

CARBONATE EVOLUTION OF GROUNDWATER  
CONTAMINATED BY HIGHLY SALINE PRODUCED  
WATER AND HYDROCARBONS

By

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Abstract: The physical properties and the major ionic concentration and stable carbon isotope composition ( $\delta^{13}\text{C}_{\text{DIC}}$ ) of dissolved inorganic carbon (DIC) was measured in groundwater at an abandoned oil production site near Lake Skiatook, Osage County, Oklahoma. The shallow aquifer is contaminated with highly saline produced water and hydrocarbons that were transported through a trench and stored in an unlined earthen pit. Results show the groundwater to have high concentrations of  $\text{Cl}^-$  and  $\text{Na}^+$  from the mixing of produced water with natural groundwater. The produced water also contributed moderately high concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , but extensive weathering and ion exchange has added significant quantities of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to the groundwater. Weathering of aquifer carbonates and dissolution of  $\text{CO}_{2(\text{g})}$  from root respiration and hydrocarbon degradation has altered the carbonate chemistry, adding DIC to the groundwater with an average  $\delta^{13}\text{C}_{\text{DIC}}$  value of approximately -12‰. Continued weathering and precipitation due to dedolomitization has added isotopically enriched DIC to the groundwater and has shifted the  $\delta^{13}\text{C}_{\text{DIC}}$  to higher than -12‰, indicating greater influence from carbonate dissolutions on the isotopic value of many groundwater samples. Residual hydrocarbons still exist throughout the site and are being degraded, further adding  $\text{CO}_2$  to the groundwater and weathering aquifer minerals. It is concluded that the addition of high concentrations of ions and degradation of residual hydrocarbons has altered the saturation state of carbonate minerals calcite and dolomite and dissolution and precipitation of these minerals alters the DIC concentration in the groundwater and enriches the groundwater in  $^{13}\text{C}$ .

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## 1.0 Introduction

Highly saline produced waters (brine) containing hydrocarbons from oil field operations are a major source of groundwater contamination at thousands of sites across the US and the world (Kharaka and Otton, 2007; Otton et al., 2007). Produced waters are treated as environmental contaminants and investigation of contaminated sites are focused on defining the spatial extent of contaminant plumes (Herkelrath et al., 2007; Kharaka et al., 2007; Whittemore, 2007). The chemical evolution of fresh groundwater can be determined from equilibrium and mass balance approaches based on weathering of watershed and aquifer rocks (Drever, 1997). However, seepage of highly saline produced water into freshwater aquifers contributes to the total dissolved solids (TDS), which may perturb the chemical evolution. This chemical perturbation may cause oversaturation of solute species (e.g., chloride and sodium) and their subsequent precipitation in groundwater. Alternatively, because of the common ion effect, chemical species that would naturally be released from weathering may be impeded by the high TDS concentrations (Drever, 1997). If we assume that the petroleum in the produced water is transformed by chemical and microbial processes, the resulting  $\text{CO}_{2(g)}$ , which forms carbonic acid, can also cause further weathering of aquifer minerals. This should be clearly evident in the dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) concentrations and the stable carbon isotopes ( $\delta^{13}\text{C}$ ).

Many studies have investigated the effects of the biodegradation of petroleum products (e.g., jet fuel or diesel) on natural groundwater, and have focused on the effects of these biodegraded products on the evolution of carbonate systems by measuring DIC concentrations and stable carbon isotopic composition of the groundwater (e.g., Fang et al., 2000; Godsy et al., 2003; Atekwana et al., 2005; Scow and Hicks, 2005; Whittemore, 2007; Parker et al., 2012). Recently, Su et al. (2013) investigated a site contaminated by hydrocarbons from oil field activities, but highly saline produced water was not part of the contaminants at the site. Most studies investigating the effects of high salinity are in areas where hydrocarbon contamination is not a concern (Cates et al., 1996; Nicholson and Fathepure, 2005; Ulrich et al., 2009; Currell and Cartwright, 2011). This study aims to investigate a natural groundwater system that has been contaminated by unprocessed hydrocarbons in highly saline produced waters.

The overarching goal of this study is to develop a fundamental understanding of the chemical and isotopic evolution of the carbonate system in freshwater aquifers contaminated by oilfield produced waters. The hypothesis tested in this study is *“Microbial degradation of hydrocarbons in highly saline produced waters produce  $CO_{2(g)}$  that increases the dissolved inorganic carbon concentrations, altering the weathering of aquifer solids and the chemical evolution of fresh groundwater in shallow aquifers”*. The objective of this study is to assess (1) the spatial and temporal chemical characteristics during the interaction of highly saline produced waters with fresh groundwater and (2) the fate of hydrocarbon contaminants in the highly saline produced water and its effect on the carbonate equilibrium during this interaction.

## **2.0 Study Site**

### *2.1 Site history*

The study site is located at an abandoned oil production site in Skiatook Lake, in northeast Oklahoma USA (Figure 1), and is typical of many older contaminated production sites throughout the continental U.S. This study is in addition to a multidisciplinary investigation, Osage-Skiatook Petroleum Environmental Research (OSPER) project, studying the effects of produced water contamination in fresh groundwater, led by the US Geological Survey (USGS) ([http://toxics.usgs.gov/sites/produced\\_water](http://toxics.usgs.gov/sites/produced_water), 4/28/2014). The project included two study sites, an abandoned oil production site (site A) and an active oil production site (site B). This study site was conducted at site A, the abandoned oil production site. Between the mid 1910's to the late 1970's, more than 150,000 m<sup>3</sup> of produced water was generated during oil production. The produced water and oil were processed at this site at a tank battery located uphill and to the south of the pits that were used to temporarily store produced fluids. The pits used to store the produced fluids were unlined, earthen pits and the fluids was transported by a trench running from the tank battery to the pits (Kharaka et al., 2005; Otton et al., 2007). The southern edges of the two pits are located on the local drainage divide (Figure 1). Over time, the produced water seeped into the ground creating a high salinity hydrocarbon plume (Herkeleath et al., 2007). The produced water

was also discharged into an ephemeral creek to the north of the site creating a salt scar that originated from the pits to the north cove of Skiatook Lake (Figure 1) (Kharaka et al., 2005; Otton et al., 2007). The salt scar, with erosion up to 2 m below the surface, extends from the pits to the lakeshore of the NE cove of Skiatook Lake. Skiatook Lake was constructed in 1987, creating a peninsula where site A exists (Figure 1).

## *2.2 Geology*

The study site is nested in a saddle between two hills, with a drainage divide running generally NW-SE through the middle of the site (Figure 1). Detailed geology of the study site is reported by Otton et al. (2007) and is briefly summarized below. Five units have been identified from surface mapping and coring (Figure 2). All the units are Pennsylvanian in age, in the Wann Formation. The surficial sediments consist of unconsolidated very fine-grained eolian sands and colluvium of sandstone in a sandy to clayey matrix. Unit 1, a weathered sandstone, is of limited areal distribution within the site and is only found in three holes, AA05, AA12 and AA13. Unit 2 is widespread and consists of weathered, very fine-grained sandstone and clayey sandstone with variable amounts of Fe oxyhydroxide cement. Unit 3 intertongues with Unit 2 and consists mostly of weathered shale, sandy siltstone, sandy mudstone, and sandstone. Unweathered shale containing abundant pyrite was observed in this unit, and gypsum was found in weathered shale and along exposed surfaces within the salt scar. Unit 4 consists of dolomite-cemented, unweathered sandstone, clay partings, and thin shale beds that are

carbonaceous and have fossil detritus. Unit 5 contains interbedded muddy sandstone, shale, siltstone, and mudstone, with the sandstone cemented by dolomite.

The bedrock at site A strikes N25°E and dips 1°25'NW. A structural lineament extends across the site along a topographic low trending N45°E from the southwest cove to the northeast cove. Vertical and subvertical fractures and faults are common and have slickensided surfaces and juxtaposed lithologies (Figure 2). Vertical movement is estimated to be less than 1 m. Several NE-trending fault segments were mapped in the area surrounding the study site by Gardner (1957).

### *2.3 Hydrology*

The study site is in a temperate semi-arid climate. The average annual precipitation in the region is 89 cm and the annual potential evapotranspiration is estimated at 180 cm (Herkeleth et al., 2007). A drainage divide extending NW–SE across the study site directs surface water flow to one of two coves (Figure 1). Surface runoff north of the divide near the pits flow NW and turn NE to discharge into the north cove. Surface waters south of the divide flow SSW and then turn to the SW to discharge flow into the SW cove.

Groundwater flow paths follow the dip of the bedrock to the NW, flowing along bedding plans and penetrating deeper through the units via the fractures and faults (Figure 2). The aquifer has an average recharge rate of about 1 cm/a (Herkeleth et al., 2007). Hydraulic conductivity of the aquifer ranges from 0.3 to 7.0 cm/day and averages 1.9 cm/day (Herkeleth et al., 2007). The sandstone aquifer units (units 1-5) are confined

by clay parting throughout the units and not well connected to soil and surface water except where the salt scar exists and all soil has been removed (Herkelrath et al., 2007). Groundwater levels in wells do not respond to individual rainfall events, however, there is a seasonal variation reflecting the seasonal rainfall pattern (Herkelrath et al., 2007). Groundwater is recharged from January to June and groundwater level declines from July to December.

## **3.0 Methods**

### *3.1 Sample Collection*

#### 3.1.1 Groundwater

As part of the OSPER project, the USGS installed 34 monitoring wells, distributed inside and outside the visible salt scar (Figure 1). Each well location corresponds to two wells drilled to different depths, shallow (s) and deep (d), except well locations AA10 and AA11 which have three well depths; shallow (s), medium (m), and deep (d). The well depths range from 1.22 to 23.46 m deep.

Water samples were collected from the monitoring wells. Sampling for water was conducted seasonally in October 2008, February 2009, June 2009, and May 2010. Prior to collecting the samples, depth to water was measured with an electronic water-level tape. Following this, the wells were purged using a peristaltic pump or a submersible pump. During purging, the specific conductance (SPC) and pH were monitored using a Yellow Spring Instruments (YSI) multi-parameter probe until the readings were stable, indicating complete purging of the well bore. When the SPC and pH were stable; SPC, total dissolved solids (TDS), dissolved oxygen (DO), pH and oxidation-reduction potential (ORP) was recorded from the YSI probe.

All samples were filtered through a 0.45  $\mu\text{M}$  filter before collection. Samples for major cations analysis were collected in 60 mL polypropylene bottles and acidified to a pH <2 with high purity nitric acid. Samples collected for major anions and silica analysis were collected unacidified in 30 mL polypropylene bottles. Samples for dissolved organic carbon (DOC) were collected in pre-combusted 60 mL amber glass vials and later acidified with hydrochloric acid. Samples for benzene, toluene, ethylbenzene, and xylenes (BTEX) analysis were collected during the May 2010 sampling event and stored in 30 mL glass vials pre-acidified with hydrochloric acid. Samples to measure dissolved inorganic carbon (DIC) and stable carbon isotopes ( $\delta^{13}\text{C}_{\text{DIC}}$ ) were collected in vacutainers containing magnets and pre-acidified with phosphoric acid as described by Atekwana and Krishnamurthy (1998). All the samples were cooled on ice in the field and transported to the laboratory where they were stored at 4°C until analysis.

### 3.1.2 Lake Water

Samples were collected from the north cove of the lake along the shore from three locations (Figure 1). The SPC, TDS, DO, pH, and ORP were measured and recorded using a YSI probe immersed into lake water. Water was collected by the grab technique using a 1 L polypropylene bottle attached to the end of a telescoping pole approximately 3 m from the water's edge. From the 1 L bottle, samples were collected for various analyses and preserved as described above.



### 3.1.3 Leachate

Leachate from the asphaltic material in the tar pit was collected by squeezing water from the material into 50 mL centrifuge tubes that were taken back to the lab and filtered through 0.45  $\mu\text{M}$  filters using a vacuum pump. Aliquots of samples were collected for cations and anions, metals, and DOC in the lab as described above. Samples to measure DIC and stable carbon isotopes were collected as described above in the field. Samples were not collected for major ions and metals during the May 2010 sampling event.

### 3.2 Sample Analysis

Dissolved iron was measured by colorimetry (CHEMetrics, 2004) and alkalinity was determined by acid titration (Hach, 1992) in the field immediately after filtration. Major anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{2-}$ ) were measured by ion chromatography and cations ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) were analyzed by ion chromatography and inductively coupled plasma-optical emission spectrometry. DOC concentrations were analyzed by combustion followed by coulometric titration of  $\text{CO}_{2(\text{g})}$  using a UIC, Inc. CM 5014 coulometer. Silica concentration was determined by colorimetry (CHEMetrics, 2004). Analysis of samples for BTEX was performed by Ecological Research and Management Incorporated (ERMI Environmental Laboratories, Dallas, TX).

DIC concentrations were determined by extraction and cryogenic purification of  $\text{CO}_{2(\text{g})}$  using a vacuum line and the  $\text{CO}_{2(\text{g})}$  was stored in 6 mm Pyrex tubes for stable carbon isotope measurements (Atekwana and Krishnamurthy, 1998). Stable carbon

isotopes were measured using a Thermo Finnigan Delta plus XL isotope ratio mass spectrometer. Stable isotope ratios for carbon in DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ) are reported in the delta ( $\delta$ ) notation in per mil (‰):

$$\delta(\text{‰}) = ((R_{\text{sample}}/R_{\text{standard}}) - 1) \times 1000$$

where  $R$  is  $^{13}\text{C}/^{12}\text{C}$ . The  $\delta$  values for C isotopes are reported relative to the Vienna Pee Dee Belemnite standard (VPDB). Routine isotopic measurements of in-house standards and samples have an overall precision (1- $\sigma$  standard deviation) of better than 0.1‰.

### *3.3 Determination of water types and mineral saturation indices*

The results of the chemical analysis were uploaded to AquaChem where water types were determined and plotted on a Piper diagram. PhreeqcI version 2 was then used to calculate mineral saturation indices and  $\text{pCO}_2$  using cation and anion results, pH, alkalinity, DIC, and temperature (Parkhurst and Appelo, 1999).

## 4.0 Results

### 4.1 TDS, DO, and pH

The results of the physical, chemical, and isotopic parameters are presented in (Table 1). For all the groundwater samples, the average TDS concentration was  $6112 \pm 5154$  mg/L with a range of 632 to 18,750 mg/L. The TDS concentration for lake samples averaged  $149 \pm 15$  mg/L and ranged from 137 to 176 mg/L. Field parameters for the tar pit were measured once in June 2009 after a rainfall event (4.11 cm), which occurred over seven days and caused water to be pooled in a hole dug in the tar pit. The TDS concentration for this sampling event was 4816 mg/L. The DO concentrations in groundwater averaged  $2.65 \pm 2.12$  mg/L (29.0 $\pm$ 24.1%), but had a large range of 0.31 to 9.53 mg/L (3.5% -129.8%). For lake samples, the DO concentrations were much higher, with an average value of  $10.01 \pm 3.27$  mg/L (110.5 $\pm$ 15.9%) and ranged from 6.87 to 16.59 mg/L (87.0%-135.7%). The DO concentration in the tar pit was 1.82 mg/L (27.1%). The pH of groundwater ranged from 4.45 to 7.62 and averaged  $6.14 \pm 0.76$ . The pH of lake samples was more alkaline which ranged from 6.03 to 8.76 and averaged  $7.79 \pm 0.75$ . The tar pit sample had a pH value of 6.53.

#### 4.2 Alkalinity, $Cl^-$ , and $SO_4^{2-}$

In groundwater samples, the alkalinity concentrations ranged from less than 1 mg/L to 618 mg/L and averaged  $227 \pm 144$  mg/L. Lake samples had alkalinity concentrations that ranged from 27 to 96 mg/L and averaged  $59 \pm 16$  mg/L. Alkalinity in the tar pit was 17.4 mg/L. In groundwater,  $Cl^-$  concentrations ranged from 35.5 to 10,476.3 mg/L and averaged  $2918.1 \pm 2872.7$  mg/L. The  $Cl^-$  concentrations for lake samples averaged  $22.6 \pm 3.3$  mg/L and ranged from 19.1 to 28.3 mg/L. The average  $Cl^-$  concentration for the tar pit was 31,189.9 mg/L and ranged from 1076.5 to 64,700.4 mg/L. The  $SO_4^{2-}$  concentrations were typically low, as it is not a major constituent of the produced waters (Kharaka and Otton, 2003), but some samples showed significant concentrations relative to  $Cl^-$  concentrations. For the groundwater, the average  $SO_4^{2-}$  concentration was  $339.4 \pm 383.7$  mg/L with a range of 1.4 to 1267.7 mg/L. Lake samples had an averaged  $SO_4^{2-}$  concentration of  $10.4 \pm 2.1$  mg/L which ranged between 7.1 and 12.8 mg/L. The tar pit had very little  $SO_4^{2-}$  relative to  $Cl^-$  with an averaged  $SO_4^{2-}$  concentration of  $43.9 \pm 6.1$  mg/L and a range from 38.4 to 52.5 mg/L.

#### 4.3 $Na^+$ , $Ca^{2+}$ , $Mg^{2+}$ , and $Fe$

$Na^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  were the major cations with notable concentrations in the groundwater.  $Na^+$  averaged  $1088. \pm 942.3$  mg/L in the groundwater samples and ranged from 75.4 to 3445.5 mg/L. Lake samples had low concentrations of  $Na^+$  with an average of  $12.1 \pm 4.1$  mg/L and a range between 6.4 and 18.0 mg/L. In contrast, the tar pit had

high concentrations of  $\text{Na}^+$  which averaged  $17,069.8 \pm 13,364.1$  mg/L and ranged from 743.0 to 33,477.9 mg/L.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were similar in concentrations relative to  $\text{Cl}^-$  for groundwater and tar pit samples, but  $\text{Ca}^{2+}$  concentrations are typically higher than  $\text{Mg}^{2+}$  in lake samples. The averaged concentrations for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  for groundwater samples were  $496.4 \pm 530.7$  and  $340.48 \pm 418.0$  mg/L, respectively, with high concentrations of 2623.2 and 1858.2 mg/L, respectively, and low concentrations of 19.8 and 4.5 mg/L, respectively. In lake samples the averaged  $\text{Ca}^{2+}$  concentration was  $22.7 \pm 1.7$  mg/L and the average  $\text{Mg}^{2+}$  concentrations was  $5.4 \pm 1.4$  mg/L. In the lake samples,  $\text{Ca}^{2+}$  concentrations ranged from 20.0 to 26.3 mg/L and  $\text{Mg}^{2+}$  concentrations ranged from 2.0 to 7.0 mg/L. The tar pit had an averaged  $\text{Ca}^{2+}$  concentration of  $3051.0 \pm 2362.6$  mg/L and a range between 156.3 and 5943.5 mg/L and an averaged  $\text{Mg}^{2+}$  concentration of  $805.5 \pm 625.0$  mg/L with a range between 95.1 and 1616.1 mg/L. The total Fe concentrations within the groundwater ranged from none detected to 16.0 mg/L and averaged  $2.5 \pm 3.9$  mg/L. Lake samples had very little total iron with an averaged concentration of  $0.1 \pm 0.04$  mg/L and range from 0.01 to 0.1 mg/L. The total Fe concentrations in the tar pit averaged  $83.0 \pm 94.8$  mg/L with a range from 0.4 to 215.8 mg/L.

#### 4.4 *BTEX, DOC, DIC, and $\delta^{13}\text{C}_{\text{DIC}}$*

BTEX concentrations were below detection limits in all groundwater samples and only trace quantities were detected from the pit samples. DOC concentrations were analyzed for groundwater and lake samples collected in October 2008 and May 2010. In groundwater, the averaged concentration of DOC was  $65.4 \pm 30.1$  mg C/L and ranged

from 31.4 to 156.8 mg C/L. The averaged concentration of DOC in lake water was  $32.4 \pm 4.1$  mg C/L and ranged from 24.4 to 36.0 mg C/L. DOC concentrations were only measured for the tar pit in October 2008, with a result of 238.8 mg/L. DIC concentrations for groundwater averaged  $67.7 \pm 31.4$  mg C/L and ranged between 7.6 to 194.4 mg C/L, while lake samples averaged concentration for DIC was  $11.3 \pm 2.3$  mg C/L and ranged from 6.0 to 14.1 mg C/L. Groundwater  $\delta^{13}\text{C}_{\text{DIC}}$  values averaged  $-15.3\text{‰} \pm 3.7\text{‰}$  and ranged from -8.6 to -23.5‰. The  $\delta^{13}\text{C}_{\text{DIC}}$  of lake samples averaged  $-7.7\text{‰} \pm 1.4\text{‰}$  and ranged from -5.4 to -9.1‰. Only two samples for DIC and subsequent isotopic analysis were collected from the tar pit: February 2009 (DIC concentration of 37.1 mg C/L and a  $\delta^{13}\text{C}_{\text{DIC}}$  value of 5.9‰) and May 2010 (DIC concentration of 81.8 mg C/L and a  $\delta^{13}\text{C}_{\text{DIC}}$  value of 10.7‰).

#### 4.5 *Spatial and Seasonal Distribution*

Transect A-A' (Figure 1) is used to display the spatial variation of select physical, chemical, and isotopic measurements with respect to the salt scar along the general groundwater flow path (Figure 3). The transect depicts evolution of the groundwater as it flows from the source downgradient through the different units (Figure 2). Transect A-A' begins south of the pits (AA10), crosses the drainage divide and the pits, and follows the general groundwater flow paths ending at the edge of the lake on the northeast side of the study site (AA61).

The longitudinal variations in TDS,  $\text{Cl}^-$ , pH, DO,  $\text{SO}_4^{2-}$ , alkalinity,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , DOC,  $\log \text{pCO}_2$ , DIC, and  $\delta^{13}\text{C}_{\text{DIC}}$  are shown for October 2008, February 2009, June 2009, and

May 2010. It is clear from the plots that the concentration of the parameters south of the drainage divide are generally lower and less variable compared to the north portion of the site (Figure 3). North of the drainage divide, variations at each location are seasonal. For example, the changes in the concentration of TDS and  $\text{Cl}^-$  (a conservative tracer) appear to be related to seasonal influx of freshwater, with concentrations that are lower during recharge in the spring and summer and higher in the fall and winter. June 2009 had the lowest concentrations for TDS and  $\text{Cl}^-$  and October 2008 and February 2009 had the highest concentrations (Figure 3). The pH increases from approximately 5.5 near the drainage divide northwards to approximately 7.0 at the lake. The DO and  $\text{Na}^+$  concentration are depressed and the alkalinity,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  concentrations are highly elevated relative to the upgradient and downgradient wells (Figure 3).

DOC,  $\text{pCO}_2$ , and DIC all have a similar pattern along the transect. For all the sampling events, values south of the drainage divide were relatively consistent; 50 mg C/L, -1.7 atm, and 60 mg C/L, respectively (Figure 3). Across the drainage divide, DOC,  $\text{pCO}_2$ , and DIC concentrations generally decrease from the pits northward toward the lake. Despite this, the DOC concentration for October 2008 spikes at well AA01 and the DIC concentration for February 2009 spikes at well AA01 and then decrease to well AA61 near the lake (Figure 3).  $\delta^{13}\text{C}_{\text{DIC}}$  values range from -16.0 to -21.0‰ south of the drainage divide, and north of the divide,  $\delta^{13}\text{C}_{\text{DIC}}$  values increase from well AA02 near the drainage divide towards the lake to well AA61 (Figure 3). This increase in the  $\delta^{13}\text{C}_{\text{DIC}}$  values is concomitant with the decrease in DIC concentrations along the flow path.

## 5.0 Discussion

### 5.1 *Extent of highly saline produce water contamination of groundwater*

The USGS identified the produced water to be a Na-Ca-Cl brine with high concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{NH}_4^+$  and low  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$  (Kharaka and Otton, 2003). Typically,  $\text{HCO}_3^-$  is a dominant anion of natural groundwaters, while  $\text{Cl}^-$  is in relatively low concentrations (Drever, 1997). To verify continued contamination by produced water,  $\text{Cl}^-$  was plotted against TDS (Figure 4). There is a positive relationship between  $\text{Cl}^-$  and TDS suggesting that groundwater with high TDS was impacted by produced water. Therefore, groundwater locations that have  $\text{Cl}^-$  as their dominant anion and low concentrations of  $\text{HCO}_3^-$  are considered contaminated, while locations that have  $\text{HCO}_3^-$  as their dominant anion and low concentrations of  $\text{Cl}^-$  are considered uncontaminated. The uncontaminated samples have lower TDS and clearly lie off a trend for TDS-Cl defined best by samples from the tar pit for the contaminated samples (Figure 4). It was also observed that the extent of the groundwater contamination by produced water has decreased over time. Compared to the data collected by the USGS in 2002-2005, when the maximum TDS was 20,000 mg/L, a 30% decrease has occurred during the intervening five year period. Also, Cl in the tar pit was 64,700 mg/L and in the former salt pit was only 5 mg/L. The significantly low concentration in the salt pit



indicate that the tar pit might be the current source of production water leachate to the groundwater.

The relative proportion of cations and anions are presented in a Piper diagram (Figure 5). The water samples cluster in three anion groupings; chloride-rich, bicarbonate-rich, and sulfate-rich. In contrast, the water samples show cation proportions that have nearly 50%  $Mg^{2+}$  and vary between more than 60%  $Ca^{2+}$  to more than 90%  $Na^+$  plus  $K^+$ . The USGS sampled two wells (Bolin Well and Hum Well) considered to be uncontaminated and representative of background conditions. All water samples that have  $Cl^-$  concentrations within the range of the Bolin and Hum wells (23.9 to 216 mg/L) have  $HCO_3^-$  or  $SO_4^{2-}$  as their dominant anion. Several groundwater samples belong to the  $SO_4^{2-}$  anion group and are not contaminated by the highly saline produced water as evidenced by  $Cl^-$  concentrations that are within the range of background groundwater (Figure 5). On the other hand, there are several groundwater samples that are contaminated by produced water that have high  $Cl^-$  concentrations and elevated concentrations of  $SO_4^{2-}$  similar to the  $SO_4^{2-}$  dominant anion water types (Table 1). Based on the brine composition, and subsequently, the modeled water types, all groundwaters at the site appear to be contaminated to some degree with produced water, except the groundwater sampled at wells AA13-S and AA13-D (Table 1).

Along the groundwater flow path from the pit source towards the north into the lake, the facies of the water changes from a Na-Cl water type (e.g. AA02-S; Table 1) to a mixed-cation-Cl water type (e.g. AA61; Table 1). This suggests that the concentrations of cations cannot be solely attributed to contaminant migration and mixing with fresh

groundwater. Other processes such as rock-water interactions appear to be influencing the relative concentration of cations along the groundwater flow path.

Since  $\text{Cl}^-$  has been shown to be a conservative ion at the study site,  $\text{Cl}^-$  is also used to distinguish the degree to which the groundwater is contaminated. The magnitude of contamination at the site varies spatially in a radial pattern from the pits (source). As surface water infiltrates near the source, solutes are dissolved into the groundwater, transported away from the source, and subsequently, diluted as the contaminated groundwater mixes with fresh groundwater. North of the source, wells show a radiating pattern with the degree of contamination dependent on the distance from the source and the season, corresponding to the relative amount of fresh water recharge, “pushing” through the aquifer. The highest concentrations are found centrally at the site, directly along the main flow path from the source towards the lake cove to the north (Table 1). South of the drainage divide, groundwater at some locations have anion proportions that are dominated by  $\text{Cl}^-$ , suggesting some level of produced water contamination. Southwest of the pits and south of the drainage divide is an old trench that was used to transport the oil and produced water to the pits (Figure 1). Residual oil and produced water from the trench is likely the major source of contamination in groundwater south of the drainage divide.

## *5.2 Chemical Evolution of Groundwater Contaminated by Highly Saline Produced Water*

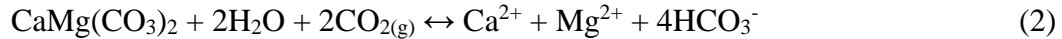
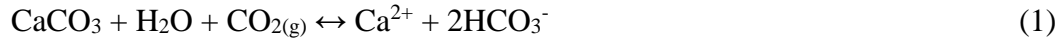
The chemical evolution of the natural groundwater at the study site can be attributed to mixing between production water and fresh groundwater, rock-water interactions

involving the dissolution and precipitation of minerals, microbial degradation of organic material and biodegradation of dissolved hydrocarbons. The USGS modeled the transport of the produced water since it was first released through 2006 (Herkehrath et al., 2007). Based on the nearly 60-year period of production, the produced water contamination was naturally attenuated by mixing and flushing until 1987 when Skiatook Lake was filled. Creation of Skiatook Lake created a natural boundary of high head, which essentially caused the plume to “stagnate” and ceasing the natural attenuation of the high salinity. Although the overall concentration of the contaminants has decreased from the time USGS first sampled groundwater at the study site (2002) to the time of the last sampling during this study (2010), only wells (AA01-D, AA07-S, AA07-D, and AA06-S) with the greatest concentrations of TDS have decreased significantly and some wells have shown an increase in the concentration of the production water contaminants. Also, as part of the USGS sampling of the study site, water was sampled beneath and immediately outside the brine pit to determine if contaminants were still being added to the groundwater from the open pit that was used to store the produced water. The TDS concentrations for all samples collected around the pit were below 500 mg/L, indicating that brine is no longer being added to the groundwater system from the pit and the existing plume is not being flushed.

The high  $\text{Cl}^-$  concentrations in the groundwater is the result of contamination by produced water. Assuming that well AA13 (shallow and deep) represents background conditions, since it has low TDS and  $\text{Cl}^-$  concentrations. As the produced water contamination migrates through the groundwater system, it is anticipated that  $\text{Cl}^-$  concentrations will increase at a constant ratio with TDS (Figure 4). Furthermore, its

anticipated that the chemical evolution of the groundwater might occur by means of reverse ion-exchange. Typically, clays prefer cations with a higher valence charge (e.g.  $\text{Ca}^{2+} > \text{Na}^+$ ). However, when ions with a lower valence charge exist in concentrations elevated as compared to that of ions with a higher valence charge, reverse ion exchange can occur (Hounslow, 1995; Cates et al., 1996; Appelo and Postma, 2007). As seen in Figure 6a, the  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  rich water types plot with a Na:Cl ratio greater than 1, which is typical of natural groundwaters ( Hounslow, 1995; Cates et al., 1996; Drever, 1997; Appelo and Postma, 2007). The pit samples (source) trend parallel to the 1:1 ratio line, but for the Cl-rich water types the ratio starts at a 1:1 ratio and as the contaminants increase ( $\text{Cl}^-$  concentration increases) the ratio of  $\text{Na}^+$  decreases, suggesting that  $\text{Na}^+$  is removed as the contaminated groundwater flows through the groundwater system. As the Na:Cl ratio decreases with increasing  $\text{Cl}^-$ , the cation composition goes from Na-rich to mixed cation to Ca- or Mg-rich groundwater. In Figure 6b,  $\text{Ca}^{2+}$  vs.  $\text{Cl}^-$  is plotted and the Ca:Cl ratio in the Cl-rich water types increases relative to the trend of the pit samples. The ratio of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to  $\text{Cl}^-$  increases as the degree of contamination increases and, similar to Ca:Cl ratios, Mg:Cl ratios for Cl-rich groundwaters deflect above the trend of the pit samples and increase with increasing contamination (Figures 6b and 6c). Reverse ion exchange is likely not a significant source of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and other geochemical processes are additionally responsible for generating these ions in significant quantities such as dissolution of carbonates.

The dissolution of carbonates, calcite and dolomite, can be a major source of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as well as DIC. Calcite and dolomite dissolution proceed as shown in reactions 1 and 2:



Alkalinity concentrations will increase as calcite and dolomite are weathered (dissolved) which should lead to a positive relationship between  $\text{Ca}^{2+}$  concentration or  $\text{Mg}^{2+}$  concentration with DIC concentration (Figure 7a). The Cl-rich waters have a positive correlation between alkalinity and DIC, but there is some scatter in the data.

In addition to the generation of DIC by carbonate weathering, there are still likely residual dissolved hydrocarbons that are undergoing microbial degradation (Godsy et al., 2003). When Godsey and others (2003) studied the microbial population at the study site, they found large populations of aerobic and anaerobic microbes with aerobic populations being predominant near the surface and iron-reducing anaerobic populations predominating downslope. Interestingly, they found large populations of sulfate-reducing bacteria, but there were no signs that they were active (low concentrations of  $\text{S}^{2-}$ ) despite large concentrations of  $\text{SO}_4^{2-}$ . As microbial populations degrade hydrocarbons,  $\text{CO}_{2(\text{g})}$  is generated in addition to the  $\text{CO}_{2(\text{g})}$  generated from respiration in the root zone.

The continual generation of  $\text{CO}_{2(\text{g})}$  from bacterial respiration decreases groundwater pH. The  $\text{CO}_{2(\text{g})}$  generated does not alter the total DIC concentration, but rather the relative proportions of the carbonate species ( $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ). Figure 7b shows this effect. Most waters show a trend of increasing DIC and decreasing pH with an increase of  $\text{pCO}_2$ , but there are several samples that show a drop in pH with no corresponding change in  $\text{pCO}_2$ . This excess  $\text{CO}_2$  may lead to continued weathering of minerals.

It was initially thought that the produced water would inhibit the dissolution of calcite and dolomite due to the common ion effect (Drever, 1997). However, the saturation indices for many of the sampled groundwaters indicate that the water is undersaturated with respect to calcite and dolomite (Figure 8a). Most of the Cl-rich water types that are also undersaturated with respect to these minerals also have the highest concentration of produced-water contaminants. Also, there is a positive relationship between alkalinity and the saturation indices of calcite. Therefore, extensive weathering of the carbonate rocks of the aquifer is an additional source of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to the groundwater.. The extensive weathering of these minerals is increasing the DIC concentration by adding  $\text{HCO}_3^-$  and  $\text{CO}_{2(g)}$  to the groundwater system.

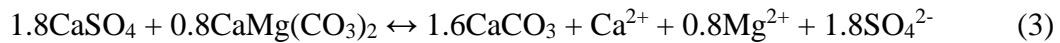
### 5.3 *Carbon Isotopic Evolution of Groundwater*

In natural groundwaters, major sources of DIC are (1) the dissolution of soil  $\text{CO}_{2(g)}$  derived from root respiration and decay of labile organic matter and (2) the dissolution of carbonates (Drever, 1997; Appelo and Postma, 2007). Soil  $\text{CO}_{2(g)}$  dissolves in groundwater, giving the groundwater an approximate  $\delta^{13}\text{C}_{\text{DIC}}$  value of -23‰ (Clark and Fritz, 1997). The dissolved  $\text{CO}_{2(aq)}$  then aids in the dissolution of carbonates with an approximate  $\delta^{13}\text{C}$  value of about 0‰ (Clark and Fritz, 1997). In an open system  $\text{CO}_{2(g)}$  and  $\text{CO}_{2(aq)}$  remain in equilibrium and the  $\delta^{13}\text{C}_{\text{DIC}}$  increases to approximately -16‰, but in a closed system, carbonate weathering results in  $\delta^{13}\text{C}_{\text{DIC}} \approx -12\text{‰}$ , ideally resulting from equal proportions of  $\text{CO}_{2(g)}$  dissolution and carbonate dissolution (Appelo and Postma, 2007).

Figure 9a shows that in the DIC concentration vs.  $\delta^{13}\text{C}_{\text{DIC}}$ , the Cl-rich groundwater show a positive relationship of increasing DIC with increasing  $\delta^{13}\text{C}_{\text{DIC}}$  to values as high as -8.5‰. The natural, uncontaminated groundwater ( $\text{HCO}_3$ -rich water type) has an average  $\delta^{13}\text{C}_{\text{DIC}}$  value of -13.1‰ and  $\text{SO}_4$ -rich groundwater, has an average  $\delta^{13}\text{C}_{\text{DIC}}$  value of -11.2‰. Furthermore, Hu and Burdige (2007) have demonstrated that the slope of  $\delta^{13}\text{C}_{\text{DIC}} \cdot \text{DIC}$  vs. DIC is the average isotopic value of the DIC being added to the groundwater system (Figure 9b). Table 2 shows the average isotopic value of the DIC being added to each water type group. The average  $\delta^{13}\text{C}_{\text{DIC}}$  for all Cl-rich groundwater is -12.8‰, but interestingly Cl-rich water types within the salt scar have an average isotopic value of -16.6‰ indicating that the groundwater system within the salt scar is “open” to the soil zone  $\text{CO}_{2(\text{g})}$ . The salt scar is an area of extensive weathering where almost all the overburden has been removed and in some places groundwater seeps to the surface. Sulfate-rich water types have an average isotopic value higher than that of bicarbonate-type waters because the isotopic value of DIC added to the groundwater is -9.4‰ (Table 2).

Appelo and Postma (2007; and references therein) have demonstrated that many aquifers show  $\delta^{13}\text{C}_{\text{DIC}}$  enrichment beyond -12‰ with increasing residence time. Explanations for continued enrichment are renewed dissolution such as dedolomitization, loss of  $\text{Ca}^{2+}$  to ion exchange, or methanogenesis by bacteria. Reverse ion exchange is likely occurring as explained above so  $\text{Ca}^{2+}$  is likely gained through ion exchange reactions. Methane concentration were not measured in this study, but Godsy et al. (2003) found that methanogenic microorganisms exist in very low numbers in this system and only trace amounts of  $\text{CH}_4$  were detected. If groundwaters are saturated or near

saturation for dolomite and calcite and dissolution of gypsum is occurring, then dedolomitization likely will occur (Figure 10a). Dedolomitization generates 1.6 moles of calcite precipitate for every 0.8 mole of dolomite dissolved according to the stoichiometry of the reaction:



Also, Reaction (3) indicates that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  must increase with the increase of  $\text{SO}_4^{2-}$  at ratios of 1:1.8 and 0.8:1.8, respectively. Figures 10b and 10c are scatter plots of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  vs.  $\text{SO}_4^{2-}$ , respectively, along with lines showing the Ca: $\text{SO}_4$  and Mg: $\text{SO}_4$  ratios according to Reaction (3). Bicarbonate-rich groundwater and sulfate-rich groundwater fall along the expected ratios according to the stoichiometry of dedolomitization. Many of these waters are at saturation or near saturation with respect to calcite and dolomite.

According to Figures 10b and 10c, dedolomitization does not appear to be occurring for Cl-rich groundwater although many samples exhibit high concentrations of  $\text{SO}_4^{2-}$  and the isotopic value for many Cl-rich samples are enriched beyond -12‰. It is likely that the effects of dedolomitization are masked by mixing of waters with high  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations. The calcite and dolomite saturation indices for many Cl-rich groundwater indicate saturation concurrently with high  $\text{SO}_4^{2-}$  concentrations similar to  $\text{SO}_4$ -rich groundwater. On close examination of Figures 10b and 10c,  $\text{Ca}^{2+}$  concentrations are significantly lower than  $\text{Ca}^{2+}$  concentrations found in the pit samples, but there are several samples with  $\text{Mg}^{2+}$  concentrations as high as or greater than the highest pit samples and increase with increasing  $\text{SO}_4^{2-}$  concentrations.



## 6.0 Conclusions

Highly saline production water and hydrocarbons produced over a sixty-year period were stored in unlined earthen pits. Over time the produced water and hydrocarbons seeped into the subsurface and mixed with the natural groundwater creating a high-salinity plume. Until the creation of Skiatook Lake (1987) the contaminants were flushed through the groundwater system, but the filling of the lake created a high head boundary which stopped the flushing of the contaminants. The hydrocarbons have been microbially degraded and likely only residual hydrocarbons exist.

$\text{Na}^+$  from the produced water is exchanging for  $\text{Ca}^{2+}$  in clays. Contrary to the initial hypothesis, high ionic concentrations did not inhibit weathering of aquifer carbonates (common ion effect). Many of the groundwater samples were undersaturated with respect to calcite and dolomite. The additional  $\text{CO}_{2(g)}$  generated from continued weathering of carbonates lead to dedolomitization. Concurrent weathering of gypsum with carbonate weathering caused some waters to be saturated with respect to calcite, resulting in precipitation of calcite.

Carbonate evolution of the groundwater system is a mixing of two end members, dissolution of soil  $\text{CO}_{2(g)}$  and dissolution of carbonate rocks. In a plot of  $\delta^{13}\text{C}_{\text{DIC}} \cdot \text{DIC}$  vs. DIC the average isotopic value of the DIC being added ( $\delta^{13}\text{C}_{\text{DIC-added}}$ ) is represented by the slope of the regression line. In a closed system when DIC is added from both soil  $\text{CO}_{2(g)}$  and dissolution of carbonates the  $\delta^{13}\text{C}_{\text{DIC}}$  moves towards -12‰ and in Cl-rich

groundwater the  $\delta^{13}\text{C}_{\text{DIC-added}}$  is -12.7‰. Continued dissolution and precipitation of carbonates can further enrich the DIC with  $^{13}\text{C}$ . The  $\delta^{13}\text{C}_{\text{DIC-added}}$  for  $\text{SO}_4^{2-}$  groundwater is -9.4‰ and for many of the Cl-rich groundwater samples the isotopic value of DIC added is greater than -12‰. In the outer parts of the high salinity plume, residual hydrocarbons are likely still being degraded and the additional generation of  $\text{CO}_{2(\text{g})}$  is causing the excess weathering of carbonates and generation of  $\text{SO}_4^{2-}$  from dedolomitization.

Further work should be done to model more precisely the isotopic change from mixing of carbonate dissolution and  $\text{CO}_{2(\text{g})}$  dissolving into solution. Also, direct effects from biodegradation of the hydrocarbon on the  $\delta^{13}\text{C}_{\text{DIC}}$  were not fully investigated. This would provide data to determine if biodegradation of residual hydrocarbons is still impacting the  $\delta^{13}\text{C}_{\text{DIC}}$ .

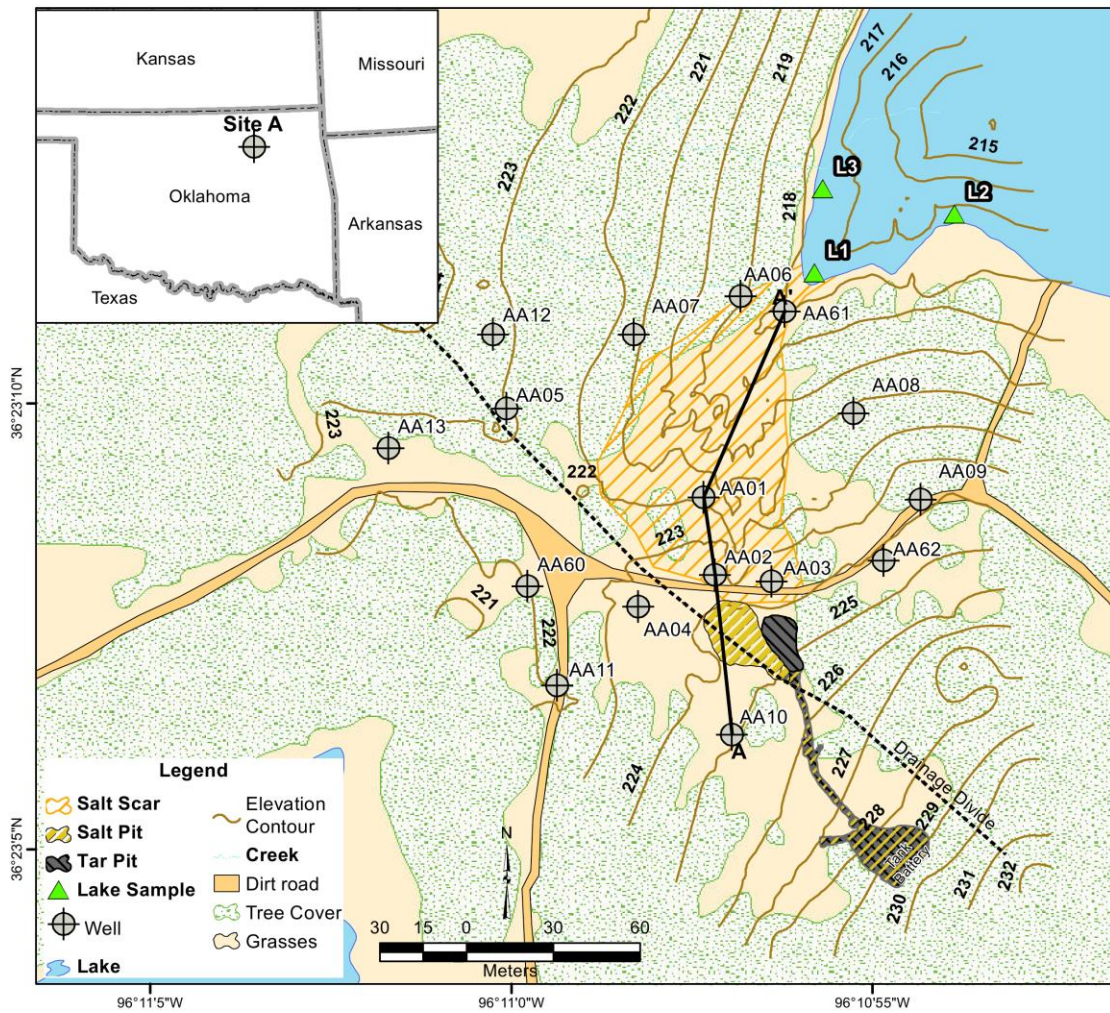
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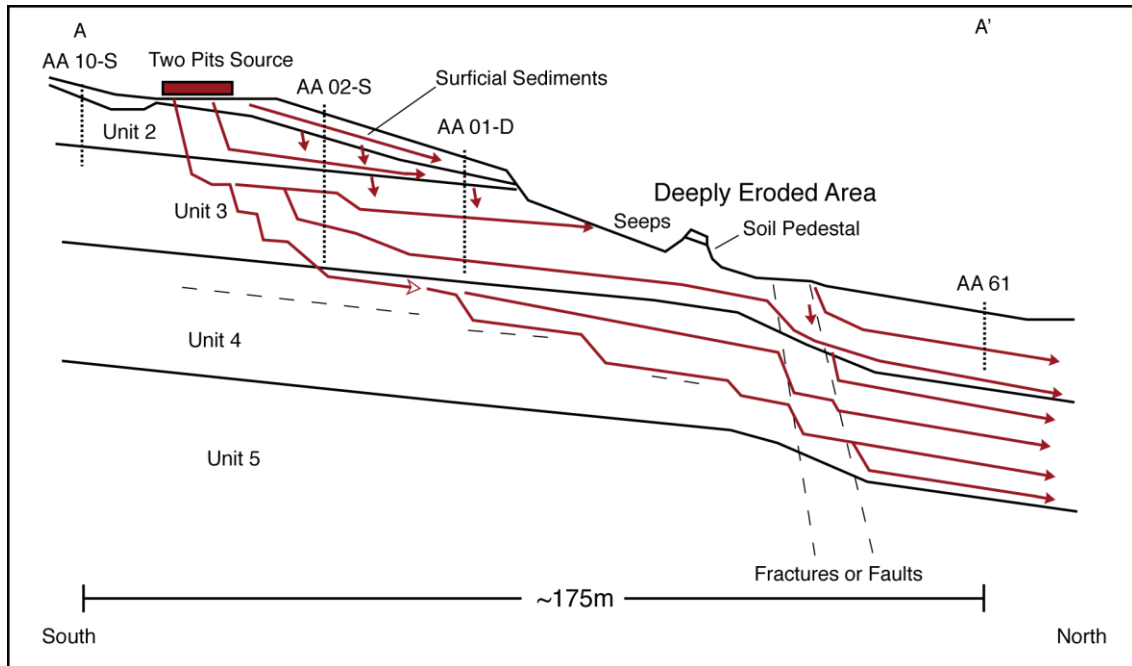
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**Figure 1.** Map of Site A at Skiatook Lake, Osage County, Oklahoma. Within this map are all the monitoring well locations, salt scar, oil and salt pit, drainage divide, and transect A – A’.



**Figure 2.** Conceptual schematic of geologic units along Transect A – A'. Along this transect, likely groundwater flow paths caused by the weathering effects of the produced water and hydrocarbon contaminants are shown. Modified from Otten et al. (2007).



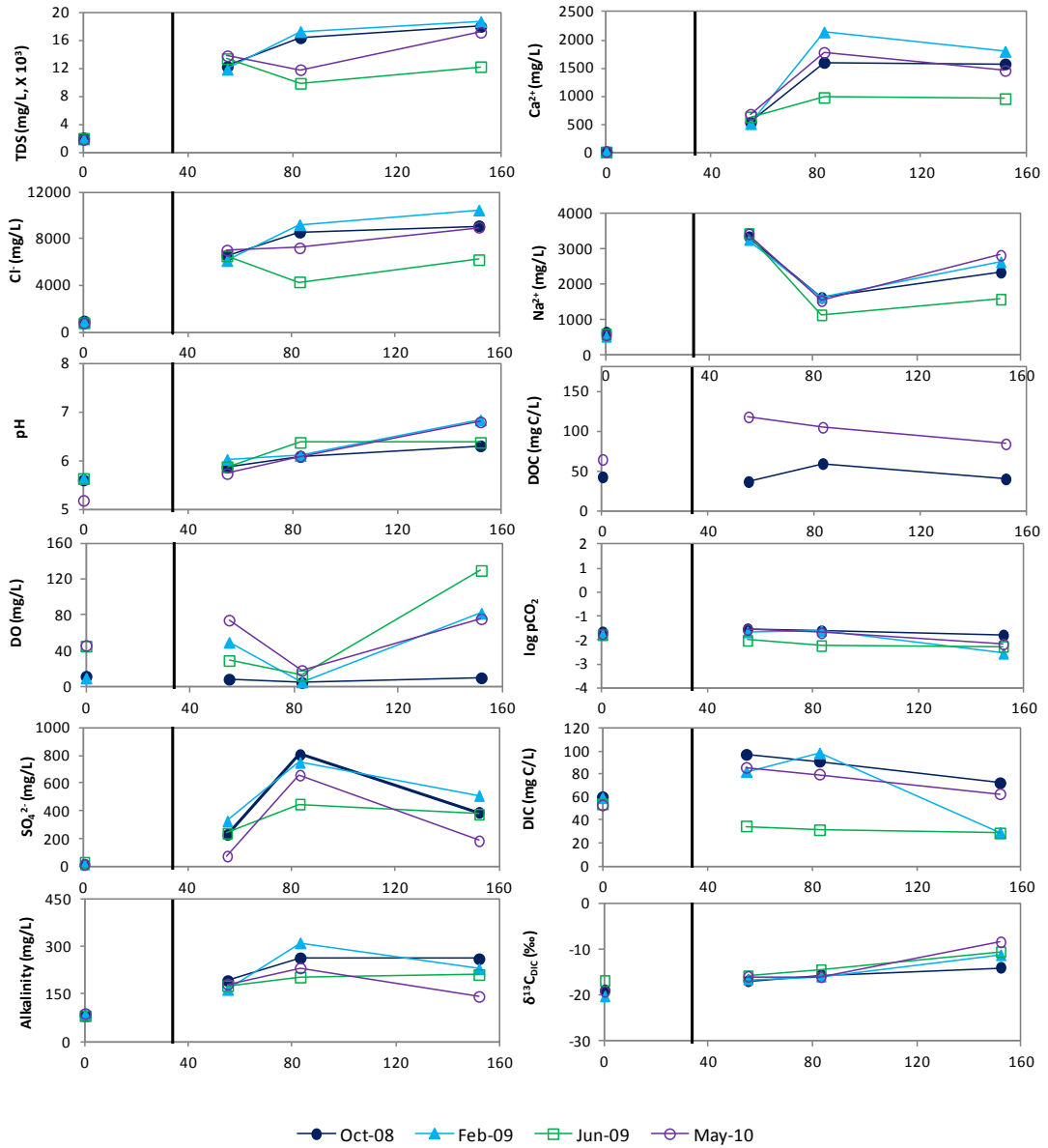
**Table 1** Summary of physical, chemical, and isotopic ratio results for wells sampled at the OSPEP Site A, Skiatook Lake, Oklahoma.

Well ID	Date	Temp (°C)	Watertype	SPC (µS/cm)	TDS (mg/L)	DO (mg/L)	pH	Alk (mg/L as CaCO <sub>3</sub> )	HCO <sub>3</sub> (mg/L)	DOC (mg C/L)	DIC (mg C/L)	δ <sup>13</sup> C <sub>DIC</sub> (‰)	Log pCO <sub>2</sub> (atm)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	Na <sup>+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)	Ca <sup>2+</sup> (mg/L)	Fe Total (mg/L)
<i>Fall 2008 (9/27/2008 - 9/30/2008)</i>																			
AA01-D	9/27/2008	19.40	Mg-Ca-Na-Cl	25,314	16,430	0.44	6.09	265	318	59.61	90.82	-15.7	-1.6	8583	806	1641	1363	1607	7.74
AA02-S	9/30/2008	18.68	Na-Cl	18,931	12,310	0.78	5.87	193	232	37.12	96.78	-17.0	-1.5	6597	233	3356	258	546	ND
AA02-D	9/30/2008	17.98	Na-Cl	18,913	12,290	0.99	6.33	236	283	38.75	54.65	-14.8	-1.9	6554	180	2894	438	747	0.63
AA03-D	9/30/2008	20.15	Na-Cl	9604	6243	0.66	6.58	238	286	34.16	57.35	-17.0	-2.0	3032	20	1709	102	245	ND
AA04-S	9/30/2008	24.42	Na-Cl	7799	5070	0.55	5.04	11	13	32.54	46.48	-20.3	-1.7	2563	1	1438	48	141	ND
AA04-D	9/30/2008	20.76	Na-Cl	8200	5329	0.77	5.97	99	119	36.85	56.01	-18.3	-1.8	2613	28	1413	68	194	0.04
AA05-S	9/30/2008	21.23	Na-Ca-Mg-Cl	17,154	11,150	0.76	5.70	87	104	31.44	54.73	-19.0	-1.7	6293	20	2102	518	952	0.34
AA05-D	9/30/2008	20.54	Mg-Ca-Na-SO4-HCO3	1791	1163	1.62	7.06	448	538	48.32	109.81	-11.2	-2.1	55	434	95	115	146	ND
AA06-S	9/27/2008	20.62	Na-Mg-Ca-Cl	15,142	9843	0.49	6.32	185	222	34.80	59.95	-12.5	-1.9	5190	152	1443	683	936	0.13
AA07-S	9/30/2008	18.79	Ca-Mg-Na-Cl	25,549	16,610	1.38	4.51	0.1	0.1	36.96	111.49	-22.8	-1.4	9218	971	1737	1433	2452	5.46
AA07-D	9/30/2008	19.33	Ca-Mg-Na-Cl	27,556	17,910	0.75	5.39	130	156	63.76	111.85	-14.3	-1.4	9901	1115	1763	1537	2623	7.19
AA08-S	9/27/2008	19.39	Na-Mg-Cl	13,960	9090	2.95	6.63	419	503	63.03	114.55	-14.1	-1.8	5162	358	1677	759	645	0.04
AA08-D	9/27/2008	19.05	Mg-Ca-SO4-HCO3	2954	1920	0.67	6.78	371	445	41.31	101.15	-10.7	-1.9	47	1233	98	217	291	0.35
AA10-S	9/30/2008	21.00	Na-Cl	3232	2106	1.07	5.61	82	98	43.01	59.93	-19.0	-1.7	967	19	665	7	23	0.17
AA10-M	9/30/2008	19.51	Na-Cl	4417	2871	6.88	6.94	166	199	42.09	41.81	-13.2	-2.4	1259	22	693	46	134	ND
AA11-S	9/30/2008	20.00	Na-Ca-Mg-Cl	19,130	12,430	0.50	6.15	232	278	—	84.19	-16.1	-1.7	6695	95	2355	492	1159	3.94
AA11-M	9/30/2008	21.15	Na-Ca-Mg-Cl	4920	3199	0.85	6.73	332	398	—	94.19	-12.1	-1.9	1280	269	475	163	322	1.56
AA11-D	9/30/2008	19.52	Na-Ca-Mg-Cl	4361	2833	0.39	6.73	324	389	40.82	80.57	-11.8	-2.0	1076	262	384	150	301	ND
AA12-S	9/30/2008	20.22	Na-Ca-Mg-Cl-HCO3	1399	907	0.52	7.13	269	323	46.14	67.78	-15.8	-2.4	229	69	153	36	88	0.00
AA12-D	9/30/2008	20.64	Ca-Mg-SO4	2164	1407	5.39	7.32	208	250	40.05	45.98	-12.4	-2.7	81	980	101	139	241	ND
AA13-S	9/30/2008	22.61	Na-Ca-Mg-HCO3-Cl	1101	715	0.85	7.04	342	410	40.52	82.68	-13.7	-2.2	92	86	119	35	79	0.10
AA13-D	9/30/2008	25.66	Na-Ca-Mg-HCO3-Cl	1075	648	1.33	7.07	347	416	43.91	83.18	-13.3	-2.2	85	86	112	35	78	0.10
AA60-S	9/30/2008	25.18	Na-Cl	7660	4979	7.00	6.22	87	104	33.92	33.92	-19.0	-2.1	2855	3	1379	75	203	8.23
AA60-D	9/30/2008	20.65	Na-Ca-Cl	3562	2315	1.39	6.98	226	271	37.15	58.12	-19.0	-2.3	930	37	424	74	176	ND
AA61	9/27/2008	20.59	Mg-Na-Ca-Cl	27,779	18,050	0.82	6.31	262	314	40.43	72.09	-14.1	-1.8	9127	391	2356	1441	1581	15.96
L1	9/27/2008	28.55	Ca-Na-Mg-HCO3-Cl	212	138	7.93	8.24	48	58	30.18	12.26	-8.4	-4.1	20	9	12	5	21	ND
L2	9/27/2008	27.91	Ca-Na-Mg-HCO3-Cl	210	137	7.78	8.27	53	64	24.37	12.19	-8.4	-4.1	19	7	12	5	22	ND
L3	9/27/2008	27.40	Ca-Li-HCO3-Cl	213	139	6.87	8.76	51	61	33.75	11.85	-9.1	-4.7	19	7	6	2	20	ND
Tar Pit	9/30/2008	—	Na-Cl	—	—	—	—	—	—	238.75	—	—	—	64,700	41	33478	1616	5944	32.84
<i>Winter 2009 (2/7/2009 - 2/8/2009)</i>																			
AA01-D	2/8/2009	18.50	Mg-Ca-Na-Cl	26,683	17,330	0.50	6.11	312	374	—	97.94	-16.0	-1.6	9228	750	1649	1858	2146	9.00
AA02-S	2/7/2009	17.11	Na-Cl	18,320	11,910	4.42	6.03	165	198	—	81.89	-16.6	-1.7	6143	329	3278	165	521	ND
AA02-D	2/7/2009	16.85	Na-Ca-Cl	17,706	11,510	2.57	6.44	289	347	—	80.70	-14.7	-1.8	5940	230	2592	392	744	ND
AA03-D	2/7/2009	17.59	Na-Cl	11,430	7431	4.57	6.88	281	337	—	71.50	-15.8	-2.2	3625	46	1984	92	335	ND
AA04-S	2/8/2009	13.83	Na-Cl	7176	4665	3.40	5.00	44	53	—	34.42	-21.3	-1.9	2307	3	1285	32	137	ND
AA04-D	2/8/2009	16.37	Na-Cl	7375	4787	2.80	5.50	21	25	—	34.69	-20.5	-1.9	2286	4	1265	35	145	ND
AA05-S	2/7/2009	16.32	Na-Ca-Cl	14,557	9431	2.73	5.47	36	43	—	45.91	-21.7	-1.8	4951	24	2218	282	590	ND
AA05-D	2/7/2009	17.79	Mg-Ca-Na-SO4-HCO3	1809	1172	6.29	7.35	370	444	—	97.29	-10.7	-2.4	59	424	108	131	149	ND
AA06-S	2/7/2009	16.74	Na-Mg-Ca-Cl	12,234	7959	0.87	6.71	162	194	—	46.03	-11.7	-2.2	4312	120	1213	507	740	1.54
AA07-S	2/7/2009	16.69	Mg-Na-Ca-Cl	16,259	10,560	3.55	4.45	0.1	0	—	43.27	-20.9	-1.8	5560	852	1453	777	1154	ND

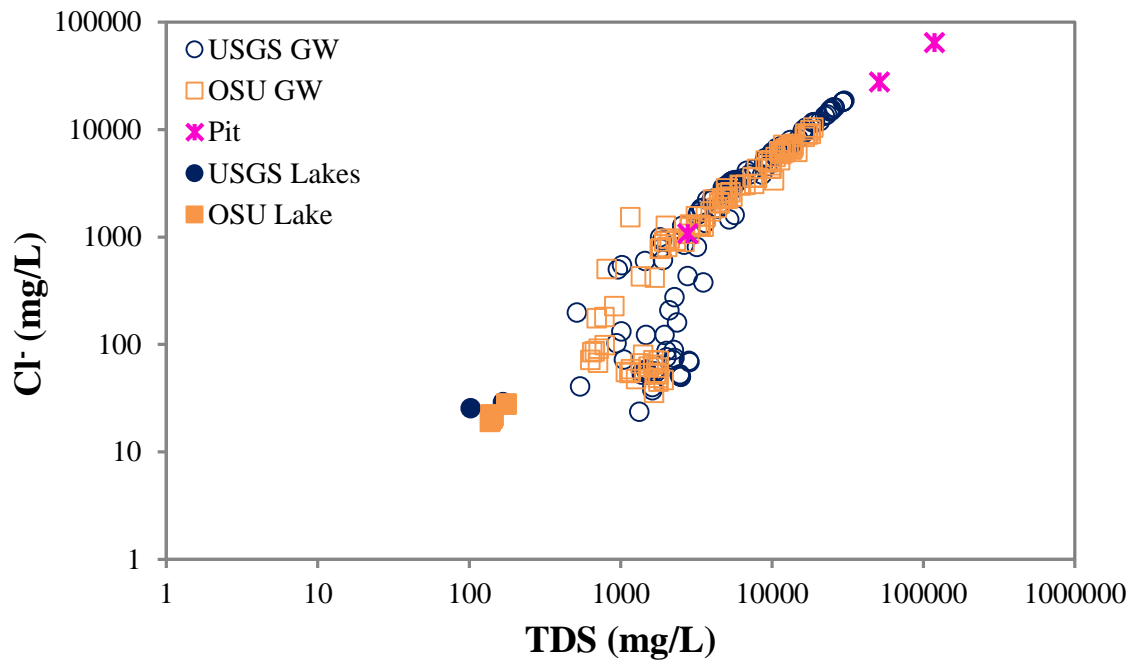
AA07-D	2/7/2009	16.96	Mg-Ca-Na-Cl	19,882	12,920	6.79	4.64	0.1	0	—	—	—	29.70	-17.8	-2.0	6947	1260	1401	1187	1735	ND
AA08-S	2/7/2009	17.38	Mg-Na-Ca-Cl	21,272	13,830	1.08	6.56	353	424	—	—	—	118.78	-14.2	-1.7	7388	673	2031	1432	1098	0.13
AA08-D	2/7/2009	17.28	Mg-Ca-SO4	2654	1724	2.85	7.24	248	298	—	—	—	86.13	-9.8	-2.4	61	1268	105	256	298	0.39
AA09-S	2/7/2009	18.36	Na-Mg-Ca-Cl	12,259	7968	2.56	6.65	618	742	—	—	—	194.44	-13.4	-1.6	3578	1121	1315	678	575	3.26
AA09-D	2/7/2009	17.58	Mg-Ca-SO4-HCO3	2748	1784	0.88	6.88	392	470	—	—	—	116.45	-10.5	-2.0	71	1163	100	259	294	3.49
AA10-S	2/8/2009	13.49	Na-Cl	2995	1943	1.05	5.64	86	103	—	—	—	59.10	-20.3	-1.8	910	21	546	4	24	0.02
AA10-M	2/8/2009	16.70	Na-Cl	4425	2877	3.88	6.39	161	193	—	—	—	41.24	-13.5	-2.1	1307	25	692	32	138	ND
AA11-S	2/8/2009	17.18	Na-Ca-Cl	17,523	11,390	6.33	6.62	193	232	—	—	—	44.14	-12.5	-2.2	6186	101	2179	316	929	ND
AA11-M	2/8/2009	18.00	Na-Ca-Mg-Cl	5201	3379	1.00	6.81	342	410	—	—	—	89.13	-12.5	-2.0	1305	293	474	149	323	1.39
AA11-D	2/8/2009	17.47	Na-Ca-Mg-Cl	5625	3657	1.49	6.75	299	359	—	—	—	68.29	-11.4	-2.1	1561	258	539	156	371	0.29
AA12-S	2/7/2009	18.18	Na-Ca-Mg-Cl-HCO3	1202	781	3.20	6.84	224	269	—	—	—	62.82	-15.4	-2.2	181	70	125	36	98	0.54
AA12-D	2/7/2009	17.52	Mg-Ca-SO4	2532	1646	1.02	6.66	226	271	—	—	—	60.04	-13.1	-2.1	72	1218	111	204	317	0.68
AA13-S	2/8/2009	16.01	Na-Ca-Mg-HCO3-Cl	1040	676	2.14	5.90	338	406	—	—	—	74.70	-13.8	-1.7	87	80	127	33	87	ND
AA13-D	2/8/2009	15.98	Na-Ca-Mg-HCO3	973	632	2.67	7.03	379	455	—	—	—	73.33	-13.6	-2.3	72	73	111	30	81	ND
AA60-D	2/8/2009	17.49	Na-Ca-Mg-Cl	4428	2876	5.87	7.21	215	258	—	—	—	48.85	-16.8	-2.6	1236	41	430	98	246	0.09
AA61	2/7/2009	14.99	Mg-Na-Ca-Cl	28,870	18,750	7.44	6.84	230	276	—	—	—	29.02	-11.4	-2.5	10,476	513	2646	1691	1803	0.00
L1	2/7/2009	11.04	Ca-Na-HCO3-Cl	213	139	14.89	7.48	74	89	—	—	—	11.79	-7.3	-3.5	22	9	13	4	23	0.11
L2	2/7/2009	9.66	Ca-Na-HCO3-Cl	219	142	15.02	6.67	96	115	—	—	—	11.09	-7.5	-2.9	22	9	14	5	23	0.10
L3	2/7/2009	5.85	Ca-Na-Mg-Cl-HCO3	210	138	16.59	7.37	27	32	—	—	—	6.02	-9.0	-3.7	22	10	13	5	22	0.10
Tar Pit	2/8/2009	—	Na-Cl	—	—	—	—	—	—	—	—	—	37.09	5.9	—	27,793	38	16988	705	3053	215.83

Summer 2009 (6/3/2009 - 6/9/2009)

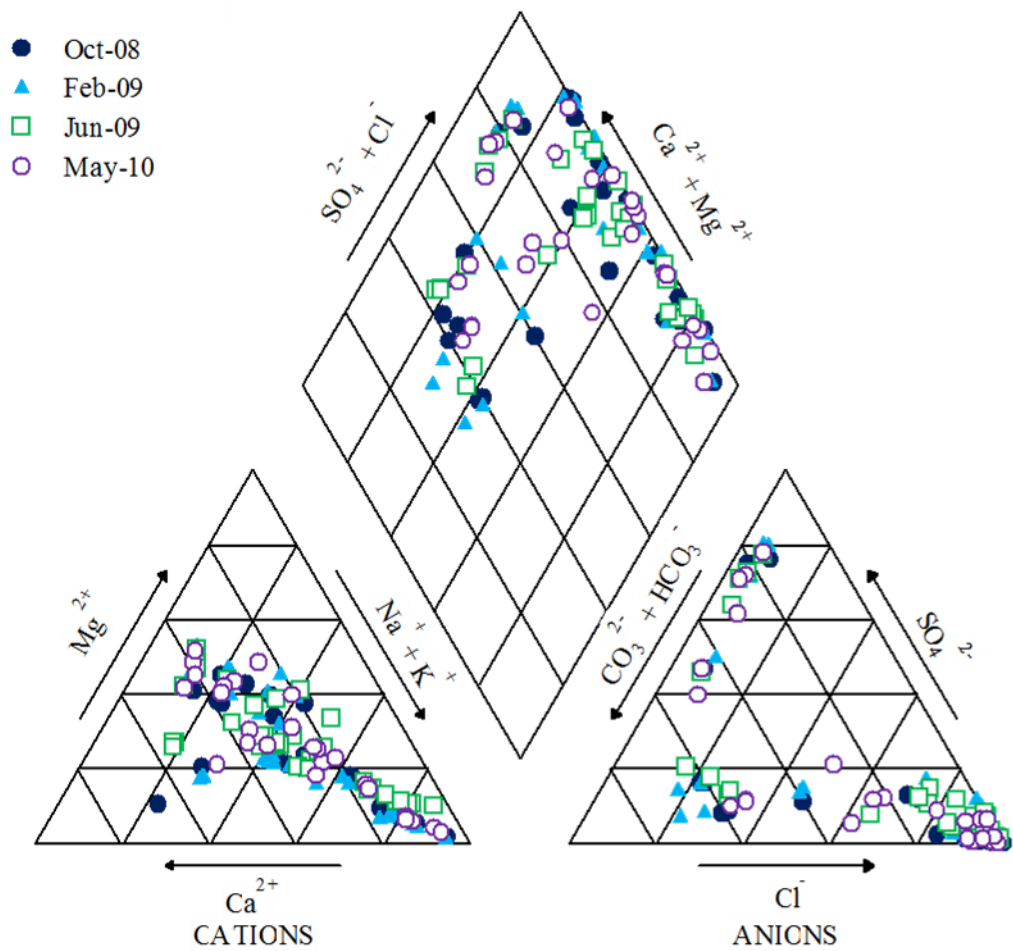
AA12-D	6/9/2009	17.14	Ca-M-g-SO4	2526	1641	2.23	6.36	251	301	—	45.89	-12.6	-2.0	65	1110	101	174	303	ND
AA13-S	6/3/2009	15.94	Na-Ca-M-g-HCO3	1089	708	5.80	7.62	353	424	—	59.40	-12.7	-2.9	68	111	106	42	79	ND
AA13-D	6/3/2009	16.60	Na-Ca-M-g-HCO3-Cl	1212	786	2.20	7.48	342	410	—	60.49	-13.0	-2.8	99	98	113	46	89	ND
AA60-S	6/3/2009	18.53	Na-Cl	3063	1994	8.49	6.66	127	152	—	46.02	-2.2	-2.2	1276	17	599	54	91	13.26
AA60-D	6/3/2009	16.80	Ca-M-g-Na-Cl	5111	3321	5.42	6.85	223	268	—	41.42	-14.3	-2.4	1289	107	333	191	375	ND
AA61**	6/9/2009	16.38	M-g-Na-Ca-Cl	18,910	12,290	9.53	6.38	212	254	—	28.42	-10.7	-2.3	6222	378	1594	906	965	ND
AA62	6/3/2009	16.75	Na-M-g-Ca-Cl	2785	1811	4.04	6.12	63	76	—	12.98	-16.3	-2.5	776	150	389	99	127	ND
L1	6/9/2009	27.64	Ca-M-g-HCO3-Cl	220	143	7.91	8.32	54	65	—	10.22	-8.8	-4.3	21	13	7	6	22	ND
L2	6/9/2009	26.00	Ca-M-g-HCO3-Cl	224	145	7.59	8.06	58	70	—	9.81	-9.0	-4.0	21	13	7	6	22	ND
L3	6/9/2009	25.63	Ca-M-g-HCO3-Cl	218	142	7.87	7.96	54	65	—	8.50	-8.7	-4.0	20	13	7	6	22	0.01
Salt Pit	6/9/2009	36.81	—	54	35	6.35	7.93	0.4	0	—	—	—	—	5	3	2	0	2	ND
Tar Pit	6/9/2009	34.10	Na-Cl	7409	4816	1.82	6.53	17.4	21	—	—	—	—	1077	52	743	95	156	0.44
<i>Spring 2010 (5/23/2010 - 5/24/2010)</i>																			
AA01-D	5/24/2010	16.96	M-g-Ca-Na-Cl	18,241	11,860	1.69	6.10	233	280	104.97	79.59	-16.2	-1.7	7235	659	1551	1473	1785	8.66
AA02-S	5/24/2010	18.31	Na-Cl	21,311	13,850	6.37	5.74	182	218	117.96	85.44	-16.1	-1.6	7047	78	3440	419	688	ND
AA02-D	5/24/2010	17.12	Na-Cl	21,049	13,680	2.02	5.98	179	215	96.88	68.14	-15.2	-1.7	6775	126	3353	379	670	ND
AA03-S	5/23/2010	18.67	Na-Cl	1780	1158	3.31	4.86	45	54	47.64	26.05	0.0	-2.0	1537	16	801	18	50	0.36
AA03-D	5/23/2010	17.34	Na-Cl	6059	3940	4.54	5.19	182	218	67.79	46.74	-16.6	-1.8	1733	12	1047	46	125	1.52
AA04-S	5/23/2010	18.42	Na-Cl	7853	5104	5.11	5.32	50	60	67.59	46.92	-20.2	-1.8	2290	6	1349	49	138	ND
AA04-D	5/23/2010	15.36	Na-Cl	7639	4965	1.23	5.22	85	102	76.61	59.70	-18.7	-1.7	2281	13	1303	57	161	ND
AA05-S	5/24/2010	18.09	Na-Ca-Cl	18,946	12,320	2.87	5.31	51	61	91.59	50.13	-21.1	-1.7	6263	21	1919	397	718	ND
AA05-D	5/24/2010	16.78	M-g-Ca-Na-SO4-HCO3	1754	1140	3.21	6.17	478	574	126.71	103.41	-10.7	-1.6	55	460	111	114	157	0.63
AA06-S	5/24/2010	17.94	Na-M-g-Ca-Cl	26,482	17,210	6.53	6.80	143	172	84.20	62.53	-8.6	-2.2	8999	187	2833	1075	1464	ND
AA07-S	5/24/2010	16.65	Na-M-g-Ca-Cl	6630	4309	0.89	5.03	11	13	70.37	57.42	-23.5	-1.7	1877	182	745	189	270	1.09
AA07-D	5/24/2010	16.56	Na-M-g-Ca-Cl	7644	4969	1.40	5.18	17	20	41.09	30.69	-21.7	-2.0	2266	214	861	232	339	0.06
AA08-S	5/23/2010	16.01	M-g-Na-Ca-Cl	15,100	9815	0.80	5.39	444	533	120.42	131.99	-16.0	-1.4	4681	399	1442	770	666	0.10
AA08-D	5/23/2010	15.81	M-g-Ca-SO4-HCO3	2746	1783	3.46	5.70	390	468	94.00	90.52	-9.6	-1.6	53	1120	98	213	282	0.03
AA09-S	5/23/2010	17.65	M-g-Na-Ca-Cl	11,698	7606	1.14	5.23	608	730	156.78	184.74	-12.7	-1.2	3134	467	790	743	601	0.71
AA09-D	5/23/2010	16.35	M-g-Ca-SO4-HCO3	2741	1780	1.99	5.74	417	500	104.62	103.48	-10.0	-1.5	45	1113	85	221	267	1.72
AA10-S	5/23/2010	16.03	Na-Cl	2859	1857	4.54	5.19	89	107	64.77	52.83	-19.3	-1.7	791	17	582	9	28	0.36
AA10-D	5/23/2010	16.82	M-g-Ca-SO4-HCO3	2080	1352	0.37	6.13	363	436	99.49	100.92	-12.5	-1.6	67	684	85	148	218	1.17
AA11-S	5/23/2010	17.81	Na-Ca-Cl	15,209	9886	0.45	4.70	282	338	76.99	76.32	-18.0	-1.5	4388	63	1775	310	721	14.79
AA11-M	5/23/2010	17.72	Ca-Na-M-g-Cl-HCO3	2592	1682	0.31	5.22	334	401	93.04	93.69	-11.6	-1.5	419	238	213	100	195	0.29
AA11-D	5/23/2010	17.06	Na-Ca-M-g-Cl	4075	2640	0.59	5.61	420	504	92.40	96.24	-11.5	-1.5	905	224	404	142	290	8.55
AA12-S	5/24/2010	17.96	Ca-Na-M-g-Cl-HCO3	1256	810	5.48	6.31	373	448	69.28	60.75	-14.9	-1.9	505	55	196	78	181	0.09
AA12-D	5/24/2010	17.42	Ca-M-g-SO4	2358	1532	3.31	6.44	249	299	68.77	63.70	-11.8	-1.9	63	1124	109	181	323	0.06
AA13-S	5/24/2010	17.21	M-g-Ca-Na-HCO3-SO4	2551	1658	4.35	6.56	250	300	92.70	88.86	-11.5	-1.9	36	187	75	73	109	0.07
AA62	5/23/2010	19.66	Na-M-g-Ca-Cl-HCO3	1074	697	1.61	5.02	93	112	42.99	28.57	-18.2	-1.9	176	43	108	23	32	0.10
L1	5/24/2010	25.11	Ca-Na-M-g-HCO3-Cl	271	176	9.08	6.03	60	72	35.99	13.65	-5.6	-2.4	28	12	17	7	24	0.12
L2	5/24/2010	24.84	Ca-Na-M-g-HCO3-Cl	271	176	9.05	8.16	62	74	35.93	14.08	-5.5	-4.0	28	12	18	7	26	0.10
L3	5/24/2010	25.67	Ca-Na-M-g-HCO3-Cl	270	176	9.57	8.17	72	86	34.37	13.88	-5.4	-4.0	28	12	17	7	25	0.13
Tar Pit	5/24/2010	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
SPC = specific conductance; DO = dissolved oxygen; pH = standard units; Alk = alkalinity; — = not available; ND = below detection level																			



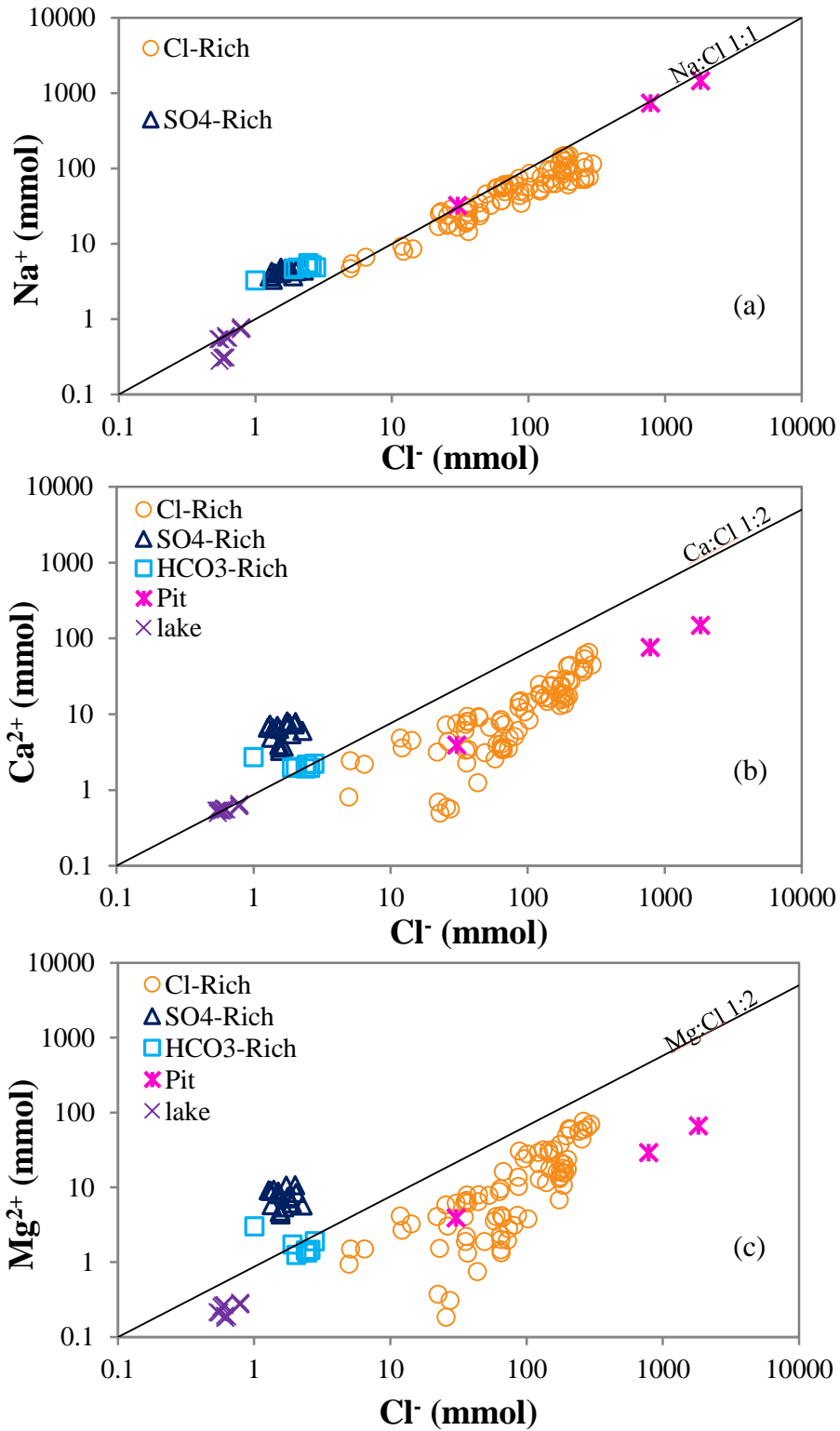
**Figure 3.** Spatial variation of TDS, Cl<sup>-</sup>, pH, DO, Na<sup>+</sup>, Alkalinity, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, DOC, log pCO<sub>2</sub>, DIC, and δ<sup>13</sup>C<sub>DIC</sub> along transect A to A'. Vertical line represents the position of the drainage divide. Refer to Figure 1 for transect location.



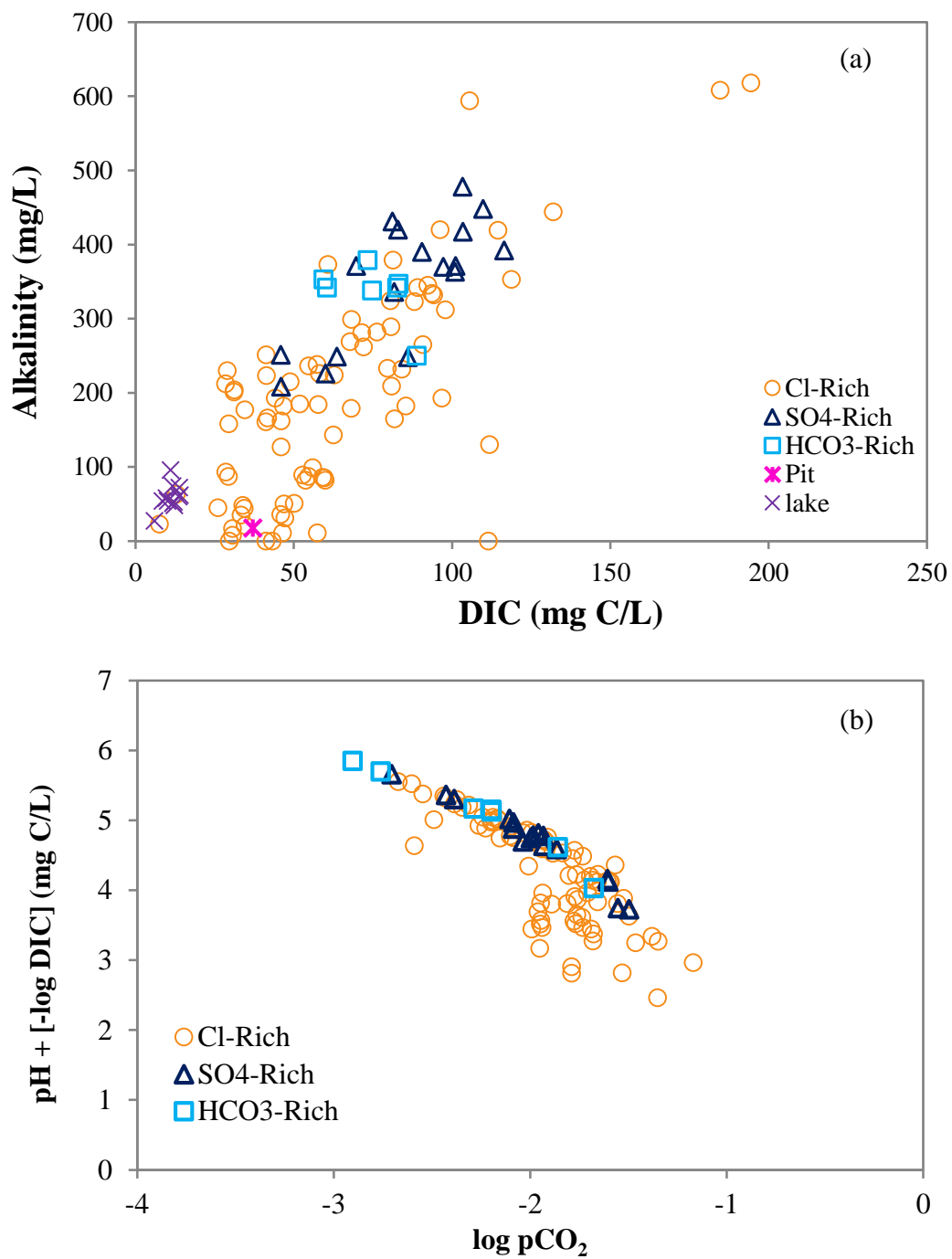
**Figure 4.** Plot total dissolved solids (TDS) vs.  $\text{Cl}^-$ .  $\text{Cl}^-$  has a constant ratio to TDS indicating that  $\text{Cl}^-$  is a dominant constituent of the produced water and it is a conservative ion in the groundwater system. Note that the TDS values were calculated from the linear regression of the groundwater samples for the two pit samples with high  $\text{Cl}^-$ .



**Figure 5.** Piper plot showing the various groundwater types at site A;  $\text{SO}_4^{2-}$ -rich water types,  $\text{HCO}_3^-$ -rich water types (background water), and  $\text{Cl}^-$ -rich water types.  $\text{Cl}^-$ -rich water types indicate those waters contaminated by produced water.

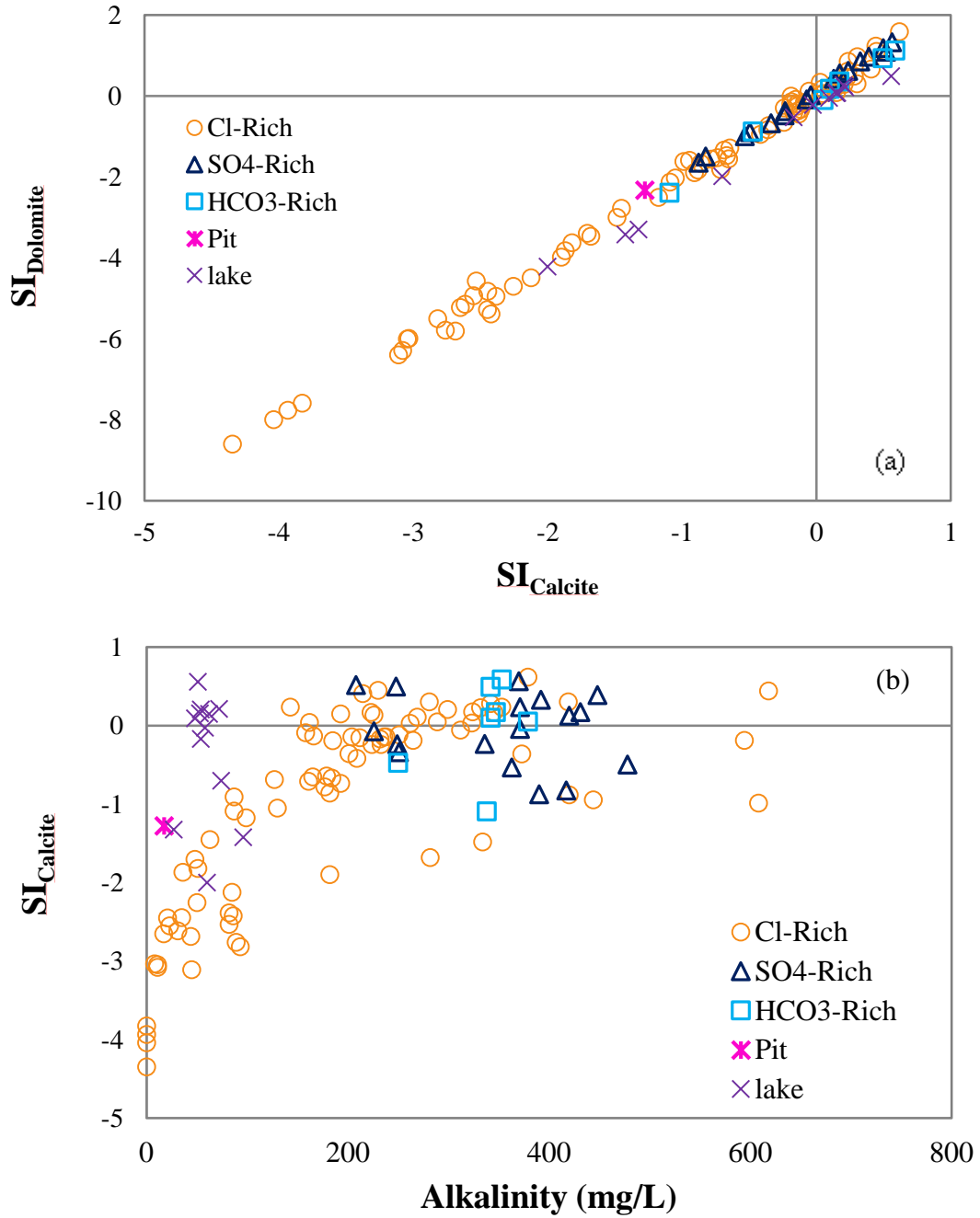


**Figure 6.** Scatter plots of cation concentration relative to degree of contamination. (a)  $\text{Na}^+$  vs.  $\text{Cl}^-$ , (b)  $\text{Ca}^{2+}$  vs.  $\text{Cl}^-$  and (c)  $\text{Mg}^{2+}$  vs.  $\text{Cl}^-$ . Groundwaters are identified according to their anion facies.

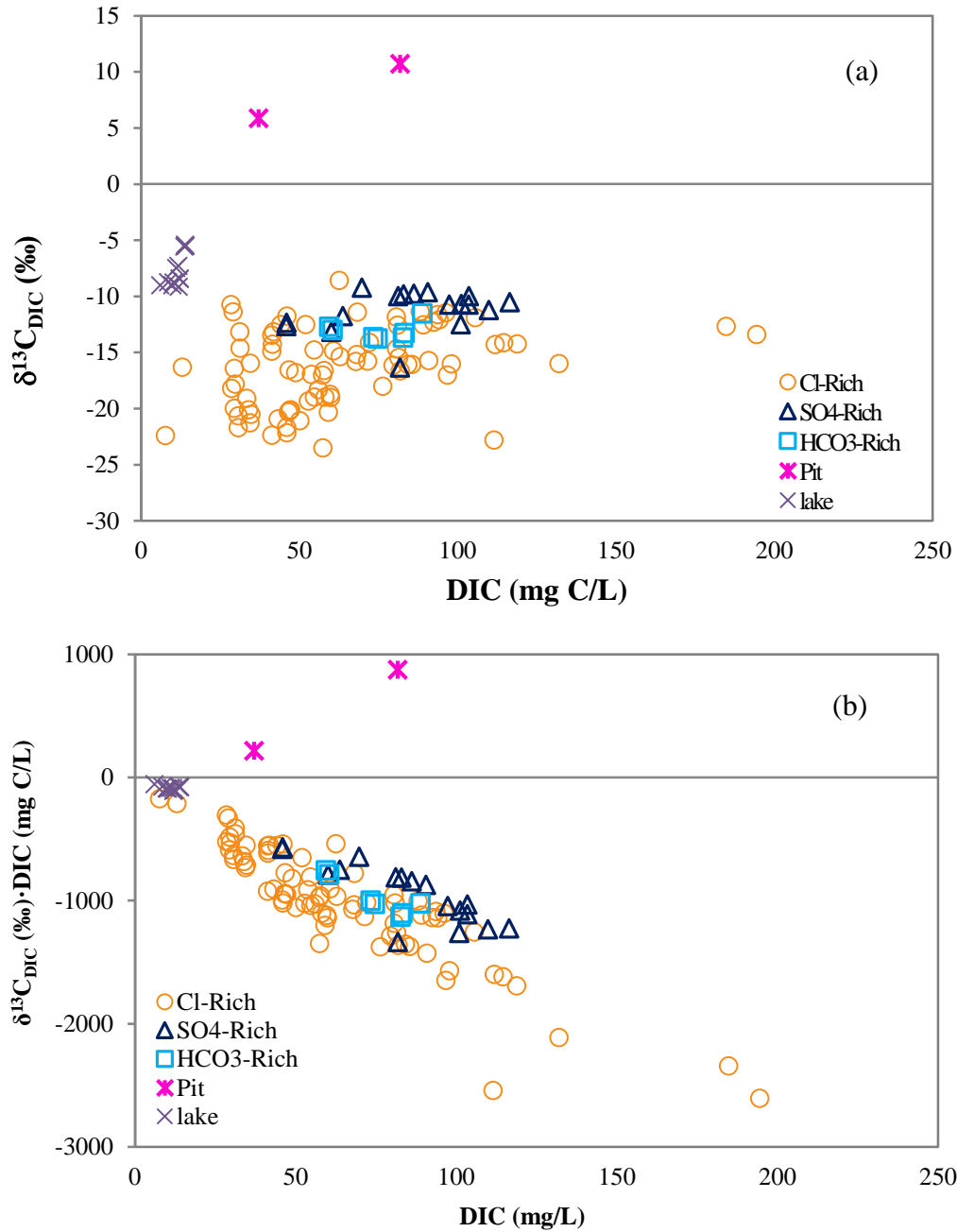


**Figure 7.** Generating DIC vs. Alkalinity and excess CO<sub>2</sub> within groundwater DIC. (a) Alkalinity vs. DIC and (b) pH + [-log DIC] vs. log pCO<sub>2</sub>. Groundwaters are identified according to their anion facies.





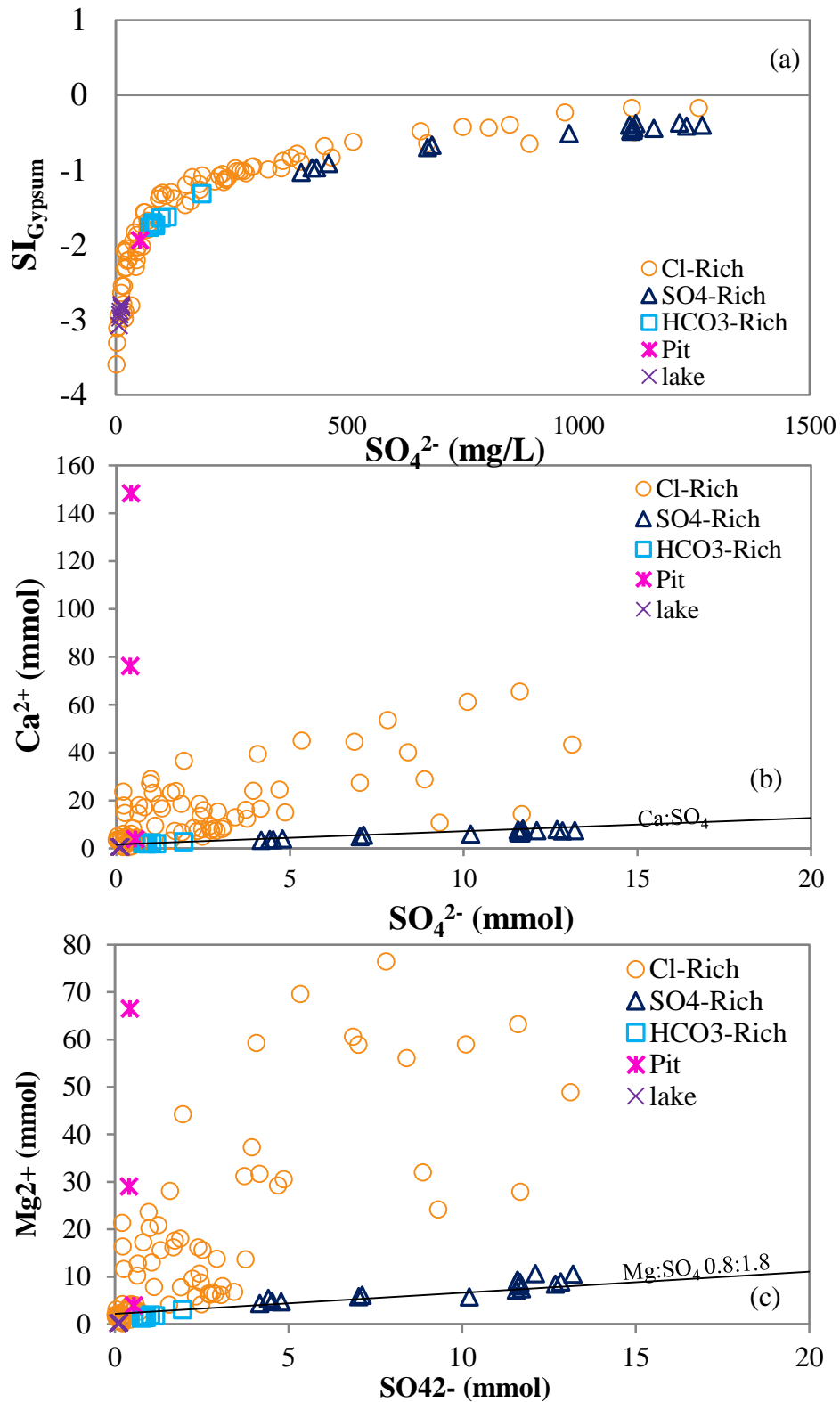
**Figure 8.** The saturation state of calcite and dolomite and calcite relative to alkalinity. (a) Saturation indices of calcite vs. dolomite and (b) Saturation indice for calcite vs. Alkalinity. Groundwaters are identified according to their anion facies.



**Figure 9.** Isotopic value of groundwater DIC and average isotopic value of DIC added to groundwater. (a)  $\delta^{13}C_{DIC}$  vs. DIC and (b)  $\delta^{13}C_{DIC} \cdot DIC$  vs. DIC. Slope of the linear regression of the groundwater samples is the average DIC added to the groundwater. Groundwaters are identified according to their anion facies.

Table 2. Isotopic value of the DIC added to groundwater.

Water Sample Group	$\delta^{13}\text{C}_{\text{DIC-added}}$
Cl-rich groundwater	-12.7 ‰
SO <sub>4</sub> -rich groundwater	-9.4 ‰
HCO <sub>3</sub> -rich groundwater	-11.6 ‰
Lake samples	-2.6 ‰
Pit samples	14.7 ‰



**Figure 10.** Saturation state of gypsum and ratio of  $Ca^{2+}$  and  $Mg^{2+}$  to  $SO_4^{2-}$ . Scatter plots of (a)  $SO_4^{2-}$  vs. gypsum saturation indice, (b)  $SO_4^{2-}$  vs.  $Ca^{2+}$  and (c)  $SO_4^{2-}$  vs.  $Mg^{2+}$ . Groundwaters are identified according to their anion facies.

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