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Abstract: Selenium (Se) contamination of public lands and water is a result of irrigated agriculture and mining activities in areas rich in Se geologic deposits. Pariette Draw is part of the northern Colorado Plateau and is an area of concern for Se contamination in the Pariette Wetlands. Pariette Wetlands, a wetland built in the 1970s to provide wildlife habitat, is distinguished by its arid climate and a short growing season of hot dry summers followed by cold winters with several months below freezing. An understanding of how Se is mobilized and removed within the wetland will provide management strategies that minimize and mitigate Se contamination and promote sustainable ecosystem services. The data collected in 2012 and 2014 was the first comprehensive spatial and temporal analysis of Se in all environmental compartments (bird eggs, macroinvertebrates, plants, sediments, and water) of an arid wetland ecosystem in the Colorado Plateau. Water, sediment, and plant tissue samples were collected and analyzed to determine Se's spatial and temporal variation in Pariette Wetlands. Se concentrations in water, sediment, and plants were evenly distributed throughout wetlands. No significant differences were found in plant Se concentrations between samples collected in 2012  $(447 \pm 44 \text{ ug kg}^{-1})$  or 2014  $(541 \pm 42 \text{ \mu g kg}^{-1})$ , indicating that plant Se did not vary temporally during sampling. Aquatic plant species (e.g., pondweed (*Potamogeton filiformis*),  $743 \pm 66 \ \mu g \ kg^{-1}$  and watermilfoil (*Myriophyllum spicatum*),  $874 \pm 122 \ \mu g \ kg^{-1}$ ) accumulated more Se than plant species growing at the edges of the ponds (e.g., hardstem bulrush (*Schoenoplectus acutus*),  $368 \pm 37 \ \mu g \ kg^{-1}$ and cattail (Typha),  $420 \pm 43 \ \mu g \ kg^{-1}$ ). Plant roots ( $1045 \pm 110 \ \mu g \ kg^{-1}$ ) accumulated more Se than above ground vegetation (flowers,  $228 \pm 17 \ \mu g \ kg^{-1}$  or stems,  $224 \pm 19 \ \mu g \ kg^{-1}$ ). Relative to Se retained by sediments (75%), plants were not an extensive reservoir of wetland Se (<5%) but still may pose a risk to animals feeding on plant tissue. Thus, phytoremediation of Se does not appear to be a viable tool for Se mitigation in wetlands of arid climates with a short growing season, such as those located in the Colorado Plateau.

Keywords: selenium; constructed wetland; biogeochemistry; Pariette Wetlands; Colorado Plateau

# 1. Introduction

Selenium (Se) is an essential micronutrient for both animals and plants that is known to be beneficial in low doses and toxic in high doses [1]. Similar to sulfur (S), the physiochemical characteristics allow Se to non-specifically bind in place of S during protein synthesis [2]. Plants typically uptake Se non-specifically as S analogs and following the uptake, they are incorporated by sulfate assimilation pathways into selenocysteine and selenomethionine and other organic S compounds by transporters in the root cell membrane [3]. In other wetlands with a longer growing season, plants can be used to remove Se from areas of concern via bioremediation and potentially harvesting for commercial biofortification [4].

In lower doses, Se plays an essential role in reducing oxidative stress in cells with selenoenzymes and selenoproteins. Selenocysteine, an amino acid at the center of the glutathione peroxidase (GSH) enzyme, inhibits peroxide formation during metabolism



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and acts as a powerful antioxidant through the GSH pathway to produce compounds that are part of the reactive oxygen species (ROS) scavenging system and cell detoxification process [5,6]. Other studies have reported on the importance of Se in the protection of cells [7,8] and its toxicity when taken at more than toxic thresholds [2,9–12].

In human health, at low doses, Se is an important component of several metabolic pathways which include thyroid hormone metabolism, immune function, and antioxidant defense systems [13]. At higher doses, Se has the potential to cause the following health problems in humans: (1) short-term: fatigue and irritability; hair and fingernail changes; damage to the peripheral nervous system; (2) long-term: damage to the nervous and circulatory systems; damage to kidney and liver tissue; and hair and fingernail loss [14]. However, in veterinary medicine, Se deficiency diseases causing toxicosis have also been reported [15]. High concentrations of Se cause toxicity in plants which impedes plant growth and development and causes chlorosis, necrosis, and reduced protein biosynthesis [16,17]. Most plants can avoid toxicity by metabolizing selenomethionine into a volatile dimethyllselenide a form of organic Se [18].

Se occurs naturally in sedimentary rock formations, especially those formed from marine deposits during the Tertiary and Cretaceous Ages [19]. The weathering of these formations by natural or anthropogenic causes, such as precipitation, runoff, or irrigation return water can oxidize Se into more soluble and mobile species [20]. Once mobilized, Se becomes bioavailable and in high concentrations leads to accumulation in plants and wildlife in aquatic ecosystems [21]. Se has four oxidative states: Selenate (Se<sup>6+</sup>), Selenite (Se<sup>4+</sup>), elemental Se (Se<sup>0</sup>), and Selenide (Se<sup>2-</sup>), and the oxidative state of Se determines its bioavailability [22]. Selenate, the more oxidized state, and some organic forms of selenium are more soluble and, therefore, more available for plant uptake [23].

Kesterson National Wildlife Refuge in the San Joaquin Valley, California is an example of an environmental contamination disaster caused by Se caused by agricultural irrigation return water drainage [24]. High concentrations of Se resulted in high rates of embryonic deformity and death in aquatic wildlife [25]. Similarly, the middle Green River area of the Uinta Basin, Utah has been identified as an area with significantly high Se contamination. Several studies conducted in the 1980s by the US Geological Survey (USGS), US Fish and Wildlife Service (USFWS), and the US Bureau of Land Management (BLM) identified three areas of concern for Se contamination, including Stewart Lake Waterfowl Management Area (SLWM), Ouray National Wildlife Refuge (ONWR), and Pariette Wetlands (Figure 1) [26]. Pariette Wetlands, the focus of the USGS study, led to the mediation of Se contamination by replacing flood irrigation with sprinkler irrigation methods to reduce erosion of geologic formations with high concentrations of Se [27].

Sediments serve as a reserve source of Se and dissolved Se is depleted by plant uptake. Desorption from sediments can replenish the dissolved Se to feed plant uptake. The dominant mechanism driving the distribution and accumulation of salts and soluble Se in the upper horizons of the wetlands soils are attributed to capillary migration caused by a fluctuating water table influenced by a deluge of irrigation return water and high evapotranspiration rates coupled with low precipitation [28]. The accumulation and distribution of Se within plant tissues are determined by the plant's metabolism processes. The uptake of Se in plants begins at the roots and is influenced by the concentration of Se in water and sediment. Plants actively take up selenate through sulfate transport proteins. Selenite is taken up through passive diffusion and can be inhibited by phosphate [29].

Surface water samples collected at Pariette Wetlands by the Utah Division of Water Quality's TMDL report [30] from 1995 to 2010 showed spatial and seasonal variation with a yearly average Se concentration at the inlet  $(5.8 \pm 4.2 \ \mu g \ L^{-1})$  slightly higher than at the outlet  $(3.7 \pm 3.6 \ \mu g \ L^{-1})$  [30,31]. The highest Se concentrations occurred at low flow during the winter months (December, January, and February). The lowest Se concentrations occurred during the peak irrigation season (June, July, and August), indicating that irrigation water addition to the wetlands tended to dilute soluble Se levels already in the wetlands. Although Se concentrations tended to be lower in the Desilt Pond,

a larger pond and wetlands after the inlet of the Flood Control Structure (Figure 1). Se concentrations tended to remain relatively constant as water traversed the wetland ponds. The change in Se concentration at the outlet of the wetland was significantly less than that at the inlet [31].



**Figure 1.** Upper map of Pariette Draw and Pariette Wetlands in the red box. Lower map is Pariette Wetland's plant, sediment, and water sample sites for the summer field season of 2012 and 2014 (Modified from Jones et al.) [31].

Jones et al. [31] found that 75% of the input Se into the Pariette Wetland is retained within the wetland with sediment storage accounting for most retained Se. Moreover, plant uptake accounted for 3 to 16% removal of Se per year within the wetland, while volatilization was a minor removal process of 0.4 to 1% per year. However, Jones et al. [31] did not examine many aspects of plant removal of Se, such as spatial distribution within the wetland, Se uptake over time, which plant species accumulated the most Se, and Se accumulation by plant part.

The purpose of this study was to determine the natural attenuation processes responsible for mitigating Se within the Pariette wetland. An understanding of these processes will result in best management practices that will minimize and mitigate Se contamination and promote sustainable ecosystem services. Specifically, we wanted to determine if wetland plants accumulated and retained enough Se to make phytoremediation of Se a viable best management practice. We hypothesize that because wetland species roots are in close contact with dissolved Se in the wetland water column and Se sorbs to wetland sediments, plant roots are likely to store the most Se before translocation into other parts of the plant, such as stems, leaves, and flowers. Various representative plant species and plant parts within each species were sampled throughout the Pariette Wetlands to test these hypotheses.

### 2. Materials and Methods

#### 2.1. Description of Study Area

Pariette Wetlands is in the northeastern corner of Utah (Figure 1). In 1975, the BLM constructed surface flow wetlands to provide a habitat for wildlife as well as to filter runoff from irrigation and return water from upstream agricultural fields. The complex encompasses 3656 ha, 1023 ha of which are classified as wetlands or riparian areas, and the remaining 2633 ha area is arid desert shrub rangelands [32]. The wetland's emergent vegetation communities include common reed (*Phragmites australis* (Cav.) Trin. ex Steud.), cattail (*Typha domingensis* Pres. *and Typha latifolia* L.), hardstem bulrush (*Schoenoplectus acutus* Muhl. ex Bigelow), and alkali bulrush (*Schoenoplectus maritimus* L.) while the submerged aquatic vegetation consists of Chara (*Chara spp.* L.), Pondweed (*Potamogeton filiformis* L.), and Watermilfoil (*Myriophyllum spicatum* L.).

Pariette Wetlands Complex currently consists of 20 ponds filled using water diverted from the Pariette Draw through a series of water-diversion structures and canals [33]. The BLM designed the system (dikes, dams, outlet pipes, and trickle tubes) to maintain constant water levels throughout the summer. The spatial distribution of dissolved selenium flows through Pariette Wetlands ponds from the inlet at Flood Control Structure to the ponds of Desilt, Felter's, Big Island, Pintail, Gadwall, and exits the outlet of Redhead (Figure 1) [27].

#### 2.2. Field Methods

During the 2012 and 2014 field seasons, water samples were collected in clean polyethylene bottles that had been rinsed three times in the field from the various ponds of the Pariette Wetlands Complex (Figure 1). Water samples collected in the field were stored in a cooler on ice until returned to the lab for storage. At the lab, samples and field blanks were filtered through a 0.45-µm filter and acidified with trace-metal grade concentrated HNO<sub>3</sub>. Water samples were kept refrigerated at 4 °C until ready for digestion and then analysis [34].

Whole emergent and vegetative plants were dug by shovel and tissues were separated by flower, stem, and root for Se concentration analysis. During the active growing season of 2012, eleven plant sample sites were selected based on vegetation type and distributed throughout the Pariette Wetlands Complex. Sample sites of the wetlands were selected based on proximity to water sampling sites (inlet and outlet) and predominant vegetation communities along the wetlands' edge (Figure 1).

Se sediment concentrations used for the 2012 statistical analysis were taken from a soil pit in the Flood Control area approximately 10 m from the edge of wetlands in somewhat poorly drained soils. The methods are as described in Jones et al. [28]. During the 2014 field season, sampling was expanded to include co-located samples of plant, sediment, and water samples. At each sample site, three random sediment core samples were collected using a Kajak-Brinkhurst (KB) corer. Whole wetland plant samples (*P. australis, Typha, S. acutus,* and *S. maritimus*) and submerged aquatic plants (*Chara, P. filiformis* and *M. spicatum*) 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.

Utah State University's Astrid Jacobson Lab analyzed plant, sediment, and water samples for Se concentration.

#### 2.3. Laboratory and Statistical Analysis

Water samples were digested using the sulfuric acid-potassium peroxydisulfate method. Total Se was analyzed by hydride generation atomic absorption spectroscopy (HG-AAS) (EPA Method 7741A) [35,36]. 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 [37]. 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 [38]. Samples were then analyzed using HG-AAS [35]. Details for sediment sample processing, analysis, and quality control for water, plant, and sediment samples can be found in Jones et al. [31]. Statistical analysis and graphing were performed with Deducer, a GUI interface for R [39]. Data is available at https://digitalcommons.usu.edu/all\_datasets/204/, accessed on 12 December 2022).

### 3. Results

### 3.1. Temporal Variation of Plant Se Concentration

The focus of plant species sampling in 2012 was to assess plant uptake by common wetland species throughout the wetland complex at the inlet, Flood Control Pond, to the interior Desilt Pond, and then to the outlet ponds, Gadwall and Redhead Ponds. While in 2014, the focus of sampling was to assess the risk of Se to biota in the interior ponds (Desilt, Felters, Big Island, Pintail, Gadwall, and Redhead Ponds) [32]. Both plant datasets were combined to determine if there was any change between years. Although the 2014 sampling was more extensive than that in 2012, both datasets were sufficient to indicate that in the overall plant mean Se concentrations between years were not significantly different with a *p*-value of 0.12 using a Welch two-sample *t*-test.

### 3.2. Spatial Distribution of Se in Water, Sediments and Plants

A combined and log-scaled spatial comparison of the datasets for water, sediment, and plant samples showed the spatial changes in the Se concentration within the wetland complex (Figure 2). The average total Se concentration in water was the highest at the inlet of Flood Control Pond (5.4  $\pm$  1.9 µg L<sup>-1</sup>), lowest at the Desilt Pond (0.7  $\pm$  0.03 µg L<sup>-1</sup>), and Gadwall Pond (0.9  $\pm$  0.2 µg L<sup>-1</sup>). The interior ponds, Felters (1.3  $\pm$  0.03 µg L<sup>-1</sup>), Big Island  $(1.2 \pm 0.1 \text{ µg L}^{-1})$ , and Pintail  $(1.4 \pm 0.2 \text{ µg L}^{-1})$ , have similar Se concentrations. The Se concentration in the water at Redhead Pond was the third lowest (Figure 2). The average Se concentration in the sediment was the highest in Gadwall Pond (3154  $\pm$  283  $\mu$ g kg<sup>-</sup> 1) and Redhead Pond (2252  $\pm$  436  $\mu$ g kg<sup>-1</sup>) near the outlet to the wetlands complex. The lowest concentration was at the Flood Control Pond ( $16 \pm 8 \,\mu g \, kg^{-1}$ ). However, the Flood Control sample was not a KB core sample taken within the pond but taken from a soil pit taken adjacent to the pond. The interior ponds Desilt (1186  $\pm$  786 µg kg<sup>-1</sup>), Felters  $(1881 \pm 399 \ \mu g \ kg^{-1})$ , Big Island  $(2206 \pm 786 \ \mu g \ kg^{-1})$ , and Pintail  $(2070 \pm 609 \ \mu g \ kg^{-1})$ ponds had similar concentrations (Figure 2 and Table 1). The average plant Se concentration remained relatively constant throughout the length of the Pariette Wetlands (Figure 2 and Table 1). The highest Se concentrations averages were the interior ponds, Big Island Pond  $(906 \pm 180 \ \mu g \ kg^{-1})$ , and Pintail Pond  $(680 \pm 101 \ \mu g \ kg^{-1})$ . The lowest average was at the inlet at the Flood Control Pond (259  $\pm$  21 µg kg<sup>-1</sup>). The other ponds were not significantly different from each other, Desilt Pond (319  $\pm$  26 µg kg<sup>-1</sup>), Felters Pond (439  $\pm$  57 µg kg<sup>-1</sup>), Gadwall Pond (449  $\pm$  47 µg kg<sup>-1</sup>), and Redhead Pond (502  $\pm$  49 µg kg<sup>-1</sup>) (Figure 2 and Table 1).





Summary Statistics	n	$\begin{array}{l} \mbox{Mean} \pm \mbox{Std Err} \\ \mbox{$\mu g$ $L^{-1}$ or} \\ \mbox{$\mu g$ $kg^{-1}$} \end{array}$	Min μg L <sup>-1</sup> or μg kg <sup>-1</sup>	Max μg L <sup>-1</sup> or μg kg <sup>-1</sup>
Water				
Flood Control	4	$5.4 \pm 1.9$	1.8	9.3
Desilt	3	$0.7\pm0.03$	0.7	0.8
Felters	3	$1.3\pm0.03$	1.3	1.4
Big Island	3	$1.2\pm0.06$	1.1	1.3
Pintail	3	$1.4\pm0.2$	1.1	1.7
Gadwall	3	$0.9\pm0.2$	0.6	1.3
Redhead	3	$1.0\pm0.2$	0.6	1.4
Sediment				
Flood Control	3	$16.1\pm7.8$	3.5	30.2
Desilt	9	$1186\pm786$	482	7031
Felters	9	$1881\pm399$	868	4090
Big Island	9	$2206\pm786$	132	7031
Pintail	9	$2070\pm609$	257	5344
Gadwall	9	$3154\pm283$	2092	4458
Redhead	9	$2252\pm436$	602	4559
Plant *				
Flood Control	24	$259\pm21$	110	430
Desilt	67	$319\pm26$	50	980
Felters	45	$439\pm57$	41	1709
Big Island	57	$906 \pm 180$	43	6476
Pintail	45	$680\pm101$	55	3262
Gadwall	65	$449\pm47$	0.6	1479
Redhead	100	$502\pm49$	26	2800

**Table 1.** Summary statistics of selenium concentration in water ( $\mu$ g L<sup>-1</sup>), sediment, and plants ( $\mu$ g kg<sup>-1</sup>) samples taken from Pariette Wetlands during the field season 2012 and 2014.

Note: \* average is pooled across all plant sample.

# 3.3. Plant Species and Part Se Concentration

Submerged aquatic plant species chara (*Chara* spp.), pondweed (*P. filiformis*), and watermilfoil (*M. spicatum*) had significantly higher average Se concentrations than emergent vegetation with *M. spicatum* with the highest whole plant concentration of  $874 \pm 122 \ \mu g \ kg^{-1}$ (Figure 3 and Table 2). Emergent plant species alkali Bulrush (*S. maritimus*), bulrush (*S. acutus*), catail (*Typha*), and common reed (*P. australis*) had lower average Se concentrations with *S. maritimus* highest average Se concentration  $534 \pm 147 \ \mu g \ kg^{-1}$  and *S. acutus* with the lowest  $368 \pm 37 \ \mu g \ kg^{-1}$  of emergent vegetation (Figure 3 and Table 2).



**Figure 3.** Box and whisker plot of log scale of Se concentrations ( $\mu$ g kg<sup>-1</sup>) by plant species alkali bulrush (*S. maritimus*), bulrush (*S. acutus*), catail (*Typha*), common reed *P. australis*), chara (*Chara spp.*), pondweed (*P. filiformis*), and watermilfoil (*M. spicatum*) of emergent and submerged vegetation from Pariette Wetlands (the pink and blue dots represent outliers to the data set).

**Table 2.** Summary statistics of selenium concentrations ( $\mu g k g^{-1}$ ) by plant species in the root, stem, flower, and whole plant tissue.

Species	Root (µg kg <sup>-1</sup> )	Stem (µg kg <sup>-1</sup> )	Flower (µg kg <sup>-1</sup> )	Whole Plant (µg kg <sup>-1</sup> )
Emergent Vegetatior	ı			
S. maritimus	$1188 \pm 128$	$278\pm25$	$235\pm20$	$534\pm147$ *
S. acutus	$743\pm72$	$227\pm35$	$152\pm15$	$368 \pm 37$ *
Typha	$897\pm97$	$196.0\pm30.0$	$207\pm22$	$420\pm43$ *
P. australis	$2755\pm768$	$240\pm28$	$376\pm42$	$832\pm226$ *
Submerged Vegetation	on			
Chara spp.	$929 \pm 194$	$656 \pm 173$	$675\pm162$	$637\pm26$
P. filiformis	NA	NA	NA	$775\pm68$
M. spicatum	NA	NA	NA	$874 \pm 122$

Note: \* average is pooled across all plant sample.

There was a significant difference (*p*-value  $1.2 \times 10^{-31}$ ) using a Kruskal–Wallis chisquared test in Se concentration between roots compared to stems and flowers in plant tissue samples collected during the study period (Figure 4). The highest average value was in the root tissue of *P. australis* (2755 ± 768 µg kg<sup>-1</sup>) and *S. maritimus* (1188 ± 128) (Figure 4 and Table 2). The lowest average values were in the stems and flowering portions of *S. maritimus*, *S. acutus*, and *Typha* (Figure 4 and Table 2). *S. acutus* and *Typha* had somewhat similar average Se concentrations  $368\pm 37 \ \mu g \ kg^{-1}$  (*n* = 110) and  $420 \pm 43 \ \mu g \ kg^{-1}$ (*n* = 149), whereas *S. maritimus* had a higher average Se concentration ( $534 \pm 147 \ \mu g \ kg^{-1}$ (*n* = 10)) (Table 2).



**Figure 4.** Box and whisker plot of log scale of Se concentrations ( $\mu$ g kg<sup>-1</sup>) by part of plant tissue of root, stem, and flower from the vegetation of Pariette Wetlands (the black dot is an outlier of the data set).

### 4. Discussion

#### 4.1. Mass Balance of Selenium

It is imperative for land managers seeking to manage Se contamination in wetland ecosystems in arid climates within the Colorado Plateau, such as Pariette Wetlands, to consider the short length of the growing season for plants to accumulate Se for bioremediation. Therefore, adequate water saturation of wetland sediments is key to the anaerobic conditions that sorb Se to the surface of sediments preventing bioavailability.

In a previous study, a mass balance of Se indicated that sediments retained an impressive 75% of the dissolved Se entering the Pariette Wetlands [31]. On average 1530 kg of Se per year enters via the inlet, groundwater, and runoff and 380 kg per year exits via the outlet, evapotranspiration, and seepage of the wetlands complex. The most notable portioning processes for the storage of Se are sorption onto sediments, followed by bioaccumulation by plants and animals, and the least by volatilizations. The sediment fraction constituted a majority of Se sorbed (296–3633 kg), bioaccumulation (9–47 kg), and volatilization (1.4–4.5  $\mu$ g) constituted minor storage processes in this wetlands complex [31].

At Pariette Wetlands, the total amount of Se accumulated and stored in the aboveground biomass was from 9 to 47 kg. The above-ground biomass of Se is a relatively small fraction of the total amount of Se stored (1150 kg Se) in the wetland (<5%), a calculation that assumed the aboveground dry matter (DM) biomass yield ranged from 2.2 to 12 kg m<sup>-2</sup> [31]. The average aboveground Se concentration of plants in the wetland was 0.4 mg kg<sup>-1</sup> DM, and Pariette Wetlands cover an area of approximately 1023 hectares [40]. The consensus of data from similarly constructed wetlands exposed to Se contamination similarly reports higher concentrations at the inlet than at the outlet, indicating that the wetland acts as a sink for Se removal from water entering the wetlands [41–44]. Most of the Se was immobilized as a result of sorption to sediments as well as bioaccumulation and volatilization by plants and microbes [41–44]. A 36-hectare constructed wetland located at the Chevron Refinery Marsh adjacent to San Francisco Bay, California reported a similar amount of removal of Se (70%) from the inflow of water Se concentration of 20–30 µg L<sup>-1</sup> and outflow of <5 µg L<sup>-1</sup> [43]. Biological volatilization accounted for 10 to 30% of the Se removed. The remaining Se was removed by sediments and plants [43].

Figure 2 shows that Se is widely distributed in water, sediment, and plant tissue of the Pariette Wetlands. Se accumulation in plants ranged from 0.03 to 6.5 mg kg<sup>-1</sup> and is

similar to elevated concentrations reported by Hansen [43], Garcia-Hernandez [45], and Pollard [46]. The highest concentrations of Se at Pariette Wetlands were in the roots of *P. australis* (6.5 mg kg<sup>-1</sup>) and *Typha* (3.2 mg kg<sup>-1</sup>). The spatial distribution data of Se supports the high degree of mobility of Se in these wetlands as documented in previous papers [28,31]. No short-term year-to-year differences in plant accumulation were found, indicating a relatively constant level of input, output, and storage of Se in the wetlands. Plant roots accumulated significantly more Se than aboveground plant parts because of the continuous close contact of roots with seleniferous water and sediment [47]. Although submerged aquatic plants tended to accumulate more Se than emergent plants at the wetland edges, the large extent of variability precluded significant differences in the averages between emergent and submerged vegetation. Regardless of location within the wetland or the species, Se is so widely distributed within the wetland components that the level of risk of Se impact on aquatic and terrestrial species remains uniform throughout the wetland complex.

#### 4.2. Selenium Uptake in Plant Tissue

Se's seasonal precipitation/dissolution replenishes dissolved Se concentrations, thereby contributing to the plant uptake of Se. Due to the close contact with dissolved Se in the water column, Se becomes immediately available for plant roots to uptake and disperse to the stem and then to the flower. Between dissolved Se inputs, desorption from sediments, and seasonal dissolution of soluble salt associated with Se, there is an ample supply of Se for plant uptake throughout the wetland. It is reasonably evident that Se plant concentrations from pond to pond through the wetlands are constant (Figure 2 and Table 1). We would expect roots to have the highest Se concentrations with root tissue in the closest contact with dissolved and sediment 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 the shoot [48,49]. Submerged and emergent plant differences may be due to the submerged plant growing entirely underwater and being exposed to the soluble Se species in the water throughout the entire plant.

Other constructed wetlands with Se contamination (Table 3) are Chevron Refinery Marsh in San Francisco, California, and the root and shoot Se concentrations in plants ranged from 5 to 20 mg kg<sup>-1</sup> [43]. On the lower Colorado River at the Cienega de Santa Clara Wetland, Mexico, Se concentration in plants ranged from 0.03 to 0.2 mg kg<sup>-1</sup> [45]. A constructed wetland near Las Vegas at the Clark County Wetland Park, Nevada reported Se concentrations in plant species results in plant species similar to ours. The highest Se concentrations were in the *Typha* vegetative material  $2.8 \pm 0.5$  mg kg<sup>-1</sup> [46]. Our study and the San Francisco study, cited above, indicated a consistently higher concentration of Se in the root than in the plant's vegetative material [43,50].

**Table 3.** Comparison of four constructed wetlands: mean annual temperature (degree C), mean annual precipitation (mm), area (ha), plant taxa, and plant Se concentrations (mg kg<sup>-1</sup>).

Variable	Chevron Refinery Marsh, California [43]	Cienega de Santa Clara Wetland, Mexico [45]	Clark County Wetlands Park, Nevada [46]	Pariette Wetlands, Utah [31]
Mean annual temp, deg C	14.4	14.4	20.8	8.2
Mean annual Precip, mm	274	63	106	178
Area, ha	36	4200	53	1023
Principal plant taxa	Scirpus spp. Scirpus fornicus Distichlis spicata Grindelia stricta	Typha spp. Phragmites spp. Distichlis palmeri	<i>Scirpus</i> spp. <i>Typha</i> spp. <i>Najas</i> spp. <i>Chara</i> spp.	<i>Scirpus</i> spp. <i>Typha</i> spp. <i>Phragmites</i> spp. <i>Chara</i> spp.
Plant Se Concentration mg kg <sup>-1</sup>	5 to 20	0.03 to 0.17	0.3 to 2.81	0.03 to 6.5

# 5. Conclusions

In conclusion, the toxicological impact of the micronutrient Se is essential to the management of constructed wetlands. Land managers who are responsible for constructed wetlands must understand how Se is mobilized and removed so that they can determine management strategies to avoid, minimize, and mitigate Se contamination and promote sustainable ecosystem services in an arid climate, such as the Pariette Wetlands in the Colorado Plateau.

The widespread distribution of Se in water, sediment, and plants in the Pariette Wetlands indicates that retention of Se in sediments provides an ecological service to the local area. Se concentrations in plant tissue analyzed at Pariette Wetlands are near or below typical levels found in the Western United States. The Se levels in plants are important to understanding the potential for trophic transfer and bioremediation. The mechanisms that control oxidation and reduction of Se in constructed wetlands, such as the Pariette Wetlands Complex, are a guide for the most efficient use of resources in an arid climate. The feasibility of using Pariette Wetlands as Se removal and storage from drainage water is dependent on the availability of water and keeping the sediments wet and anaerobic which is essential to a functioning wetland. However, due to arid conditions and the short growing season, the use of plants for bioremediation is not the best method for Se removal [31].

Aquatic ecosystems are complex with complex biogeochemical cycles regulating the bioavailability of Se to aquatic species. Aquatic species, such as fish and bird endpoints, are at the greatest risk of exposure to chronic effects of exposure to total Se in water. Even though there are benefits of low doses of Se exposure, chronic and high dose exposure have reproductive effects on aquatic populations of these endpoints. The USEPA published in 2016 described the final national tissue-based Se criterion with four elements (fish egg-ovary element, fish whole-body and/or muscle element, water column element, and water column intermittent element). The tissue-based criterion was established based on toxicity studies that involved extended duration dietary exposure and measurement of total Se in the tissue of the target organism [12]. The future analysis focuses on bioaccumulation and a hazard assessment approach that uses spatial explicit exposure modeling to visualize and quantify the risk to fish and birds within wetlands based on ecosystem components water, sediment, benthic macroinvertebrates, plants, fish, and bird tissue.

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# References

- Hasanuzzaman, M.; Bhuyan, M.H.M.B.; Raza, A.; Hawrylak-Nowak, B.; Matraszek-Gawron, R.; Nahar, K.; Fujita, M. Selenium Toxicity in Plants and Environment: Biogeochemistry and Remediation Possibilities. *Plants* 2020, 9, 1711. [CrossRef] [PubMed]
- Bodnar, M.; Konieczka, P.; Namiesnik, J. The properties, functions, and use of selenium compounds in living organisms. *J. Environ.* Sci. Health Part C 2012, 30, 225–252. [CrossRef] [PubMed]

- Rizwan, M.; Ali, S.; Rehman, M.Z.u.; Rinklebe, J.; Tsang, D.C.W.; Tack, F.M.G.; Abbasi, G.H.; Hussain, A.; Igalavithana, A.D.; Lee, B.C.; et al. Effects of selenium on the uptake of toxic trace elements by crop plants: A review. *Crit. Rev. Environ. Sci. Technol.* 2021, 51, 2531–2566. [CrossRef]
- 4. White, P.J.; Broadley, M.R. Biofortification of crops with seven mineral elements often lacking in human diets–iron, zinc, copper, calcium, magnesium, selenium and iodine. *New Phytol.* **2009**, *182*, 49–84. [CrossRef] [PubMed]
- Hartikainen, H.; Xue, T.; Piironen, V. Selenium as an anti-oxidant and pro-oxidant in ryegrass. *Plant Soil* 2000, 225, 193–200. [CrossRef]
- Bellinger, F.P.; Raman, A.V.; Reeves, M.A.; Berry, M.J. Regulation and function of selenoproteins in human disease. *Biochem. J.* 2009, 422, 11–22. [CrossRef] [PubMed]
- Lanza, M.G.D.B.; Reis, A.R.d. Roles of selenium in mineral plant nutrition: ROS scavenging responses against abiotic stresses. *Plant Physiol. Biochem.* 2021, 164, 27–43. [CrossRef]
- Gui, J.-Y.; Rao, S.; Huang, X.; Liu, X.; Cheng, S.; Xu, F. Interaction between selenium and essential micronutrient elements in plants: A systematic review. *Sci. Total Environ.* 2022, *853*, 158673. [CrossRef]
- 9. Gupta, M.; Gupta, S. An overview of selenium uptake, metabolism, and toxicity in plants. *Front. Plant Sci.* 2017, 7, 2074. [CrossRef]
- Ohlendorf, H.M.; Kilness, A.W.; Simmons, J.L.; Stroud, R.K.; Hoffman, D.J.; Moore, J.F. Selenium Toxicosis in Wild Aquatic Birds. J. Toxicol. Environ. Health 1988, 24, 67–92. [CrossRef]
- 11. Lemly, A.D. Environmental hazard of selenium in the Animas La Plata water development project. *Ecotox. Environ. Safe.* **1997**, 37, 92–96. [CrossRef] [PubMed]
- 12. US EPA. Aquatic Life Ambient Water Quality Criteria for Selenium—Freshwater; US EPA: Washington, DC, USA, 2016.
- 13. Levander, O.A.; Burk, R.F. Update of human dietary standars for selenium. In *Selenium: Its Molecular Biology and Role in Human Health*, 2nd ed.; Hatfield, D.L., Berry, M.J., Gladyshev, V.N., Eds.; Springer: New York, NY, USA, 2006.
- 14. Ge, K.Y.; Yang, G.Q. The Epidemiology of Selenium Deficiency in the Etiologic Study of Endemic Diseases in China. *Am. J. Clin. Nutr.* **1993**, *57*, S259–S263. [CrossRef] [PubMed]
- Tiwary, A.K.; Stegelmeier, B.L.; Panter, K.E.; James, L.F.; Hall, J.O. Comparative toxicosis of sodium selenite and selenomethionine in lambs. J. Vet. Diagn. Investig. 2006, 18, 61–70. [CrossRef]
- Mroczek-Zdyrska, M.; Strubińska, J.; Hanaka, A. Selenium improves physiological parameters and alleviates oxidative stress in shoots of lead-exposed Vicia faba L. minor plants grown under phosphorus-deficient conditions. *J. Plant Growth Regul.* 2017, 36, 186–199. [CrossRef]
- 17. Molnár, Á.; Kolbert, Z.; Kéri, K.; Feigl, G.; Ördög, A.; Szőllősi, R.; Erdei, L. Selenite-induced nitro-oxidative stress processes in Arabidopsis thaliana and Brassica juncea. *Ecotox. Environ. Saf.* **2018**, *148*, 664–674. [CrossRef] [PubMed]
- Terry, N.; Zayed, A.M.; de Souza, M.P.; Tarun, A.S. Selenium in higher plants. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* 2000, 51, 401–432. [CrossRef]
- Seiler, R.L. Prediction of Areas Where Irrigation Drainage May Induce Selenium Contamination of Water. J. Environ. Qual. 1995, 24, 973–979. [CrossRef]
- Gao, S.; Tanji, K.K.; Dahlgren, R.A.; Ryu, J.; Herbel, M.J.; Higashi, R.M. Chemical status of selenium in evaporation basins for disposal of agricultural drainage. *Chemosphere* 2007, 69, 585–594. [CrossRef] [PubMed]
- Bañuelos, G.S.; Lin, Z.Q. Acceleration of selenium volatilization in seleniferous agricultural drainage sediments amended with methionine and casein. *Environ. Pollut.* 2007, 150, 306–312. [CrossRef]
- Ohlendorf, H.M.; Covington, S.M.; Byron, E.R.; Arenal, C.A. Conducting site-specific assessments of selenium bioaccumulation in aquatic systems. *Integr. Environ. Assess. Manag.* 2011, 7, 314; Erratum in *Integr. Environ. Assess. Manag.* 2012, 8, 210. [CrossRef]
- Zhang, Y.Q.; Zahir, Z.A.; Frankenberger, W.T. Fate of colloidal-particulate elemental selenium in aquatic systems. J. Environ. Qual. 2004, 33, 559–564. [CrossRef] [PubMed]
- Ohlendorf, H.M.; Hoffman, D.J.; Saiki, M.K.; Aldrich, T.W. Embryonic mortality and abnormalities of aquatic birds: Apparent impacts of selenium from irrigation drainwater. *Sci. Total Environ.* 1986, 52, 49–63. [CrossRef]
- 25. Presser, T.S. The Kesterson effect. Environ. Manag. 1994, 18, 437–454. [CrossRef]
- Stephens, D.W.; Waddell, B.; Peltz, L.A.; Miller, J.B. Detailed Study of Selenium and Selected Elements in Water, Bottom Sediment, and Biota Associated with Irrigation Drainage in the Middle Green River Basin, Utah 1988–90; U.S. Geological Survey: Salt Lake City, UT, USA, 1992.
- 27. Williams, D. Pariette Wetland Manager of the Bureau of Land Management Green River District—Vernal Field Office. 2011. Available online: https://www.blm.gov/press-release/bureau-land-management-conduct-pariette-wetlands-prescribed-fire (accessed on 12 December 2022).
- 28. Jones, C.P.; Grossl, P.R.; Amacher, M.C.; Boettinger, J.L.; Jacobson, A.R.; Lawley, J.R. Selenium and salt mobilization in wetland and arid upland soils of Pariette Draw, Utah (USA). *Geoderma* **2017**, *305*, 363–373. [CrossRef]
- Pilon-Smits, E.A.H. Selenium in Plants. In *Progress in Botany: Vol.* 76; Lüttge, U., Beyschlag, W., Eds.; Springer International Publishing: Cham, Switzerland, 2015; pp. 93–107.
- 30. Wingert, S.; Adams, C. TMDLs for Total Dissolved Solids, Selenium, and Boron in the Pariette Draw Watershed; US EPA: Washington, DC, USA, 2011.

- 31. Jones, C.P.; Amacher, M.C.; Grossl, P.R.; Jacobson, A.R. Selenium mass balance and flux in water of Pariette Wetlands, Utah (USA). *Appl. Geochem.* **2020**, *113*, 104517. [CrossRef]
- 32. Jones, C.P.; Isanhart, J.P.; Jackson, A.K. *Hazard Assessment of Born, Mercury, and Selenium in Biota from Pairette Wetland Complex, Utah*; Final Report for Utah Department of Water Quality; Utah State University: Logan, UT, USA, 2015; p. 128.
- Zalunardo, D. Myton Habitat Management Plan—Diamond Mountain Resource Area Vernal District; Diamond Mountain Resource Area Resource Management Plan and Environmental Impact Statement; United States Bureau of Land Management: Washington, DC, USA, 1979.
- Wilde, F.D. Water-Quality Sampling by the US Geological Survey: Standard Protocols and Procedures; U.S. Geological Survey: Salt Lake City, UT, USA, 2010; Volume 312.
- 35. Cutter, G.A. Speciation of Selenium and Arsenic in Natural Waters and Sediments; EPRI EA-4641; Electric Power Research Institute: Palo Alto, CA, USA, 1986.
- US Environmental Protection Agency (USEPA). Method 7741A—Selenium (Atomic Absorption, Gaseous Hydride). Available online: https://www.epa.gov/sites/production/files/2015-12/documents/7741a.pdf (accessed on 12 December 2022).
- 37. Pilon-Smits, E.A.H.; de Souza, M.P.; Hong, G.; Amini, A.; Bravo, R.C.; Payabyab, S.T.; Terry, N. Selenium volatilization and accumulation by twenty aquatic plant species. *J. Environ. Qual.* **1999**, *28*, 1011–1018. [CrossRef]
- Zasoski, R.J.; Burau, R.G. Rapid nitric-perchloric acid digestion method for multi-element tissue analysis. Commun. Soil Sci. Plant Anal. 1977, 8, 425–436. [CrossRef]
- 39. Fellows, I. Deducer: A data analysis GUI for R. J. Stat. Softw. 2012, 49, 1–15. [CrossRef]
- Authority, S.N.W.; Acharya, K.; Adhikari, A. A Comparison of Water Quality Improvements from Three Different Wetland Types in the Las Vegas Valley Watershed. 2010. Available online: <a href="https://www.lvwash.org/assets/pdf/resources-wqresearch-wetlands.pdf">https://www.lvwash.org/assets/pdf/resources-wqresearchwetlands.pdf</a> (accessed on 12 December 2022).
- 41. Azaizeh, H.; Salhani, N.; Sebesvari, Z.; Shardendu, S.; Emons, H. Phytoremediation of selenium using subsurface-flow constructed wetland. *Int. J. Phytorem.* 2006, *8*, 187–198. [CrossRef]
- 42. Dicataldo, G.; Hayes, D.F.; Miller, T.G.; Scanlan, L. Selenium speciation and distribution in a wetland system of the Great Salt Lake, Utah. *Environ. Eng. Sci.* 2010, 27, 777–788. [CrossRef]
- Hansen, D.; Duda, P.J.; Zayed, A.; Terry, N. Selenium removal by constructed wetlands: Role of biological volatilization. *Environ. Sci. Technol.* 1998, 32, 591–597. [CrossRef]
- 44. Karlson, U.; Parker; Frankenberger, W.T.; Calderone, S.J. Influence of temperature and organic amendments on the mobilization of selenium in sediments. *Soil Biol. Biochem.* **1990**, *22*, 615–620.
- 45. Garcia-Hernandez, J.; Glenn, E.P.; Artiola, J.; Baumgartner, D.J. Bioaccumulation of selenium (Se) in the Cienega de Santa Clara Wetland, Sonora, Mexico. *Ecotoxicol. Environ. Saf.* **2000**, *46*, 298–304. [CrossRef]
- 46. Pollard, J.; Cizdziel, J.; Stave, K.; Reid, M. Selenium concentrations in water and plant tissues of a newly formed arid wetland in Las Vegas, Nevada. *Environ. Monit. Assess.* 2007, 135, 447–457. [CrossRef] [PubMed]
- 47. White, P.J. Selenium metabolism in plants. Biochim. Biophys. Acta BBA-Gen. Subj. 2018, 1862, 2333–2342. [CrossRef]
- Zayed, A.; Lytle, C.M.; Terry, N. Accumulation and volatilization of different chemical species of selenium by plants. *Planta* 1998, 206, 284–292. [CrossRef]
- Feng, R.; Wang, L.; Yang, J.; Zhao, P.; Zhu, Y.; Li, Y.; Yu, Y.; Liu, H.; Rensing, C.; Wu, Z. Underlying mechanisms responsible for restriction of uptake and translocation of heavy metals (metalloids) by selenium via root application in plants. *J. Hazard. Mater.* 2021, 402, 123570. [CrossRef] [PubMed]
- Bitterli, C.; Bañuelos, G.S.; Schulin, R. Use of transfer factors to characterize uptake of selenium by plants. J. Geochem. Explor. 2010, 107, 206–216. [CrossRef]

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