

**Preliminary Results of Reductive Dechlorination
Conducted at the X-749/X-120 Area of the DOE
Portsmouth Gaseous Diffusion Plant, Piketon, Ohio**

D. E. Rieske, D. R. Baird, N. E. Lawson
CDM Federal Programs
P.O. Box 789, Piketon, OH 45661

ABSTRACT

Reductive dechlorination is being implemented at the X-749/X-120 trichloroethene (TCE) plume South Barrier Wall containment site at the Department of Energy (DOE) Portsmouth Gaseous Diffusion Plant (PORTS). The purpose of this paper is to present the effectiveness of the reductive dechlorination at PORTS. Reductive dechlorination is an *in situ* remediation technology that utilizes existing subsurface microbes to biologically degrade volatile organic compounds in groundwater. Monitoring in the barrier wall area reveals the presence of Hydrogen Release Compound¹ (HRC) injected in the spring of 2004 in two groundwater monitoring wells closest to the injection points. Oxidation/reduction potential in these two wells has decreased steadily since injection, but has not yet reached optimal reducing levels for TCE degradation. Monitoring the effectiveness of the injection is hampered by near-stagnant groundwater flow due in part to the South Barrier Wall.

The X-749/X-120 TCE groundwater plume lies beneath approximately 91 acres in the southern portion of PORTS, and extends southward threatening to cross the DOE property boundary. A 1,077-foot long subsurface bentonite barrier wall was installed in 1993 at the southern DOE property boundary to restrict movement of contaminated groundwater from traveling off-site until other remedial technologies could be implemented. In 2003, TCE was detected on the south side of the barrier wall (but still within DOE property) above drinking water standards of 5 micrograms per liter. Monitoring has also detected TCE in groundwater beyond the western edge of the barrier wall.

In the spring of 2004, DOE initiated the injection of a reductive dechlorination compound known as Hydrogen Release Compound-extended release formula¹ (HRC-X) into the subsurface using direct push technology (DPT). The HRC-X was injected within the saturated zone from the top of bedrock to 10 feet above bedrock as the probe was withdrawn from the push. A total of 180 DPT points were completed within three treatment zones: north, west, and south of the X-749 South Barrier Wall.

The HRC-X (glycerol tripoly lactate) degrades chlorinated organic compounds, such as TCE, into non-toxic compounds such as ethene and ethane. Upon being injected into the subsurface, HRC-X slowly reacts with groundwater and releases lactic acid. As the anaerobic microbes (which are naturally present in the subsurface) metabolize the lactic acid, low concentrations of dissolved hydrogen are produced. These hydrogen molecules strip the chlorinated (TCE) molecules of their chlorine atoms. During the chemical process of this reductive dechlorination, the lactic acid degrades to pyruvic acid and finally to acetic acid. As the subsurface environment becomes more anaerobic, the TCE degrades.

Lactic acid and acetic acid were detected in two wells immediately downgradient from the HRC-X injection areas. The oxidation/reduction potential has dropped in these two monitoring wells, but did not reach ideal levels for reductive dechlorination of the TCE until after June 2005. The methane concentration in the two wells has increased since the injection of HRC-X, but has not likely reached extreme methanogenesis levels that may restrict the dechlorination process. Through June 2005, concentrations of TCE and TCE degradation products had not yet changed significantly in response to reductive dechlorination. However, by November 2005 the concentration of TCE at monitoring well X749-45G had decreased from a high of 59 µg/L (April 2005) to 9.6 µg/L. At well

¹ HRC and HRC-X are trademarked products of Regenesys Corporation.

X749-97G TCE had decreased from a high of 6.3 µg/L (June 2005) to 2.6 µg/L in November 2005. Groundwater monitoring of the wells for reductive dechlorination effectiveness will continue on a semiannual basis in order to track the chemical and biochemical changes in the groundwater.

INTRODUCTION

The Portsmouth Gaseous Diffusion Plant (PORTS), which is owned by the U.S. Department of Energy (DOE), was constructed in the early 1950s and was operated to enrich uranium for electric power generation. PORTS is approximately 80 miles south of Columbus and 20 miles north of Portsmouth near Piketon in south-central Ohio. The industrialized portion of PORTS is approximately 1,000 acres of a 3,714-acre DOE reservation. As with many industrial sites, solvents and degreasers were used to clean miscellaneous machine parts and tools. Unfortunately, the cleaning practices were not clearly defined and disposal of these solvents and degreasers were not monitored effectively. Investigations conducted since the late 1980s have identified five distinct groundwater contaminant plumes composed of volatile organic compounds (VOCs) at PORTS. The largest of these plumes, known as the X-749/X-120 Groundwater Plume, is located near the southern end of the reservation and has advanced southward to the DOE property boundary. The X-749/X-120 Groundwater Plume is located in a five-foot thick gravelly sandy clay layer 25 to 30 feet deep known as the Gallia Sand. The Gallia is underlain by the 10- to 20-foot thick black Mississippian Sunbury Shale that acts as an effective aquitard preventing migration of contaminants to deeper bedrock layers. Two known sources of the VOC contamination (primarily trichloroethene [TCE]) in the area were the X-749 Landfill and the former X-120 Goodyear Atomic Corporation Training Facility. The X-120 Facility housed both machine shops and training rooms that were used during plant construction. The X-749 Landfill containing solvents, waste oils, and low-level radioactive materials was capped and closed in accordance with Ohio Hazardous and Solid Waste Regulations in 1993.

The X-749/X-120 Groundwater Plume lies beneath the X-749 Landfill, expands west underneath the area where the former X-120 Goodyear Training Facility was located, east under the southern end of the X-749B Peter Kiewit Landfill, and south of Perimeter Road near the DOE reservation property boundary (Fig. 1).

In 1994, a subsurface bentonite barrier wall was installed at the southern end of the DOE property boundary to retard off-site migration of the TCE-contaminated groundwater plume. Once the barrier wall was completed, groundwater monitoring wells were installed at various points along the barrier wall and were closely monitored. In recent years, the monitoring results indicated that TCE concentrations were increasing north of the barrier wall and TCE was detected above the drinking water Maximum Contaminant Level (MCL) of 5 micrograms per liter (µg/L) in monitoring wells south and west of the barrier wall, adjacent to the DOE property boundary.

DOE decided to induce *in situ* reductive dechlorination as a measure to degrade the VOCs in the groundwater plume before they migrate off site. During March and April 2004, DOE injected approximately 10,728 pounds of reductive dechlorination compound known as Hydrogen Release Compound-extended release formula (HRC-X) into the subsurface using direct push technology (DPT). This application was accomplished by injecting 180 points in three zones, creating a reactive curtain that is expected to intercept and treat the groundwater as it moves through the reactive area. Also, DOE added several new monitoring wells south of the X-749 South Barrier Wall including four on private property. There were three areas within the X-749 South Barrier Wall area where HRC-X was applied: the western end of the barrier wall (Western Treatment Zone), north of the barrier wall (Northern Treatment Zone), and south of the barrier wall (Southern Treatment Zone) (Fig. 1). HRC-X was injected within the saturated zone from the top of bedrock to 10 feet (ft) above bedrock. The HRC-X was injected as the probe was withdrawn from the push, thereby filling the void within the contaminated saturated zone. A total of 180 DPT points were completed within the treatment zones of the X-749 South Barrier Wall area. Approximately 40 pounds of HRC-X was injected into each of the DPT points in the Western and Southern Treatment Zones, and 70 pounds was injected into each point in the Northern Treatment Zone. A total of 10,728 pounds of HRC-X was injected. The HRC-X is expected to accelerate the natural attenuation of TCE (through reductive dechlorination) in the southern portion of the X-749/X-120 Groundwater Plume. Injections of the HRC-X started on March 31, 2004 and were completed on April 28, 2004.

WM'06 Conference, February 26–March 2, 2006, Tucson, AZ

Groundwater sampling was conducted from August 2004 until June 2005 on selected wells (X749-44G, X749-45G, X749-67G, X749-97G, X749-102G, X749-PZ03G, X749-PZ04G, X749-PZ05G, and background well X749-PZ06G) in the vicinity of the X-749 South Barrier Wall to determine the effectiveness of the HRC-X on the X-749/X-120 Groundwater Plume. Additional sampling after June 2005 is planned to continue on a semiannual basis.

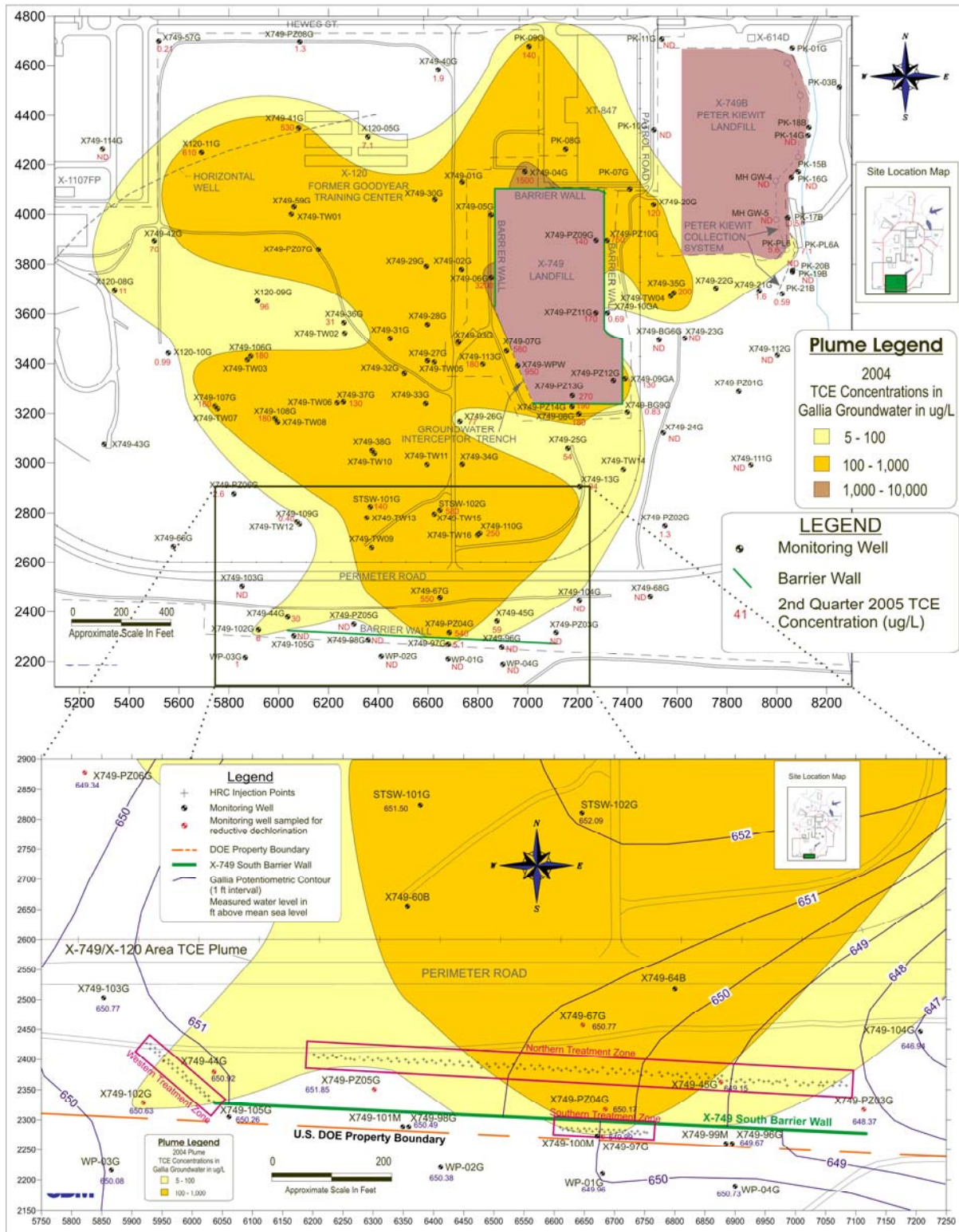


Fig. 1. Second Quarter 2005 TCE Plume at X-749/X-120/Peter Kiewit Landfill Area and HRC Injection Points with Gallia Potentiometric Surface Contours

GENERAL PROCESS

HRC is a proprietary polylactate ester that, upon being deposited into the subsurface, slowly releases lactate. Lactate is metabolized by naturally occurring microorganisms, resulting in the creation of anaerobic aquifer conditions and the production of hydrogen. Naturally occurring microorganisms capable of reductive dechlorination then use the hydrogen to progressively remove chlorine atoms from chlorinated hydrocarbon contaminants.

HRC is manufactured as a viscous gel that can be injected into the saturated zone in grid or barrier configurations for either localized area or cutoff-based treatment approaches. The use of HRC for groundwater remediation offers a comparatively simple and cost-effective remediation alternative for sites that would otherwise require unacceptably long periods of time for natural attenuation or the high levels of capital investment and operating expense associated with active remediation technologies such as pump-and-treat.

An extended release formulation of HRC, known as HRC-X, will release lactic acid for more than 3 years. The HRC-X (glycerol tripolylactate) degrades chlorinated organic compounds, such as TCE, into non-toxic compounds such as ethane and ethene. Upon being injected into the subsurface, HRC-X slowly reacts with groundwater and releases lactic acid. As the anaerobic microbes (which are naturally present in the subsurface) metabolize the lactic acid, low concentrations of dissolved hydrogen are produced. The dissolved hydrogen is used as an energy source by bacteria that perform reductive dechlorination. The hydrogen is used as the electron donor, while the chlorinated solvents are used as the electron acceptors. The result is a process that sequentially removes chlorine atoms and replaces them with hydrogen atoms. The ultimate products of the chlorinated hydrocarbon degradation process are the non-toxic compounds ethane and ethene (Fig. 2). Monitoring of the parent chlorinated solvents (i.e., TCE) as well as the reductive daughter products in the groundwater allows for assessment of the extent of dechlorination.

Another important set of sampling parameters are those used to track the distribution of electron donors derived from the HRC-X. During the chemical process of this reductive dechlorination, the lactic acid that is generated from HRC-X can be fermented to volatile fatty acids such as pyruvic acid, acetic acid, and propionic acid (Fig. 2). Each of these fatty acids can in turn also be used by bacteria as additional electron donors. Measurement of these “secondary” electron donors allows for an assessment of the area that has been impacted by the electron donor.

Reductive dechlorination requires strongly reducing conditions in order to proceed to completion (i.e., to ethene and ethane). In fact, data from many sites has shown that methanogenic conditions are optimal for complete dechlorination. Therefore, the electron donor must consume the competing electron acceptors present in the aquifer (e.g., dissolved oxygen, ferric iron, nitrate, and sulfate). Generation of methane in the subsurface is an indication that the appropriate reducing conditions have been reached.

The specific sampling parameters for monitoring reductive dechlorination include VOCs (particularly TCE, TCE degradation products, chloride, ethane, and ethene), oxidation-reduction (redox) parameters (nitrate, nitrite, sulfate, methane, dissolved oxygen, and redox potential), electron donor parameters (acetic acid, butanoic acid, lactic acid, propanoic acid, pyruvic acid, and total organic carbon), and pertinent water quality parameters (conductivity, pH, and alkalinity).

RESULTS OF MONITORING

Injections of HRC-X were completed from March 31, 2004 through April 28, 2004. Analytical sampling was conducted in the X-749 South Barrier Wall Area every other month following injection of the HRC-X to monitor the progression of the reductive dechlorination process.

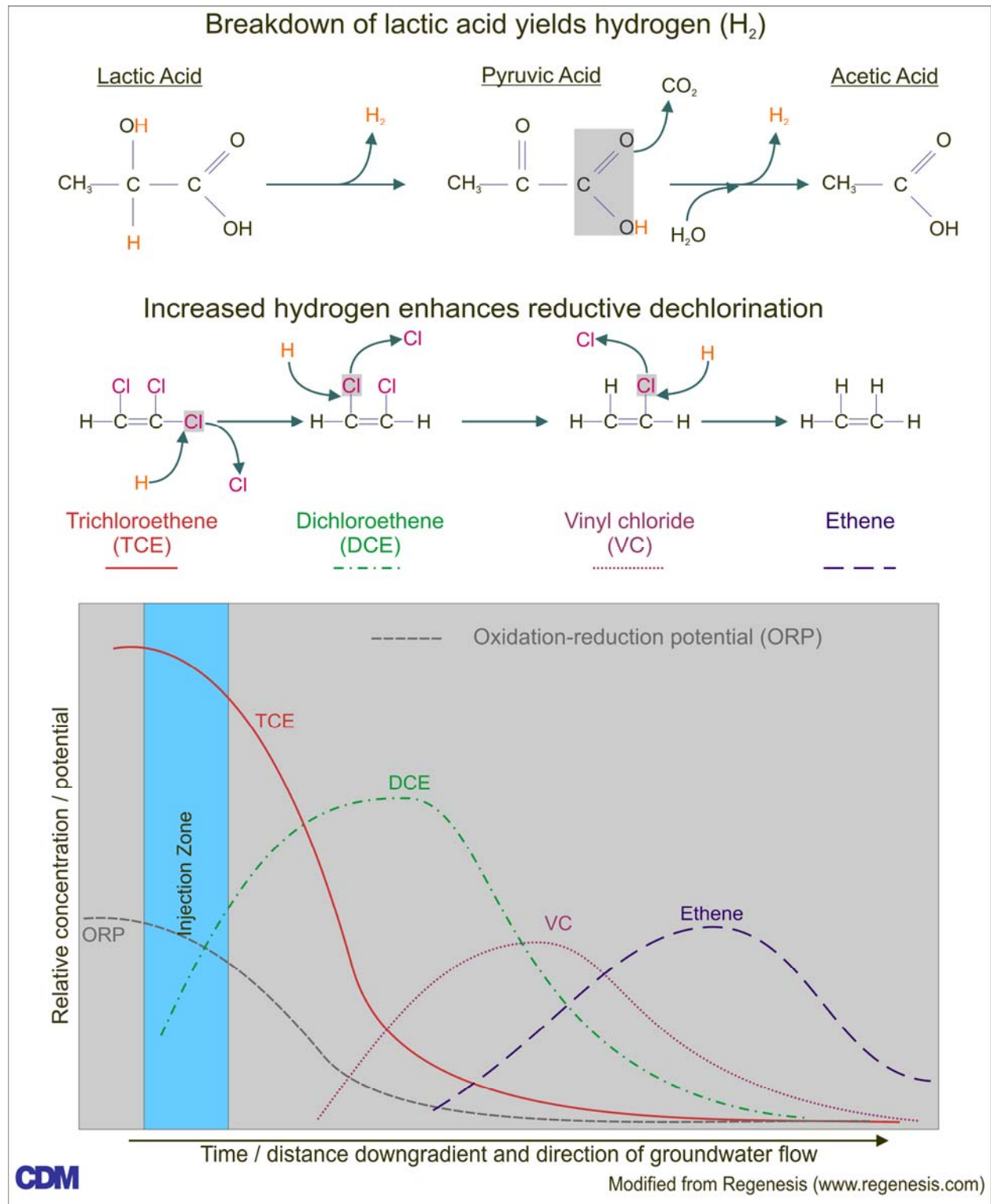


Fig. 2. Schematic Diagram of Hydrogen Released from Lactic Acid Enhancing Reductive Dechlorination of TCE

To monitor the effectiveness of the HRC-X™ injection, nine wells were sampled (see Fig. 1). These wells include:

- X749-44G Upgradient of Western Treatment Zone HRC injection area
- X749-45G Downgradient of Northern Treatment Zone HRC injection area
- X749-67G Upgradient of Northern Treatment Zone HRC injection area
- X749-97G Downgradient of Southern Treatment Zone HRC injection area
- X749-102G Downgradient of Western Treatment Zone HRC injection area
- X749-PZ03G Downgradient of Northern Treatment Zone HRC injection area
- X749-PZ04G Downgradient of Northern Treatment Zone HRC injection area
- X749-PZ05G Downgradient of Northern Treatment Zone HRC injection area
- X749-PZ06G Background well; upgradient of all treatment zones and outside of TCE plume

Northern Treatment Zone

In the Northern Treatment Zone, some evidence of electron donor arrival, redox changes, and reductive dechlorination are apparent in monitoring well X749-45G located immediately downgradient of the injection area in comparison to upgradient well X749-67G. As the groundwater flows through the injection areas, lactic acid is dissolved in the groundwater and acts as a hydrogen donor, subsequently degrading to volatile fatty acids such as pyruvic acid and acetic acid. Lactic acid and acetic acid were detected at levels of up to approximately 90 milligrams per liter (mg/L) in the samples collected from monitoring well X749-45G during each sampling event. Pyruvic acid was only detected in well X749-45G (7.95 mg/L) in August 2004. Other monitoring wells located further downgradient from the Northern Treatment Zone injection area (X749-PZ03G, X749-PZ04G, and X749-PZ05G) do not show evidence of reductive dechlorination at this time. In general, groundwater flows from north to south in the X-749/X-120 area at an approximate velocity of 0.01ft/day. Therefore, the HRC-X compound has not had sufficient time to reach the downgradient wells. Figure 3 shows the concentrations of lactic acid, pyruvic acid, and acetic acid at monitoring well X749-45G.

Another indication that conditions are beginning to become favorable for reductive dechlorination in the Northern Treatment injection area is the decrease in the redox potential at monitoring well X749-45G. In response to the HRC-X injections, competing electron acceptors such as dissolved oxygen, nitrate, and sulfate are reduced as electron donors derived from HRC-X are consumed. This reduction of competing electron acceptors causes a corresponding decrease in the redox potential of the groundwater. The redox potential in monitoring well X749-45G decreased from 65.5 millivolts (mV) in August 2004 to -48 mV in June 2005. Preliminary results reveal a redox potential of -124 mV measured in December 2005. The redox potential needs to be below about -130 mV in order to reach the ideal reducing conditions for dechlorinating TCE. Preliminary results from November 2005 sampling indicates that the concentration of TCE at monitoring well X749-45G has decreased from a high of 59 µg/L (April 2005) to 9.6 µg/L. These results suggest that the aquifer in the Northern Treatment zone is becoming more anaerobic, and has just begun to reach the reducing environment levels for optimal dechlorination. This interpretation is further supported by an evaluation of other redox parameters, namely methane, ferrous iron, and sulfate. Methane levels detected in well X749-45G have increased to 1590 µg/L in June 2005 as the redox potential has dropped (Fig 3). Ferrous iron has decreased from 4 mg/L in August 2004 to 2.4 mg/L in June 2005. Sulfate, however, still remains relatively high at 67 mg/L in June 2005. These data demonstrate that methanogenic conditions are just becoming established at this monitoring location. It should be noted that no significant change in redox parameter values has occurred at this time in the other downgradient monitoring wells as a result of the low groundwater flow rate.

Preliminary fourth quarter 2005 data indicates that ideal redox conditions have begun to be established for optimal dechlorination of TCE to occur and decreasing values in TCE concentrations have been observed. Subsequently, concentrations of TCE degradation products have also begun to decrease, as vinyl chloride and ethene have not been detected. The concentration of TCE and TCE degradation products through June 2005 at well X749-45G are shown in Fig. 3.

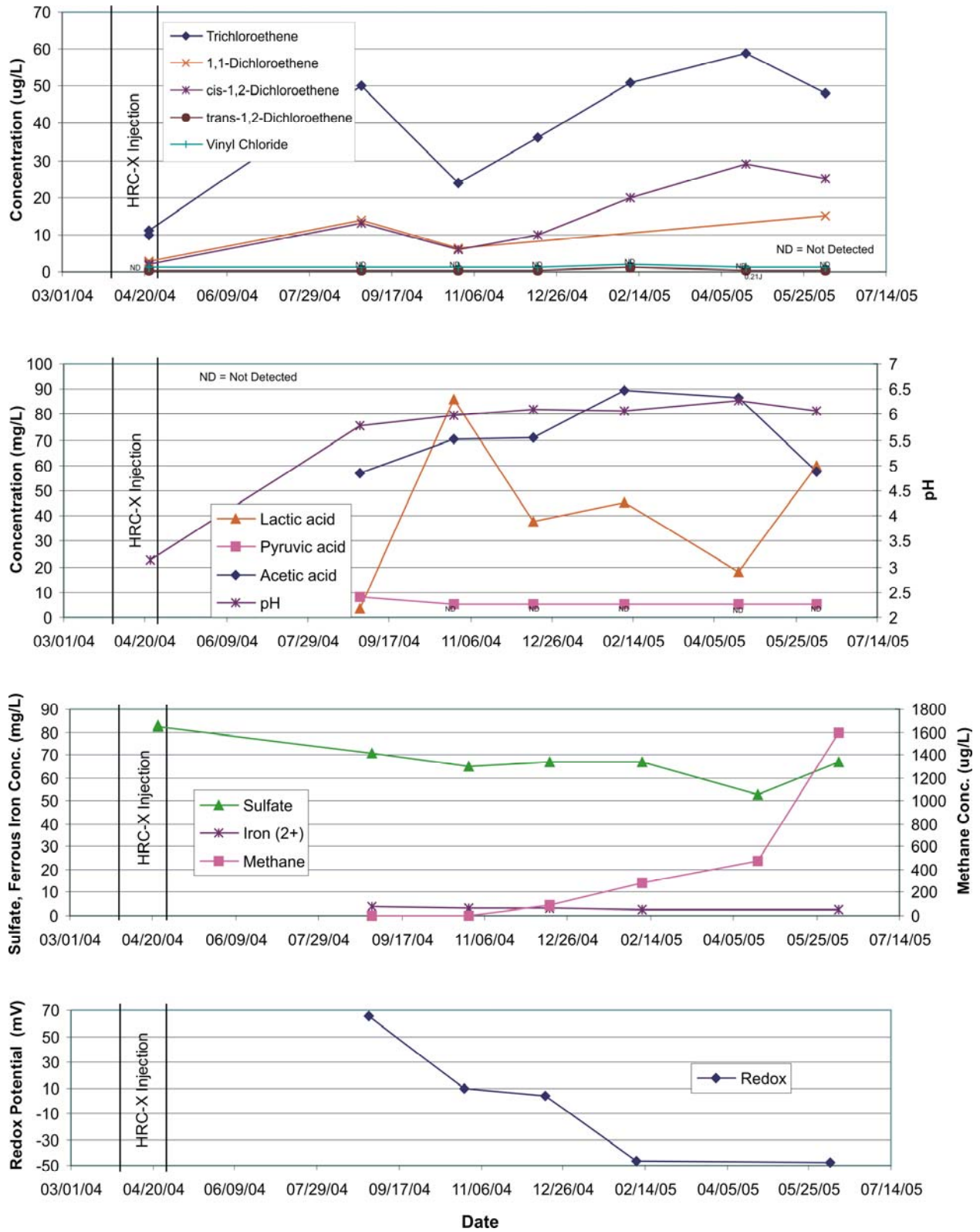


Fig. 3. Comparison of Selected Monitoring Parameters in Well X749-45G through Time

Southern Treatment Zone

In the Southern Treatment Zone, there is some evidence that conditions are becoming favorable for reductive dechlorination. Acetic acid was detected at low concentrations (less than 12 mg/L) in samples collected from monitoring well X749-97G. Lactic acid and pyruvic acid were not detected above trace amounts in this well (Fig. 4). Redox conditions have begun to progress toward sufficiently reducing conditions. For example, the redox potential in monitoring well X749-97G decreased from 133.1 mV in August 2004 to -99 mV in June 2005. Levels of ferrous iron have been measured at approximately 2 to 4 mg/L while sulfate decreased from 120 mg/L to less than 10 mg/L. Levels of methane detected in well X749-97G have increased to 3180 µg/L in June 2005. These results indicate that a reducing environment in the groundwater is developing south of the barrier wall. The near-stagnant flow south of the barrier wall may be contributing to the rise in methane at X749-97G. A graph of the redox parameters (redox potential, ferrous iron, sulfate, and methane concentrations) in X749-97G through time is depicted in Fig. 4.

The redox potential measured in June 2005 at -99 mV was approaching, but had not yet decreased to, the ideal range for dechlorination of TCE to occur. However, preliminary results reveal a redox potential of -170 mV measured at well X749-97G in December 2005. Consequently, TCE concentrations have decreased at well X749-97G from a high of 6.3 µg/L (June 2005) to 2.6 µg/L in November 2005. Preliminary results indicate that concentrations of TCE degradation products have also decreased in November 2005. Vinyl chloride and ethene have not been detected. The concentration of TCE and TCE degradation products through June 2005 at well X749-97G are shown in Fig. 4.

Western Treatment Zone

In the Western Treatment Zone, strong evidence that reductive dechlorination processes are occurring is not apparent at this time. The groundwater velocity in this area is approximately 25 ft/year.² However, monitoring well X749-102G is located approximately 75 ft downgradient from the injection zone. Therefore, the effect of the HRC-X compound on the groundwater has not yet reached monitoring well X749-102G.

² Groundwater velocity was calculated using the 2nd Quarter 2005 hydraulic gradient between monitoring wells X749-44G and WP-03G, with an estimated hydraulic conductivity of 6.0 ft/day, and an effective porosity of 30%.

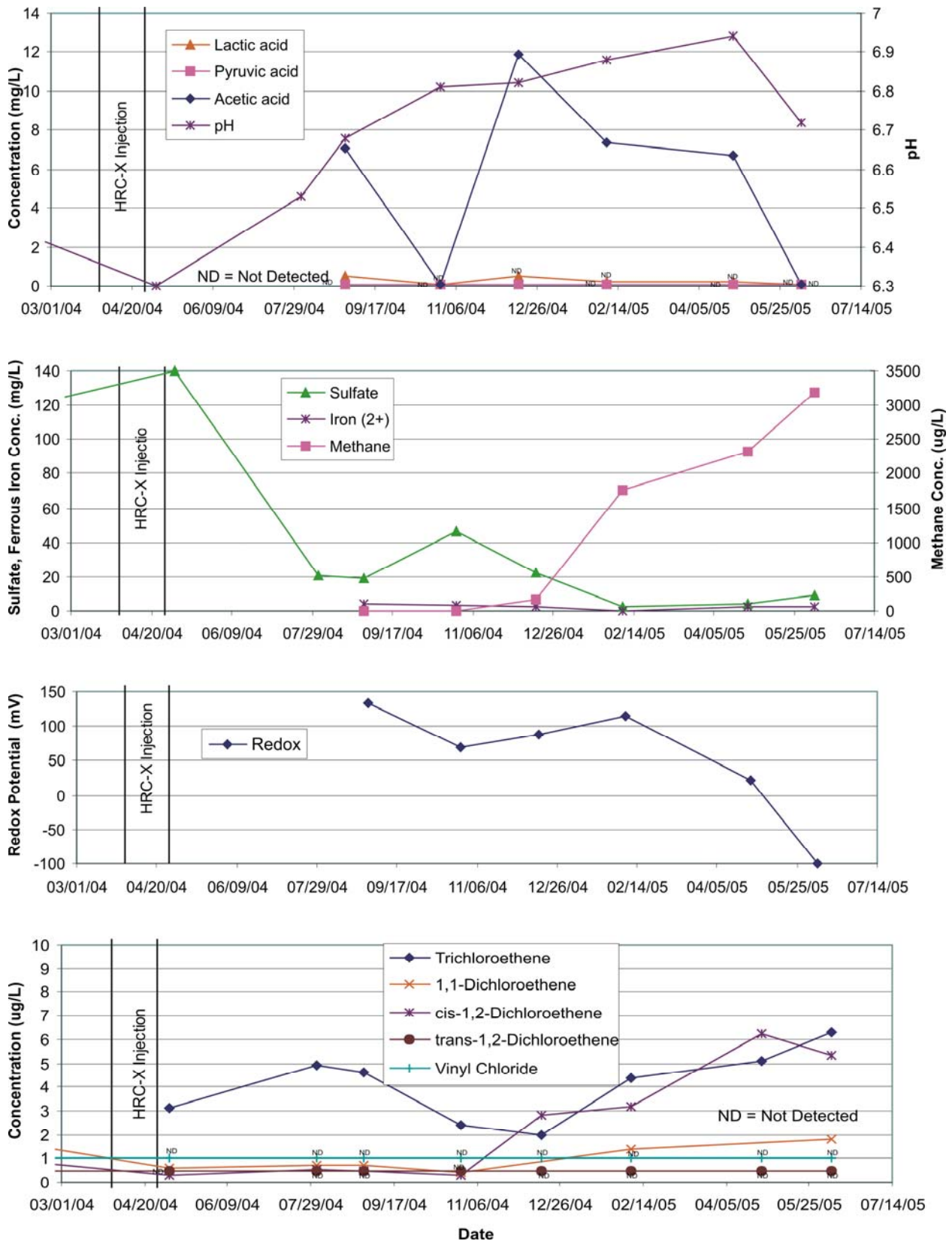


Fig. 4. Comparison of Selected Monitoring Parameters in Well X749-97G through Time

CONCLUSION

In order to monitor the effectiveness of the interim action, Integrated Groundwater Monitoring Plan (IGWMP) sampling and HRC-X effectiveness sampling were conducted to monitor the progression of the reductive dechlorination process at the X-749 South Barrier Wall. According to the data, the beginning stages of appropriate redox conditions for optimal reductive dechlorination are apparent in the groundwater monitoring wells (X749-45G and X749-97G) closest to the injection points. Lactic acid and acetic acid were detected in wells X749-45G and X749-97G, indicating the presence of electron donors derived from HRC-X in the groundwater immediately downgradient from the injection areas. The redox potential has dropped in these two monitoring wells, but did not reach ideal levels for reductive dechlorination of the TCE until after monitoring conducted in June 2005. Methane concentrations in wells X749-45G and X749-97G have increased since the injection of HRC-X, but have not likely reached extreme methanogenesis levels that may restrict the dechlorination process. Through June 2005, concentrations of TCE and TCE degradation products had not yet changed significantly in response to reductive dechlorination. However, by November 2005 the concentration of TCE at monitoring well X749-45G had decreased from a high of 59 µg/L (April 2005) to 9.6 µg/L. At well X749-97G TCE had decreased from a high of 6.3 µg/L (June 2005) to 2.6 µg/L in November 2005. The concentration of the TCE degradation products, 1,1-dichloroethene and cis-1,2-dichloroethene, also decreased in the two wells in November 2005. The reaction of the groundwater to the HRC-X injection is proceeding as expected, but slowly, mostly due to the very low groundwater velocities in the area both upgradient and downgradient of the X-749 South Barrier Wall.

Given that HRC-X has an expected longevity on the order of 3 years in the subsurface, monitoring of the wells should continue as planned in order to track the chemical and biochemical changes in the groundwater. Groundwater sampling for HRC-X effectiveness will continue on a semiannual basis as delineated in the IGWMP.

REFERENCES

1. DOE 2004. *Work Plan for the Injection of a Reductive Dechlorination Compound at the X-749 South Barrier Wall Area for the Portsmouth Gaseous Diffusion Plant Piketon, Ohio*, DOE/OR/11-3144&D1, United States Department of Energy Office of Environmental Management, January 2004.
2. DOE 1994. *Interim Measures Plan Containment/Diversion Wall for the X-749/X-120 Contaminant Plume Portsmouth Gaseous Diffusion Plant*, DOE/OR/1-14-28/05.005, United States Department of Energy Office of Environmental Management, January 1994.
3. DOE 1995. *The X-749 Groundwater Containment Wall Interim Remedial Measures*, PORTS/ER/0019 United States Department of Energy Office of Environmental Management, Spring 1995.
4. *Regenesis Online*. 10 Jan. 2004. Leaders in Accelerated Natural Attenuation. Oct. 2004 <<http://www.regenesis.com>>.