Ground Water Monitoring & Remediation

Groundwater Sampling at ISCO Sites: Binary Mixtures of Volatile Organic Compounds and Persulfate

by Scott G. Huling, Saebom Ko, and Bruce Pivetz

Abstract

In situ chemical oxidation involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming groundwater contaminants into harmless by-products. Owing to oxidant persistence, groundwater samples collected at hazardous waste sites may contain both the contaminant(s) and the oxidant in a "binary mixture." Binary mixtures composed of sodium persulfate (2.5 g/L; 10.5 mM) and volatile organic compounds (VOCs) (benzene, toluene, *m*-xylene, perchloroethylene, trichloroethylene) were analyzed to assess the impact on the quality of the sample. A significant decline (49 to 100%) in VOC concentrations was measured in binary mixtures using gas chromatography (GC) purge and trap, and GC mass spectroscopy headspace methods. Preservation of the binary mixture samples was achieved through the addition of ascorbic acid (99 to 100% VOC average recovery). High concentrations of ascorbic acid (42 to 420 mM) did not interfere in the measurement of the VOCs and did not negatively impact the analytical instruments. High concentrations of ascorbic acid favored the reaction between persulfate and ascorbic acid while limiting the reaction between persulfate and VOCs. If an oxidant is detected and the binary sample is not appropriately preserved, the quality of the sample is likely to be compromised.

Introduction

Binary Mixtures of Oxidant and Organic Contaminants in Groundwater Samples

In situ chemical oxidation (ISCO) involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming groundwater or soil contaminants into less harmful chemical by-products (Rivas 2006; Ferrarese et al. 2008; Kao et al. 2008). An integral component of ISCO is the collection and analysis of groundwater samples to assess ISCO treatment performance. Often, groundwater samples collected specifically to analyze organic contaminants may contain the oxidant and the organic contaminants in a "binary mixture." This commingling of organic contaminants and oxidants in the groundwater sample represents a condition in which there is significant potential for oxidative transformation of the contaminants after sample collection. Consequently, the quality of the groundwater sample is compromised and a false negative may result. The oxidant may also potentially affect the analytical instruments used to quantify the concentration of groundwater analytes. To mitigate this potential problem, detection of the oxidant in binary mixtures and neutralization of the oxidant are needed immediately after sample collection, and prior to analysis.

A site-specific critical analysis of contaminant and oxidant fate and transport conditions is needed to help understand the cause of binary mixtures. Several subsurface fate and transport conditions exist that result in commingling of organic contaminants and oxidant residuals in groundwater samples. The main cause of commingling is attributed to heterogeneities in aquifer materials and heterogeneous distribution of oxidants and contaminants in the subsurface. Groundwater solutes can enter a monitoring well screen from different lithologic zones, containing different levels of oxidant and contaminant. These groundwater solutes may be transported disproportionately in preferential pathways as separate solutes from different lithologic zones or as a binary mixture from the same lithologic zone (Figure 1). Insufficient contact time between the oxidant and contaminant prior to, or after, entering the well leads to binary mixtures. High levels of contamination, including dense nonaqueous phase liquids (DNAPLs) or light nonaqueous liquids (LNAPLs) immobilized in porous media near the monitoring well (i.e., in the source zone), will impart high levels of contaminant concentrations to the groundwater. During groundwater sampling, mobilization of LNAPL or DNAPL droplets from inside the well or from contaminated porous media near the well may result in high contaminant concentrations in the groundwater samples. Cold groundwater temperature or poor activation chemistry, and the resulting limited reaction

doi: 10.1111/j1745-6592.2011.01332.x

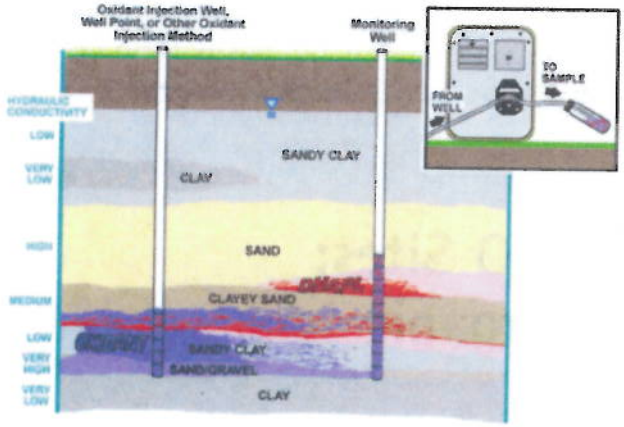

Figure 1. Conceptual model of hydrogeologic, and oxidant and contaminant fate and transport conditions that contribute to binary mixture groundwater samples. The oxidant illustrated in purple conceptually represents any oxidant (persulfate, permanganate, peroxide) used for in situ chemical oxidation.

between oxidant and contaminants, may permit oxidant and contaminants to coexist in porous media or a monitoring well for extended periods of time.

Reasons to Sample and Analyze Binary Mixtures

The rationale for collecting and analyzing binary mixture groundwater samples varies. In some cases, a preliminary assessment of ISCO performance may be needed to validate treatment performance. Groundwater samples may also be used to help assess whether redistribution of the contaminant plume may have resulted from ISCO activities. Interim ISCO pilot-scale studies are implemented to establish design parameters for full-scale ISCO deployment. Often, the criteria for completion of these studies include rapid turnaround of field data and information to meet specified milestones and deadlines for full-scale remedy selection, design, construction, and implementation. Regulatory-driven goals and specified timelines may result in added pressure on project managers to rapidly complete pilot- and full-scale testing and deployment of ISCO. For these reasons, significant emphasis may be placed on the collection of groundwater samples at ISCO sites prior to complete reaction of the oxidant. Interpretation of data derived from the collection and analysis of binary samples requires a critical analysis of site-specific conditions and scientific judgment and is not the subject of this study.

Oxidation of Organic Contaminants in Groundwater Samples

The oxidation of organic contaminants found in binary mixtures, after sample collection, may significantly compromise the quality of groundwater samples. Given the four main oxidants used at ISCO sites (i.e., permanganate [MnO_4^-], persulfate [$S_2O_8^{2-}$], hydrogen peroxide [H_2O_2], ozone [O_3]), persulfate and permanganate persist the longest in the subsurface and represent the greatest potential for binary mixture groundwater samples. H_2O_2 and O_3 reaction in the subsurface is rapid (Huling and Pivetz 2006) and no cases could be found where the excessive persistence of H_2O_2 or O_3 was problematic in groundwater. The focus of this study involves persulfate. Permanganate persistence also represents a significant potential for binary mixtures, and groundwater sample preservation methods for this oxidant are being investigated in a separate detailed study.

Persulfate

Persulfate oxidation of organic contaminants can either occur by direct reaction between the persulfate and the contaminant, or persulfate can be activated thermally (i.e., at temperatures approximately ≥30 °C) (Johnson et al. 2008), by base chemicals (i.e., KOH, NaOH) or by ferrous iron (Fe(II)) (rxns 1 to 3, Table 1), resulting in the formation of the sulfate radical ($\cdot SO_4^-$), a stronger oxidant (2.4 V) than the persulfate anion ($S_2O_8^{2-}$) (2.1 V) (rxn 4, Table 1). Minimal persulfate reaction is expected after the groundwater sample has been removed from the subsurface. However, under some conditions, activators or activated persulfate (i.e., Fe(II), KOH, thermal) may be captured in the groundwater sample, allowing the persulfate-activation reaction to continue after the sample has been collected. Under all three activation conditions, significant reaction of persulfate may occur after the sample is collected and may alter the quality of the groundwater sample. Ultraviolet (UV) light activation of persulfate can occur if the groundwater sample vial is exposed to sunlight. Persulfate activation can also occur after sample collection and/or during analytical procedures. For example, automated analytical procedures that involve heating the aqueous sample will thermally activate the persulfate. High concentrations of sodium persulfate, typical at ISCO sites, in conjunction with relatively low concentrations of organic contaminants, may result in significant loss of the contaminant, despite the slow direct-oxidation reaction kinetics typical of the inactivated persulfate anion ($S_2O_8^{2-}$).

The objectives of this study were (1) to determine whether the quality of an aqueous sample containing persulfate and VOCs (benzene, toluene, *m*-xylene, perchloroethylene [PCE], trichloroethylene [TCE]) is impacted after the sample is collected and (2) to evaluate and validate the addition of a reductant (i.e., ascorbic acid) to the groundwater sample to neutralize the oxidant and preserve the quality of the groundwater sample.

Methods, Materials, Analytical Procedures

Aqueous Sample Preparation (Binary Mixtures)

Aqueous samples were prepared in 40-mL borosilicate glass vials with Teflon-coated septa. In experiments conducted involving binary mixtures of persulfate and VOCs, solutions were added to the reactors in the following order: De-ionized water, VOCs (benzene, toluene, *m*-xylene, PCE, TCE), and persulfate. The fate of individual VOCs was evaluated in the binary mixture and VOCs were not combined in the same reactor. The target concentration of sodium persulfate was high (2.5 g/L; 10.5 mM) and is representative of the concentration range found in groundwater at ISCO sites (Liang and Lee 2008). VOC- and persulfate-free control reactors were prepared similarly to assess VOC and

Table 1

Persulfate Activation and Chemical Oxidation Reactions

Persulfate activation	
Thermal : $S_2O_8^{2-} \xrightarrow{heat} 2 \cdot SO_4^-$	(rxn 1)
Base: $S_2O_8^{2-} + KOH \rightarrow \cdot SO_4^- + K^+ + SO_4^{2-} + OH$	(rxn 2)
Ferrous iron: $S_2O_8^{2-} + Fe^{2+} \rightarrow \cdot SO_4^- + Fe^{3+} + SO_4^{2-}$	(rxn 3)
Chemical oxidation	
$\cdot SO_4^- + e^- \rightarrow SO_4^{2-}$	(rxn 4)
$S_2O_8^{2-} + AH^- \rightarrow \cdot SO_4^- + \cdot A^- + SO_4^{2-} + H^+$	(rxn 5)
$S_2O_8^{2-} + AH_2 \rightarrow \cdot SO_4^- + \cdot A^- + SO_4^{2-} + 2H^+$	(rxn 6)
$\cdot SO_4^- + AH^- \rightarrow \cdot A^- + SO_4^{2-} + H^+$	(rxn 7)
$\cdot SO_4^- + AH_2 \rightarrow \cdot A^- + SO_4^{2-} + 2H^+$	(rxn 8)
$\cdot SO_4^- + benzene \rightarrow$	(rxn 9)
$C_6H_8O_6 + 10\ Na_2S_2O_8 + 6\ H_2O \rightarrow 6\ CO_2 + 20\ Na^+ + 20\ HSO_4^-$	(rxn 10)
$\cdot SO_4^- + S_2O_8^{2-} \rightarrow \cdot SO_4^{2-} + S_2O_8^-$	(rxn 11)

oxidant persistence. A set of control vials were prepared the same way, but without persulfate. All samples were immediately stored in the refrigerator (4 °C) until analyzed. VOC sample sets (i.e., benzene, toluene, *m*-xylene, PCE, TCE) were removed from the refrigerator and analyzed separately to assure that each group was maintained at the same temperature regime throughout the sample analysis procedure. In separate experiments conducted to investigate the use of ascorbic acid as a preservative, ascorbic acid was amended to the reactors prior to the VOCs and persulfate. The concentration of the ascorbic acid (0 to 420 mM) in the reactors was varied to assess the ratio of ascorbic acid to persulfate (mol/mol) (0, 4, 7, 10, 13, and 40) on VOC recovery. Preliminary experiments were conducted to investigate the possible use of other preservatives (sodium bisulfite, sodium thiosulfate), but were abandoned because of the formation of precipitates that potentially could damage the analytical instruments.

Analytical

An automated headspace gas chromatography/mass spectrometry (GC/MS) method was used to confirm the identity and quantity of purgeable VOCs in the water samples (40-mL VOA vials). This method is used in EPA Methods 5021A and 8260C and used to quantify over 60 VOCs in drinking water, including aromatics, haloalkenes, haloalkanes, haloaromatics, and fuel oxygenates. This automated method involves the transfer of an aqueous subsample (10 mL) to a sealed headspace vial which is heated from room temperature to 80 °C in 30 min. A sample of the headspace gas is then transferred to the capillary column in the GC.

An automated purge and trap GC (Agilent, Model 6890, Wilmington, Delaware) method was used to quantify benzene, toluene, and *m*-xylene (BTX) in water (40-mL VOA vials) samples. This method is most similar to EPA Methods 602 and 8020, but shares similarities with several other EPA methods that involve purge and trap, including EPA Methods 501, 502.2, 503.1, 524.2, 601, 602, 624, 8010, 8020, 8021, 8240, and 8260. In this method, a subsample (10 mL) is transferred to a sparge chamber and rigorously purged with helium (6 min). The volatile VOCs are transferred to a K VOCARB 3000 Encon trap and dry purged with helium at room temperature to remove water vapor. The VOCs are thermally desorbed (i.e., heated from room temperature to 260 °C in 25 min) and transferred to the GC column for separation and measurement. Sample transfer is through a heated 1.9 mm × 1.0 m Silcosteel (Restek, Bellefonte, Pennsylvania) transfer line coupled directly to the analytical column. Following separation on the column, the presence of VOCs is determined with photoionization and flame ionization detectors.

A spectrophotometric method was used to analyze persulfate concentration in the solution. Samples were prepared by combining 0.1 mL of aqueous sample, 0.9 mL of DI water, 10 mL of 2.5 N H_2SO_4 solution, and 0.1 mL of 0.4 N ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) solution. The contents were mixed and allowed to react (40 min) after which an NH_4SCN (0.6 N) solution (0.2 mL) was added. The absorbance ($\lambda = 450$ nm) was measured with a spectrophotometer (Huang et al. 2002; Huling et al. 2011).

Results

GC/MS and GC Analysis of Binary Mixture (Persulfate + VOCs)

A significant decrease (49 to 100%) in benzene, toluene, and xylene aqueous concentrations was measured in binary mixture samples using both the GC/MS headspace and the GC purge and trap methods (Table 2). Complete removal (100%) of PCE and TCE was measured using the GC/MS headspace method (Table 2). In persulfate-amended VOC control samples (i.e., prepared specifically to analyze for persulfate), the persulfate concentration prior to GC/MS

Table 2

Transformation of VOCs in Binary Mixtures Containing Persulfate (2.5 to 2.6 g/L; 10.5 to 10.9 mM) Using the GC/MS Headspace and GC Purge and Trap Methods[1]

Analytical Method/Analyte	Initial Concentration (μM)	Final Concentration (μM)	Percent Loss (%)
GC/MS headspace			
Benzene	7.7 (7.3–8.1)	3.9 (3.9–4.0)	49
Toluene	7.9 (7.6–8.2)	2.3 (2.21–2.35)	71
m-Xylene	5.7 (5.58–5.90)	0.54 (0.29–0.79)	91
PCE	3.0 (2.98–3.11)	ND	100
TCE	4.8 (4.72–4.87)	ND	100
GC purge and trap			
Benzene	10.2 (10.1–10.4)	2.4 (2.1–2.7)	76
Toluene	8.7 (8.3–9.0)	0.52 (0.18–0.86)	94
m-Xylene	6.2 (5.9–6.4)	ND	100

[1]All aqueous samples prepared in triplicate; average value reported (n = 3); 95% confidence interval in parentheses.

headspace analysis after 2 to 14 d storage (4 °C) indicated no loss of the initial persulfate concentration (2.5 g/L). Temperature-dependent reaction rate constants for persulfate in de-ionized water indicate that the half-life of $S_2O_8^{2-}$ at 60, 70, and 80 °C is approximately 34, 11, and 2 min, respectively (Johnson et al. 2008). These values indicate that thermal activation of persulfate during GC/MS analysis resulted in a significant decrease in persulfate concentration when the 10-mL subsample was heated from room temperature to 80 °C over a 30-min timeframe. Consequently, significant VOC oxidation is projected under this aggressive thermally activated persulfate oxidation condition either by the rapid reaction with $\cdot SO_4^-$ or by direct reaction with $S_2O_8^{2-}$.

Generally, greater loss of BTX was measured during GC analysis than GC/MS analysis (Table 2). The temperature-dependent reaction rate constant (4.3×10^{-3}/d) for persulfate in de-ionized water at 24 °C was estimated from an Arrhenius plot of thermal decomposition of persulfate (Johnson et al. 2008) and used to calculate persulfate loss at room temperature (24 °C) over the 1- to 4-h analysis period. The method of estimating the persulfate reaction rate constant was subject to error because of the very slow and uncertain reaction rate of persulfate known to occur at room temperature (24 °C). Approximately, a 0.02 to 0.07% loss in persulfate concentration was projected. However, based on the concentrations of persulfate measured in the 10-mL subsample after sample purging was completed, the actual difference between the initial concentration of 2.57 g/L (95% confidence interval 2.54 to 2.61 g/L) and the final concentration 2.50 g/L (95% confidence interval 2.48 to 2.52 g/L) accounted for a 2.6% loss. No known persulfate activation agent (i.e., thermal, base, iron, UV light) appears to have played a role in the GC sparge vessel and currently we cannot provide a firm explanation for the loss in persulfate.

It is proposed that the loss of VOCs may have resulted from the formation of aerosol droplets containing persulfate during the helium sparge step and the transport into the VOCARB 3000 Encon trap. Subsequently, during the VOC thermal desorption step where the trap was heated from room temperature to 260 °C, the persulfate residing in the trap may have been thermally activated resulting in the oxidation of the VOCs in the trap. Similarly, highly efficient oxidation of organics immobilized in granular-activated carbon media by thermally activated persulfate has been reported elsewhere (Huling et al. 2011). Overall, the seemingly minor loss in persulfate concentration (i.e., ≈70 mg/L) and/or persulfate solution was sufficient to account for significant losses in VOCs in aqueous samples.

Ascorbic Acid Stabilization

The addition of ascorbic acid resulted in the preservation of the quality of the groundwater VOC concentrations (Table 3) relative to the ascorbic acid-free aqueous samples (Table 2). The overall average recovery of VOCs was 99 and 100% in the GC/MS headspace method and GC purge and trap methods, respectively. There was no negative impact on the instruments used in the GC/MS headspace or GC purge and trap methods and no interference in the sequential analysis of aqueous samples despite high concentrations of ascorbic acid (42 to 420 mM).

Discussion

Ascorbic Acid

Ascorbic acid reacts with persulfate to initiate the production of the sulfate radical ion ($\cdot SO_4^-$) (Curtin et al. 2004). Consequently, the oxidation of ascorbic acid can either occur by direct reaction with $S_2O_8^{2-}$ or by $\cdot SO_4^-$ (rxns 5 to 8, Table 1). The symbols AH_2, AH^-, and $\cdot A^-$ represent ascorbic acid, hydrogen ascorbate, and oxidized dehydroascorbic acid species, respectively. The pK_a values associated with these ascorbate species are AH_2, pK_{a1} = 4.10; AH^-, pK_{a2} = 11.79 (Lide 1993). The direct reaction between persulfate and ascorbic acid is relatively limited (k_5 = 0.35 and k_6 = 0.02/M s) compared to oxidation of ascorbic acid by $\cdot SO_4^-$ ($k_7 = 1 \times 10^9$ and $k_8 = 1 \times 10^8$/M s) (Curtin et al. 2004).

Table 3

Preservation of VOCs by Amending Ascorbic Acid to Binary Mixtures Containing Persulfate (2.5 g/L; 10.5 mM) and VOCs[1]

Analytical Method/ Analyte	Ascorbic Acid/Persulfate (mmol/mmol)[2]	Initial Concentration (μM)	Final Concentration (μM)	Percent Recovery (%)
GC/MS headspace				
Benzene	0	7.29 (7.09–7.49)		
	4		7.32 (7.29–7.34)	100
	7		7.29 (7.15–7.43)	100
	10		7.23 (7.09–7.37)	99
	13		7.47 (7.38–7.57)	103
	40		6.88 (6.87–6.90)	94
Toluene	0	6.39 (6.16–6.62)		
	4		6.40 (6.19–6.61)	100
	7		6.43 (6.29–6.56)	100
	10		6.29 (6.08–6.51)	98
	13		6.42 (6.36–6.48)	100
	40		6.02 (5.98–6.07)	94
m-Xylene	0	3.35 (3.17–3.52)		
	4		3.19 (2.93–3.44)	95
	7		3.28 (3.20–3.36)	99
	10		3.42 (3.38–3.46)	102
	13		3.48 (3.43–3.53)	104
	40		3.27 (3.25–3.29)	98
PCE	0	1.63 (1.60–1.66)		
	4		1.54 (1.52–1.55)	94
	7		1.53 (1.48–1.58)	94
	10		1.55 (1.48–1.62)	95
	13		1.60 (1.56–1.64)	98
	40		1.61 (1.56–1.66)	99
TCE	0	4.29 (4.21–4.38)		
	4		4.41 (4.26–4.56)	103
	7		4.28 (4.03–4.53)	100
	10		4.31 (4.21–4.40)	100
	13		4.34 (4.26–4.42)	101
	40		4.12 (4.00–4.24)	96
GC purge and trap				
Benzene	0	11.16 (11.06–11.26)		
	4		10.85 (10.75–10.95)[3]	97
	7		11.12 (10.98–11.26)	100
	10		11.12 (10.97–11.26)	100
	13		11.27 (11.14–11.40)	101
	40			

Table 3 Continued

Analytical Method/ Analyte	Ascorbic Acid/Persulfate (mmol/mmol)[2]	Initial Concentration (μM)	Final Concentration (μM)	Percent Recovery (%)
Toluene	0	10.20 (9.80–10.61)		
	4		9.85 (9.79–9.91)[3]	97
	7		9.95 (9.82–10.07)	
	10		9.98 (9.91–10.06)	98
	13		10.18 (10.00–10.35)	98
	40			100
m-Xylene	0	10.20 (10.05–10.35)	10.11 (9.91–10.31)	99
	4		10.36 (10.23–10.49)	102
	7		10.30 (10.10–10.49)	101
	10		10.58 (10.50–10.65)[3]	104
	13			
	40			

Note: Aqueous samples were analyzed using GC/MS headspace and GC purge and trap methods.
[1]All aqueous samples prepared in triplicate; average value reported (n = 3); 95% confidence interval in parentheses.
[2]The value 0 represents the ascorbic acid- and persulfate-free samples used to establish baseline.
[3]Data invalidated because of inverted septa.

However, given the reaction rate equation ($dAH_2/dt = k_6 [S_2O_8^{2-}] [AH_2]$) representative of the conditions in this experiment (pH < 4.1; $[S_2O_8^{2-}]$ = 10.5 mmol/L, $[AH_2]$ = 42 mmol/L), the initial rate of persulfate reaction was estimated to be high (30.2 mmol/h) and could account for significant consumption of persulfate. Furthermore, formation of $\cdot SO_4^-$ as a result of rxn 6, and rapid reaction between $\cdot SO_4^-$ and ascorbic acid (rxn 8, Table 1), would result in even faster reaction and depletion of persulfate.

The success of ascorbic acid reactions involving the depletion of persulfate and the effective preservation of the groundwater sample quality is attributed to the rapid reaction kinetics between persulfate (i.e., $S_2O_8^{2-}$ and $\cdot SO_4^-$) and ascorbic acid, and less favorable reaction kinetics between persulfate and the VOCs. This result requires that the overall reaction rate between either $S_2O_8^{2-}$ or $\cdot SO_4^-$ and ascorbic acid must be significantly greater than with the VOCs. Although the reaction between benzene and $\cdot SO_4^-$ is potentially fast (i.e., $k_9 = 3 \times 10^9$/M s) (rxn 9) (Neta et al. 1988), the high concentrations of ascorbic acid relative to benzene (11.2 μmol/L) predominantly favors the reaction between $\cdot SO_4^-$ and ascorbic acid. Specifically, the relative rate of reaction (R_R) of ascorbic acid and benzene (Equation 1) under the conditions of these experiments (pH < 4.1; $[S_2O_8^{2-}]$ = 10.5 mmol/L; $[AH_2]$ = 40 to 420 mmol/L; [benzene] = 11.2 μmol/L) indicates favorable reaction between $\cdot SO_4^-$ and ascorbic acid relative to benzene (i.e., $R_R >> 1$).

$$R_R = k_8 [\cdot SO_4^-] [AH_2]/k_9 [\cdot SO_4^-] [\text{Benzene}] \approx 125\text{-}1250 \quad (1)$$

The balanced reaction for persulfate mineralization of ascorbic acid indicates that 1 mol of ascorbic acid is required for 10 mol of $S_2O_8^{2-}$ (rxn 10, Table 1). In this study, the minimum ratio of ascorbic acid to persulfate tested was 4 (i.e., 4 mmol ascorbic acid/mmol $S_2O_8^{2-}$). Greater quantities of ascorbic acid are projected to effectively deplete the persulfate and stabilize VOC concentrations than is estimated using ideal reaction stoichiometry. This is because of the excess ascorbic acid required to favor the reaction between $\cdot SO_4^-$ and ascorbic acid and to minimize the reaction between $\cdot SO_4^-$ and VOCs. However, two sources of persulfate oxidation inefficiency may contribute to lowering the consumption of ascorbic acid: (1) nonproductive persulfate reactions that do not yield $\cdot SO_4^-$ and (2) $\cdot SO_4^-$ scavenging reactions. An example of both is provided by the scavenging reaction (rxn 11, Table 1) where $\cdot SO_4^-$ is scavenged by $S_2O_8^{2-}$, resulting in the consumption of both $\cdot SO_4^-$ and $S_2O_8^{2-}$. The second-order reaction rate constant for this reaction is moderately low ($k_{11} = 1.2 \times 10^6$ L/mol s; Buxton et al. 1988), but significant scavenging of $\cdot SO_4^-$ is probable because of the high $S_2O_8^{2-}$ concentrations.

Contaminant Rebound Interpretation

Contaminant rebound at ISCO sites involves the condition in which the contaminant concentrations in groundwater are reduced or non-detectable soon after the oxidant is injected, but steadily increase, or rebound in groundwater after oxidant concentrations have diminished and the aquifer re-equilibrates (Huling and Pivetz 2006). Rebound is attributed to extended periods of slow mass transfer and mass transport mechanisms of the residual contaminants. These mechanisms include, but are not limited to, the slow dissolution of contaminants from NAPL, slow desorption from aquifer materials, slow advective transport in groundwater, and slow diffusive transport of contaminants from low-permeability materials. Furthermore, if monitoring wells are not located near the source zone/ISCO area, the prolonged time required for groundwater transport, sampling, and detection of contaminants may also contribute to the perception of contaminant rebound.

Given the results presented earlier, GC/MS or GC analysis of unpreserved binary mixture groundwater samples may indicate reduced or non-detect concentrations of groundwater contaminants and the misconception of uncontaminated groundwater samples. Later, collection and analysis of oxidant-free, groundwater samples from the same well may reveal the detection of high concentrations of contaminants. Under this set of conditions, these results could be misinterpreted as "contaminant rebound" even in the absence of contaminant mass transport or mass transfer limitations.

The binary mixture condition in groundwater samples and the subsequent misconception of results also extend to bench-scale chemical oxidation studies where the feasibility of ISCO is under investigation. For example, collection and analysis of binary mixture aqueous samples from bench-scale soil reactors may also yield false-negative results. For this reason, detection and quantification of oxidant concentrations and preservation of aqueous samples also extend to bench-scale studies where binary mixture aqueous samples are analyzed for organic contaminants.

Field Methods Used to Measure Oxidant Concentrations in Groundwater

Detection of oxidants in groundwater samples is the first step in assuring that appropriate steps can be taken to mitigate the potential impact of oxidants on the quality of the groundwater sample. Field analytics are useful for providing quick, real-time measurements to detect and quantify the oxidant. Subsequently, field staff responsible for collecting groundwater samples can make a decision on whether to take the appropriate steps to preserve the groundwater sample for subsequent analysis.

Persulfate is colorless and requires field measurement at the well head to determine whether it is present in the groundwater sample and at what concentration. Field test kits are available to measure persulfate concentrations in aqueous samples. Selection of the test kit is dependent on whether the persulfate activator is base or thermal (test kit "K"), or whether persulfate is activated by iron chelates or H_2O_2 (test kit "C") (FMC 2010). Persulfate concentrations can also be measured in groundwater samples using the ferrous ammonium sulfate method and a field spectrophotometer, as described earlier in section "Analytical."

Other

Ascorbic acid has a high solubility and can be prepared in a concentrated solution (620 g/L at 25 °C; 780 g/L at 75 °C) and added to the groundwater sample at the well head. The volume of ascorbic acid solution added to the groundwater sample should be recorded so that appropriate dilution adjustments to the final contaminant concentrations can be made. Alternatively, appropriate quantities of solid-phase ascorbic acid could be added to the sample vessel prior to sample collection or added to the groundwater sample vial at the well head. Preservation of the sample after it is shipped to the laboratory is generally not recommended because of the potential for oxidative reactions in transit and inappropriately preserved (i.e., unrefrigerated) samples.

The use of reductants other than ascorbic acid has been reported in various site reports, but definitive information on the use of these chemicals to neutralize oxidants in groundwater samples is limited. These reductants may be as effective as ascorbic acid but have not been rigorously investigated and reported. These reductants include, but are not limited to, sodium bisulfite, sodium thiosulfate, sodium metabisulfite, manganese sulfate, hydrazine hydrate, hydrazine sulfate, H_2O_2, and hydrochloric acid. In one study, it was reported that different quenching agents and the concentration of the quenching agents could introduce some variability during headspace analysis of PCE (Dai and Reitsma 2004). The variability was hypothesized to be because of the changes in PCE vapor pressures.

The persistence and presence of oxidants in groundwater represents a transient condition of chemical nonequilibrium. Groundwater samples collected and analyzed in the presence of oxidants represent transient nonequilibrium conditions. Contaminant concentrations measured under these conditions may vary widely, and an accurate assessment of the treatment performance is limited. Assuming early groundwater sample collection and analysis is not critical to the wise and effective management of the ISCO remedy, it is recommended that oxidant concentrations decline to non-detect levels prior to groundwater sampling (Huling and Pivetz 2006; Palaia et al. 2010). In one study, 80 d was permitted after the MnO_4^- oxidant dropped below the detection limit before the groundwater was sampled for organic contaminants (Thomson et al. 2007). Consequently, the effects of oxidant residuals on the quality of the groundwater sample can be avoided, and the chemical conditions in the groundwater will become more representative of stabilized conditions.

Summary and Conclusions

ISCO involves the injection of an oxidant, such as sodium persulfate, to oxidize toxic chemicals to nontoxic by-products. Persistent sodium persulfate and other oxidants injected into the subsurface may be accidentally captured in groundwater samples collected during groundwater monitoring events, resulting in a binary mixture of oxidant and contaminants.

In this study, binary mixtures of sodium persulfate (2.5 g/L) and volatile organic compounds (VOCs) (benzene, toluene, xylene, PCE, TCE) (500 to 1100 µg/L) resulted in a significant decline in VOC concentrations (49 to 100%) during the analytical process. Oxidative transformation of these VOC compounds occurred either by direct reaction with the persulfate anion ($S_2O_8^{2-}$) or by reaction with the sulfate radical ($\cdot SO_4^-$) that formed as a result of persulfate activation. Thermal activation of persulfate is known to occur at approximately ≥30 °C (Johnson et al. 2008). During GC/MS headspace analyses of aqueous samples, a 10-mL subsample undergoes a heating step (room temperature to 80 °C in 30 min). During this heating step, the thermal activation of persulfate and formation of $\cdot SO_4^-$ resulted in the oxidation of VOCs present in the aqueous sample. However, a significant decline in VOC concentration was also measured during GC analysis where the aqueous sample was not heated. Seemingly minor losses (1 to 3%) in persulfate concentration (10.5 mM), typical of ISCO sites, were sufficient to

account for significant loss (76 to 100%) of VOCs (10.2 to 11.2 μM), despite limited reaction kinetics.

Groundwater samples containing binary mixtures of VOCs and persulfate were effectively preserved through the addition of ascorbic acid (≥4 mM ascorbic acid/mM sodium persulfate; lower molar ratios were not tested). The overall average recovery of VOCs was 99 and 100% in the GC/MS headspace method and the GC purge and trap method, respectively. No interference by ascorbic acid was detected in sequential analysis of aqueous samples despite high concentrations of ascorbic acid (42 to 420 mM). The addition of excess ascorbic acid is recommended: It does not negatively impact either the quality of the groundwater sample or the analytical instruments used in the GC/MS headspace or GC purge and trap methods. Higher concentrations of ascorbic acid favor the reaction between $S_2O_8^{2-}$ or $\cdot SO_4^-$ and ascorbic acid and limit the reaction between persulfate and the target contaminants, an important requirement in sample preservation.

Detection of oxidants in groundwater samples collected at the well head is required to take appropriate preservation steps. Field methods are available that can be used to detect the presence and concentration of persulfate and other oxidants in groundwater samples. Assuming the oxidant is detected, the sample must be preserved if it is to be analyzed by GC/MS (headpace) or GC (purge and trap). If an oxidant is detected and the binary mixture sample is not appropriately preserved, the quality of the sample is at stake and its use in ISCO remedy decision making is compromised.

Acknowledgments

The authors acknowledge R. Weber, the Superfund Technical Liaison in U.S. EPA Region 7 (Kansas City, Kansas), for his valuable input on the impact of binary mixtures at U.S. EPA Superfund sites; and M. Blankenship, J. Cox, and T. Pardue (Shaw Environmental & Infrastructure, Inc., Ada, Oklahoma) for their analytical assistance.

Notice

The U.S. Environmental Protection Agency, through its Office of Research and Development, funded and managed the research described here. It has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

References

Buxton, G.V., C. Greenstock, W.P. Hellman, and A.B. Ross. 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms, and hydroxyl radicals (·OH/·O⁻) in aqueous solution. *Journal of Physical and Chemical Reference Data* 17, no. 2: 513–886.

Curtin, M.A., I.A. Taub, K. Kustin, N. Sao, J.R. Duvall, K.I. Davies, C.J. Doona, and E.W. Ross. 2004. Ascorbate-induced oxidation of formate by peroxodisulfate: Product yields, kinetics and mechanism. *Research on Chemical Intermediates* 30, no. 6: 647–661.

Dai, Q., and S. Reitsma. 2004. Kinetic study of permanganate oxidation of tetrachloroethylene at a high pH under acidic conditions. *Remediation: The Journal of Environmental Cleanup Costs, Technologies & Techniques*, Autumn: 67–79.

Ferrarese, E., G. Andreottolaa, and I.A. Oprea. 2008. Remediation of PAH-contaminated sediments by chemical oxidation. *Journal of Hazardous Materials* 152, no. 1: 128–139.

FMC Environmental Solutions. 2010. News and Events—Klozur® Persulfate Field Test Kits Now Available from FMC. http://envsolutions.fmc.com/EnvironmentalSolutions/NewsEvents.aspx?itemId=961 (accessed September 2010).

Huang, K.C., R.A. Couttenye, and G.E. Hoag. 2002. Kinetics of heat-assisted persulfate oxidation of methyl *tert*-butyl ether. *Chemosphere* 49, no. 4: 413–420.

Huling, S.G., and B. Pivetz. 2006. In-Situ Chemical Oxidation – Engineering Issue. EPA/600/R-06/072. Ada, Oklahoma: US Environmental Protection Agency, National Risk Management Research Laboratory, R.S. Kerr Environmental Research Center.

Huling, S.G., S. Ko, S. Park, and E. Kan. 2011. Persulfate-driven oxidation of contaminant-spent granular activated carbon. *Water Research* (in review).

Johnson, R.L., P.G. Tratnyek, and R.B. Johnson. 2008. Persulfate persistence under thermal activation conditions. *Environmental Science Technology* 42, no. 24: 9350–9356.

Kao, C.M., K.D. Huang, J.Y. Wang, T.Y. Chen, and H.Y. Chien. 2008. Application of potassium permanganate as an oxidant for in situ oxidation of trichloroethylene-contaminated groundwater: A laboratory and kinetics study. *Journal of Hazardous Materials* 153, no. 3: 919–927.

Liang, C., and I.L. Lee. 2008. In situ iron activated persulfate oxidative fluid sparging Treatment of TCE contamination—A proof of concept study. *Journal of Contaminant Hydrology* 100, no. 3–4: 91–100.

Lide, D.R., ed. 1993. *CRC Handbook of Chemistry and Physics*, 74th ed. Boca Raton, Florida: CRC Press.

Neta, P., R.E. Huie, and A.B. Ross. 1988. Rate constants for reactions of inorganic radicals in aqueous solution. *Journal of Physical and Chemical Reference Data* 17: 1027–1284.

Palaia, T., B. Smith, and R. Lewis. 2010. Chapter 12. ISCO Performance Monitoring. Remediation of Contaminated Groundwater. In *In-Situ Chemical Oxidation for Remediation of Contaminated Groundwater*, ed. R.L. Siegrist, M.L. Crimi, and T.J. Simpkin. In-Situ Chemical Oxidation—Technical Practices Monograph Book. Thousand Oaks, California: Springer Publications, Inc. (In press).

Rivas, F.J. 2006. Polycyclic aromatic hydrocarbons sorbed on soils: A short review of chemical oxidation based treatments. *Journal of Hazardous Materials* 138, no. 2: 234–251.

Thomson, N.R., E.D. Hood, and G.J. Farquhar. 2007. Permanganate treatment of an emplaced DNAPL source. *Ground Water Monitoring and Remediation* 27, no. 4: 74–85.

Biographical Sketches

Scott G. Huling, *Ph.D., corresponding author, is at U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, P.O. Box 1198, Ada, OK 74820; (580) 436-8610; fax: (580) 436-8614; huling.scott@epa.gov.*

Saebom Ko, *Ph.D., is at National Research Council, Robert S. Kerr Environmental Research Center, P.O. Box 1198, Ada, OK 74820; (580) 436-8742; ko.saebom@epa.gov.*

Bruce Pivetz, *Ph.D., is at Shaw Environmental & Infrastructure, Inc., Robert S. Kerr Environmental Research Center, P.O. Box 1198, Ada, OK 74820; (580) 436-8998; pivetz.bruce@epa.gov.*