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Mass balance on water column trace metals in a free-surface-flow-constructed wetlands in Sacramento, California

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Abstract

A mass balance has been performed on trace metals concentrations and hydrology observed between 1994 and 1996 at the Sacramento Demonstration Constructed Wetlands using a first-order areal plug flow model. Water losses to infiltration and evapotranspiration from a typical cell are estimated to average 35 and 7% of influent flow, respectively. The wetlands effluent metals concentrations consistently meet proposed discharge criteria. Annual total mass loadings for all trace metals average 14.0 kg ha^{-1} yr^{-1}, 88% of which consists of zinc, copper, and nickel. Effluent metals leaving the wetland average 3.1 kg ha^{-1} yr^{-1}, 79% of which consists of the same three metals. Annual vegetation harvest events do not appear to account for more than 5% of annual trace metals mass removal, although harvest does appear to represent a significant loss pathway for some metals like mercury, lead, nickel, and chromium. Metals mass removals resulting from first-order removal interactions within the wetland range from 27 to 81%, with the exception of arsenic and nickel which display poor mass removals in part due to their high dissolved concentrations. An average of 7.6 kg ha^{-1} yr^{-1}, or 54% of influent metals loadings, is sequestered within the internal wetland compartments.

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1. Introduction

This paper documents a mass balance on trace metals for a free-water surface flow constructed wetland that provides polishing treatment on disinfected secondary municipal effluent. Trace metals loadings and removal rates are calculated based on trace metal influent and effluent concentrations and wetland inflows and outflows. The mass balance design model incorporates the observed impacts of perceived 'minor' effects like infiltration, evaporation, and vegetative transpiration on effluent metals concentrations. Measurements of trace metals concentrations in distinct wetland compartments (water, sediment, vegetation, and biota) allow conclusions to be drawn about the fate of these metals in wetland environments. Also assessed is the applicability of comparing trace metals concentrations observed to water quality risk criteria. Another predictive tool, the Constructed Wetlands Fate and Transport Evaluation model (CWFATE), has been developed to model the long-term fate of trace metals in wetland environments. The application of the CWFATE model is discussed in other articles (Perry et al., 1996).

Designers of constructed wetlands must be aware of the loadings, fate, and impacts of trace metals present in applied wastewaters and sediments in treatment wetlands. The potential hazard to organisms from exposure to trace metals in the wetland ecosystem (influent, sediment reflux) can be great due to the extreme toxicity of trace metals (Guilizzoni, 1991). However, the impact of metals to organisms are dependent on numerous mechanisms, including: pathway of exposure, the trace metal concentration and physiochemical state (i.e. speciation) in the environment, and the uptake mechanisms (Nieboer and Richardson, 1980).

Constructed wetlands attract a host of aquatic and aquatic-dependent organisms. An improved understanding of trace metal-biotic interactions may assist in an improved merging of designs that optimize the treatment and habitat functions of constructed wetlands. This merger can result in exceptionally functional systems that provide simultaneous water quality improvement and valuable habitat. This multipurpose nature, typical of natural wetland environments, is where the substantial returns on investment and cost effectiveness of treatment wetlands lie (Amell and Eastlick, 1996).

This paper discusses the fate of total trace metal concentrations in wetland environments. It does not attempt to address the fate and transport of organic chemicals and other persistent compounds. Throughout this text, the term 'trace metals' is used to refer to the twelve metals considered in this study (Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Zn). Using an existing classification of metals which separates them into three categories, class A 'oxygen seeking', class B 'nitrogen/sulfur seeking', and borderline, the metals considered in this study consist of; one class

A metal ion (Be), two are class B metal ions (Ag and Hg), and eight borderline metal ions (As, Cd, Cr, Cu, Ni, Pb, Se, Sb, and Zn). The metals considered in this study were chosen primarily for their classification as potential water quality criteria in the proposed California Inland Surface Waters Plan (ISWP, 1991). Some ISWP metals (Be and Th) were dropped from the testing program at an early date because they were not observable at concentrations above the detection limits.

1.1. Sacramento demonstration constructed wetlands

The Sacramento Regional County Sanitation District (District) has developed an 8.9 ha (22 acre) free-water surface flow (FWS) constructed wetland. The facility functions as a demonstration wastewater polishing unit to the largest inland surface discharger in California, the Sacramento Regional Wastewater Treatment Plant in Elk Grove.

A main objective of the Sacramento Demonstration Constructed Wetlands (SDCW) is to demonstrate the effectiveness of constructed wetlands to remove trace metals from secondary municipal effluents to levels in compliance with proposed California Inland Surface Waters Plan (ISWP, 1991) and California Toxics Rule (CTR, 1997) discharge risk criteria. The SDCW were constructed in two phases in 1993, and started operation in March 1994. An intensive 5-year monitoring program is presently in effect through December 1998. The analysis presented in this paper represents monitoring results for the first three project years (1994–1996).

Approximately 3785 $m^3\ d^{-1}$ (1.0 mgd) of secondary effluent is discharged to one of ten wetland treatment cells after being treated with ultraviolet disinfection (Williams et al., 1996). An additional cell supplied with groundwater serves as the project control. Within the treatment system there are five different treatment processes: plug flow, batch discharge, plug flow with recycle, overland flow/plug flow combination, and subsurface flow/plug flow combination. A 0.81-ha (2-acre) habitat cell receives effluent from the treatment cells to monitor toxicity. The wetland treatment cells are 384 m long by 15.2 m wide with a typical operating depth of 0.46 m. As noted in Fig. 1, the flow into each cell is introduced at the north end of a half-cell and proceeds to the south end. At this end flow crosses into a parallel half-cell through a 30.5-cm (12-in) culvert and returns to the north end. The treatment cells, control cell, and habitat cell are closely monitored for water quality, sediment character, vegetation types and growth, and wildlife quantity and diversity. The results of wetland monitoring are summarized annually (Nolte and Associates, 1995, 1996, 1997).

The near-surface soils consist predominantly of medium-stiff silty clay to depths of about 0.6–1.0 m. Below these surface clay soils, dense-to very-dense, cemented sandy silt is encountered to depths exceeding 3.5 m. All native material was used in construction of the unlined wetland cells, with the exception of 30.5 cm of kaolinite clay sealant which were applied to the bottom surface of Cell 9 (Kleinfelder Inc., 1992). Groundwater is encountered at depths of 12.2 m with a regional gradient to the southeast of 0.001 m m^{-1}. Quarterly sampling of the monitoring wells has not

indicated an increase in nitrogen or trace metals attributable to the wetlands (Nolte and Associates, 1997).

Vegetation at the site is diverse, however, two predominant species inhabit the treatment cells: *Schoenoplectus acutus* and *Typha latifolia*. Shallow areas are densely vegetated with average densities on the order of 320 live and dead plants per square meter. Six open water areas evenly distributed throughout each cell occupy approximately 19% of the total wetland cell area and are commonly covered with *Lemna minor*. The remaining 81% of the cell is vegetated. The overland flow regions are primarily occupied with *Cyperus eragrostis*. Treatment cells are typically harvested annually to assist in the management of biomass growth and mosquito populations. The treatment cells are annually inoculated with mosquito fish, *Gambusia affinis*, to aid in mosquito control.

1.2. Review of trace metal interactions

The behavior of metals in aquatic systems is complex and may include interactions among or between the major wetland compartments, above-ground plant parts, roots, litter, biofilms, soils, and water (Kadlec and Knight, 1996). Volatilization of metals into a gaseous phase occurs with mercury, selenium, and arsenic to a lesser degree. Trace metals introduced into the wetland can exist in several particulate or dissolved forms.

Dissolved metals can adsorb onto particles, or exist complexed to inorganic and organic ligands, or be present in solution in the free-ion state. Chemical reactions,

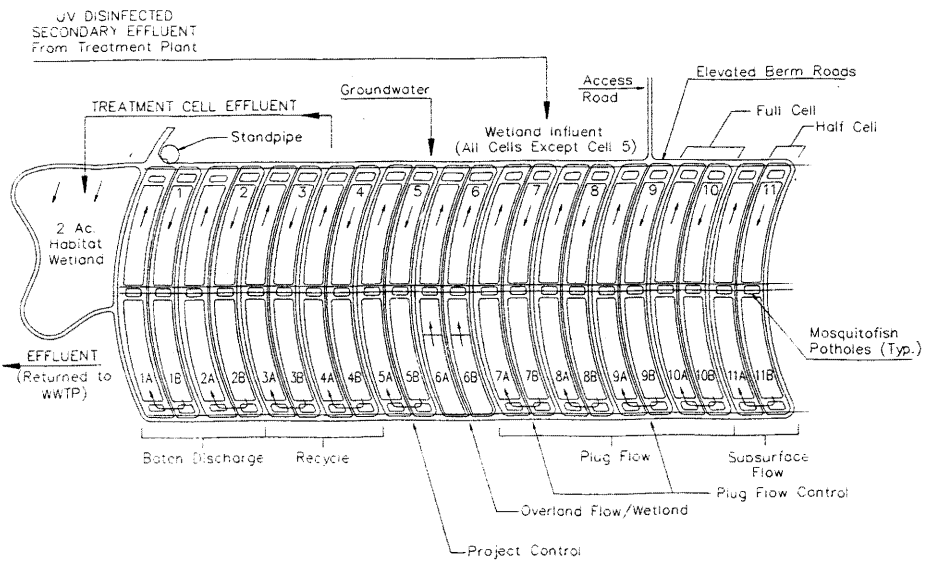

Fig. 1. The flow into each cell.

including; acid-base, precipitation, complexation, oxidation-reduction, and sorption, all play a role in removing metal-ions from the water column, resulting in the metal-ion complex more or less rapidly settling to the sediments (Yong, 1995).

The free metal ion is the most biologically available fraction (Bufflap and Allen, 1995). Therefore, the bioavailability of metal ions is partially related to the solubility of the metal ion at environmental pH values. Due to the presence of large quantities of dissolved organic matter in wetland environments, complexation of metals with organic ligands is considered to be the single most important abiotic factor in reducing metal toxicity (Guilizzoni, 1991).

Sediments can serve as both sinks and reservoirs for trace metals. The exchange of trace metals between the sediments and water column, although dominated in wetland environments by settling, is directly controlled by environmental conditions. Chemical reactions like sorption, precipitation, and complexation contribute to the flux of trace metals to and from the sediments. Flow- or wind-induced currents can resuspend and transport metals to a different location. Interactions between benthic invertebrates and sediment, referred to collectively as bioturbation, can be significant. Mixing, uptake, and aeration may disperse contaminants through sediments and/or release metals to the water column (WERF, 1995).

1.2.1. Metal toxicity

Metal toxicity to an organism results from one metal replacing another in a biomolecule, such as an enzyme, which changes the structure and function of the molecule. Nieboer and Richardson (1980) divide the mechanisms of metal-ion toxicity into the following three categories: (1) blocking of essential biological functional groups of biomolecules, (2) displacing the essential metal ion in biomolecules and (3) modifying the active conformation of biomolecules. The net result of the binding of metal ions to reactive sites not normally requiring them, is often inhibitory. These effects can result in acute and chronic toxicity impacts in organisms.

The uptake of metals by organisms is related to the intrinsic biology of the organism, which regulates the net uptake of the metals, and the biological behavior of the organism, which is expressed in its life cycle, life history, and the trophic situation in which it grows (Guilizzoni, 1991). The presence of tolerance mechanisms may also be determinative (Nieboer and Richardson, 1980).

1.3. Assumptions

An assumption is made that the available water mass balance data, which covers the final quarter of the second project year and first three quarters of the third project year (September 1996 to September 1997), can be applied to trace metal concentration data for different project years. Without this assumption, trace metal mass balances cannot be conducted for the initial two project years, due to a lack of reliable water balance data. Variations in inflow, rainfall, and outflow between the available water balance data and the initial project year's conditions may be

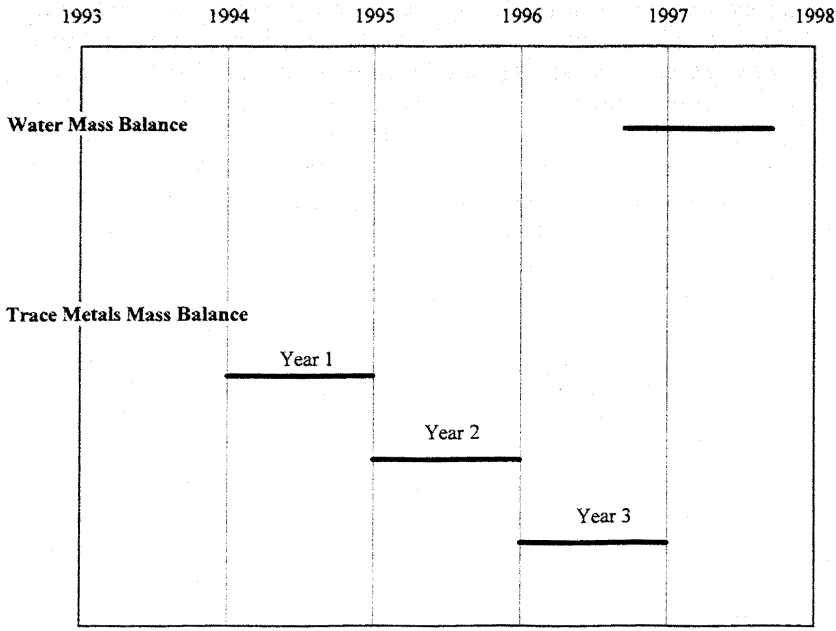

Fig. 2. The availability of the data used for each mass balance.

significant, but are not readily identifiable, without similar simplifying assumptions. Although the lack of reliable water balance data precludes dynamic modeling prior to September 1996, useful information can be obtained from a simpler static model. This assumption is considered reasonably valid for the annual basis at which trace metals mass balances are performed for the first two project years. A monthly trace metals mass balance is also conducted under a similar assumption using non-synchronous trace metal and water balance data.

2. Experiment materials and methods

The mass balance design model presented in this paper is based on simultaneous analysis of two mass balance equations for water and for trace metals m the wetland cells. Monthly (at a minimum) average monitoring results are available for all but one variable in each of the mass balance equations, resulting in the analysis of two equations with two unknowns.

Three annual events, corresponding to the average annual metals concentrations observed in all wetland treatment cells for each of the first three years of the operation of the marsh, are analyzed in this manner. Fig. 2 shows the availability of the data used for each mass balance. Each year's trace metals mass balance is solved using the same water balance data set (September 1996 to September 1997),

corresponding to the earliest period for which reliable data could be collected for each water balance variable. A monthly trace metals mass balance is also performed for the latest periods for which both monthly trace metals data and monthly water balance data are available. The methodology used to obtain the hydraulic and wetland compartment data are summarized below.

2.1. Water mass balance

A water balance for the constructed wetlands has been prepared by summing inflows and outflows, as shown in Fig. 3.

$$Q_I + P(A + \psi A_c) = ET(A) + Q_{GW} + Q_E \pm S \quad (1)$$

where: Q_I, wastewater addition, ($m^3\ d^{-1}$); P, precipitation rate, ($m\ d^{-1}$); A, wetland surface area, (m^2); ψ, catchment runoff coefficient; A_c, catchment area, (m^2); ET, evapotranspiration rate, ($m\ d^{-1}$); Q_{GW}, infiltration to groundwater, ($m^3\ d^{-1}$); Q_E, outflow, ($m^3\ d^{-1}$); S, storage in wetland, ($m^3\ d^{-1}$).

Measurements of influent and effluent flow rates, precipitation, evaporation, and transpiration are used to determine the quantities of water lost to infiltration in the unlined treatment cells. Meters on the influent distribution pipe and effluent flow channel measure flow rates. Influent flow is logged on a weekly basis. Effluent flow is logged every 15 min and is converted to a daily basis for use in this water balance.

Influent and effluent flow rates measured in Cell 7 are presented in the water balance. Daily precipitation is recorded by an onsite rain gauge. Precipitation falling on a catchment area of 0.13 ha equal to one-half the width of the levees that surround a typical cell, adjusted with a 0.8 runoff coefficient, is assumed to contribute to wetland inflows. The wetland cells are not operated to store water.

Evaporation rates are measured at the site using pans placed in the open and vegetated areas of the treatment cells and a reference pan placed on a levee near the aquatic habitat cell. Open water pan evaporation values measured over nine months in 1996 averaged 88 percent of reference pan evaporation values and a

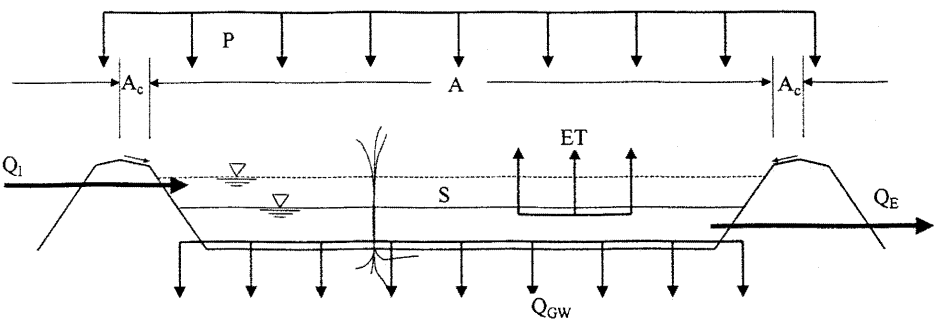

Fig. 3. Schematic of water mass balance for a typical wetland cell.

strong correlation (corr = 0.99) between the two was observed (Nolte and Associates, 1997). Vegetated evaporation values measured over the same period were approximately 46% of the open water evaporation values. Consequently, it can be interpreted that evaporation from a typical wetland cell accounts for approximately 49.5% of reference pan evaporation values. The vegetated area of a typical wetland cell occupies approximately 81% of the total wetland area.

Monthly transpiration measurements have been underway since June 1997 using twelve wetland mesocosms located within vegetated areas in three wetland cells. Individual rhizomes of *Scirpus* were planted in 15 cm of soil within 114-l (30-gallon) containers. The containers were sealed with clear plastic, allowing only the shoots to protrude. The plants were allowed to establish normal growth, defined as at least four shoots of three meters or more, at which time the containers were raised onto wooden platforms so 10 cm of freeboard could be maintained. The water levels were adjusted and monitored to determine transpiration per unit area. Estimates of vegetation biomass were made using a correlation between plant length and dry weight to determine transpiration per unit biomass.

Wetland evapotranspiration is considered equivalent to lake evaporation, and is typically estimated as 80% of reference pan evaporation rates (DWR, 1974). This assumption, combined with the assumptions stated above for vegetated evaporation, implies that wetland transpiration rates from a typical wetland cell can be estimated as 30.5% of reference pan evaporation rates, or approximately 50 cm per year. The total transpiration for a typical cell estimated from the available mesocosm data (June to October 1997) on a transpiration per unit area basis is approximately 87 cm. Transpiration rates determined from transpiration per unit biomass estimates exceed those determined from transpiration per unit area estimates by an order of magnitude. Although these higher transpiration rates are not used in the water balance presented in this article, the impact of these rates on metals removal is considered in the discussion.

The large values of observed transpiration rates are not unreasonable in light of the observation that small wetlands can display larger values of evapotranspiration than otherwise estimated using standard ratios of reference pan and lake evaporation (Kadlec and Knight, 1996). It is likely that the extrapolation of small-scale mesocosm transpiration results over a large-scale wetland area results in inaccurate overestimates of wetland transpiration. The use of the mesocosm transpiration per unit area estimates in this water balance is considered a reasonable estimate of wetland cell transpiration until additional information can be provided to accurately define the magnitude of each water loss pathway. Additional transpiration and evaporation measurements made in the months of November and May will provide an improved understanding of the role of transpiration in the water balance. Measurements of the water lost from cells where influent and effluent flows have been shut off will provide an improved understanding of the magnitude of infiltration in comparison to evapotranspiration.

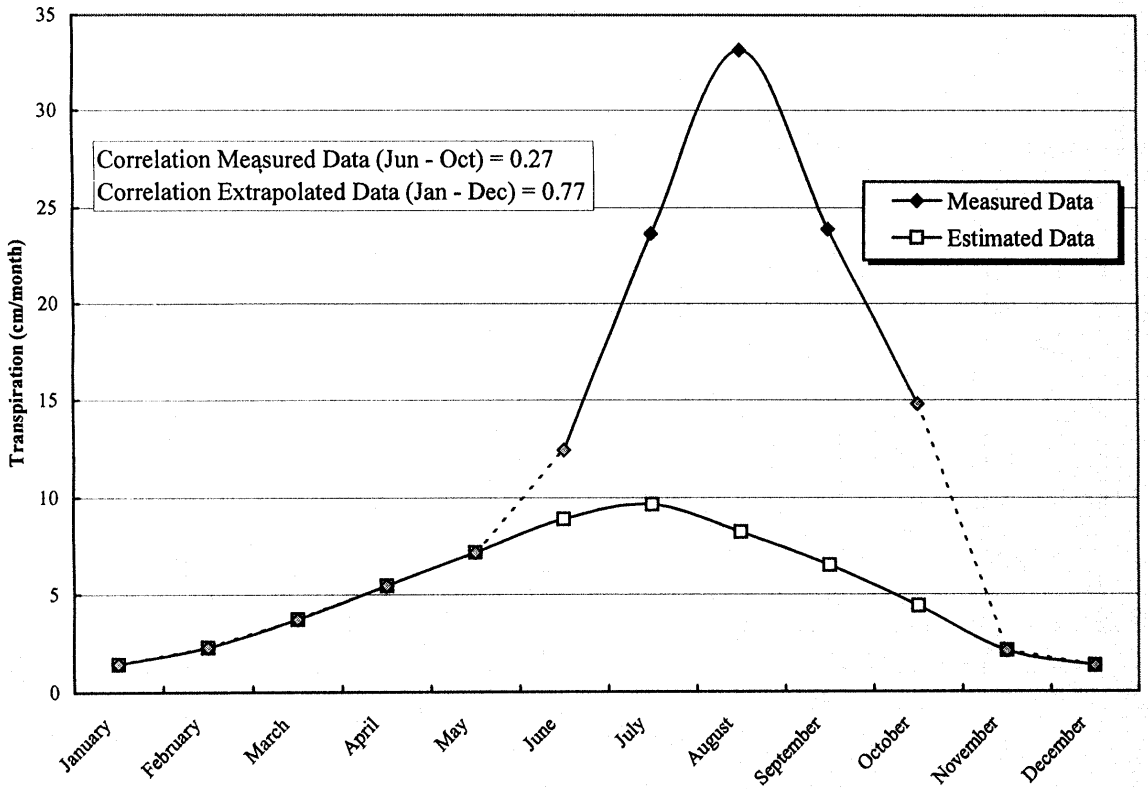

Fig. 4. Comparison of measured and estimated transpiration rates.

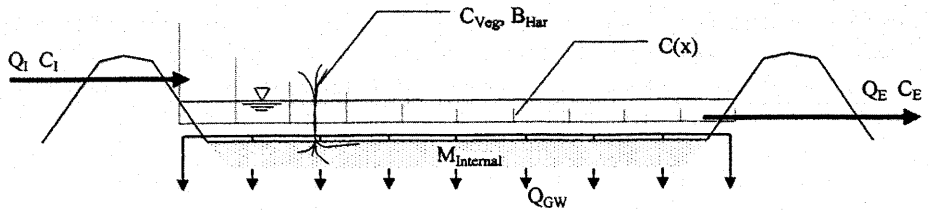

Fig. 5. Schematic of trace metals mass balance for a typical wetland cell.

The transpiration data appears to indicate that the standard assumption for transpiration significantly underestimates the seasonal impact of wetland transpiration in densely vegetated wetlands. The measured transpiration rate curve is poorly correlated (corr = 0.27) with that estimated as 30.5% of reference evaporation data (See Fig. 4). If the remaining months for which measured transpiration rates are not available are estimated as 30.5% of reference pan evaporation rates, an annual transpiration rate of 106 cm is observed for a typical wetland cell. Therefore, an annual wetland evapotranspiration rate of 187 cm is estimated for a typical wetland cell at the SDCW (see Table 1).

2.2. Trace metals mass balance

In Fig. 5, a mass balance is presented for trace metals in the wetland cells which includes the volume of trace metals accumulated over the operation of the wetland (i.e. the bulk solids layer between the initial and current wetland bottom). This mass balance can be described as the mass of metal entering the wetland plus the mass of metal residing in the wetland minus the sum of the mass of metals observed exiting the wetland, the mass of metal transported below the accreted sediment layer, and the mass of metal removed from the wetland by alternative means such as harvesting or transport through biota. The simplifying assumption that trace metals residing in any of several wetland compartments can be lumped together as a single term allows trace metals mass removals to be readily identified.

$$Q_I C_I + M_{Internal} = Q_E C_E + Q_{GW} C(x) + C_{Veg} \frac{B_{Har}}{t_{Har}} \tag{2}$$

where: C_I, trace metal concentration in inflow, (μg l^{-1}); $M_{internal}$, mass of trace metal residing in wetland, (mg d^{-1}); C_E, trace metal concentration in outflow, (μg l^{-1}); $C(x)$, trace metal concentration in wetland water column at distance x from inlet, (μg l^{-1}); C_{Veg}, trace metal concentration in vegetation tissue, (mg kg^{-1}); B_{Har}, biomass removed during harvest event, (kg); t_{Har}, frequency of harvest event, (d).

Table 1
Water balance for a typical wetland cell (September 1996–September 1997)

Month	Inflow[a]			Outflow[b]			Precipitation[c]			Evaporation[d]			Transpiration[e]			Estimated water loss[f]		
	(gpm)	(Mgal)	(m mo^{-1})	(gpm)	(Mgal)	(m mo^{-1})	(in)	(Mgal)	(m mo^{-1})	(in)	(Mgal)	(m mo^{-1})	(in)	(Mgal)	(m mo^{-1})	(Mgal)	(m mo^{-1})	(%ofinfluent)
January	62.2	2.78	1.80	46.0	2.05	1.33	15.7	0.72	0.40	0.7	0.03	0.02	0.46	0.01	0.01	1.40	0.91	51
February	57.5	2.32	1.50	36.8	1.49	0.96	0.4	0.02	0.01	1.2	0.05	0.03	0.73	0.02	0.02	0.78	0.51	34
March	62.3	2.78	1.80	30.0	1.34	0.86	0.3	0.01	0.01	1.9	0.08	0.05	1.19	0.04	0.03	1.34	0.87	48
April	47.9	2.07	1.34	23.0	0.99	0.64	0.3	0.01	0.01	2.8	0.11	0.07	1.74	0.06	0.04	0.92	0.60	45
May	68.5	3.06	1.98	45.6	2.04	1.32	0.0	0.00	0.00	3.7	0.15	0.09	2.29	0.07	0.06	0.80	0.52	26
June	93.1	4.02	2.60	67.5	2.92	1.89	1.1	0.05	0.03	4.6	0.18	0.12	3.96	0.13	0.10	0.85	0.55	21
July	69.5	3.10	2.01	38.2	1.71	1.10	1.3	0.06	0.03	5.0	0.20	0.13	7.54	0.24	0.19	1.02	0.66	33
August	73.5	3.28	2.12	46.3	2.07	1.34	0.2	0.01	0.00	4.3	0.17	0.11	10.58	0.34	0.27	0.72	0.46	22
September	72.1	3.12	2.01	45.5	1.97	1.27	0.0	0.00	0.00	3.4	0.13	0.09	7.62	0.24	0.19	0.77	0.50	25
October	69.3	3.10	2.00	40.7	1.82	1.18	0.4	0.02	0.01	2.3	0.09	0.06	4.72	0.15	0.12	1.06	0.68	34
November	69.6	3.01	1.94	46.3	2.00	1.29	1.3	0.06	0.03	1.1	0.04	0.03	0.67	0.02	0.02	1.00	0.65	33
December	69.6	3.11	2.01	46.2	2.06	1.33	7.1	0.33	0.18	0.7	0.03	0.02	0.43	0.01	0.01	1.33	0.86	43
Total	—	35.74	23.11	—	22.44	14.51	27.9	1.28	0.71	31.7	1.24	0.80	41.9	1.33	1.06	12.00	7.76	—
Average	67.9	2.98	1.93	42.7	1.87	1.21	2.3	0.11	0.06	2.6	0.10	0.07	3.5	0.11	0.09	1.00	0.65	35
S.D.	10.7	0.5	0.3	10.8	0.5	0.3	4.6	0.2	0.1	1.5	0.1	0.0	3.4	0.1	0.1	0.2	0.2	10

[a] Average weekly influent flows measured from September 1996 to September 1997.
[b] Average daily effluent flows measured from September 1996 to September 1997.
[c] Daily precipitation data measured et treatment plans September 1996 to September 1997. Includes precipitation falling on wetland surface area of 0.59 ha and catchment area of 0.13 ha. A catchment coefficient of 0.8 was used to estimate overland runoff from berm surfaces.
[d] Average monthly pan evaporation for the Sacramento Valley (DWR, 1974). Multiplied by 0.88 factor to estimate open water wetland evaporation and by 0.405 factor to estimate vegetated wetland evaporation.
[e] Average of weekly mesocosm areal transpiration rates measured between June and October 1997. Other months estimated as 30.5% of pan evaporation rates.
[f] Determined as Inflow + Precipitation − Outflow − Evaporation − Transpiration.

Influent and effluent total metals concentrations in each wetland treatment cell have been monitored on a monthly basis for the duration of the project. Wetland influent is sampled at the standpipe that distributes disinfected secondary flows to the ten wetland treatment cells. Grab samples of wetland effluent are obtained immediately upstream of the effluent weir outside the outfall box. Measurements of dissolved wetland metals concentrations were also made on samples obtained along the wetland treatment cell profiles in July 1996.

Trace metal water column concentration profiles can be determined from average influent and effluent trace metals concentrations using a first-order areal plug flow model adjusted for a distance variable flow rate that accounts for the effects of uniform precipitation, infiltration, and evapotranspiration (Kadlec and Knight, 1996).

$$C(x) = C_a + (C_i - C_a)\left(\frac{q_i + ax}{q_i}\right)^{-(1+(k+I)/a)} \tag{3}$$

where: I, infiltration rate, (m yr^{-1}); C_P, trace metal concentration in rain, (g m^{-3}); C^*, background trace metal concentration, (g m^{-3}); k, first order areal reduction rate constant, (m d^{-1}).

$$a = P - ET - I \tag{4}$$

$$C_a = \frac{[PC_P + kC^*]}{(p - ET + k)} \tag{5}$$

$$q_i = \frac{Q_i}{A_T} \tag{6}$$

$$y = \frac{x}{L} \tag{7}$$

In the case of trace metals, the concentration in rain and as the background concentration is considered to be very low relative to the influent and are therefore assumed to equal zero. The processes of infiltration and evapotranspiration act to slow incoming water and increase detention time. Rainfall has the opposite effect. Evapotranspiration also concentrates the trace metal remaining in the wetland, while infiltration carries trace metals to the subsurface, thereby contributing to the accumulation of metals in the sediments and transport of metals to groundwater. The assumption that the concentration of trace metals in the infiltrated water equals the overlying water concentration results in a conservative estimate of the mass of metal carried outside of the wetland cell to underlying groundwater layers. The volatilization of metals is assumed to be negligible.

Metals may leave the system through pathways other than outflow or infiltration, such as by the removal of harvested vegetation or by biotic uptake and subsequent transport outside of the system. The latter term is assumed to be negligible. Trace metal removals due to vegetation harvest can be estimated based on the trace metal

concentrations observed annually in live shoots, average observed wetland cell vegetation biomass values, and an estimate of 68% biomass removal for each harvest event (Nolte and Associates, 1997). Although several vegetation harvest frequencies and methods have been tested at the SDCW, an annual harvest event is presented in the mass balance. Cell 7 has never been harvested, so this term can be neglected for this cell.

Due to the complex interaction of trace metals between wetland compartments, M_{Internal} is used to describe the trace metal stored in the wetland over the period of the mass balance. The M_{Internal} term is considered to be the sum of trace metal accumulated in the sediment layer, residing in vegetation (e.g. macrophytes, algae, and *Lemna*) or biota tissue, or attached to settleable detrital particles. Metals residing in any one of these compartments can be considered to either be stored within the wetland or cycling through the wetland. Since the fate and transport of trace metals within the wetland system is complex, with multiple interactions between each of the wetland compartments, it is easier to solve for the metals residing internally within the wetland as a lumped parameter.

3. Results

The results of the water mass balance and trace metal mass balances are presented.

3.1. Water mass balance

The results of the water balance conducted to date, presented in Table 1 and Fig. 6, indicate average annual water losses to infiltration on the order of 35% of influent flow. Infiltration remains fairly constant during summer months and demonstrates a strong positive correlation with precipitation (corr = 0.69) and a weak correlation (corr = 0.12) with the sum of inflow and precipitation. Outflow ranges from 48 to 74% of inflow, and demonstrates a strong positive correlation with the sum of inflow and precipitation (corr = 0.93). Water year 1996 demonstrates a concentrated wet season, with precipitation averaging 26% of inflow in January and 11% of inflow in December. Precipitation averaged less than 2% of inflow during all other months. Evapotranspiration exhibits a typical seasonal curve with a peak in mid-August and ranged from slightly greater than 1–15.4% of inflow on a monthly basis.

3.2. Trace metals mass balance

Annual average, minimum, maximum, and the number of influent and effluent samples analyzed for total metals within all ten treatment cells for 1994 (Year 1) through 1996 (Year 3) are presented in Table 2. The results of dissolved metals analysis performed in 1996 are also presented. The metals concentrations observed in the groundwater-fed control cell (Cell 5) are not presented. Detection limits have

Table 2
Influent and effluent trace metals concentrations observed in Sacramento demonstration constructed wetlands (1994–1996)

Metal	Influent concentration ($\mu g\,l^{-1}$)				Effluent concentration ($\mu g\,l^{-1}$)				Apparent concentration removal[e] (%)	Aboveground vegetation tissue concentration[f] ($mg\,kg^{-1}$)
	Average	Minimum	Maximum	Number	Average	Minimum	Maximum	Number		
1994[a]										
Silver (total)[g]	0.70	0.70	0.70	1	0.29	0.05	0.42	9	58	NA
Arsenic (total)	3.25	2.00	4.50	2	2.65	2.00	5.00	17	18	1.15
Beryllium (total)[c]	0.581	0.05	1.10	2	0.05	0.05	0.05	9	91	NA
Cadmium (total)	0.11	0.10	0.11	2	0.05	0.05	0.10	13	49	NA
Chromium (total)	1.70	0.50	3.50	3	0.98	0.50	4.00	17	42	0.72
Copper (total)	6.77	6.00	8.20	3	2.44	0.50	4.20	17	64	1.01
Mercury (total)	0.013	0.008	0.018	2	0.005	0.002	0.009	17	62	NA
Nickel (total)	2.70	2.70	2.70	1	2.84	2.20	4.00	13	−5	0.57
Lead (total)	2.30	1.50	3.40	3	0.38	0.17	0.50	17	84	0.39
Antimony (total)	0.34	0.34	0.34	1	0.12	0.10	0.13	9	64	NA
Selenium (total)[d]	0.53	0.50	0.55	3	0.62	0.50	1.30	21	−16	NA
Zinc (total)	49.00	34.00	67.00	4	10.90	2.50	73.00	25	78	3.00
1995[a]										
Silver (total)	0.28	0.21	0.35	4	0.04	0.01	0.06	30	85	NA
Arsenic (total)	2.42	1.70	4.40	6	2.51	0.55	4.50	31	−4	NA
Cadmium (total)	0.12	0.05	0.29	12	0.05	0.01	0.19	49	59	NA
Chromium (total)[g]	2.47	0.55	8.60	11	1.18	0.50	4.20	49	52	NA
Copper (total)	7.21	5.20	13.00	12	3.47	1.90	6.70	49	52	2.37
Mercury (total)	0.010	0.008	0.013	6	0.003	0.001	0.010	35	66	0.07
Nickel (total)	7.26	3.60	9.80	12	6.79	1.40	12.00	49	6	4.92
Lead (total)	1.39	0.25	4.80	12	0.19	0.05	0.73	49	86	0.37
Antimony (total)	0.64	0.25	1.50	6	0.28	0.05	1.10	30	55	NA
Zinc (total)	35.20	24.00	84.00	10	3.26	0.50	8.30	38	91	8.25
1996[a,b]										
Silver (total)	0.34	0.21	0.40	6	0.05	0.01	0.10	41	86	0.06
Arsenic (total)	1.75	1.00	2.20	4	2.18	1.00	3.80	38	−25	0.32
Cadmium (total)	0.10	0.02	0.20	7	0.06	0.01	0.20	44	41	0.05
Chromium (total)	1.05	0.50	1.40	11	1.35	0.50	6.80	52	−28	1.64

Table 2 (*Continued*)

Metal	Influent concentration ($\mu g\,l^{-1}$)				Effluent concentration ($\mu g\,l^{-1}$)				Apparent concentration removal[e] (%)	Aboveground vegetation tissue concentration[f] ($mg\,kg^{-1}$)
	Average	Minimum	Maximum	Number	Average	Minimum	Maximum	Number		
Copper (total)	8.90	6.20	11.00	11	4.42	3.20	9.50	52	50	1.88
Mercury (total)	0.011	0.007	0.017	4	0.005	0.001	0.017	34	60	0.01
Nickel (total)	6.85	4.50	9.50	11	8.41	6.00	16.00	52	−23	0.70
Lead (total)	0.85	0.59	1.00	11	0.25	0.10	0.79	52	71	0.50
Antimony (total)	0.43	0.38	0.49	6	0.18	0.12	0.36	42	58	NA
Selenium (total)[d]	1.00	1.00	1.00	1	1.00	1.00	1.00	8	0	NA
Zinc (total)	37.00	30.00	47.00	11	7.58	1.40	39.00	52	80	10.00
Silver (dissolved)	0.06	0.05	0.06	7	0.01	0.01	0.01	6	83	NA
Arsenic (dissolved)	2.46	2.10	2.90	8	2.42	1.80	2.90	6	2	NA
Cadmium (dissolved)	0.10	0.01	0.46	8	0.01	0.01	0.02	6	88	NA
Chromium (dissolved)	1.00	1.00	1.00	8	1.13	1.00	1.80	6	−13	NA
Copper (dissolved)	7.38	5.50	9.70	8	2.13	1.80	2.60	6	71	NA
Mercury (dissolved)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Nickel (dissolved)	7.90	7.80	8.10	8	6.93	6.50	8.00	6	12	NA
Lead (dissolved)	0.10	0.10	0.11	8	0.10	0.10	0.10	6	1	NA
Antimony (dissolved)	0.26	0.24	0.28	8	0.11	0.10	0.13	6	56	NA
Selenium (dissolved)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Zinc (dissolved)	23.38	22.00	24.00	8	2.93	1.60	4.70	6	87	NA

NA, Not available.

[a] Wetland cell water quality data collected monthly in ten wetland treatment cells between March 1994 and December 1996.

[b] Dissolved inlet and outlet concentration taken during July 1996 water quality profiles.

[c] Beryllium sampled only in 1994.

[d] Selenium sampled in 1994 and 1996 only.

[e] Apparent concentration removal does not factor out effects of infiltration and evapoconcentration on trace metal concentration.

[f] Average trace metal concentration observed in live vegetation shoots (Nolte and Associates, 1997; Table 4–14).

[g] One outlier concentration value removed from influent (standpipe) data set. Influent silver concentration in 1994 corresponds to 85th percentile concentration values. Influent chromium concentration in 1995 corresponds to 88th percentile concentration values.

steadily decreased over the course of the monitoring program due to improved analytical techniques, with one-half the detection limit used when values are below the detection limit. The apparent concentration removal, determined as the difference between average influent and effluent concentrations are presented on this table. Average aboveground vegetation tissue concentrations are also presented in this table.

Influent trace metals concentrations are typically measured in parts per billion ($\mu g\ l^{-1}$) levels, with the exception of mercury, which is measured at parts per trillion (ng l^{-1}) levels. For each of the first 3 years, apparent trace metals concentration removals have ranged between 40 and 90% removal for all metals, with the exception of arsenic and nickel which display low removals and/or increases. Arsenic and nickel both enter the wetland in a predominantly dissolved form and the chemistry of these metals inhibits their removal from solution. The low or negative removals observed for arsenic, nickel, and chromium do not necessarily correspond to a net positive release of trace metal from the wetland. As discussed below, evapotranspiration, rainfall, and infiltration all effect the concentration profile, consequently further mass balance analysis is needed to ascertain the degree of removal attributable to each water balance element.

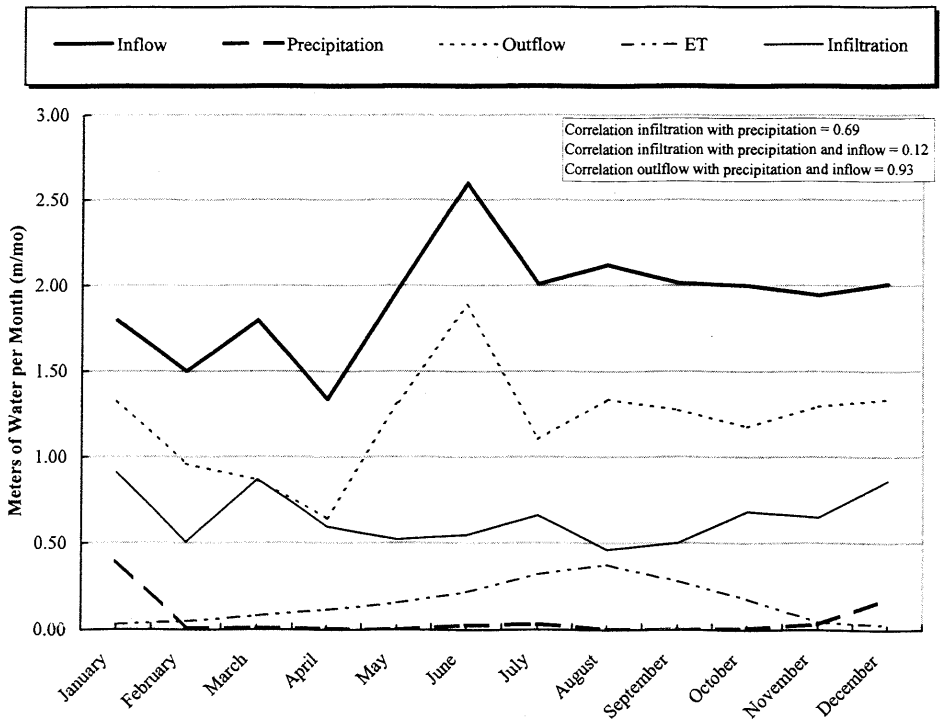

Fig. 6. Monthly water balance for a typical wetland cell (September 1996–September 1997).

Selenium has not been measured in concentrations far above the detection limit and has not been regularly tested. Analysis of variation on the metals data obtained during the initial 3 years has not indicated any statistically significant differences among treatment cells or treatment processes with regard to effluent metals concentrations (Nolte and Associates, 1997).

Annual mass balances for trace metals in the water column are presented in Table 3. The mass removal fractions attributable to outflow, infiltration, and harvest are presented on this table. The mass of trace metal residing internally within the wetland, M_{Internal}, is determined for both cases with and without an annual harvest event. Annual total mass loadings for all trace metals average 14.0 kg ha^{-1} yr^{-1}, 88% of which consists of zinc, copper, and nickel. Effluent metals leaving the wetland average 3.1 kg ha^{-1} yr^{-1}, 79% of which consists of the same three metals. A total of 42.1 kg ha^{-1} yr^{-1} of trace metals have been applied to the wetland cells during the 3-year period.

Annual mass removals for trace metals in the water column are presented in Table 4. It can be seen in all years that all metals exhibit positive apparent mass removals. Infiltration of metals to subsurface soils consistently averages 20% and ranges from 13 and 38% of annual inflow trace metals. Annual vegetation harvest events do not appear to account for more than 5% of annual trace metals mass removal, although harvest does appear to represent a significant loss pathway for some metals like mercury, lead, nickel, and chromium. Metals mass removals resulting from first order removal interactions within the wetland range from 27 to 81%, with the exception of arsenic and nickel which display poor mass removals.

A mass balance performed for monthly (January to December 1996) total zinc concentrations is presented in Table 5. The annual total mass loadings correspond closely with those estimated for zinc in the 1996 annual mass balance presented in Table 3. A single annual harvest event conducted in April represents 87% of that month's zinc leaving the wetland cell, however, this accounts for only 7% of the annual zinc removed from the wetland cell.

4. Discussion

The treatment wetlands regularly demonstrate significant removals of many trace metals monitored in the program. Judging from the detailed surveys of fish, invertebrates, and avian species in comparison with neighboring natural systems, the constructed wetlands system is thriving biologically (Nolte and Associates, 1997). The performance of the constructed wetlands in achieving compliance with proposed discharge standards is presented in Table 6. The applicable proposed California Toxics Rule (CTR, 1997) and proposed Inland Surface Waters Plan (ISWP, 1991) metals concentration discharge standards are included in this table. Neither the CTR nor the ISWP have yet been adopted. It is very likely however, that the CTR will be adopted in spring of 1998 and the ISWP will be revised and adopted sometime in 1999 (Grovhaug, 1998). While the exact discharge or receiving water limitations may change, it is unlikely they will change significantly from the

Table 3
Trace metals annual mass loadings for a typical wetland cell

Metal	Trace metal mass loading ($kg\ ha^{-1}\ yr^{-1}$)									
	Influent			Effluent			Infiltration[b]	Harvest[c]	Internal	
	Total	Dissolved	Particulate	Total	Dissolved	Particutate			w/Harvest	w/o Harvest
1994										
Silver (total)	0.16	NA	NA	0.04	NA	NA	0.04	0.001[d]	0.08	0.08
Arsenic (total)	0.75	NA	NA	0.38	NA	NA	0.23	0.021	0.11	0.13
Beryllium (total)[a]	0.13	NA	NA	0.01	NA	NA	0.02	NA	0.11	0.11
Cadmium (total)	0.02	NA	NA	0.01	NA	NA	0.01	0.001[d]	0.01	0.01
Chromium (total)	0.39	NA	NA	0.14	NA	NA	0.10	0.013	0.13	0.15
Copper (total)	1.56	NA	NA	0.35	NA	NA	0.34	0.019	0.85	0.87
Mercury (total)	0.0030	NA	NA	0.0007	NA	NA	0.0007	0.0007[d]	0.0009	0.0016
Nickel (total)	0.62	NA	NA	0.41	NA	NA	0.22	0.011	−0.02	−0.01
Lead (total)	0.53	NA	NA	0.05	NA	NA	0.09	0.007	0.38	0.39
Antimony (total)	0.08	NA	NA	0.02	NA	NA	0.02	NA	0.04	0.04
Selenium (total)[a]	0.12	NA	NA	0.09	NA	NA	0.05	NA	−0.01	−0.01
Zinc (total)	11.32	NA	NA	1.58	NA	NA	2.07	0.056	7.61	7.67
1994 Subtotal	15.70	NA	NA	3.09	NA	NA	3.17	0.130	9.30	9.43
1995										
Silver (total)	0.07	NA	NA	0.01	NA	NA	0.01	0.0019[d]	0.05	0.05
Arsenic (total)	0.56	NA	NA	0.36	NA	NA	0.19	0.023[d]	−0.02	0.00
Cadmium (total)	0.03	NA	NA	0.01	NA	NA	0.01	0.0016[d]	0.01	0.01
Chromiurn (total)	0.57	NA	NA	0.17	NA	NA	0.14	0.038[d]	0.22	0.26
Copper (total)	1.66	NA	NA	0.50	NA	NA	0.41	0.075	0.68	0.75
Mercury (total)	0.0023	NA	NA	0.0005	NA	NA	0.0005	0.0023	−0.0010	0.0013
Nickel (total)	1.68	NA	NA	0.99	NA	NA	0.55	0.157	−0.02	0.14
Lead (total)	0.32	NA	NA	0.03	NA	NA	0.05	0.012	0.23	0.24
Antimony (total)	0.15	NA	NA	0.04	NA	NA	0.03	NA	0.07	0.07
Zinc (total)	8.13	NA	NA	0.47	NA	NA	1.12	0.263	6.27	6.54

Table 3 (*Continued*)

Metal	Trace metal mass loading ($kg\ ha^{-1}\ yr^{-1}$)									
	Influent			Effluent			Infiltration[b]	Harvest[c]	Internal	
	Total	Dissolved	Particulate	Total	Dissolved	Particutate			w/Harvest	w/o Harvest
1995 Subtotal	13.16	NA	NA	2.58	NA	NA	2.52	0.573	7.49	8.06
1994–95 Subtotal	28.86	NA	NA	5.67	NA	NA	5.69	0.703	16.79	17.49
1996										
Silver (total)	0.08	0.01	0.06	0.01	0.00	0.01	0.01	0.003	0.06	0.06
Arsenic (total)	0.40	0.57	0.00	0.32	0.35	0.00	0.15	0.014	−0.08	−0.07
Cadmium (total)	0.02	0.02	0.00	0.01	0.00	0.01	0.01	0.002	0.01	0.01
Chromium (total)	0.24	0.23	0.01	0.20	0.16	0.03	0.09	0.071	−0.12	−0.05
Copper (total)	2.06	1.70	0.35	0.64	0.31	0.33	0.51	0.081	0.82	0.90
Mercury (total)	0.0026	NA	NA	0.0007	NA	NA	0.0006	0.0003	0.0011	0.0014
Nickel (total)	1.58	1.82	0.00	1.22	1.01	0.21	0.60	0.030	−0.26	−0.23
Lead (total)	0.20	0.02	0.17	0.04	0.01	0.02	0.04	0.022	0.10	0.12
Antimony (total)	0.10	0.06	0.04	0.03	0.02	0.01	0.02	NA	NA	0.05
Zinc (total)	8.54	5.40	3.15	1.10	0.43	0.67	1.52	0.432	5.50	5.93
1996 Subtotal	13.23	NA	NA	3.55	NA	NA	2.95	0.655	6.02	6.72
1994–96 Subtotal	42.09	NA	NA	9.22	NA	NA	8.64	1.359	22.81	24.22

[a] Trace metal dropped from monitoring program in 1995.

[b] Determined using first-order areal plug flow model that accounts for effects of *P*, *I*, and *ET*. Assumes that metals concentrations in overlying water column are carried to underlying groundwater layers at observed infiltration rate.

[c] Typical harvest values based on average vegetation tissue concentrations presented in Table 2, average wetland cell biomass values stated below, and average harvest biomass removal rate of 68% (Nolte and Associates, 1997).

[d] Aboveground vegetation tissue trace metal concentration data unavailable. Estimated as average of available abovegroumd vegetation tissue trace metal concentration data.

NA, Not applicable.

Inlet hydraulic loading rate: 68 gpm = 6.33 cm d^{-1}
Outlet hydraulic loading rate: 43 gpm = 3.98 cm d^{-1}
Infiltration: 23 gpm = 2.13 cm d^{-1}
Wetland cell biomass
1994 2.74 kg dw m^{-2}
1995 4.68 kg dw m^{-3}
1996 6.36 kg dw m^{-4}

Table 4
Trace metals annual mass removal for a typical wetland cell

Metal	Mass removal[b] (%)					
	Apparent		Infiltration	Harvest	First order	
	Total	Dissolved			w/Harvest	w/o Harvest
1994						
Silver (total)	74	NA	23	NA	50	50
Arsenic (total)	49	NA	31	3	15	18
Beryllium (total)[a]	95	NA	13	NA	81	81
Cadmium (total)	68	NA	24	NA	44	44
Chromium (total)	64	NA	27	3	34	37
Copper (total)	77	NA	22	1	54	55
Mercury (total)	76	NA	22	NA	54	54
Nickel (total)	34	NA	35	2	−3	−1
Lead (total)	90	NA	16	1	72	73
Antimony (total)	78	NA	22	NA	56	56
Selenium (total)[a]	27	NA	37	NA	−10	−10
Zinc (total)	86	NA	18	0	67	68
1994 Subtotal	80	NA	20	1	59	60
1995						
Silver (total)	91	NA	16	NA	75	75
Arsenic (total)	35	NA	35	NA	0	0
Cadmium (total)	74	NA	23	NA	51	51
Chromium (total)	70	NA	24	NA	46	46
Copper (total)	70	NA	25	5	41	45
Mercury (total)	79	NA	22	101	45	56
Nickel (total)	41	NA	33	9	−1	8
Lead (total)	91	NA	16	4	72	76
Antimony (total)	72	NA	24	NA	48	48
Zinc (total)	94	NA	14	3	77	80
1995 Subtotal	80	NA	19	4	57	61
1994–95 Subtotal	80	NA	20	2	58	61
1996						
Silver (total)	91	89	16	3	72	76
Arsenic (total)	22	38	38	3	−20	−16
Cadmium (total)	63	93	27	9	27	36
Chromium (total)	20	29	39	29	−48	−19
Copper (total)	69	82	25	4	40	44
Mercury (total)	75	NA	23	11	41	52
Nickel (total)	23	45	38	2	−17	−15
Lead(total)	82	38	20	11	50	61
Antimony (total)	74	72	23	NA	NA	51
Zinc (total)	87	92	18	5	64	69

Table 4 (*Continued*)

Metal	Mass removal[b] (%)					
	Apparent		Infiltration	Harvest	First order	
	Total	Dissolved			w/Harvest	w/o Harvest
1996 Subtotal	73	77	22	5	45	51
1994–96 Subtotal	78	77	21	3	54	58

[a] Trace metal dropped from monitoring program in 1995.
[b] Mass removals determined from mass loadings presented in Table 3.
NA, Not applicable.
Inlet hydraulic loading rate: 68 gpm = 6.33 cm d^{-1}
Outlet hydraulic loading rate: 43 gpm = 3.98 cm d^{-1}
Infiltration: 23 gpm = 2.13 cm d^{-1}
Wetland cell biomass
1994 2.74 kg dw m^{-2}
1995 4.68 kg dw m^{-3}
1996 6.36 kg dw m^{-4}

proposed values. The District has been able to compare average effluent metals concentrations to the ISWP 4-day standard (comparable to the CTR Criteria Continuous Concentration), while maximum effluent metals concentrations are compared to the ISWP 1-h standard (comparable to the CTR Criteria Maximum Concentration) (SRWTP, 1996).

The influent metals concentrations entering the wetlands have been in compliance with all discharge standards for all metals but copper, lead, and mercury. It is important to note that under the ISWP the discharge standards for copper and lead fluctuate with the receiving water hardness concentration. As seen in Table 6, the wetlands effluent metals concentrations meet CTR and ISWP discharge criteria for all metals.

Quantities of trace removed by the wetlands demonstrate a 3-year decreasing trend, from an average of 9.3 kg ha^{-1} yr^{-1} in 1994 to 6.08 kg ha^{-1} yr^{-1} in 1996. This trend is partially explained by the lower annual loading of trace metals in the last 2 years, however mass removal rates also mirror this decreasing trend.

Dissolved metals appear tc undergo significant removal rates within the wetland. Dissolved nickel and arsenic have been measured in greater concentrations than total concentrations. Therefore particulate nickel is not considered to be a factor in nickel removal. Dissolved nickel in wastewater is dominated by 'strong' organic nickel-ligand (NiL) complexes (Sedlak et al., 1997). The strength of the bonds in these NiL complexes limit nickel removal within the constructed wetland. Arsenic is an oxidation-reduction metal. It may be reduced in the wetlands from As(VI) to As(III), the more particle reactive state. Future water column speciation work will confirm these hypotheses (Phinney, 1997).

Table 5
Monthly zinc mass loadings for a typical wetland cell

Metal	Trace metal mass loading (kg ha^{-1} yr^{-1})					Mass removal (%)				
	Influent	Effluent	Infiltration[a]	Harvest[b]	Internal	Apparent	Infiltration	Harvest	First order	Exit system
January	0.84	0.13	0.227	0.0	0.49	85	27	0	58	15
February	0.53	0.06	0.092	0.0	0.37	88	18	0	70	12
March	0.63	0.05	0.155	0.0	0.42	91	25	0	67	9
April	0.50	0.03	0.105	0.432	−0.08	93	21	87	−15	7
May	0.77	0.07	0.093	0.0	0.61	91	12	0	79	9
June	1.07	0.07	0.094	0.0	0.90	93	9	0	84	7
July	0.76	0.15	0.161	0.0	0.46	81	21	0	60	19
August	0.72	0.05	0.068	0.0	0.61	93	9	0	84	7
September	0.75	0.10	0.099	0.0	0.55	87	13	0	74	13
October	0.60	0.06	0.100	0.0	0.44	91	17	0	74	9
November	0.62	0.17	0.141	0.0	0.31	73	23	0	50	27
December	0.78	0.17	0.209	0.0	4.1	79	27	0	52	21
Total	8.57	1.10	1.54	0.43	5.49	—	—	—	—	—
Average	0.71	0.09	0.13	0.04	0.46	87	18	7	61	13

[a] Determined using first-order areal plug flow model that accounts for effects of *P*, *I*, and *ET*. Assumes that metals concentrations in overlying water column are carried to underlying groundwater layers at observed infiltration rate.
[b] Typical harvest values based on average vegetation tissue concentrations presented in Table 2, average wetland cell biomass values stated in Table 3, and average harvest biomass removal rate of 68% (Nolte and Associates, 1997).

Table 6
Comparison of wetlands effluent metals concentrations and discharge standards

Metal	Sacramento wetlands effluent metals concentrations ($\mu g\,l^{-1}$)[a]						Potential discharge standard[b]				
	1994		1995		1996		CTR		ISWP[f]		
	Average	Maximum	Average	Maximum	Average	Maximum	CCC[c]	CMC[c]	Aquatic life (4-day average)	Aquatic life (1-h average)	Human health (30-day average[d])
Silver	0.29	0.42	0.04	0.06	0.05	0.10[e]	–	3.4	—	2.3[g]	50
Arsenic	2.65	5.00	2.51	4.50	2.18	3.80	150	340	190	360	5
Beryillium	0.05	0.05	NA	NA	NA	NA	—	—	—	—	—
Cadmium	0.05	0.10	0.05	0.19	0.06	0.20	2.2	4.3	0.88	2.7	10
Chromium	0.98	4.00	1.18	4.20	1.35	6.80	11	16	11	16	50
Copper[h,j]	2.44	4.20	3.47	6.70	4.42	9.50	9	13	8.9	13	1000
Mercury[i]	0049	0.0093	0.0034	0.0098	0.0046	0.0170	0.77	1.4	—	2.4	0.012
Nickel	2.84	4.00	6.79	12.00	8.41	16.00	52	470	119	1074	600
Lead[h]	0.38	0.50	0.19	0.73	0.25	0.79	2.5	65	2.1	54	50
Antimony	0.12	0.13	0.28	1.10	0.18	0.36	—	—	—	—	—
Selenium	0.62	1.30	NA	NA	1.00	1.00	—	—	—	—	—
Zinc	10.90	73.00	3.26	8.30	7.58	39.00	120	120	80	89	5000

[a] Average and maximum metals concentrations observed in wetlands each year presented in Table 2.
[b] Proposed discharge standards for the protection of freshwater under the California Toxics Rule (CTR, 1997) and the Inland Surface Waters Plan (ISWP, 1991). Based on receiving water hardness of 72 $mg\,l^{-1}$.
[c] CTR Proposed Criteria Maximum Concentrations (CMC) and Criteria Continuous Concentrations (CCC) from Federal Register, 5 August 1997.
[d] Limits apply to waters that are either existing or potential sources of drinking water.
[e] Dashes indicate no value limitation has been set.
[f] Average metals concentrations typically compared to ISWP 4-day standard. Maximum metals concentrations typically compared to ISWP 1-h standard.
[g] Instantaneous maximum.
[h] Average influent metals concentration has exceeded ISWP aquatic life 4-day average limit; 1994 for lead and 1996 for copper.
[i] Average influent metals concentration has exceeded ISWP human health 30-day average limit; 1994 for mercury.
[j] Maximum influent metals concentration has exceeded ISWP aquatic life 1-h average limit and CTR CMC limit for copper in 1995.

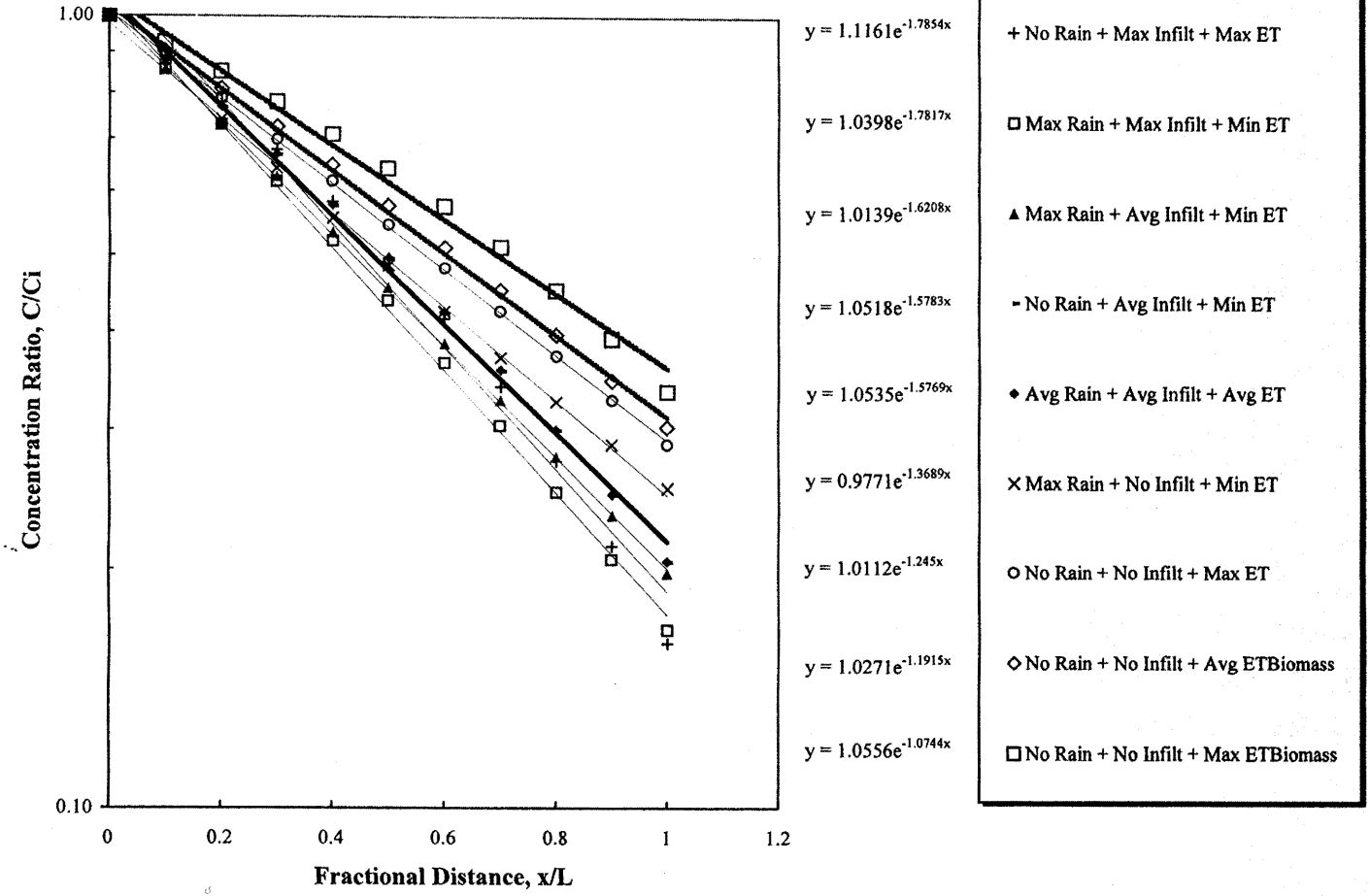

Fig. 7. Effects of rainfall, evapotranspiration, and infiltration on zinc concentration profiles and first-order removal constant.

An average of 7.6 kg ha^{-1} yr^{-1}, or 54% of influent metals loadings, is sequestered within the internal wetland compartments summarized by $M_{Internal}$. An accurate mass balance on the components of $M_{Internal}$ cannot be conducted due to insufficient spatial and temporal information on the magnitude of trace metals sequestered in the multiple wetland compartments. Metals partitioning work, water column speciation, sediment speciation, and the CWFATE model could provide an improved identification of the fraction of accumulated metal immobilized in sediments.

Between 13 and 39% of annual inflow trace metals are assumed to be carried to subsurface soils. The fate of trace metals in the deep, unsaturated soils is not clear, however, no statistically significant increases in groundwater trace metals concentrations have been observed to date. It is likely that trace metals carried below the wetland are effectively immobilized by the adsorption capacity of the highly organic accreted layer and/or subsurface soils.

Annual trace metal mass balances are performed in this article based on annual average hydrological conditions for inflow, outflow, precipitation, evapotranspiration, and infiltration. The impact of monthly variations in hydrological conditions can be significant, as viewed by the range of first order mass removal rates from 50 to 84% estimated in the monthly mass balance for zinc in Table 5.

The impact of individual hydrologic components on trace metals removal can be estimated using an analysis of the first-order areal plug flow model presented in this paper. Several normalized concentration profiles (along the 1260 ft length of the wetland) for zinc are plotted in Fig. 7. Each curve presented on Fig. 7 represents different variations of rainfall, infiltration, and evapotranspiration ranging from zero, minimum, average, and maximum conditions. The case for average rainfall, infiltration, and evapotranspiration conditions falls in the middle of the curves presented in Fig. 7.

Four of the cases considered have curves that fall above the average case, meaning that the removal constant for zinc is lower then that present for the average case. This is a result in each case of either higher evapotranspiration rates, which act to concentrate the trace metal remaining in the wetland, or higher rates of rainfall, which decreases detention time resulting in decreased removal performance. The removal constant is estimated to be up to 21% lower then the case of average conditions for the range of conditions observed in water year 1996/1997. The removal constant is estimated to be up to 32% lower then the case of average conditions when the peak transpiration rate estimated per unit biomass is considered (the peak transpiration rate occurs when there is no rainfall and implies that there is no infiltration). The four curves that fall below the average case each represent conditions where either the effect of evapoconcentration is minimized in comparison to the average case or the rate of infiltration is greater then the average case. The case where infiltration is estimated to peak results in a removal rate 13% greater then the average case. The significant range in trace metals removal rates demonstrates the need for an accurate accounting of water loss pathways.

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