1 **Dosing of Ozone in Oxidation of Methyl *tert*-Butyl Ether while Minimizing**
2 **Hexavalent Chromium Formation in Groundwater**

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Abstract

Co-oxidation of trivalent chromium (Cr(III)) to hexavalent chromium (Cr(VI)) during ozonation of organic pollutants represents a common problem facing the implementation of in situ chemical oxidation (ISCO) for environmental remediation. A laboratory study was conducted by using groundwater and saturated soil samples from a field site in Sacramento, California, to determine optimal O₃ dosage to achieve satisfactory remediation of MTBE while minimizing co-oxidation of Cr(III) to Cr(VI). Total oxidant demand was determined (28.33 mg O₃ L⁻¹) and used as the benchmark to establish a range of ozone dosages for the study. Concentration changes in MTBE and chromium were monitored at O₃ dosages less than and greater than the benchmark. The results indicate that MTBE is preferentially oxidized by ozone at and below the indicated benchmark dosage prior to the oxidation of Cr(III) to Cr(VI). The resultant O₃ dosage of 28.33 mg L⁻¹ was successfully applied in the field implementation, verifying that the O₃ can be applied in a controlled manner to remediate MTBE while minimizing the formation of Cr(VI).

Keywords: Remediation; advanced oxidation processes; hexavalent chromium; in situ chemical oxidation; total oxidant demand

1. Introduction

Methyl *tert*-butyl ether (MTBE) is a gasoline-additive that has contaminated groundwater from leaking underground storage tanks [1, 2,] and other sources. The water solubility of MTBE is 50,000 mg L⁻¹ and it has an effective water solubility of 5,000 mg L⁻¹ when in a typical gasoline mixture [3]. MTBE also has a low tendency for adsorption to soil particles. As such, MTBE readily dissolves into groundwater and experiences little retardation resulting in migration nearly equal to the groundwater flow rate and the potential for widespread migration. MTBE also creates taste and odor problems in drinking water at relatively low concentrations. The California Department of Health Services adopted primary and secondary maximum contaminant levels (MCLs) for MTBE of 13 µg L⁻¹ and 5 µg L⁻¹, respectively [4].

In-situ chemical oxidation (ISCO) using ozone (O₃) is a remediation technology that has been successfully applied at MTBE contaminated sites. Delivery approaches include fine-bubble sparging, gas injection, and aqueous injection technologies using O₃ and O₃/hydrogen peroxide [2, 5-10]. Tertiary-butyl formate (TBF) and tertiary-butyl alcohol (TBA) are common intermediate by-products of MTBE oxidation with O₃ under the following predominant degradation pathway [6]:

Ozone can also react with metals in groundwater and the soil matrix. In particular, trivalent chromium (Cr(III)), which is ubiquitous in soil, can be oxidized by oxidants such as O₃ to form the toxic hexavalent chromium (Cr(VI)) [8, 11-13]. Research found that oxidation of Cr (III) to Cr (VI) was largely attributed to hydroxyl radicals in advanced oxidation process by ozone [14]. Few, if any, peer-reviewed studies have been

done on Cr(VI) formation during or after ISCO implementation. The USEPA drinking water standard is 0.1 mg L⁻¹ for total chromium, which includes all forms of chromium. Chromium form, Cr(VI) is much more soluble than Cr(III); therefore, proper dosing of O₃ oxidation is critical for achieving remedial goals while preventing Cr(VI) formation.

A field pilot test was conducted at a MTBE-contaminated site, where in situ injections of O₃ were conducted. Field monitoring indicated that MTBE was oxidized prior to Cr(VI) formation, and it was assumed that over dosing of O₃ might have caused the elevated Cr(VI). The following study was conducted to test this assumption and a series of ozone dosages were tested to determine the optimal dosage for oxidizing MTBE while limiting the co-oxidation of Cr(III). The optimal dosage was then applied during the remediation of MTBE-impacted groundwater.

2. Materials and Methods

2.1 Field site history

A field pilot test was conducted at a leaking underground storage tank (LUST) site located in Sacramento, California. The MTBE released from the former gasoline service station migrated to and impacted a municipal water supply well. Ozone injection was tested as a potential remedial alternative for removing MTBE from groundwater. In the field pilot test, ozone was injected into the MTBE impacted groundwater at approximately 24.4 m below ground surface (bgs). Monitoring wells were located 4.6 m down-gradient (MW-4B) and 6.1 m cross-gradient (MW-13B) from injection well OZ-2, as shown in Figure 1. An existing shallow interval monitoring well (MW-4A), screened from 10.7 to 15.2 m bgs and located 6.1 m down-gradient, was also included in the test.

Ozone injection was successful in reducing MTBE concentrations from approximately 10,000 $\mu\text{g L}^{-1}$ to approximately 300 $\mu\text{g L}^{-1}$ after 2 weeks and non-detect ($< 0.5 \mu\text{g L}^{-1}$) after 7 weeks. These results were complicated by Cr(VI) increasing from non-detect ($<1.0 \mu\text{g L}^{-1}$) after 3 weeks to nearly 400 $\mu\text{g L}^{-1}$ after 10 weeks. The pilot test was shutdown after 5 weeks, and the Cr(VI) impacts were observed to be persistent. A temporary groundwater extraction system was used to remove the Cr(VI).

2.2 Field sampling

Groundwater and soil samples were collected from the field site in Sacramento, California, two weeks prior to conducting the laboratory experiments. Groundwater samples were collected from each using a bailer (purging groundwater equivalent to three times the well volume before collecting the sample). Groundwater samples (18.9 L) were collected from MW-4B, MW-3 (located up-gradient to MW-4B), and MW-4A (located adjacent to MW-4B) to establish a site baseline and assist in evaluating site heterogeneity. Field parameters of pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), and electrical conductivity (EC) were measured at these locations during the sampling. During this sampling event, a new well (EW-1B) was completed using a sonic drill rig. Core samples taken during drilling were characterized in the field and a well log was produced. Soil samples were taken from the drilling core above the impacted interval, in the interval, and just below the interval at depths of 21.9 to 22.6 m, 24.4 to 25.0 m, and 25.3 to 25.9 m, respectively. The soil and groundwater samples were shipped at 4°C to Western Research Institute (Laramie, WY) for analyses and laboratory experiments.

2.3 Sample characterization

Soil and groundwater were analyzed to establish baseline characteristics. Analytes included: pH, EC, DO, ORP, total organic carbon (TOC), dissolved organic carbon (DOC), anions including Fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), total and dissolved metals including iron (Fe), manganese (Mn), copper (Cu), nickel (Ni), zinc (Zn), lead (Pb), chromium (Cr(III) and Cr(VI)), as well as MTBE and its intermediates.

The pH was measured by using an Orion 9106BNWP ion-selective probe (Thermo Electron Corp, Waltham, MA) attached to an Orion 720A+ meter (Thermo Electron Corp, Waltham, MA). Temperature was measured during the analyses for data correction. Oxidation-reduction potential (ORP) was measured by using an Orion 9678BN redox electrode connected to the Orion 720 A+ meter. Electrical conductivity (EC) was measured using an Orion 150A+ meter equipped with an Orion 013005D conductivity cell. Dissolved oxygen (DO) was measured using a YSI (Yellow Springs, OH) Model 58 DO meter. Anions were analyzed using a Dionex (Sunnyvale, CA) DX-100 ion chromatograph (IC) equipped with an IonPac AS14 Pack Column. Total and dissolved metals were analyzed by using inductively coupled plasma mass spectrometry (ICP-MS; PE SCIEX Model Elan 6000) with a method equivalent to EPA Method 200.8. Cr(VI) analysis was performed within 24-h of the sampling event using EPA method 7196A. Samples for MTBE were analyzed using EPA Method 8260 and a gas chromatograph-mass spectrometer (GC-MS; model 6890/5973, Agilent Technologies, Palo Alto, CA) equipped with a purge and trap system. The TOC and were analyzed using a Shimadzu TOC analyzer (Columbia, MD) by following standard methods.

2.4 Total oxidant demand

Total oxidant demand (TOD) was measured to estimate a benchmark based ozone dosage. Due to the difficulty in quantifying residual ozone, a TOD protocol was established using sodium percarbonate ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$) as a surrogate oxidant equivalent, due to its relative stability and simple measurability. The TOD was determined by reacting site groundwater and soil samples (10% w/v of soil) with a solution of $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ (10,000 mg L⁻¹). Sodium percarbonate concentrations were evaluated by determining the residual H_2O_2 concentrations from reacting with titanium (IV) oxysulfate [15] and analyzing the solution on a Shimadzu UV min 1240, UV-VIS spectrophotometer (Columbia, MD).

The O_3 demand was calculated based on an oxidizing potential of 2.1 V for O_3 and 1.8 V for H_2O_2 (1.8 V) from $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$. The O_3 demand was then determined based on the stoichiometric relationship of 0.85 mol O_3 being equivalent to 1.0 mol H_2O_2 . Since there are 3 mol H_2O_2 in 1 mol $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, the relationship in terms of $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ is 0.28 mol O_3 mol⁻¹ $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$.

2.5 Bench-scale study

Microcosm reactors were established in 500-ml amber glass bottles using composite groundwater and soil samples collected from the site. Soil was set at 10% (w/v) of the total volume in the reactors. A range of O_3 dosages were used corresponding to 0, 25, 50, 100, 200, and 400% of the benchmark dosage. Ozone was delivered at a steady rate by an Absolute Ozone AE15MC ozone generator (Edmonton, AB, Canada) with micro bubble emitters placed at the bottom of the reactors. The testing flow rates and system specifications are summarized in Table 1. The reactors were set up in triplicates and oxidation was performed at field-measured temperature in a water bath.

Based on the flow rate, a sampling schedule was established to collect samples when set dosages were obtained (Table 2). Temperature, ORP, and pH was measured and the samples were analyzed for MTBE and Cr(VI). Anions and total and dissolved metals were also monitored to determine if other substances were oxidized, released and/or precipitated during the O₃ test.

2.6 Field implementation

Four O₃ injection wells were established in the field and designated as AS-1, OZ-2B, and OZ-3A/B. Wells AS-1 and OZ-2B were located on the down-gradient side of the source area in the shallow and deep groundwater intervals, respectively (Figure 1). Wells OZ-3A and OZ-3B were located in the former UST area on the up-gradient side of the site. A groundwater extraction and treatment (GET) system was installed on the down-gradient edge to capture groundwater from both groundwater intervals. The GET system was designed to enhance in-situ biodegradation by accelerating groundwater flow and distributing the O₃-oxygenated water across the site and capture any Cr(VI) that may have formed. The O₃ generator was capable of injecting 0.68 kg d⁻¹ of O₃ in an air/ozone mixture at a flow rate of approximately 85.0 dm³ min⁻¹, and at pressure up to 276 kPa and the O₃ loading rate could be varied by adjusting the percent of total capacity. Ozone was injected into each well sequentially, allowing an off time after injection into a particular well. As such, the amount of applied ozone was controlled by the generator output and by the ON/OFF cycle times. MTBE, TBA, Cr(VI), and DO were monitored at nearby groundwater monitoring wells to evaluate ozone application and MTBE treatment and potential formation of Cr(VI). Groundwater monitoring samples were collected from wells MW-3, MW-4A, and MW-4B at times 0, 3, 6, and 9 months. Groundwater samples

were collected from each using a bailer (purging groundwater equivalent to three times the well volume before collecting the sample).

3. Results and discussion

3.1 Baseline characterization

Field measurements from monitoring wells MW-3, MW-4A, and MW-4B are shown in Table 3. The redox potential of the groundwater was in a low DO to oxygen-depleted state, indicated by the DO measurements and verified by the negative ORP measurements. The neutral pH and presence of organic carbon may suggest that microbial activity may be responsible for the oxygen depletion. Monitoring well MW-4A had the highest DO at 1.22 mg L^{-1} which corresponded with a low DOC of 0.32 mg L^{-1} (Table 4).

Results of other analytes are summarized in Table 5. Similar concentrations of anions were found in each well. The lower concentrations of common electron acceptors such as nitrate and sulfate indicate that the groundwater onsite is relatively homogeneous and under reducing conditions. Nitrate data from MW-4B samples was not reported due to system error during the analysis. Elevated concentrations of dissolved Mn ($2602 \text{ } \mu\text{g L}^{-1}$) and Zn ($227.7 \text{ } \mu\text{g L}^{-1}$) were detected in groundwater collected from MW-3 and MW-4A, respectively, where possible subsurface lenses differed in metal content. No Cr(VI) (below detection limit of $1.7 \text{ } \mu\text{g L}^{-1}$) was detected in groundwater samples collected from all three wells. Analytical results for organic compounds including TOC, DOC, and MTBE are summarized in Table 4. Organic content appears to be low in the groundwater, except for the contribution from MTBE in MW-4B.

3.2 Total Oxidant Demand

Total oxidant demand (TOD) is a form of oxidant demand that is commonly evaluated in bench tests and utilized for ISCO remedies. It is an important parameter for proper design of field scale deployment of chemical oxidation for effective removal of target contaminants, as well as for evaluation of economic feasibility of treatment [16-19]. TOD comprises of stoichiometric demand from contaminants and other oxidant sinks including demand from reduced metal, oxidizable organic carbon, soil oxidant demand, oxidant auto-decomposition. Estimate of oxidant demand from target contaminants alone will result in underestimate of injection. A number of chemical and physical factors could have impacts on TOD [16, 17].

The TOD for complete oxidation of the soil/water slurry was determined to be 558 mg L⁻¹ through titration with 2Na₂CO₃·3H₂O₂. The TOD was then utilized to obtain a benchmark ozone dosage of 28.33 mg L⁻¹ as described in the methods and materials section. All the dosages in the bench-scale test were based on this 100% dosage. As described in 2.4, the O₃ demand was calculated based on an oxidizing potential of 2.1 V for O₃ and 1.8 V for H₂O₂ (1.8 V) from 2Na₂CO₃·3H₂O₂. As a reference, Zingaretti et al. [20] reported TOD value of soil sampled from MTBE contaminated groundwater of 3383 ppm. The O₃ demand was then determined based on the stoichiometric relationship of 0.85 mol O₃ being equivalent to 1.0 mol H₂O₂. Since there are 3 mol H₂O₂ in 1 mol 2Na₂CO₃·3H₂O₂, the relationship in terms of 2Na₂CO₃·3H₂O₂ is 0.28 mol O₃ mol⁻¹ 2Na₂CO₃·3H₂O₂.

3.3 Bench-scale study

As shown in Figure 2, detectable concentrations of Cr(VI) appear after 2 times the benchmark dosage (28 mg O₃ L⁻¹). At this point, an average of 17.3 µg L⁻¹ of Cr(VI) was measured. Sparging additional O₃ did not increase the amount of oxidized Cr, and levels of Cr(VI) remained stable. It is possible that total Cr was dissolved from the soil matrix at an O₃ dosage of 56 mg L⁻¹ and simultaneously or within a short time most of this dissolved Cr was oxidized to Cr(VI). As such, it appears that the formation of Cr(VI) was related to the total Cr in the soil and the quantity of applied O₃.

The MTBE concentration substantially decreased with increasing O₃ application. Approximately 60% of the MTBE was depleted at 28 mg L⁻¹ O₃ and greater than 90% was depleted at 56 mg L⁻¹. However, no further decreases in MTBE concentrations were observed at O₃ dosages above 56 mg L⁻¹, where the average final MTBE concentration of the treated reactors was approximately 18 µg L⁻¹.

Changes in pH, ORP, and temperature were insignificant during the tests. Similarly, anions and total metals remained stable throughout the tests, except for Mn, which decreased at an O₃ dosage of 112 mg L⁻¹. This may be attributed to the oxidation of Mn at elevated O₃ dosages. The soil/groundwater slurries with O₃ applied (as well as those exposed to the atmosphere) demonstrated that MTBE concentration decreased after ozonation. This suggests that O₃ dosage in the full-scale field implementation could be further reduced to eliminate the formation of Cr(VI).

Follow-up testing of the laboratory samples also indicated that intrinsic biodegradation could be stimulated by adding oxygen. The soil/groundwater slurries that were exposed to the atmosphere and those with applied O₃ demonstrated decreasing MTBE concentrations following the ozone application. This suggests an ozone dosage in

the full-scale field implementation could be lower than stoichiometrically designed to eliminate MTBE and prevent the formation of Cr(VI) while the oxygen-enhanced aquifer would stimulate biodegradation of residual MTBE. Although this practice may not completely deplete MTBE during ozonation, it could substantially reduce the mass of MTBE for in situ biodegradation to eventually achieve the remedial goal.

3.4 Field application

As shown in Figure 2, a 28 mg O₃ L⁻¹ dosage was used for the full-scale benchmark. This dosage was chosen based on the results from bench-scale study showing that no substantial Cr(VI) was formed at this concentration. The volume of groundwater to be treated was calculated for each location based on the expected radius of influence and anticipated depth interval. Using a modeled groundwater flow velocity, the groundwater flux through the treatment zone was also estimated. From these approximations, the benchmark application rates were calculated to be 113 g d⁻¹ in Interval A and 209 g d⁻¹ in Interval B. Approximately 75% of the dosage was applied to the up-gradient injection wells (OZ-3A and OZ-3B) and 25% applied to the down-gradient injection wells (AS-1 and OZ-2B). Ozone generator settings and cycle times were determined based on having an average injection period of 20 minutes, followed by approximately 60 min of off time for each well while ozone injection is cycled through the other wells. As shown in Table 6, monitoring results from well MW-4B showed rapid reduction in MTBE (73 µg L⁻¹ to non-detect 0.5 µg L⁻¹) and TBA (53 µg L⁻¹ to non-detect 0.5 µg L⁻¹) concentrations, while concentrations of Cr (VI) were nearly unchanged before (4.0 µg L⁻¹) and after (4.5 µg L⁻¹) ozonation.

After 3 months of operation, the Cr(VI) concentration increased to 9.6 mg L⁻¹, but decreased to 4.5 mg L⁻¹ after an additional 6 months. Based on the results from the previous field application of ozonation (described in 2.1), the Cr(VI) concentrations were 42 – 100 times less when the O₃ dosage determined from TOD was injected into the groundwater. Therefore, the field test results indicate that using the TOD determined in the laboratory using a different oxidant (e.g., percarbonate) can estimate the optimal dosage O₃ that can be applied in situ for degrading MTBE without substantially increasing Cr(VI) concentration in groundwater.

The complete oxidation of MTBE by O₃ follows the following equation where 5 mol O₃ is required to completely oxidize 1 mol MTBE,

Other compounds and minerals present in the contaminated aquifer can consume the oxidant; therefore, to ensure complete oxidation of MTBE, excess O₃ is typically used for ISCO applications. With an over excess of O₃, the O₃ and its decomposition products can react with other materials, such as inorganic minerals composed of Cr(III). The decomposition of O₃ are shown in the following equations [21, 22]:

The hydroxyl radical ($\bullet\text{OH}$) has a higher oxidation potential than O_3 , where an excess of $\bullet\text{OH}$ can react with Cr(III) to form Cr(VI) . Even with O_2 present in groundwater, Cr(III) can be oxidized as shown below:

Due to the risk of Cr(VI) formation from the over addition of O_3 , it is important that the O_3 dosage be suitable for contaminant degradation while minimizing the oxidation of Cr(III) ; therefore, determining the O_3 dosage by using a simple TOD method test can minimize this hazard as demonstrated by both the laboratory and field studies.

4. Conclusions

Results from the laboratory study indicate that a benchmark dosage of O_3 can be established using the TOD test results and assuming a different oxidant. Based on the benchmark results, MTBE can be effectively oxidized prior to oxidizing Cr(III) to Cr(VI) . The results also suggest Cr is dissolved from the soils and further oxidation of Cr(III) to Cr(VI) will occur as O_3 dosages increase. In addition, the total potential for Cr(VI) production may be estimated from the total Cr present in the soil matrix.

In past field applications O_3 dosage was usually limited by the O_3 generator and subsurface application technologies. As such, it may have been fortuitous that MTBE destruction was occurring without extensive Cr(VI) production. As generation and delivery technologies improve, greater quantities of ozone are being effectively applied to

the subsurface and rapid remediation may be feasible. At the same time, the potential for Cr(VI) formation is also greater.

Results from this study demonstrate that a TOD test can be used to resolve the O₃ dosage problem by establishing a site-specific benchmark dosage for field ozone applications. In addition, soluble Cr(III) and Cr(VI) in groundwater and total Cr in soil should be tested to understand the potential for Cr(VI) formation. Prudent field applications of the benchmark dosage can be used to reduce the risk of creating Cr(VI).

Acknowledgement

The authors thank Western Research Institute (WRI) for partially conducting the laboratory work. This work was partially supported by the United States Department of Energy (DoE) through WRI's Cooperative Agreement No. DE-FC26-98FT40322 with DoE. Field work was conducted under oversight from the State of California Regional Water Quality Control Board (Central Valley Region) with reimbursement for remediation activities provided by the State of California Underground Storage Cleanup Fund. Any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not reflect the view of the DoE or the State of California.

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Figure Captions

Figure 1. Ozone Field Pilot Layout

Figure 2. MTBE Degradation vs. Cr(VI) Production. At 56 mg L^{-1} (200% of the benchmark dosage), MTBE (●) is shown to have the highest degradation. Likewise, at this same dosage, oxidizable Cr begins to produce detectable ($>1.7 \text{ } \mu\text{g L}^{-1}$) Cr(VI) (▲).

Figures

Fig. 1

Fig. 2

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Tables

Table 1. Ozone generator parameters.

Ozone Flow Rate	0.13 dm ³ min ⁻¹
Ozone Production	1440.00 mg h ⁻¹
Ozone Dosage Rate/Bottle	2.00 mg h ⁻¹
Flow To Manifold	0.0013 dm ³ min ⁻¹
Flow To Manifold	0.0015 dm ³ min ⁻¹
Or	1.49 cm ³ min ⁻¹ (2195 m elevation)
N ₂ Mix Flow For 72%	1.87 cm ³ min ⁻¹ (2195 m elevation)

Table 2. Dosage schedule

Dosage (% of TOD)	Benchmark Dosage (mg ozone)	Treatment Time (min)
0%	0.00	0
25%	4.00	90
50%	7.00	180
100%	14.00	360
200%	28.00	720
400%	57.00	1440

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643 **Table 3. Field measurements.**

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645	Well ID	pH	DO (mg L ⁻¹)	ORP(mV)	EC (μS cm ⁻¹)
646	MW-3	6.85	0.89	-5.8	556
647	MW-4A	7.17	1.22	29.5	643
648	MW-4B	7.09	0.57	-66.6	802
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672 **Table 4. Baseline organic compound concentrations.**

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674	Well ID	TOC (mg L ⁻¹)	DOC (mg L ⁻¹)	MTBE (µg L ⁻¹)
675	MW-3	1.34	0.38	1.20
676	MW-4A	0.32	0.32	4.60
677	MW-4B	6.50	6.22	110.00

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699 **Table 5. Baseline anions, cations, and metals concentrations.**

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701	Anion (mg L ⁻¹)	MW-3	MW-4A	MW-4B
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703	Flouride (F ⁻)	<1.5	<1.5	<1.5
704	Chloride (Cl ⁻)	36.9	31.5	35.1
705	Bromide (Br ⁻)	<3.0	<3.0	<3.0
706	Nitrate (NO ₃ ⁻)	<0.1	<0.1	N/A
707	Phosphate (PO ₄ ³⁻)	<3.0	<3.0	<3.0
708	Sulfate (SO ₄ ²⁻)	30.9	36.2	30.7
709	Na (mg L ⁻¹)	21.7	23.0	24.9
710	Mg (mg L ⁻¹)	29.0	34.4	38.8
711	K (mg L ⁻¹)	1.2	3.2	3.3
712	Ca (mg L ⁻¹)	61.8	63.3	80.0
713	Cr (µg L ⁻¹)	2.2	2.6	3.5
714	Cr ⁶⁺ (µg L ⁻¹)	<1.7	<1.7	<1.7
715	Mn (µg L ⁻¹)	2,602.2	936.4	152.4
716	Fe (mg L ⁻¹)	0.7	0.8	1.1
717	Ni (µg L ⁻¹)	6.7	10.9	1.3
718	Cu (µg L ⁻¹)	0.8	1.2	0.4
719	Zn (µg L ⁻¹)	9.8	227.7	3.8
720	Pb (µg L ⁻¹)	0.0	0.1	0.0
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734 **Table 6. Summary of monitoring data from MW-4B.**

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Date	MTBE ($\mu\text{g L}^{-1}$)	TBA ($\mu\text{g L}^{-1}$)	Cr(VI) ($\mu\text{g L}^{-1}$)
8/20/07	73	53	4
11/20/07	<0.5	<5	9.6
2/19/08	<0.5	<5	6.4
5/20/08	<0.5	<5	4.5

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