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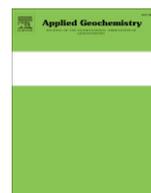
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Diel variation of selenium and arsenic in a wetland of the Great Salt Lake, Utah

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ABSTRACT

Diel (24-h) changes in Se and As concentrations in a freshwater wetland pond bordering the Great Salt Lake (GSL) were examined. Selenium concentrations (filtered and unfiltered) changed on a diel basis, i.e., were depleted during early morning and enriched during daytime over August 17–18. During the May 24–25, 2006 and September 29–30 diel studies, no significant 24-h trends were observed in Se concentrations compared to August, which showed daily maximums up to 59% greater than the daily minimum. Both filtered and unfiltered As concentrations also varied on a diel cycle, with increased concentrations during early morning and decreased concentrations during daytime. Filtered As concentrations increased 110% during the May 24–25, 2006 diel study. Selenium varied in phase with pH, dissolved O₂ (DO), and water temperature (*T_w*) whereas As varied opposite to Se, pH, DO and *T_w*. Changes in pH, DO and *T_w* showed a direct linear correlation ($r = 0.74, 0.75, \text{ and } 0.55$, respectively) to filtered Se. Also pH, DO and *T_w* were inversely correlated to filtered As concentration ($r = -0.88, -0.87, \text{ and } -0.84$, respectively). Equilibrium geochemical speciation and sorption models were used to examine the potential oxidation state changes in Se and As, and sorption and desorption reactions corresponding to the observed 24-h variations in pe and pH. In this wetland it was postulated that diel Se variation was driven by sorption and desorption due to photosynthesis-induced changes in pH and redox conditions. Diel variations of As were hypothesized to be linked to pH-driven sorption and desorption as well as co-precipitation and co-dissolution with mineral phases of Mn.

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1. Introduction

Potential ecological risks can arise from underestimation of trace element loads due to temporal variation in trace element concentrations (including Se and As) caused by sampling biases (i.e., daytime measurements) (Gammons et al., 2007). An increasing body of evidence indicates that the concentration of many trace elements in streams with acidic to alkaline pH can change over a 24-h period. Currently, the data are limited to Hg, Fe, Mn, Zn, Al, Cu, Cd, Ni, As and rare earth elements (REE) (McKnight and Bencala, 1988; Brick and Moore, 1996; Nimick et al., 2003, 2007; Jones et al., 2004; Gammons et al., 2005).

The mechanisms driving these diel changes were linked to photosynthesis- and respiration-induced pH variation and photoredox processes affecting mass transfer of these elements (McKnight and

Bencala, 1988). Mass transfer processes include adsorption and desorption, precipitation and dissolution, biological uptake, volatilization, sedimentation and resuspension (Nimick et al., 2003; Morris et al., 2005; Diaz et al., 2009b; Dicaldo et al., 2010). Other mass transfer mechanisms may include daily upstream element loading changes and daily inflow changes (e.g., tributary and groundwater) (Nimick et al., 2003; Jones et al., 2004).

The Great Salt Lake (GSL) is the largest hypersaline lake in North America, and the fourth largest terminal lake in the world (Brix et al., 2004). The GSL and its associated wetlands have been designated as a site of hemispheric importance for supporting millions of shorebirds and waterfowl (Aldrich and Paul, 2002). Selenium is a trace element that has gained recent interest due to the effects of elevated Se loads to migratory birds using the GSL (Diaz et al., 2009a; Oliver et al., 2009). Elevated levels of Se were recently reported in eared grebes (*Podiceps nigricollis*), California gulls (*Larus californicus*), and greenwinged teal (*Anas crecca*) (Vest et al., 2009; Conover and Vest, 2009a,b). No studies have been reported for As in the GSL birds; however elevated levels of As are well

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known to cause deformities and death in birds (Eisler, 1988; Baos et al., 2006; Albert et al., 2008).

Selenium exists in four oxidation states (+6, +4, 0, -2) and in several compound types (oxyanions, sulfides, organoselenides and metal selenides) (Zhang and Moore, 1996). Sorption of selenate (+4 oxidation state) and selenite (+6 oxidation state) oxyanions on Al oxides and goethite surfaces has been demonstrated to increase with decreasing pH (Zhang and Sparks, 1990). Selenite has been shown to sorb more strongly than selenate on goethite, hematite, hydroxyapatite and fluorapatite (Duc et al., 2003).

Arsenic is present as arsenate, As(V), in oxic environments and with a pH ranging from 7 to 11, whereas arsenite, As(III), is favored in reducing conditions and low pH (Hem, 1986). In general, arsenate sorbs more strongly than arsenite to oxyhydroxide surfaces (Lakshmipathiraj et al., 2006). In alkaline rivers and streams, diel changes in dissolved As (as arsenate) concentration were attributed to pH changes caused by daily photosynthesis and respiration processes driven by biological activity, coupled with adsorption-desorption of arsenate (e.g., HAsO_4^{2-}) to/from suspended particulate, and sediment Fe oxyhydroxide deposits (Fuller and Davis, 1989; Nimick et al., 1998; Gammons et al., 2007; Barringer et al., 2007).

This paper examines the effects of 24-h changes in pH and water temperature (T_w) on diel changes in Se and As concentrations in a freshwater wetland of Ambassador Duck Club (ADC). It also explores the possibility that changes in aqueous Se oxidation state coupled to pH-driven variations in Se (and As) sorption/desorption, and redox-driven As co-precipitation and co-dissolution with oxides of Mn, drove their mass transfer to/from the water column, yielding observed diel cycles in their aqueous concentrations.

This wetland is an important test-bed in understanding Se and As diel concentration and geochemical variations, and associated ecological risks of these contaminants to migratory birds using

these wetlands and other similar systems in this region (Aldrich and Paul, 2002; Dicaldo et al., 2010). This site is part of a larger sampling effort conducted by the main author, the Utah Division of Water Quality (UDWQ) and EPA Region 8 since 2003, to understand the potential trace element contamination in these wetlands representative of a typical freshwater wetland pond in this area.

2. Materials and methods

2.1. Location

The ADC wetland pond that is the focus of this research is located on the southern shoreline of the GSL near to the Salt Lake City International airport (Fig. 1). The ADC wetland pond covers about 21.5 hectares (53 acres), its depth varies from 0.15 m to 0.85 m, with salinity ranging from 500 to 1000 mg L^{-1} . The area and volume of the pond were computed using available aerial photographs of the site and the Geographical Information System software, and were approximately 214,300 m^2 and 107,150 m^3 , respectively. The average daily inflow over the study period (2005–2006) to the wetland from the Jordan River, obtained from the Utah Division of Water Rights and measured at the Lower Jordan River Utah Club or Utah Storet number 4985315, was 3600 $\text{m}^3 \text{h}^{-1}$. The computed average residence time of water in the wetland (determined as volume of wetland divided by the average through flow) was about 30 h.

The wetland provides a habitat for ducks, and other biota. Submerged aquatic plants (e.g. *Stuckenia* sp.) have been observed during late Spring, Summer and early Fall. This wetland receives nutrient-rich water, Se and As inputs by a series of canals from the Jordan River. Sources of Se and As include waste discharge from

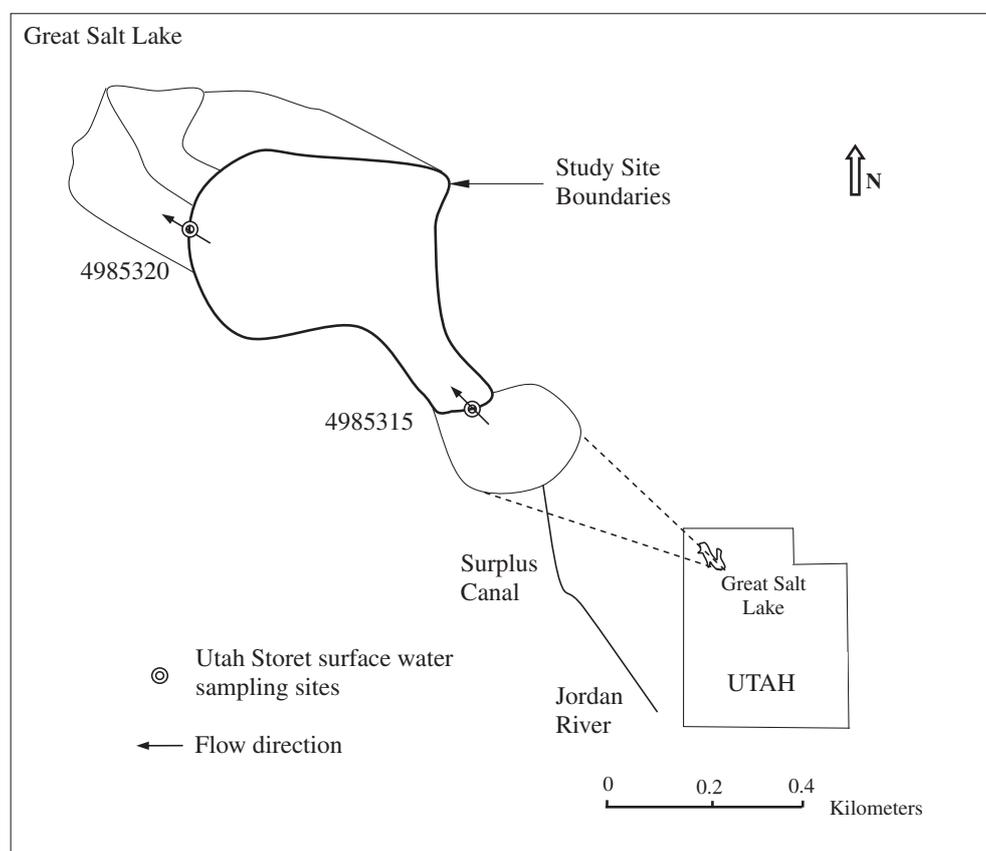


Fig. 1. Site map of the wetland. "Storet" refers to the Utah Storet number. The Storet numbers for this site are shown below the inlet and outlet of the wetland pond.

municipal and industrial facilities, natural tributaries, urban runoff, and irrigation return flows (Aldrich and Paul, 2002).

2.2. Field measurements

To understand the diel fluctuations and seasonal changes of Se concentration amplitudes three 24-h sampling events were performed. Arsenic samples were collected only in one diel study, in May 2006, since Se was the initial focus of this study. Also, surface water samples were collected in this wetland pond and other ponds of the ADC throughout the study period (2005–2006) as presented by Dicaldo et al. (2010).

Filtered Se samples were collected every 1–2 h from the outlet of the wetland pond (Storet Site number 4985320) on September 29–30, 2005 ($N = 23$). Filtered samples were collected using 0.45 μm Millipore sterile filters and represent dissolved ionic forms of Se and Se associated with colloidal matter of various size passing the filter ($<0.45 \mu\text{m}$). Diel studies are labor intensive and expensive; therefore, to verify the existence of diel changes of Se, only filtered Se samples were collected during the first 24-h study in September. May 24–25, 2006 ($N = 83$) samples were collected at the same site, for unfiltered and filtered Se, Ag, Al, As, Ba, B, Cd, Cu, Cr, Fe, Hg, Mn, Ni, Pb and Zn, major ions (HCO_3^- , CO_3^{2-} , Cl^- , SO_4^{2-} , Mg^{2+} , K^+ , Ca^{2+} and Na^+), unfiltered nutrients (NO_3^- , P and NH_3), and chlorophyll a. August 17–18, 2007 samples ($N = 42$) were collected at the same site for filtered and unfiltered Se, Al, Fe, Hg and Mn, and major ions (SO_4^{2-} , Cl^- , Na^+ , Mg^{2+} , K^+ and Ca^{2+}).

Replicate surface water samples for trace element analyses were collected in 250 mL plastic bottles. One replicate was filtered (0.45 μm) and both replicates were preserved in the field (0.8% HNO_3). Surface water samples for nutrient analyses (unfiltered) were collected in 500 mL plastic bottles, and preserved with 0.4% H_2SO_4 . Surface water samples for major ion analyses were collected in 1 L plastic bottles with no preservative or filtration. Chlorophyll a samples were collected in 500 mL opaque plastic bottles with no preservative or filtration, and were immediately put on ice and kept frozen. Holding time was 6 months for trace elements, 28 days for nutrients and SO_4^{2-} , 21 days for chlorophyll a, and less than 21 days for other ions.

Dissolved O_2 , pH, Eh, and water temperature (T_w) were measured using Troll 9000 and 9500 probes (In-Situ, Inc., Ft. Collins, Colorado) in the wetland pond concurrently with the collection of surface water samples. Eh was measured using a Pt sensor with a Ag/AgCl reference electrode. The data were recorded after stabilization of the probes. Calibration of the pH probe was performed using a 3-point calibration (pH of 4, 7, and 10) and Zobell's solution for Eh (In-Situ, 2010a). Dissolved O_2 optical instrument calibration was carried out by the saturation method as detailed by In-Situ (In-Situ, 2010b).

Ten water samples were collected on June 13 and August 17–18, 2007 to measure volatile Se concentration according to the methods described in Diaz et al. (2009b) using a purge and cryotrap system. The trap process was performed in the field in order to avoid degradation of the water samples during transport and holding. For more details refer to Diaz et al. (2009b).

2.3. Laboratory measurements

Filtered Se samples collected in September 2005 were analyzed (with laboratory duplicates) by hydride generation atomic absorption spectroscopy (HGAAS) methods at the Utah Public Health (UPH) laboratory. Filtered and unfiltered Se samples collected in May 2006 were analyzed by HGAAS methods at UPH laboratory. Filtered and unfiltered Se concentrations were determined by pre-digesting the samples in potassium persulfate and HCl, and determined by HGAAS (AAAnalyst 400; Perkin Elmer Corporation) using

modified Standard Method 3114 C (Clesceri et al., 1998). Other trace elements were determined in May 2006 samples (filtered and unfiltered) by inductively coupled plasma (ICP Optima 4300 DV; Perkin Elmer Corporation) optical emission spectrometry. May samples were also analyzed for major ions (HCO_3^- , CO_3^{2-} , Cl^- , SO_4^{2-} , Mg^{2+} , K^+ , Ca^{2+} and Na^+), other trace elements, and nutrients at the UPH laboratory as detailed in Dicaldo et al. (2010). Chlorophyll a colorimetric measurements ($N = 11$) for May samples were performed at the UPH laboratory with a UV/Vis Spectrometer (Beckman DU 520) by Standard Method 10200H (Clesceri et al., 1998).

Water samples collected on August 17–18, 2007 for unfiltered and filtered Se, major ions (Cl^- , SO_4^{2-} , Mg^{2+} , K^+ , Ca^{2+} and Na^+), and trace metals (Fe, Mn, Al and Hg) were analyzed at the UU laboratory by ICP-MS with a collision cell (Agilent 7500ce). Samples for volatile Se analyses were processed and analyzed using the ICP-MS with collision cell at the UU laboratory as detailed in Diaz et al. (2009b). Sample concentrations were corrected to the recovery of Se due to losses in the purge and cryotrap system (Diaz et al., 2009b). The volatile Se mass transfer was computed by multiplying the volatile Se flux by the surface area of the wetland pond (214,300 m^2).

2.4. Quality control

Quality control of HGAAS analyses (at the UPH laboratory) included check standards (CSTD) (acceptable within $\pm 10\%$), laboratory spiked blanks (LSB) (within $\pm 10\%$), laboratory spiked matrix (LSM), and laboratory spiked matrix duplicate (LSMD) (LSM/LSMD recovery within $\pm 30\%$ and relative percent difference (RPD) of LSM/LSMD $\leq 15\%$). Laboratory analyses of field samples (unfiltered and filtered Se) and matrix spiked samples ($N = 32$) were performed in triplicate (% Relative Standard Deviation (RSD) < 8.0) to validate the accuracy of the HGAAS method. The Standard Reference Material (SRM) recovery was within $\pm 10\%$, while the calibration curve was accepted if the R^2 (correlation coefficient) was > 0.997 . The minimum detection limit (MDL) for Se with this method was 0.18 $\mu\text{g L}^{-1}$.

Quality control on As and other elements determined at the UPH laboratory included initial calibration verification (ICV), continuing calibration verifications (CCV) (acceptable within 90–110% of calibration standards), initial calibration blanks (ICB) and continuing calibration blanks (CCB) acceptable if below the estimated quantitation limit (EQL). The MDL for As using the ICP-MS method was 0.12 $\mu\text{g L}^{-1}$. Quality control on unfiltered and filtered Se, and elements determined by ICP-MS (at the UU laboratory) included ICV, CCV (acceptable within 90–110% of calibration standards), ICB and CCB that were accepted if below the EQL. The MDL for Se using the ICP-MS method was 0.007 $\mu\text{g L}^{-1}$. All water surface laboratory data sets passed QC.

2.5. Statistical analysis

The relationship between Se, As, Fe, Mn, pH and T_w in the water column were determined using correlation analysis (95% confidence level or $\alpha = 0.05$) with a two-tailed t -test and Pearson's product-moment correlation coefficient (r). All statistical analyses were performed using Excel® 2003 Statistical Analysis tools.

2.6. Geochemical modeling

Aqueous speciation and saturation indices (SI) of mineral phases of Se, As, Fe and Mn were estimated with PHREEQC using the thermodynamic database Minteq.v4 in (Parkhurst and Appelo, 1999) (Table 1). PHREEQC uses observed water chemistry data to compute the distribution of aqueous species by an ion-association

Table 1

Saturation Indices (SI) for Se, Mn, and Fe solid phases computed from analyses of the GSL wetland-water samples collected on August 17–18, 2007, using PHREEQC Minteq.v4 database (Parkhurst and Appelo, 1999). The data was normalized to ferrihydrite (Hfo).

Solid phase	Formula	Min SI	Max SI
Achavalite	FeSe	−9.9	−3.3
Ferroselite	FeSe ₂	−15.2	−4.5
Iron selenite	Fe ₂ (SeO ₃) ₃ ·2H ₂ O	−5.5	−3.2
Iron hydroxide selenite	Fe ₂ (OH) ₄ SeO ₃	−2.2	−1.1
Manganese selenite	Mn SeO ₃	−1.8	−1.4
Manganese selenide	MnSe	−11.1	−6.0
Selenium dioxide	SeO ₂	−3.9	−3.1
Selenium trioxide	SeO ₃	−10.5	−9.3
Ferrihydrite	Fe ₅ HO ₈ ·4H ₂ O	0.3	0.6
Bixbyite (Mn Fe oxide)	(Fe, Mn) ₂ O ₃	−2.4	0.7
Magnetite	Fe ₃ O ₄	2.0	3.2
Maghemite	Fe ₂ O ₃ , γ-Fe ₂ O ₃	0.7	1.2
Hematite	Fe ₂ O ₃	2.2	2.7
Goethite	α-FeO(OH)	0.8	1.1
Lepidocrocite	γ-FeO(OH)	0.7	1.0
Manganite	MnO(OH)	−1.2	0.3
Pyrolusite	MnO ₂	−2.4	0.0
Hausmannite	Mn ²⁺ Mn ₃ ⁺ O ₄	−2.9	0.8

aqueous model. In addition, SI were computed as the log IAQ/K, where IAQ is the ion activity quotient, and K is the equilibrium constant for the mineral dissolution reaction (Parkhurst and Appelo, 1999). Positive values of SI indicate potential oversaturation and possible precipitation of an aqueous species. Major ion concentrations (i.e., HCO₃[−], CO₃^{2−}, Cl[−], SO₄^{2−}, Mg²⁺, K⁺ and Na⁺) determined during the study period (2005–2007) (Dicaldo et al., 2010) were used in the diel August PHREEQC simulations to close the charge balance and understand if mineral phases containing Se and As were thermodynamically favored.

Measurements of individual oxidation states of Se and As are ideal in constraining the speciation of these trace elements in many surface waters. However, Se(IV) concentrations were below the detection limit where measured, possibly because it is more strongly adsorbed to metal oxides than Se(VI) at pH < 8 (Duc et al., 2003). Likewise, As(VI) is the thermodynamically favorable species at the pH measured in the ADC pond (consistently >7.5), and As species were not determined in this study.

May 2006 measured Eh values using a Pt electrode (yielding pe values of 4.4–7.8) showed good agreement with the PHREEQC calculated values using the NH₃/NO₃ redox couple (4.4–8.4) measured in the surface water concurrently during the diel period (Supplementary data). Ammonia and NO₃ data were not measured during the September 2005 and August 2007 sampling periods. For these periods, Pt electrodes were used to measure Eh and compute speciation of Se, As, and trace elements in solution. While Eh measurements are well-known to provide good qualitative information regarding redox potential, they are routinely used despite their limitations (Holm and Curtiss, 1989; Hinckey and Schaffner, 2005). Redox values calculated by Carling et al. (in press) via PHREEQC using NO₃/NO₂ concentrations in the same wetland pond (August 20–21, 2008), compared well (pe ranging from 4 to 7) with the pe estimated in this study (pe ranging from 3.5 to 6.5) using Eh values from a Pt electrode (August 17–18, 2007). Studies conducted by Holm and Curtiss (1989) showed that Eh calculated from the As(V)/As(III) redox couple correlated fairly well with measured Pt-electrode potentials (Eh) in shallow groundwater.

Sorption and desorption simulations of Se on ferrihydrite commonly referred to as hydrous ferric oxide (Hfo) (Johnson et al., 2005) were developed via PHREEQC (Parkhurst and Appelo, 1999). The simulation used the generalized two-layer model of

Dzombak and Morel (1990) with a single adsorption phase and competitive adsorption of H⁺, AsO₄^{3−}, PO₄^{3−}, SO₄^{2−}, Ca²⁺, Mn²⁺, Mg²⁺, Zn²⁺, Cu⁺ and Pb²⁺. The simulations used a single adsorption site with concentrations ranging from of 2.0 × 10^{−4} to 2.0 × 10^{−2} moles L^{−1}, a surface area of 600 m² g^{−1}, and a mass of solid concentration of 3.4 × 10^{−4} g L^{−1}. These values were computed according to the method described by Dzombak and Morel (1990) and are based on the maximum water concentration of particulate Fe measured in 48 samples during the study period from the Utah Storet Site number 4985320.

3. Results

3.1. Diel variations in T_w, DO, pH

Strong diel variations were observed in T_w, DO and pH during all three sampling periods (September 29–30, 2005; May 24–26, 2006; August 17–18, 2007) (Fig. 2), with all three parameters varying in phase with each other, showing low values during nighttime (e.g., 0600 h) and high values during day time (e.g., 1600 h). During these three sampling periods water temperatures (T_w) ranged from 11.8 to 20.4 °C (September), 17.1 to 27.9 °C (May), and 19.9 to 25.8 °C (August). Dissolved O₂ concentrations ranged from 4.3 to 13.4 mg L^{−1} (September), 0.55 to 22.9 mg L^{−1} (May), and 0.20 to 15.4 mg L^{−1} (August). Values of pH ranged from 8.2 to 8.8 (September), 7.5 to 9.4 (May), and 7.5 to 9.1 (August). Notably the amplitude of the diel changes in these three parameters was higher during the warmer months (May and August) relative to September. Usually water temperatures on August 17–18 would be expected to be warmer than on May 24–25 in this wetland pond. However, starting on May 12, 2006, air temperature was 5.5–10 °C warmer than normal, reaching historical record highs on May 15 and 16 (31–32 °C actual vs. 21 °C average normal), explaining the warmer water temperatures in May as compared to August (Fig. 2).

3.2. Diel changes in Se, As and Mn

Significant diel variations were observed for filtered Se, As and Mn during the same 24-h cycle (Figs. 3 and 4). Filtered As concentration increased 110% in May 24–25, showing a maximum concentration of 13.2 μg L^{−1} occurring at 0300 h, and a minimum concentration of 6.3 μg L^{−1} occurring at 1900 h. Filtered Mn concentrations increased rapidly during suboxic (low to near-zero DO concentration) conditions (mostly early morning) and decreased during oxic periods (daytime) (Fig. 3). Filtered Mn concentration during the diel cycle varied across a factor of 37 in August, ranging from a minimum of 2.9 μg L^{−1} at 1700 h (August 17) to a maximum of 111.5 μg L^{−1} at 0700 h (August 18).

Unfiltered As and Mn concentrations (Fig. 3) generally exceeded filtered As and Mn concentrations during nighttime hours, suggesting the possible association of As and Mn with particulates (>0.45 μm) under these conditions. However, unfiltered and filtered concentrations of As and Mn were equivalent during daylight hours (Fig. 3), indicating removal from the water column of As and Mn particulates that formed during early-morning hours (Fig. 3). Filtered As showed a strong inverse linear relationship with pH ($r = -0.88$, $p < 0.05$), DO ($r = -0.87$, $p < 0.05$), and T_w ($r = -0.84$, $p < 0.05$), whereas Mn showed a fairly good inverse linear correlation with pH ($r = -0.59$, $p < 0.05$), and T_w ($r = -0.65$, $p > 0.05$). Manganese did not correlate with DO.

Filtered Se concentrations in the wetland pond were depleted during nighttime-early morning and enriched in daytime during August (Fig. 4) with an amplitude difference between the minimum and maximum filtered Se concentration of 59%. The September

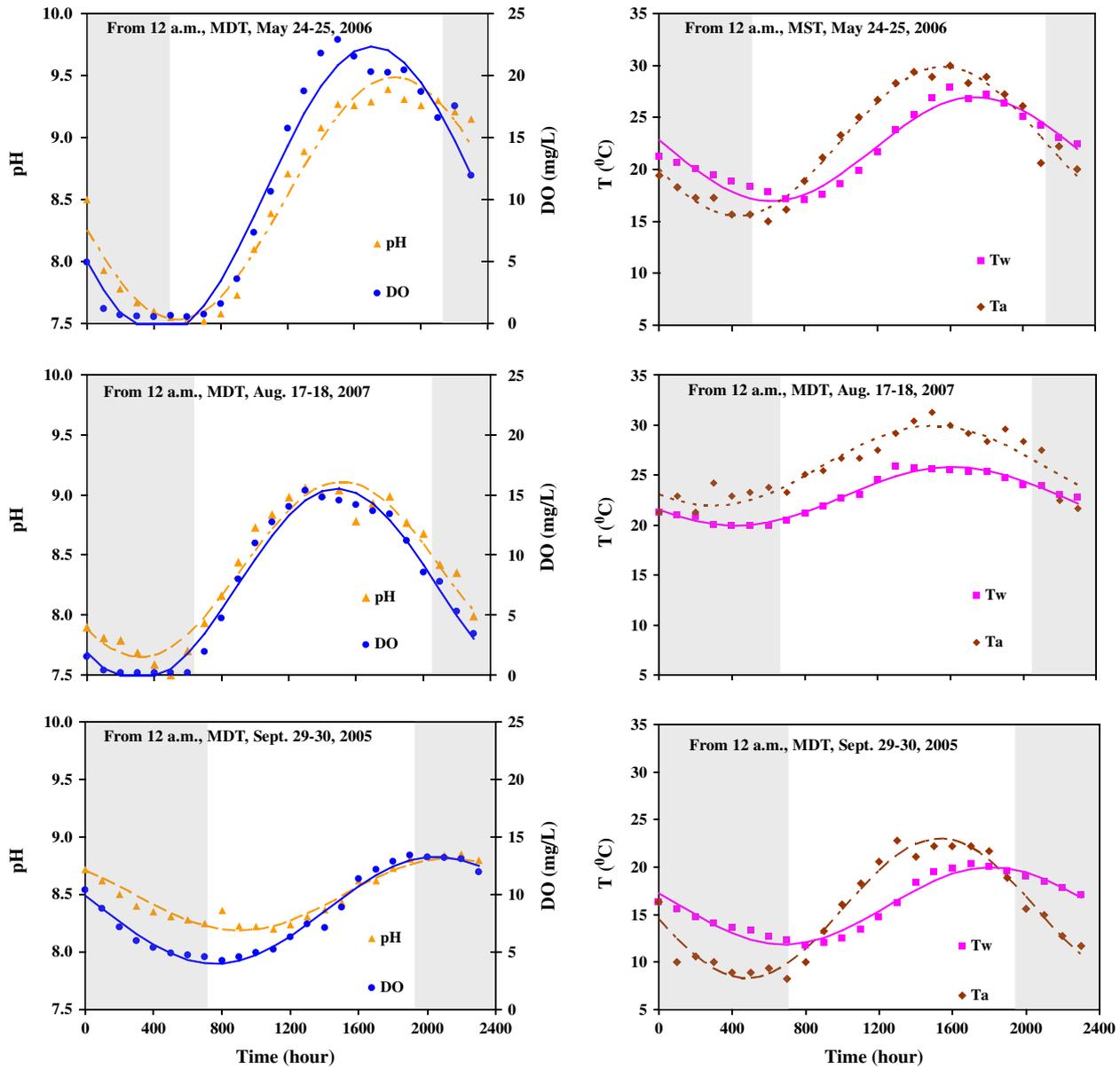


Fig. 2. Hourly (24-h) DO, pH, T_w and air temperature (T_a) observed during May 24–25, 2006, August 17–18, 2007, and September 29–30, 2005, in the GSL wetland. The shaded areas represent nighttime hours.

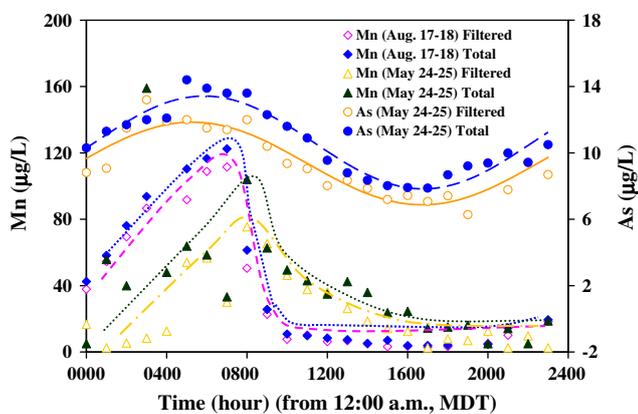


Fig. 3. Diel (24-h) filtered and total (unfiltered) Mn and As concentrations during May 24–25, 2006, and filtered and total (unfiltered) Mn in August 17–18, 2007, in the ADC wetland.

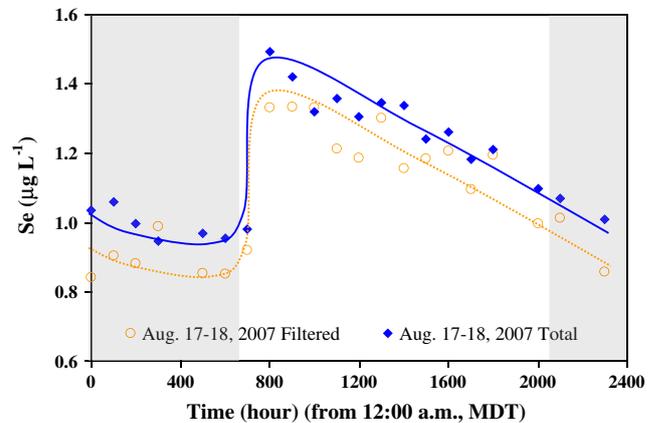


Fig. 4. Diel (24-h) filtered and total (unfiltered) Se concentrations during August 17–18, 2006 in the GSL wetland. The shaded areas represent nighttime hours. Sunrise occurred at 6:40 AM and sunset was recorded at 8:23 PM.

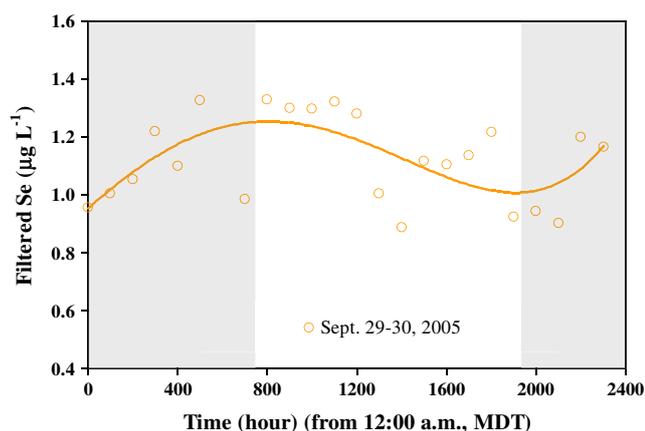


Fig. 5. Diel (24-h) filtered Se concentrations during September 29–30, 2005 in the GSL wetland. The shaded areas represent nighttime hours. Sunrise occurred at 7:23 AM and sunset at 7:11 PM.

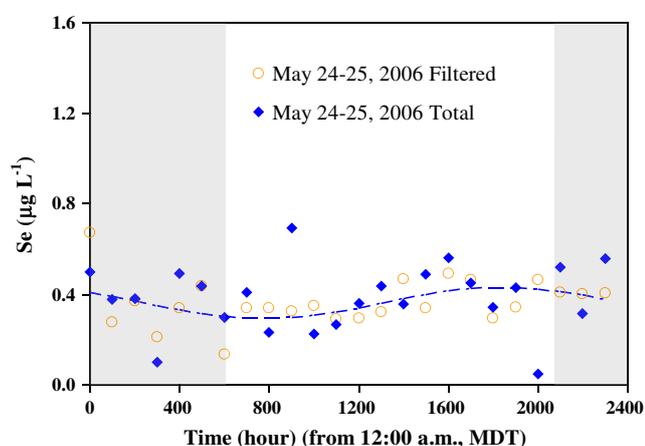


Fig. 6. Observed daily (24-h) dissolved Se concentrations during May 24–25, 2006 in the GSL wetland. The shaded areas represent nighttime hours. Sunrise was recorded at 6:03 AM and sunset at 8:43 PM.

observations do not indicate a clear diel trend, indicating a reduction in the diel cycle magnitude concurrent with the diminished variation in pH, DO, and T_w (Figs. 2 and 5). May observations of filtered Se concentrations showed no clear diel trend and decreased Se concentrations, probably due to unusual high flows (twice the normal flow) (Fig. 6). The seasonal trends in filtered Se concentrations described above are corroborated by recent data (Carling et al., in press).

Unfiltered Se concentrations were practically equivalent to filtered Se concentrations over the diel cycle (Fig. 4), indicating that the vast majority of Se was nominally dissolved. The peak Se concentrations were out-of-phase with peak concentrations of As and Mn (Figs. 3 and 4), with Se concentrations peaking after sunrise, whereas As and Mn concentrations generally peaked during the night. The peak in Se concentration corresponded to a rapid increase in pH and DO concentrations, during the morning when the wetland geochemistry transitioned from suboxic to oxic conditions (Figs. 2 and 4). Selenium appeared to be sensitive to pH (DO) changes particularly between 0700 h and 0900 h when the pH (DO) increased from 7.9 to 8.4 (2–8 mg L⁻¹) and filtered Se increased from 0.93 µg L⁻¹ to 1.30 µg L⁻¹. Filtered Se showed a good linear correlation with pH ($r = 0.74$, $p < 0.05$), DO ($r = 0.75$, $p < 0.05$), and a fairly good relationship with T_w ($r = 0.55$, $p < 0.05$).

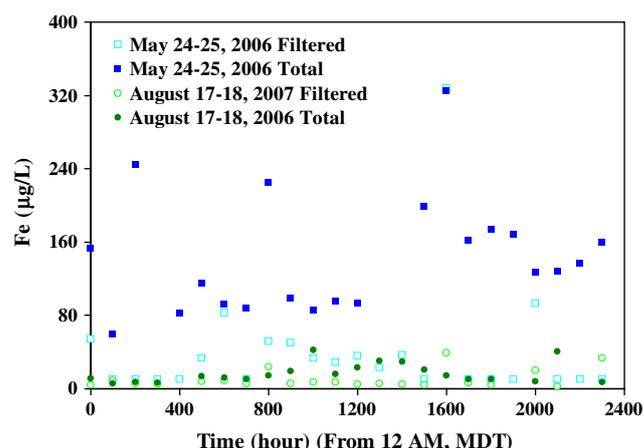


Fig. 7. Observed daily (24-h) dissolved and total Mn and As concentrations during May 24–25, 2006, and total and dissolved Mn in August 17–18, 2007, in the ADC wetland.

3.3. Diel changes in Fe and other elements

Unfiltered Fe concentrations varied by a factor of 6.4 in August 2007, and by a factor of 16 in May 2006 (Fig. 7). Unfiltered Fe concentrations ranged from a minimum of 2.6 µg L⁻¹ at 2100 h (nighttime) to a maximum of 38.8 µg L⁻¹ at 1600 h (daytime) in August, and a minimum of <20 µg L⁻¹ at 2100 h to a maximum of 328 µg L⁻¹ at 1600 h in May (Fig. 7). Comparison of unfiltered and filtered Fe concentrations during the diel period (August) indicated significant formation of particulate Fe (up to 38 µg L⁻¹) (Fig. 7). Filtered Fe did not show any linear correlation with filtered Se and filtered As.

Since diel variations in trace element concentrations can be driven by redox, sorption and other processes, a wide variety of trace elements including Ag, Al, Ba, B, Cd, Cu, Cr, Hg, Ni, Pb, and Zn were monitored during 24-h cycles to determine if they showed diel variation. However, these elements showed no apparent diel changes (Fig. S1, Supplementary material).

Major ions in the wetland pond did not show any apparent diel variation. Effluent concentrations of some major ions varied from May to August. Sulfate and Mg were higher in May (149 mg L⁻¹ and 227 mg L⁻¹, respectively) than August (105 mg L⁻¹ and 56 mg L⁻¹, respectively). Sodium, Ca and K were higher in August than May (221 mg L⁻¹ vs. 104 mg L⁻¹, 89 mg L⁻¹ vs. 55 mg L⁻¹ and 19 mg L⁻¹ vs. 9 mg L⁻¹, respectively). Chloride concentration was as high as 143 mg L⁻¹ in May and <500 mg L⁻¹ in August.

4. Discussion

The Jordan River and its associated canals transport nutrient-rich water to the ADC wetland pond. Intense solar radiation and photosynthetic algal and submerged plant activity drive diel changes in pH, DO, and T_w in this wetland, where algal activity is visually apparent in the form of green mats on the pond surfaces as well high turbidity with green coloration. Chlorophyll a samples ($N = 11$) measured in May 2006 indicated algal cell activity and algal mass, but varied from a minimum of 3.2 µg L⁻¹ at 1900 h to a maximum of 14.1 µg L⁻¹ at 0500 h corresponding to a 344% variation in chlorophyll a during a 24-h period. Although chlorophyll a concentrations varied inversely with DO, pH, and T_w , chlorophyll a concentrations alone may not correlate to algal mass since other chlorophyll components exist that were not measured. The vigor of photosynthesis and respiration processes was evident in the significant DO and pH diel changes. Filtered Se and As were sensitive to changes in pH, DO and water temperature as demonstrated by

the Pearson's coefficient with $r = 0.74$, 0.75 , and 0.55 ($p < 0.05$ for both) for Se with pH, DO and T_w , respectively; and $r = -0.88$, -0.87 , and -0.84 ($p < 0.05$ for both) for As with pH, DO and T_w .

The similarity between unfiltered and filtered concentrations for Se and As throughout the observed diel periods in May and August (Figs. 3 and 4) indicates that the diel variation cannot be explained simply by Se and As mass transfer between dissolved and particulate phases. Furthermore, it suggests that the dissolved Se and As mass was cyclically introduced to, and/or removed from, the water column. Possible mass transfer mechanisms causing the Se diel variation include: (1) daily upstream trace element loading changes, (2) continuous loading with diel volatilization, (3) settling and resuspension of Se precipitants, and (4) sorption and desorption to settling or moored oxyhydroxides.

Daily upstream elemental loading changes represent a possible mechanism of diel changes in filtered and unfiltered Se concentrations. However, if trace element load changes caused diel variations in Se concentrations, it would be difficult to understand how they produced out-of-phase responses in As and Mn concentrations. The hourly inflows did not vary significantly ($5301\text{--}5607\text{ m}^3\text{ h}^{-1}$), further weakening the possibility that the diel variations represent changes in elemental loads to the wetlands.

Continuous loading to the wetland and Se removal by volatilization (Diaz et al., 2009b) may explain the daily variation in filtered Se if the daily volatilization mass removal rate is large enough to justify the shortfall of Se between nighttime and daytime. Volatilization is largely controlled by the concentrations of dissolved volatile Se (Chasteen, 1998), which ranged between 0.4 and 3.7 ng L^{-1} . The volatile Se flux corresponding to the high measured dissolved volatile Se concentration (3.7 ng L^{-1}) as described in Dicaldo et al. (2010), ranged from 0.17 to $0.20\text{ (}\mu\text{gSe m}^{-2}\text{ h}^{-1}\text{)}$, which translates to a volatile Se flow range of $3.58 \times 10^{-5}\text{ kg h}^{-1}$ – $4.21 \times 10^{-5}\text{ kg h}^{-1}$. This volatile Se flux is far too low a removal flow (by three orders of magnitude) to yield the observed mass loss (over the 12-h period) in August (e.g., $107,150\text{ m}^3 \times 0.5\text{ }\mu\text{g L}^{-1} = 5 \times 10^{-2}\text{ kg}$).

Settling of Se precipitants coupled with resuspension and dissolution may represent another mechanism of Se replenishment and removal from the water column. Redox-driven changes in Se speciation may result in the conversion of selenate and selenite (predominantly dissolved species) to mineral phases of Se; e.g., Se(0), and Se(-II), which can settle out of the water column. However, equilibrium geochemical speciation simulations in PHREEQC do not support the production of Se(0) or Se(-II) precipitants during suboxic conditions.

Periodic resuspension processes caused by carp, duck, bird, and macroinvertebrate populations living in this wetland, or via wind or other external causes may affect replenishment of Se in the water column (Carling et al., in press). However, periodic resuspension is an unlikely source to replenish the water column, since both unfiltered and filtered Se (As and Mn) concentrations showed diel variations; whereas resuspension alone would result in only the particulate concentration increase (unfiltered but not filtered). Furthermore, as was true for variable loading, it is difficult to explain how resuspension would yield Se diel variations that were out-of-phase with Mn and As.

Sorption and desorption reactions induced by changes in speciation and pH to settling or moored hydroxides may also explain the rapid changes in filtered Se in the early morning. Because of their prominence in natural environments, Fe oxides (e.g., amorphous Fe-oxyhydroxides) have been found to be important scavengers of Se in wetlands (Masscheleyn and Patrick, 1993). Desorption of selenite species from hydroxides of Fe and/or Mn, induced by the rapid increase in pH ($7.5\text{--}9.1$) between 0700 h and 0900 h may have driven the observed increase in water column Se (Fig. 4). Subsequent decreases in pH and DO during the afternoon, evening and, especially, nighttime (Fig. 2), may allow sorp-

tion of selenite to metal oxyhydroxides removed from the water column by settling or attachment to moored substrates, thereby potentially explaining the depletion of Se in the water column. Similar combinations of speciation and mass transfer may also drive the observed variations in As (and Mn) concentrations.

Simulations of Se and As speciation were performed using PHREEQC (Parkhurst and Appelo, 1999) to determine whether significant changes in Se, and As speciation can be expected in response to the observed pH, DO and T_w variations. Hourly speciation and mass distribution of Se and other trace element species and mineral/gas phases (via SI) were simulated using hourly field-measured data and measured Eh using a Pt electrode, as described in Section 2.

The speciation predictions showed that from 2100 h to 1200 h (suboxic conditions), selenite species (SeO_3^{2-} and HSeO_3^-) were predominant. In contrast, selenate species were predominant during most of the daytime and oxic conditions (1300–2000 h). PHREEQC simulations predicted undersaturation with respect to Se minerals during the diel period, with SI consistently below 0 (ranging from a minimum of -15.2 to a maximum of -1.1) (Table 1). The simulations show that Se precipitation was not favored, and that settling of mineral phases of Se is an unlikely removal mechanism of Se from the water column during the 24-h period. PHREEQC simulations also indicated the production of insignificant concentrations (1.0×10^{-40} – 5.5×10^{-32} (moles kg^{-1})) of selenium hydride (H_2Se) during suboxic conditions.

Simulations in PHREEQC showed that formation of significant mineral phases of Mn is favored including Mn oxyhydroxides, whereas Fe minerals including Fe-oxyhydroxides are consistently oversaturated in the water column. Among the oxides, ferrihydrite or Hfo ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), manganite ($\text{MnO}(\text{OH})$), and pyrolusite (MnO_2) are expected to precipitate ($\text{SI} > 0$). Therefore, the favorability of oxyhydroxide minerals as sorbing surfaces in the water column provides some evidence of the likelihood of sorption and desorption reactions as major mechanisms of mass transfer for Se. PHREEQC simulations indicated dominance of filtered Mn (mostly as Mn^{2+}) under suboxic conditions. Hourly PHREEQC simulations for May data showed also that As(V) was the major species of As in the wetland under both oxic and suboxic conditions.

To test the plausibility of sorption as a possible mechanism driving the diel changes in Se (As) a sorption model was developed using Hfo as an equilibrium phase in PHREEQC. Sorption simulations of Se onto Hfo particles show strong binding of Se (mostly selenite) by Hfo for pH values below 8.0. At $\text{pH} < 8.0$ (at 0700 h) the percentage of Se sorbed was as high as 76%, whereas for $\text{pH} > 8.5$ (after 0900 h) Se sorption decreased dramatically to 35% (Fig. 8), potentially explaining the rapid and significant increase in filtered Se concentration between 0700 and 0900 h in August (Fig. 4). This rapid increase in Se resembles a “step function” indicating high sensitivity of Se speciation and desorption to changes in redox condition and pH, respectively.

The simulated sorption to Hfo surfaces was relatively insensitive to the ratio of Se concentration to Hfo concentration. For example, for $\text{pH} = 7.9$, a range in the ratio from 3.4×10^{-3} to 3.4×10^{-7} produced a range in peak percentage sorbed Se from 76% to 66%. For $\text{pH} = 8.7$ the same range in ratio yielded a range in peak percentage sorbed Se from 35% to 15%, indicating that the observed pH increase during 0700–0900 h can be expected to drive Se from the Hfo surfaces regardless of the Se:Hfo concentration ratio.

To explain the observed diel variations by Se sorption onto and desorption from Hfo, the Hfo particles could be either suspended and $< 0.45\text{ }\mu\text{m}$ in size (“dissolved”) or $> 0.45\text{ }\mu\text{m}$ and permanently attached to plants or moored substrates in the wetland pond since both filtered and unfiltered Se concentrations changed similarly during the 24-h period. Plant surfaces were not sampled for Se during

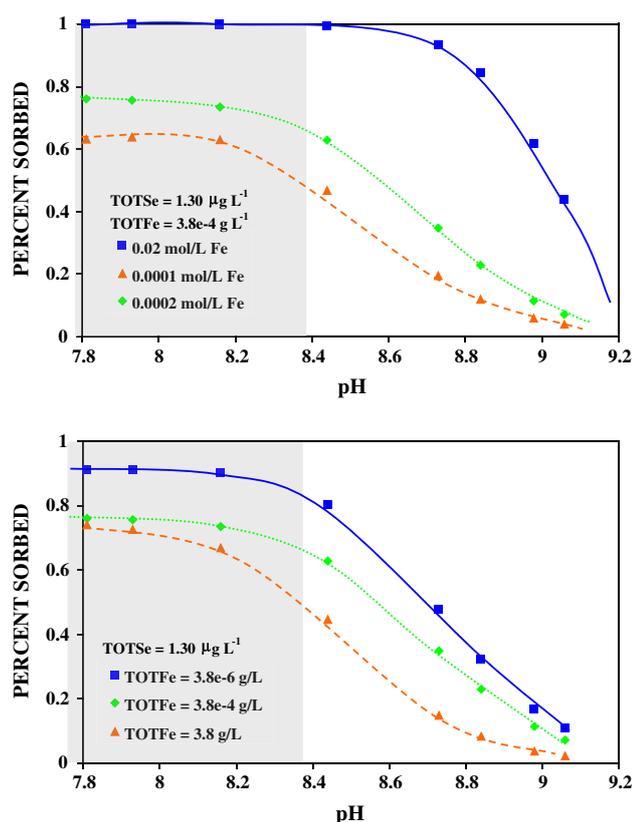


Fig. 8. PHREEQC simulations of percent Se sorbed vs. pH with various site densities of total Fe. The bottom figure was modeled using a site density of 2×10^{-4} moles L^{-1} . The surface area for all models was $600 \text{ m}^2 \text{ g}^{-1}$. The percent sorption of Se was also compared to different concentrations of Fe oxides (Hfo). The sorption edge for Se showed to decrease about 15% with significant decrease in site density of Hfo (two orders of magnitude) and 5% with significant increase in Hfo concentration (four orders of magnitude) at a pH around 8. Shaded areas represent nighttime periods.

the diel study. However, earlier measurements (July 2005) of submerged plants (e.g., *Stuckenia* sp.) in the wetland showed concentrations of total Se equal to $1.91 \pm 0.35 \text{ mg kg}^{-1}$, which, is more than three orders of magnitude greater than the concentration of unfiltered Se in the water column ($1.4 \mu\text{g L}^{-1}$) (Dicaldo et al., 2010).

Reductive dissolution of settled Mn (suboxic condition) can potentially explain the replenishment of filtered and unfiltered Mn concentrations during early morning; whereas precipitation and subsequent rapid settling or attachment to plants of newly formed Mn oxyhydroxide particulates during transition between suboxic and oxic conditions (0700–0900 h) may explain the daytime depletion of Mn (both unfiltered and filtered) (Fig. 3). Apparently, the pH increase that drove Se from Hfo also prevented Se sorption to these Mn oxyhydroxides. It is hypothesized that during the early-morning hours (suboxic conditions), the Mn oxyhydroxides reductively dissolved, as predicted by PHREEQC simulations thereby replenishing Mn in the water column.

Diel variations of dissolved As have previously been linked to pH-induced adsorption onto, and desorption from, surfaces (Fuller and Davis, 1989; Stollenwerk, 2003; Cong et al., 2005), wherein sorption generally decreases with increasing pH (Cong et al., 2005; Appelo and Postma, 2006). In the present study, filtered As concentrations decreased with increasing pH suggesting that mechanisms in addition to sorption governed the As diel behavior. The fact that filtered As concentrations varied in phase with filtered and unfiltered Mn concentrations suggests a possible relationship between Mn and As. This leads us to conclude that during transition between suboxic and oxic conditions, filtered

As(V) sorbed to newly formed Mn oxyhydroxides (and Hfo), which rapidly settled or attached to moored substrates, thereby depleting both As and Mn water column concentrations during daytime. The increase in As concentration during the night may have occurred in response to dissolution of Mn oxyhydroxides under suboxic conditions. The filtered As pattern – high at night and low during daytime – does not resemble the general diel pattern of dissolved As in rivers and streams (Nimick et al., 2003; Gammons et al., 2007). However, river studies by Barringer et al. (2007) showed a similar pattern at one site where As, Mn and Fe increased at night and decreased during the day.

In contrast to Se, As was not driven from Mn oxyhydroxides or Hfo (based on lack of daytime increases in As concentrations), and this is corroborated by PHREEQC simulations of As sorption to Hfo, which showed that As (which occurred mostly as arsenate) was consistently 100% sorbed to Hfo for the measured range of pH (7.5–9.1). In addition, under these conditions As sorption would be expected to increase with temperature, as generally observed for ion adsorption (Nimick et al., 2003; Jones et al., 2004), and is consistent with the observed inverse relationship between filtered As and temperature, although this relationship may also reflect covariation of temperature and pH.

5. Conclusions

The diel variations of Se and As (the latter indirectly) appear to be ultimately driven by algal photosynthesis and respiration, via increased pH (DO concentrations) in the water column during daytime hours and pH (DO) depletion during the early-morning hours.

Algal driven photosynthesis and respiration add or remove dissolved CO_2 or H_2CO_3^* from the carbonate system in the wetland. Hence, removal of CO_2 and concomitant addition of DO by photosynthesis resulted in both pH and DO increase. Conversely, addition of CO_2 and simultaneous removal of DO caused a decrease in pH and DO during hours when respiration dominates over photosynthesis (Chapra, 1997).

Based on equilibrium geochemical speciation simulations it is reasonable to expect that these biologically-driven changes in pH (and DO) drive speciation, which in turn drives phase change, and observed diel variations in the concentrations of filtered (unfiltered) Se, As and Mn.

Although diel cycling of other trace elements (including As and Mn) have been reported elsewhere, the authors are unaware of any other reports on diel Se concentration cycling prior to this study. While the results are based on only one 24-h period in August 2007, they provide evidence that Se responds quickly to the biogeochemical cycles and pH (DO) observed in the wetland studied. An implication of the findings is that overestimation of Se loads in wetlands and other similar aquatic environments may occur if water quality monitoring is performed predominantly during daylight periods. In contrast, As and Mn loads would be grossly underestimated if water samples were collected only during daytime when they reach their lowest concentrations.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.apgeochem.2010.10.011](https://doi.org/10.1016/j.apgeochem.2010.10.011).

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