain by silty clay and clay to a depth of 9 to 10 feet below ground surface. Debris (e.g., brick, wood, and rubber fragments) were found to depths of at least 5 feet. Sand with varying amounts of gravel and silt was found below the silty clay. This sand zone was the target of the reagent injections. The analyses of the pre-injection soil samples' average zinc concentrations of 347 mg/kg with a range of 313 to 423 mg/kg. Leachable zinc concentrations ranged from <0.020 to 0.0552 mg/L and averaged 0.0390 mg/L. However, the concentration of <0.020 mg/L appears to be a low outlier, with 5 of 6 samples ranging from 0.0192 to 0.0552 mg/L.

The zinc concentration in MW-3A was 21.2 mg/L and the pH was 4.91 SU. The groundwater samples from the temporary wells (PIB-1 and PIB-2) yielded zinc concentrations about 60 times less than the zinc concentration in MW-3A and the pH was higher (5.71 to 5.79 SU). The well screens of the temporary wells were about 5 feet higher than the MW-3A well screen. It may therefore be possible that the chemistry difference is a result of vertical



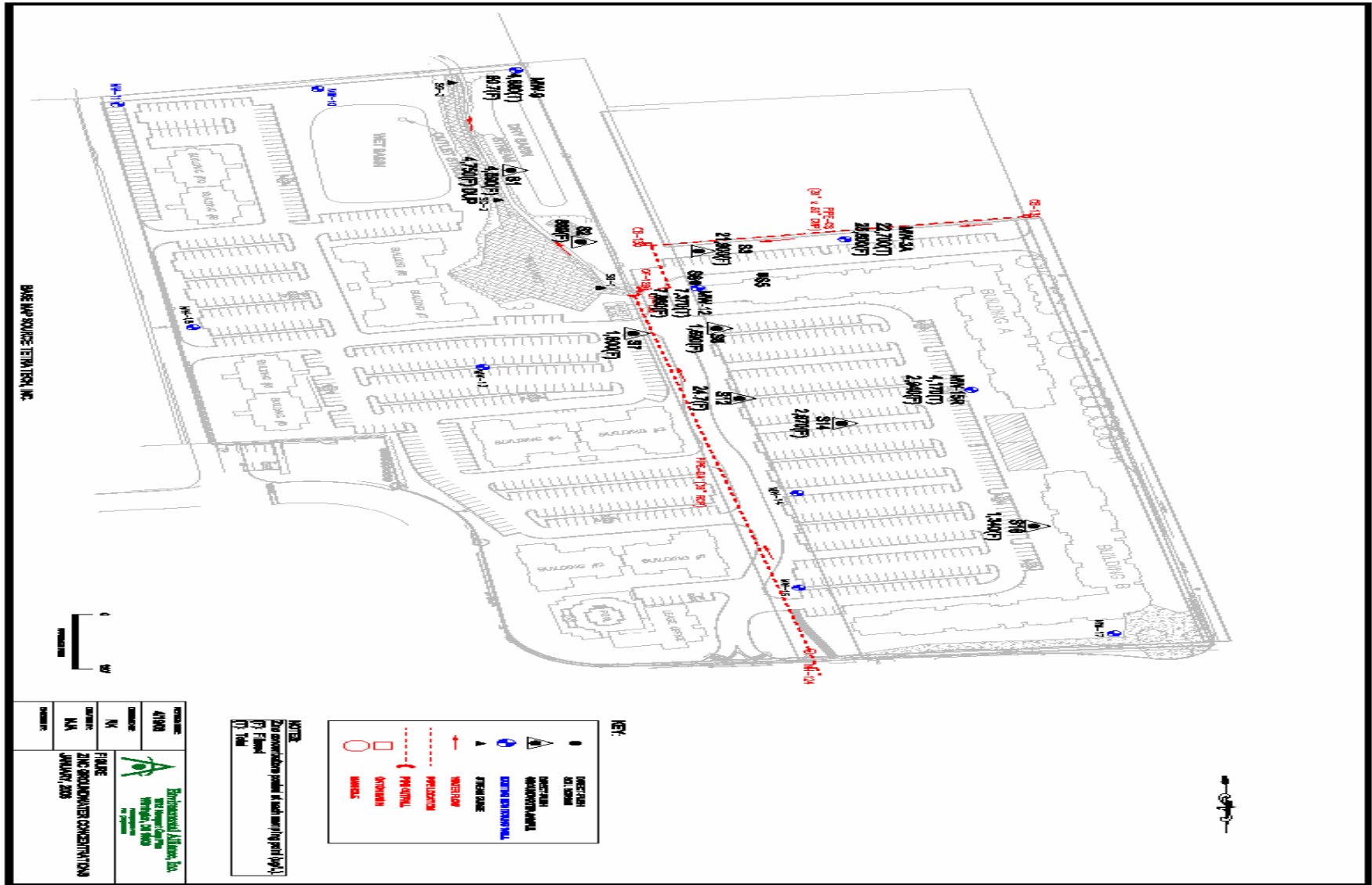


Figure 1. Site map.

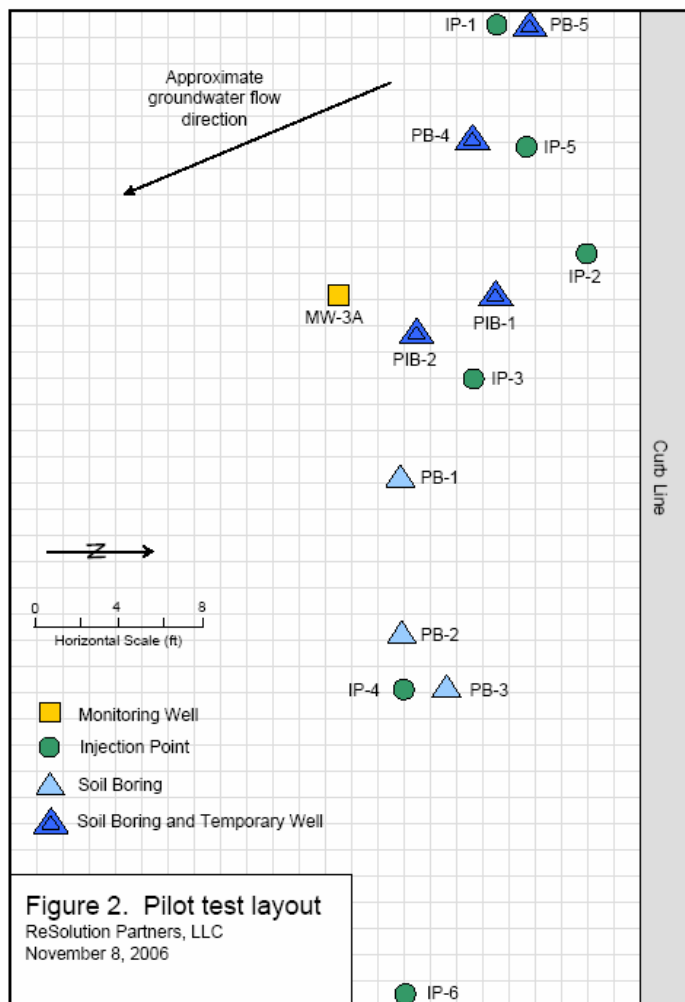


Figure 2. Pilot test map.

stratification of the zinc plume. The borings suggest that the permeability of the soil may increase with depth (i.e., increasing gravel and decreasing silt content). This suggests that zinc was present in a preferential flow zone in the deeper sandier soil.

The plan was to inject the AquaMag into two locations with four injection depths per location. The injection of 4,200 gallons of diluted AquaMag was completed in two days. Injection flow rates were typically on the order of 5 to 10 gallons per minute (gpm) at injection pressures of about 20 to 40 pounds per square inch (psi). Injected volumes ranged from 30 to 550 gallons per interval due to break-through of the injection solution at the ground surface. A total of six injection points were advanced to complete the test. Some of the breakthroughs occurred at the boreholes advanced prior to the injection. These could often be plugged by driving 3-in diameter direct push tools into the original 2-in diameter boreholes. However there were also breakouts at locations not associated with earlier borings these could not be plugged and resulted in the cessation of injection.

The portion of the area immediately upgradient of monitoring well MW-3A received about 66-percent of the total injection with approximately 240 tons of soil receiving a 2 wt % of reagent. The shallowest injection zones received the lowest doses because of slurry discharge at the ground surface. However, if the hypothesis that the zinc plume is mostly at depth is correct, the incomplete injection at shallower depths should have little effect on the performance of the remedy as measured at MW-3A.

Soil borings were advanced approximately 10 feet, 3 feet, and 2 feet from the injection locations to evaluate the distribution of treatment reagents in the soil. Visual observations and soil pH measurements found evidence of the injection in discrete thin seams. The pH at the seams was between 9 and 10 SU and a "halo" of pH greater than 7 SU commonly extended about 1 foot from the seam (compared to untreated soil pH that ranged from 5.5 to 6.5 SU). The AquaMag seams were no thicker than 0.03 ft. Soil samples from PB-4 and PB-5 for laboratory analyses were compared to the pre-injection data from borings PIB-1 and PIB-2, the average magnesium concentrations approximately doubled as a result of the injections but the concentration range was comparable to the pre-injection levels of about 2,600 mg/kg to as high as 11,800 mg/kg. This is consistent with the visual observations and pH screening that indicates the reagent distribution is spatially heterogeneous. Temporary wells in post-injection borings PB-4 and PB-5 found the post injection groundwater pH at 8.00 and 8.94 SU. The bench scale testing indicated that pH values in this range would result in zinc precipitation. This was confirmed by the field results where the zinc concentrations determined by the laboratory analyses of two groundwater samples were <0.020 and an estimated 0.0094 mg/L. The post-injection groundwater sample results from PB-4 and PB-5 indicated successful treatment of the groundwater in these locations.

The post-injection results of the monitoring well MW-3A re-sampling are summarized in Table 4. Within about two weeks following the injections, the pH began to increase at the monitoring wells and the zinc concentration decreased from 21.4 to 8.44 mg/L. From October 2006 through February 2007 the pH rose slowly and the zinc concentrations decreased slowly. From February to May 2007 the pH rose by 2.5 SU to 9.3 SU and the zinc concentration fell by 650 percent to 0.986 mg/L.

Table 4. Post-injection groundwater chemistry.

Sample Date	Zinc (mg/l)	pH (SU)
9/28/2006	21.4	5.0
10/12/2006	8.44	5.7
10/27/2006	6.54	6.5
11/22/2006	5.74	7.0
12/20/2006	7.87	5.8
1/25/2007	7.63	6.1
2/12/2007	6.43	6.8
3/9/2007	4.68	7.6
4/13/2007	0.614	8.6
5/10/2007	0.986	9.3
6/13/07	6.60	8.2
8/10/07	13.2	6.2

In spite of the apparent heterogeneous spatial distribution of AquaMag suggested by the post-injection soil borings, the groundwater results from the monitoring well downgradient of the injection area clearly shows a decrease in the dissolved zinc concentrations through the first nine months of treatment as a result of the injections. On the basis of this performance the regulatory agency approved the full-scale implementation of an IRB upgradient of the surface water receiving the zinc-bearing groundwater.

A rebound of the zinc concentrations (and lower pH) was observed since May 2007. This increase suggests that the limited spatial distribution and dose applied during the pilot test may be affected by the continued flux of acidic and zinc-bearing groundwater. Additional injections were planned in the area of the pilot test as part of the full-scale remedy.

## **6. FULL-SCALE IMPLEMENTATION**

Approval for the full-scale implementation of the remedy was received on 25 July 2007. Vironex, Inc. was retained by Environmental Alliance to provide injection services. Site preparation including staging area construction, utility clearance, and additional monitoring well installations began the first week of August and injection began on 6 August.

An estimated total of 35,000 gallons of undiluted reagent was successfully injected into the zinc treatment barrier (Figure 3). An estimated total volume of 45,000 gallons of diluted and undiluted reagent was injected on-site in 63 injection locations. The injections were performed over a 4-week period. Groundwater monitoring will continue for a period of 2 years.

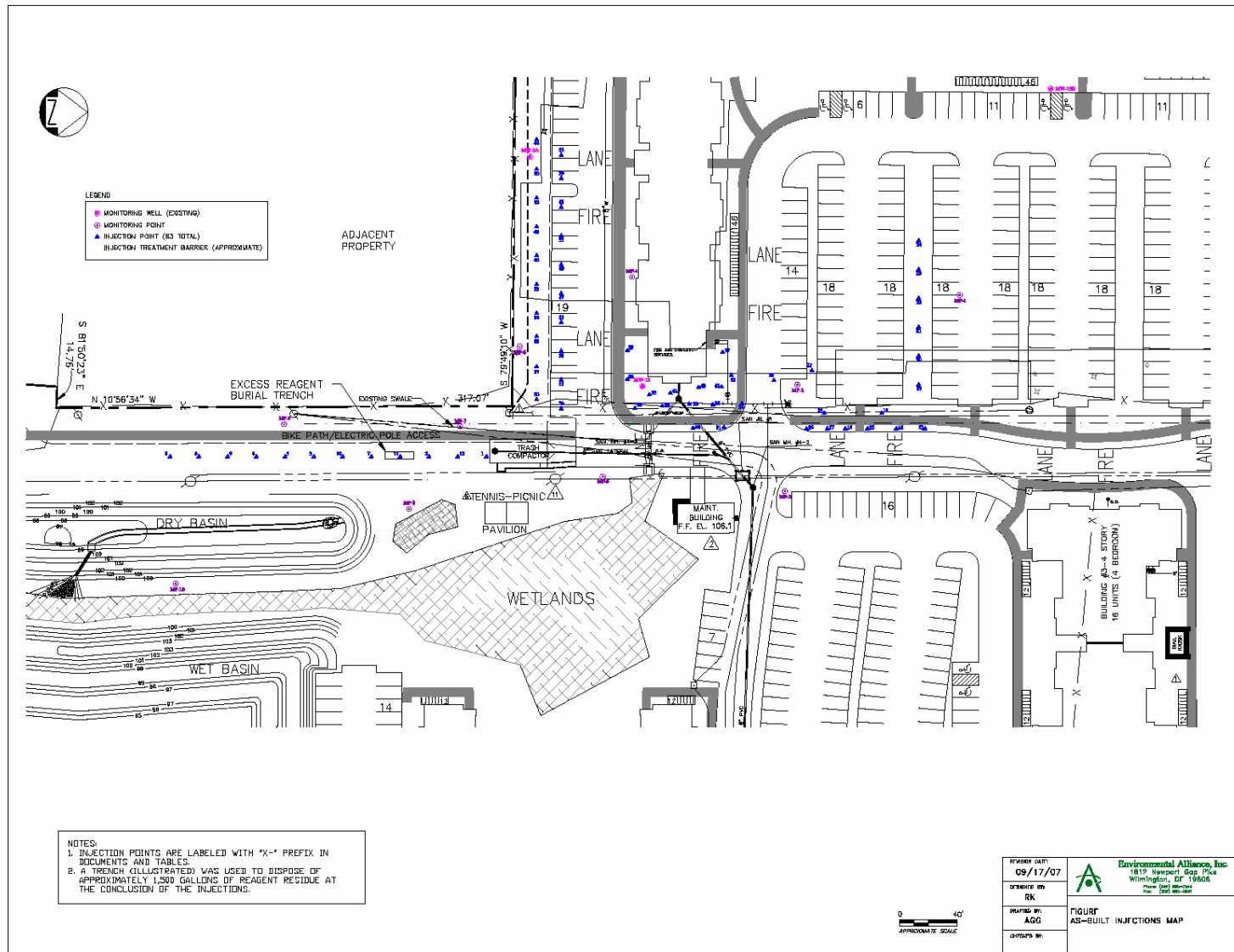


Figure 3. Full-scale injection locations.

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