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## Cycling of oxyanion-forming trace elements in groundwaters from a freshwater deltaic marsh

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#### A R T I C L E I N F O

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#### ABSTRACT

Pore waters and surface waters were collected from a freshwater system in southeastern Louisiana to investigate the geochemical cycling of oxyanion-forming trace elements (i.e., Mo, W, As, V). A small bayou (Bayou Fortier) receives input from a connecting lake (Lac des Allemands) and groundwater input at the head approximately 5 km directly south of the Mississippi River. Marsh groundwaters exchange with bayou surface water but are otherwise relatively isolated from outside hydrologic forcings, such as tides, storms, and effects from local navigation canals. Rather, redox processes in the marsh groundwaters appear to drive changes in trace element concentrations. Elevated dissolved S(-II) concentrations in marsh groundwaters suggest greater reducing conditions in the late fall and winter as compared to the spring and late summer. The data suggest that reducing conditions in marsh groundwaters initiate the dissolution of Fe(III)/Mn(IV) oxide/hydroxide minerals, which releases adsorbed and/or co-precipitated trace elements into solution. Once in solution, the fate of these elements is determined by complexation with aqueous species and precipitation with iron sulfide minerals. The trace elements remain soluble in the presence of Fe(III)- and SO<sup>2</sup><sub>4</sub>- reducing conditions, suggesting that either kinetic limitations or complexation with aqueous ligands obfuscates the correlation between V and Mo sequestration in sediments with reducing or euxinic conditions.

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#### 1. Introduction

Deltaic wetlands are important sites for carbon cycling and ecosystem productivity and provide a barrier for inland communities against storms (Chmura et al., 2003; Day et al., 2007; Kemp et al., 2014). Owing to their dynamic nature, deltaic wetlands are sensitive recorders of changing hydrologic regimes, anthropogenic influence, and sea level rise (Paola et al., 2011). Particularly important is their function as a filter for anthropogenic contaminants between upland regions and the ocean (Windom et al., 1989; Alewell et al., 2008). The biogeochemical reactions that occur within deltaic wetlands can ultimately impact marine biogeochemistry and fluxes of constituents to the ocean (Bianchi and

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Allison, 2009). Although many studies have focused on the influence of large river fluxes to the ocean (e.g., Martin and Whitfield, 1983; Shiller and Boyle, 1987; Bianchi and Allison., 2009) or the biogeochemistry of shallow pore waters (e.g., Kostka and Luther, 1995; Sundby et al., 2003), much less is known about biogeochemical processes at depth in deltaic marsh systems and how these processes may affect fluxes of constituents to the coast (Beck et al., 2008).

In this study we focus on the biogeochemical cycling of redox sensitive trace elements (i.e., Fe, Mn, Mo, W, As, V) in marsh groundwaters exchanging with an interdistributary lake of the Mississippi River Delta system. The fate of these trace elements in coastal systems has important consequences for biological cycles, potential contamination in the environment, and because of their redox sensitivity, their use in paleoredox reconstructions in paleoceanographic studies (Bone et al., 2006; O'Connor et al., 2015). Owing to the seasonal variation in redox reactions, cycling of trace elements is dynamic, and concentrations are representative of







numerous processes, including biologically mediated redox reactions, adsorption/desorption reactions, and ion-exchange reactions occurring within the marsh system. For example, in natural dilute oxic waters, Mo and W occur as fully deprotonated oxyanions in the hexavalent state ( $MOQ_4^{2-}, WO_4^{2-}$ ), whereas V and As exist as hydrolyzed oxyanions in the pentavalent state, where the degree of protonation depends on pH (e.g.,  $H_2VO_4^{-}, HVO_4^{-}, H_2AsO_4^{-}, HAsO_4^{-};$ Cruywagen, 2000; Smedley and Kinniburgh, 2002; Wright and Belitz, 2010; Gustafsson, 2003). As oxyanions, desorption from mineral surfaces occurs at alkaline pH where mineral surface charges become increasingly negative (Hingston et al., 1967; Stumm and Morgan, 1996). Adsorbed oxyanions will also be released to solution upon reductive dissolution of Fe(III)/Mn(IV) oxide/oxyhydroxide host phases (Davison, 1993; Lovley, 1987).

Under sulfate reducing conditions, the production of dissolved sulfide can also influence the speciation and reactivity of these trace elements as S(-II) can act as both a reducing agent or complexing ligand (Clarke and Helz, 2000; Erickson and Helz, 2000; Planer-Friedrich et al., 2007; Mohajerin et al., 2014). For example, vanadate can be reduced by H<sub>2</sub>S to the more particle reactive V(IV) or V(III) oxidation states, leading to decreasing aqueous concentrations (Wanty, 1986; Breit and Wanty, 1991), whereas under sulfate reducing conditions, Mo, W, and As are converted to thioanions with or without reduction (Cullen and Reimer, 1989; Erickson and Helz, 2000; Vorlicek et al., 2004; Planer-Friedrich et al., 2007; Dahl et al., 2013; Mohajerin et al., 2014). Less described but equally important is the role of organic matter affecting the solubility of these trace elements through complexation or adsorption processes (e.g., Wehrli and Stumm, 1989; Tribovillard et al., 2006; Koutsospyros et al., 2006). Polymeric forms of Mo, W, and V also exist but are negligible at the typically low metal concentrations (i.e., nanomolal, picomolal) and circumneutral pH values observed in most natural waters (Baes and Mesmer, 1976; Wesolowski et al., 1984; Wanty and Goldhaber, 1992; Cruywagen, 2000).

Detailed studies of trace element cycling in marsh groundwaters (1-6 m depth) are lacking, especially in Mississippi River Delta groundwaters, and to the best of our knowledge there have been no investigations of trace element cycling between deeper groundwaters and surface waters in the Mississippi River Delta region. Consequently, we sampled groundwaters and surface waters at an interdistributary freshwater deltaic lake (i.e., Lac des Allemands) over the course of a year to investigate processes that control trace element cycling in the system. Trace element concentrations are discussed within the context of redox chemistry of the marsh and comparison with nearby surface water samples. We highlight the importance of competition between redox processes acting to release or sequester trace elements in the sediments and complexation with dissolved ligands, which can act to increase the effective solubility of some of the studied trace elements, while enhancing the removal of others from solution.

#### 2. Study site

The study site is located at Lac des Allemands, an interdistributary lake in the Mississippi River Delta (Fig. 1). The Mississippi River Delta formed by a series of river avulsion events beginning ~7000 years ago and built around 25,000 km<sup>2</sup> of river deposits with each of the 6 lobes observable today (Fisk et al., 1954; Roberts, 1997). Upon abandonment of a lobe, fine-grained deposits associated with interdistributary bays, tidal flats and marshes overlaid the coarser-grained river deposits (Coleman, 1988; Seybold et al., 2007). The Lac des Allemandes systems lies between Bayou LaFourche, which was the main channel of the Mississippi River from about 1300 years before present to about 500 years before present, and the modern mainstem of the Missisippi River. During this period, the region accumulated a complex stratigraphy of organic matter, as well as fine and coarse-grained material, with each depositional facies related to the proximity of the outlet and crevasses in the Mississippi River (Kosters et al., 1987; Torngvist et al., 1996; Roberts, 1997). Lac des Allemands is hydrologically connected to the southern portions of Barataria Basin by Bayou des Allemands (Fig. 1A). Barataria Basin is presently under a transgressive phase, experiencing subsidence, saltwater intrusion, and erosion (Kosters et al., 1987; Kolker et al., 2013; Couvillion et al., 2011; Roberts, 1997). Furthermore, anthropogenic levee structures that constrain Mississippi River flow in the southern Mississippi River Delta prevent future river migration and land building by overbank flow. Consequently, the adjacent sediment-starved wetlands in the southern portion of the basin are left vulnerable to sea level rise and storm surge inundation (Reed, 2002). Lac des Allemands is also considered to lie within the "industrial corridor" of the delta that includes abundant industrial facilities and a number of Superfund waste sites (Catallo et al., 1995).

The region surrounding Lac des Allemands is classified as freshwater marsh, and the marsh is dominated by freshwater spikerush species, such as Panicum hemitomon (maidencane), Typha latifolia, and Eleocharis macrostachya Britton (Kosters et al., 1987; CRMS). There are no surface water sources to the upper Barataria Basin, although the Davis Pond Diversion opens to Lakes Salvador and Cataouatche to the south of Lac des Allemands (Fig. 1A). Precipitation is the main surface water input, of which about 40% is available for runoff (Inoue et al., 2008, and references therein). Runoff from agricultural and industrial areas accumulates nutrients, which may then accumulate in the lake. Lac des Allemands is a hypereutrophic and fresh lake, with salinities below 0.5 ppt (Ren et al., 2009). Lac des Allemands waters are considered to be Nlimiting, and the cyanobacteria species Anabaena spp., Anabaenopsis spp., Cylindrospermopsis raciborskii spp., and Aphanizomenon spp. constitute the predominant phytoplankton species within the lake. The depth of Lac des Allemands ranges between 2 and 3 m and is therefore likely a polymictic lake (Ren et al., 2009).

#### 3. Methods

#### 3.1. Field methods

A number of small bayous extend from the lake and terminate in the adjacent wetlands (Fig. 1B). We focused on Bayou Fortier, which is the largest and most northern of these bayous because it extends north to near the natural levee of the Mississippi River and within 5.4 km of the river (Fig. 1C). Six piezometers (W1-W6) were installed in September 2013 along Bayou Fortier using vibracoring techniques (Lanesky et al., 1979). A marsh fire the following winter cleared enough vegetation to allow the installation of three additional piezometers farther inland (W7–W9; Fig. 1C). Piezometer W4 is the closest to the Mississippi River and is located within the cypress swamp near the northern reach of Bayou Fortier (Fig. 1C). Additionally, a piezometer was installed on farmland in Edgard, Louisiana (EDG), directly north of Bayou Fortier and 0.88 km south of the Mississippi River, and two piezometers were installed at different depths (183 cm and 488 cm) along the western edge of Lac des Allemands on farmland in the town of Vacherie, LA (Fig. 1B). These "farmland cores" were taken using a Geoprobe® technical drilling machine, and the piezometers were emplaced in the resulting boreholes. All piezometers were constructed from PVC pipes connected to a PVC Well Point that contained a 0.91 m screened interval. In addition to the groundwater samples collected from the piezometers, surface water samples were collected from Bayou Fortier as well as Lac des Allemands (Fig. 1B). Additionally, a



**Fig. 1. A.** Map of Barataria Basin in the Mississippi Delta region of southern Louisiana. **B.** Map of Lac des Allemands. Surface sites are labeled as magenta diamonds and piezometers installed on farmlands are labeled as green circles. The orange dashed line indicates the region of a buried sand unit that extends from the Mississippi River levee to the head of Bayou Fortier, and the green dashed arrow indicates the hypothesized direction of groundwater flow. The black dashed line outlines inset **C**. Map of Bayou Fortier. Marsh piezometers are labeled as yellow circles and surface sites as magenta diamonds. Maps constructed using high resolution ortho imagery downloaded from USGS Earth Explorer for input into ArcGIS. Location details for the sample sites are listed in Appendix A. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

surface water sample was also collected at a bayou (St 8) along LA route 3127 located 3.4 km south of the Mississippi River and 2 km north of Lac des Allemands piezometer W4 (Fig. 1B). Cores collected from Lac des Allemands sample W4 and all three of the farmland cores reveal coarse-grained sediments at depth in contrast to the very fine-grained organic-rich units constituting the remaining Lac des Allemands samples (W1-3, W5-9; Fig. 2).

Surface water samples were collected April, May, July and September of 2013 and in February, April, May, and September of 2014. Groundwater samples from the marsh piezometers were collected October of 2013 and again in February, April, May, and September of 2014 (Appendix A). Groundwater samples from the piezometers on farmland (VACW1, VACW2, and EDG) were sampled during the May and September sampling campaigns of 2014. All sampling equipment used to collect water samples was cleaned prior to sampling according to trace-metal clean procedures, and sample bottles were rinsed three times prior to collection with filtered sample water (e.g., Johannesson et al., 2004). Surface water samples were collected just below the bayou and lake surface using a peristaltic pump with Teflon® tubing attached to a 0.45 µm Gelman Sciences (polysulfone ether membrane) in-line filter. Groundwater samples were similarly sampled using a peristaltic pump after measuring depth to water level. Approximately 30 mL of filtered water sample was passed through anion exchange columns (Biorad prefilled AG® 1-X8 Resin converted to acetate form) in order to separate As(V) and As(III) species. At neutral pH and oxic to ferruginous conditions, As(V) occurs as the ionized, arsenate oxyanion (e.g.,  $H_2As^VO_4^-$  and  $HAs^{V}O_{4}^{2-}$ ) and is therefore retained on the column, whereas As(III) occurs as fully protonated arsenic acid (i.e.,  $H_3As^{III}O_3^0$ ), which because it is a neutral species, passes through the column to be collected in a pre-cleaned HDPE bottle (Ficklin, 1983; Wilkie and Hering, 1998). Total As(III) is measured in this eluted fraction, and total As is measured from a separate fraction, both by sector-field ICP-MS as described below (sec. 3.2). Total As(V) is then determined as the difference between As<sub>Total</sub> and As(III) (Wilkie and Hering, 1998; Haque and Johannesson, 2006). Total As(III) is assumed to consist of both As(III) bound with O as an



Fig. 2. Schematic cross section from Lac des Allemands to the Mississippi River with core profiles from Breaux (2015). The Lac des Allemands cores shown are the samples closest to the bayou edge (W1,W3,W5, W4). Abbreviations: MULO: muddy loam, SICLA: silty clay, CLALO: clay loam, SANLO: sandy loam, SCL: silty clay loam, FINSAND: fine sand, SILLO: silty loam.

oxyanion and As(III) bound with S as a thioanion. Similarly, total As(V) is assumed to consist of both the arsenate oxyanion and thioarsenate. This approach is imperfect because thioarsenite species may also bind to the anion-exchange column and lead to underestimation of As(III) species (Jay et al., 2004; Yang et al., 2015), but without the ability to immediately measure speciation with HPLC (e.g., Planer-Friedrich et al., 2007), this is the most accurate method.

Filtered samples were acidified with ultrapure HNO<sub>3</sub>, chilled with ice in the field and transferred to a refrigerator at Tulane University where they were stored at 4 °C until analysis. Field blanks and duplicates were collected to control for contamination and to evaluate reproducibility during sample and analysis. Trace element analysis of the major cation and trace element samples was completed within two weeks of sample collection.

A YSI handheld multiparameter sonde was used to measure temperature, salinity, conductivity, and dissolved oxygen, and an Oakton<sup>®</sup> meter was used to measure pH. Alkalinity was determined by titration (Hach method 8203) using phenolphthalein and bromocresol green-methyl red indicators and 0.16 Eq L<sup>-1</sup> or 1.6 Eq L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. Total iron, Fe(II), S(-II), and SO<sub>4</sub><sup>2-</sup> were determined using a portable Hach DR 2800 UV-VIS spectrophotometer. The FerroVer<sup>®</sup> method was used to determine total iron and the 1,10-phenanthroline method to determine Fe(II) (detection limits 0.36 µmol kg<sup>-1</sup>; Eaton et al., 1995a). Ferric iron was determined as the difference between Fe<sub>Total</sub> and Fe(II). Sulfate was determined by the SulfaVer<sup>®</sup> method (detection limit 0.02 mmol kg<sup>-1</sup>; Eaton et al., 2005), and S(-II) was measured using the methylene blue method (detection limit 0.31 µmol kg<sup>-1</sup>; Eaton et al., 1995b), which is based on Cline (1969).

#### 3.2. Major cation and trace element analysis

The concentrations of a suite of major cations and trace elements were determined using a Thermo Fisher Element II high resolution (magnetic sector) inductively coupled plasma mass spectrometer (HR-ICP-MS). Major ions (Na, Mg, K, Ca, Sr, Ba) were diluted 100- to 10,000-fold with 2% (v/v) ultrapure HNO<sub>3</sub> (Optima grade) before introduction to the HR-ICP-MS for quantification. The trace elements were measured in separate runs on undiluted aliguots of each water sample. We monitored <sup>88</sup>Sr. <sup>138</sup>Ba. <sup>95</sup>Mo. <sup>182</sup>W. and <sup>23</sup>Na in low resolution mode and corrected for instrumental drift using a Re spike (220.2 nmol kg<sup>-1</sup>) as the internal standard. Additionally, <sup>51</sup>V, <sup>55</sup>Mn, <sup>56</sup>Fe, <sup>27</sup>Al, <sup>24</sup>Mg, and <sup>44</sup>Ca were monitored under medium resolution, and <sup>75</sup>As and <sup>39</sup>K were monitored in high resolution mode to distinguish from potential ArCl<sup>+</sup> and ArH<sup>+</sup> interferences, respectively (Olesik, 2014). A Sc spike  $(222.4 \text{ nmol kg}^{-1})$  was used as the internal standard for both medium and high resolution analyses. Calibration standards were made in concentrations ranging from 5 ng kg<sup>-1</sup> to 2.5 mg kg<sup>-1</sup> from SPEX CertiPrep® ICP-MS Multi-Element Solution 2 in 2% HNO<sub>3</sub>. Tungsten and Mo standards were made separately from SPEX CertiPrep<sup>®</sup> W and Mo standards, respectively. Due to instabilities in low resolution mode during analysis, W and Mo data are unavailable for the September sampling event. The accuracy of each analysis was checked using calibration check standards and a suite of certified reference material. Percent error using check standards and certified reference material is less than 20% and generally less than 10%. Although W concentrations are not reported for SLRS-4 and SLEW-3, Mohajerin et al. (2016) and Yeghicheyan et al. (2001) report W concentrations of ~70 pmol/kg for SLRS-4. We

did not detect W in the SLRS-4 standard but measured relatively constant W concentrations in the SLEW-3 standard (average  $\pm \sigma = 34 \pm 7 \text{ pmol/kg}$ ). Detection limits were calculated as three times the standard deviation of the blank, where the standard deviation was calculated from the blank concentrations for all analyses (Appendix B).

#### 3.3. Geochemical modeling

Geochemical modeling was conducted using the Spec8 and React programs of Geochemist's Workbench<sup>®</sup> (version 9.0; Bethke, 2008) to calculate the thermodynamically stable dissolved species and mineral saturation states. The default thermodynamic database (Lawrence Livermore National Laboratory Database; Delany and Lundeen, 1990) was modified for As, Mo, and W to include sulfidation reactions by incorporation of data from Helz and Tossell (2008), Erickson and Helz (2000), and Mohajerin et al. (2014), respectively, as described by Yang et al. (2015). Thiomolybdate and thiotungstate formation constants have been determined experimentally by Erickson and Helz (2000) and Mohajerin et al. (2014), respectively. The sulfidation reactions for As, however, are estimated from *ab* initio computations, and although this dataset is preliminary, it provides the most current dataset available (Helz and Tossell, 2008). In addition to the sulfidation reactions, the modified database of As speciation includes dissociation constants of arsenous and arsenic acids (Nordstrom et al., 2014) and solubility constants for As-bearing minerals from Webster (1990), Eary (1992), Nordstrom and Archer (2003), and Nordstrom et al. (2014). We assumed that all measured As(III) was available for sulfidation reactions to form thioarsenite and all calculated As(V) was available to form thioarsenate species in the modeling (Yang et al., 2015). As mentioned above, this approach suffers from the potential interaction of thioarsenites with the column. However, without sulfur speciation data, specifically, quantification of zerovalent sulfur, it is not possible to systematically model As speciation between As(III) and As(V) species using the total dissolved As concentration (Helz et al., 2014). With these limitations acknowledged, the model is capable of predicting As redox and thioanion



**Fig. 3.** Piper diagram of surface (A) and groundwaters (B). Shapes indicate sample location. Circles: bayou surface water, squares: lake surface water, triangles: groundwaters from fine-grained sediment, diamonds: groundwaters from coarse-grained sediment. Colors indicate time. Grey: October, green: February, blue: April, magenta: May, orange: September, C. Linear relationship between Mg and Ca concentrations in Bayou surface water (samples S5, S6, and S7). Upper and lower 95% confidence intervals are plotted as dashed lines. Mississippi River samples are plotted as grey symbols. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

formation at the order of magnitude level in Lac des Allemands waters and therefore broadens our ability to understand As cycling in these waters (Yang et al., 2015). The database also includes the solubility data for the iron sulfide minerals, mackinawite and greigite, taken from Rickard et al. (2006) and Morse et al. (1987), respectively, in addition to a possible Fe–Mo–S mineral species of the form FeMo<sub>0.6</sub>S<sub>2.8</sub> proposed by Helz et al. (2011). Recent work suggests that the hexavalent Mo in this species may be partially reduced, but the effects on the resulting equilibrium constant are negligible in shallow sediment pore waters (Helz et al., 2014; Mohajerin et al., 2016).

#### 4. Results

#### 4.1. General geochemistry of surface waters and groundwaters

Hydrogeochemical facies for surface waters and groundwaters are presented on Piper diagrams to classify the waters based on relative proportions of major cations and anions (Fig. 3A and B; Santos et al., 2008). The major ion data are consistent with interpretations that groundwater derived from the Mississippi River is transported through a buried sand channel and discharges at the head of Bayou Fortier in the vicinity of surface site S7 (Kim, 2015). In particular, the bayou surface waters plot in a more  $Ca^{2+}$  enriched region than the lake surface waters, reflecting input from the Mississippi River, which is enriched in  $Ca^{2+}$  relative to the lake surface waters (Appendix C; Fig. 3A). Furthermore, Swarzenski et al. (2008) demonstrate that water derived from the Mississippi River has a constant Ca–Mg ratio, and Fig. 3C shows that the bayou waters show a significant correlation between Ca and Mg with Mississippi River water samples. The major cation data is therefore consistent with groundwater derived from the Mississippi River discharging at the head of Bayou Fortier and subsequent dilution of this water upon mixing in Lac des Allemands.

The major ion composition of the groundwaters suggests that there is hydrological communication between the bayou and the marsh groundwaters (Fig. 3A and B). Specifically, Lac des Allemands groundwaters contain low  $SO_4^{2-}$  concentrations and comparable proportions of HCO<sub>3</sub> and Cl<sup>-</sup> to the surface waters. The cation data, however, are more scattered. For example, although the groundwater samples have relatively constant proportions of Mg<sup>2+</sup>, the relative proportions of Na<sup>+</sup> and Ca<sup>2+</sup> are variable (Fig. 3B). More specifically, the groundwater samples from the farmland piezometers and Lac des Allemands piezometer W4, are enriched in Ca<sup>2+</sup> relative to the other samples, suggesting greater hydrological influence from the Mississippi River. The major cation data imply that



Fig. 4. Concentrations of trace elements in surface waters from the Mississippi River, Bayou Fortier, and Lac des Allemands as a function of distance from the River. The green vertical line represents the transition from Bayou Fortier to the open Lac des Allemands. A linear regression and 95% confidence intervals for the average of all sampling events at each location is also shown. Shown are dissolved Fe (A), Mn (B), Mo (C), W (D), As (E), and V (F). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the sand-rich units present at EDG, VACW1, VACW2, and W4 are probably laterally continuous to the Mississippi River levee sand deposits (Kim, 2015).

Using dissolved Fe as a proxy for anoxia ( $Fe \ge 100 \ \mu g \ L^{-1}$  or 1.8  $\mu$ mol kg<sup>-1</sup>), all of the groundwater samples, except for the May VACW1 sample, are classified as anoxic (Wright et al., 2014; McMahon and Chapelle, 2008). Additionally, based on the classification scheme of Berner (1981), the groundwaters were both anoxic and sulfidic (S(-II) > 1  $\mu$ mol kg<sup>-1</sup>) at all locations during the October and February sampling events (Appendix D). Together, these classifications indicate that groundwaters were generally reducing and favored the dissolution of Fe(III)/Mn(IV) oxides/oxy-hydroxides, especially during the autumn and winter. Moreover, all groundwaters exhibited acidic to neutral pH, reflecting the high organic content of freshwater marsh sediments (Appendix D; Feijtel et al., 1988; Nyman et al., 1990; Neubauer et al., 2005; Swarzenski et al., 2008).

## 4.2. Trace element geochemistry of surface waters and groundwaters

Surface water concentrations of trace elements (Fe, Mn, Mo, W, As, and V) are presented as a function of distance from the Mississippi River (Fig. 4). Manganese and Fe concentrations are low in the Mississippi River and Lac des Allemands surface waters, but elevated concentrations of Mn and Fe are observed in Bayou Fortier surface waters (Fig. 4A and B; Appendix C). Bayou Fortier is a slow moving body of water with visible suspended matter. The dissolved Fe and Mn concentrations in Bayou Fortier surface waters are therefore likely released to surface waters from suspended sediment. In the groundwater samples, Fe and Mn concentrations are generally high (Fe =  $54.6 \pm 83.3$ , Mn =  $23.2 \pm 21.7 \,\mu$ mol kg<sup>-1</sup>), demonstrating the reducing conditions of the local groundwaters.

Of the trace elements, only Mo concentrations show a statistically significant variation as a function of distance from the river in surface waters from Bayou Fortier and Lac des Allemands (Fig. 4C). Vanadium and As concentrations vary between 4.31 and 140.0 nmol kg<sup>-1</sup> and 7.44–189 nmol kg<sup>-1</sup>, respectively, and show no discernible trend as a function of distance (Appendix C; Fig. 4E and F). The surface water samples with exceptionally high concentrations of V and As (e.g., S3 and S5 in July) that occur seemingly randomly throughout time and location may arise from resuspension of bottom sediments within the lake. Conversely, W concentrations in the surface waters from Bayou Fortier and Lac des Allemands are low, with 90% of the sample concentrations below the detection limit (39 pmol/kg; Fig. 4D).

In contrast to the surface waters, trace element concentrations (Mo, W, As, V) of the groundwater samples vary through time and with location (Fig. 5). Two trends in the data are particularly notable. First, trace element concentrations are generally greatest in groundwaters extracted from coarse-grained sediment units. The average Mo, W, and As concentrations are 12, 2, and 10 times greater in the groundwaters from coarse-grained sediments as compared to the fine-grained sediments (Fig. 5; Appendix D). The average V concentrations, however, are not substantially different between locations with different grain-sized sediments. Second, trace element concentrations are generally elevated in October and February as compared to April, May, and September.

The computed speciation of the trace metals is shown in Fig. 6A and Appendix E. During times of elevated sulfide concentrations (i.e., October, February), thiomolybdates are predicted to form, whereas the molybdate oxyanion dominates during the spring and early fall when dissolved sulfide is substantially lower. Conversely, thioarsenate formation is predicted to occur during all seasons, although in much greater percentages in the winter and late fall.



**Fig. 5.** Dissolved S(-II) and trace element concentrations of groundwaters from Lac des Allemands separated by samples from coarse-grained, low organic content sediments and samples from fine-grained, organic-rich sediments. Shown are (A) S(-II), (B) Fe, (C) Mn, (D) Mo, (E) W, (F) As, (G) V. Two outliers (W2, W8) from the April sampling event are excluded from further analysis.

Thiotungstate formation is not predicted to be an important process during any season. The predicted speciation is consistent with measurements of thiotungstate formation constants, which indicate that W is less reactive towards S(-II) than Mo (Mohajerin et al., 2014, 2016). Formation of thiovanadates has not been reported in natural waters (Steudel, 1996), and the speciation of V is dominated by the vanadyl cation ( $VO^{2+}$ ).

Geochemical modeling also predicts that Fe–S minerals are likely to form during all seasons, especially during the late fall and winter (Fig. 6B). More specifically, mackinawite is near or below saturation, whereas pyrite is consistently oversaturated. Formation of As–S minerals is expected to be negligible.

#### 5. Discussion

#### 5.1. Redox conditions in the marsh

Lac des Allemands experiences negligible tidal activity, and the marsh is perpetually saturated, prohibiting aerobic conditions and hence, oxidation of deep pore waters and sediments. Thus, it is not surprising that the marsh experienced reducing conditions during all sampling events of this study. Dissolved S(-II) concentrations are not expected to be particularly high in freshwater marshes as compared to brackish and saline marshes, owing to a greater distance from an oceanic  $SO_4^{2-}$  source compared to salt marshes (DeLaune et al., 2002a; Neubauer et al., 2005). For example, gaseous H<sub>2</sub>S emissions from freshwater marshes in Louisiana are 12 and 27 times lower than emissions from brackish and salt marshes. respectively (DeLaune et al., 2002a,b). Instead, in freshwater marshes, Fe(III) reduction has been shown to be the most important redox buffer in the early summer followed by methanogenesis later in the year (Neubauer et al., 2005). High dissolved Fe and Mn concentrations in local pore water supports the notion that redox is buffered by reductive dissolution of Fe(III)/Mn(IV) oxides/oxyhydroxides throughout the year in Lac des Allemands groundwaters. However, occasional high dissolved S(-II) concentrations in Lac des Allemands groundwaters also insinuate a seasonal S cycle. Groundwater S(-II) concentrations are high in October and February and decrease substantially by April and May. Low dissolved S(-II) concentrations continue into September, when dissolved SO<sub>4</sub><sup>2-</sup> concentrations increase (Appendix D). Dissolved S(-II), in turn, affects the dissolved Fe(II) concentrations either by reducing Fe(III) oxides/oxyhydroxides and/or precipitating with Fe to form iron sulfide mineral phases (Dos Santos Afonso and Stumm, 1992; Kostka and Luther, 1995). Geochemical modeling indicates that pyrite is likely an important sink for Fe in this system (Fig. 6B; Appendix F).

#### 5.2. Input from Mississippi River

Previous studies suggest that Bayou Fortier is hydrologically connected to the Mississippi River via a buried; sand-rich crevasse splay deposit that truncates near the W4 well (Figs. 1 and 2; Breaux, 2015; Kim, 2015). For example, Kim (2015) used radon as a tracer to estimate that between 0.4 and 14.6 cm day<sup>-1</sup> ( $2.2 \cdot 10^4$  m<sup>3</sup> day<sup>-1</sup>) of Mississippi River derived groundwater is discharged at the head of Bayou Fortier. The surface water concentrations of dissolved trace elements observed on a transect from the Mississippi River to Lac des Allemands, suggest that the Mississippi River has the potential to supply Lac des Allemands with dissolved V, Mo and W, whereas the As concentration in the river is less than that observed in the lake, indicating that the Mississippi River is not a source of As to Lac des Allemands (Fig. 4). Tungsten, and to a greater extent, Mo, decrease significantly with distance from the river, decreasing from 1.67 nmol kg<sup>-1</sup> to below detection and 19.6 to 2.46 nmol kg<sup>-1</sup>,

respectively, between the river and station 7 during the October sampling (Appendix C). Vanadium similarly decreases with distance from the river, but variability in the open lake concentrations obscures a definitive trend (Fig. 4). The magnitude of hydraulic head difference driving groundwater flow from the Mississippi River to the interdistributary basin varies as a function of river stage, suggesting that any transport of trace elements from the river to the lake is likely to vary seasonally (Kolker et al., 2013). Additionally, the concentrations of trace elements increased in the river between the May and October sampling trips, whereas the river stage decreased over this time, suggesting that trace element concentrations in the Mississippi River are not directly related to discharge (Fig. 4; Appendix C). For example, previous work in the Mississippi River showed that Fe and Mn are highest in the fall and decrease in the spring, whereas V and Mo display the opposite trend (Shiller, 1997). The variability in the concentration of these trace elements in Mississippi River water reflects redox processes in the river basin rather than hydrologic factors (Shiller, 1997). Better temporal resolution of the trace element concentrations in the Mississippi River as well as a hydrological constraint on the amount of water entering Lac des Allemands from Bayou des Allemands are necessary to estimate the trace element flux from surface reservoirs. However, trace element concentrations in the groundwaters at Lac des Allemands fluctuate independently of surface water variability, suggesting that in situ conditions in the deep marsh sediments overwhelm the signal from changes in surface water supply (Figs. 4 and 5). The correspondence of increased dissolved trace metal concentration with dissolved sulfide suggests that trace metals are released from the sediment under reducing conditions in the late fall and winter.

#### 5.3. Redox-sensitive trace elements

#### 5.3.1. Molybdenum

Previous work has demonstrated that Mo solubility decreases under reducing conditions owing to formation of thiomolybdates and subsequent sequestration as Fe–Mo–S solids. Erickson and Helz (2000) describe a geochemical switch at dissolved S(-II) concentrations greater than 11  $\mu$ mol kg<sup>-1</sup>, where the molybdate oxyanion, MoO<sub>4</sub><sup>2-</sup>, is converted to thiomolybdate complexes by reaction with H<sub>2</sub>S. More recent investigations point out that thiomolybdate anions are more particle reactive than the molybdate oxyanion, which ultimately leads to Mo removal from solution (Erickson and Helz, 2000; Vorlicek et al., 2004; Helz et al., 2014). A mechanism proposed by Vorlicek et al. (2004) attributes formation of Mo–Fe–S cuboidal clusters on pyrite formed by ligand-induced reduction of Mo(VI) by polysulfides.

However, Mo in Lac des Allemands groundwaters exhibits the opposite behavior: Mo is liberated under reducing conditions. Although the geochemical modeling predicts formation of thiomolybdates, sustained dissolved S(-II) concentrations greater than 11 µmol kg<sup>-1</sup> are required for formation and persistence of thiomolybdates and sequestration of excess Mo by sediments (Erickson and Helz, 2000; Adelson et al., 2001). Thus, at the seasonal scale, Mo speciation is kinetically controlled, and Mo may still exist as molybdate in Lac des Allemands groundwaters (Erickson and Helz, 2000). Another possibility for this anamolous behavior is the influence of Fe. Low dissolved Fe concentrations favor the formation of organic S (Zaback and Pratt, 1992; Mongenot et al., 2000; Tribovillard et al., 2004), and a study of S speciation in Louisiana freshwater marsh soils indicates that organic sulfur as ester-sulfate or carbon-bonded sulfur accounts for greater than 70% of the total sulfur in local marsh soils, with minor contributions from mackinawite and pyrite (Krairapanond et al., 1992). Hence, Mo may also be associated with organic matter via bonding with S-compounds



Fig. 6. A. Trace element speciation shown as percent of total element concentration. Data for additional months and wells in Appendix E. B. Saturation Indices (log Q/K) for pyrite and mackinawite. Data for additional months and wells in Appendix F.

(Helz et al., 1996; Tribovillard et al., 2004; Algeo and Lyons, 2006). Finally, reductive dissolution of Fe(III)/Mn(IV) oxides/oxyhydroxides may have occurred and released adsorbing ions such as molybdate (Froelich et al., 1979). For example, during October and February, Mo is positively correlated with Mn ( $R^2 = 0.46$ ; p < 0.0005), an association commonly recruited to explain Mo behavior (e.g., Bertine and Turekian, 1973; Crusius et al., 1996; Tribovillard et al., 2006). It is unlikely that such unexepected Mo

behavior is unique to Lac des Allemands groundwaters, and further study of Mo in seasonally variabe redox settings will help elucidate these observations.

#### 5.3.2. Tungsten

Similar to Mo, W also exhibits higher concentrations in Lac des Allemands groundwaters in the autumn and winter than in the spring and summer (Fig. 5E; *t*-test, p < 0.05). Tungsten also significantly correlates with Fe in the fall/winter ( $R^2 = 0.53$ , p < 0.05), a relationship that is not observed in the spring. Given that the pH does not change appreciably between seasons, the elevated W concentrations in the fall and winter likely result from dissolution of Fe(III) oxides/oxyhydroxides rather than desorption reactions.

The molal Mo/W ratio of Lac des Allemands groundwaters  $(72.3 \pm 113)$  is less than that in the surface waters  $(111 \pm 31.9)$  (Mann-Whitney test, 5% significance level), which is consistent with observations of greater W enrichment in pore waters relative to surface waters in other Mississippi Delta pore waters (Mohajerin et al., 2016). Tungsten adsorption onto ferromanganese oxides is typically greater than Mo adsorption owing to the octahedral coordination and inner sphere complexation of W onto these metal oxides/oxyhydroxides as opposed to the tetrahedral coordination and outer sphere complexation of Mo adsorption (Kashiwabara et al., 2010, 2013; Gustafsson, 2003).

Arnórsson and Óskarsson (2007) also observed elevated Mo/W ratios in peat soil groundwaters, which they attributed to adsorption of W onto organic matter, clay minerals and/or Fe(III) hydroxide. Furthermore, in organic-rich sediments, adsorption onto organic matter and clays may be more important than Fe(III)/ Mn(IV) oxide/oxyhydroxide surfaces (Arnórsson and Óskarsson, 2007). Tungsten adsorption experiments also indicate that W adsorption is strongest on soils with the highest organic content, but the interaction with humic substances is not detailed (Koutsospyros et al., 2006). The relationship between W and organic matter warrants further study.

Although W concentrations in the groundwaters show a seasonal trend, W concentrations in the surface waters do not vary substantially through space or time, and surface water concentrations are mostly below detection (Fig. 4D). Therefore, although W is released from the sediments into the groundwaters, most of the generated W is probably readsorbed onto marsh sediment near the sediment-water interface. The W concentrations at the bayou surface sites (S6 and S7) in October and February are detectable in contrast to the other surface water sites, which may suggest that marsh sediments release some W to the bayou, which is then scavenged by bayou bottom sediments.

#### 5.3.3. Arsenic

Similar to the other trace elements, As concentrations in groundwaters from Lac des Allemands are higher in the fall and winter than in the spring and late summer, coincident with high dissolved S(-II) concentrations. In sulfidic waters, As(V) is predicted to form thioarsenate species (Fig. 6A). As thioarsenate, arsenic is less likely to be sequestered in the sediments (Van der Weijden et al., 1990; Kirk et al., 2010; Burton et al., 2013). Furthermore, groundwater dissolved As concentrations may be higher in the fall and winter compared to the spring because thioarsenite and thioarsenate sorb more strongly to Fe oxides/oxyhydroxides than to pyrite, and the groundwaters are more saturated with respect to pyrite during the fall and winter (Couture et al., 2013).

Nevertheless, groundwater As concentrations are less than those observed in the bayou surface waters, signifying that the deep marsh groundwaters likely serve as a sink for dissolved As. Previous studies argue that As is generally removed from waters where sulfate reduction is occurring via precipitation of arsenicsulfide minerals or co-precipitation with iron sulfide minerals (Kirk et al., 2004, 2010; Bostick et al., 2004; Wolthers et al., 2005). Geochemical modeling indicates that these groundwaters are all undersaturated with respect to As-S species (e.g., realgar, orpiment) during all sampling events. Precipitation of arsenic sulfide species is favored under conditions of low pH (pH = 4-6), elevated As concentrations, and dissolved S(-II) concentrations low enough to prevent formation of thioarsenates/thioarsenites (Wilkin and Ford, 2006; Kirk et al., 2010). Groundwaters from Lac des Allemands generally have a circumneutral pH (5.3-8.2) and low dissolved As concentrations  $(55.0 \pm 103 \text{ nmol kg}^{-1})$ , indicating that precipitation of arsenic-sulfide species is not an important sink for As. Of the iron sulfide mineral phases, mackinawite is typically the first to precipitate (Schoonen and Barnes, 1991; Wolthers et al., 2005). Yet, the Lac des Allemands groundwaters are undersaturated with respect to mackinawite but are oversaturated with respect to pyrite (Appendix F). Furthermore, laboratory experiments indicate that As co-precipitation with iron sulfides occurs predominantly with pyrite (Kirk et al., 2010). Therefore, the measured dissolved As concentrations and geochemical modeling of mineral saturation states of Lac des Allemands waters are consistent with sequestration of As in pyrite.

#### 5.3.4. Vanadium

During October and February, the groundwaters at Lac des Allemands exhibited relatively high V concentrations compared to the concentrations in the surface waters from Bayou Fortier. Conversely, the April, May, and September sampling reveal similar concentrations between the groundwaters and surface waters or, in some cases, higher V concentrations in the surface waters than the groundwaters (Figs. 4F and 5G). Therefore, during the fall and winter, the groundwaters appear to serve as a source of V to the bayou. However, because the groundwaters are relatively more reducing during the fall and winter, V is predicted to exist as vanadyl and should be less soluble due to its greater affinity for particle surfaces under reducing conditions (Fig. 6A; Breit and Wanty, 1991). Vanadium is known to sorb to Fe(III)/Mn(IV) oxides/oxyhydroxides, organic matter, and clays (McBride, 1979; Wehrli and Stumm, 1989). Yet, if the potential host phases adsorbing V dissolve, V concentrations would increase in the groundwaters. As discussed above, Fe(III)/Mn(IV) oxides/oxyhydroxides are likely undergoing reductive dissolution in deep marsh sediments in the study region. However, V does not covary with dissolved Fe concentrations ( $R^2 = -0.16$ , p > 0.05), indicating that upon reductive dissolution, Fe and V concentrations are regulated by separate mechanisms. Whereas dissolved Fe precipitates with dissolved sulfide to form iron sulfide minerals, dissolved V may be stabilized in solution by complexation with organic matter (Breit and Wanty, 1991; Wanty and Goldhaber, 1992; Lu et al., 1998; Pourret et al., 2012).

## 6. Summary and implications for redox sensitive trace element cycling in the Mississippi River Delta

Analysis of redox-sensitive trace elements indicates that reductive dissolution of Fe(III)/Mn(IV) oxides/oxyhydroxides during the reducing conditions of the fall and late winter are important processes for supplying trace elements to pore waters. Therefore the source of trace elements may be related to the supply of reducible Fe/Mn oxides/oxyhydroxide minerals of coatings on sediment grains. Dissolved Mn concentrations increase with



**Fig. 7.** Distribution of abandoned distributaries in the upper Barataria Basin (yellow). Channels were traced using Mississippi River Deltaic Plain 15-min quadrangle maps from the U.S. Army Corps and overlain on a compilation of high resolution orthoimagery from the USGS EarthExplorer database. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

increasing grain size of the surrounding sediment, which explains why the farmland wells and Lac des Allemands well W4 have relatively high dissolved Mn concentrations and commonly exhibit higher trace element concentrations. This relationship is not observed for dissolved Fe concentrations, but Fe is reprecipitated as sulfide mineral as dissolved S(-II) concentrations increase. These results suggest that buried sand units with Fe(III)/Mn(IV) oxide/ oxyhydroxide coatings throughout the delta may serve as sources of dissolved trace element to pore waters and possibly surface waters, but more work to quantify the association of trace elements in the solid phase is necessary to determine the exact source of the trace elements. Fig. 7 shows a distribution of sand units throughout the Lac des Allemands region, which indicates numerous abandoned distributary channels that extend to the natural levee deposit of the Mississippi River. Where the distributary channels are connected to interdistributary lakes and bayous, they may serve as a source of trace elements to the basin and ultimately the Gulf of Mexico.

The marsh pore waters are also tightly coupled to redox reactions, including not only Fe(III) and Mn(IV) reduction but also sulfate reduction. In particular, trace element concentrations (Mo, W, As, V) increase in October and February, coinciding with more reducing conditions in marsh groundwaters. The increase in concentration is expected for W and As and is most pronounced for W. The increase in Mo and V concentrations, however, requires further explanation as both elements are expected to be more particle reactive under reducing conditions. The unexpected solubility of V has been demonstrated in other reducing basins, such as Framvarren Fjord and is attributed to aqueous complexation with dissolved organic carbon (Emerson and Huested, 1991). Such a mechanism is likely also operating in the organic-rich waters at Lac des Allemands. The cause of Mo solubility under reducing conditions is less certain as most studies in reducing basins report sequestration of Mo even with sporadic H<sub>2</sub>S (e.g., Tribovillard et al., 2006). Molybdenum's persistence in reducing waters is likely related to kinetic effects. If so, this study suggests that in pore waters with seasonally variable redox conditions, Mo sequestration may not record paleoredox conditions as well as previously thought.

The marsh surrounding Lac des Allemands is typical of freshwater marsh systems and demonstrates that local groundwaters are rich in organic matter and electron acceptors that actively drive redox reactions. These reactions, in turn, affect trace element sequestration in sediments and potential supply to the interdistributary basin. This study also underscores the need for a better understanding of organic matter interaction with trace elements that form aqueous complexes with sulfur.

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Appendix A. Sample identification and location for surface water and groundwater sites

Sample Name	Latitude	Longitude	Location Type	Well Depths (cm below surface)	Dates Sampled
Mississippi River (MSR)	29.9383	-90.3547	Surface Water	NA	2013: May, Oct.
LdA-S0	29.8809	-90.5278	Surface Water	NA	2014: Feb., April
LdA-S1	29.8875	-90.5392	Surface Water	NA	2013: April, May, July, Oct.
					2014: Feb, April, Sept.
LdA-S2	29.9260	-90.5525	Surface Water	NA	2013: April, May, July, Oct. 2014: Feb. April, Sept.
LdA-S3	29.9520	-90.5612	Surface Water	NA	2013: April, May, July, Oct.
LdA-S5	29.9701	-90.5628	Surface Water	NA	2014: Feb. 2013: April, May, July, Oct. 2014: Feb. April Sont
LdA-S6	29.9837	-90.5529	Surface Water	NA	2014: Teb, April, Sept. 2013: April, May, July, Oct.
	20.0044	00 5 4 4 1	Curfo on Maton	NA	2014: Feb, April, Sept.
LuA-S7	29.9944	-90.5441	Surface water	INA	2013: April, May, July, Oct. 2014: Feb., April, May, Sept.
LdA-S8	29.9372	-90.6251	Surface Water	NA	2013: April, May, July, Oct.
					2014: Feb., Sept.
LdA-S9	29.9244	-90.6231	Surface Water	NA	2013: April, May, July, Oct.
144 610	20.0111	00 50 49	Surface Water	NA	2014: Feb.
LuA-310	29.9111	-90.3946	Sullace vvalel	INA	2013: April, May, July, Oct. 2014: Feb., Sept.
LdA-S11	29.9210	-90.5852	Surface Water	NA	2013: July, Oct.
					2014: Feb.
St-8	30.0139	-90.5431	Surface Water	NA	2013: July, Oct.
					2014: Feb., May
LdA-W1	29.9743	-90.5581	Marsh	200	2013: Oct.
	20.07.17	00 5500		100	2014: Feb., April, Sept.
LdA-W2	29.9747	-90.5582	Marsh	108	2013: Oct.
	20,0022	00 5522	D.f well		2014: April
LdA-W3	29.9822	-90.5533	Marsh	55	2013: UCL
	20.0045	00 5444	March	175	2014: FeD., April
Lux-w4	29.9940	-90.3444	IVIdI SII	175	2013. Oct. 2014: Feb April May
Ida_W/5	20 0878	90 5528	March	280	2014. Feb., April, May 2013: Oct
Lun-ws	23,3070	-50.5528	Wai Sii	280	2013: Oct. 2014: Feb April May
Ida-W6	29 9880	-90 5531	Marsh	345	2013: Oct
	2010000	0000001	inter bir	5.15	2014: Feb., April
LdA-W7	29.9770	-90.5584	Marsh	196	2014: April. Sept.
LdA-W8	29.9770	-90.5583	Marsh	235	2014: April
LdA-W9	29.9885	-90.5535	Marsh	254	2014: April. May. Sept.
EDG	30.0461	-90.5714	Farmland	875	2014: May, Sept.
VAC-1	29.9356	-90.6667	Farmland	183	2014: May, Sept.
VAC-2	29.9356	-90.6667	Farmland	488	2014: May, Sept.

#### Appendix B. Detection limits were calculated as three times the standard deviation of the blank, where the standard deviation was calculated from the blank concentrations of each element for all ICP-MS analyses

	Detection Limits	Reported as $DL/\sqrt{2}$
Мо	82 pmol/kg	58 pmol/kg
W	39 pmol/kg	28 pmol/kg
U	22 pmol/kg	16 pmol/kg
V	175 pmol/kg	124 pmol/kg
Mn	917 pmol/kg	648 pmol/kg
Fe	31 nmol kg <sup>-1</sup>	22 pmol/kg
Al	$10 \mathrm{nmol}\mathrm{kg}^{-1}$	7 pmol/kg
As	674 pmol/kg	477 pmol/kg

#### Appendix C. Temperature, pH, conductivity, salinity, major solute, and trace element concentrations in surface waters from Lac des Allemands, Bayou Fortier, and the Mississippi River

		MSR	LdA-S0	LdA-S1	LdA-S2	LdA-S3	LdA-S5	LdA-S6
Temperature (°C)	Apr-13	ND	ND	23.40	22.70	22.00	25.90	24.50
	May-13	ND	ND	26.23	27.16	28.26	29.24	28.48
	Jul-13	ND	ND	30.94	30.57	30.53	32.48	32.2
	Oct-13	ND	ND	28.00	28.30	29.10	28.30	29.50
	Feb-14	ND	18 90	19.60	20.10	18 90	1920	19 20
	Apr-14	ND	18 37	18.02	18 12	ND	17.65	17.04
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sen_14	ND	ND	26.30	26.72	ND	27.46	27.21
Conductivity ( $\mu$ S cm <sup>-1</sup> )	Sep-14	ND .	ND	20.50	20.72	ND	27.40	27.21
conductivity (µs cm <sup>-</sup> )	Apr-13	ND	ND	ND	ND	ND	ND	ND
	May_13	ND	ND	0.125	0.16	0 150	0 130	0.154
	Iviay-15	ND	ND	0.125	0.10	0.153	0.155	0.134
	Jui-13 Oct 12	ND	ND	0.14J	0.141	0.135	100	195
	Oct-15	ND	100	100	172	ND 104	100	100
	Feb-14	ND	180	100	172	164	233	234
	Apr-14	ND	183	174	170	ND	180	200
	Ividy-14	ND	ND	ND 152	ND 1.40	ND	ND 152	ND 100
	Sep-14	ND	ND	153	148	ND	153	160
Salinity (psu)								
	Apr-13	ND	ND	0.07	0.07	0.07	0.07	0.07
	May-13	ND	ND	0.06	0.07	0.07	0.06	0.07
	Jul-13	ND	ND	0.07	0.06	0.07	0.08	0.10
	Oct-13	ND	ND	0.07	0.07	0.08	0.08	0.09
	Feb-14	ND	0.10	0.08	0.09	0.09	0.12	0.13
	Apr-14	ND	0.09	0.08	0.08	ND	0.09	0.09
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	0.07	0.07	ND	0.07	0.07
pH								
-	Apr-13	ND	ND	ND	ND	ND	ND	ND
	May-13	ND	ND	9.65	10.08	10.11	9.35	7.46
	Jul-13	ND	ND	8.94	8.64	9.23	9.13	7.74
	Oct-13	ND	ND	6.95	ND	ND	6.70	6.61
	Feb-14	ND	8.54	8.82	9.24	9.38	7.71	7.04
	Apr-14	ND	7 51	7 77	8 88	ND	ND	6.80
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sen-14	ND	ND	7.60	8 37	ND	8 90	7.88
$DOC \pmod{I^{-1}}$	Sep 11	11D	n.b	7.00	0.57	ND .	0.50	7.00
	Apr-13	ND	ND	ND	ND	ND	ND	ND
	May_13	ND	ND	ND	ND	ND	ND	ND
	Iviay-15	ND	ND	ND	ND	ND	ND	ND
	Jui-13 Oct 12	ND	ND	0.974	0.974	0.769	1 16	1 10
	Oct-15	ND	ND 0.705	0.674	0.874	0.700	1.10	1.19
	rep-14		0.795	0.5/0	0.720	1.02 ND	0.501	1.00
	Apr-14	ND	2.01	1.87	1.90	ND	2.19	2.35
	May-14	ND	ND	ND	ND	ND	ND	ND
mr. ( 1 1.)	Sep-14	ND	ND	0.967	0.796	ND	0.773	0.742
TN ( $\mu$ mol L <sup>-+</sup> )								
	Apr-13	ND	ND	ND	ND	ND	ND	ND
	May-13	ND	ND	ND	ND	ND	ND	ND
	Jul-13	ND	ND	ND	ND	ND	ND	ND
	Oct-13	ND	ND	49.3	48.4	49.1	52.8	53.1
	Feb-14	ND	50.3	49.4	43.4	49.8	38.9	30.4
	Apr-14	ND	60.8	49.9	51.8	ND	54.7	45.9
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	54.6	44.9	ND	41.5	43.0
mmol kg <sup><math>-1</math></sup>	-							
Mg								
-	Apr-13	ND	ND	0.20	0.19	0.20	0.21	0.28
	Mav-13	0.275	ND	0.15	0.20	0.15	0.16	0.19
	Jul-13	ND	ND	0.16	0.16	0.15	0.17	0.26
	Oct-13	0.649	ND	0 223	0214	0.215	0 247	0.280
	Feb-14	ND	0.246	0.225	0.214	0.213	0.247	0.200
	Δpr 14	ND	0.240	0.217	0.210	0.214 ND	0.292	0.332
	May 14	ND	0.213 ND	0.109 ND	0.200 ND	ND	0.222 ND	0.202 ND
	ividy-14			ND 0.140	UND 0.172		ND 0.195	ND 0.159
	Sep-14	ND	ND	0.149	0.172	ND	0.185	0.158

		MSR	LdA-S0	LdA-S1	LdA-S2	LdA-S3	LdA-S5	LdA-S6
Ca								
cu	Apr-13	ND	ND	0.158	0 148	0.150	0 1 8 9	0.281
	May_13	0 325	ND	0.109	0.150	0.105	0.119	0.172
	Jul_13	0.525 ND	ND	0.105	0.101	0.105	0.117	0.253
	Oct-13	0.613	ND	0.100	0.150	0.153	0.202	0.250
	Feb-14	ND	0.210	0.142	0.193	0.190	0.284	0.345
	Apr-14	ND	0.267	0.130	0.302	ND	0.233	0.291
	May_14	ND	ND	0.240 ND	ND	ND	0.235 ND	ND
	Sop 14	ND	ND	0.100	0.216	ND	0.227	0.229
Na	3ep-14	ND	ND	0.199	0.210	ND	0.227	0.238
INd	Apr 12	ND	ND	0.54	0.52	0.52	0.42	0.51
	Apr-13 May 12	0.424	ND	0.34	0.52	0.33	0.43	0.31
	Ividy-15	0.454 ND	ND	0.40	0.56	0.44	0.40	0.56
	Jui-13 Oct 12	1.62	ND	0.45	0.45	0.40	0.48	0.50
	Oct-15	1.02	ND 1.04	0.037	0.541	0.040	0.015	0.550
	rep-14	ND	1.04	0.829	0.794	0.005	0.805	0.720
	Api-14	ND	1.25 ND	0.750	1.00	ND	0.721	0.039
	Ividy-14	ND	ND	ND 0.279	ND 0.459	ND	ND 0.500	ND 0.472
*502-	Sep-14	ND	ND	0.378	0.458	ND	0.509	0.472
504	Amn 12	ND	ND	ND	ND	ND	ND	ND
	Apr-13	ND	ND	ND 0.105	ND	ND	ND	ND
	May-13	ND	ND	0.125	0.021	0.014	0.021	0.014
	Jul-13	ND	ND	ND	ND	ND	ND	ND
	Oct-13	ND	ND	0.014	0.014	0.014	0.014	0.014
	Feb-14	ND	0.014	0.014	0.014	0.014	0.014	0.014
	Apr-14	ND	0.014	0.014	ND	ND	0.014	ND
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	1.67	1.15	ND	0.014	0.014
Alkalinity (as HCO <sub>3</sub> )								
	Apr-13	ND	ND	ND	ND	ND	ND	ND
	May-13	ND	ND	ND	ND	ND	ND	ND
	Jul-13	ND	ND	ND	ND	ND	ND	ND
	Oct-13	ND	ND	6.79	8.23	9.75	10.5	11.2
	Feb-14	ND	0.880	0.896	0.688	0.872	1.18	1.50
	Apr-14	ND	1.60	1.04	0.960	ND	0.960	1.12
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	0.510	ND	ND	0.680	1.27
$\mu mol \ kg^{-1}$								
K								
	Apr-13	ND	ND	50.26	46.09	47.32	33.72	36.18
	May-13	45.9	ND	42.14	56.76	43.19	38.29	37.94
	Jul-13	ND	ND	49.63	46.83	45.73	43.49	51.59
	Oct-13	97.5	ND	51.2	47.2	49.8	61.0	66.3
	Feb-14	ND	73.4	64.3	65.7	62.5	81.8	82.7
	Apr-14	ND	182	$57.3 \pm 5.40$	144	ND	55.3	73.2
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	76.9	74.5	ND	73.9	70.5
Ba								
	Apr-13	ND	ND	ND	ND	ND	ND	ND
	May-13	ND	ND	0.23	0.27	0.27	0.23	0.25
	Jul-13	ND	ND	ND	ND	ND	ND	ND
	Oct-13	0.576	ND	0.310	0.355	0.367	0.374	0.302
	Feb-14	ND	ND	ND	ND	ND	ND	ND
	Apr-14	ND	$.966 \pm 0.403$	$0.374 \pm 0.087$	0.436	ND	0.330	0.383
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	0.392	2.58	ND	0.350	0.398
Sr								
	Apr-13	ND	ND	0.57	0.55	0.56	0.58	0.81
	May-13	0.873	ND	0.40	0.55	0.38	0.38	0.54
	Jul-13	ND	ND	0.42	0.42	0.46	0.44	0.74
	Oct-13	2.60	ND	0.742	0.748	0.764	0.855	0.947
	Feb-14	ND	1.10	1.02	1.043	1.07	1.29	1.364
	Apr-14	ND	$1.94 \pm 0.819$	$0.852 \pm 0.085$	0.945	ND	0.759	0.954
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	1.05	0.752	ND	0.856	0.976
Fe	*						-	-
	Apr-13	ND	ND	0.72	1.23	1.98	11.38	10.43
	Mav-13	0.520	ND	1.00	0.53	1.24	2.78	7.10
	Jul-13	ND	ND	0.26	0.41	0.27	1.89	8.98
	Oct-13	$0.124 \pm .0400$	ND	0.585 + 0.078	0.145	0.284 + 0.071	5.87	8.48
	Feb-14	ND	1.02	0.927	0.813	0.915	3.32	3.93
	Apr-14	ND	1.66	0.820	0.981	ND	2.37	1.67
								atinued on most march
							(CO1	itinueu on next page)

249

		MSR	LdA-S0	LdA-S1	LdA-S2	LdA-S3	LdA-S5	LdA-S6
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	3.12	2.51	ND	1.13	4.85
*Fe(II)								
	Apr-13	ND	ND	0.72	0.36	ND	1.79	1.97
	May-13	0.179	ND	0.90	0.36	0.255	5.37	1.25
	Jul-13	ND	ND	ND	ND	ND	ND	ND
	Oct-13	ND	ND	0.255	0.720	0.900	0.180	2.52
	Feb-14	ND	1.43	1.25	1.07	0.716	1.25	4.12
	Apr-14	ND	4.30	0.255	3.04	ND	6.09	7.70
	May-14	ND	ND	ND	ND	ND	ND	ND
* <b>P</b> -	Sep-14	ND	ND	0.255	0.255	ND	0.255	0.255
Fe <sub>Total</sub>	Apr 12	ND	ND	10.4	2.04	ND	27.0	<u></u>
	Apt-15 May 12	ND		10.4 ND	5.94 ND	ND	27.0 ND	ZZ.Z
	Ividy-15	ND	ND	ND		ND		ND
	Jui-13 Oct-13	ND	ND	ND	ND	ND	ND	ND
	Feb-14	ND	9.85	12.4	877	7.52	12.2	25.1
	Apr-14	ND	10.9	12.4	9.49	ND	27.9	36.9
	May_14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	4 83	1.07	ND	1 79	2.69
Mn	bep 11		112	1.05	1107	112		2100
	Apr-13	ND	ND	0.031	0.033	0.031	2.54	3.03
	Mav-13	0.031	ND	0.057	0.078	0.097	0.199	3.07
	Iul-13	ND	ND	0.054	0.051	0.120	0.167	3.92
	Oct-13	$0.077 \pm 0.008$	ND	$0.052 \pm 0.024$	0.054	$0.057 \pm 0.004$	1.24	9.30
	Feb-14	ND	$0.028 \pm 0.015$	$0.021 \pm 0.004$	0.023	0.026	0.867	3.01
	Apr-14	ND	0.200	$0.058 \pm 0.010$	0.061	ND	1.74	1.80
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	0.112	1.16	ND	0.111	0.922
*S(-II)								
	Apr-13	ND	ND	1.53	1.28	ND	0.655	0.530
	May-13	6.55	ND	1.50	1.90	2.03	1.53	0.81
	Jul-13	ND	ND	ND	ND	ND	ND	ND
	Oct-13	ND	ND	0.811	1.22	1.37	1.22	0.312
	Feb-14	ND	2.68	2.00	2.46	2.40	1.40	3.80
	Apr-14	ND	1.56	3.21	2.99	ND	4.80	3.59
	May-14	ND	ND	ND	ND	ND	ND	ND
1	Sep-14	ND	ND	0.219	0.219	ND	0.717	1.22
nmol kg <sup>-1</sup>								
Мо		ND	ND	5.07	2.50	2.70	4 55	2.02
	Apr-13	ND	ND	5.67	3.59	3.78	1.//	2.93
	IVIAY-13	9.9 ND	ND	2.74	3.45	3.00	3.71	4.20
	Jui-13 Oct 12	ND 10.6	ND	4.29	4.11	3.33	3.44	3.70
	Cct-15 Eab 14	19.0 ND	2.04	2.97	2.35	2.50	2.49 4.19	2.72
	rep-14	ND	2.94	2.91	2.30	2.00 ND	4.10	0.20
	May_14	ND	ND	ND	1.20 ND	ND	2.39 ND	2.01 ND
	Sep-14	ND	ND	ND	ND	ND	ND	ND
W	5cp-14	ND	0.989	ND	ND	ND	ND	ND
	Apr-13	ND	ND	0 203	0.028	$0.112 \pm 0.245$	0.028	0.028
	May-13	0 105	ND	0.028	0.028	0.028	0.028	0.028
	Iul-13	ND	ND	0.028	0.028	0.028	0.028	0.028
	Oct-13	1.674	ND	0.028	0.028	0.028	0.028	0.047
	Feb-14	ND	0.028	0.028	0.028	0.028	0.028	0.056
	Apr-14	ND	0.028	0.028	0.028	ND	0.028	0.028
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	ND	ND	ND	ND	ND
U	-							
	Apr-13	ND	ND	ND	ND	ND	ND	ND
	May-13	ND	ND	ND	ND	ND	ND	ND
	Jul-13	ND	ND	ND	ND	ND	ND	ND
	Oct-13	4.11	ND	$0.411 \pm 0.055$	0.612	0.553	0.232	0.102
	Feb-14	ND	0.636	0.688	0.605	0.663	$0.611 \pm 0.155$	0.583
	Apr-14	ND	0.548	0.749	1.04	ND	0.289	0.431
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	0.281	0.231	ND	0.210	$0.251 \pm .0462$
V								
	Apr-13	ND	ND	8.89	5.74	6.50	6.95	8.01
	May-13	29.0	ND	16.5	30.4	31.2	19.8	19.1
	Jul-13	ND	ND	47.8	57.2	104	140	10.1
	Oct-13	62.0	ND	21.5	44.0	37.6	12.1	4.39
	Feb-14	ND	5.99	5.00	4.46	5.17	10.5	15.8

		MSR	LdA-S0	LdA-S1	LdA-S2	LdA-S3	LdA-S5	LdA-S6
	Apr-14	ND	7.91	7.21	8.92	ND	10.1	9.95
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sop 14	ND	ND	20.1	10.0	ND	10.0	12.4
۵1	Sep-14	ND	ND	20.1	10.0	ND	10.9	15.4
74i	Apr-13	ND	ND	ND	ND	ND	ND	ND
	May_13	ND	ND	ND	ND	ND	ND	ND
	Ividy-15	ND		ND	ND	ND	ND	ND
	Jul-13	ND	ND	ND	ND	ND	ND	ND
	Oct-13	1363	ND	139	275	270	220	232
	Feb-14	ND	2242	2612	2494	2827	1245	1079
	Apr-14	ND	2513	1107	1173	ND	320	160
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND						
As								
	Apr-13	ND	ND	7 44	$7.02 \pm 1.07$	7 91	187	27.6
	May_13	14.6	ND	15.3	101	24.6	20.3	30.3
	Int 12	ND	ND	82.0	057	140	190	55.5
	Jui-15	ND 2.40	ND	82.0	65.7	140	169	54.0
	Oct-13	2.19	ND	47.8	60.7	56.3	57.0	/5.3
	Feb-14	ND	9.05	$11.5 \pm 4.03$	9.01	10.4	16.0	38.3
	Apr-14	ND	9.98	11.2	11.5	ND	20.2	20.4
	May-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	21.4	19.4	ND	17.9	22.5
As (III)								
()	Apr-13	ND	ND	$0.850 \pm 0.147$	ND	ND	1.82	2.37
	May 12	ND	ND	ND	ND	ND	ND	ND
	Iviay-13		IND					
	Jul-13	ND	ND	ND			NU	
	Oct-13	ND	ND	$1.57 \pm 0.254$	$1.03 \pm 0.200$	$0.933 \pm 0.240$	3.89	$245 \pm 30.1$
	Feb-14	ND	1.57	1.60	2.10	1.86	2.19	8.47
	Apr-14	ND	2.41	1.78	1.97	ND	3.51	3.31
	Mav-14	ND	ND	ND	ND	ND	ND	ND
	Sep-14	ND	ND	2.35	3 94	ND	313	5.23
	140	\$7			1010	<u>\$10</u>		Ct 9
		-37				-310		51-0
Temperature (°C)	24.5	50	ND	ND	ND		ND	ND
	27.4	1	28.56	28.04	27.6	3	ND	ND
	30.4	L.	33.05	34.31	31.3	9	31.23	25.19
	26.4	0	31.00	31.90	31.5	0	29.90	ND
	19.1	0	ND	ND	ND		ND	12.40
	16.7	0	ND	ND	ND		ND	ND
	24.9	20	ND	ND	ND		ND	26.00
	24.0	1	ND	ND	ND		ND	20.90
Conductivity (Constitution	27.4	1	ND	ND	ND		ND	ND
Conductivity (µS cm <sup>-1</sup> )	ND		ND	ND	ND		ND	ND
	ND		ND	ND	ND	_	ND	ND
	0.14	4	0.151	0.141	0.11	6	ND	ND
	0.23	8	0.169	0.175	0.13	6	0.126	0.193
	190		ND	ND	ND		ND	ND
	239		ND	ND	ND		ND	189
	238		ND	ND	ND		ND	ND
	159		ND	ND	ND		ND	342
	167		ND	ND	ND		ND	ND
Salinity (psu)	157			110	110			
samily (psa)	0.07	,	ND	ND	ND		ND	ND
	0.07	,	0.07	0.07	0.05		ND	ND
	0.07		0.07	0.07	0.05			
	0.11		0.08	0.08	0.06		0.06	0.09
	0.09	)	0.08	0.08	0.08		0.09	ND
	0.13	1	ND	ND	ND		ND	0.09
	0.11		ND	ND	ND		ND	ND
	0.07	,	ND	ND	ND		ND	0.15
	0.07	,	ND	ND	ND		ND	ND
рH								
<b>r</b> '	ND		ND	ND	ND		ND	ND
	7		0.07	0.70	0.15		ND	ND
	7	,	0.07	5.70	5.13		7.02	C 01
	7.67		9.27	9.46	8.03		7.92	0.81
	6.70	)	ND	ND	ND		ND	ND
	7.05	5	9.10	8.58	9.26		9.50	7.20
	6.85	;	ND	ND	ND		ND	ND
	6.82	2	ND	ND	ND		ND	7.09
	7.50	)	8.35	ND	8.21		ND	ND
DOC (mmol $L^{-1}$ )					-121			
(	ND		ND	ND	ND		ND	ND
			ND	ND			ND	ND
	IND		ND	IND	ND		ND .	IND.

(continued on next page)

	144 57	144 69		144 610	LdA C11	C+ 0
	LuA-S7	LuA-58	LUA-59	LaA-STO	LuA-STT	51-8
	ND	ND	ND	ND	ND	ND
	1.39	0.924	0.941	0.874	0.858	ND
	0.908	0.858	0.874	1.36	0.966	ND
	2.67	ND	ND	ND	ND	ND
	1.38	ND	ND	ND	ND	1.45
	0.950	0.915	ND	0.668	ND	ND
TN ( $\mu$ mol L <sup>-1</sup> )						
	ND	ND	ND	ND	ND	ND
	ND	ND	ND	ND	ND	ND
	ND	ND	ND	ND	ND	ND
	08.3	58.6	58.1	56.3	53.4	ND
	48.5	J0.0 46 0	52.0	96.2	19.5	ND
	48.0	40.2 ND	JZ.0	80.5 ND	40.J	ND
	47.5	ND	ND	ND	ND	120
	108.4	ND C2.5	ND	12.2	ND	150
	59.3	62.5	ND	43.3	ND	ND
mmol kg						
Mg						
	0.29	0.19	0.20	0.20	ND	ND
	0.21	0.18	0.13	0.18	ND	ND
	0.29	0.18	0.18	0.17	0.17	0.30
	0.272	0.212	0.200	0.211	0.242	0.260
	0.356	0.216	0.208	0.218	0.210	0.418
	0.305	ND	ND	ND	ND	ND
	0.172	ND	ND	ND	ND	0.394
	0.200	0.159	ND	0.151	ND	ND
Ca						
	0.282	0.150	0.165	0.141	ND	ND
	0.204	0.144	0.098	0.140	ND	ND
	0.285	0.134	0.134	0.108	0.115	0.313
	0.247	0.156	0.147	0.132	0.142	0.243
	0.369	0 198	0 201	0 191	0.184	0.457
	0 330	ND	ND	ND	ND	ND
	0.330 $0.244 \pm 0.025$	ND	ND	ND	ND	0.483
	0.270	0.227	ND	0 198	ND	0.405 ND
Na	0.270	0.227	ND	0.150	ND	ND
INa	0.55	0.51	0.50	0.56	ND	ND
	0.55	0.51	0.30	0.30	ND	ND
	0.51	0.51	0.37	0.43	0.42	ND 0.47
	0.61	0.40	0.48	0.42	0.42	0.47
	0.566	0.576	0.539	0.611	0.697	0.538
	0.793	0.741	0.699	0.790	0.751	0.496
	0.740	ND	ND	ND	ND	ND
	0.193	ND	ND	ND	ND	$0.408 \pm 0.053$
+ <sup>2</sup>	0.561	0.457	ND	0.346	ND	ND
$*SO_4^2$						
	ND	ND	ND	ND	ND	ND
	0.010	0.229	0.010	0.479	ND	ND
	ND	ND	ND	ND	ND	0.014
	0.014	0.014	1.000	0.014	0.014	ND
	0.014	0.312	0.073	1.312	2.040	ND
	1.000	ND	ND	ND	ND	ND
	0.094	ND	ND	ND	ND	ND
	0.014	0.562	ND	0.014	ND	ND
Alkalinity (as $HCO_3^-$ )						
	ND	ND	ND	ND	ND	ND
	ND	ND	ND	ND	ND	ND
	ND	ND	ND	ND	ND	ND
	20.1	10.0	10.7	8.15	9.51	ND
	1.55	0.576	0.808	0.936	0.816	1.72
	1.60	ND	ND	ND	ND	ND
	0.160	ND	ND	ND	ND	0.640
	0.510	0.510	ND	2.12	ND	ND
$\mu$ mol kg <sup>-1</sup>	0.010	0.010		22		
K						
	34 55	<b>43 80</b>	43 30	49.52	ND	ND
	AU 05	52.00		52.05		ND
	40.33 50 FF	J2.0J	J1.97 A0 10	10.03	E1 70	100 54
	59.55 70.5	40.70 51.6	40.19	45.04	51./0	109.04
	/0.5	0.10	DU.I	51.7	52.0	00.Z
	ð3./	08.0	/3.0	05.9	64.3 ND	12.2
	0.0	ND	ND	ND	ND	ND 05-0
	60.8	ND	ND	ND	ND	85.8
	66.9	72.6	ND	66.2	ND	ND

(continued	1)

	A-S7 I	.dA-S8	LdA-S9	LdA-S10	LdA-S11	St-8
Ва	、		ND	ND	ND	ND
ND		ND 0.19	ND 0.19	ND 0.18	ND	ND
0.2		J.16	0.10 ND	U.10		ND
0.2	) 987 (	1 3 3 5	0 303	0 304	0 336	0 355
0.2 ND	)	ND	ND	ND	ND	ND
0.3	374 ľ	ND	ND	ND	ND	ND
0.4	114 I	ND	ND	ND	ND	0.510
0.4	413 (	0.345	ND	0.323	ND	ND
Sr						
0.8	32 (	0.53	0.52	0.53	ND	ND
0.6	67 (	0.52	0.35	0.51	ND	ND
0.7	79 (	).49	0.44	0.45	0.45	0.89
0.9	928 (	0.758	0.727	0.712	0.782	0.907
1.4	17 (	).982	1.03	0.979	0.976	1.60
1.1	1 0	ND	ND	ND	ND	ND
ND	1 (	ND	ND	ND	ND	ND
0.8	380 (	0.901	ND	0.781	ND	ND
Fe			1.40	0.07		N/D
8.7	/1	1.49	1.48	0.87	ND	ND
6.7		1.18	1.10	1.65	ND 1.01	ND 0.67
0.9		J.94 J.240	0.34	0.50	1.01	9.07
7.1	76	5.12	6.19	0.012	0.175	5.64
4.7	50 1		ND	0.051 ND	0.922 ND	5.04 ND
	36 I	ND	ND	ND	ND	11.2
3.8	30	1.78	ND	1.81	ND	ND
*Fe(II)						
1.6	51 1	1.25	1.07	0.36	ND	ND
0.9	90 (	0.255	0.255	0.36	ND	ND
ND	1 (	ND	ND	ND	ND	2.86
2.1	16 (	0.180	0.255	0.180	0.360	ND
4.8	33 1	1.07	1.97	ND	ND	3.22
3.7	76 1	ND	ND	ND	ND	ND
5.7	73 1	ND	ND	ND	ND	ND
0.2	255 (	0.255	ND	0.255	ND	ND
*Fe <sub>Total</sub>						
20.	.2	10.4	9.13	7.16	ND	ND
ND		ND	ND	ND	ND	ND
			ND			ND
24	ן ו כי ו	127	17.0	ND	ND	33.1
62	ע. זע 17	ND	ND	ND	ND	ND
29.	0.	ND	ND	ND	ND	ND
19.	.9	7.70	ND	3.40	ND	ND
Mn						
2.7	72 (	0.023	0.187	0.030	ND	ND
2.8	39 (	0.110	0.105	0.139	ND	ND
5.9	96 (	0.113	0.070	0.134	0.088	16.20
8.2	29 (	0.046	0.093	0.115	0.036	3.69
3.8	31 (	0.413	0.096	0.024	0.025	4.93
2.1	13 1	ND	ND	ND	ND	ND
4.6	54 1	ND	ND	ND	ND	12.9
1.8 *C( II)	3/ (	).153	ND	0.088	ND	ND
S(-II)	)1 <b>)</b>	0.15	1 77	2 50	ND	ND
0.5	50 2	1.50	1.22	2.50		ND
0.5	י ו	ND	ND	1.45 ND	ND	1.25
ND 0 3	212 1	1 15	134	1 10	1 25	1.2.5 ND
0.3	19	2 90	8 33	3.18	2 31	1 37
2.4	13 13	ND	ND	ND	ND	ND
5.0	1 36	ND	ND	ND	ND	ND
5.5 0 Q	)67 (	1 998	ND	1 40	ND	ND
nmol kg <sup>-1</sup>	(					
Мо						
2.0						
2.b	57	3.72	3.80	4.05	ND	ND
2.6	57 <u>-</u> 77	3.72 3.75	3.80 3.83	4.05 3.19	ND ND	ND ND
2.6 4.0 4.2	57 5 07 5 20 2	3.72 3.75 2.94	3.80 3.83 3.85	4.05 3.19 3.67	ND ND 3.35	ND ND 7.51

<u> </u>	LdA-S7	LdA-S8	LdA-S9	LdA-S10	LdA-S11	St-8
	2.40	2.70	2.00	2.22	2.27	2.52
	2.40	2.76	2.90	3.22	3.37	2.53
	0.57	3.02	3.33 ND	2.79	2.30	4.57
	3.84	ND	ND	ND	ND	ND 7.00
	5.51	ND	ND	ND	ND	7.88
147	ND	ND	ND	ND	ND	ND
vv	0.028	0.028	0.028	0.028	ND	ND
	0.028	0.028	0.028	0.028	ND	ND
	0.028	0.028	0.028	0.028	ND	ND
	0.028	0.028	0.028	0.028	0.028	$0.040 \pm 0.005$
	0.049	0.028	0.028	0.028	0.028	0.040 ± 0.000
	0.028	ND	ND	ND	ND	ND
	0.020	ND	ND	ND	ND	$0.053 \pm 0.005$
	ND	ND	ND	ND	ND	0.000 <u>+</u> 0.000
П	ND	ND	ND	ND	ND	ND
0	ND	ND	ND	ND	ND	ND
	ND	ND	ND	ND	ND	ND
	ND	ND	ND	ND	ND	ND
		0.505	0.561	0.420	ND 0 5 4 1	0.194
	$0.101 \pm 0.013$	0.595	0.301	0.420	0.541	0.164
	0.039	0.430	0.447 ND	0.725	0.J62	1.04 ND
	0.550	ND	ND	ND	ND	ND 1.15
	$0.077 \pm 0.172$	ND 0.276 + 0.050	ND	0.287 + 0.062	ND	1.15 ND
V	0.280 ± 0.092	$0.576 \pm 0.039$	20.3	$0.287 \pm 0.005$	ND	ND
v	6.96	7.00	0.88	9.66	ND	ND
	10.7	7.50	26.3	21.1	ND	ND
	14.6	53.1	59.0	42.0	38.2	14.3
	/ 31	45.5	43.0	36.5	J0.2 ∕/2 1	10.0
	-1.51	15.9	377	7 29	4.52	13.7
	$20.0 \pm 11.1$	ND	ND	ND	4.52 ND	ND
	27.4	ND	ND	ND	ND	26.4
	11 5	18.0	ND	16.0	ND	20.4
A1	11.5	10.5	ND	10.0	ND	ND
AI	ND	ND	ND	ND	ND	ND
	ND	ND	ND	ND	ND	ND
	ND	ND	ND	ND	ND	ND
	147	ND 471	402	660	224	102
	147 916	7721	452	2401	2205	403
	1059	ND	1J0/4	2491	209J	10J4 ND
	1036	ND	ND	ND	ND	ND 1070
	121	ND	ND	ND	ND	1070
As						
115	27.0	10.3	20.8	9.00	ND	ND
	30.5	25.1	26.5	21.3	ND	ND
	66.7	89.6	109	83.4	72.1	97.7
	71 9	58.6	53.4	57.8	60.9	62.6
	42.9	147	38.8	9.69	8 79	35.3
	33.0	ND	ND	ND	ND	ND
	25.9	ND	ND	ND	ND	60.8
	20.5	14.8	ND	11.9	ND	ND
As (III)	20.5	1 1.0	TILD .	11.5	TILD .	ND
	415	$0.948 \pm 0.160$	ND	$0.818 \pm 0.134$	ND	ND
	ND	ND	ND	ND	ND	ND
	ND	ND	ND	ND	ND	ND
	14.2	319+362	401+555	$125 \pm 0.240$	27 9	175
	117	1 73	1 78	2.05	1.60	$4.78 \pm 0.667$
	$7.54 \pm 0.894$	ND	ND	2.03 ND	ND	
	$5.34 \pm 0.834$	ND	ND	ND	ND	8 57
	5.71 ± 0.020	436	ND	4.41	ND	ND
	5.12	JU	ND	7.71		ND .

BDL: values in bold indicate value below detection limit. ±: standard deviation given where %RSD is greater than 5%. ND: not determined.

\*: measured by spectrophotometry.

# Appendix D. Temperature, pH, dissolved oxygen, conductivity, salinity, major solute, and trace element concentrations in groundwaters from Lac des Allemands, Bayou Fortier, and the Mississippi River

		LdA-W1	LdA-W2	LdA-W3	LdA-W4	LdA-W5	LdA-W6
Temperature (°C)							
	Oct-13	24.00	21.80	22.50	ND	23.90	22.60
	Feb-14	20.30	ND	19.70	ND	21.40	21.90
	Apr-14	20.65	19.88	20.56	17.27	18.29	18.54
	May-14	ND	ND	ND	21.60	22.50	ND
	Sep-14	ND	ND	ND	ND	ND	ND
Conductivity ( $\mu$ S cm <sup>-1</sup> )							
	Oct-13	1727	2110	1127	ND	1582	1517
	Feb-14	1030	ND	995	ND	1345	1451
	Apr-14	1947	2114	1084	2501	1615	308.0
	May-14	ND	ND	ND	2526	1570	ND
	Sep-14	ND	ND	ND	ND	ND	ND
Salinity (psu)							
	Oct-13	0.880	1.15	0.590	ND	0.810	0.810
	Feb-14	0.580	ND	0.550	ND	0.720	0.770
	Apr-14	0.990	1.08	0.540	1.30	0.820	0.150
	May-14	ND	ND	ND	1.31	0.790	ND
	Sep-14	ND	ND	ND	ND	ND	ND
рH							
	Oct-13	7.19	7.08	6.44	6.70	6.62	6.64
	Feb-14	7.61	ND	6.85	7.03	7.18	7.54
	Apr-14	7.30	7.04	5.27	6.80	6.85	6.83
	Mav-14	ND	ND	ND	6.60	6.45	ND
	Sep-14	ND	ND	ND	7 59	674	7 46
DOC (mmol $L^{-1}$ )	bep 11	112	112	112	100	0.7 1	7110
200(1111012))	Oct-13	3 4 9	2 55	215	3 73	5 52	9 77
	Feb-14	1 78	ND	1.07	2.63	1 58	1.69
	Apr-14	2.37	3.93	1.07	1 39	1 99	0.971
	May-14	ND	ND	ND	1 38	ND	ND
	Sep-14	2.60	ND	ND	3.00	1.09	1 46
TN (upped $I^{-1}$ )	Sep 11	2.00	T(D)	TID .	5.00	1.05	1.10
int (pillor 2 )	Oct-13	541	577	355	222	468	581
	Feb-14	547	ND	224	117	231	281
	Apr-14	536	1298	224	111	452	71 7
	May_14	ND	ND	ND	168	ND	ND
	Sen_14	655	ND	ND	142	303	114
mmol $k\sigma^{-1}$	Sep 11	000	T(D)	nD	1 12	505	
Μσ							
ivig	Oct-13	2.74	2.85	1.87	3 08	2.51	1 01
	Ech 14	2.74	2.05 ND	1.69	2.06	2.51	1.51
	Apr 14	2.52	2 47	1.00	2.55	2.39	2.20
	Apr-14 May 14	2.00	2.47 ND	1.55 ND	2.54	2.33	0.300 ND
1	Sop 14	2.65	ND	ND	2.00	2.02	0.152
63	3ep-14	2.05	ND	ND	5.00	2.37	0.152
Ca	Oct 12	1.26	1.24	0.007	2 45	1 26	1.09
	Ech 14	1.20	1.24 ND	0.337	3.45	1.20	1.00
	rep-14	1.14	ND 1.10	0.795	4.47	1.70	0.251
	Apr-14	2.29 ND	1.10	1.14 ND	4.24	1.18	0.25 I
	May-14	ND 1.74	ND	ND	3.03	1.08	ND 0.200
NI-	Sep-14	1.74	ND	ND	5.05	2.02	0.209
INd	Oct 13	10.9	10.0	E 07	9.40	0.27	0.01
	UCT-13	10.8	12.3	5.07	8.49	8.3/	8.01
	Feb-14	11.1	ND	4.42	8.55	/./6	9.07
	Apr-14	11.1	12.0	4.59	8.46	8.27	1.07
	May-14	ND	ND	ND	7.39	6.37	ND
*co <sup>2</sup> -	Sep-14	11.2	ND	ND	9.35	8.59	0.513
~SU4 <sup>-</sup>	0.1.10	0.047	0.011	0.01 -	0.04 -	0.04 -	0.011
	Oct-13	0.014	0.014	0.014	0.014	0.014	0.014
	Feb-14	0.042	ND	0.014	0.073	0.031	0.014
	Apr-14	0.014	0.014	0.014	0.014	0.014	0.014
	May-14	ND	ND	ND	0.014	0.014	ND

		LdA-W1	LdA-W2	LdA-W3	LdA-W4	LdA-W5	LdA-W6
	Sep-14	6.83	ND	ND	1.42	2.37	2.62
Alkalinity (as $HCO_3^-$ )							
	Oct-13	11.1	9.91	7.19	19.2	11.6	9.03
	Feb-14	15.0	ND	10.1	17.4	10.2	11.4
	Apr-14	10.9	8.88	7.44	13.2	6.96	1.84
	May-14	ND	ND	ND	16.2	8.88	ND
	Sep-14	6.54	ND	ND	17.2	9.69	0.935
$\mu mol \ kg^{-1}$							
K						0.10	
	Oct-13	319	375	251	66.5	243	234
	Feb-14	337	ND	253	54.2	294	317
	Apr-14	353	443 ND	438	69.4	255	67.2 ND
	Nidy-14	ND 262	ND	ND	23.0 46.1	249	ND 49 E
Pa	Sep-14	202	ND	ND	40.1	207	46.0
ba	Oct-13	1 64	1 1 9	1 95	5.65	1 89	2 15
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	1 23	1 1 8	1 29	4 14	1 44	0.400
	May-14	ND	ND	ND	630	1.11	0.400 ND
	Sep-14	1.18	ND	ND	5.37	2.07	0.339
Sr	Sep 11		112	112	5157	2107	0.000
	Oct-13	8.35	7.15	4.81	14.8	6.95	4.98
	Feb-14	8.14	ND	5.84	16.9	8.01	6.79
	Apr-14	7.02	5.74	4.59	13.2	5.92	0.943
	May-14	ND	ND	ND	14.9	5.43	ND
	Sep-14	7.07	ND	ND	13.8	7.12	0.724
Fe							
	Oct-13	60.5	14.8	42.6	84.8	13.1	82.2
	Feb-14	1.14	ND	3.34	5.92	3.61	2.48
	Apr-14	3.81	25.7	14.3	58.4	10.8	6.76
	May-14	ND	ND	ND	131	29.7	ND
	Sep-14	14.8	ND	ND	176	55.5	14.8
*Fe(II)							
	Oct-13	36.3	18.0	39.6	44.6	20.5	42.3
	Feb-14	12.4	ND	0.0898	12.7	15.0	8.95
	Apr-14	2.15	4.30	3.58	14.3	4.30	2.33
	May-14	ND	ND	ND	23.3	2.69	ND
*5	Sep-14	3.04	ND	ND	26.5	30.1	0.255
Fe <sub>Total</sub>	Oct 12	ND	ND	ND	ND	ND	ND
	Eeb-14	ND 43.7	ND	0.022	ND	32.0	32 1
	Apr-14	43.7	0.895	0.022	36.9	J2.9 11 1	5.01
	May_14	2.80 ND	0.835 ND	ND	52.8	143	ND
	Sep-14	16.5	ND	ND	158	14.5 AA A	25.1
Mn	5cp-14	10.5	ND	ND	150		25.1
	Oct-13	11.0	9.05	9.48	36.6	10.3	15.6
	Feb-14	7.41	ND	5.73	39.4	9.48	10.3
	Apr-14	6.92	9.01	8.55	46.2	9.57	1.66
	May-14	ND	ND	ND	46.1	11.0	ND
	Sep-14	7.45	ND	ND	52.9	15.3	1.22
*S(-II)							
	Oct-13	2.71	58.0	8.80	20.8	24.3	28.8
	Feb-14	21.0	ND	17.6	16.0	8.98	9.26
	Apr-14	0.499	0.748	0.219	0.156	1.65	0.499
	May-14	ND	ND	ND	0.343	0.343	ND
	Sep-14	1.59	ND	ND	0.998	0.219	2.31
nmol kg <sup>-1</sup>							
Mo	0-1-12	2.20	2 7 2 7	2.60	4 77	2.04	2.20
	UCC-13 Fob 14	2.38	2.121 ND	2.09	4.77	3.04	3.20
	Δητ. 14	2.03 1 $AA \pm 0.177$	61.8	2.00	4.05	0.536	2.55
	Apr-14 May 14	1.444 ± 0.177	ND	1.05 ± 0.240 ND	2.21	0.330	5.15 ND
	101dy - 14 Sep-14	ND	ND	ND	2.15 ND	0.410 ND	ND
W	3cp-14		ND .		ND.	ND	ND .
••	Oct-13	0.375	0.139	0.143	0.310	0.136	0.232
	Feb-14	0.175	ND	0.171	0.205	0.096	$0.131 \pm 0.027$
	Apr-14	0.028	0.139	0.028	0.042	0.028	0.028
	Mav-14	ND	ND	ND	0.067	0.120	ND
	Sep-14	ND	ND	ND	ND	ND	ND
	-						

. ,		IdA-W/1	I dA-W/2	EW-AD1	I dA-W/4	Ida-W5	Ida-W6
			LUM-VVZ	Lun-113	Lun-vv4		EU/ - VV U
U	Oct-13	0.619	0.482	0.671	185 + 113	$0.734 \pm 0.046$	0.829
	Feb-14	$1.05 \pm 0.517$	0.402 ND	1 563	1.85 ± 1.15 1.89	$0.734 \pm 0.040$ 0.308 $\pm 0.042$	$1.13 \pm 0.962$
	Apr-14	$0.258 \pm 0.050$	3.95	0.344	0.385	0.111	0.266
	Mav-14	ND	ND	ND	0.120	0.0575	ND
	Sep-14	0.194 + 0.029	ND	ND	$0.105 \pm 0.017$	$0.099 \pm 0.029$	0.153
V							
	Oct-13	16.2	$25.9 \pm 5.69$	$21.7 \pm 2.96$	14.4	14.9	$20.9 \pm 2.12$
	Feb-14	33.0	ND	$52.1 \pm 23.8$	45.1	15.5	27.2
	Apr-14	16.4	97.2	10.5	9.21	5.76	17.6
	May-14	ND	ND	ND	6.36	6.01	ND
	Sep-14	12.6	ND	ND	6.10	5.87	18.0
Al							
	Oct-13	328	1208	1729	827	1095	1732
	Feb-14	818	ND	2021	684	486	569
	Apr-14	534	15941	$511 \pm 87.1$	$225 \pm 31.4$	181	1051
	May-14	ND	ND	ND	142	150	ND
	Sep-14	ND	ND	ND	ND	ND	ND
As	0 . 15	0.00	21 5	16 7	26.1	12.0	22.0
	Oct-13	8.90	21.5	16.7	26.1	13.8	22.0
	Feb-14	$30.0 \pm 30.6$	ND	18.5	26.1	4.53	8.89
	Apr-14	3.97	81.8	5.19	9.53	4.57	22.7
	May-14	ND	ND	ND	11.1	$2.75 \pm 0.454$	ND
A.c. (III)	Sep-14	2.22	ND	ND	9.39	2.50	8.12
AS (III)	Oct 12	2.77	0.67	8 J C	15 1	014	10.4
	UCI-13 Feb 14	3.27 5.59	9.07 ND	0.20 9.91	15.1	ŏ.14 1.69	10.4
	rep-14	1.30	22.0	0.01	9.44	1.00	5.76
	Api-14 May 14	1.29 ND	55.U ND	2.52 ND	4.22	0.426	0.5Z
	Ividy-14	0.208	ND	ND	$5.15 \pm 0.414$ 1 79	0.430	ND 1.45
	3ep-14	0.238	ND	ND	1.70	0.128 ± 0.074	1.45
		LdA-W7	LdA-W8	LdA-W9	EDG	VAC-1	VAC-2
Temperature (°C)							
	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	21.44	22.01	18.80	ND	ND	ND
	May-14	ND	ND	24.06	25.50	22.90	27.50
1	Sep-14	ND	ND	ND	23.75	27.04	24.27
Conductivity ( $\mu$ S cm <sup>-1</sup> )							
	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND 20410	ND	ND	ND	ND
	Apr-14	2260	39410	2302	ND	ND	ND
	May-14	ND	ND	2270	1085	526.0	145.0
Calinity (new)	Sep-14	ND	ND	ND	//2.0	872.0	3036
saimity (psu)	Oct 12	ND	ND	ND	ND	ND	ND
	ULL-13 Fob 14			ND			
	Δpr 14	1 16	25.2	1 10	ND	ND	ND
	Api-14 May_14	1.10 ND	23.2 ND	1.19	עא 0.550	עא 0.240	0.710
	Sen-14	ND	ND	ND	0.330	0.240	1 58
рН	3CP-14	110		nD.	0,500	ULE.U	1.30
r	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	6.95	6.50	6.93	ND	ND	ND
	Mav-14	ND	ND	6.73	6.64	7.41	6.88
	Sep-14	6.77	ND	8.21	8.9(li)	7.37(li)	ND
DOC (mmol $L^{-1}$ )						G /	
, ,	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	7.64	2.51	5.50	ND	ND	ND
	May-14	ND	ND	4.69	1.22	3.03	6.59
	Sep-14	1.68	ND	1.94	3.41	5.69	3.77
TN ( $\mu$ mol L <sup>-1</sup> )	Oct-13						
/	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	772	1598	261	ND	ND	ND
	May-14	ND	ND	288	64.2	29.4	515
	Sep-14	549	ND	259	67.0	48.7	595

(continued on next page)

		LdA-W7	LdA-W8	LdA-W9	EDG	VAC-1	VAC-2
ΠΠΙΟΙ Κ <u>g</u> Μσ							
ivig	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	2.17	32.2	2.68	ND	ND	ND
	May-14	ND	ND	3.58	1.27	1.23	3.04
	Sep-14	0.998	ND	3.11	1.26	1.18	3.64
Ca							
	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	1.25	16.0	1.95	ND	ND	ND
	May-14	ND	ND	1.71	1.61	2.12	3.56
N	Sep-14	0.878	ND	2.02	2.25	2.54	4.75
Na	0-+ 12	ND	ND	ND	ND	ND	ND
	UCT-13 Eab 14	ND	ND	ND	ND	ND	ND
	Apr 14	12.2	ND 255	12.9	ND	ND	ND
	May_14	ND	ND	12.8	$0.621 \pm 0.103$	1 20	11.8
	Sen-14	5.67	ND	13.1	0.616	1.20	16.1
*SO4-	Sep 11	5.07	n.b	15.1	0.010	1.50	10.1
	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	0.014	0.014	0.014	ND	ND	ND
	May-14	ND	ND	0.042	0.104	0.021	0.014
	Sep-14	1.12		ND	1.17	0.645	2.42
Alkalinity (as $HCO_{3}^{-}$ )							
	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	7.36	3.28	11.1	ND	ND	ND
	May-14	ND 12.0	ND	15.4	5.12	7.52	19.5
$umol lug^{-1}$	Sep-14	12.9	ND	10.4	5.09	9.93	21.3
μποι κg v							
ĸ	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	0	0	0	ND	ND	ND
	May-14	ND	ND	391	128	68.5	213
	Sep-14	157	ND	359	126	51.0	237
Ba	-						
	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	2.27	84.5	2.12	ND	ND	ND
	May-14	ND	ND	2.39	2.15	2.26	6.28
6	Sep-14	1.02	ND	2.17	2.31	1.95	7.58
Sr	Oct 12	ND	ND	ND	ND	ND	ND
	Eeb-14	ND	ND	ND	ND	ND	ND
	Apr-14	5.61	91.5	7.05	ND	ND	ND
	May-14	ND	ND	10.2	8 18 + 2 86	$636 \pm 0.754$	13.8
	Sep-14	3.35	ND	7.98	4.89	5.51	14.3
Fe	- 1						
	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	9.38	268	58.7	ND	ND	ND
	May-14	ND	ND	87.0	5.67	0.129	57.1
	Sep-14	45.4	ND	30.1	32.2	47.0	414
*Fe(II)	0.10						
	Oct-13	ND	ND	ND	ND	ND	ND
	rep-14	NU 2.22	ND 7014	NU 99.1			
	May 14	5.22 ND	7914 ND	00.1 2.51	6.09	166	10.0
	Sen_14	6.45	ND	4.31	15.8	4.00	26.0
*Fe <sub>Total</sub>	3CP-14	0.40	UD.	U	13.0		20.0
• ~ 10tai	Oct-13	ND	ND	ND	ND	ND	ND
	Feb-14	ND	ND	ND	ND	ND	ND
	Apr-14	6.27	180	44.8	ND	ND	ND
	May-14	ND	ND	36.3	20.4	8.42	36.7
	Sep-14	101	ND	25.2	82.7	56.6	82.7

(	continued	)

LdA-W7 LdA-W8 LdA-W9 EDG VAC-1	VAC-2
Mn	
Oct-13 ND ND ND ND ND	ND
Feb-14 ND ND ND ND ND	ND
Apr-14 23.1 97.3 19.7 ND ND	ND
	57.6
Sep-14 6.92 ND 13.4 53.5 37.2	46.3
*S(-II)	
Oct-13 ND ND ND ND ND	ND
Feb-14 ND ND ND ND ND	ND
Apr-14 0.031 1.47 0.343 ND ND	ND
Max-14 ND ND 0967 418 265	1 15
Sep. 14 0219 ND 0156 827 253	0.218
nmol kg <sup>-1</sup>	0.210
Mo	
Oct-13 ND ND ND ND ND	ND
Feb-14 ND ND ND ND ND	ND
Apr 14 2.26 6.52 2.26 ND ND	ND
Mu: 14 ND ND 120 547 056	52.0
101dy-14 IND IND 1.59 54.7 55.0	33.9 ND
אט א	ND
	ND
OCC-13 ND ND ND ND ND	ND
rep-14 ND ND ND ND ND	ND
Apr-14 0.057 0.091 0.080 ND ND	ND
May-14 ND ND 0.040 0.153 0.327	0.537
Sep-14 ND ND ND ND ND	ND
0	
Oct-13 ND ND ND ND ND	ND
Feb-14 ND ND ND ND ND	ND
Apr-14 2.00 2.39 0.665 ND ND	ND
May-14 ND ND 0.165 9.03 27.8	7.86
Sep-14 0.205±0.029 ND 0.052 3.56 4.68	0.412
V	
Oct-13 ND ND ND ND ND	ND
Feb-14 ND ND ND ND ND	ND
Apr-14 16.7 12.5 11.9 ND ND	ND
May-14 ND ND 14.1 16.1 62.7	44.4
Sep-14 18.1 ND 14.9 4.77 8.80	23.8
Al	
Oct-13 ND ND ND ND ND	ND
Feb-14 ND ND ND ND ND	ND
Apr-14 575 36.6 ± 17.3 31.1 ND ND	ND
May-14 ND ND 214 <b>7.07</b> 88.0	$13.6 \pm 1.22$
Sep-14 ND ND ND ND ND	ND
As	
Oct-13 ND ND ND ND ND	ND
Feb-14 ND ND ND ND ND	ND
Apr-14 17.9 11.2 11.8 ND ND	ND
Mav-14 ND ND 7.61 216 55.8	186
Sep-14 9.21 ND 2.47 298 327	418
As (III)	
Oct-13 ND ND ND ND ND	ND
Feb.14 ND ND ND ND ND	ND
And $4$ 30 965 $853\pm0.074$ ND ND	ND
$M_{14}$ ND ND 152 146 102	03.3
100 - 100 - 100 - 1.32 - 140 - 19.3 - 1.32 - 140 - 19.3 - 1.32 - 100 - 52.3 - 100 - 50.3 - 100 - 50.3 - 100 - 50.3 - 5	161
3.42 <sup>-14</sup> 0.332 UN 0.234 10.9 35.2	101

BDL: values in bold indicate value below detection limit. ±: standard deviation given where %RSD is greater than 5%.

ND: not determined. \*: measured by spectrophotometry.

#### Appendix E. Aqueous speciation of trace element species modeled at equilibrium shown as percent of total trace element concentration

%		MoO <sub>4</sub> <sup>-</sup>		MoS <sub>4</sub> <sup>2-</sup>		MoOS <sub>3</sub> <sup>-</sup>		MoO <sub>2</sub> S <sub>2</sub> <sup>-</sup>	Mo	D <sub>3</sub> S <sup>2−</sup>	Fe	OOHMoS <sub>4</sub> <sup>3-</sup>
LdAW1-Oct		87.8							11.6	;;		
LDAW2-Oct		2.3		41.2		7.5		10.7	24.1		14	.1
LdAW3-Oct		36.1		4.6		9.4		14.5	35.2			
LdAW4-Oct		12.5		21.2		22.4		18.0	22.8	3	3.0	)
LdAW5-Oct		7.2		32.1		26.7		16.9	16.9	)		
LdAW6-Oct		4.6		37.8		27.0		14.6	12.6	5	3.5	5
LdAW1-Feb		60.8				2.1		6.3	29.9	)		
LdAW3-Feb		22.8				16.5		18.0	31.1	l		
LdAW4-Feb		36.4		4.7		9.4		14.4	34.7	7		
LdAW5-Feb		63.6				1.7		5.5	28.6	)		
LdAW6-FeD		//./						2.1	19.6	)		
LUAW I-April		96.1							2.0			
IdAW3-April		91.0							2.9			
LdAW4-April		98.6							1.1			
LdAW5-April		87.9							11.3	}		
LdAW6-April		96.0							3.9			
LdAW7-April		99.6										
LdAW8-April		90.1							9.1			
LdAW9-April		97.8							2.3			
LdAW4-May		96.6							3.0			
LdAW5-May		96.1							3.6			
LdAW9-May		92.4						10	7.5			
EDG-May		68.0 01.4				1.1		4.2	26.3	5		
VACW2-May		91.4							8.3			
%		55.8				W/O <sup>2-</sup>			0.0			WO \$2-
/o						00.7						W033
LUAWI-OCI						99.7						20
LDAW2-Oct						97.2						2.0
IdAW4-Oct						98.2						16
LdAW5-Oct						98.0						2.0
LdAW6-Oct						97.7						2.3
LdAW1-Feb						99.7						
LdAW3-Feb						98.9						1.2
LdAW4-Feb						99.3						
LdAW5-Feb						99.6						
LdAW6-Feb						99.9						
LdAW1-April						100.1						
LDAW2-April						100.1						
LdAW3-April						98.6						
IdaW5_April						99.9 100.0						
IdAW6-April						99.9						
LdAW7-April						99.9						
LdAW8-April						99.9						
LdAW9-April						100.0						
LdAW4-May						99.9						
LdAW5-May						100.0						
LdAW9-May						99.8						
EDG-May						99.7						
VACW1-May						100.0						
%	<u>مددع-</u>	Haleo	He Acc-	HAcs-02-	H_Acco-	99.9 HAcso <sup>2-</sup>	H-Acco-	HACC- 02-	H24cs.0-	HAc0	Н-Л-О-	Н- Л-О-
	15 1	26.1	112/1503	47.4	112ASSU2	1173203	112ASSU3	1/122/02	112/1332/02	174	H2ASU3	12ASU4
LUAW I-UCT	15.1 47.2	30.1	81	47.4 74	5.2							
LDAW2-OCL	47.2 13.1	48.8	0.1	7. <del>4</del> 36.8	J.2							
IdAW4-Oct	25.4	-10.0 54 3	10	163	2.2							
LdAW5-Oct	23.9	54.7	1.7	16.5	2.3							
LdAW6-Oct	32.8	42.5	2.2	19.3	2.1							
LdAW1-Feb	61.1	16.6		20.0	1.4							
LdAW3-Feb	30.5	44.9		21.7	1.8							
LdAW4-Feb	40.8	34.1		22.6	1.6							
LdAW5-Feb	31.5	35.7		30.9	1.0							
LdAW6-Feb	32.0	40.1		25.2	1.5	10.5	5.2	1.2				
LOAW I-April	3.U 2.1	31.9		47.0		10.5	5.2	1.2				
LDAVV2-APTI	3.1	40.0 44.7		49.0 7 3		3.2	3.U 40.0	60				
IdAW4-Anril		44 1		20.2		13.2	20.0	0.0				
							-0.0					

/ .* 1	
continued	
Continueu	

%	AsS <sub>4</sub> <sup>-</sup>	$H_3AsO_3$	$H_2AsS_3^-$	HAsS <sub>3</sub> O <sup>2-</sup>	$H_2AsSO_2^-$	HAsSO <sub>3</sub> <sup>2-</sup>	$H_2AsSO_3^-$	HAsS <sub>2</sub> O <sub>2</sub> <sup>-</sup>	$H2AsS_2O_2^-$	HAsO <sub>4</sub> -	$H_2AsO_3^-$	$H_2AsO_4^-$
LdAW5-April	6.5	42.6		49.2								
LdAW6-April	1.4	27.7		57.4		3.8	7.4	1.3				
LdAW7-April		46.6				24.0	27.4					
LdAW8-April	3.1	85.5		10.7								
LdAW9-April		71.6		19.5		3.2	3.8					
LdAW4-May	1.1	28.5		51.3		4.7	11.6	1.7				
LdAW5-May		15.9		60.0		4.1	15.6	2.7				
LdAW9-May	5.2	19.8		70.9			1.7					
EDG-May	5.4	66.7		26.9								
VACW1-May	14.4	33.6		49.7								
VACW2-May	3.6	49.8		43.3			1.2					
LDAW1-Sept	15.5	13.1		66.2		2.9						
LdAW4-Sept	9.4	18.4		57.9		9.8	2.3	1.3				
LdAW5-Sept		4.9		51.1		13.8	25.7	1.5	2.2			
LdAW6-Sept	16.4	10.1		63.6		1.1		1.4	2.1			
LdAW7-Sept				45.0		14.1	26.5					
LdAW9-Sept		9.3				81.0	4.9			2.0	1.0	
EDG-Sept	37.9	2.4		31.1			24.3	1.5			1.2	
VACW1-Sept	14.1	15.9		66.4			1.7					
VACW2-Sept		38.0				27.4	24.8			6.2		3.4
sample		$VO^{2+}$	V	(OH)	HVO2-		camplo		$VO^{2+}$	WOU	<u>۱+</u>	111/02-
F			V	(011)2	11004		sample		10	V(OII	12	HVU4
LdAW1-Oct		99.7		(011)2	11004		LdAW4-May	y	98.5	1.5	)2	HVU4
LdAW1-Oct LDAW2-Oct		99.7 99.8		(011)2			LdAW4-May LdAW5-May	y y	98.5 97.6	1.5 2.2	J2	HV0 <u>4</u>
LdAW1-Oct LDAW2-Oct LdAW3-Oct		99.7 99.8 98.2		.8	11104		LdAW4-May LdAW5-May LdAW9-May	y y y	98.5 97.6 99.3	1.5 2.2	J2	HVO4
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW4-Oct		99.7 99.8 98.2 98.9	1	.8 .2			LdAW4-May LdAW5-May LdAW9-May EDG-May	y y y	98.5 97.6 99.3 99.4	1.5 2.2	12	HV04
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW4-Oct LdAW5-Oct		99.7 99.8 98.2 98.9 98.6	1 1 1	.8 .2 .5			LdAW4-May LdAW5-May LdAW9-May EDG-May VACW1-May	y y y	98.5 97.6 99.3 99.4 99.9	1.5 2.2	)2	
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW4-Oct LdAW5-Oct LdAW6-Oct		99.7 99.8 98.2 98.9 98.6 98.9	1 1 1 1 1	.8 .2 .5 .2			LdAW4-May LdAW5-May LdAW9-May EDG-May VACW1-May VACW2-May	y y y y y	98.5 97.6 99.3 99.4 99.9 99.6	1.5 2.2	J2	HVU4
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW4-Oct LdAW5-Oct LdAW6-Oct LdAW1-Feb		99.7 99.8 98.2 98.9 98.6 98.9 99.9	1 1 1 1	.8 .2 .5 .2			LdAW4-May LdAW5-May LdAW9-May EDG-May VACW1-May VACW2-May LDAW1-Sep	y y y y y	98.5 97.6 99.3 99.4 99.9 99.6 100.3	1.5 2.2	J2	HVUą
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW4-Oct LdAW5-Oct LdAW6-Oct LdAW1-Feb LdAW3-Feb		99.7 99.8 98.2 98.9 98.6 98.9 99.9 99.9 99.5	1 1 1 1	.8 .2 .5 .2			LdAW4-May LdAW5-May LdAW9-May EDG-May VACW1-May VACW2-May LDAW1-Sep LdAW4-Sep	y y y y y t t	98.5 97.6 99.3 99.4 99.9 99.6 100.3 99.9	1.5 2.2	J2	<u>HVU4</u>
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW4-Oct LdAW5-Oct LdAW5-Oct LdAW1-Feb LdAW3-Feb LdAW3-Feb		99.7 99.8 98.2 98.9 98.6 98.9 99.9 99.9 99.5 99.9	1 1 1 1	.8 .2 .5 .2			LdAW4-May LdAW5-May LdAW9-May EDG-May VACW1-May VACW2-May LDAW1-Sep LdAW4-Sep LdAW5-Sep	y y y y tt t	98.5 97.6 99.3 99.4 99.9 99.6 100.3 99.9 99.4	1.5	12	Πνυ <u>4</u>
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW4-Oct LdAW5-Oct LdAW6-Oct LdAW1-Feb LdAW3-Feb LdAW4-Feb LdAW5-Feb		99.7 99.8 98.2 98.9 98.6 98.9 99.9 99.9 99.9 99.5 99.9 99.8	1 1 1 1 1	.8 .2 .5 .2			LdAW4-May LdAW5-May LdAW9-May EDG-May VACW1-May VACW2-May LDAW1-Sep LdAW4-Sep LdAW5-Sep LdAW5-Sep	y y y y t t t t	98.5 97.6 99.3 99.4 99.9 99.6 100.3 99.9 99.4 99.9	1.5 2.2	12	ΠνΟ
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW3-Oct LdAW5-Oct LdAW6-Oct LdAW1-Feb LdAW3-Feb LdAW3-Feb LdAW5-Feb LdAW5-Feb		99.7 99.8 98.2 98.9 98.6 98.9 99.9 99.5 99.9 99.5 99.9 99.8 99.9	1 1 1 1 1	.8 .2 .5 .2			LdAW4-May LdAW5-May LdAW9-May EDG-May VACW1-May VACW1-May VACW2-May LDAW1-Sep LdAW4-Sep LdAW5-Sep LdAW6-Sep LdAW7-Sep	y y y y t t t t t	98.5 97.6 99.3 99.4 99.9 99.6 100.3 99.9 99.4 99.9 99.4 99.9 99.4	1.5 2.2 2.1	12	ΠνΟ
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW3-Oct LdAW5-Oct LdAW6-Oct LdAW1-Feb LdAW3-Feb LdAW4-Feb LdAW6-Feb LdAW6-Feb LdAW1-April		99.7 99.8 98.2 98.9 98.6 98.9 99.9 99.5 99.9 99.5 99.9 99.8 99.9 99.7	1 1 1 1	.8 .2 .5 .2			LdAW4-May LdAW5-May LdAW9-May EDG-May VACW1-May VACW1-May VACW2-May LDAW1-Sep LdAW4-Sep LdAW5-Sep LdAW5-Sep LdAW9-Sep	y y y y t t t t t t	98.5 97.6 99.3 99.4 99.9 99.6 100.3 99.9 99.4 99.9 99.4 99.9 98.1 100.2	1.5 2.2 2.1	12	ΠνΟ
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW3-Oct LdAW5-Oct LdAW6-Oct LdAW3-Feb LdAW3-Feb LdAW4-Feb LdAW6-Feb LdAW6-Feb LdAW6-Feb LdAW1-April LDAW2-April		99.7 99.8 98.2 98.9 98.6 98.9 99.9 99.5 99.9 99.5 99.9 99.8 99.9 99.7 99.9	1 1 1 1	.8 .2 .5 .2			LdAW4-May LdAW5-May LdAW9-May EDG-May VACW1-May VACW1-May VACW2-May LDAW1-Sep LdAW5-Sep LdAW5-Sep LdAW5-Sep LdAW5-Sep LdAW9-Sep	y y y y t t t t t t	98.5 97.6 99.3 99.4 99.9 99.6 100.3 99.9 99.4 99.9 99.4 99.9 98.1 100.2 97.9	1.5 2.2 2.1	12	1.7
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW5-Oct LdAW5-Oct LdAW6-Oct LdAW3-Feb LdAW3-Feb LdAW4-Feb LdAW5-Feb LdAW6-Feb LdAW6-Feb LdAW1-April LDAW2-April		99.7 99.8 98.2 98.9 98.6 98.9 99.9 99.5 99.9 99.5 99.9 99.8 99.9 99.7 99.9 58.4	1 1 1 1 3	.8 .2 .5 .2 4.3			LdAW4-May LdAW5-May EDG-May VACW1-May VACW1-May VACW1-May LdAW1-Sep LdAW5-Sep LdAW5-Sep LdAW5-Sep LdAW5-Sep EDG-Sept VACW1-Sep	y y y y t t t t t t	98.5 97.6 99.3 99.4 99.9 99.6 100.3 99.9 99.4 99.9 98.1 100.2 97.9 99.9	1.5 2.2 2.1	12	1.7
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW5-Oct LdAW5-Oct LdAW4-Feb LdAW3-Feb LdAW3-Feb LdAW5-Feb LdAW5-Feb LdAW6-Feb LdAW6-Feb LdAW6-Feb LdAW1-April LDAW2-April LdAW3-April		99.7 99.8 98.2 98.9 98.6 98.9 99.9 99.5 99.9 99.5 99.9 99.8 99.9 99.7 99.9 58.4 99.4	1 1 1 1 3	.8 .2 .5 .2 4.3			LdAW4-May LdAW5-May EDG-May VACW1-May VACW1-May VACW1-May VACW2-May LDAW1-Sep LdAW5-Sep LdAW6-Sep LdAW6-Sep LdAW6-Sep LdAW9-Sep EDC-Sept VACW1-Sep	y y y y y t t t t t t	98.5 97.6 99.3 99.4 99.9 99.6 100.3 99.9 99.4 99.9 98.1 100.2 97.9 99.9	1.5 2.2 2.1	12	1.7
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW5-Oct LdAW5-Oct LdAW5-Oct LdAW1-Feb LdAW3-Feb LdAW4-Feb LdAW5-Feb LdAW5-Feb LdAW6-Feb LdAW1-April LdAW3-April LdAW3-April LdAW5-April		99.7 99.8 98.9 98.9 98.6 98.9 99.9 99.9 99.5 99.9 99.8 99.9 99.7 99.9 58.4 99.9 58.4 99.4 99.0	1 1 1 1 3	.8 .2 .5 .2 4.3			LdAW4-May LdAW5-May EDG-May VACW1-May VACW1-May VACW2-May LDAW1-Sep LdAW4-Sep LdAW5-Sep LdAW5-Sep LdAW5-Sep LdAW7-Sep EDG-Sept VACW1-Sep	y y y y y t t t t t t	98.5 97.6 99.3 99.4 99.9 99.6 100.3 99.9 99.4 99.9 98.1 100.2 97.9 99.9	1.5 2.2 2.1	12	1.7
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW5-Oct LdAW5-Oct LdAW6-Oct LdAW3-Feb LdAW3-Feb LdAW5-Feb LdAW5-Feb LdAW6-Feb LdAW6-Feb LdAW1-April LDAW2-April LdAW3-April LdAW5-April LdAW5-April		99.7 99.8 98.9 98.9 98.6 98.9 99.9 99.9 99.5 99.9 99.8 99.9 99.7 99.9 58.4 99.4 99.4 99.0 99.7	1 1 1 1 3	.8 .2 .5 .2 4.3			LdAW4-May LdAW5-May EDG-May VACW1-May VACW2-May LDAW1-Sep LdAW4-Sep LdAW5-Sep LdAW5-Sep LdAW5-Sep LdAW9-Sep EDG-Sept VACW1-Sep	y y y y t t t t t	98.5 97.6 99.3 99.4 99.9 99.6 100.3 99.9 99.4 99.9 99.9 98.1 100.2 97.9 99.9	1.5 2.2 2.1	12	1.7
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW3-Oct LdAW5-Oct LdAW6-Oct LdAW6-Feb LdAW3-Feb LdAW5-Feb LdAW5-Feb LdAW5-Feb LdAW6-Feb LdAW1-April LDAW2-April LdAW3-April LdAW5-April LdAW6-April LdAW6-April LdAW7-April		99.7 99.8 98.2 98.9 98.6 98.9 99.9 99.5 99.9 99.5 99.9 99.8 99.9 99.7 99.9 58.4 99.0 99.7 100.0	1 1 1 1 3	.8 .2 .5 .2 4.3			LdAW4-May LdAW5-May LdAW9-May EDG-May VACW1-May VACW1-May VACW2-May LDAW1-Sep LdAW4-Sep LdAW5-Sep LdAW5-Sep LdAW9-Sep EDG-Sept VACW1-Sep	y y y y t t t t t t	98.5 97.6 99.3 99.4 99.9 99.6 100.3 99.9 99.4 99.9 99.4 99.9 98.1 100.2 97.9 99.9	1.5 2.2 2.1	12	1.7
LdAW1-Oct LDAW2-Oct LdAW3-Oct LdAW3-Oct LdAW5-Oct LdAW6-Oct LdAW3-Feb LdAW3-Feb LdAW5-Feb LdAW5-Feb LdAW5-Feb LdAW5-Feb LdAW5-Feb LdAW5-Feb LdAW5-April LdAW5-April LdAW6-April LdAW6-April LdAW6-April LdAW8-April		99.7 99.8 98.2 98.9 98.6 98.9 99.9 99.5 99.9 99.5 99.9 99.7 99.9 58.4 99.0 99.7 100.0 97.6	1 1 1 1 3 3	.8 .2 .5 .2 4.3			LdAW4-May LdAW5-May EDG-May VACW1-May VACW1-May VACW2-May LDAW1-Sep LdAW4-Sep LdAW5-Sep LdAW5-Sep LdAW9-Sep EDG-Sept VACW1-Sep	y y y y t t t t t t	98.5 97.6 99.3 99.4 99.9 99.6 100.3 99.9 99.9 99.9 98.1 100.2 97.9 99.9	1.5 2.2 2.1	12	1.7

## Appendix F. Mineral saturation states (log Q/K) of Lac des Allemands groundwaters for sulfide-bearing minerals

Sample	Pyrite	Mackinawite	Realgar	Sample	Pyrite	Mackinawite	Realgar
LdAW1-Oct	6.93	0.37	-4.74	LdAW4-May	5.25	-1.12	-5.59
LDAW2-Oct	8.60	0.94	-2.88	LdAW5-May	4.60	-1.92	-6.42
LdAW3-Oct	7.25	-0.35	-3.56	LdAW9-May	6.12	-3.45	-5.47
LdAW4-Oct	8.29	0.65	-2.92	EDG-May	6.21	-1.20	-2.83
LdAW5-Oct	7.62	-0.16	-3.11	VACW1-May	4.41	-1.96	-4.14
LdAW6-Oct	8.59	0.76	-2.94	VACW2-May	5.83	-0.63	-3.70
LdAW1-Feb	6.93	0.03	-3.86	LDAW1-Sept	6.55	-0.18	-6.56
LdAW3-Feb	6.97	-0.53	-3.28	LdAW4-Sept	7.05	0.79	-5.99
LdAW4-Feb	7.30	-0.14	-3.44	LdAW5-Sept	5.26	-1.44	-7.49
LdAW5-Feb	6.72	-0.33	-4.48	LdAW6-Sept	6.94	0.10	-5.62
LdAW6-Feb	6.56	-0.03	-4.30	LdAW7-Sept	5.14	-1.46	-6.63
LdAW1-April	4.45	-1.44	-6.03	LdAW9-Sept	4.77	-0.09	-8.20
LDAW2-April	5.38	-0.84	-4.39	EDG-Sept	7.69	2.32	-5.44
LdAW3-April	2.43	-4.63	-6.07	VACW1-Sept	6.91	0.28	-4.08
LdAW4-April	4.45	-1.50	-5.89	VACW2-Sept	2.53	-2.35	-6.81
LdAW5-April	5.69	-1.03	-5.06				
LdAW6-April	4.71	-1.67	-5.18				
LdAW7-April	2.36	-2.86	-6.58				
LdAW8-April	6.07	-0.72	-4.29				
LdAW9-April	5.19	-0.92	-5.22				

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