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FROM WASTEWATERS: CHEVRON'S ENHANCEMENT
WETLAND AS A CASE STUDY**

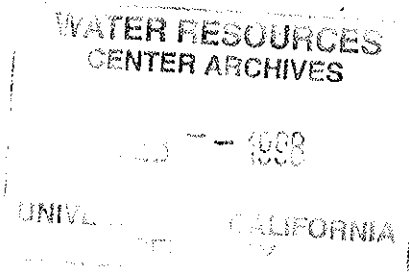
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Selenium Removal by Constructed Wetlands: Role of Biological Volatilization

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Selenium-laden effluents from oil refineries are polluting San Francisco Bay, California. One environmentally-friendly way of cleaning up selenium (Se) from effluents is by plant and microbial Se volatilization using constructed wetlands. Using mesocosms, we investigated the role of biological Se volatilization in a 36-hectare constructed wetland located adjacent to San Francisco Bay. The constructed wetland was highly effective in removing Se from selenite-contaminated oil refinery wastewater: 89% of the Se was removed. Inflow Se concentrations of 20-30 $\mu\text{g L}^{-1}$ decreased to $< 5 \mu\text{g L}^{-1}$ in the outflow. Most of the Se was removed by immobilization into sediments and plant tissues where Se concentrations reached ~ 5 and $\sim 15 \text{ mg kg}^{-1}$, respectively. Biological volatilization may have accounted for as much as 10 to 30% of the Se removed. The highest mean rates of Se volatilization for vegetated sites were 190, 180 and 150 $\mu\text{g Se m}^{-2} \text{ day}^{-1}$ (rabbitfoot grass, cattail and saltmarsh bulrush, respectively). Rates for the most dominant species, saltmarsh bulrush, varied during the year: the mean rates were 150, 70 and 25 $\mu\text{g Se m}^{-2} \text{ day}^{-1}$ in February, June and October, respectively. We conclude that biological Se volatilization is a significant pathway of Se removal in wetlands.

[Abstract figure chosen is Figure 2]

Key words: Constructed wetlands, Se volatilization, phytoremediation, wastewater cleanup, oil refinery.

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Introduction

Selenium (Se) is a metalloid which exists in a variety of oxidation states including selenide (Se^{2-}), elemental Se (Se^0), selenite (Se^{4+}), selenate (Se^{6+}), and several organic (e.g., selenomethionine) and volatile Se compounds (e.g., dimethyl selenide, DMSe). The oxidized forms of Se, selenite and selenate, are highly soluble and therefore bioavailable and potentially toxic. The reduced forms, selenide and elemental Se, are insoluble and much less bioavailable. The presence of Se in aqueous discharges from agriculture and industry is a cause for concern in many areas of the world. In the 1980's, selenate-rich agricultural drainage water was discharged into the Kesterson Reservoir marsh in California. This had very serious environmental consequences and resulted in the death and deformity of wildfowl due to Se poisoning (1). Another significant health concern is the rising Se levels in the San Francisco Bay. Much of the Se inflow comes from urban and industrial sources (2). Six oil refineries discharge into the Bay and Se discharge levels from several of the refineries substantially exceed those permitted under the guidelines established by both state and federal regulators.

Constructed wetlands constitute a complex ecosystem, the biological and physical components of which interact to provide a mechanical and biogeochemical filter capable of removing many different types of contaminants from water. They have been used to cleanup municipal wastewaters, stormwater runoff, and many other types of polluted wastewaters in the USA (3), and in Europe (4). Constructed wetlands are orders of magnitude lower in cost than other treatment systems (5); however, the science of understanding of wetland detoxification mechanisms is in its infancy. The first indication that wetlands might be useful in the removal of Se from wastewaters came from a study of a 36-hectare constructed wetland located adjacent to the San Francisco Bay, California. Analysis of the wetland inlet and outlet waters showed that the constructed wetland was successful in removing at least 70% of the Se from the wastewater passing through it (6). Although effluent levels of Se were well below the permit requirements, there remained the obvious concern that the Se retained in the wetland may eventually be harmful to wildlife. This concern led to a field study to determine Se partitioning among the sediments, water and plant material. The resulting inventory accounted for only 70% of the Se removed by the wetland (6); the fate of the remainder of the Se removed was unknown.

One explanation for the "missing Se" at the constructed wetland is that the Se had been converted to volatile forms and had escaped to the atmosphere. Both plants (7) and microbes (8,9) are able to take up Se in the form of selenate or selenite and metabolize it to volatile forms (e.g., DMSe). This process is

termed "biological volatilization". Cooke and Bruland (10) estimated that as much as 30% of the Se removed from drainage water moving through the Kesterson Ponds may have been released to the atmosphere through biological volatilization. Allen (11) also suggested that volatilization could represent a significant component of Se removal by wetlands. From a remediation standpoint, volatilization of Se is an attractive method of removing Se from wastewater because it minimizes the entry of Se into the food chain. This is because volatilization takes place mainly in the region of the roots (12) so that most of the Se volatilized escapes directly to the atmosphere, minimizing plant-bound Se available to birds and other wildlife. Furthermore, most of the volatile forms of Se (e.g., DMSe) are relatively non-toxic (13,14,15). Selenium may eventually be redeposited in areas deficient in this trace element (16,17), which is also an important nutrient (18,19). The main goals of the present work were to assess the potential importance of biological Se volatilization as a means of Se removal by constructed wetlands, and to determine how effectively the San Francisco Bay constructed wetland removes Se from oil refinery effluent.

Materials and Methods

Experimental Plan

The research was carried out at a surface-flow constructed wetland situated near the mouth of the San Pablo Bay, one of the five basins of the adjacent San Francisco Bay estuary system. Three main experiments were performed between June 23 and October 13, 1995. Experiment 1 was designed to determine 1) how efficiently the constructed wetland removed Se from the inflow, 2) how much of the Se was removed by the first 12-hectare section of the wetland, Pass 1, and 3) the chemical forms of Se in the inflow and outflow of Pass 1. Experiment 2 determined how rates of biological Se volatilization varied with time for five wetland plant species and for the inlet channel, i.e., a 2 m wide, 0.9 m deep channel through which oil refinery wastewater was supplied to the wetland. Selenium concentrations were measured in roots and shoots, sediments and sediment pore water. Experiment 3 determined the effect of detopping (shoot removal) on the rate of volatilization of saltmarsh bulrush (*Scirpus maritimus* and *S. robustus*). pH, redox potentials and EC values were measured on all water samples.

A preliminary set of volatilization measurements (with no accompanying measurements of pore water, sediment or plant tissue Se) was carried out in Spring 1995 (from February 7 to April 18). These were made non-systematically over the southern half of Pass 1 to determine how Se volatilization rates varied with different wetland plant species and among different non-vegetated sites. The four vegetated sites measured included saltmarsh bulrush, cattail (*Typha angustifolia*, *T. domingensis* and *T. latifolia*), brass

buttons (*Cotula coronopifolia*), and rabbitfoot grass (*Polypogon monspeliensis*); non-vegetated sites included the inlet channel, fungal mats, algal puddles and bare sediments.

The Study Site

The 36-hectare, surface flow constructed wetland was divided into three nearly equal sections, referred to as Passes 1, 2 and 3 (Fig. 1). Treated wastewater from the refinery entered the wetland at the south-west corner of Pass 1 ("Inlet", Fig. 1), and flowed down the inlet channel which runs north between Passes 1 and 2. Inlet water was then distributed laterally in an easterly direction across Pass 1, and was collected in a canal which transfers the water to Pass 2. Figure 1 shows the generalized flow of water through Passes 1, 2 and 3. Outlet water from the wetland was recombined with refinery waste water, and released to San Francisco Bay. During the growing season, plant cover in Pass 1 was dominated by dense saltmarsh bulrush, with cattails being the next most populous species. Pass 2 is primarily open-water; however, stands of saltmarsh bulrush, cattails and tules (*S. acutus var occidentalis* and *S. californicus*) became established at the southern end and comprised 10 - 15 % of the area of Pass 2. The vegetation in Pass 3 is similar to Pass 1, although plant stands are smaller and the coverage not as thick as in Pass 1. Other plant species common to fresh-brackish water wetlands in the area have become established, e.g., brass buttons, saltgrass (*Distichlis spicata*), and marsh gumweed (*Grindelia stricta var angustifolia*) (B. Ertter, pers. comm.). The five wetland plant species chosen for Experiment 2 included saltmarsh bulrush, cattail, brass buttons (the 3 most common species in Pass1), saltgrass and rabbitfoot grass (minor common species). Experiment 2 measurements were made in an area measuring approximately 75 X 75 m located in Pass 1 (Primary Study Site, Fig. 1). This site was chosen because it was central to dense, monotypic stands of each of the chosen plant species. Because saltgrass was established only near the southern end of Pass 1, the saltgrass measurements were made at a 10 X 40 m "saltgrass site" in a different location (Fig. 1). The mean water height at the primary study site was 5.3 ± 3.4 cm.

Water, Sediment and Plant Se Concentrations

For Experiment 1, total Se concentrations of the Pass 1 inlet and outlet waters, and of Pass 3 outlet water, were sampled weekly during the 16-week study period. The sampling and analytical procedures were conducted according to EPA Method #270.3 ; this method measured total Se (dissolved and particulate-bound forms of Se). In addition, total dissolved Se concentrations of Pass 1 inlet and outlet waters were measured by our laboratory at UC Berkeley. These latter samples were made using Rhizon

water samplers (pore size = 0.1 μm) with 10 ml Vacutainers. Pass 1 inlet and outlet waters were sampled horizontally at a depth of 10 cm. For Experiment 2, samples of sediment pore water, sediments and plant tissues were collected weekly. Sediment pore-water was sampled directly adjacent to the Plexiglas chambers (used to measure Se volatilization, see below) at a depth of 0 - 10 cm and at a distance of 0 - 5 cm from the chamber. The Rhizon samplers were carefully washed and flushed with deionized water and then were air dried in-between uses. Water chemistry measurements for all water samples were made in the field. Sample pH was determined with a gel-filled combination electrode (Fisher Scientific, Pittsburgh, PA); electrical conductivity (EC) was determined with a conductivity meter (Model CDH-80MS, Omega Engineering, Stamford, CT), and redox potential (Eh) was determined with a combination platinum-reference electrode (Ag-AgCl) (Fisher Scientific, Pittsburgh, PA). Water samples were then brought back to the lab and were stored at -80°C until the end of the experiment for Se analysis. Total dissolved Se in water samples was determined by heating 2.25 ml sample with 0.5 ml 2% ammonium persulfate at 95°C for 25 minutes, then adding 2.25 ml concentrated HCl and heating at 95°C for 25 minutes (20). Total dissolved selenite was determined by introducing the sample directly into the hydride generator for atomic absorption spectrophotometry. In Experiment 2, sediments were sampled from each chamber location during the 4-week period commencing June 23 and during the 4-week period ending October 13. A hand auger was used to sample sediments 10 - 15 cm outside the chamber and from a depth of 0 - 10 cm. Fresh samples were brought to the lab where they were dried, cleaned of organic matter, milled and stored for analysis at the end of the project. Sediment samples were prepared for analysis of total Se as described by Zawislanski and Zavarin (21). Plants were sampled weekly by collecting 4 - 5 whole plants from within 5 - 20 cm from volatilization chambers. Shoots and roots were cleaned of debris, rinsed with deionized water, separated and dried at 70°C . Whole shoot and root samples were ground and mixed to ensure sample homogenization. Plant tissue samples were prepared for analysis using a nitric acid- hydrogen peroxide digestion procedure according to Martin et al. (22).

Flow rates

Water flow rates were measured twice daily. Water flow rates into Pass 1 were measured using a calibrated weir while those out of Pass 1 were estimated by monitoring changes in water levels across Pass 1. Water flow rates out of Pass 3 were recorded from a flow rate gauge on the Pass 3 outlet pump. Flow rates into and out of Pass 1 and Pass 3 did not change significantly with time over the 16-week study period; the mean values were 6.4 ± 1.4 , 6.7 ± 3.3 and 3.8 ± 0.7 million L day^{-1} . The residency time for water in the entire wetland was 7 to 10 days (6).

Selenium volatilization

Rates of Se volatilization were measured using open-bottom Plexiglas collection chambers (mesocosms) to cover selected sites, inserting the bottom edges of the chambers up to 5 cm into the sediments. Inlet and outlet ports, located on top of the chambers, held activated charcoal filter material (Booda Products, Calabasas, California) for trapping volatile Se. A vacuum applied to the outlet port caused ambient air to be drawn into the chamber. As a result, the chamber inlet filter served to scrub the incoming air of ambient volatile Se, and the outlet filter trapped volatile Se emitted from within the collection chamber. The volatile Se trapping and extraction protocols used here were adapted from Jayaweera and Biggar (23) and Biggar and Jayaweera (24). The volatilization traps each consisted of twenty 10 cm diameter discs of charcoal material (approximate mass, 70 grams). After field exposure, charcoal traps were removed and placed in sealed plastic bags for transport to the lab. Within 2 hours after being removed from the field, the total weight of the volatilization trap was recorded, then a 1/4 sub-sample of each disc was randomly cut, and the weight of the entire sub-sample was recorded. The sub-sample was placed in a 500 ml Nalgene bottle with extraction solution which consisted of: 160 ml of 0.05 M NaOH and 40 ml of 30% H₂O₂. The caps of the bottles were slightly loosened for 24 hours, to prevent pressure build-up. Samples were prepared for analysis by heating a 500 μ L sample of extraction solution with 500 μ L 30% H₂O₂ at 91°C for 25 minutes. After cooling, 5 mL of concentrated HCl was added to the samples which were heated again at 91°C for 25 minutes. Samples were then diluted to a 10 mL final volume with distilled deionized water. Samples of charcoal material that had not been exposed in the field were extracted and prepared for each analysis. No Se was detectable in these matrix blanks. All Se concentrations were determined using a Perkin-Elmer atomic absorption spectrophotometer (Model# 2280), equipped with a Varian hydride-generator (Model # VGA-76). Two sub-samples were prepared for analysis from each field sample; Se concentration values were recorded as the average of these two separate determinations. Volatilization rates were calculated as the mass of Se trapped in the outlet filter, divided by the collection time and by the basal area (0.81 m²) of the collection chamber. The efficiency of the volatile Se collection apparatus was tested in the laboratory using recovery experiments in which small (5 μ L) and large (25 μ L) aliquots of dimethylselenide (DMSe) were introduced into the chamber. After numerous experiments were made to optimize the flow rate and trap thickness, close to 100% recovery of standard DMSe was obtained.

The collection chambers (mesocosms) were open-bottom cubes measuring 90 cm on each side. Chamber inlet and outlet ports were made of 10 cm wide, 25 cm tall Plexiglas cylinders. Inlet ports were open to the atmosphere on top of the chambers (except for a small rain shield), and were connected inside the chamber to a length of 4 cm diameter tubing, which distributed scrubbed inlet air to the bottom of the collection chambers. The chamber outlet ports were sealed to the outside atmosphere and each was connected to a vacuum supply and regulator to ensure that the flow of air through each chamber was the same. Air flow through each chamber provided one air-exchange approximately every 2 hours. For cattail measurements, extra chamber modules were stacked together which increased the chamber height to 180 cm. Two separate gaskets were used on all chamber connections to ensure against leaks. Experiment 2 chambers were fitted with 12 volt (DC) mixing fans which were rated to move approximately $3 \text{ m}^3 \text{ air min}^{-1}$. Also, the tops of the chambers were covered in shade cloth to minimize heat build-up inside the chambers. Temperature inside and outside of the chambers at mean plant height was monitored continuously throughout measurements using two Hobo (Onset Instruments, Pocasset, Massachusetts) temperature data loggers. Analysis of the temperature data from the study period showed that mean daily temperature inside the chambers was $22.4 \pm 3.3 \text{ }^\circ\text{C}$ and the mean daily temperature outside the chambers was $18.7 \pm 2.1 \text{ }^\circ\text{C}$. The difference between inside and outside temperatures was $3.75 \pm 1.76 \text{ }^\circ\text{C}$. The sampling procedure for Experiment 2 was as follows. Six collection chambers were used to monitor Se volatilization rates (over 1-week periods) from two different sites (plant species or inlet channel) each week, using three replicate chambers for each measurement. Chambers were moved weekly to randomly selected sites within the study areas as follows. During the first week, three chambers were used to monitor volatilization rates for saltmarsh bulrush, and three chambers for saltgrass. The second week, the chambers were moved to monitor volatilization rates for brass buttons and the inlet channel. During the third week saltmarsh bulrush was again monitored, along with detopped saltmarsh bulrush sites. In the fourth week, the chambers were used to monitor sites populated with cattails and rabbitfoot grass. This 4-week cycle was repeated four times during the 16-week period (some additional measurements with time were taken for bulrush, 9/1-9/15). The charcoal traps for any given chamber were routinely changed twice per week; the volatilization values reported are the average of these two separate determinations.

Results and Discussion

Selenium removal by the constructed wetland

The oil refinery wastewater flowing into the constructed wetland contained 20 to 30 $\mu\text{g Se L}^{-1}$; the water exiting the wetland contained $< 5 \mu\text{g Se L}^{-1}$ (Fig. 2A). Neither the inlet or outlet Se concentrations (of the entire wetland) changed significantly with time over the study period (June 23 to October 13, 1995). The mass of Se removed by the wetland was calculated from measurements of flow rate and inlet and outlet Se concentrations (Fig. 2B). The amount of Se removed daily over the 16-week study period by the entire wetland (which also did not change significantly with time) was $156 \pm 13 \text{ g day}^{-1}$ (Fig. 2B). Expressed as a percentage of the mass per day of Se delivered in the inflow, the proportion of Se removed was constant with time at 89.4 ± 0.6 percent (Fig. 2C). Over the first half of the study period, most of the Se removed by the wetland was removed by the first 12-hectare section of the wetland (Pass 1, Fig. 2B,C), although Pass 1 became progressively less effective in removing the Se from the 9th to the 16th weeks (i.e., August 18 to October 13) (Fig. 2B,C). The decrease in the effectiveness of Pass 1 in removing Se from the inflow may have been due to a seasonal decline in plant uptake and microbial reduction of Se associated with cooler temperatures in the Fall. However, if one considers the entire wetland, it is clear that the wetland was remarkably effective in removing Se from wastewater throughout the 16-week study period.

Three chemical forms of Se were measured in the inlet and outlet waters of Pass 1, i.e., total Se, including particulate Se, total dissolved Se, and selenite Se (Fig. 3A,B; Table 1). The data show that nearly all of the Se in the inlet and outlet waters was in dissolved forms, mainly selenite: only in the last 4-week period did selenite Se concentration decrease significantly below total Se, or total dissolved Se, concentrations (Fig. 3A,B). Thus, the forms of Se in the outlet water of Pass 1 were similar to, and apparently governed by, the forms of Se in the inlet water. The percentage of Se as selenite decreased in the sediment pore water compared to the inlet or outlet waters; it also decreased with time in the inlet water (Table 1; Fig. 3C).

Changes in pH, redox potential (Eh) and electrical conductivity (EC) were determined for inlet and outlet waters and for samples of sediment pore water taken at each chamber location. Inlet water pH increased to a small extent with time over the 16-week period from 7.2 to 7.5 ($P < 0.02$); outlet water pH (7.31 ± 0.19) and sediment pore water pH (7.22 ± 0.21) did not change significantly with time. Inlet, outlet and sediment pore water redox potentials each declined linearly with time over the period measured (July 22

to October 13). The initial inlet, outlet and sediment pore water redox potentials were similar, 141, 128 and 118 mV, respectively; the corresponding final values were considerably lower, 22, 50 and 30 mV, respectively (all values calculated from linear regressions of data with time). The redox potentials and pH values obtained at the study site were favorable for the conversion of Se to more reduced forms such as organo-Se or elemental Se (25,26,27), which become immobilized in the sediments, and for conversion to organic forms suitable for volatilization.

The ECs of the inlet and outlet waters were similar to one another and both ECs changed with time in the same way, i.e., they were relatively constant with time over the first 8 weeks then decreased over the remaining part of the 16-week period. The mean ECs for Weeks 1-8 were $4100 \pm 200 \mu\text{S cm}^{-1}$ for the inlet water and $4500 \pm 80 \mu\text{S cm}^{-1}$ for the outlet water; from Weeks 9-16, the mean ECs declined to 3000 ± 500 and $3400 \pm 600 \mu\text{S cm}^{-1}$ for the inlet and outlet waters, respectively. The higher salt levels in the outlet versus the inlet waters may have been due to the evaporative concentration of salts in the ponded waters and/or to the diffusion of salt from the sediments to surface waters. The EC of the sediment pore water exceeded the inlet and outlet water ECs substantially: the mean value over the study period was $6700 \pm 4400 \mu\text{S cm}^{-1}$. Thus, it appears that the inlet water, which had a lower salt concentration than the sediment pore water, resulted in the removal of some salt from the first pass, but not enough to significantly lower the EC of the sediment pore water.

Distribution of Se in the sediments, sediment pore water and plant tissues

There are three potential fates for the soluble Se entering the wetland: 1) it may become chemically reduced and immobilized in the sediments, 2) it may be absorbed by plants and accumulated in root and shoot tissues, and 3) it may be volatilized by plants or microbes to the atmosphere. Total Se concentrations in the wetland sediments adjacent to the volatilization chambers were much higher than those of the sediment pore water: they ranged from 2.1 to 6.7 mg Se kg⁻¹ dry sediment, compared to 5.0 to 9.8 $\mu\text{g Se L}^{-1}$ in the sediment pore water (Table 2). Sediments taken from the saltgrass and rabbitfoot grass sites contained ~2 mg Se kg⁻¹ dry sediment, compared to values of around 6 mg Se kg⁻¹ dry sediment at bulrush, cattail or brass buttons' sites (Table 2). There were no statistically significant changes in sediment total Se with time over the 4-month period at any of the species-associated sites.

Large amounts of Se were accumulated in plant tissues. In most instances, Se concentrations in roots ranged from 11 to 21 mg Se kg⁻¹ dry weight and from 5 to 8 mg Se kg⁻¹ dry weight in shoots (Table 2).

Selenium concentrations were substantially higher in roots than shoots of all the species tested; in bulrush, for example, Se concentrations were up to 3-fold higher in roots than in shoots. In general, plant tissue Se concentrations did not change significantly with time, the two exceptions being roots of bulrush and rabbitfoot grass: the total Se concentration of bulrush roots decreased from 32 ± 14 to 14 ± 6.3 mg Se kg^{-1} , while total Se of rabbitfoot grass roots increased from 16.3 ± 4.2 to 34.4 ± 7.3 mg Se kg^{-1} , over the 16-week time period. The concentrations of Se in shoot tissue differed remarkably little among species, ranging from 5.2 mg kg^{-1} in bulrush to 7.9 mg kg^{-1} in rabbitfoot grass (Table 2). Thus, the data show that 1) Se concentrations in sediments and plant tissues were orders of magnitude higher than those of the sediment pore water, 2) Se concentrations in roots were greater than those of shoots, 3) shoot Se concentrations did not differ significantly among plant species, and 4) plant Se concentrations varied significantly with time in only two instances (bulrush and rabbitfoot grass root tissue).

Volatilization of Se

In the preliminary set of measurements carried out in Spring 1995, rates of volatilization of Se were measured non-systematically over a variety of sites located in Pass 1. Some of the sites measured were vegetated with the most common plant species in the wetland, i.e., saltmarsh bulrush, cattail, rabbitfoot grass, saltgrass and brass buttons. Some of the sites were unvegetated, i.e., the inlet channel, fungal mats, detritus floating on water, algal puddles and unvegetated sediments. In Experiment 2, we monitored the changes in the rates of Se volatilization with time for five vegetated sites and for one site over the inlet channel. The period of measurement was June 23 to October 13 (16 weeks). The five vegetated sites were populated with saltmarsh bulrush, cattail, rabbitfoot grass, saltgrass or brass buttons. Since bulrush was the most populous species in the wetland, we chose bulrush as a reference species against which volatilization from other species might be compared. Thus, bulrush was sampled most frequently during the 16-week measuring period (Fig. 4A).

The maximum rates of Se volatilization recorded at the different sites throughout 1995 (i.e., including preliminary and Experiment 2 data), together with their dates of measurement, are shown in Table 3. The maximum rates shown are the means of several measurements made at specific sites over periods of one or two weeks. The most populous species in the wetland were saltmarsh bulrush and cattail. In February, these two species (more precisely, the sites populated by these species) attained their maximum mean rates of 150 and 180 $\mu\text{g Se m}^{-2} \text{day}^{-1}$, respectively. The rabbitfoot grass site attained the highest mean rate of all sites in March, i.e., 190 $\mu\text{g Se m}^{-2} \text{day}^{-1}$, and the highest individual measurement of 330

$\mu\text{g Se m}^{-2} \text{ day}^{-1}$. Among the non-vegetated sites measured, the highest mean rate of Se volatilization was attained by the inlet channel to Pass 1, i.e., $170 \mu\text{g Se m}^{-2} \text{ day}^{-1}$. The lowest maximum mean rate attained was for unvegetated sediments, i.e., $20 \mu\text{g Se m}^{-2} \text{ day}^{-1}$, while rates for an algal puddle, detritus floating on water and fungal mats, the rates were 50, 100 and $110 \mu\text{g Se m}^{-2} \text{ day}^{-1}$, respectively.

In Experiment 2, the highest mean value for the bulrush sites was attained in Week 1 (June 23-30), i.e., $71 \pm 36 \mu\text{g Se m}^{-2} \text{ day}^{-1}$ (Fig. 4A). Thereafter the rate of volatilization for bulrush remained low, at or below $25 \mu\text{g Se m}^{-2} \text{ day}^{-1}$ (except for an increase at Week 13). Rates of volatilization for brass buttons and saltgrass increased with time (Fig. 4B,C). Rates of volatilization for cattail and rabbitfoot grass did not change with time; the mean rates for each of the two species over the 16-week period were $10 \pm 7 \mu\text{g Se m}^{-2} \text{ day}^{-1}$ and $9 \pm 5 \mu\text{g Se m}^{-2} \text{ day}^{-1}$, respectively. Rates of volatilization over the inlet channel were initially higher than for the vegetated sites, possibly because the Se concentrations were substantially higher in the inlet channel ($17 \pm 1.8 \mu\text{g Se L}^{-1}$) than in the sediment pore water ($6 \pm 4 \mu\text{g Se L}^{-1}$); however, volatilization over the inlet channel declined with time to values comparable to those of the vegetated sites (Fig. 4D). Increased Se concentration may also have been responsible for the increase in volatilization rate of saltgrass with time: volatilization rate was positively correlated with total Se in the pore water ($P < 0.04$; $r^2 = 0.36$). To summarize, volatilization rates changed with time over the 16-week measuring period in different ways for the different sites: volatilization over the inlet channel and over the bulrush site decreased with time, volatilization of the cattail and rabbitfoot grass sites did not change with time, while volatilization of brass buttons and saltgrass sites increased.

One concern about using constructed wetlands to remove Se from wastewater is that Se may build up in the wetland to biologically hazardous levels. One approach to dealing with this problem is to periodically harvest and remove Se-containing vegetation (e.g., by drying the wetland and mowing). Shoot removal may have the additional benefit of promoting Se volatilization: studies in our laboratory showed that shoot removal led to substantially increased rates of Se volatilization by the remaining root system (12). Because removal of Se from wetlands through biological volatilization minimizes toxicity to wildlife, we investigated whether it is possible to accelerate volatilization under field conditions through shoot removal (Experiment 3). Volatilization rates were measured over bulrush populated sites from which we removed all of the bulrush shoots (Fig. 4E). Volatilization of bulrush plants detopped in September and October was measured continuously for 7 days immediately after detopping; detopped sites exhibited 2- to 4-fold increases in volatilization (Fig. 4E). Thus, the results suggest that detopping can accelerate

volatilization under field conditions, at least for short periods. This finding corresponded to that of the earlier laboratory study which showed that volatilization increased 72 hours after detopping and then decreased (12).

It should be possible to develop other management options to increase volatilization. Volatilization rate depends on such factors as Se concentration (28), temperature (29) and water (8,29,30). Dacey et al. (31) found that dimethyl sulfide (DMS, chemically analogous to DMSe) emissions from vegetated (*Spartina alterniflora*) salt marsh sediments may be increased by varying water levels. Zhang and Moore (32) found that rates of Se volatilization were increased by transferring wetland microcosms from a flooded to a drying condition. Thus, varying the water level could be an important management tool for increasing Se emission in constructed wetlands.

How high are the volatilization rates obtained in the present work compared to other measurements of Se volatilization in wetlands? Unfortunately, very few published data are available. Zawislanski et al. (21) measured Se volatilization rates over a variety of manipulated and unmanipulated vegetated sites of the Kesterson Reservoir (which was a wetland marsh). Originally their study site was dominated by cattails but at the time of volatilization measurement, it was dry and vegetated with grass species such as *Polypogon* and *Bromus*. Their volatilization rates (mean values) for control (unmanipulated) sites ranged from 50 to 175 $\mu\text{g Se m}^{-2} \text{ day}^{-1}$ in 1993 (May 27 to December 8) and 40 to 100 $\mu\text{g Se m}^{-2} \text{ day}^{-1}$ in 1994 (January 12 to October 23). However, Zawislanski et al.'s study site contained much higher concentrations of Se than those found in the constructed wetland. The total sediment Se concentrations at the Kesterson site were around 35-40 mg kg^{-1} , compared to $\sim 5 \text{ mg kg}^{-1}$ for our constructed wetland, while soluble Se concentrations in their sediment water extracts (0 to 10 cm depth) ranged from 2 to 12 mg L^{-1} , i.e., approximately 1000 times higher than the values for Se in the pore water at our sites. Using enclosures placed over plants at the Kesterson Reservoir, Weres et al. (20) obtained rates of Se volatilization ranging from 24 to 192 $\mu\text{g Se m}^{-2} \text{ day}^{-1}$; however, they obtained very much higher rates over other surfaces (e.g., peat, muck). Weres et al. (20) concluded that volatilization was enhanced by the presence of decaying organic matter, increasing temperature and increased soil moisture. Zhang and Moore (32) obtained rates of Se volatilization of 1-50 $\mu\text{g Se m}^{-2} \text{ day}^{-1}$ from microcosms consisting of Se-containing water (3 $\mu\text{g Se L}^{-1}$, including 12-15% organic Se), sediment (containing 1-7 mg Se kg^{-1}), and plant materials, collected from a wetland system from Benton Lake, Montana. Their results showed that

plants and sediments were the major producers of volatile Se and that volatilization was increased with increase in temperature, air-flow rate and decomposition of wetland plants.

The main goal of our volatilization research was to determine if plant and microbial volatilization represents a significant pathway for the removal of Se by the constructed wetland. We may calculate the percentage of Se removed by volatilization compared to the total mass of Se removed by the wetland as follows. The constructed wetland has a total area (A) of $3.64 \times 10^5 \text{ m}^2$, and, over the 16-week study period, removed Se at the rate of $W \text{ } \mu\text{g Se day}^{-1}$ (i.e., $W = 156 \text{ g Se day}^{-1}$, Fig. 2B). If the total amount of Se volatilized is assumed to be the average daily rate, V , $\mu\text{g Se m}^{-2} \text{ day}^{-1}$ multiplied by A , then the percent of the Se removed from the wetland by volatilization, P , is $VA/W \times 100$, i.e., $P = 0.234 V$. The actual value of V for the entire constructed wetland is unknown: our measurements were confined to a small area of Pass 1 and to limited time periods. However, we may calculate P for various values of V . For example, the highest rate of volatilization obtained in the wetland was $330 \text{ } \mu\text{g Se m}^{-2} \text{ day}^{-1}$ (rabbitfoot grass in March), and if the whole wetland volatilized at this rate, 77% of the Se removed would be through volatilization. The lowest values attained were around $10 \text{ } \mu\text{g Se m}^{-2} \text{ day}^{-1}$; this would give a P value of 2.34%. The most dominant species in the wetland was bulrush. Bulrush exhibited different rates according to the time of the year measured. In February, June and October the mean rates were 150, 70 and $25 \text{ } \mu\text{g Se m}^{-2} \text{ day}^{-1}$; these rates correspond to percent removals of 35%, 17% and 6%, respectively. Thus, the present study shows that both high and low rates of volatilization occur in the constructed wetland. The proportion of Se removed from this wetland through volatilization may be determined accurately only after a more comprehensive study is made which systematically takes spatial and temporal variation of volatilization into account. However, we believe that volatilization *could* account for as much as 10 to 30% of the daily amounts of Se removed by the wetland. Such a proportion is consistent with the view put forward by Cooke and Bruland (10) who calculated that as much as 30% of the Se entering the Kesterson Reservoir was volatilized.

We conclude that 1) the constructed wetland is highly effective in removing Se from oil refinery wastewater, 2) high rates of volatilization are present in the constructed wetland, over vegetated as well as non-vegetated sites, and 3) there is potential to increase the extent of Se removal through volatilization by wetland management. It may be possible, for example, to manipulate volatilization rates through management of water levels, temperature or plant and microbial factors. The success of the constructed wetland in removing Se from wastewater provided the impetus for a new study to determine if Se levels

in agricultural drainage water can be reduced using constructed wetland treatment systems. For this study (supported by the University of California and the Tulare Lake Drainage District), ten quarter-acre experimental wetland cells have been constructed at Corcoran, CA, to treat selenate-contaminated drainage water (containing up to $30 \mu\text{g Se L}^{-1}$). The wetland cells have been planted with a variety of different plant species to determine which type of wetland plants would be the most effective in removing and volatilizing Se. It is hoped that this method of Se removal will greatly lower the Se concentrations of drainage water entering the evaporation ponds.

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TABLE 1. Selenite Se (Se^{IV}) expressed as percentage of total dissolved Se in wetland waters sampled over four successive 4-week intervals from June 23 - October 13. Values shown are means (\pm SD) where n=4 (Pass 1 inlet and outlet waters), n=21 (sediment pore water; n=32 over Interval 4).

% Se^{IV}	Interval 1	Interval 2	Interval 3	Interval 4
Inlet	101 \pm 19.7	90.1 \pm 13.1	86.1 \pm 18.3	51.3 \pm 24.9
Outlet	55.0 \pm 4.36	87.4 \pm 11.4	61.2 \pm 20.3	54.9 \pm 21.4
Pore water	49.2 \pm 25.3	47.7 \pm 16.0	31.6 \pm 15.6	18.2 \pm 11.3

TABLE 2. Selenium concentrations in sediment pore water, sediment and plant tissues sampled from wetland sites populated with five different plant species. For sediments, n=6 for all species. For pore water and plant tissue Se, n=39 for bulrush, n=9 for cattails; n=12 for brass buttons, saltgrass and rabbitfoot grass. Note that Se concentrations in sediments, roots and shoots, are many times higher than those of the sediment pore water.

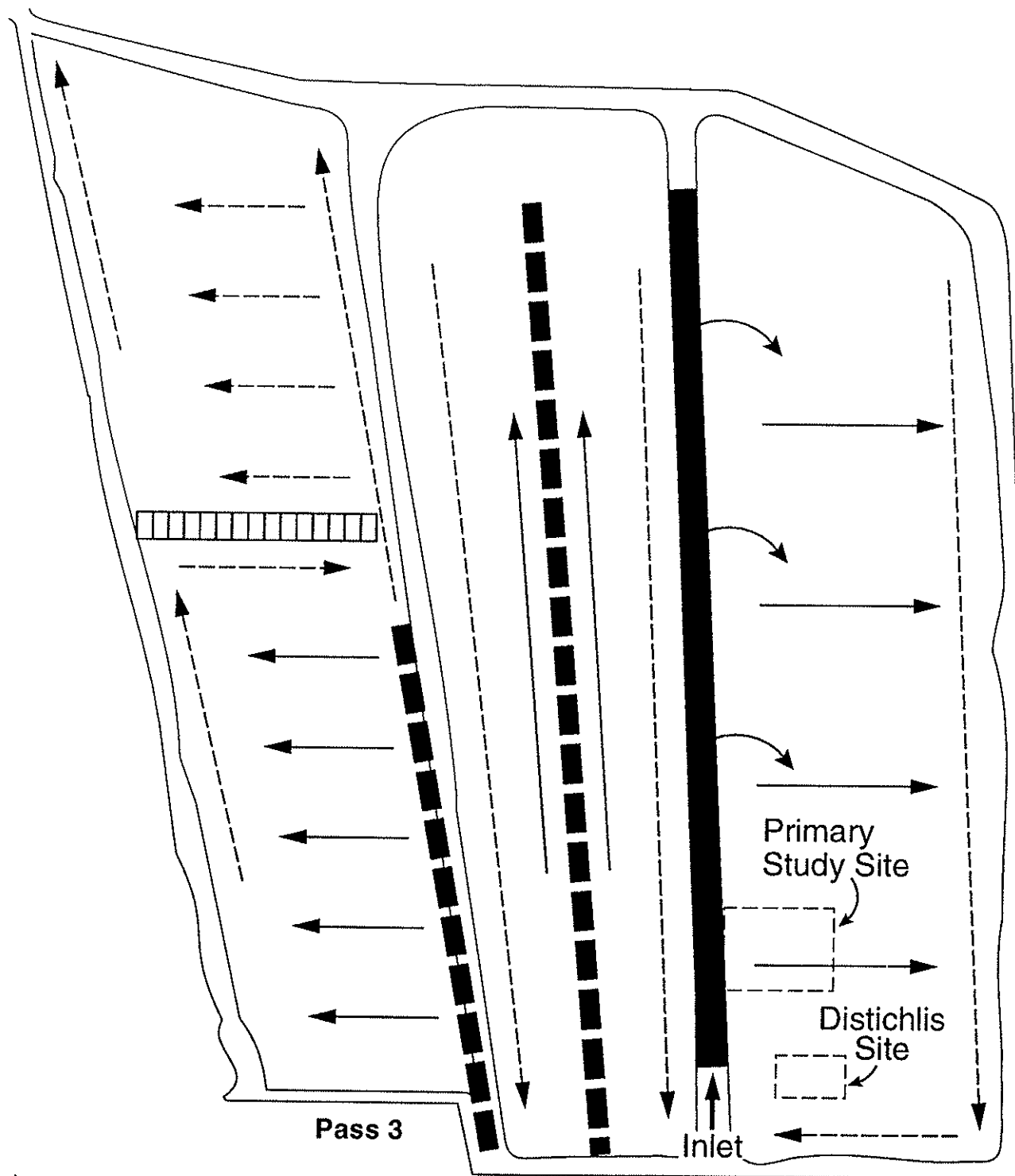
Se concentration	Bulrush	Cattail	Brass buttons	Saltgrass	Rabbitfoot grass
pore water ($\mu\text{g Se L}^{-1}$)	5.0 ± 3.2	5.2 ± 3.2	5.4 ± 2.8	7.7 ± 3.8	9.8 ± 5.8
sediment (mg Se kg^{-1})	4.6 ± 3.5	5.9 ± 5.3	6.7 ± 5.1	2.3 ± 0.8	2.1 ± 0.6
roots (mg Se kg^{-1})	15.5 ± 11.4	14.0 ± 7.8	15.1 ± 6.0	11.0 ± 3.3	20.7 ± 10.8
shoots (mg Se kg^{-1})	5.2 ± 3.2	6.1 ± 1.6	7.8 ± 3.2	7.1 ± 4.6	7.9 ± 6.2




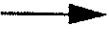
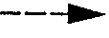
TABLE 3. Maximum rates of Se volatilization and dates of measurement for various vegetated and non-vegetated sites in the constructed wetland. Values shown are means (\pm SD) of a number of measurements, n, made at each site over the period shown.

Site	Volatilization Rate ($\mu\text{g Se m}^{-2} \text{ day}^{-1}$)	n	Dates Measured
<u>Vegetated sites:</u>			
Rabbitfoot grass	190 \pm 150	3	3/8 - 3/17
Cattail	180 \pm 100	4	2/7 - 2/24
Saltmarsh bulrush	150 \pm 40	3	2/10 - 2/24
Saltgrass	80 \pm 40	3	8/18 - 8/25
Brass buttons	60 \pm 30	3	9/22 - 9/29
<u>Non-vegetated sites:</u>			
Inlet channel	170 \pm 30	3	6/30 - 7/7
Fungal mat	110 \pm 60	2	2/24 - 3/3
Detritus on water	100 \pm 110	3	3/17 - 2/28
Algal puddle	50 \pm 20	7	3/3 - 3/17
Unvegetated sediment	20 \pm 10	6	4/7 - 4/18

Legends to Figures

- Figure 1.** Schematic of the constructed wetland showing the pattern of water flow and location of study sites.
- Figure 2.** Removal of Se from wastewater by the constructed wetland from June 23 - October 13. Concentrations of total Se in wastewater entering the wetland (Inlet), after passage through Pass 1 (Outlet - Pass 1), and after passage through the entire wetland (Outlet - Pass 3) (A). Rates of Se removal from wastewater after passage through Pass 1, and through the entire wetland (B). Percent Se mass removed from wastewater after passage through Pass 1, and the entire wetland (C).
- Figure 3.** Total Se (unshaded), total dissolved Se (shaded) and dissolved $\text{Se}^{(\text{IV})}$ (hatched) in the wetland inlet (A), Pass 1 outlet (B), and study site sediment pore water (C) over successive 4-week intervals (June 23 - October 13). Note that most of the Se in the inlet and outlet waters was in dissolved forms, especially selenite, and that selenite in the sediment pore water was rapidly converted to other forms of Se.
- Figure 4.** Changes in the rate of Se volatilization with time over the 16-week study period for saltmarsh bulrush (A), brass buttons (B), saltgrass (C), inlet channel (D) and for detopped bulrush (E). Values shown are means (\pm SD), where $n=3$ (in some instances $n=6$ or 9). Note large increases in Se volatilization rate when shoots are removed (E).



EXPLANATION	
	Inlet Channel
	HDPE Soaker Line
	Diversion Dike
	Generalized Water Flow (Influent)
	Generalized Water Flow (Effluent)

Pass 2

Pass 1



