NOAA Technical Memorandum ERL PMEL-77

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Contribution No. 980 from NOAA/Pacific Marine Environmental Laboratory

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IN THE MAIN BASIN OF PUGET SOUND

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ABSTRACT. Municipal, industrial and atmospheric sources contributed 66% of the total Pb added to the main basin of Puget Sound. Advective inputs were the major sources of total Cu and Zn (~40%) while riverine and erosional sources contributed about 30%. The discharge of the particle-bound trace metals from rivers minimized the impacts of particulate anthropogenic sources, which constituted 50%, 23% and 18% of the total particulate Pb, Cu and Zn inputs, respectively. While advective transport was the major source of dissolved Cu and Zn (~60% of all dissolved inputs), industrial, municipal and atmospheric inputs contributed 85%, 30% and 38% of the dissolved Pb, Cu and Zn inputs, respectively. Diffusion of dissolved Mn was the major source of Mn to the main basin.

About 75% of the dissolved Pb discharged into the main basin of Puget Sound was lost from the dissolved phase and was balanced by a similar gain in the particulate phase. Because of the effective retention of particles within the main basin, extensive scavenging resulted in about 70% of the total Pb added to the main basin being retained in the underlying sediments. The sources of dissolved and particulate Cu and Zn were comparable with the sinks within the errors of the analyses indicating their quasi-conservative nature. Advection removed about 60% of the total Cu and Zn added to the main basin while 40% was deposited in the sediments of Puget Sound. The rapid oxidative precipitation allowed only 10% of the dissolved Mn added to the main basin to leave the main basin in the dissolved form.

1. INTRODUCTION

Recently, the total inputs of trace metals have been determined for Narragansett Bay (Santschi *et al.*, 1984), New York Harbor (Klinkhammer and Bender, 1981), New York Bight (Mueller *et al.*, 1976), Chesapeake Bay (Helz, 1976), Southern California Bight (SCCWRP, 1973) and Puget Sound (Romberg *et al.*, 1984). The identification and quantification of the sources of trace metals to a complete estuarine system help to put the discharge rate of a specific source into a system-wide perspective. With this system-wide perspective, the overall impact of the development of an estuary can be evaluated by comparing the natural sources of these metals from riverine, erosional and oceanic sources with the anthropogenic inputs from municipal, industrial and atmospheric inputs. While riverine sources do not presently originate completely from natural weathering processes and not all atmospheric deposition is man-made, this general

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classification provides an initial insight into man's impact on an estuary. However, lack of knowledge of the partitioning of these metals between the dissolved and particulate phase prevents scientists and managers from predicting whether a discharge will have a greater impact on the water column or the sediments. By constructing individual dissolved and particulate mass balances for the system, we can begin to understand how different sources will impact the concentrations of these metals in both the water column or the sediments. By comparing the sources and sinks of a specific phase (i.e. the dissolved phase), we can determine if geochemical reactions are progressing to an extent that will alter the fate of these metals discharged into the marine environment.

Mass balance calculations for dissolved, particulate and total Pb, Cu, Zn and Mn for the years 1980-1983 were performed for the study area which included central and southern main basin and the urban bays of Seattle and Tacoma, WA (Fig. 1). Advective, riverine, erosional, municipal and industrial sources were considered along with sources from atmospheric deposition and diffusion from the sediments. The sinks of trace metals included advective transport from the main basin and sedimentation.

2. GEOGRAPHICAL SETTING

The main basin of Puget Sound is a long, narrow, deep basin situated between two shallow sills, Admiralty Inlet in the north and the Narrows in the south (Fig. 1). In the central and southern main basin, depths exceed 200 m for much of its 70 km length. Two side channels, Hood Canal and Possession Sound, join with the main basin south of Admiralty Inlet. On the eastern side of the main basin, the Duwamish River flows into Elliott Bay while the Puyallup River discharges into Commencement Bay. The sediments of the waterways of Elliott Bay and Commencement Bay adjacent to the industrial areas of Seattle and Tacoma, respectively, are highly contaminated with metals (Harper-Owes, 1983; Malins *et al.*, 1980). While Commencement Bay was the only marine region to be on the first list of ten Superfund sites, parts of Seattle's industrial area have since been added to the extended list. Point and non-point discharges from primary and secondary metal smelting activities, ship building and repair, chemical manufacturing and paper making (Harper-Owes, 1983; Johnson *et al.*, 1984) are thought to contribute to the metal burden in these embayments. Municipal effluents from storm drains, combined sewer overflows and primary and secondary treatment plants also discharge metals into Puget Sound (Romberg *et al.*, 1984). The urbanized areas of the Lake Washington drainage basin also show enrichments of metals in the sediments although not to the extent observed in the industrial waterways (Romberg *et al.*, 1984).

The mass balances of dissolved and particulate trace metals are partially based on the budgets of water and sediment. Because of the constrains of water and salt flux, the budget for water is well balanced (Table 1). The advective transports of water across the sills at the Tacoma
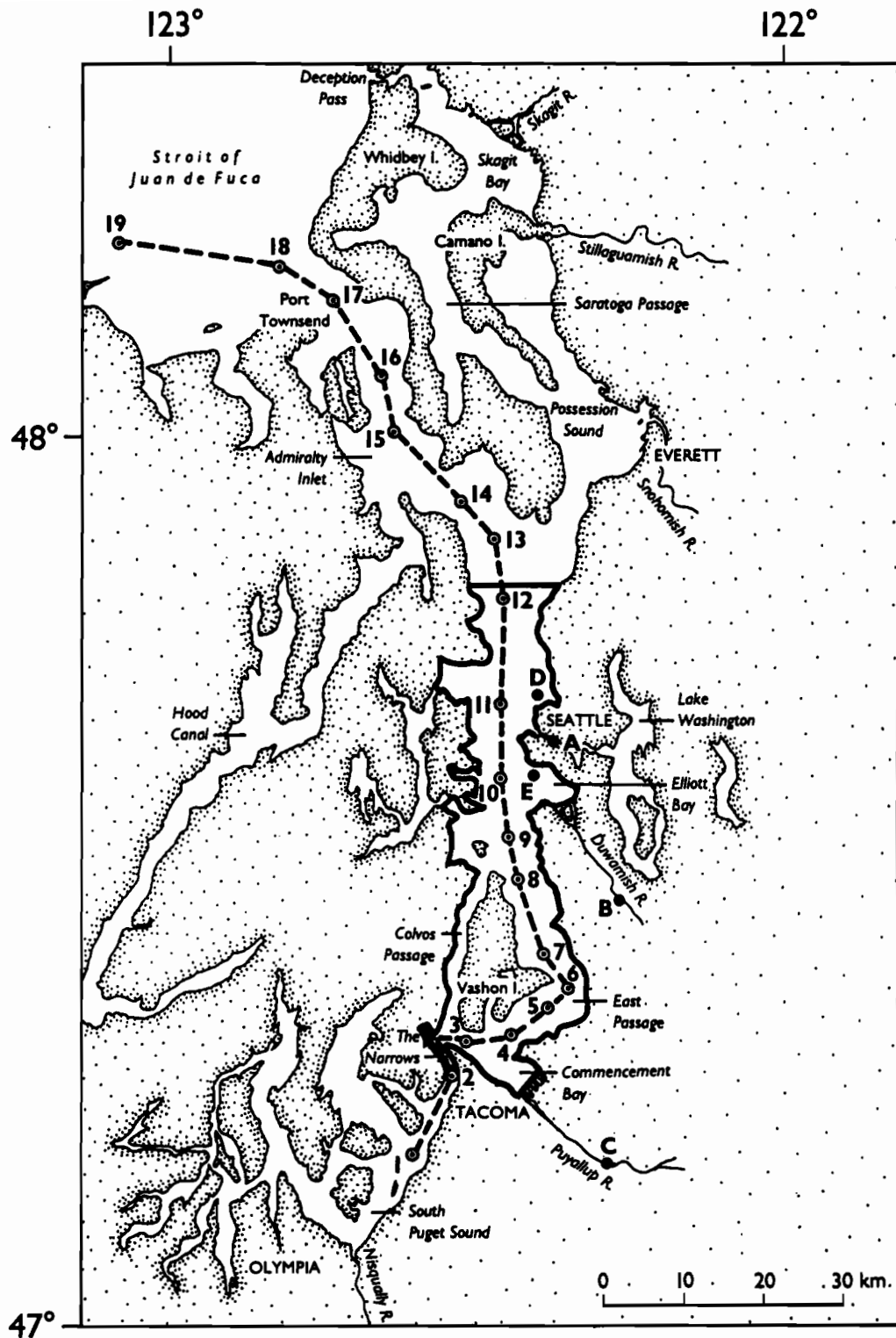
Figure 1.--Map of Study Area. The dotted line shows the December transect. Locations A-C are river sampling sites. Location D and station 5 are lander flux chamber sites while stations 5 and 11 and location E are pore water sites. The bold line marks the boundary of our box for mass balance calculations.

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Table 1. Water Transport Data and Sediment Budget for the Main Basin of Puget Sound.

	Water ($m^3 \times 10^9$/yr)	(Ref)	Sediment (mt/yr)	(Ref)
Sources				
Rivers				
Duwamish	1.2 ±0.2	(1)	170,000 ±160,000	(2)
Puyallup	3.3 ±0.3	(1)	530,000 ±530,000	(3)
Lake Washington Ship Canal	1.2 ±0.2	(4)	3,000 ±3,000	(5)
Erosional			380,000 ±380,000	(6)
Municipal & Industrial	0.4	(5)	30,000 ±15,000	(5)
Advective				
Straits of Juan de Fuca	197 ±50 (est)	(7)	P.S. is net exporter	(8)
South Puget Sound	175 ±45 (est)	(7)	?	
TOTAL SOURCES	378 ±66		1,110,000 ±670,000	

Table 1. (continued).

	Water ($m^3 \times 10^9$/yr)	(Ref)	Sediment (mt/yr)	(Ref)
Sinks				
Sedimentation				
Elliott Bay			158,000 ±158,000	(9)
Commencement Bay			212,000 ±212,000	(10)
Main Basin			1,600,000 800,000	(6)
Advective				
Strait of Juan de Fuca	196 ±50 (est)	(7)	?	
South Puget Sound	171 ±45 (est)	(7)	?	
TOTAL SINKS	367 ±65		1,970,000 ±840,000	

References
1) U.S.G.S. (1980-1983)
2) Santos and Stover (1972)
3) Downing (1983)
4) Schell *et al.* (1977)
5) This study
6) Lavelle *et al.* (1986)
7) From Puget Sound reflx model described by Cokelet *et al.* (1984)
8) Baker (1984)
9) Curl *et al.* (1982)
10) Crecelius *et al.* (1985)

Narrows and Admiralty Inlet are taken from a model described by Cokelet *et al.* (1984). Since the refluxing of seaward-flowing surface into the landward-flowing bottom layer near Admiralty Inlet is considered to be internal to the box of this model, refluxed water is not considered an input to the box. The freshwater flows are taken from USGS data and Schell *et al.* (1977). In lieu of adequate trace metal data and mass budgets for Hood Canal and Whidbey Basin, the net transports of metals between the main basin of Puget Sound and these side channels are assumed to be negligible. While the Duwamish and Puyallup Rivers contribute 700,000 mt/yr of suspended matter to Puget Sound, erosional sources add 380,000 mt/yr. The rate of sedimentation is calculated to be 1,970,000 mt/yr, which is about 800,000 mt/yr higher than the sources. However, this difference may not be significant in view of the large errors (50%) on both sides of the sediment budgets. While advective transport over the sills could constitute a net source of suspended matter, it is thought that Puget Sound is a net exporter of suspended particles (Baker, 1984). Other possible sources of sediment which are not included in this sediment budget include submarine erosion or transport from the rivers draining into Whidbey Basin (Lavelle *et al.*, 1986).

3.   METHODS

Dissolved trace metal samples were collected at stations 1, 5-6, 10-12 and 19 (Fig. 1) in April and December of 1983, with modified 12-l General Oceanic Go-Flo bottles attached to a Kevlar line. Standard Go-Flo bottles were modified by replacing all O-rings with silicone O-rings, replacing spigots with Teflon stopcocks and replacing brass sleeves with aluminum sleeves. Filtration in a closed system in a clean van was performed by passing seawater through acid-cleaned 0.2 μm Nuclepore filters held in all-Teflon Savillex filter holders. After discarding the first 500 ml of filtrate, one-liter samples were retained, acidified and bagged in plastic for transport. Field filtering blanks were obtained by passing quartz-distilled water (Q-water) through the filtration system in the field. Trace metal concentrations were determined by pre-extraction employing the flow controlled Chelex-100 ion-exchange method of Paulson (1986) followed by analyses by graphite furnace atomic absorption spectrometry (GFASS). Determinations of Mn, Pb, Cu and Zn in the CASS-1 and NASS-1 standards were within the tolerance ranges (Paulson, 1986). The field filtering blanks for Mn, Pb, Cu and Zn were $1 \pm 1, 2 \pm 1, 3 \pm 1$ and 59 ± 14 ng for the April cruise and <8, 4 ± 3, <6 and 85 ± 25 ng for the December cruise, respectively.

During the April and December cruises, samples for the determinations of total suspended matter and particulate trace metals concentrations were collected on separate CTD-rossette hydrowire casts using standard 12-l Go-Flo bottles. Seawater was filtered in closed systems through pre-tared, acid-cleaned 0.4 μm Nuclepore filters. The filters were removed from their Teflon holders in a clean van, stored in individual acid-cleaned, plastic petri dishes and desic-

cated over sodium hydroxide. Total suspended matter concentrations were determined gravimetrically on electrobalances. The total elemental compositions of suspended particulate matter were determined by X-ray primary- and secondary-emission spectrometry using the thin-film technique (Baker and Piper, 1976; Holmes, 1981; Feely *et al.* 1986). A Kevex Model 7077-0700 X-ray energy spectrometer with a rhodium X-ray tube was used in the direct and secondary-emission (Ge and Zr targets) mode to obtain maximum efficiency for excitation of individual elements in the sample. Calibrations were performed by preparing thin-film standards from suspensions of finely ground U.S.G.S, N.B.S. and N.R.C.C. standard reference materials.

Dissolved and particulate trace metal samples from the Lake Washington Ship Canal, Duwamish River and Puyallup River were collected between 1980 and 1984, at locations A-C, respectively (Fig. 1). These waters were sampled under a variety of flow stages from low flow conditions in the summer to flooding in the winter. Dissolved Mn and Zn in riverwater were determined by direct injection GFASS methods with standard additions. Dissolved Cu and Pb concentrations in riverwater were determined by Chelex-100 extraction followed by GFASS analysis, which resulted in extraction efficiencies of $100\% \pm 10\%$ and $78\% \pm 13\%$, respectively. The field filtering blanks for Pb, Cu and Zn were 20 ± 20, 80 ± 80 and 200 ± 100 ng/l, respectively. Particulates in riverwater were analyzed by the thin film X-ray emission spectrometry method. An examination of the partitioning between dissolved and particulate phases in primary and secondary sewage effluents was also performed.

4. RESULTS

The advective input terms from South Puget Sound (SPS) and the Strait of Juan de Fuca (SJF) were determined from the water transports across the sills into the main basin (Table 1) and the average dissolved and particulate concentrations in the respective bottom waters (Table 2). The errors in advective fluxes of dissolved metals were estimated from the variance of the dissolved concentrations and an estimated 25% error in the water transports while the errors in the particulate fluxes were estimated to be 100% because of our imprecise knowledge of particulate transport across sills.

The riverine fluxes of dissolved metals were derived from the dissolved metal concentrations in the rivers and the freshwater flow while the riverine particulate fluxes were calculated from the metal concentration on the particulates and the sediment discharge rate (Table 1). The concentrations of dissolved Pb, Cu and Zn in the Duwamish and Puyallup Rivers averaged 30 ng/l, 640 ng/l and 1600 ng/l, respectively (Table 3). In the Lake Washington Ship Canal (LWSC), dissolved concentrations were much higher and averaged 130 ng/l, 1700 ng/l and 3900 ng/l, respectively. In contrast, the dissolved Mn concentrations in the Lake Washington Ship Canal averaged 4 µg/l and were much lower than the river concentrations (27 µg/l). The high Mn concentrations on LWSC particulates suggest that dissolved Mn had been scavenged in

Table 2. Average Water Column Concentrations Used for Advective Transport Terms.

Location	Layer[1]	Phase	Pb ng/l	Cu ng/l	Zn ng/l	Mn μg/l	n
ADVECTIVE INPUT FROM:							
Eastern Strait of Juan de Fuca (STA. 19)	B	Dis.	15 ±90%	140 ±10%	190 ±42%	1.2 ±33%	4
		Part.	23 ±20%	67 ±50%	150 ±25%	1.2 ±25%	9
South Puget Sound (STA. 1)	B	Dis.	19 ±66%	310 ±25%	370 ±25%	1.3 ±10%	2
		Part.	24 ±66%	30 ±66%	60 ±50%	3.9 ±25%	5
ADVECTIVE EXPORT FROM:							
Central Main Basin (STA. 10-12)	S	Dis.	38 ±60%	390 ±20%	790 ±20%	1.3 ±38%	7
		Part.	43 ±60%	60 ±200%	120 ±100%	2.6 ±30%	16
East Passage (STA. 5-6)	S&B	Dis.	28 ±50%	300 ±25%	480 ±20%	3.3 ±140%	18
		Part.	55 ±100%	50 ±80%	50 ±80%	3.2 ±55%	39

[1] S = Surface Layer; B = Bottom Layer

Lake Washington basin because of its long residence time. LWSC particulates also contained higher Pb, Cu and Zn concentrations than those found on riverine particulates. Particulate Mn, Pb and Zn concentrations from the Duwamish River were higher than those of the Puyallup River. The particulate metal contributions from erosional sources were computed from the erosional discharge rate of 380 000 mt/yr (Lavelle *et al.*, 1986) and the metal concentrations of Puget Sound regions soils (D. Pevear as cited in Dexter *et al.*, 1981).

The estimates of total metal discharges from municipal and industrial point sources were obtained from local and state monitoring agencies. Since the current regulations require monitoring of only total metal concentrations, the partitioning of metals between dissolved and particulate phases must be known before these inputs can be applied to separate dissolved and particulate metal budgets. The partitioning of different types of effluents is shown in Table 4. The discharges of dissolved and particulate metals from monitored point sources were calculated

Table 3. Dissolved and Particulate Concentrations in Riverwater.*

Phase/Location	Metal							
DISSOLVED	Pb		Cu		Zn		Mn	
	ng/l		ng/l		ng/l		µg/l	
Lake Washington Ship Canal	130 ±120	(2)	1700 ±800	(5)	3900 ±800	(2)	4 ±3	(5)
Duwamish River	20 ±20	(4)	620 ±290	(6)	1100 ±400	(4)	30 ±17	(6)
Puyallup River	40	(1)	650 ±200	(5)	2200 ±800	(2)	23 ±9	(6)
PARTICULATE	Pb		Cu		Zn		Mn	
	(ppm)							
Lake Washington Ship Canal	205 ±70	(4)	150 ±103	(5)	556 ±203	(5)	2695 ±950	(5)
Duwamish River	45 ±9	(5)	42 ±6	(5)	150 ±84	(5)	1150 ±332	(6)
Puyallup River	15 ±9	(4)	78 ±24	(6)	90 ±30	(6)	590 ±100	(6)

* Values in parentheses are n's.

based on the total metal discharges and the appropriate partitioning values (Table 4). An attempt was made to account for flocculation reactions which may alter the partitioning in seawater. Paulson *et al.* (1984) found that about 50% of the dissolved Cu from a secondary sewage treatment plant (STP) that was discharged into freshwater flocculated upon entering the salt wedge. This change in partitioning was taken into consideration but had little impact on the Cu mass balances since most of the effluents were primary and were discharged directly into marine waters. Changes in the partitioning of primary effluents discharged into marine waters have been reported in the literature but the results are conflicting. While Rohatgi and Chen (1975) reported extensive release of particulate metals from primary effluents upon mixing with seawater, Morel *et al.* (1975) and Galloway (1979) reported little release. Incorporation of partitioning changes upon mixing with seawater was not attempted for these mass balances because of these conflicting results.

Table 4. Percentage of Effluents in the Dissolved Form.

Effluent	% Dissolved				Reference
	Pb	Cu	Zn	Mn	
Primary Treated[1]	25 ±17	56 ±11	55 ±21	91 ±1	This work
Secondary Treated[2]	40 ±20	90 ±5	90 ±6	66 ±22	This work
Storm Drains	9	40	35	--	Tomlinson et al. (1980)
Combined Sewer Overflow	35	27	38	--	"

[1] n = 3
[2] n = 7

The fluxes of metals from non-point sources are more difficult to quantify. Harper-Owes (1983) found that much of the inventory of many contaminants in the West Duwamish Waterway adjacent to the industrial area of Seattle did not originate from known point sources. To account for industrial non-point sources from the West Duwamish Waterway, metal:salinity plots were constructed for samples taken in Elliott Bay during May, 1980 and August, 1981 (Paulson and Feely, 1985; Feely, unpublished data). The y-intercepts from these plots were then multiplied by the daily averaged flow to calculate the total transport in each phase (Boyle et al., 1974; Rattray and Officer, 1981). The industrial non-point fluxes were then calculated by subtracting known discharges from the total. The results of these analyses are given in Table 5. The large industrial discharge of Pb from the Waterway is thought to originate from a secondary Pb smelter which has contaminated the land, air and water around the site. Pb concentrations in storm water as high as 2.1 mg/l have been found in an adjacent storm drain that discharges into the West Water-way (Harper-Owes, 1983). The high discharge of Cu and Zn is thought to originate from drydock activities (Harper-Owes, 1983; Paulson et al., in prep.). The discharge of total metals from Tacoma non-point sources has been studied by Johnson et al. (1984).

The atmospheric deposition of metals onto the surface waters of the main basin was taken from Romberg et al. (1984). Atmospheric data cited in PSAPCA (1981), Larson et al. (1975) and Hardy and Crecelius (1981) were used to calculate the atmospheric input to the urban bays. The solubilization of Pb, Cu and Zn from Puget Sound air particulates after contacting seawater

for one hour (Hardy and Crecelius, 1981) was used as the initial partitioning at the air-seawater interface (58%, 42% and 69%, respectively). The errors were set at 100% to account for uncertainties in the settling velocity of particulates and temporal variability. The diffusive fluxes of dissolved metals from the sediments were taken from Paulson *et al.* (submitted).

The removal of metals from the main basin by advection was calculated based on their concentrations in the surface waters of the central main basin and the entire water column in East Passage (Table 2) and the advective transport of water (Table 1). The sedimentation of Pb, Cu and Zn was derived from the average surface sediment concentrations (Curl *et al.*, 1982; Romberg *et al.*, 1984; Crecelius *et al.*, 1985; Lavelle *et al.*, 1986) and sedimentation rates (Table 1). The average surface sediment concentrations in Elliott Bay, Commencement Bay and the main basin were 90, 32 and 36 ppm for Pb; 88, 56 and 44 ppm for Cu and 165, 90 and 115 ppm for Zn, respectively. The deposition of particulate Mn was calculated using the average Mn concentration in particulates 20 m above the bottom (3880 ppm) and the sedimentation rate. The burial rate of Mn was calculated from an average sediment concentration of 450 ppm at sediment depths greater than 100 cm. The known inputs of total, dissolved and particulate Pb, Cu, Zn and Mn from advective, riverine, erosional, municipal, industrial, diffusive and atmospheric sources are summed in Table 6. These sources are balanced by advective and sedimentation sinks. The method of progression of errors was used for the errors on all calculations.

Table 5. Municipal and Industrial Inputs from Seattle and Tacoma for the years 1980-1983 (in metric tons/year)

Source	Type/Degree[a]	Phase[b]	Pb	Cu	Zn	Mn	Ref.
Seattle							
West Point STP	M/P	T	13.7 ±28%	16.4 ±40%	26.8 ±45%		g
		T				40 ±20%	h
Renton STP	M/S	T	1.3 ±50%	1.5 ±12%	3.5 ±27%		g
						2.9 ±62%	h
Alki STP	M/P	T	3.7 ±17%	4.7 ±36%	5.3 ±22%	0.9 ±16%	i
Small STP	M/P	T	0.6 ±100%	0.8 ±33%	3.1 ±100%	0.9 ±20%	g
Combined Sewer Overflows	M	T	1.1 ±100%	0.2 ±50%	2.2 ±50%	---	j
Industrial Non-Point Sources[c]	I	D	12.2[d]	9.3 ±90%	35[d]	---	h
		P	0.7[d]	1.1[d]	4[d]	---	h
Seattle Total		T	33	34	80	45	
		D[e]	18	22	59	40	
		P[e]	15	12	21	5	

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Table 5. (continued).

Source	Type/Degree[a]	Phase[b]	Pb	Cu	Zn	Mn	Ref.
Tacoma							
Tacoma STP	M/P	T	2.7 ±74%	0.4 ±36%	8.1 ±50%	6.6 ±26	g,k,l
Ruston STP	M/P	T	0.1[d]	2.0 ±50%	2.2	---	k
Pulp Mill	I/S	T	4.1 ±47%	7.0 ±36%	3.2 ±25%	31 ±100%	i,k
Cu Smelter[f]	I	T	0.9 ±50%	4.3 ±65%	5.0 ±100%	---	i
Other Point Sources[f]	I	T	0.1	1.3	0.1	62	i,k
Non-Point Sources	I/SD	T	7	1.6	2.2	---	k
Tacoma Total		T	15	17	21	100	
		D[e]	3	11	12	56	
		P[e]	12	6	9	54	

a) Type: M = Municipal, I = Industrial. Degree: P = Primary,
   S = Secondary, CSO = Combined Sewer Overflow, SD = Storm Drain
b) Phase: T = Total, D = Dissolved, P = Particulate.
c) Industrial Non-Point Sources calculated from the advective
   transport from Elliott Bay minus known point source discharges.
d) Values based on measurement at one time period; errors assumed
   to be ±100%.
e) Based on the total values above and the partitioning presented in
   Table 4.
f) No partitioning data available; % dissolved assumed to be 50%±25%.
g) Romberg et al., 1984.
h) This study.
i) NPDES Monitoring Reports.
j) Tetra Tech, 1986.
k) Johnson et al., 1984.
l) PSAPCA, 1981.

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Table 6. Known sources and sinks of total, dissolved and particulate Mn, Pb, Cu and Zn for the main basin of Puget Sound for the years 1980-1983 (metric tons per year).

Sources	Pb T	Pb D	Pb P	Cu T	Cu D	Cu P	Zn T	Zn D	Zn P	Mn T	Mn D	Mn P
Advection from:												
SJF	7.5 ±5.4	3.0 ±3.0	4.5 ±4.5	40 ±15	28 ±7	13 ±13	66 ±36	36 ±17	30 ±30	303 ±237	66 ±23	236 ±236
SPS	7.5 ±4.8	3.3 ±3.3	4.2 ±4.2	69 ±20	54 ±19	5 ±5	76 ±25	65 ±23	11 ±11	910 ±684	227 ±61	682 ±682
	15 ±7	6 ±4	9 ±6	100 ±25	82 ±21	18 ±14	141 ±43	101 ±29	40 ±3	1212 ±723	293 ±65	918 ±722
Riverine	17 ±12	0.3 ±0.2	16 ±12	54 ±44	5 ±1	49 ±44	88 ±58	13 ±3	75 ±58	632 ±376	117 ±31	516 ±375
Erosional	6 ±6	--	6 ±6	8 ±8	--	8 ±8	30 ±30	--	30 ±3	266 ±266	--	266 ±266
Municipal	24 ±14	6 ±3	17 ±5	26 ±7	14 ±4	12 ±3	50 ±13	29 ±10	22 ±9	51 ±10	46 ±10	5 ±2
Industrial	25 ±15	15 ±12	10 ±7	25 ±13	19 ±11	6 ±3	50 ±40	41 ±35	8 ±5	93 ±69	51 ±37	54 ±48
Diffusive	0.1 ±0.1	0.1 ±0.1	--	0.5 ±0.5	0.5 ±0.5	--	1.5 ±1.5	1.5 ±1.5	--	7615 ±4600	7615 ±4600	--
Atmospheric	23 ±23	13.3 ±13.3	9.7 ±9.7	9 ±9	4 ±4	5 ±5	7 ±7	1.5 ±1.5	2 ±2	2.7 ±2.7	1.3 ±1.3	1.4 ±1.4
TOTAL INPUTS	109 ±34	41 ±19	68 ±19	222 ±54	125 ±24	97 ±47	369 ±89	192 ±47	177 73	9873 ±4650	8123 ±4600	1760 ±857

Table 6. (continued)

Sinks	Pb			Cu			Zn			Mn		
	T	D	P	T	D	P	T	D	P	T	D	P
Advection to:												
SJF	15.8 ±9.7	7.4 ±4.8	8.4 ±8.4	88 ±27	76 ±24	12 ±12	179 ±54	155 ±50	24 ±24	764 ±536	254 ±167	509 ±509
SPS	14.2 ±9.8	4.8 ±2.7	9.4 ±9.4	66 ±23	51 ±18	15 ±5	96 ±30	82 ±26	14 ±14	1110 ±994	564 ±830	547 ±547
	30 ±14	12 ±5	18 ±13	155 ±36	128 ±30	27 ±19	275 ±63	236 ±56	37 ±27	1875 ±1129	819 ±847	1056 ±750
Sedimentation	78 ±37	--	78 ±37	96 ±45	--	96 ±45	229 ±108	0	229 ±108	7690 ±3500	--	7690 ±3500
TOTAL OUTPUTS	108 ±40	12 ±5	96 ±39	251 ±58	128 ±30	123 ±49	504 ±124	237 ±56	266 ±111	9565 ±4650	819 ±847	8746 3589

T = TOTAL; D = DISSOLVED; P = PARTICULATE; SJF = Strait of Juan de Fuca and SPS = South Puget Sound.

5. DISCUSSION

5.1 *Lead*

Municipal, industrial and atmospheric sources each contributed about 22% of the 109 mt/yr of total Pb added to the main basin (Fig. 2). The known sources of Pb in Puget Sound were balanced by the sedimentation (72%) and by advection from the main basin (28%). Because of the solubilization of atmospheric particulates and the prevalence of the dissolved Pb in industrial discharges, sources that are mostly anthropogenic contributed about 85% of the 41 mt/yr of dissolved Pb added to Puget Sound. In contrast to other sources, greater than 95% of the 17 mt/yr of total Pb from riverine sources was in the particulate phase. Because of this large input of particulate riverine Pb, anthropogenic sources added only 55% of the 68 mt/yr of particulate Pb. It was found that the sinks of particulate Pb (sedimentation and advection) were 31 mt/yr greater than the amount of particulate Pb being added to the main basin of Puget Sound (Table 6). This excess was balanced by a loss of 29 mt/yr of Pb from the dissolved phase (Fig. 3). While the difference in the particulate budget was within its 50% error, the difference between the sources and sinks of dissolved Pb in the main basin was significant. This significant difference confirms the importance of scavenging of dissolved Pb in controlling its ultimate fate.
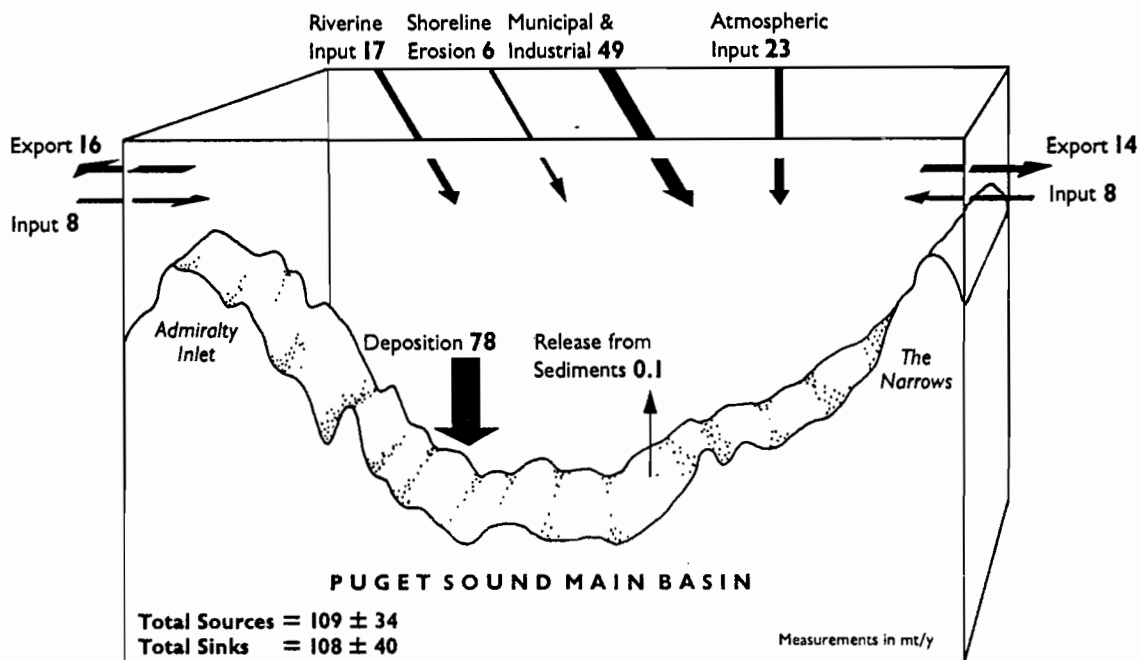
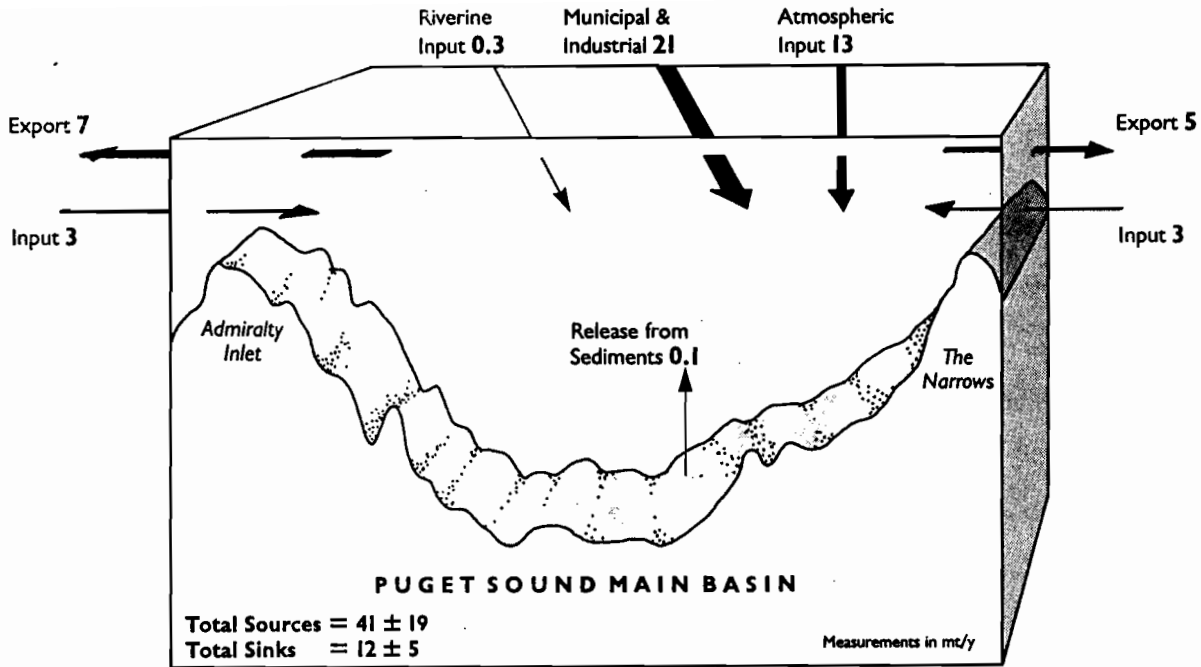Figure 2.--Known sources and sinks of total Pb in the main basin of Puget Sound. Values in metric tons/yr.

Figure 3.--Known sources and sinks of dissolved Pb in the main basin of Puget Sound. Values in metric tons/yr.

5.2 Copper

Advection from the Strait of Juan de Fuca and South Puget Sound contributed 45% of the 222 mt/yr of Cu added to the main basin while riverine and erosional sources added 28% (Table 6 and Fig. 4). Municipal and industrial sources contributed about 11% each. The sinks of total Cu balanced the sources of total Cu within the errors of the budget calculations. About 40% of the total Cu remained within the sediments of Puget Sound while 60% was advected from the main basin.

The combination of riverine and erosional sources were the more significant sources of particulate Cu (59% of the 97 mt/yr of particulate Cu) while the advective sources added 19%. Municipal, industrial and atmospheric inputs added about 23% of the total particulate Cu. The sources of particulate Cu were balanced by the removal by sedimentation (78%) or by advective transport (22%). This agreement between the sources and sinks of particulate Cu suggests that Cu in the main basin did not participate in adsorption reactions to an extent that we were able to detect (i.e. Cu was quasi-conservative within the 50% error of the analysis).

Advection contributed about 66% of the 125 mt/yr of dissolved Cu while riverine sources added 4% of the dissolved Cu to the main basin (Fig. 5). The configuration of the box for these mass balances overstated the importance of the advective term in that the southern boundary of the box (the Narrows) is connected a terminal basin (South Puget Sound). The fact that the flux
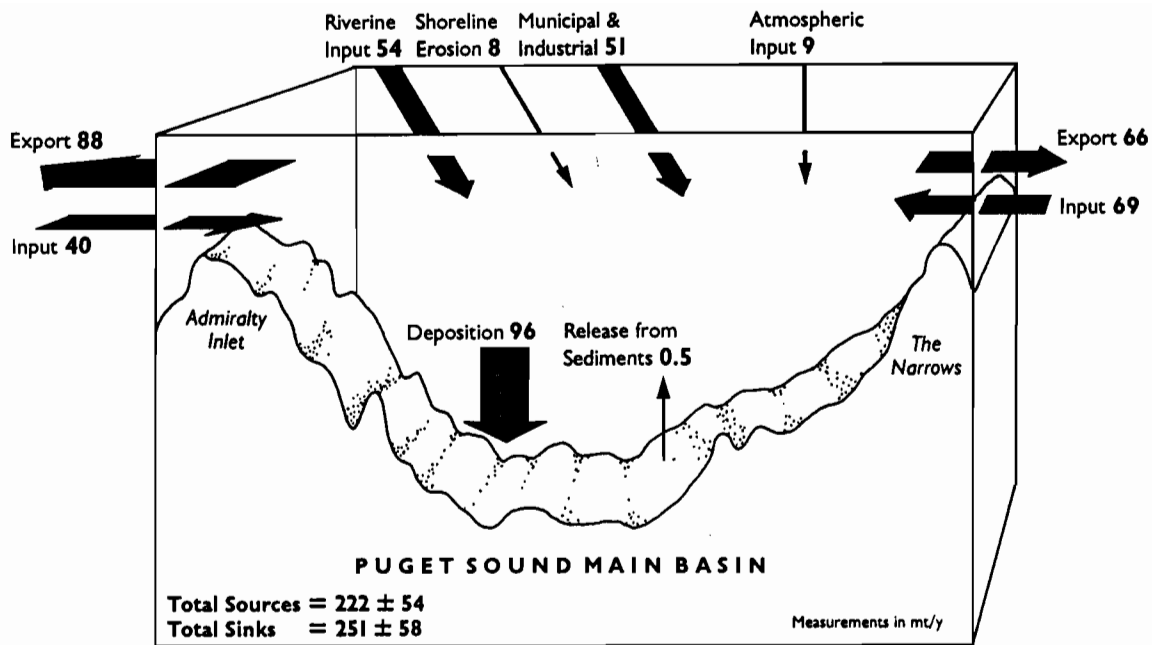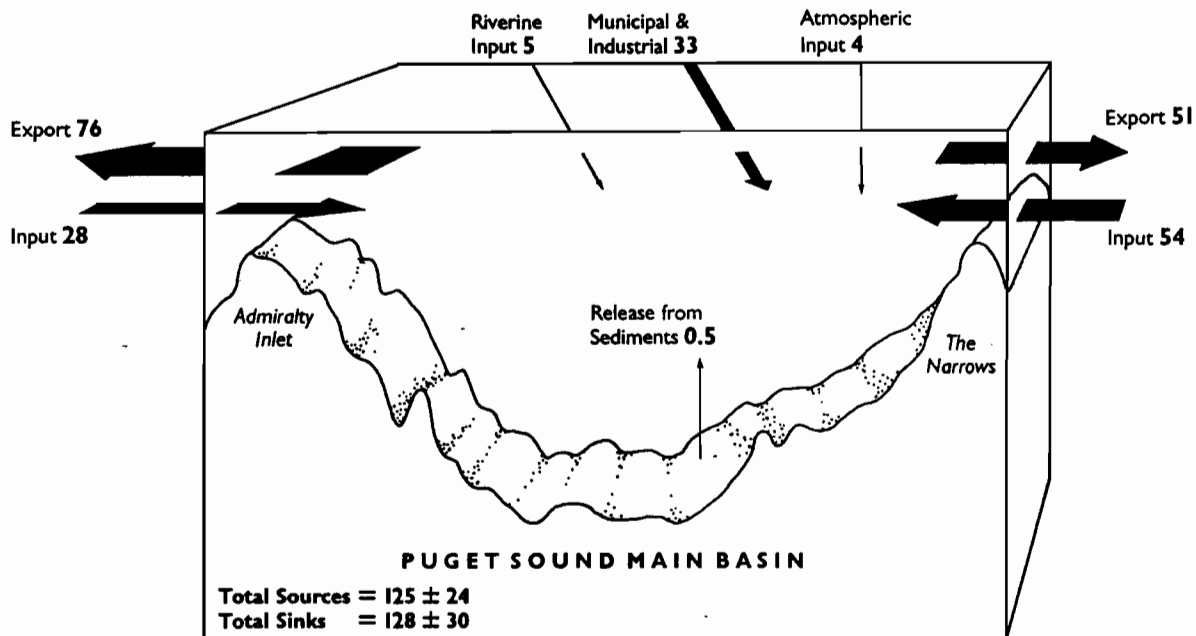
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Riverine   Shoreline   Municipal &   Atmospheric
Input 54   Erosion 8   Industrial 51   Input 9

Export 88

Input 40

Admiralty
Inlet

Deposition 96   Release from
                Sediments 0.5

The
Narrows

Export 66

Input 69

PUGET SOUND MAIN BASIN

Total Sources = 222 ± 54
Total Sinks   = 251 ± 58   Measurements in mt/y

Figure 4.--Known sources and sinks of total Cu in the main basin of Puget Sound. Values in metric tons/yr.

Riverine   Municipal &   Atmospheric
Input 5   Industrial 33   Input 4

Export 76

Input 28

Admiralty
Inlet

Release from
Sediments 0.5

The
Narrows

Export 51

Input 54

PUGET SOUND MAIN BASIN

Total Sources = 125 ± 24
Total Sinks   = 128 ± 30

Figure 5.--Known sources and sinks of dissolved Cu in the main basin of Puget Sound. Values in metric tons/yr.

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of dissolved Cu advected across the Narrows from the main basin was equal to the amount advected from South Puget Sound suggests that main basin water is merely recycled through South Puget Sound. This would suggest that baseline Cu concentrations in South Puget Sound are controlled by inputs to the main basin of Puget Sound. The impact of this recycling can only be evaluated using a model which includes movement of water through the southern main basin such as that described by Cokelet *et al.* (1984). Municipal, industrial and atmospheric sources added most of the remaining 30% of the dissolved Cu inputs. The diffusion of Cu from the sediment porewaters did not seem to be a significant source of dissolved Cu. Advection of dissolved Cu from the main basin, the only sink for dissolved Cu, balanced the sources within the 20% errors of the budgets. The smaller errors of dissolved Cu budget compared to the particulate Cu budget offered the better sensitivity to demonstrate the quasi-conservative nature of Cu within the boundaries of this box model.

5.3 *Zinc*

The sources and sinks of Zn were similar to those of Cu. Advective sources contributed 38% of the 369 mt/yr of Zn added to the main basin while the combination of riverine and erosional sources contributed 32% (Fig. 6). Municipal and industrial sources each contributed 14% of the Zn. Atmospheric deposition and diffusion from the sediments contributed less than 2%. Like Cu, the advective sources were a more important sources of dissolved Zn (53% of the 192 mt/yr dissolved Zn) than particulate Zn (22% of the 177 mt/yr particulate Zn). In contrast,
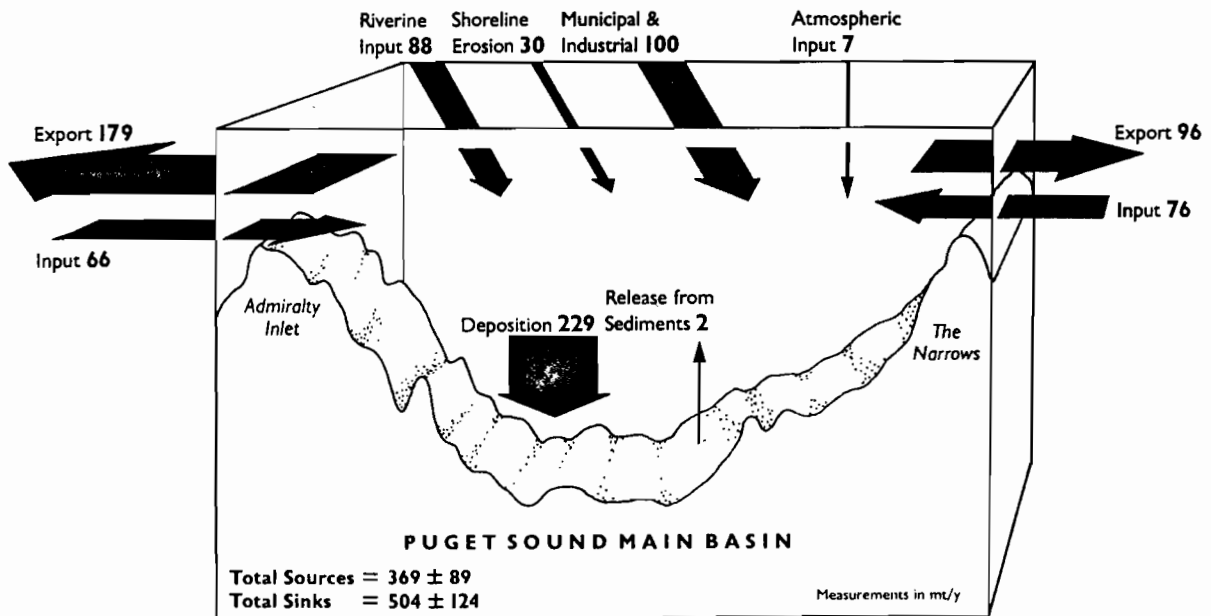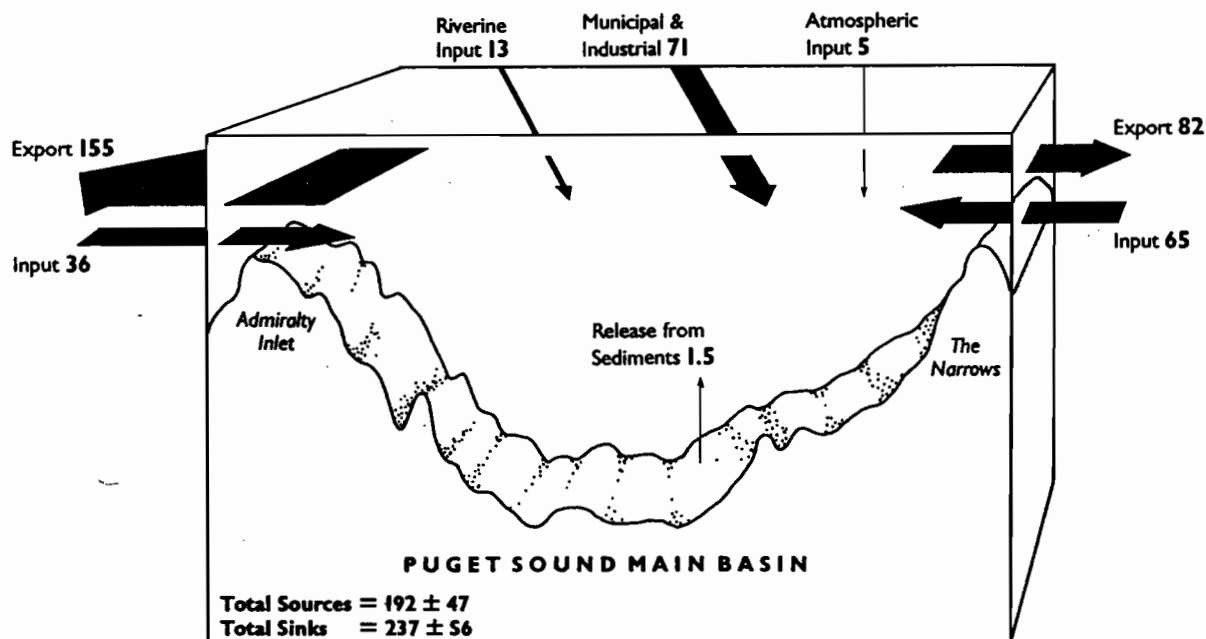

Figure 6.--Known sources and sinks of total Zn in the main basin of Puget Sound. Values in metric tons/yr.

riverine and erosional sources added 59% of the total particulate Zn but only 7% of the dissolved Zn. Like Cu, municipal and industrial sources seemed to a more important source of dissolved Zn (37% of dissolved Zn) than of particulate Zn (17% of the particulate Zn). The sources of particulate Zn were comparable to the sinks within the large 40% error of the budget calculation. The sources of dissolved Zn were also comparable to the advection of Zn from the main basin within the 25% error (Fig. 7). These observation suggest that Zn is also quasi-conservative within the main basin of Puget Sound. The sinks of Zn were also similar to those of Cu. About 45% of the total Zn remained within the sediments of the main basin Puget Sound while 55% was advected from the main basin (47% as dissolved Zn and 7% as particulate Zn).

Figure 7.--Known sources and sinks of dissolved Zn in the main basin of Puget Sound. Values in metric tons/yr.

5.4 Manganese

Diffusion of dissolved Mn from the sediments contributed 77% of the 9900 mt/yr of Mn added to the main basin of Puget Sound (Table 6). However, less than 10% of the dissolved Mn added to the main basin was advected from the main basin (Fig. 8b). This substantial loss of dissolved Mn was a result of the rapid formation of particulate Mn from the oxidative precipitation of dissolved Mn (Feely et al., 1983; 1986). This particulate Mn then settled to the bottom sediments, where it again redissolved due to reducing conditions in the sediments (Fig. 8a). This rapid cycling of Mn between the oxidative precipitation and reductive dissolution cycles provides a large amount of oxide surfaces for metals which have a high scavenging affinity for manganese oxide surfaces such as Pb (Paulson et al., submitted).
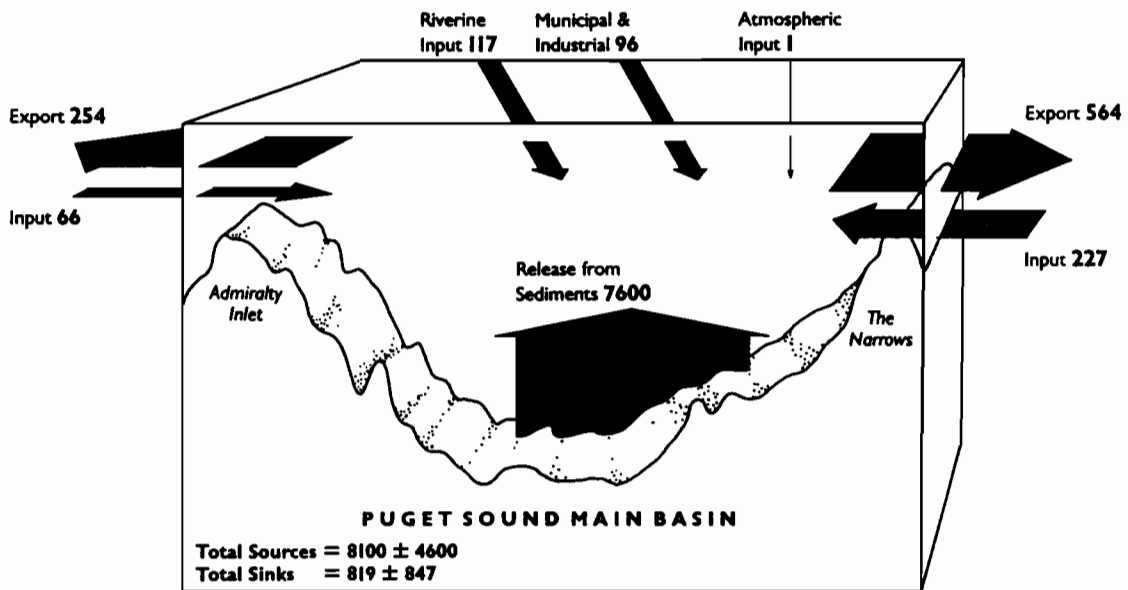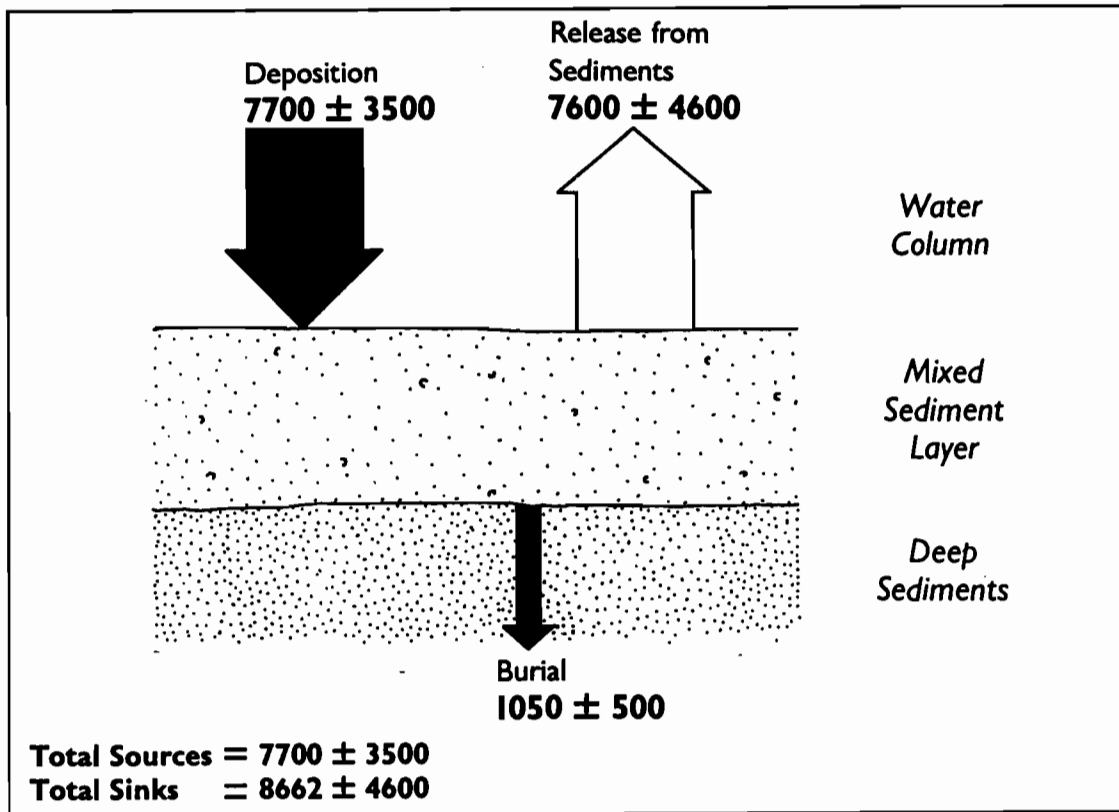
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Figure 8.--Known sources and sinks of Mn in main basin of Puget Sound. (a) Total Mn in the sediment column (The open arrows are for dissolved Mn while the solid arrows are for particulate Mn). (b) Dissolved Mn in the water column. Values in metric tons/yr.

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6. CONCLUSION

Construction of individual dissolved and particulate mass balances for trace metals allows one to evaluate the impacts of changing anthropogenic inputs on both the water column and the sediments and the occurrence of scavenging reactions. Municipal, industrial and atmospheric inputs added 85% of total input of dissolved Pb to the main basin. However, comparison of the sources and sinks of dissolved Pb indicated that 75% of the dissolved Pb added to the main basin was scavenged onto particulates. This scavenging of anthropogenic dissolved Pb tended to result in the retention of anthropogenic Pb in the sediments of the main basin of Puget Sound. The net effect of this scavenging and the discharge of particulate Pb from rivers and anthropogenic sources was the sedimentation within the main basin of 72% of the total Pb input. The sources and sinks of dissolved Cu and Zn were comparable, which indicated their quasi-conservative geochemical nature. Apparently, the fates of Cu and Zn were mainly determined by their partitioning between the dissolved and particulate phases in different source discharges. For particulate Cu and Zn, riverine and erosional sources added about 60% while 30% originated from industrial, municipal and atmospheric inputs. The impact of anthropogenic inputs on dissolved Cu and Zn concentrations in the water column cannot be fully evaluated without an understanding of the effects of recirculation within the Puget Sound system. The nature of discharges to the main basin of Puget Sound resulted in only 40% of the total Cu and Zn being retained in the main basin sediments while 60% was advected from the system. Diffusion of dissolved Mn from reducing sediments and its subsequent oxidative precipitation onto particles controlled the fate of Mn.

These budgets were constructed from data collected between the years 1980-1983. Since that time, many economic and regulatory actions have occurred in the Puget Sound basin which will result in the reduction of trace metal discharge rates to the main basin. The decrease in the content of Pb in gasoline has already resulted in decreased rates of atmospheric deposition. The closing of the Tacoma and Seattle smelters and the economic demise of Puget Sound shipbuilding facilities will result in lower discharge rates in our urban embayments. The hardening of drinking water by the Seattle Water Department has also resulted in decreased discharge of some metals from METRO's municipal sewage treatment plants. The regulatory requirement to implement secondary treatment will further decrease discharge rates of trace metals from municipal sources throughout Puget Sound, especially those in the particulate phase. The hypotheses put forth by this work will be able to be tested in the next decade when the effects of these actions have had their impact on the concentrations of metals in the water column and sediments. The use of this trace metal mass balance approach for management purposes would benefit from further research that would decrease the uncertainties in the budgets of water and, especially, sediments which form the foundation of these trace metal budgets.

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7. ACKNOWLEDGMENTS

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