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TECHNICAL MEMORANDUM FOR FOCUSED TECHNOLOGY SCREENING FOR CHLORINATED ORGANIC CONTAMINATION IN GROUNDWATER NIROP FRIDLEY MN
4/12/2000
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TECHNICAL MEMORANDUM

FOCUSED TECHNOLOGY SCREENING FOR CHLORINATED ORGANIC CONTAMINATION IN GROUNDWATER ANOKA COUNTY PARK NAVAL INDUSTRIAL RESERVE ORDNANCE PLANT FRIDLEY, MINNESOTA

On April 12 and 13, 2000, a technical subcommittee met to discuss issues related to environmental cleanup at Naval Industrial Reserve Ordnance Plant (NIROP) Fridley. The subcommittee included members of the Minnesota Pollution Control Agency (MPCA), the United States Environmental Protection Agency (USEPA), the Southern Division Naval Facilities Engineering Command (SOUTHDIV), and two NavyCLEAN contractors: Tetra Tech NUS, Inc. (TtNUS) and CH2MHill. Among the issues discussed was an area of trichloroethene (TCE)-contaminated groundwater underneath Anoka County Park. This technical memorandum presents a focused technology screening for remediation of the TCE contamination. The final recommendation is to implement anaerobic bioremediation with vegetable oil or cometabolic processes. Treatability studies should be conducted to compare and contrast the two technologies. If the schedule or funding is limited, it is recommended that the Navy implement anaerobic bioremediation with vegetable oil.

In order to address the groundwater contamination, the subcommittee identified the following objectives: 1) to achieve the regulatory standard (MCL) of 5 ug/l of TCE at the point of compliance - the Mississippi River, and 2) to achieve overall reduction of contaminant mass. A secondary objective is to gather sufficient technology information to evaluate alternative solutions for the TCE source area underneath the NIROP Fridley building. In the meantime, this source area will be addressed with a new groundwater extraction well, the existing extraction well containment system, and on-site treatment at the existing groundwater treatment plant. In addition to the objectives, the following considerations were identified:

- Overall cost
- Cost versus reduction of contamination
- Schedule
- Impacts to the park; security requirements
- Requirements for permitting variances from the State of Minnesota
- Utility requirements in the park; technology constructability
- Climate – groundwater temperature ranges from 11 to 14 degrees Celsius
- Remediation breakdown/residual products and their impacts on the Mississippi River
- Drought conditions in Minnesota are affecting groundwater levels
- The ability to deliver reagents
- Capture of the upgradient plume
- The UDLP plume and its impacts on Anoka County Park

The subcommittee discussed the feasibility of implementing numerous remedial technologies at Anoka County Park. Based on this discussion, a list of potentially applicable technologies was finalized. The list includes the following in situ technologies:

1. Chemical Oxidation
   - Fenton's Reagent (hydrogen peroxide applied with an iron catalyst)
   - Potassium Permanganate

2. Enhanced Anaerobic Bioremediation
   - Slow-releasing Substrates: Hydrogen Releasing Compound (HRC)/Vegetable Oil
   - Metered Substrates: Molasses/Lactic Acid

3. Cometabolic Processes

TtNUS, Inc. was tasked with conducting a focused screening of these potentially applicable technologies. This technical memorandum presents the focused screening, which includes a technical description of each technology followed by an evaluation of the technology and its applicability at Anoka County Park. The evaluation is conducted using three generalized criteria: effectiveness, implementability, and cost. Section 1.0 addresses chemical oxidation, Section 2.0 addresses anaerobic bioremediation, and Section 3.0 addresses cometabolic processes. Section 4.0 recommends the most appropriate technology/technologies and proposes a plan of action. Section 5.0 provides a list of references.

Description of the TCE Contamination

The TCE contamination was investigated during the Remedial Investigation at NIROP Fridley (TtNUS, 1999) and during subsequent sampling for the Annual Monitoring Report (TtNUS, 2000). Figures 1 and 2 present isoconcentration contours for TCE in the shallow and intermediate aquifers, respectively. As shown, the contamination exists in an area where a groundwater mound is present. The center of the TCE contamination flows outward in a radial direction towards the west (Mississippi River), south, and east. The maximum concentration detected in the shallow aquifer was 18,000 ug/l. The maximum concentration detected in the intermediate aquifer was 1,600 ug/l.

The geochemistry at Anoka County Park indicates that the shallow aquifer is marginally aerobic and the intermediate aquifer is marginally anaerobic. In the shallow aquifer, the dissolved oxygen concentration is 1.5 mg/l, which only slightly exceeds the indicator of 0.5 mg/l for aerobic conditions. Thus, the shallow aquifer appears to be slightly aerobic. In the intermediate aquifer, the dissolved oxygen concentration is 0.3 mg/l, which is less than 0.5 mg/l, indicating anaerobic conditions. In addition, there is evidence of iron and manganese reduction in the intermediate aquifer, which further supports the existence of marginally anaerobic conditions. More detailed geochemical information is located in the Field Investigation Report (TtNUS, 2000).

1.0 CHEMICAL OXIDATION

Chemical oxidation is a technology that is widely used for the treatment of wastewater and drinking water. In situ chemical oxidation involves the injection of chemical oxidants into a contaminated aquifer. The oxidants break down organic chemical bonds forming simpler organic compounds, which are then oxidized to carbon dioxide, water, and ferric or manganese salts. The primary oxidation reaction is:

Oxidant + Organic Compound → Reduced Oxidant + CO_2 + H_2O

The final oxidation products are generally benign in the subsurface (BEM and ENSR, 2000).

This memo will evaluate the in situ application of two chemical oxidants: Fenton's reagent and potassium permanganate ($KMnO_4$).

1.1 Fenton's Reagent

Fenton's reagent was developed in the late 19th century. The reagent is a chemical solution of dilute hydrogen peroxide and ferrous iron. The iron acts as a catalyst to increase the oxidation potential of the hydrogen peroxide. This results in the generation of highly reactive hydroxyl radicals. These radicals react with organics to create water, carbon dioxide, oxygen, and dilute hydrochloric acid as by-products. The following reactions describe the process:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + 2HO^-$$
$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + HO^-$$
$$H_2O_2 + HO^\bullet \rightarrow H_2O + HO_2^\bullet$$
$$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^\bullet \Leftrightarrow H_2O_2$$
$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + H^+ + O_2$$
$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + H^+ + O_2$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+$$

The hydroxyl radicals are then available to react with the organic compounds as described below (BEM and ENSR, 2000):

$$RH + HO^\bullet \rightarrow R^\bullet + H_2O$$
$$R^\bullet + H_2O_2 \rightarrow ROH + HO^-$$
$$R^\bullet + HO^\bullet \rightarrow ROH$$
$$2R^\bullet \rightarrow R\text{-}R$$
$$R^\bullet + Fe^{3+} \rightarrow Fe^{2+} + R$$
$$R^\bullet + Fe^{2+} \rightarrow Fe^{3+} + RH$$

The following sections evaluate the effectiveness, implementability, and cost of implementing in situ chemical oxidation with Fenton's reagent at the Anoka County Park site.

1.1.1 Effectiveness

- Based on bench scale studies, chemical oxidation with Fenton's reagent is effective at reducing chlorinated organic concentrations. The reagent completely oxidizes chlorinated ethenes such as TCE.
- Chemical oxidation may increase the rate of solubilization of dense non-aqueous phase liquids (DNAPLs) because the oxidation reaction occurs at the aqueous phase/DNAPL boundary.
- The treatment processes take place underground and will not significantly disrupt park activities.
- In situ chemical oxidation is a relatively new technology that is not well-demonstrated.

- The ability to distribute the reagent throughout the aquifer is critical to the success of this technology..
- The most favorable temperature range is 20 to 40 degrees Celsius (BEM and ENSR, 2000). At Anoka County Park, the temperature is 14.8°C in the shallow and 11.7°C in the intermediate, which is not ideal.
- The most effective pH range is 3-6, which is moderately acidic. At Anoka County Park, the pH is 7.38 in the shallow and 7.19 in the intermediate, which is not ideal.
- If the aquifer is altered to lower pH, its acidic nature could mobilize metals.
- The reagent will remove almost all organics through oxidation and carbonates through pH reduction. However, this will reduce the structural stability of the soil, which is a concern at a public park.
- Due to its radical nature, the technology is most effectively applied to small volumes of very highly contaminated groundwater. At Anoka County Park, the volume of contaminated groundwater is relatively large.
- The effectiveness depends on the availability of unchelated iron, which is difficult to maintain because of the chelating properties naturally occurring in soil and groundwater.
- Formation of gas bubbles may reduce the movement of liquid (liquid-phase oxidants and groundwater) through the formation. The gaseous end-products of the oxidation reaction occupy a portion of the void space within the saturated zone, hence decreasing the effective permeability of the soil.
- There is a potential for chemical oxidation to destroy indigenous microorganisms. This will complicate the implementation of bioremediation as an alternative technology in the event that chemical oxidation is ineffective.
- There is a potential to alter contaminant flow patterns and redistribute contaminant concentrations within less impacted areas of the plume.
- Chemical oxidation is likely to meet scheduling requirements. The treatment time is expected to be between 3 months and one year.

1.1.2 Implementability

- Fenton's reagent is an explosive chemical. Security measures must be enforced because the site is a public park. In addition, stabilizers may be required as an additional injection component to reduce the volatility.
- Prior to injection, aboveground mixing of the Fenton's reagent will be required. This will require safety measures and temporarily disrupt park activities.
- The oxidant will be injected using direct push technology. This technology may be implemented with minimal disturbances to the site and the park activities. The park is readily accessible to direct push installation equipment.
- Once injected, operation and maintenance (O&M) is relatively easy. The treatment processes occur underground. There is no aboveground equipment to operate or maintain. Groundwater sampling will be required.
- Based on bench-scale studies, several injections of Fenton's reagent may be required compared to potassium permanganate (BEM and ENSR, 2000).
- If the Fenton's reagent adversely affects the soil stability at Anoka County Park, major earthwork could be required.
- Bench and pilot scale treatability studies should be conducted.
- Permitting variances from the State of MN will be required.
- A thorough monitoring program will be required to evaluate the technology's effectiveness. This could involve the installation of additional monitoring wells at Anoka County Park.

- Reagent mixing and injection requires more above ground processes and equipment than permanganate.

1.1.3 Cost

- Capital costs are moderate.
- O&M costs are low to moderate, depending on the number of applications required.
- Reagent costs are $1.30/lb (vendor quote).
- A pilot scale study for Fenton's reagent was $105,000; its counterpart, a pilot scale study for potassium permanganate, was $110,00 (BEM and ENSR, 2000).

1.2 Potassium Permanganate

Chemical oxidation using potassium permanganate ($KMnO_4$), involves the reduction of manganese as follows:

$KMnO_4^- + 8H + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Examples of oxidation reactions using $KMnO_4$ are:

Divalent Manganese: $3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_{2(s)} + 4H^+$

Divalent Fe^{2+}: $3Fe^{2+} + MnO_4^- + 4H \rightarrow MnO_{2(s)} + 3Fe^{3+}{}_{(s)} + 2H_2O$

Hydrogen Sulfide H_2S: $3H_2S + 4MnO_4^- \rightarrow 2SO_4^{2-} + S^0 + MnO_{2(s)} + 3MnO_{(s)} + 3H_2O$

The heptavalent state of the manganese is thus reduced to the divalent state. The electrons are transferred from the organic compounds to the manganese ions, using water as a transfer medium (BEM and ENSR, 2000).

The following sections evaluate the effectiveness, implementability, and cost of implementing in situ chemical oxidation with potassium permanganate at the Anoka County Park site.

1.2.1 Effectiveness

- Based on bench scale studies, chemical oxidation with potassium permanganate is effective at reducing chlorinated organic concentrations. The reagent completely oxidizes chlorinated ethenes such as TCE.
- Chemical oxidation may increase the rate of solubilization of DNAPLs because the oxidation reaction occurs at the aqueous phase/DNAPL boundary.
- Both aqueous and non-aqueous liquid media can accommodate permanganate oxidation.
- The treatment processes take place underground and will not significantly disrupt park activities.
- In situ chemical oxidation is a relatively new technology that is not well-demonstrated.
- The ability to distribute the reagent throughout the aquifer is critical to the success of this technology.
- The source material for potassium permanganate is an ore that may contain impurities. The ore may contain metals such as manganese and chromium that could further contaminate the aquifer.

- Potassium permanganate has a high solubility in water. This should facilitate its movement with the groundwater into remote portions of the aquifer.
- Using potassium permanganate, many reaction paths are available to achieve oxidation. In addition, many oxidation states are available to manganese, which range from divalent to heptavalent states.
- Potassium permanganate will not persist in the subsurface environment. The breakdown products of the oxidation reaction should be readily neutralized by the soil.
- Unlike Fenton's reagent, potassium permanganate appears to be effective at a wide range of temperatures. The reagent successfully treated TCE at a U.S. Army Corps of Engineers Hanover site where the average temperature is 7°C. At Anoka County Park, the temperature is 14.8°C in the shallow aquifer and 11.7°C in the intermediate aquifer.
- Unlike Fenton's reagent, potassium permanganate is effective at a wide range of pH levels.
- Formation of gas bubbles may reduce the movement of liquid (liquid-phase oxidants and groundwater) through the formation. The gaseous end-products of the oxidation reaction occupy a portion of the void space within the saturated zone, hence decreasing the effective permeability of the soil.
- There is a potential for chemical oxidation to destroy indigenous microorganisms. This will complicate the implementation of bioremediation as an alternative technology in the event that chemical oxidation is ineffective.
- There is a potential to alter contaminant flow patterns and redistribute contaminant concentrations to less impacted areas of the plume.
- Chemical oxidation is likely to meet scheduling requirements. The treatment time is expected to be between 3 months and one year.

1.2.2 Implementability

- Security measures will be required at Anoka County Park, but they will not be as critical as those required with Fenton's reagent. Fenton's reagent is far more volatile than potassium permanganate. In addition, potassium permanganate may be transported and handled without significant safety concerns.
- Compared to Fenton's reagent, preparation and injection of the permanganate will require less aboveground equipment.
- Injection of the permanganate will temporarily disrupt park activities.
- The oxidant will be injected using direct push technology. This technology may be implemented with minimal disturbances to the site and the park activities. The park is readily accessible to direct push installation equipment.
- Once injected, O&M is minimal. The treatment processes occur underground. There is no aboveground equipment to operate or maintain. Groundwater sampling will be required.
- Based on bench-scale studies, several injections of Fenton's reagent may be required compared to potassium permanganate (BEM and ENSR, 2000).
- The reaction rate may be increased by introducing an alcohol or surfactant that will increase the solubility of the chlorinated compound in water.
- Bench and pilot scale treatability studies should be conducted.
- Permitting variances from the State of MN will be required.
- A thorough monitoring program will be required to evaluate the technology's effectiveness. This could involve the installation of additional monitoring wells at Anoka County Park.

1.2.3 Cost

- Capital costs are moderate. The cost of potassium permanganate is higher than the cost of Fenton's reagent.
- O&M costs are low.
- Treatment costs are expected to be on the order of $16-23/cubic yard (vendor quote).
- A pilot scale study for Fenton's reagent was $105,000; its counterpart, a pilot scale study for potassium permanganate, was $110,00 (BEM and ENSR, 2000).
- A pilot scale study for potassium permanganate involving 2 injection points and 3 days of operation cost $45,000. The site was the Former News Publisher Facility in Framinham, MA (USEPA, 1998).
- A pilot and full scale study cost $235,000 at an Active Industrial Facility in Clifton, NJ (USEPA, 1998).

2.0 ENHANCED ANAEROBIC BIOREMEDIATION

Bioremediation involves the use of microorganisms to break down hazardous organic contaminants into non-toxic or less toxic forms. Enhanced bioremediation attempts to accelerate subsurface biodegradation processes by providing nutrients, electron acceptors, competent degrading microorganisms, and substrates for existing microorganisms that may otherwise be limiting the rapid conversion of contaminants.

Chlorinated organics primarily degrade through anaerobic processes, which occur in an oxygen-deficient environment. Anaerobic bacteria may use nitrate, sulfate, salts of iron III, or carbon dioxide as electron acceptors. The following reactions describe the anaerobic processes (Chapelle, 1996):

Nitrate Reduction: $4NO_3 + 4H^+ + 5CH_20 \rightarrow 4NO_2 \rightarrow 2N_2 + 5CO_2 + 7H_2O$

Iron III Reduction: $4Fe(OH)_3 + CH_2O + 8H^+ \rightarrow 4Fe^{2+} + CO_2 + 11H_20$

Sulfate Reduction: $2CH_2O + SO_4^{2+} + H^+ \rightarrow 2CO_2 + HS^- + 2H_20$

Methanogenesis: $2CH_2O \rightarrow CH_4 + CO_2$

The injection of substrates into the contaminated aquifer will provide a carbon energy source for anaerobic microorganism growth, thereby stimulating the degradation of TCE. Two types of substrates will be considered: slow-releasing substrates such as HRC or vegetable oil, and metered substrates such as lactic acid and molasses. The slow-releasing substrates are injected into the aquifer in single doses and gradually release in the subsurface. The metered substrates are released on a continuous basis from metered equipment located aboveground. The metered substrates are not capable of gradually releasing over time in the subsurface.

The following sections evaluate the effectiveness, implementability, and cost of using HRC/vegetable oil and lactic acid/molasses at Anoka County Park.

2.1 HRC/Vegetable Oil

2.1.1 Effectiveness

- Based on the geochemistry, both the shallow and intermediate aquifers have the potential to be driven towards an anaerobic environment in the presence of an appropriate substrate. As a result, enhanced anaerobic bioremediation should be an effective treatment solution.
- HRC and vegetable oil provide a carbon source that anaerobic microorganisms will consume, thus driving the natural anaerobic degradation of contaminants.
- Anaerobic bioremediation is effective for the degradation of chlorinated ethenes and ethanes.
- The treatment processes take place underground and will not significantly disrupt park activities.
- Anaerobic bioremediation will occur at a wide range of temperatures. However, lower temperatures will make the process proceed at a slower rate. At Anoka County Park, the aquifer temperatures are likely to slow the biodegradation process.
- In situ bioremediation involves a natural environmental cleanup solution that should be generally acceptable to the public.
- Applications of HRC and vegetable oil are time-releasing and long-lasting in the subsurface. Compared to using molasses or lactic acid, fewer injections of HRC and vegetable oil will be required.
- HRC and vegetable oil are readily degradable by a large number of microorganisms.
- HRC is a patented substrate sold by Regenesis. Vegetable oil is a common food substance that may be obtained from many sources.
- Vegetable oil has a high energy content.
- When mixed with water, vegetable oil forms small droplets. In a soil matrix, these droplets become trapped on the soil particles and form an organic filter. Organics in the groundwater partition into the oil as the contaminant plume passes the "filter", depending on the relative affinity of the contaminant for the oil. Thus, the oil concentrates or strips the organics, in addition to providing a carbon source for microorganisms.
- Vegetable oil may be emulsified to increase its effectiveness.
- Methanogens compete with reductive dehalogenators for the use of hydrogen. The methanogens use the hydrogen for conversions to methane and carbon dioxide. The methanogens are more competitive at higher doses of hydrogen. Slow-release compounds (i.e., HRC and vegetable oil) will keep hydrogen levels low, favoring reductive dehalogenators.
- An HRC Case Study from a site in New York indicated a 67% reduction in mass of TCE in groundwater after 273 days of treatment (Regenesis).
- An HRC Case Study from a site in Hurlburt Field, Florida indicated a 71% reduction in mass of TCE in groundwater after 103 days of treatment (Regenesis).
- Delivery of the HRC or vegetable oil to all portions of the contaminated aquifer is crucial to the effectiveness of treatment. The hydraulic travel time for delivery of nutrient could be a limiting factor.
- HRC and vegetable oil are relatively new technologies that are not well-demonstrated.
- Anaerobic TCE dechlorination produces cis 1,2-DCE, and vinyl chloride, which are toxic by-products.
- As TCE degrades, it forms vinyl chloride, which degrades under aerobic conditions. ORC may be necessary following HRC treatment, depending on the vinyl chloride levels that are produced.

- If concentrations of H_2 are high, reductive dechlorination will be relatively efficient leading to the sequential dechlorination of PCE to TCE to DCE to vinyl chloride to ethylene. Conversely, if H_2 concentrations are low, reductive dechlorination will be relatively inefficient and may lead to dechlorination only as far as vinyl chloride or DCE (Chapelle, 1996).
- HRC and vegetable oil are most effective on dissolved phase plumes and the associated hydrophobically sorbed contaminant. They are not necessarily effective for free-phase DNAPL.
- High contaminant concentrations may be toxic to microorganisms.

2.1.2 Implementability

- HRC and vegetable oil provide a constant, steady hydrogen source. As a result, O&M is less compared to substrates that require repeated or continuous injections (i.e., molasses and lactic acid).
- The substrate will be injected using direct push technology. This technology may be implemented with minimal disturbances to the site and the park activities. The park is readily accessible to direct push installation equipment.
- Once injected, O&M is minimal. The treatment processes occur underground. There is no aboveground equipment to operate or maintain. Groundwater sampling will be required.
- The oil can be injected into the appropriate location at or below the contamination, or it can be pooled on the surface and permitted to percolate down to the contamination.
- Bench and pilot scale treatability studies should be conducted.
- Permitting variances from the State of MN will be required.
- A thorough monitoring program will be required to evaluate the technology's effectiveness. This could involve the installation of additional monitoring wells at Anoka County Park.

2.1.3 Cost

- Capital costs are moderate.
- O&M costs are low.
- Since enhanced bioremediation is a passive, in situ technology, O&M and capital costs are less than an actively engineered treatment technology.
- Typical treatment costs range from $20 to $80 per cubic yard.
- HRC cost is $6/lb required; the application rate is 5 lbs per vertical foot (Regenesis vendor quote).

2.2 <u>Lactic Acid/Molasses</u>

2.2.1 Effectiveness

- Based on the geochemistry, both the shallow and intermediate aquifers have the potential to be driven towards an anaerobic environment in the presence of an appropriate substrate. As a result, enhanced anaerobic bioremediation should be an effective treatment solution.
- Molasses and lactic acid provide a carbon source that anaerobic microorganisms will consume, thus driving the natural anaerobic degradation of contaminants.
- Anaerobic bioremediation is effective for the degradation of chlorinated ethenes and ethanes.
- The treatment processes take place underground and will not significantly disrupt park activities.

- Anaerobic bioremediation will occur at a wide range of temperatures. However, lower temperatures will make the process proceed at a slower rate. At Anoka County Park, the aquifer temperatures are likely to slow the biodegradation process.
- In situ bioremediation involves a natural environmental cleanup solution that should be generally acceptable to the public.
- Applications of molasses and lactic acid require repeated, continuos injections. A metered, engineered aboveground system will be required. HRC and vegetable oil require fewer injections and less complicated aboveground equipment.
- Repeated injection could introduce oxygen into the aquifer, thus working against the anaerobic conditions.
- Molasses and lactic acid are readily degradable by a large number of microorganisms.
- Molasses contains both carbohydrates and sulfates. The molasses carbohydrates mix with the dissolved oxygen in groundwater to form carbon dioxide and water. This results in the formation of anaerobic conditions. As a result of the anaerobic conditions, sulfates present are reduced to form sulfide ions, which then react with heavy metal ions to form a solid precipitate that is eventually filtered out by the soil matrix. The precipitate remains in the subsurface because it is insoluble and harmless.
- Delivery of the molasses and lactic acid to all portions of the contaminated aquifer is crucial to the effectiveness of treatment. The hydraulic travel time for delivery of nutrient could be a limiting factor.
- Molasses and lactic acid are relatively new technologies that are not well-demonstrated.
- Anaerobic TCE dechlorination produces cis 1,2-DCE, and vinyl chloride, which are toxic by-products.
- As TCE degrades, it forms vinyl chloride, which degrades under aerobic conditions. Further aerobic treatment may be required, depending on the vinyl chloride levels that are produced.
- If concentrations of H_2 are high, reductive dechlorination will be relatively efficient leading to the sequential dechlorination of PCE to TCE to DCE to vinyl chloride to ethylene. Conversely, if H_2 concentrations are low, reductive dechlorination will be relatively inefficient and may lead to dechlorination only as far as vinyl chloride or DCE (Chapelle, 1996).
- Molasses and lactic acid are most effective on dissolved phase plumes and the associated hydrophobically sorbed contaminant. They are not necessarily effective for free-phase DNAPL.
- High contaminant concentrations may be toxic to microorganisms.

2.2.2 Implementability

- Compared to HRC and vegetable oil, molasses and lactic acid require aboveground, engineered equipment for repeated/continuous injections. This results in more O&M requirements.
- The substrate will be injected using direct push, temporary geoprobe technology. This technology may be implemented with minimal disturbances to the site and the park activities. The park is readily accessible to direct push installation equipment.
- The oil can be injected into the appropriate location at or below the contamination, or it can be pooled on the surface and permitted to percolate down to the contamination.
- Bench and pilot scale treatability studies should be conducted.
- Permitting variances from the State of MN will be required.
- A thorough monitoring program will be required to evaluate the technology's effectiveness. This could involve the installation of additional monitoring wells at Anoka County Park.

2.2.3 Cost

- Capital costs are moderate.
- O&M costs are moderate.
- Since enhanced bioremediation is a passive, in situ technology, O&M and capital costs are less than an actively engineered treatment technology.
- Like vegetable oil, molasses is inexpensive.

3.0 COMETABOLIC PROCESSES

Cometabolic processes involve the fortuitous metabolic degradation of a contaminant by a microorganism growing on a primary organic substrate (Donofrio, 1999). Under cometabolism, methane and oxygen are injected into an aquifer to stimulate aerobic biodegradation of TCE. The addition of methane to the aquifer encourages the growth of methanotrophic bacteria. Methanotrophs are capable of breaking down TCE in an aerobic environment. Thus, oxygen is injected into the aquifer to enhance aerobic conditions.

Methanotrophs initiate the break down of TCE through oxidation to form an epoxide. (Semprini, et. al., 1991). The epoxide is removed from the bacterial cell and is released into the aquifer where it is metabolized further to form carbon monoxide, formate, glyoxylate, and dichloroacetate. These products are further broken down by methanotrophs and heterotrophs (Henry & Grbic-Galic, 1994). The final breakdown products are stable and non-toxic.

The following sections evaluate the effectiveness, implementability, and cost of implementing cometabolic processes at the Anoka County Park site.

3.1 Effectiveness

- Based on the geochemistry, both the shallow and intermediate aquifers have the potential to be driven towards an aerobic environment. As a result, cometabolism should be an effective treatment solution.
- The treatment processes take place underground and will not significantly disrupt park activities. However, aboveground equipment is required to mix and inject methane and oxygen on a continuous basis.
- Aerobic bioremediation will occur at a wide range of temperatures. However, lower temperatures will make the process proceed at a slower rate. At Anoka County Park, the aquifer temperatures are likely to slow the biodegradation process.
- In situ bioremediation involves a natural environmental cleanup solution that should be generally acceptable to the public.
- Cometabolism appears to be generally acceptable at government sites. It is currently being used at the Naval Ammunitions Site in Hastings, Nebraska and at the Savannah River Site. (Terry Hazen, phone call 4-28-00).
- The aerobic degradation of TCE does not produce toxic daughter products like cis 1,2-DCE and vinyl chloride. Aerobic TCE cometabolism transforms TCE into a TCE epoxide. The TCE epoxide is further broken down into benign products such as carbon dioxide, water, and chloride ions.
- Cometabolism appears to degrade TCE about 10 times faster than anaerobic bioremediation (Terry Hazen, phone call 4-28-00).
- Petroleum contaminants assist the biodegradation rate.

- Time needed to achieve 95% contaminant removal should be less than 4 years.
- Methanotropic bacteria most efficiently degrade chlorinated organics under copper-depleted conditions (Bettencourt, et. Al., 1999). At Anoka County Park, copper concentrations are low: 8.6 ppb in the shallow aquifer and 0.9 ppb in the intermediate aquifer, which is not ideal.
- Cometabolism is most effective under a neutral pH (Bettencourt, et. Al., 1999). At Anoka County Park, the pH is approximately neutral: 7.38 in the shallow aquifer and 7.19 in the intermediate aquifer.
- Separate pulse injections of methane and oxygen prevents their mixing within the well and creating biofouling. Methane and oxygen will mix gradually during transport through the aquifer (Roberts et. Al., 1991).
- Delivery of the cometabolite to all portions of the contaminated aquifer is crucial to the effectiveness of treatment. The hydraulic travel time for delivery could be a limiting factor. Where the subsurface is heterogeneous, it is difficult to circulate the methane solution throughout every portion of the contaminated zone.
- By adding a carbon source to encourage the cometabolic degradation of a specific compound, preferential degradation of the added substrate may inhibit the degradation of the compounds of interest.
- Under anaerobic conditions, sulfate, iron, or nitrate addition to the aquifer may be required to increase the availability of the preferred electron acceptor.
- In an anaerobic aquifer, cometabolism may be applied, but the enzyme systems utilized are dehalogenases rather than the oxygenase systems of the aerobic microorganisms. Accumulation of toxic chlorinated daughter products may become an issue.
- The cometabolites are themselves toxic substances (toluene, phenol, methanol, propane, methane). They are also explosive and corrosive.
- A co-metabolite known as Compound C has been developed by BioRemedial Technologies, Inc. According to the vendor, Compound C is non-toxic, non-corrosive, and non-explosive, unlike other cometabolites.
- Extreme temperatures may inhibit microbial activity.
- High contaminant concentrations may be toxic to microorganisms.

3.2 Implementability

- Methane is an explosive chemical. Security measures must be enforced at Anoka County Park during system operation.
- An aboveground, engineered system will be required to mix and continuously inject the methane and oxygen. This system will disrupt park activities for the duration of the treatment. O&M will be more complicated than a passive treatment approach.
- Case studies indicate a treatment time of 6 to 18 months (Terry Hazen, phone call 4-28-00).
- The park is readily accessible to installation equipment.
- Although methane is explosive, it is injected at 4 percent of the lower explosive limit in air, which is safe. Equipment will require gauges and meters to ensure the injection amount does not exceed 4 percent. In an aerobic environment, methane will not accumulate to a level that exceeds the lower explosive limit. Methane also has an odor that indicates leaks in the system.
- Bench and pilot scale treatability studies should be conducted.
- Permitting variances from the State of MN will be required.
- A thorough monitoring program will be required to evaluate the technology's effectiveness. This could involve the installation of additional monitoring wells at Anoka County Park.

3.3 Cost

- Capital costs are moderate.
- O&M costs are moderate.
- Although this technology involves a more complicated aboveground system, may not exceed the costs of anaerobic bioremediation due to an increased treatment time.

4.0 RECOMMENDATIONS

Since the technologies evaluated are relatively new and innovative, it is recommended that the Navy conduct treatability studies at Anoka County Park. The studies should be conducted to compare and contrast two technologies: anaerobic bioremediation with vegetable oil and cometabolism.

The geochemistry results indicate that the shallow aquifer is marginally aerobic and the intermediate aquifer is marginally anaerobic. Based on these marginal conditions, both aquifers have the potential to be driven towards an aerobic environment or an anaerobic environment. Cometabolism is effective at aerobically degrading TCE and anaerobic bioremediation with vegetable oil is effective at anaerobically degrading TCE. Enhanced anaerobic bioremediation requires little O&M and disruption at the park. Vegetable oil is injected using direct push technology. The treatment processes occur in the subsurface; the vegetable oil is a time-releasing, long-lasting substrate. In addition, vegetable oil is a common, food-grade substance with a low material cost. Although cometabolism requires an aboveground system to mix and continuously inject methane and oxygen, the aerobic degradation of TCE is expected to be much faster than the anaerobic degradation of TCE. In addition, the aerobic degradation does not generate potentially toxic daughter products. This is a particularly important issue considering the proximity of the Mississippi River to the contaminated area. Based on this information, it is worthwhile to test cometabolism versus anaerobic bioremediation with vegetable oil at Anoka County Park.

If the ~~schedule or~~ funding is limited, it is recommended that the Navy proceed with a treatability study for one technology: anaerobic bioremediation with vegetable oil. This technology is preferable because it requires less O&M and aboveground processes than cometabolism. Groundwater monitoring will attempt to track the accumulation of toxic degradation by-products. If concentrations exceed regulatory limits, safety measures could be implemented.

Chemical oxidation with Fenton's reagent is not recommended due to the volatility of the reagent and potential safety concerns at a public park. In addition, the temperature and pH in the contaminated aquifers are not ideal for the application of Fenton's reagent. Chemical oxidation with potassium permanganate is not recommended because of the impurities contained within the source material (ore) that could further contaminate the aquifer. Compared to chemical oxidation, bioremediation presents a more natural, environmental solution that utilizes indigenous microorganisms to breakdown the contamination. Vegetable oil is recommended over molasses and lactic acid because it does not require a metered, continuous injection system. Vegetable oil is recommended over HRC because it is a readily available substance that can be inexpensively obtained through more than one source.

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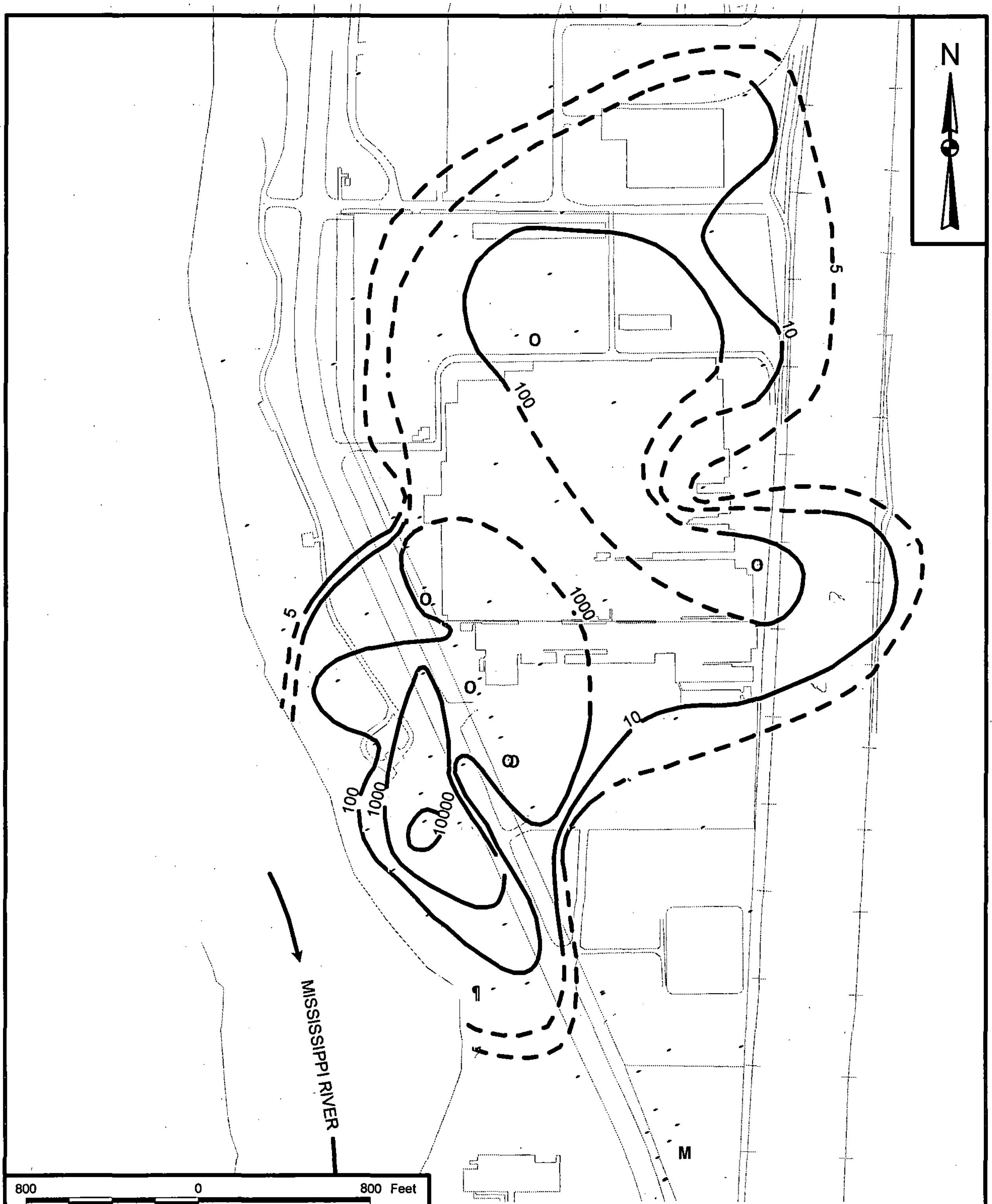

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CHECKED BY — DATE —	TCE CONCENTRATIONS (ug/l) SHALLOW MONITORING INTERVAL NIROP FRIDLEY, MINNESOTA	APPROVED BY — DATE —	
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