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SECTION 8.0

METALS MASS BALANCE

INTRODUCTION

In the previous sections of this report, metals are discussed with respect to water quality (Section 3), sediment quality (Section 4), vegetation (Section 5), and biota (Section 6). In this section, an attempt is made to account for the overall fate of metals by examining the water quality, sediment, vegetation, and biota data together. Nine metals are examined: silver, arsenic, cadmium, chromium, copper, mercury, nickel, lead, and zinc. While other metals, such as antimony, selenium, and manganese were measured in the water, sediment, vegetation, or biota section, they were not measured in all four and were therefore excluded from this analysis.

METHODOLOGY

To account for the fate of each metal, a mass balance equation was developed. The derivation of the mass balance equation is presented below.

0 = Mass into wetland (M_i) - Mass out of wetland (M_o) – Mass accumulated in wetlands (M_a) [8-1]

Where,

M_i = Metals mass in influent wastewater (MM_i) + Metals mass deposited from atmosphere (MM_a) [8-2]

M_o = Metals mass lost in effluent (MM_e) + Metals mass lost to percolation (MM_p) + Metals mass lost to plant harvest (MM_h) + Metals mass lost to volatilization (MM_v) [8-3]

M_a = Metals mass accumulated in above ground plant shoots (MM_s) + Metals mass accumulated in below ground plant roots (MM_r) + Metals mass accumulated in sediment (MM_g) [8-4]

Substituting equations [8-2], [8-3], and [8-4] into equation [8-1] results in the following equation:

$$0 = (MM_i + MM_a) - (MM_e + MM_p + MM_h + MM_v) - (MM_s + MM_r + MM_g) \quad [8\text{-}5]$$

Where,

MM_i	=	Influent flow (Q_i) x average influent metals concentration (C_i)	[8-6]
MM_a	=	Deposition from atmosphere is assumed to be zero	
MM_e	=	Effluent flow (Q_e) x average effluent metals concentration (C_e)	[8-7]
MM_p	=	Percolation flow (Q_p) x average metals concentrations ($C_i + C_e$)/2	[8-8]
MM_h	=	Mass of shoots (W_s) x Percent harvested (V_h) x Average shoot biomass concentration (C_s)	[8-9]
MM_v	=	Volatilization is assumed to be zero	
MM_s	=	Mass of shoots (W_s) x Average shoot biomass concentration (C_s)	[8-10]
MM_r	=	Mass of roots (W_r) x Average root biomass concentration (C_r)	[8-11]
MM_g	=	Mass of "A" layer (W_a) x ("A" layer concentration (C_a) – "C" layer concentration (C_c))	[8-12]

Substituting equations [8-6] through [8-12] into equation [8-5] results in the following mass balance equation:

$$0 = (Q_i \times C_i) - \{(Q_e \times C_e) + (Q_p \times (C_i+C_e)/2) + (W_s \times C_s \times V_h)\} - \{(W_s \times C_s) + (W_r \times C_r) + (W_a \times (C_a - C_c))\} \qquad [8\text{-}13]$$

Where,

W_s	=	Area of wetlands (A_w) x Above ground biomass density (D_s) x Fraction of wetlands vegetated (A_v)	[8-14]
W_r	=	Area of wetlands (A_w) x Above ground biomass density (D_s) x Root:Shoot ratio (R:S) x Fraction of wetlands vegetated (A_v)	[8-15]
W_a	=	Area of wetlands (A_w) x Depth of "A" layer (H_a) x Density of "A" layer (D_a) x Solids content of "A" layer (S_a)	[8-16]

Finally, by substituting equations [8-14], [8-15], and [8-16] into equation [8-13], the following metals mass balance equation is derived.

$$0 = (Q_i \times C_i) - \{(Q_e \times C_e) + (Q_p \times (C_i+C_e)/2) + (A_w \times A_v \times C_s \times V_h)\} - \{(A_w \times A_v \times D_s \times C_s) + (A_w \times A_v \times D_s \times R{:}S \times C_r) + (A_w \times H_a \times D_a \times S_a \times (C_a - C_c))\} \qquad [8\text{-}17]$$

ASSUMPTIONS

The mass balance was conducted over the five years of operation using average data for all the treatment wetlands combined. Values used in equation [8-17] are listed in Table 8-1 and 8-2, respectively. Flow rates and biomass and sediment masses are presented in Table 8-1. Measured mean metal concentrations in the influent and effluent from the wetlands, within the wetland vegetation shoots, within the wetland vegetation roots, and within the sediment "A" layer and "C" layer are presented in Table 8-2.

The accumulation of metals in the sediment is assumed to be the difference between the background concentration and the final concentration. It can be seen in the mass balance equation that the background sediment metals concentration is assumed to equal to the metals concentration in layer "C" while the final sediment metals concentration is assumed to be the concentration in layer "A".

RESULTS

The results of the mass balance are presented in Table 8-3. For each metal, the mass of introduced to the wetlands (in), the mass of exiting the wetlands (out), and the mass stored within the wetlands (accumulation) is listed. All values are in pounds. It can be seen in Table 8-3 that the model had varying success in accounting for the fate of each metal. The quantity of metal allocated to each compartment relative to the incoming metal mass is presented in Figure 8-1. A column with a height of one would mean that incoming metal was perfectly accounted for through outflows and accumulation. Columns that exceed a value of one represent metals where the sum of the outflow and accumulation terms exceed the mass input. Conversely, values less than one represent metals where the sum of the outflow and accumulation exceed the metal mass input.

It can be seen in Figure 8-1, that the most dominant terms for accumulation and outflow are surface flow through the wetland and accumulation in the sediment. The next largest term for most of the metals was accumulation in plant roots and infiltration to groundwater. The smallest compartments for metals appear to be accumulation in plant shoots and in harvested plant material.

Four of the metals (As, Cr, Ni, and Pb) were found to have outflow and accumulation terms that exceeded inflow. Chromium data, in particular, was found to produce results that were far from equilibrium. Specifically, the difference in chromium concentrations found in the "A" and "C" layers generated an extremely large accumulation term. Resolution of the mass balance equation for nickel, arsenic, and lead produced outflow and accumulation to inflow ratios of 1.89, 1.56, 1.53, respectively. It can be seen in Figure 8-1, that the surface outflow terms alone for arsenic and nickel equal the inflow. The large value for lead, on the other hand, is primarily attributed to an apparent accumulation in the sediment.

Resolution of the mass balance equation for silver, cadmium, mercury, and zinc produced opposite results; the mass of metal leaving via effluent, infiltration, and plant harvesting plus the mass accumulated in plant tissue and sediment were less than that entering the wetlands in the wastewater. Silver data, in particular, tended to underestimate the quantity of metal leaving or accumulating in the system.

Only the copper data generated results that were balanced, with the sum of metal mass leaving the wetlands via effluent, infiltration, plant harvesting and accumulation in plant shoots, roots, and sediment almost exactly (off by less than two percent) equaling the mass of metal entering the wetlands.

TABLE 8-1
ASSUMPTIONS USED IN MASS BALANCE EQUATION
SACRAMENTO CONSTRUCTED WETLANDS DEMONSTRATION PROJECT

Variable	Description	Units[a]	Value	Source
Q_i	Average influent flow rate	gal/min·cell	70	Table 2-6
Q_e	Average effluent flow rate	gal/min·cell	61.4	Table 2-6
Q_p	Percolation rate	in/hr	0.0144	Figure 2-5
A_w	Surface area of wetlands	ft^2	630,000	1260 ft long x 50 ft wide
A_v	Vegetated portion of wetlands	percent	75	A_w less mosquito fish potholes
D_s	Above-ground biomass density	lb/ft^2 DW	0.46	Table 5-3
R:S	Root to shoot ratio	unitless	3.8	Table 5-4
D_a	Below-ground biomass density	lb/ft^2 DW	1.76	$D_a = D_s \times R:S$
V_h	Mass of plant harvested	% of biomass production	20	Estimated value
H_a	Depth of "A" sediment layer	ft	0.5	Section 4
S_a	Solids content of "A" sediment layer	percent	6.8	Section 4
W_s	Mass of above ground biomass	lb DW	219,000	Equation [8-14]
W_r	Mass of below ground biomass	lb DW	833,000	Equation [8-15]
W_a	Mass of active sediment (A layer)[a]	lb DW	1,344,000	Equation [8-16]

[a]DW=dry weight

TABLE 8-2
CONCENTRATION OF METALS IN WETLAND SYSTEM
SACRAMENTO CONSTRUCTED WETLANDS DEMONSTRATION PROJECT

Metal	C_i Average Influent Concentration[a] ug/L	C_e Average Effluent Concentration[b] ug/L	C_s AverageAbove Ground Biomass Concentration[c] mg/kg DW[g]	C_r Average Below Ground Biomass Concentration[d] mg/kg DW	C_a Average "A" Layer Concentration[e] mg/kg DW	C_c Initial Sediment Concentration (C Layer)[f] mg/kg DW
Ag - Silver	0.32	0.033	0.05	0.10	1.56	0.13
As - Arsenic	2.2	2.5	1.09	4.12	9.99	3.14
Cd - Cadmium	0.1	0.0245	0.03	0.26	0.41	0.07
Cr - Chromium	1.2	0.55	1.87	3.77	155.68	77.96
Cu - Copper	7.3	3.3	3.09	7.37	65.55	27.92
Hg - Mercury	0.0096	0.0033	0.006	0.012	0.07	0.02
Ni - Nickel	6	7.1	1.41	5.12	103.43	58.77
Pb - Lead	0.67	0.175	0.79	1.48	15.63	7.28
Zn - Zinc	32	4.25	9.93	35.85	228.66	49.23

[a]Values from Table 3-12
[b]Values from Table 3-12
[c]Values from Table 5-8
[d]Values from Table 5-8
[e]Values from Table 4-23
[f]Values from Table 4-23
[g]DW=dry weight

TABLE 8-3
RESULTS OF MASS BALANCE EQUATION
SACRAMENTO CONSTRUCTED WETLANDS DEMONSTRATION PROJECT

Variable	Description	Units	Metal								
			Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Mass of Metals into Wetlands											
MM_i	Influent Mass	lb	4.9	33.7	1.5	18.4	111.7	0.15	91.8	10.2	489.5
Mass of Metals out of Wetlands											
MM_e	Effluent Mass	lb	0.4	33.5	0.3	7.4	44.3	0.04	95.3	2.3	57.0
MM_p	Percolation Mass	lb	0.4	4.8	0.1	1.8	10.9	0.01	13.5	0.9	37.3
MM_h	Harvest Biomass Mass	lb	0.0	0.2	0.0	0.4	0.7	0.00	0.3	0.2	2.2
Accumulation of Metals in Wetlands											
MM_s	Above-Ground Mass	lb	0.0	0.2	0.0	0.4	0.7	0.00	0.3	0.2	2.2
MM_r	Below Ground Mass	lb	0.1	3.4	0.2	3.1	6.1	0.01	4.3	1.2	29.9
MM_g	Sediment Mass	lb	1.9	9.2	0.5	104.4	50.6	0.07	60.0	11.2	241.2
In - Out - Accumulation[a]		lb	2.1	-17.8	0.4	-99.2	-1.6	0.01	-81.9	-5.8	119.8

[a]A positive number means that the data indicates that a greater mass of metals entered the wetland than exited or accumulated.

Total

FIGURE 8-1
FATE OF METALS AS A FRACTION OF INCOMING MASS, ALL TREATMENT CELLS FROM 1994 TO 1998
SACRAMENTO CONSTRUCTED WETLANDS DEMONSTRATION PROJECT