Persulfate injection into a gasoline source zone

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ABSTRACT

One pore volume of unactivated sodium persulfate was delivered into an emplaced gasoline residual source zone at CFB Borden. Concentrations of inorganic species (S2O8 2−, SO4 2−, Na +, dissolved inorganic carbon (DIC)) and selected gasoline compounds (benzene, toluene, ethylbenzene, xylenes, trimethylbenzenes and naphthalene) were monitored across a transect equipped with 90 multilevel sampling points for >10 months post-injection. Mass loading (M) of compounds constructed from the transect data was used for assessment purposes. Breakthrough of inorganic species was observed when the injection slug crossed the monitoring transect. An increase in M SO2/CO4 indicated persulfate consumption during oxidation of gasoline compounds or degradation due to the interaction with aquifer materials. MDIC increased by >100% suggesting some mineralization of gasoline compounds during treatment. Mass loading for all the monitored gasoline compounds reduced by 46 to 86% as the inorganic slug crossed the monitoring transect. The cumulative mass discharge across the monitoring transect was 19 to 58% lower than that expected without persulfate injection. After the inorganic injection slug was flushed from the source zone a partial rebound (40 to 80% of baseline levels) of mass discharge of the monitored gasoline compounds was observed. The ensemble of data collected provides insight into the fate and transport of the injected persulfate solution, and the accompanying treatment of a gasoline the source zone.

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1. Introduction

Gasoline is one of the most extensively used petroleum hydrocarbon (PHC) mixtures used worldwide and its accidental release, spill or leakage often causes soil and groundwater contamination (Park et al., 2008). Gasoline is primarily comprised of C6 to C16 compounds including acutely toxic and highly persistent aromatics such as benzene, toluene, ethylbenzene and xylenes (BTEX) in addition to trimethylbenzenes and naphthalene (Prince et al., 2007). Benzene and ethylbenzene are established human carcinogens, and health impacts of BTEX compounds, in general, include neurological impairment and hematological effects (ATSDR, 2004). Gasoline and other PHC source zones are persistent, and hence act as long-term sources of groundwater contamination until the source zone is removed, quarantined, attenuated by natural processes or treated in place (Lundegaard and Johnson, 2007).

Contemporary efforts to remediate gasoline-contaminated soil and groundwater have included the use of various technologies (e.g., biodegradation, air-sparging, pump-and-treat, phyto-remediation), but physical and geochemical subsurface heterogeneities, and contaminant characteristics can significantly limit the benefits of these technologies (Kunukcu, 2007; Dadkhah and Akgerman, 2006; Zhou et al., 2005; ITRC, 2001; Nadim et al., 2000). In situ chemical oxidation (ISCO) offers an alternative and aggressive remediation option either alone or as an important step within a “treatment train” (Tsai and Kao, 2009; Tsonitaki et al., 2006). During the past 5 years, persulfate (S2O8 2−) has emerged as a potentially useful oxidant for the destruction of a wide range of organic contaminants including PHCs. Its effectiveness in the treatment of these organic compounds has been reported in a number of bench-scale investigations (Crimi and Taylor, 2007; Huang et al., 2005; Liang et al., 2004, 2008; Sra et al., 2013). Sra et al.
(2013) specifically demonstrated the ability of unactivated and activated persulfate to destroy a mixture of gasoline compounds. However, the peer-reviewed literature reporting its usefulness and application at pilot- or full-scale sites with gasoline contamination is scarce.

To establish reasonable treatment goals, it is important to understand the response of a source zone following the injection of persulfate. While reduction in the aqueous phase concentration or mass discharge (loading) emanating from a treatment area may be a useful performance metric, overlooking system rebound (Suthersan et al., 2010; Thomson et al., 2008) or dilution caused by the injected solution (Payne et al., 2008) may lead to an erroneous estimation of treatment efficiency and effectiveness. This is particularly important immediately following treatment. Rebound of organic concentrations or mass loadings occurs when the oxidant is removed from or consumed within the treatment area, and dissolution or mass transfer of compounds from the untreated contaminant mass takes place (Mundle et al., 2007; Suthersan et al., 2010). Similarly, mixing of the uncontaminated solution with contaminated ambient groundwater during oxidant injection can potentially dilute the organic concentrations and over-estimate oxidation efficiency. Frequent and timely monitoring of target organics, potential inorganic by-products and other geochemical indicators is required to accurately assess treatment performance.

In this investigation, we undertook persulfate injection into a gasoline source zone at the Canadian Forces Base (CFB) Borden near Alliston, Ontario Canada. The objective of this pilot-scale investigation was to collect appropriate high resolution data to provide insight into the fate and transport of the injected persulfate solution, and the concomitant treatment of a gasoline residual source zone. Over a 4 month period following a single persulfate injection episode the evolution and breakthrough of organic compounds, residual persulfate, and oxidation by-products (e.g., SO$_4^{2-}$, Na$^+$, dissolved inorganic carbon (DIC)) were frequently examined. At 10 months post-treatment, groundwater samples were collected to assess the rebound of nine gasoline organic compounds of interest. Treatment performance was estimated from organic and inorganic concentrations and/or mass loading across a monitoring transect down-gradient of the target treatment area. A systematic evaluation was undertaken to differentiate changes in the organic mass loading due to persulfate oxidation from the effects of dilution.

1.1. Site description

The aquifer material at CFB Borden is generally homogenous and is composed of well-sorted fine to medium grain sand (hydraulic conductivity $6.0 \times 10^{-6}$ to $2.0 \times 10^{-4}$ m/s) with some microscale heterogeneity in the form of silty sand and coarse sand lenses (Mackay et al., 1986). The water table is usually located at ~1 m below ground surface (bgs) but varies seasonally. The underlying aquitard is located at ~11 m bgs and is ~8 m thick. A historical leachate plume exists >5 m bgs and is responsible for an elevated pre-injection concentration of SO$_4^{2-}$ and Na$^+$ starting at about 4.5 m bgs (MacFarlane et al., 1983).

A 48 kg gasoline fuel source (American Petroleum Institute; API 94-01) with 5% methyl tert-butyl ether (MTBE) and 5% tert-butyl alcohol (TBA) was emplaced below the water table as part of another study that evaluated distribution and mass loading of dissolved PHCs through an extensive network of monitoring transects perpendicular to the groundwater flow (Freitas et al., 2011). The monitoring network consisted of 4 transects identified as Row 1 to Row 4 installed 6 m apart in the direction of groundwater flow (Fig. 1). Each transect contained 6 multilevel monitoring wells (MW1 to MW6) separated by 1.2 m (Fig. 1(a)) and equipped with 14 multilevel (ML) sampling points (ML1 to ML14) vertically spaced by 18 cm with the shallowest multilevel (ML1) starting at 1.5 m bgs (Fig. 1(b)). The polyvinyl chloride (PVC) center stalk was screened from 4.84 to 5.34 m bgs and represents ML15. The gasoline source was emplaced between Row 1 and Row 2 using 15 PVC injection wells (internal diameter 5 cm) screened from 2.25 to 4.5 m. These gasoline injection wells were arranged in 2 rows spaced 30 cm apart located 3.5 m up-gradient of Row 2 (Fig. 1(a)).

Based on observed organic concentrations from groundwater samples collected from the down gradient monitoring network over a 5-year period prior to this study, the mass depleted from the emplaced gasoline source was estimated at ~8 kg. Hence, at the time of persulfate application ~40 kg of gasoline remained in the source zone and occupied a volume ($V_{source}$) of 7.1 m$^3$. No MTBE or TBA was detected after the first year of monitoring following emplacement suggesting that these mobile and highly soluble constituents had been depleted from the source zone. Soil cores extracted from the source zone and analyzed one year after emplacement of the gasoline showed that the majority of the mass was limited between 3.0 to 4.2 m bgs (Yang, 2009). Significant and relatively constant total petroleum hydrocarbon (TPH) concentrations up to 35 mg/L were observed in the Row 2 monitoring transect over a 2-year period prior to treatment.

2. Materials and methods

2.1. Persulfate injection

Sra et al. (2013) demonstrated that unactivated persulfate at a concentration of 20 g/L was effective for significant to near-complete destruction of nine (9) monitored gasoline compounds (MGCs) (benzene, toluene, ethylbenzene, p, m-xylene and o-xylene (>99%), 1,2,3-trimethylbenzene, 1,2,4 trimethylbenzene and 1,3,5-trimethylbenzene (>95%), and naphthalene (>70%)) over a 28-day reaction period. Significant oxidation (<80%) of PHC fractions F1 (C$_6$ to C$_{10}$) and F2 (C$_{10}$ to C$_{16}$), and TPH was also reported (Sra et al., 2013). Natural activation conditions using Borden aquifer material exhibited slightly higher oxidation rate coefficients (up to 1.8 times higher) for the MGCs as compared to the experimental systems with no aquifer solids present. Acknowledging the balance between density-driven migration of the injected persulfate solution and overall reaction rates, a concentration of unactivated persulfate of 20 g/L was selected for injection into the gasoline source zone for this investigation.

In order to achieve the required spatial coverage during persulfate injection, 3 of the 15 injection wells used by Freitas et al. (2011) as identified on Fig. 1(a) were used to inject ~2000 L of persulfate. This volume was sufficient for complete coverage of the assumed source zone (pore volume (PV) of ~2100 L). The
injection water was collected in a 2200 L polyethylene (PE) tank from a nearby uncontaminated well at the research facility. Following addition of persulfate mass (~40 kg; Klozur, FMC), the solution was mechanically stirred using an electrically-operated drill mixer. Concurrently, to enhance dissolution of the solid persulfate and to obtain a homogenous concentration throughout the tank, solution was withdrawn from an outlet at the bottom of the tank and re-cycled back into the top of the tank at a flow rate of 30 L/min. The pump was equipped with a ball-valve flow controller and connected to the tank using PE pipes (internal diameter 2.54 cm). After mixing and recycling for ~1 h, the pump and mixer were switched off, and the pump outlet was then connected to an injection manifold. The manifold distributed the injection solution to three outlet PE pipes using a combination of 90° and T-shape galvanized steel barb-fittings. A cumulative flow meter was placed between the pump and the three injection outlets. Each of these outlets was equipped with a flow control gate valve, a vent valve and a pressure gauge (0–100 kPa) to enable flow control during injection. PE pipes were used to connect manifold outlets to the riser pipes of the three injection wells which were remodeled to accommodate 2.54 cm barb-fittings. The persulfate solution was injected into the three wells under a pressure of 14 to 21 kPa at an average flow rate of 13 L/min/well for ~1 h. Samples from the injection line were collected every 20 min to quantify the injected persulfate concentration.

The intent of this single persulfate injection episode was to degrade a fraction of the mass in the gasoline source zone. Assuming that the ~40 kg of gasoline that remained in the source zone at the time of treatment was all benzene, then the 40 kg of sodium persulfate injected could theoretically oxidize <5% of the mass in the source zone based on

\[
C_8H_8 + 15S_2O_8^- + 12H_2O \rightarrow 6CO_2 + 30SO_4^{2-} + 30H^+ \quad (1)
\]

In contrast, the fraction of source zone mass that could be degraded is <1% if the overall bulk gasoline stoichiometry for unactivated persulfate of 120 g of S_2O_8^- per g of TPH destroyed determined by Sra et al. (2013) is used. Irrespective of the low fraction of source zone mass that theoretically could be destroyed, we believed that partial treatment was sufficient to observe the fate and transport of the injected persulfate, and the response to the source zone to generate a dissolved plume. Note that the delivery of 1 PV of persulfate solution into the source zone is greater than the typical number of PVs delivered into target treatment zones (Krembs et al., 2010).

2.2. Performance monitoring

Breakthrough of inorganic (S_2O_8^-, SO_4^{2-}, Na^+, DIC) and MGC concentrations were anticipated to be useful in the overall assessment. Na^+ and SO_4^{2-} are released upon dissociation and degradation of sodium persulfate and can be used to identify the transport and evolution of the injected solution. While Borden aquifer material has a low cation exchange capacity (CEC ~0.5 meq/100 g), Na^+ may be potentially retarded (retardation factor of 1 to 2) due to sorption or ion exchange processes (Dance and Reardon, 1983; Kjeldsen and Christensen, 1984). Assuming non-sulfate reducing conditions at shallow depths (MacFarlane et al., 1983), the S_2O_8^-/SO_4^{2-} system was employed to capture the transport of the injected persulfate solution through the aquifer. SO_4^{2-} is a by-product of persulfate degradation and in conjunction with Na^+ can be used as a potential measure for the overall persulfate degradation as a result of oxidation of organics and/or interaction with aquifer materials. Based on stoichiometry, 1 mole of sodium persulfate will yield 2 moles of Na^+ and 2 moles of SO_4^{2-} assuming complete degradation. Therefore, when persulfate is completely degraded, the injection slug should contain ~4.2 g SO_4^{2-} per 1 g of Na^+ assuming that both these species are conservative. Therefore, the relative strength of the two species is indicative of the overall extent of persulfate degradation. Complete mineralization of the target organics leads to CO2 production and therefore, oxidation of PHCs, if proceeding to completion, will elevate the CO2(aq) Concentration and hence the DIC concentration. In a calcite-rich subsurface geochemical environment such
as the Borden aquifer, carbonate equilibrium may influence the DIC concentration.

To capture the fate of the injected persulfate and changes in the concentration of the MGCs as a result of treatment, only the Row 2 monitoring wells were used. In addition to the breakthrough concentration (BTC) profiles at individual monitoring points, mass loading of the inorganic species, MGCs and PHC fractions across the Row 2 transect was also determined. The temporal variation in mass loading for all monitored species and compounds was used to provide a unified perspective. The mass loading (M) defined as the mass of a compound or species crossing the Row 2 transect per unit time was estimated as the integration of the mass flux (Einarson and Mackay, 2001; Thomson et al., 2007). Each multilevel sampling point with a given compound or species concentration (C_i) was assigned a representative area (A_i). Specific discharge (q) was assumed to be constant and was estimated from the average travel time of the centre of mass (t_m) of the injected solution.

Samples collected from MW1 and MW6 in the Row 2 transect 16 months prior to treatment indicated that the concentration of all the MGCs was below the method detection limits (MDLs) and hence these wells were excluded from the monitoring program. Monitoring of MW2 to MW5 was conducted 2 weeks prior to persulfate injection to establish pre-injection or baseline conditions. Monitoring was continued for >4 months post-injection (weekly for the first 2 months and then biweekly for the next 2 months) and samples were analyzed for organic and inorganic compounds. The first post-injection sampling event was conducted 8 days after persulfate injection. One sampling event for organics was conducted 10 months after injection (Day 315). At least triplicate samples were collected from each multilevel sampler using a sampling glass vial (40 mL) placed between the multilevel and a peristaltic pump. For sample collection, the glass vial was fitted to an in-line, stainless steel screw cap sample head. Several (2–3) volumes of groundwater (>120 mL) were passed through the vial before it was detached from the sample head. Two samples were used for organic and/or DIC analysis, and the third sample was used for inorganic analyses (e.g., \( \text{SO}_4^{2-} \), \( \text{SO}_3^{2-} \) and \( \text{Na}^+ \)). Samples for organic analysis were preserved with sodium azide (0.4 mL of 10% solution) and sealed with Teflon lined screw caps. All samples were stored at 4 °C and held for 14 days prior to analysis at the University of Waterloo.

2.3. Analytical methods

Organic analysis of benzene, toluene, ethylbenzene, p,m-xylene, o-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene and naphthalene were performed using gas chromatography (Freitas and Barker, 2008). This comprehensive suite of analytes (MGCs) was assumed to sufficiently capture the total contaminant load and provide evidence of source zone treatment. Concentrations of PHC fractions F1 (MDL 5 μg/L) and F2 (MDL 5 μg/L), and TPH were also quantified and used to explore changes in the bulk organic mass load. The PHC Fraction F1 (C_6 to C_10) included integration of all area counts on a PHC chromatogram beginning just after the hexane (nC_6) peak to the apex of the decane (nC_10) peak, while the PHC Fraction F2 (C_10 to C_16) included integration from the apex of the decane peak to the apex of the hexadecane (nC_16) peak. TPH was estimated as the sum of the PHC F1 and F2 fractions.

Inorganic analysis consisted of \( \text{SO}_4^{2-} \), \( \text{SO}_3^{2-} \), \( \text{Na}^+ \) and DIC concentrations. Persulfate was measured following the approach used by Huang et al. (2002). Persulfate analytical reagents were prepared using ACS grade ferrous ammonium sulfate (FAS) (Fe(NH_4)_2(SO_4)_2·6H_2O) (EMD, Gibbstown, NJ), ammonium thiocyanate (NH_4SCN) (J.T. Baker, Phillipsburg, NJ) and sulfuric acid (H_2SO_4) (EMD, Gibbstown, NJ) in Milli-Q water. Analyses for \( \text{SO}_4^{2-} \) and \( \text{Na}^+ \) were conducted using ion chromatograph (Dionex, DX-3000) (MDL for \( \text{Na}^+ \) of 0.1 mg/L, and for \( \text{SO}_4^{2-} \) of 0.3 mg/L). For DIC analysis a 20 mL aliquot was withdrawn from the bottom of the sample vial into a 30 mL glass syringe containing 10 to 20 mL of pre-purified helium. The syringe was shaken and allowed to equilibrate for several hours at room temperature. Then a 6 mL aliquot of the gas phase from the syringe was injected into a 2 mL gas sample loop where a valve switch introduced the sample into the carrier gas stream of a GOW-MAC (Series 350GP) gas chromatograph equipped with a thermal conductivity detector. Peak areas were measured by a HP3380A integrator. The MDL for DIC was 0.98 mg/L.

3. Results and discussion

The average MGC concentrations along the Row 2 transect obtained 2 weeks before the persulfate injection episode were within ±15% of the average concentrations for ethylbenzene, p,m-xylene, the trimethylbenzenes, and naphthalene observed >16 months previously. The general similarity between these MGC concentrations over this period indicated that, in the absence of any treatment, the concentrations and, by implication, mass loadings across the Row 2 transect would have remained consistent with the pre-injection levels for the duration of this pilot-scale trial monitoring period. The situation for benzene, toluene and o-xylene was not the same since the concentration of these three compounds showed a decreasing trend prior to injection and hence in the absence of any treatment this decreasing trend would presumably have persisted.

The pre-injection concentration profiles along MW3 and MW4 showed a distinct and consistent trend with lower MGC concentrations (e.g., <200 μg/L ethylbenzene) to a depth of 2.8 m bgs and higher MGC concentrations (e.g., 1200 to 3500 μg/L ethylbenzene) between 2.8 and 4.0 m bgs (Fig. 2(a)). This is consistent with the profile of bulk soil concentrations from soil core extracted from the source zone which indicates the presence of a higher residual gasoline mass between 3 and 4.2 m bgs (Fig. 2(b)). This is consistent with the profile of bulk soil concentrations from soil core extracted from the source zone which indicates the presence of a higher residual gasoline mass between 3 and 4.2 m bgs (Fig. 2(b)).

(Yang, 2009). The pre-injection MGC concentrations at ML15 sampling points were insignificant (<2.4 μg/L).

The pre-injection \( \text{SO}_4^{2-} \) and \( \text{Na}^+ \) concentrations along MW3 and MW4 were low (1 to 40 mg/L for \( \text{SO}_4^{2-} \), and 1 to 13 mg/L for \( \text{Na}^+ \)) but as expected, the deepest multilevel sampling points (ML15) were impacted (<200 mg/L \( \text{SO}_4^{2-} \), ~40 mg/L \( \text{Na}^+ \)) by the underlying leachate plume (MacFarlane et al., 1983) (Fig. 2(c,d)). To avoid complexity arising from interference by the leachate plume, the deepest multilevel sampling points (ML15) were neglected during the analyses of the inorganic data.
3.1. Behavior of persulfate, sulfate and sodium

Concentration temporal data for $\text{S}_2\text{O}_8^{2-}$, $\text{SO}_4^{2-}$ and $\text{Na}^+$ (Fig. 3) were used to estimate $t_{cm}$ for these three inorganic species. The average $t_{cm}$ was estimated to be 64 days for $\text{S}_2\text{O}_8^{2-}$ and $\text{SO}_4^{2-}$, and 75 days for $\text{Na}^+$. The estimated $t_{cm}$ for $\text{S}_2\text{O}_8^{2-}$ may be deemed representative of the advective transport of the inorganic slug. The $t_{cm}$ estimate for $\text{Na}^+$ is likely impacted by attenuation due to sorption (Kjeldsen and Christensen, 1984) and thus an average delay of 11 days was observed as compared to $\text{S}_2\text{O}_8^{2-}$ or $\text{SO}_4^{2-}$. Assuming an ideal distribution of the injected solution around the three injection wells, the inorganic slug length in the direction of groundwater flow was ~1.1 m. Further, assuming $\text{S}_2\text{O}_8^{2-}$ is not retarded, the travel time for this idealized plug to cross the Row 2 transect would range from 54 to 74 days. Using this information, the retardation factor for $\text{Na}^+$ was estimated to be ~1.2 which is within the span observed by Kjeldsen and Christensen (1984) for different sediments.

The first $\text{S}_2\text{O}_8^{2-}$ breakthrough at the Row 2 transect was observed on Day 21 but was limited to only two multilevel monitoring points at MW3 (ML1 and ML11). Persulfate was more consistently encountered in the subsequent sampling episodes across an increasing number of multilevel monitoring points until Day 107 after which time no further $\text{S}_2\text{O}_8^{2-}$ was detected. Within 8 days of $\text{S}_2\text{O}_8^{2-}$ injection, $\text{Na}^+$ and $\text{SO}_4^{2-}$ concentrations were up to 10 times higher than the pre-injection concentrations at some of the monitoring points (e.g., ML11 to ML14, ML11 and ML12 in both MW3 and MW4). A significant increase in $\text{Na}^+$ and $\text{SO}_4^{2-}$ concentrations was observed in all monitoring wells leading to an average concentration of $>100$ mg/L for $\text{SO}_4^{2-}$ and $>15$ mg/L for $\text{Na}^+$ until Day 107. Hydrodynamic dispersion and the presence of preferential flow pathways caused an earlier breakthrough of $\text{S}_2\text{O}_8^{2-}$, $\text{Na}^+$ and $\text{SO}_4^{2-}$ (Fig. 3) than that anticipated from an ideal plug flow response. Earlier arrival of $\text{SO}_4^{2-}$ relative to $\text{S}_2\text{O}_8^{2-}$ indicates either oxidation of gasoline compounds or persulfate degradation in the presence of Borden aquifer material (Sra et al., 2010). Persulfate concentration at individual monitoring points was generally $\leq 500$ mg/L indicating significant mixing between ambient and injected water and/or persulfate degradation in the presence of aquifer materials and MGCs. $\text{SO}_4^{2-}$ and $\text{Na}^+$ concentrations were $<1000$ mg/L and $<300$ mg/L, respectively, and the maximum concentrations were 10 to 20 times lower than those anticipated from the injection concentrations. $\text{SO}_4^{2-}$ concentrations decreased after Day 71 whereas $\text{Na}^+$ concentrations generally began to decrease after Day 107. These concentrations appeared to approach the pre-injection conditions after Day 121 suggesting that the majority of the injection slug had crossed the Row 2 monitoring transect. Sampling for inorganic species was terminated on Day 135.
investigation, we choose to employ Na+ which is slighted vasive tracer was added to the injected solution in this and ~5400 mg-S/L for S2O8− retarded, and the sum of S2O8− concentration in the injection solution (~4000 mg/L for Na+, SO42− and ~290 mg-S/L for the sum of S2O8− concentration detected at the Row 2 transect was 280 mg/L for Na+ (Day 93) and for 290 mg-S/L for the sum of S2O8− (expressed as equivalent sulfur concentration) as tracers. The maximum concentration detected at the Row 2 transect was 280 mg/L for Na+ (Day 93) and for 290 mg-S/L for the sum of S2O8− and SO42− (Day 79). These values represent <10% of their concentration in the injection solution (~4000 mg/L for Na+, and ~5400 mg-S/L for S2O8−) and suggest that >90% of the injected solution was diluted by the ambient groundwater or that the injection volume displaced or diluted <10% of the ambient contaminated groundwater.

3.1.1. Mass loading of sulfate, sodium, and DIC

As expected from the observations made from the time series data, the MNa+ and MSO4− were initially observed to increase over time, reach a maximum value and then decrease as the monitored inorganic species migrated through the treatment zone (Fig. 4(a)). Consistent with the time series data, the initial increase in MSO4− was faster than for MNa+, suggesting that Na+ was slightly retarded by ion exchange or sorption. The increase in MNa+ after Day 71 is indicative of a typical desorption response as ambient groundwater migrates through sediments loaded with Na+ (Kjeldsen and Christensen, 1984). The maximum MSO4− and MNa+ was observed at Day 44. The maximum SO42− to Na+ mass ratio of 9.1 was observed at Day 21 as a result of the retardation of Na+. The subsequent decrease in the SO42− to Na+ mass ratio to <4.2 corresponded with significant S2O8− breakthrough in almost all monitoring wells (as high as 130 mg/L at some sampling points) implying that not all S2O8− was consumed or decomposed to generate SO42− and hence a SO42− to Na+ mass ratio of <4.2 was not surprising. As these inorganic species migrated from the treatment zone the mass load across the Row 2 transect was observed to decrease. The MNa+ increase due to desorption and consequently the SO42− to Na+ mass ratio remained <4.2. However, the estimated average concentration of SO42− and Na+ in the inorganic slug indicated that the overall SO42− (112.9 mg/L) to Na+ (26.5 mg/L) mass ratio was ~4.3 which was very similar to that expected based on stoichiometry.

Complete oxidation of gasoline compounds would potentially result in their mineralization to CO2 and hence the mass load of DIC was expected to increase as the slug of injected solution was transported across the Row 2 transect. This behavior was indeed observed as the DIC mass load increased in tandem with the increase in SO42− and Na+. The maximum MDIC at Day 44 corresponded with the maximum mass load of SO42− and Na+. Beyond Day 44, MDIC gradually reduced indicating a decrease in the complete mineralization of some gasoline compounds.

The cumulative mass of S2O8− and SO42− that was transported across the Row 2 transect was 0.7 kg and 3.8 kg respectively. This represents ~14% of the total mass of sulfur injected into the source zone as persulfate indicating that only a portion of the injected slug was captured by the high resolution Row 2 monitoring network. Density differences between the injected solution and the ambient groundwater were likely responsible for an increase in the body force that caused the persulfate solution to migrate downwards. Schincariol and Schwartz (1990) showed that even slight density differences (as low as 0.8 g/L) can create significant flow instabilities. The monitoring transects were equipped with only one sampling point deeper than 4.5 m bgs (ML15 was screened from 4.84 and 5.34 m bgs) which was the lower extent of the injection zone (Fig. 1(b)). Although concentration data at this depth are convoluted by the presence of the historical leachate plume, higher S2O8− concentrations were observed at ML15 relative to ML14 for two sampling rounds (Day 44 and Day 51). This suggests that density driven flow influenced the transport of the injected inorganic species despite the lower persulfate concentration (20 g/L) employed in this investigation. Nevertheless, we feel that the findings reported from this effort are representative of this system and provide insight the behaviour of these inorganic species following the persulfate injection episode.

![Fig. 3. Concentration time series data for (a) persulfate, (b) sulfate and (c) sodium at selected sampling points along MW3 (ML 7 and ML 12) and MW4 (ML 7 and ML 13).](image)
3.2. Concentration of MGCs

To illustrate changes in the concentration of the MGCs as a result of the persulfate injection episode, ethylbenzene and naphthalene were selected since they capture the range of first-order oxidation rate coefficients as reported by Sra et al. (2013) and show a typical response for this system. The following discussion can be qualitatively extrapolated to the other MGCs since the relative response of concentration and mass loading of all MGCs was consistent (see Fig. S1 and Fig. S2, Supplementary materials).

The pre-injection concentration of MGCs appeared to primarily occur between 3.0 and 4.0 m bgs (Fig. 2(a)), and MW3 exhibited higher concentrations than MW4. Consistent with the breakthrough of inorganic species, depletion of MGC concentrations occurred as the inorganic slug moved across the Row 2 transect (Fig. 5). The largest decrease in MGC concentrations was observed between Day 65 and 79 and corresponded to the tail of the idealized inorganic slug. Ethylbenzene concentration was reduced significantly by Day 79 with very low concentrations (<200 μg/L) in MW4, and relatively much lower concentrations (<1400 μg/L) in MW3 as compared to the pre-injection concentrations (Fig. 2(a)). Similarly, the naphthalene concentration was <90 μg/L in MW4 and <380 μg/L in MW3 (Fig. 5(b)). The decrease in MGC concentrations was more evident at MW4 compared to MW3 particularly during early time which corresponded with the occurrence of higher SO₄²⁻ and Na⁺ concentrations in MW4. After the inorganic slug had migrated down-gradient of the Row 2 transect, re-equilibration of up-gradient uncontaminated groundwater with the gasoline source resulted in partial rebound in the MGC concentrations. As a result, the concentrations of all the MGC were observed to increase up to Day 315.

3.2.1. Mass loading of the MGCs

Mass loading across the Row 2 transect for all MGCs and PHC fractions were normalized to the pre-injection mass loading (Mₒ) (Fig. 4(b), and Fig. S1 and Fig. S2, Supplementary materials). These normalized data clearly demonstrate that by Day 28 a significant reduction in M/Mₒ crossing the Row 2 transect was observed for all MGCs. The mass loading appears to increase temporarily but then further decreased to a minimum M/Mₒ of 14 to 54% between Days 65 and 79 (Table 1). The minimum mass loading for toluene was observed ~14 days earlier than the other compounds presumably
because it has the highest oxidation rate coefficient among all MGCs (Sra et al., 2013).

The initial decrease of M/M_p at Day 44 corresponds with the maximum Na^+ , SO_4^{2−} and DIC mass loading implying significant oxidation of gasoline compounds during this time. As indicated earlier, dilution of MGCs due to mixing of ambient groundwater and the injected solution may have also contributed to this initial decrease. Further reduction in M/M_p after Day 44 was due to the continual oxidation of the MGCs. Theoretically, the injected persulfate solution was spread around its center of mass which arrived at the Row 2 transect at Day 64. The tail of this inorganic slug resulted in continual decrease of the concentration of the MGCs. The Mo ratio for the MGCs after Day 79 either: (i) consistently increased (ethylbenzene, p,m-Xylene, and trimethylbenzenes), (ii) increased to a plateau and then remained relatively constant (naphthalene), or (iii) increased to a plateau and then followed a decreasing trend (benzene, toluene, o-Xylene) until monitoring was terminated at Day 315. The decreasing M/M_p trend for benzene, toluene, o-Xylene is consistent with observed decreasing trend prior to injection. The M/M_p ratio of the other MGCs were all < 1 at Day 315 (0.59 to 0.71) suggesting that perhaps the strength of this source zone was partially reduced in response to the persulfate injection episode. We acknowledge that there was only one sampling round collected after Day 135 and that additional data would have been useful to provide a clearer understanding of these longer term trends.

Similar to the observations for the MGCs, a significant decrease in M_F1, M_F2, and M_TPH was also observed (Fig. 4(b) and Fig. S2, Supplementary materials). The maximum reduction of M_F1 (75%) and M_TPH (69%) occurred between Day 71 and 79, whereas for M_F2 the maximum decrease was 54% at Day 51. As expected from bench-scale studies (Sra et al., 2013), the decrease in M_F2 was lower than that for M_F1 or M_TPH but the maximum decrease in M_F2 occurred earlier than any of the MGCs or the F1 fraction mass loadings. Sra et al. (2013) observed during a gasoline treatability study that a 60% decrease in PHC F2 fraction concentration occurred quickly (<10 days) followed by very slow rate of destruction, unlike the MGCs or PHC F1 fraction. This suggested that the PHC F2 fraction consists of a readily oxidizable sub-fraction. Therefore, the fast destruction of this oxidizable portion in the PHC F2 fraction resulted in the minimum M_F2 occurring earlier than the MGCs and the other bulk measures. Similar to the naphthalene mass loading, M_F1, M_F2, and M_TPH increased after Day 79 to a plateau and then remained relatively constant. When monitoring was terminated at Day 315 M_F1, M_F2, and M_TPH were 58, 54, and 56% of the pre-injection mass loadings, respectively.

In general, the decrease in mass loadings for MGCs and PHC fractions may be caused by persulfate oxidation of gasoline compounds resulting in the reduction of the source mass strength and also by dilution of organic compounds following the injection of persulfate solution. As identified above, the maximum decrease in the MGC mass loadings across the Row 2 transect with respect to pre-injection conditions was between 14 and 54%, and the injection volume displaced or diluted <10% of the ambient contaminated groundwater based on the maximum concentration of Na^+ and sum of SO_4^{2−} and SO_2^{4−}. These two observations in conjunction with the elevated DIC concentrations suggest that the decrease of MGC concentrations was due to oxidation rather than dilution (Fig. 4) (Payne et al., 2008). In order to further distinguish between the reduction in organic mass load due to physical dilution by 2000 L of injection solution and due to oxidation by persulfate, the observed cumulative mass curve and two theoretical cumulative mass curves for each MGC crossing the Row 2 transect were constructed. The observed cumulative mass was calculated by assuming that mass loading between two sampling episodes was representative of the average of mass loading over the time interval. One theoretical cumulative mass represented the expected cumulative mass crossing the Row 2 transect based on the pre-injection conditions and was assumed to be constant over 315 days given that these concentrations along the Row 2 transect were similar

Table 1
Summary of changes to the gasoline source zone strength in response to the single persulfate injection episode.

<table>
<thead>
<tr>
<th>Gasoline compound or bulk measure</th>
<th>Method detection limit</th>
<th>Maximum decrease in mass loading</th>
<th>Mass loading at Day 315</th>
<th>Cumulative mass reduction at Day 315</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[μg/L]</td>
<td>[%]</td>
<td>[mg/day]</td>
<td>[mg/day]</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.4</td>
<td>52^a</td>
<td>4.2</td>
<td>3.4</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.1</td>
<td>86^b</td>
<td>19</td>
<td>11</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>1.5</td>
<td>84^c</td>
<td>100</td>
<td>48</td>
</tr>
<tr>
<td>p,m-Xylene</td>
<td>2.6</td>
<td>85</td>
<td>150</td>
<td>74</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>1.8</td>
<td>86</td>
<td>31</td>
<td>13</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>1.2</td>
<td>57</td>
<td>13</td>
<td>9.2</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>1.0</td>
<td>64</td>
<td>46</td>
<td>27</td>
</tr>
<tr>
<td>1,2,3-Trimethylbenzene</td>
<td>1.0</td>
<td>63</td>
<td>12</td>
<td>6.4</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>2.2</td>
<td>46</td>
<td>12</td>
<td>8.2</td>
</tr>
<tr>
<td>PHC fraction F1 (C6 to C10)</td>
<td>5.0</td>
<td>75^d</td>
<td>500</td>
<td>290</td>
</tr>
<tr>
<td>PHC Fraction F2 (C10 to C16)</td>
<td>5.0</td>
<td>54^e</td>
<td>140</td>
<td>75</td>
</tr>
<tr>
<td>TPH</td>
<td>5.0</td>
<td>69^f</td>
<td>640</td>
<td>360</td>
</tr>
</tbody>
</table>

Notes:

^a Obseved on Day 79.
^b Obseved on Day 65.
^c Obseved on Day 71.
for ~16 months prior to treatment. The second theoretical cumulative mass curve was constructed using the pre-injection conditions but incorporating the potential dilution by the addition of 2000 L of uncontaminated injection solution. To represent the “worst-case” scenario for complete dilution, it was assumed that the 2000 L did not contain any dissolved gasoline compounds as it crossed the Row 2 transect implying that the 2000 L led to 100% displacement of the ambient groundwater. This assumption led to a cumulative mass curve that coincided with the theoretical pre-injection cumulative mass curve until Day 54 when the leading edge of the idealized injection slug reached the Row 2 transect. The total volume crossing the Row 2 transect from Day 54 to 74 consisted of a portion of injection slug with no gasoline compounds while the remaining portion carried MGC concentrations consistent with the pre-injection conditions. Therefore, the increase in mass was minimal from Day 54 to Day 74 after which the increase in cumulative mass was again consistent with the pre-injection loading conditions.

The cumulative mass curves for the MGCs demonstrated that the observed cumulative mass was significantly lower than the dilution-embedded cumulative mass (Fig. 6). By Day 315, the observed cumulative mass was 19 to 58% lower than that expected after incorporating dilution (Table 1), clearly indicating that persulfate treatment led to a significant decrease in the mass load across the Row 2 transect. A larger decrease was observed for ethylbenzene, xylenes and toluene (>42%) than for TMBs, benzene (19%) and naphthalene (32%) which was expected from the treatability study results (Sra et al., 2013).

Overall, the relative decrease in observed cumulative mass for the MGCs was also synonymous with earlier observations related to the inorganic data in which dilution of the ambient groundwater was shown to play only a minor role. The slope of the cumulative mass curve at Day 315 can be assumed to provide a quantitative estimate of the source zone strength since it represents the overall MGC dissolution rate. Slopes of the observed cumulative mass curves were 19 to 58% lower than those for dilution-embedded cumulative mass curves at Day 315 (Table 1) indicating that the source zone strength was diminished following the single persulfate injection episode. Bulk dissolution rates for ethylbenzene and naphthalene decreased from 99.5 and 12.3 mg/day, respectively, for the dilution-embedded cumulative mass to 48 and 8.2 mg/day, respectively, for the observed cumulative mass.

4. Summary

The mass loading of SO$_4^{2-}$, Na$^+$ and DIC increased as the injection slug crossed the monitoring transect; however, Na$^+$ transport was retarded relative to persulfate and SO$_4^{2-}$ due to ion exchange or sorption with the aquifer material. The increase in SO$_4^{2-}$ signified consumption of persulfate during oxidation of gasoline compounds or degradation in the presence of aquifer materials. Increases in DIC mass loading was due to mineralization of gasoline compounds as a result of persulfate oxidation. The oxidation of gasoline compounds was also captured by the decrease in mass loading for the MGCs and PHC fractions. The overall maximum decrease in mass loadings was consistent with reaction rates of the MGCs reported from bench-scale investigations. The decrease in the cumulative mass of the MGCs crossing the monitoring transect was primarily (60 to 80%) due to persulfate oxidation. Based on the maximum concentration of inorganic species observed downgradient of the source zone the injection volume displaced or diluted <10% of the ambient contaminated groundwater. Soil cores were not collected from the source zone to quantify mass depletion due to significant contaminant heterogeneity that would prevent any meaningful statistical conclusions to be obtained. After the inorganic slug migrated from the source zone, the mass loadings for the inorganics species decreased as expected and a partial rebound of the MGCs was observed.

The results from this study suggest that prolonged and frequent sampling is required following the delivery of persulfate to assess fate and transport of the residual persulfate, generated inorganic species (e.g., SO$_4^{2-}$, Na$^+$, DIC) and to capture the rebound of organic compounds. The decrease in concentrations of the inorganic species is followed by an increase in the organic compound concentrations as the dissolution within the source zone establishes a new equilibrium. This rebound phase, as captured by the mass discharge across a high-resolution monitoring transect, indicated that after 315 days post persulfate injection the system had not yet reached this new equilibrium for some of the monitored organic compounds.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jconhyd.2013.03.007.

References


