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Selenium mass balance and flux in water of Pariette Wetlands, Utah (USA)

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ABSTRACT

Selenium (Se) has potentially deleterious impacts on flora and fauna of aquatic ecosystems. As Se moves through a wetlands system, various processes such as sorption onto sediments, plant uptake, and volatilization into the atmosphere can attenuate Se resulting in its storage in the wetlands. A comparison of inlet and outlet Se fluxes can be used to determine the mass of Se stored in a wetlands system. Inlet and outlet total Se concentrations and water discharge were measured at the Pariette Wetlands, UT, and used to calculate Se fluxes. The difference between inputs and outputs or fluxes gave great insight into how much Se was being retained or stored in the wetlands. The average influx of Se was 1530 kg year^{-1} and outflux was 380 kg year^{-1}. On average, 75% (1150 kg year^{-1}) of Se entering the wetlands was retained or stored by some biogeochemical process. Processes associated with Se retention included bioaccumulation into the biota, volatilization by plants and sediments, precipitation of insoluble phases, and sorption to sediments, which accounted for most of the attenuated Se. Water movement through the Pariette Wetlands system did not appreciably alter annual Se attenuation rates. Input, output, storage, and fate of Se for four other wetlands were compared with Pariette Wetlands with Se storage being similar among three of the wetlands: Tulare Lake (65%), Imperial (46%), Brawley (72%), and Pariette (75%).

1. Introduction

In the Western United States, there has been increasing concern about the potentially deleterious impact of selenium (Se) contamination from irrigated agriculture and mining on aquatic ecosystems and associated flora and fauna. In an aquatic ecosystem, water is the most critical vector for mobilizing Se from the geosphere (Maher et al., 2010). For example, in Kesterson Reservoir, California, subsurface agricultural drain water was identified as the source of Se. Selenium was further identified as the cause of embryo abnormalities and mortality for several species of aquatic birds (Ohlendorf et al., 1988). The Pariette Wetlands is located approximately 1 km upstream of the mouth of the Pariette Draw to the Green River and is the oasis of the Uinta Basin in Utah (Fig. 1). Selenium levels within the Pariette Wetland Complex have exceeded the USEPA (U. S. EPA, 2016) water quality standard for wildlife is 1.5 μgL^{-1} (30-day lentic ecosystem), and the Utah State Water Quality for wildlife is 4.6 μgL^{-1} (Wingert and Adams, 2011).

Selenium is a metalloid that exists in five oxidation states; Selenate (Se^{6+}), Selenite (Se^{4+}), elemental Se (Se^{0}), Selenide (Se^{2-}), and organic Se. Selenate is the dominant species in an environment that is aerobic and pH from neutral to alkaline. Selenite and elemental Se dominate in anaerobic and lower pH environments. In certain areas, Se occurs naturally in sedimentary rock formations, especially those formed from marine deposits during the Tertiary and Cretaceous Ages (Seiler, 1995). Weathering of these formations by natural or anthropogenic causes, such as precipitation, runoff, or irrigation return water, can oxidize Se to the two more mobile species, selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}). Once mobilized, Se becomes bioavailable to plants and animals. High concentrations of Se in aquatic ecosystems leads to the accumulation of bioavailable Se by wildlife, causing damage and death (Bañuelos and Lin, 2007).

Once mobilized, dissolved Se in drainage waters may be removed by a variety of attenuation processes operating in wetlands around the drainage channels including co-precipitation with and sorption onto suspended sediment in the water column and stream and pond bed sediments, uptake by wetland vegetation, and microbially-mediated volatilization of Se from wetland soils and plants. Stillings and Amacher (2004) showed that large quantities of Se leached from

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phosphatic black shales in mine waste dumps were co-precipitated with iron oxides formed by oxidation of reduced iron in wetlands downstream from the mine waste dumps. In a companion paper to this one, Jones et al. (2017) showed that Se in wetland and upland soils of the Pariette Draw was co-precipitated and released during seasonal precipitation/dissolution of various salt minerals during alternating wetting/drying cycles. Selenium was also associated with Fe oxide minerals, primarily in the drier upland soils. These findings indicate that seasonal redox conditions play a significant role in the attenuation and release of Se in these arid region wetlands.

Selenate and some organic forms of selenium are soluble and available for plant uptake (Zhang et al., 2004). Plant uptake of Se occurs through the roots and is thus influenced by Se species concentration in water and sediment. Plants actively take up selenate through sulfate transport proteins. Selenium accumulation is determined by Se metabolism of the plant and can be distributed throughout the plant (Sors et al., 2005).

Loss of Se from plants and soils occurs as a result of volatilization. In plants, this occurs when the plant has excess supplies of Se and typically occurs from the roots (Maher et al., 2010). Plants can convert Se to organic forms that bioaccumulate in fish and wildlife (Lemly, 2002). Microbes, plants, and animals convert inorganic Se to organic Se through biomethylation. Volatilization of Se is considered a useful technique for removing Se some from contaminated sites (Hansen et al., 1998; Lauchli, 1993), but only if volatilization rates are high enough to exceed fresh inputs (Bañuelos and Lin, 2007, Bañuelos et al., 2005). On an annual basis, the warmer, somewhat wetter climate in parts of the San Joaquin Valley, CA, for example, would be expected to have higher microbially-mediated Se volatilization rates than arid-region wetlands in colder, drier climates such as at Pariette.

Because little is known about the biogeochemical processes governing Se in the Pariette Wetlands, the specific aims of our study are 1) to estimate the influx, outflux and possible net storage of Se concentration within the wetland 2) to evaluate the effect of irrigation on return flows on Se mobilization, and 3) to test the hypothesis that colder arid-region wetlands volatilize Se at lower rates than warmer, wetter wetlands such as those in the San Joaquin Valley, CA.

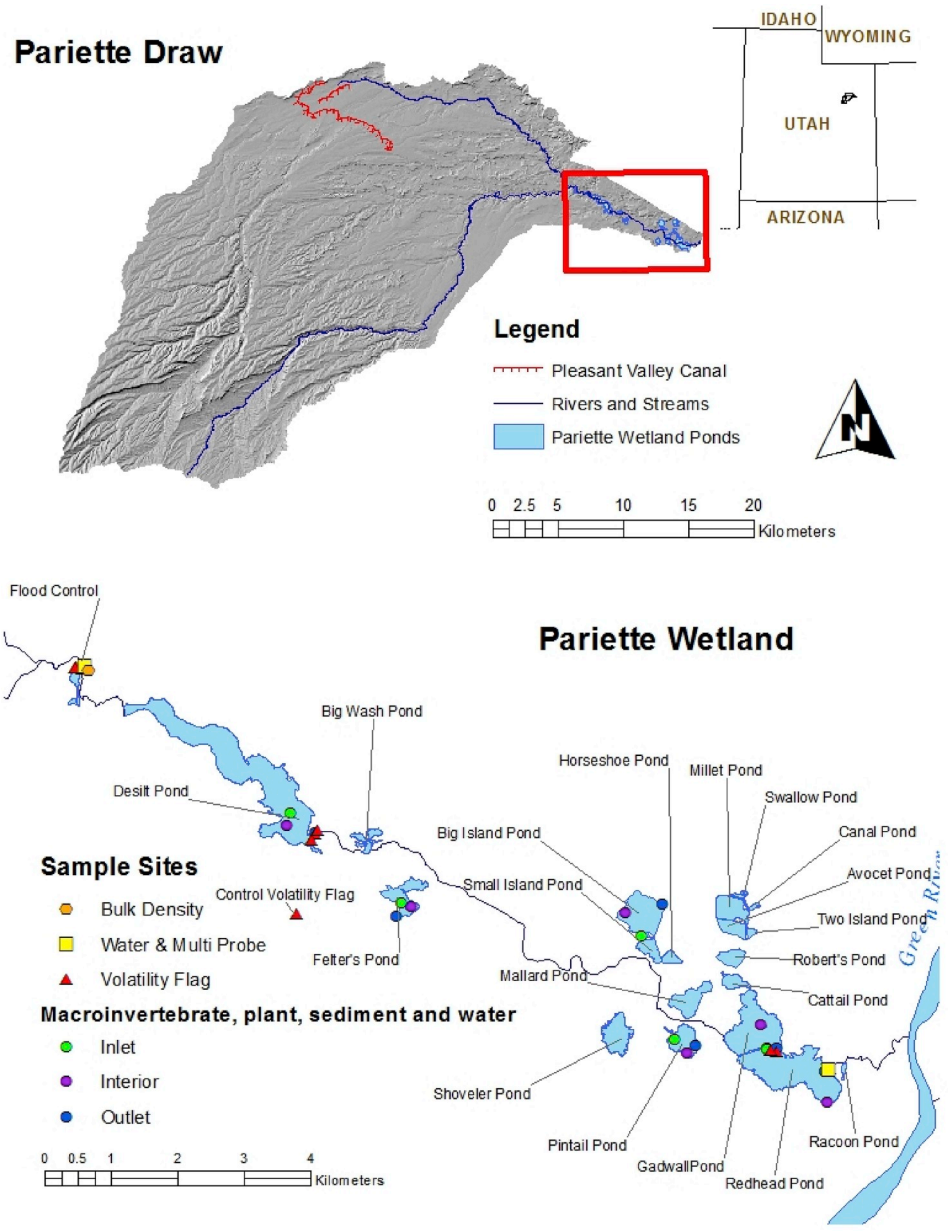

Fig. 1. Map of Pariette Draw and Wetlands, Utah, with sample site pond locations.

2. Materials and methods

2.1. Description of study area

Pariette Wetland Complex is located in the Uinta Basin of the northeastern corner of Utah (Fig. 1). The wetlands were constructed in 1975 to provide habitat for wildlife and currently consists of 20 ponds filled using water diverted from the Pariette Draw through a series of water diversions structures (Zalunardo, 1979). These water structures (dikes, dams, outlet pipes, and trickle tubes) were designed to maintain constant water levels throughout the summer (Darren Williams, personal communication, July 27, 2011). The Pariette Wetlands Complex encompasses 3656 ha, 1023 ha of which are classified as wetlands or riparian areas, and the remaining area is arid desert shrub rangelands (Jones et al., 2015). Wetlands vegetation communities include common reed *Phragmites australis* (Cav.) (Trin. ex Steud.), cattail (*Typha domingensis* Pres. *and Typha latifolia* L.), and bulrush (*Scirpus acutus* Muhl. ex Bigelow). Upland vegetation consisted of a desert shrub community with tufted hair grass (*Deschampsia cespitosa* (L.) P. Beauv.).

2.2. Field methods

Grab samples of surface water were collected monthly (April to October) from the inlet and outlet of the Pariette Wetlands during 2012 and 2014. Clean polyethylene bottles that had been rinsed three times in the field were used to collect water samples. Water samples collected in the field were stored in a cooler on ice until returned to the lab. At the lab, samples and field blanks were filtered through a 0.45-μm filter and acidified with trace-metal grade concentrated HNO_3. Water samples were kept refrigerated at 4 °C until ready for digestion and then analysis.

Water flow rates were measured using a discrete cross-sectional method (Herschy, 2008) measurements made at the time of sampling at the inlet below the Flood Control Structure and the outlet below Redhead Pond (Fig. 1). Water quality parameters and flow measurements from 1993 to 2009 were collected and measured by the Utah Department of Environmental Quality/Division of Water Quality and reported in a TMDL report for Pariette Draw Watershed (Wingert and Adams, 2011).

During the field season 2014, water samples, as well as measurements of pH and oxidation-reduction potentials (ORP), were measured at the surface and the sediment-water interface at collection sites of water and sediment samples. The instrument used to measure pH was a Thermo-Scientific Orion Star A221 handheld field meter, and the electrode used to measure ORP was an Accumet platinum Ag/AgCl combination electrode.

At the same time of the 2014 field season, co-located samples of macroinvertebrates, plant and sediment samples were collected. Three random sediment core samples were collected using a Kajak-Brinkhurst (KB) corer at each sample site. Each sample was subdivided by depth 0–2 cm, 2–5 cm and >5+. Whole wetland plant samples of common reed, cattail, bulrush, and upland tufted hair grass were collected as well. Samples were placed in plastic bags and placed on ice while in the field, and frozen at −20 °C for longer-term storage before transporting for selenium analysis (Fig. 1, Table 1 and Table 2).

Bulk density cores of known volume were collected at six locations (Xystus Amakor, personal communication) separate from the cores for total Se analysis since these were processed differently.

During the active growing season of 2012, twelve Se volatility sample sites were selected based on vegetation type and distributed throughout the wetland complex (Fig. 1 and Table 3). Eleven sites were within the wetland complex, and one upland sample sites were selected to determine if emergent plant bioaccumulation and volatilization affect Se retention within the wetlands. Wetlands sample sites were selected based on proximity to water sampling sites (inlet and outlet) and the three predominant vegetation communities along the edge of the wetlands (Fig. 1 and Table 2). Plant, sediment, and water samples were analyzed by Utah State University's Astrid Jacobson Lab.

Passive trapping of gas-phase Se species at the eleven wetland and one upland site was performed with activated charcoal air filters (BULK filter) cut to 15 cm × 9 cm and placed in a fiberglass window screening sleeve to prevent insects and debris from becoming lodged in the filters (Jayaweera and Biggar, 1996). Charcoal filters were deployed and collected every six weeks (five sampling periods) from March 30, 2012, to November 17, 2012. Each passive filter was attached to the top of a PVC pipe that was attached to a five-foot metal U-post. The filters were placed level with the top of last year's growth of vegetation. After the six weeks, traps were collected and analyzed by Utah State University's

Table 1
Total Se in sediment cores (0–5 cm) collected at various Pariette Wetland sites in 2014.

Pond	Site	Nbr of cores	Mean Total Se, g/m^2	Std err Total Se, g/m^2
Desilt	Inlet	3	0.037	0.003
	Interior	3	0.031	0.001
	Outlet	3	0.142	0.013
Felter's	Inlet	3	0.231	0.021
	Interior	3	0.073	0.015
	Outlet	3	0.066	0.011
Big Island	Inlet	3	0.076	0.009
	Interior	3	0.378	0.056
	Outlet	2	0.049	0.017
Pintail	Inlet	3	0.290	0.040
	Interior	3	0.165	0.064
	Outlet	3	0.072	0.008
Gadwall	Inlet	3	0.263	0.012
	Interior	3	0.225	0.012
	Outlet	3	0.152	0.011
Redhead	Inlet	3	0.052	0.001
	Interior	3	0.144	0.012
	Outlet	3	0.190	0.014

Table 2
Mean ± std err selenium concentrations in plant taxa (F = flower, S = vegetative material (leaves and stems), and R = root) collected in Pariette Wetlands during 2012.

Emergent Taxa	Part	n	[Se] (mg kg^{-1})
Bulrush	F	5	0.22 ± 0.15
Bulrush	S	17	0.48 ± 0.29
Bulrush	R	9	0.57 ± 0.41
Cattail	F	7	0.32 ± 0.10
Cattail	S	25	0.38 ± 0.32
Cattail	R	10	1.11 ± 0.83
Common Reed	F	6	0.27 ± 0.05
Common Reed	S	19	0.23 ± 0.13
Common Reed	R	4	0.31 ± 0.09

Table 3
Total air-borne Se captured by charcoal filters mounted at the top of the vegetation canopy during the March 30 through November 17 growing season of 2012 at the eleven wetland sites and one upland site.

Location	Plant taxa	Total Se volatilized (μg)
Flood control	Cattail	1.784
	Bulrush	1.404
	Common Reed	1.616
Desilt pond	Common Reed	2.773
	Bulrush	4.546
	Cattail	2.112
Redhead Pond	Cattail	1.956
	Bulrush	1.768
	Cattail	2.378
	Bulrush	2.378
	Common Reed	2.355
Upland BLM site	Tufted Hairgrass	1.427

Poisonous Plant Lab, using inductively coupled plasma mass spectrometry (ICP-MS) (Table 3).

2.3. Laboratory analysis

Water samples were digested using sulfuric acid-potassium peroxydisulfate method. Total Se was analyzed by hydride generation atomic absorption spectroscopy (HG-AAS) (EPA Method 7741A) (Cutter, 1986).

Wetland sediment samples were thawed immediately preceding analysis when subsamples were weighed in their moist state for digestion and moisture content. Subsamples of wetland sediment samples were prepared for Se analysis by the nitric-perchloric digestion method and reduced to selenite with hydrochloric acid (HCl) (Zasoski and Burau, 1977). Selenium was analyzed by hydride generation atomic absorption spectrometry (HG-AAS) using a Varian AA240 with a VGA 77 vapor generation accessory and a SP3 autosampler (Varian Inc., Walnut Creek, CA) (Cutter, 1986).

Bulk density cores were oven-dried at 105 °C and weighed. Bulk density was calculated as the mass of oven-dried sediment divided by the volume of each core. Total Se in each wetland sediment core, g m^{-2} was calculated from the concentration of Se in each core, mg kg^{-1} times the depth of the core, m times the bulk density of separately measured cores, Mg m^{-3}.

Plant samples were prepared by soaking them for 30 s in 0.3% sodium lauryl sulfate, 1 mM HCL, and deionized water to remove surface contamination (Pilon-Smits et al., 1999). Tissues were dried for 24 h in a convection oven at 80 °C. Dried plant tissue was then finely ground and digested with nitric acid following standard procedures (Zasoski and Burau, 1977). Samples were then analyzed using HG-AAS (Cutter, 1986).

Volatile Se filter samples were cut into smaller pieces to increase the surface area for extraction and digestion using 6% H_2O_2 in 0.05 NaOH overnight, shaken, and then filtered to remove charcoal (Wu et al., 2003). Samples were then analyzed via ICP-MS (EPA Method 6020A) (Faires, 1993). The Se concentrations in the extracts were converted from μg L^{-1} to μg of Se collected during each charcoal filter deployment period by multiplying the Se concentrations in the filter extracts by the extractant volume. The total mass of Se in μg collected at each site over the growing season was calculated by summing the amounts of Se trapped during each six-week sampling period. A Se volatilization index was calculated by dividing total Se volatilized per growing season or year by the estimated total mass of Se stored in wetland soils and sediments.

Quality control was monitored with blanks, analytical replicates, matrix-matched spiked samples, and standard reference materials consisting of National Institute of Standards and Technology (NIST) 2709a San Joaquin soil for soils and sediments or NIST 1573a tomato leaves for invertebrates and plants. The average coefficient of variation for analytical (laboratory) replicates was 9%, and spike recovery ranged from 94 to 113%. Percent recoveries of Se in NIST 1573a and NIST 2709a were 153% and 86%, respectively.

2.4. Statistical analysis and flux calculations

Statistical analysis of variance was performed with Deducer, a GUI interface for R (Fellows, 2012). Multiple comparisons of plant, sediment, and water sample variables among sites, species, tissue type, and season were conducted using a gaussian generalized linear model.

Selenium and Total Dissolved Solids (TDS) fluxes into and out of Pariette Wetlands were calculated with Equation (1):

$$F = Q^* C^*86 \quad [1]$$

where F = mass flux, g day^{-1}; Q = inflow or outflow discharge, m^3 s^{-1}; C = Se concentration, g m^{-3}, and 86,400 s day^{-1} converts seconds to days (Stillings et al., 2007) (Figs. 3 and 4).

Operation of USGS gauging stations above and below Pariette Wetlands was discontinued in 1984. After that period, irrigation practices in Pleasant Valley changed from flood to sprinkler irrigation (1985–2005) to reduce salinity load on Pariette Draw watershed (Wingert and Adams, 2011). Currently, 94% of Pleasant Valley's irrigation is sprinkler (Wingert and Adams, 2011). Average monthly flow data from 2006 to 2012 were combined with average monthly precipitation and evapotranspiration data obtained from the Utah Climate Center Myton Station (Table 4) to estimate the transit time for water and dissolved Se water to move through the wetlands (Fig. 2).

Residence time was calculated with Equation (2):

$$\tau = V / Q * 86{,}400 \quad [2]$$

where τ = residence time, day; V = total volume of wetlands estimated from area and average depth of ponds and canals, m^{-3} (Table 5); Q = flow at the outlet, m^3 s^{-1}; and 86,400 s day^{-1} converts to time to days (Stillings et al., 2007).

Comparison of flux, total sediment Se, plant uptake of Se, and volatilized Se in various selected wetlands was taken from previous studies of Tulare Lake, CA (Gao et al., 2003), Imperial Valley and Brawley, CA (Johnson et al., 2009), and Clark County Wetlands Park, NV (Pollard et al., 2007) with Pariette Wetland Complex (Jones et al., 2017) and Se concentrations from sediment, plant, and volatilized Se from this paper (Table 6).

3. Results and discussion

3.1. Wetland hydrology and Se and TDS influx and outflux

Key factors contributing to discharge were precipitation (average annual precipitation = 15.7 ± 0.7 cm (Frankenberger and Karlson, 1994; Prono, 2008)) and irrigation return water. The total volume and flow of water for the wetlands varied depending on the season and the availability of irrigation return water based on no statistical difference of regression comparison of irrigation return flow and precipitation (Fig. 3a). On average, discharge begins to increase in March due to spring runoff and decreases at the end of April until the irrigation season begins. Then, discharge peaks in June (beginning of irrigation season) and decreases in July and August at the end of irrigation season. The area will typically have a late rainy season (September through November) when discharge again increases (Fig. 3a). Most of the water entering the wetlands is diverted from the Duchesne River via the Pleasant Valley Canal (Fig. 1). On average, approximately 4.25 m^3 s^{-1} of water rights are diverted during the irrigation season, which spans from May to October. A few springs also provided a minimal source of water for the draw (Wingert and Adams, 2011).

Table 4
Average monthly precipitation (mm) and reference evapotranspiration mm d^{-1} during 2006–2012 at Myton, Utah Climate Center Station; flow at outlet (m^3 s^{-1}); and calculated residence time of water flow averaged by month from 2006 to 2012 at Pariette Wetlands.

Month	Monthly Precipitation (mm)	ET (mm d^{-1})	Flow at inlet (m^3 s^{-1})	Flow at outlet (m^3 s^{-1})	Residence Time (days)
January	6.2	0.4	–	0.10	220
February	5.6	1.0	–	0.16	142
March	5.2	2.3	1.29	0.77	30
April	9.6	3.8	0.56	0.20	116
May	18.6	5.1	1.01	0.32	72
June	15.3	6.6	3.53	0.70	33
July	19.2	6.9	0.58	0.10	230
August	13.9	6.0	0.30	0.17	134
September	21.2	4.3	1.89	0.33	68
October	21.1	2.4	0.66	0.58	39
November	4.6	1.3	0.40	0.13	179
December	20.7	0.5	–	0.07	310

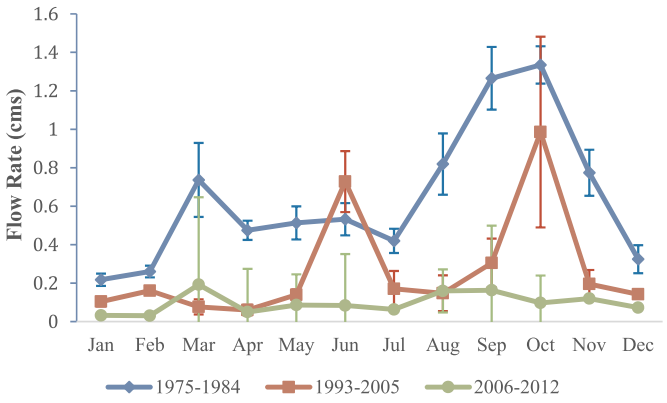

Fig. 2. Mean ± std err of flow rate (m^3s^{-1}) measured at Redhead Pond outlet of Pariette Wetlands, Utah to compare hydrology of three time periods 1975–1984 (blue diamonds - USGS gaging station), 1993–2005 (red squares - transition period from flood to sprinkler irrigation) and 2006–2012 (green circles - post-transition to sprinkler irrigation). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

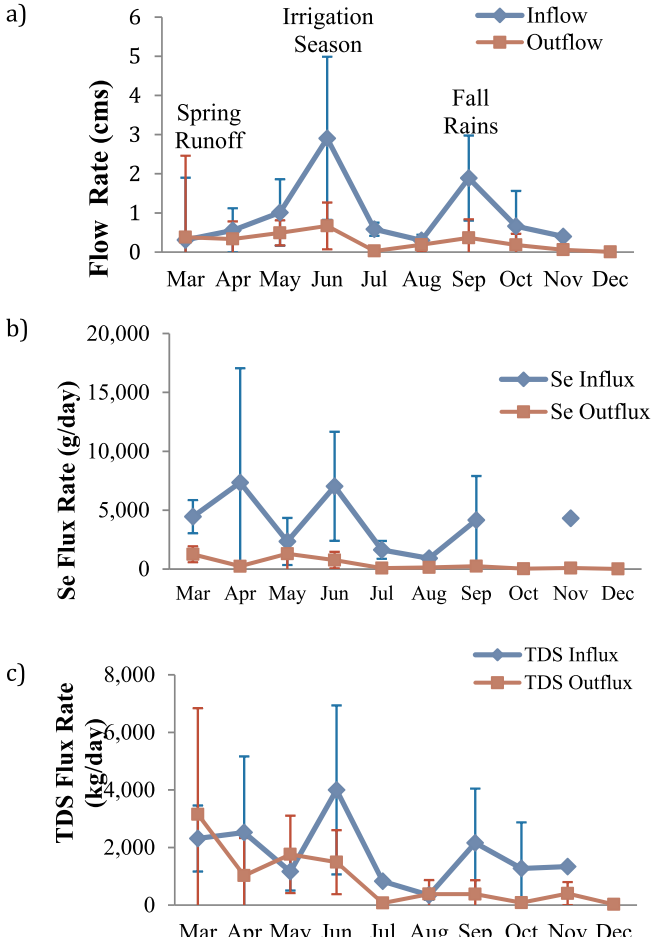

Fig. 3. Mean ± maximum and minimum a) flow rate (m^3s^{-1}), b) dissolved Se concentration flux rate (g day^{-1}), and c) Total Dissolved Solids (TDS) flux rate (g day^{-1}) at inlet (red diamonds) and outlet (blue diamonds) of Pariette Wetlands, Utah with peaks representing high flow events during spring runoff, irrigation season, and fall rains (2006–2012). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The estimated total volume of water in ponds is 1,971,939 m^3 (Table 5). Residence time is the shortest at the beginning of spring runoff in March (30 days), during peak irrigation season in June (33 days), and at the end of irrigation season in October (39 days). Calculation is based on outflow and volume. In March and October, the ponds are near empty and then refill during spring runoff and fall rains. Although discharge is higher in June than March, residence time in June is actually slightly longer than in March. In June, maximum vegetation biomass with associated transpiration of water tend to correspond with peak flow at inlet and helps retain water volume. In other words, the extra biomass causes the water to remain in the ponds longer because water velocity is reduced because the water must navigate around and through all the vegetation. Also, when ponds are nearly full, water transit pathways are much longer. Residence time is longer during winter [December (310 days), January (220 days), and February (142 days)] due to low flows. Potential sources of water loss not accounted for in this study may be evaporation, evapotranspiration, and groundwater recharge, which were not directly measured during the study. Not enough data have been collected to calculate a complete hydrologic mass balance of the wetlands.

Selenium and TDS concentrations and flow were used to calculate flux. On average, the highest influx of Se occurs in April (7342 g day-1; n = 2; range 474 to 14,209 g day^{-1}), and the lowest in August (915 g day-1; n = 4; range 545 to 1226 g day^{-1}), but Se influx in June was not significantly different than that in April (spring rains) or September (fall rains). Thus, the hypothesis that irrigation return water mobilizes as much Se as precipitation is confirmed. The Se outflux was highest in May (1303 g day^{-1}; n = 4; range 73 to 3364 g day^{-1}) and lowest in December (12 g day^{-1}; n = 1) (Fig. 3b). The average TDS flux rate follows a similar flux rate at the inlet versus the outlet (Fig. 3c). There were a few times during the year where the average TDS flux rate at the outlet exceeded the rate at the inlet (March, May, and August). The highest TDS influx occurs in June (4001 kg day^{-1}; n = 5; range 1107 to 7141 kg day^{-1}) and the lowest in August (345 kg day^{-1}; n = 4; range 164–551 kg day^{-1}). The TDS outflux was highest in March (3152 kg day^{-1}; n = 1) and lowest December (24 kg day^{-1}; n = 1). The drops in TDS influx and outflux can be a result of dissolved solids settling out in the Desilt Ponds upstream of the outlet, as evidenced by the buildup of sediments in the Desilt Pond (Darren Williams, personal communication).

3.2. Se mass balance

A mass-balance for Se was created using the mass inflow, mass outflow, and the retained components. Discharge at the inflow and outflow were used to calculate the influx, outflux, and stored or lost Se for a year. The amount of Se retained or lost in the wetlands on average was 1150 kg $year^{-1}$. About 25% of the selenium entering the wetlands exited the wetlands at the outlet. Compared to vegetation accumulation and volatilization of Se, most (about 75%) Se entering the Pariette wetland was stored in wetland sediments (Fig. 4).

3.3. Se stored in wetland sediments

Total Se in the upper 5 cm of wetland sediments collected from KB core samples ranged from 0.031 to 0.378 g m^{-2} with a mean ± std err of 0.146 ± 0.024 g m^{-2} (pond inlet, interior, and outlet total Se data in Table 1). Some ponds had more sediment Se near the inlet end (e.g., Felters and Pintail), whereas others accumulated more Se at the outlet (e.g., Desilt, Redhead). There was no clear spatial trend in wetland sediment Se accumulation. Wetland sediment core bulk densities used to calculate total sediment Se in g m^{-2} from mg kg^{-1} units ranged from 1.03 to 1.34 Mg m^{-3} with a mean ± std err of 1.16 ± 0.07 Mg m^{-3}.

Scaled over the entire 1023 ha (2529 acres) of classified wetlands within the wetland complex total Se stored in the upper 5 cm of wetland sediment was 1408 ± 226 kg. Total Se below the 0–5 cm layer of wetland sediment was less than that in the top 5 cm (Jones et al., 2015)

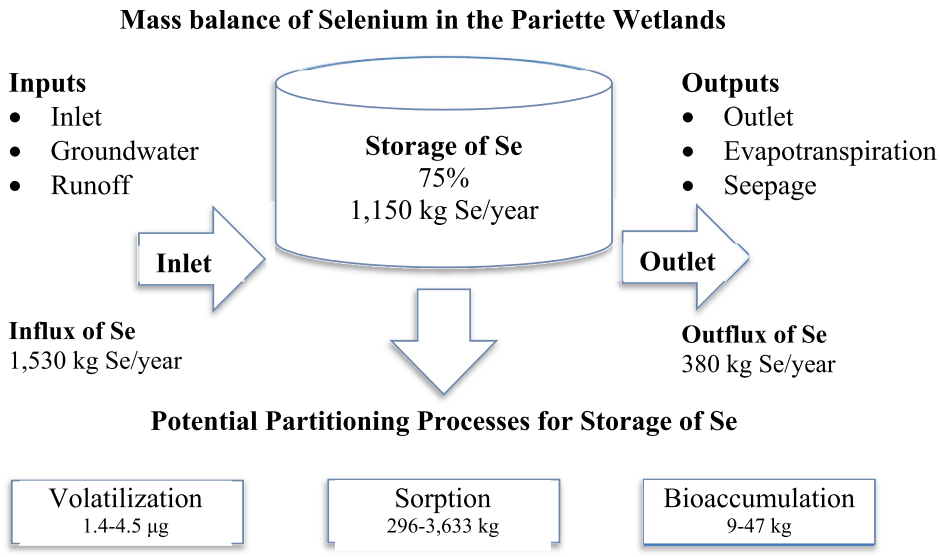

Fig. 4. Mass balance of selenium in pariette wetlands, Utah.

Table 5
Area (m^2) and estimated average depth of ponds and canals (m) used to calculate total volume (m^3) of water in Pariette Wetlands.

Pond	Area (m^2)	Average Depth (m)	Volume (m^3)
Flood Control	27,357	0.61	16,677
Desilt	801,278	0.61	488,459
Big Wash	38,000	0.46	17,374
Felter's	100,605	0.76	76,661
Small Island	43,301	0.61	26,397
Big Island	185,872	1.83	339,923
Horseshoe	22,541	0.46	10,306
Millet	88,707	0.15	13,519
Swallow	7244	0.46	3312
Canal	7891	0.46	3608
Avocet	47,955	0.15	7308
Two Island	9105	0.76	6938
Robert's	46,175	0.10	4644
Cattail	37,636	0.76	28,678
Mallard	94,373	0.46	43,147
Shoveler	108,092	0.61	65,893
Pintail	86,077	0.61	52,472
Gadwall	283,604	0.91	259,327
Redhead	411,201	1.22	501,337
Raccoon	6515	0.91	5958
Total	2,453,530	12.90	1,971,939

indicating that Se tended to accumulate in the upper sediment layer either through sedimentation or sorption onto the sediment surfaces at the bottom of the pond water column and upper sediment interface (hyporheic zone). As Se was removed from the flowing water column, it would first accumulate in the sediment at the pond water column – sediment interface. The 75% removal of Se from the inlet flux (storage) and the large amount of Se stored in wetland sediments (1405 kg) indicate that seasonal Se co-precipitation and sorption processes (Jones et al., 2017) are the main Se attenuation factors in the Pariette wetlands. Distribution of Se in soil profiles are associated with the distribution of soluble salts that mobilize by either the movement of the water table and evapotranspiration.

Biogeochemical processes play an essential role in determining which species of Se is most abundant and bioavailable to plants and wildlife inhabiting the wetland. Selenate is the primary bioavailable form of Se, and, thus, the form that poses the greatest threat to the environment, especially under alkaline pH and aerobic conditions (Ohlendorf, 2003). Measurements taken during July 2014 field season were used to construct a stability diagram based on published Eh-pH stability diagrams (Reddy and DeLaune, 2008). At the surface, the dominant Se species are selenate and selenite (Fig. 5a). Then at the sediment-water interface, the dominant Se species are selenide (Fig. 5b). Due to redox and pH conditions, selenide is sorbed to sediments and is not bioavailable for flora and fauna. However, the wetlands received their highest Se loads during spring runoff in March and again during peak irrigation season in June. These times could be problematic for waterfowl in the wetlands because it is the beginning of their breeding season. Thus, both seasonal precipitation and irrigation may cause increased mobilization of Se and lead to water quality criteria exceedances of EPA's 1.5 μgL^{-1} (30-day lentic ecosystem) (U. S. EPA, 2016). Out of the 91 water samples taken from 1993 to 2012, 86% of the samples exceed the EPA criteria.

3.4. Plant uptake of Se

Several studies have shown that Se uptake by plants begins with the roots, and depending on the Se species will determine the rate of translocation of Se from the root to shoot (Zayed et al., 1998). A generalized linear model analysis to examine differences in Se concentration between species, time of sampling, and sampling location indicated that species and date sampled were not significantly different during the sampling period. However, the sample site was significantly different with wetlands sites having notably higher concentrations than the upland site.

The Pariette Wetlands covers an area of approximately 1023 ha. Assuming that the aboveground dry matter (DM) biomass yield ranged from 2.15 to 11.50 kg m^{-2} (Acharya and Adhikari, 2010) and the average aboveground Se concentration of plants in the wetland was 0.4 mg kg^{-1} DM, the total amount of Se accumulated and stored in the aboveground biomass would range from 9 to 47 kg, a relatively small fraction of the total amount of Se stored (1150 kg Se) in the wetland (<5%).

3.5. Se volatilization

The total mass of Se volatilized and captured by the charcoal filter traps at the top of the vegetation canopy at each of the eleven wetland sites and one upland site during the 2012 growing season are listed in Table 3. A range of 1.4–4.5 µg of Se was volatilized at all wetland sites with a mean of 2.3 ± 0.45 µg. In contrast, the upland site lost 1.4 µg over the same period. Mean Se volatilization at the Flood Control, Desilt

Table 6
Comparison of Se flux, total sediment Se, plant uptake of Se, and volatilized Se in various selected wetlands.

Variable		Wetlands				
		Tulare Lake Drainage District[e], CA	Imperial[f], CA	Brawley[f], Ca	Clark County Wetlands Park, NV	Pariette, UT
Mean annual temp[a], deg C		17.3	22.5	22.25	20.75	8.2
Mean annual precip[a], mm		192	75	80	106	178
Area, ha		1.14	17.5	3.6	53	1023
Mean annual inflow, $m^c\ s^{-1}$		0.00367	0.18	0.031	0.07	6.45
Principal plant taxa		Schoenoplectus spp. Juncus spp. Spartina spp. Polypogon spp. Rupia spp. Typha spp.	Schoenoplectus spp. Tamarix spp.	Schoenoplectus spp. Tamarix spp.	Scirpus spp. Typha spp. Najas spp. Chara spp.	Scirpus spp. Typha spp. Phragmites spp.
Total Se in water, ug L^{-1}		19–22	3.6	3.1	19.6	3-6 (1991) 0.1–1.6 (2014)
Total Se flux	Inlet, kg	8.108	123	18		1530
	Outlet, kg	2.863	66	5		380
	Storage, kg	5.245	57	13		1150
Total sediment Se	Mean conc., mg kg^{-1}	Litter: 11-19 Detritus: 7-12 Sediment (0–5 cm): 1-3	0.3	0.4		2.373
	Total[b], kg	2.633	8	2		1405
Plant biomass[c]	Mean conc., kg ha^{-1}		3000	3000		$2.15–11.5 \times 10^d$
	Total[b], kg		3600	1350		$2.2–11.8 \times 10^7$
Plant Se (above ground)[c]	Mean conc., mg kg^{-1}		0.7	0.4	1.3	0.4
	Total[b], kg	0.046	0.013	0.002		9–47
Se volatilized	Mean rate, g d^{-1}	0.148	22	5		1.00×10^{-08}
	Total, g	180	49,000	11,000		2.30×10^{-06}
Volatilization factor[d], %		2	40	61		1.50×10^{-10}

Reference: Tulare Lake, CA: Gao et al. (2003).
Reference: Imperial Valley and Brawley, CA: Johnson et al. (2009).
Reference: Clark County Wetlands Park, NV: Pollard et al. (2007).
Reference: Pariette, UT: Water Se concentrations (Jones et al., 2015); soil, plant, and volatilized Se (this paper).
[a] US climate data for Corcoran, CA (Tulare Lake), Brawley, CA, Imperial, CA, and Myton, UT (Pariette) (https://www.usclimatedata.com).
[b] Total for wetland area.
[c] Total for all principal plant taxa.
[d] Total Se volatilized as percentage of input total Se.
[e] The entire drainage district is 178,000 ha. The constructed wetlands experiment was 1.14 ha (10 × 15 × 76 m cells). Inflow rate calculated from total m3 of applied water divided by the duration of the experiment. Se volatilization rate calculated from total Se volatilized divided by the duration of the experiment.
[f] Sediment and plant Se concentrations are median rather than mean values.

Pond, and Redhead Pond sites was 1.6 ± 0.1, 3.1 ± 0.7, and 2.2 ± 0.1 μg, respectively. Air-borne Se was highest at the Desilt Pond bulrush community (4.5 μg).

Air-borne Se due to microbially-mediated Se volatilization from vegetation and sediments is negligible compared to other mass balance compartments in the wetland (Fig. 4). However, it does appear that the wetland loses more Se because of volatilization than upland sites, although there was only one upland site for comparison. Plant and sediment volatilization rates are not significant contributors to Se partitioning process and removal from wetland systems (Bañuelos and Lin, 2007).

3.6. Comparison of Pariette Wetlands to other wetlands with elevated levels of Se

It is instructive to compare the input, output, storage, and fate of Se in the Pariette Wetlands with other wetlands that have elevated levels of Se (Table 6). The Tulare Lake (Gao et al., 2003), Imperial and Brawley wetlands in CA (Johnson et al., 2009), and Clark County Wetlands Park (CCWP), NV (Pollard et al., 2007) are all constructed wetlands, whereas Pariette has a natural stream with adjacent riparian areas and a series of constructed ponds with adjacent wetlands. The Tulare Lake wetlands system was experimental and was designed and constructed to test the capability of wetlands to remove Se from agricultural drainage waters. Imperial and Brawley were constructed to treat water from the New River and agricultural drainage waters. The CCWP is adjacent to the Las Vegas Wash, which conducts treated wastewater to Lake Mead.

Storage of Se was compared between constructed wetlands to determine if Pariette Wetlands Complex performs biogeochemically different than similar wetland systems. Because wetland inlet and outlet Se fluxes are dictated by both Se concentrations in the water and water discharge rates, the inlet and outlet fluxes of the wetlands listed in Table 6 vary by several orders of magnitude with discharge having the most significant contribution to Se flux. Pariette has the largest inlet and outlet fluxes even though it has the lowest Se concentrations simply because its discharge rate is so much larger than that of the other wetlands. Tulare Lake had the smallest Se flux values even though it had the highest Se concentrations because it was the smallest wetland in terms of area and water flow. Se storage in the wetlands was calculated as the difference between inlet and outlet Se fluxes. They too varied widely with the larger Pariette storing the most Se mass compared to the much smaller Tulare Lake experimental wetland. However, when expressed as a percentage of inlet flux, Se storage was much more similar among the wetlands: Tulare Lake (65%), Imperial (46%), Brawley (72%), and Pariette (75%). Thus, these wetlands stored almost half to three-quarters of their Se input.

Sediment Se concentrations varied among the wetlands ranging from 0.3 mg kg^{-1} in Imperial to 1–3 mg kg^{-1} in Tulare Lake and 2.3 mg kg^{-1} in Pariette. Tulare Lake also had data for Se concentrations of the litter and detritus fractions of the sediment. These had much higher Se concentrations. Organic fractions of wetland sediment were not assessed for the other wetlands in Table 6, but the high Se concentrations in the organic fractions in Tulare Lake sediment indicate that these fractions should be considered in other studies of the fate of wetland Se. Plant Se

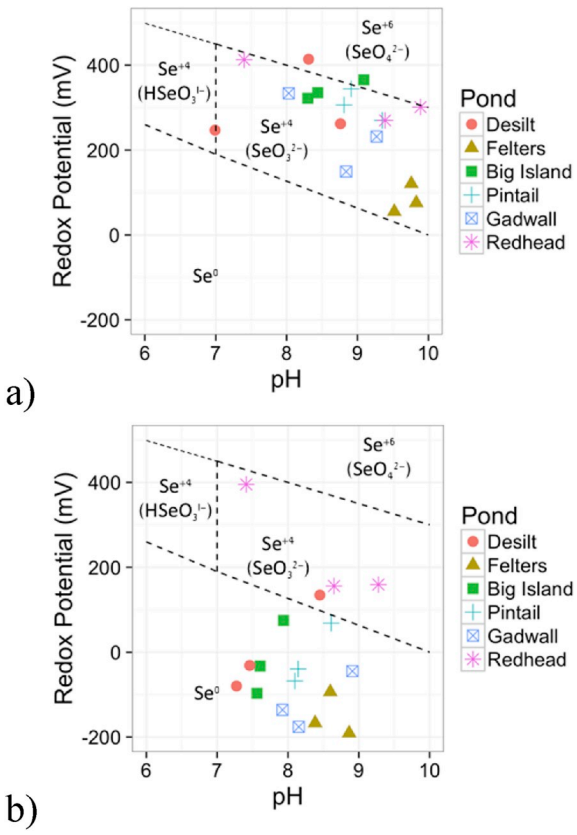

Fig. 5. Se species stability diagram: a) surface water and b) sediment-water interface (selenate = Se^{6+}, Selenite = Se^{4+}, and selenide = Se^{0}) using pH and redox potential (mV) measurements collected in July 2014 of ponds in Pariette Wetlands, Utah.

concentrations also did not vary much among the wetlands ranging from 0.4 mg kg^{-1} at Pariette, with similar concentrations at Imperial and Brawley, up to 1.3 mg kg^{-1} at CCWP, which had the same principal plant taxa as Pariette. Since Se concentrations in water at CCWP were much higher than at Pariette, the higher plant Se concentrations in the former likely reflected the fact that plant roots were in contact with higher Se concentration water. Unfortunately, sediment Se was not measured at CCWP, so we have no measure of how much Se is stored in that wetland's sediments. Although sediment and plant Se concentrations do not show an extensive range of variability among the wetlands, the total mass of Se stored in sediments and plants does vary widely, which reflects the area of each wetland; the larger the areal extent of the wetland, the greater the total Se mass it can store overall.

Se volatilization factors, as defined by the mass of Se volatilized expressed as a percentage of the mass of inlet Se varied considerably among the wetlands. The Johnson et al. (2009) paper lists Se volatilization percentages of 40% and 61% for Imperial and Brawley, respectively, far above those of Tulare Lake and Pariette. The estimated Se volatilization at Imperial and Brawley was not directly measured, but rather was calculated based on indirect assumptions. Johnson et al. (2009) did not provide a sediment sampling depth but rather stated that grab samples were taken from the sediment surface. Thus, they may have significantly underestimated the amount of Se stored in the sediments of their two wetlands. Without actual Se volatilization measurements, there is no means of determining how much Se was lost from the sediment and plant canopies via volatilization. Se volatilization rates at Tulare Lake, which has a temperature regime similar to that of Imperial and Brawley and which were measured, are far below those calculated for Imperial and Brawley and seem much more realistic. Pariette had a Se volatilization factor orders of magnitude less than Tulare Lake. Even though different Se volatilization rate methods were used at Tulare Lake (chamber-based method) and Pariette (passive trapping of air-borne Se by charcoal filters at the top of the plant canopies), we attribute the lower Se loss rate at Pariette to the far lower temperature regime. Mean annual temperature at Tulare Lake is more than double that at Pariette. The increase in Se volatilization rates with increasing temperature is well established (Frankenberger and Karlson, 1994), and the measured Se loss rates at Tulare Lake and Pariette reflect this temperature influence. Without a significant increase in Se volatilization, this is not a viable remediation method and cannot overcome much larger continuing Se inputs to the wetlands.

4. Implications to biota

The mass of Se retained in the Pariette Wetlands may be problematic to wildlife feeding in the area, depending on the mechanism of removal of Se from the water. If Se is sorbed to sediments as controlled by pH and redox potentials, then Se is not available to wildlife. However, if Se is accumulating in plants, insect, amphibians or in aquatic or benthic organisms that wildlife feed on, there is potential for bioaccumulation of Se to toxic levels detrimental to egg-laying organisms such as waterfowl and fish (Henry et al., 2019; Lemly, 2002; Ohlendorf, 2002; Presser, 1994). Based on mass-balance calculations, the wetlands received its highest Se loads during spring runoff in March and again during peak irrigation season in June. March could be problematic for waterfowl in the wetlands because it is the beginning of their breeding season.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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