Transport and Behavior of Trace Metals in the Tsengwen River and Estuary

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ABSTRACT

Studies on the transport mechanisms and behaviors of six trace metals (Fe, Mn, Cd, Cu, Pb and Zn) in the Tsengwen river and estuary were performed for the high-flow and low-flow seasons. Dissolved metals in the Tsengwen river are slightly higher than those in the pristine rivers but much lower than those in the heavily polluted rivers of the world. The riverborne dissolved Fe, Mn, Cu, Pb and Zn exhibited significant removals in the early estuarine transport; for Cd, however, this was likely controlled by the mixing process in the estuary. Particulate and sediment metals, similar to dissolved metals, showed elevated concentrations in the middle river, but there was little difference throughout estuarine locations. The enriched levels of particulate and sediment metals with reference to backgrounds (shale's metals) were found in a sequence of Pb, $Cd > Zn$, $Cu > Fe$, Mn.

Trace metals were principally transported by suspended particulates, accounting for over 93 % of the total gross fluxes. Particulate Fe and Pb are mostly concentrated in the Fe-Mn hydroxides and crystalline fractions. Particulate Mn, Cu, Zn and Cd distribute rather significantly, in addition to Fe-Mn hydroxides and crystalline fractions, in exchangeable and carbonate phases, carbonate and organic phases, carbonate phase, and exchangeable phase, respectively. The particulate speciation shows little difference between riverwater and estuarine water. The net fluxes of metals out of the estuary are modeled to be approximately 56 %, 76 %, 114 %, 67 %, 84 % and 73 % of dissolved influxes as well as 35 %, 32 %, 28 %, 29 %, 39 % and 50 % of particulate influxes, respectively for Fe, Mn, Cd, Cu, Pb and Zn. The imbalance of metals between the dissolved and particulate phases is thought to result from metal deposition in the estuary.

1. INTRODUCTION

The riverine fluxes of trace metals to the oceans may depend greatly upon reactions that occur in estuaries (Li *et al.*, 1984; Byrd and Andreae, 1986). A

large modification was usually found when the riverine metals passed through an estuary with great salinity gradients. Despite decades' of efforts towards understanding the behaviors of trace metals in the land-sea boundary, there continues to be considerable uncertainty about the estuarine processes involved in controlling the fate of riverborne metals (Sholkovitz, 1978; Windom *et al.*, 1983; Keeney-Kennicutt and Presley, 1986; Byrd and Andreae, 1986; Waslenchuck and Windom, 1987). The study on the transport mechanisms of riverine trace metals is therefore necessary in understanding the biogeochemical cycles of metals in a regional land-sea system.

Numerous studies concerning the transport and flux of elements from the rivers of the world have been reported (Gibbs, 1973, 1977; Eaton, 1979; Yeats and Bewers, 1982; Stallard and Edmond, 1983; Maest, 1984; Byrd and Andreae, 1986; Keeney-Kennicutt and Presley, 1986). Martin and Meybeck (1979) have also compiled the data of elemental transport for twenty-two major rivers in the world. The estimated global flux of metals into the oceans, however, has been rather uncertain due to the lack of data in many countries. It has been evident that data supplied from areas in Asia would be especially valuable.

In order to understand the transport and behavior of the riverine trace metals, it is usually necessary to determine the distributions of trace metals in the dissolved, suspended and sedimented matters in a river system. The growing data show that the fluxed metals are mainly transported by the suspended matter, and the fate and toxic effects of the fluxes are highly dependent on specific forms rather than total inputs (Calmano and Forstner, 1983; Forstner and Wittmann, 1979; Salomons and Forstner, 1984). Therefore, the determination of trace metal speciation in the suspended particulate matter is important for understanding the environmental significance and biogeochemical cycles of metals.

Very few reliable data are available for a systematic description of metal geochemistry in the rivers and estuarys in Taiwan. We are concerned here with behavior of trace metals in the Tsengwen river system not only because the riverwater is essential to the agriculture of the river basin, but also as the estuary is an important area with regard to maricultures and fisheries. The aims of this study are to decribe the transport modes, distributions and behaviors of metals in the Tsengwen riverine system.

2. MATERIALS AND METHODS

a. Sampling and pre-treatment

Samples of water and sediment in the Tsengwen river and estuary were collected in September, 1986, and January, 1987, which represent the periods of
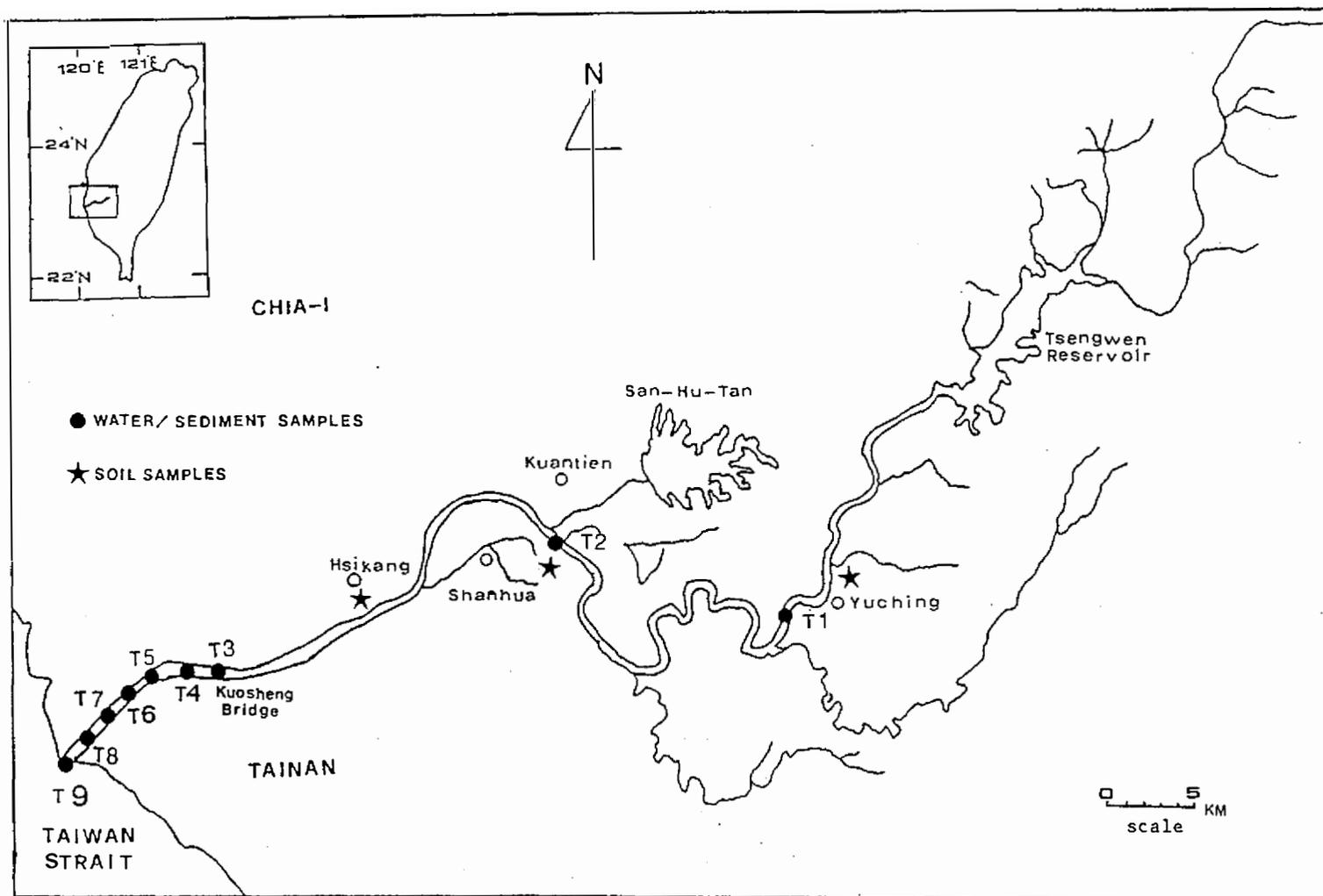
Fig. 1. Location and sampling stations on the Tsengwen river and estuary.

high-flow and low-flow, respectively. The sampling locations are shown in Fig.
1. A large volume of water (60 L) for each sample was taken, 25 cm below
the surface by a horizontal water sampler (Ekman Birge) from the highway
bridges over the river part and from aboard fishing boats in the estuary. Salin-
ity was measured in situ with a salinometer (Hydro-Bios) and then precisely
determined in the laboratory from solution density; the density was measured
with a densitometer (Parr DMA 602). Sediments were taken with an Ekman
Birge dredge. Soil samples were taken from the surface horizon of the drainage
basin. Sediment and soil samples were air-dried, ground, and pestled to pass
through a 1 mm nylon sieve, and then stored in plastic bottles.

We made two other cruises on June, 1987, (high-flow) and December, 1987,
(low-flow) to take small volume (2 L) samples only for the analyses of dissolved
metals. The sampling stations in the estuary, however, were physically much
denser than those indicated in Fig. 1, by which the behaviors of dissolved metals
in the estuary were expected to show up more clearly. An intensive survey of
profile salinity in the estuary was also performed during the inter-tidal period
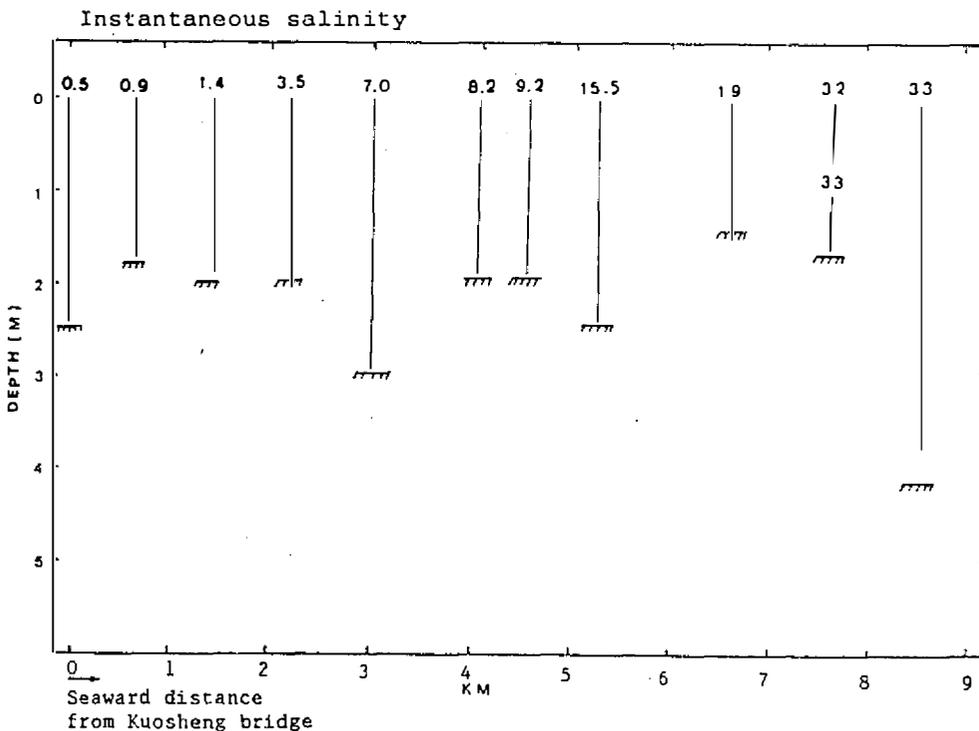of the last cruise, and the results are shown in Fig. 2.

Fig. 2. Salinity profile of the Tsengwen estuary.

Two liters of each water sample were filtered through a 0.45 μm Nalgene
membrane filter which was pre-washed with acid. The filtered water was acid-

ified to pH 1-2 and stored at $4^\circ C$ for further analyses of dissolved metals. The remaining water of each sample from the first two cruises was ultracentrifuged at 12,000 rpm (Hitachi, model SCR 20 B) to recover suspended matter, which was then dried in an oven at $105^\circ C$ until a constant weight was reached. The dried samples were stored in a desiccator.

A portion of dried sediments and suspended particulates were resuspended in distilled-deionized water (DDW) to separate the clay fraction ($< 2\mu m$) from other fractions by ultracentrifugation according to the Stokes' sedimentational principle (Osipow, 1977). The recovered clays from the sediments were dried again in an oven at $105^\circ C$ and stored in a desiccator.

b. Methods of analyses

Reagents and apparatus

All reagents used in the experiments were analytical grade (Merck) and purified with Chelex-100 resin (Biorad, 200-400 mesh) whenever possible. Acids were subboiled (HNO_3, H_2SO_4) or superpure ($HClO_4$, HF, Merck). All plasticware used in the analyses was cleaned by soaking in 10 % HCl and rinsed thoroughly with DDW. Standard solutions for atomic absorption spectrophotometry were prepared by dilution of Merck Titrisol standard solution with 0.2 % subboiled HNO_3.

Teflon lined acid digestion bombs (Parr Instrument Co.) were used to decompose soils, sediments, and suspended particulates for total metal determinations, whereas the polycarbonate centrifuge tubes (Nalgene, 50 ml) were used for sequential extraction. The Perkin-Elmer 2380 atomic absorption spectrophotometer (AA) with a D_2 background corrector and equipped with an HGA 400 graphite furnace (GFAA) was used for trace metal determinations.

Analytical procedures

Dissolved trace metals (Fe, Cd, Cu, Pb and Zn) were analyzed using the chelation back extraction method modified from Danielsson *et al.*, (1982) and Statham (1985). Metals in a 500 ml aliquot of riverine/estuarine water were preconcentrated by chelation with ammonium pyrrolidinedithiocarbonate (APDC) and diethylamonium diethyldithiocarbamate (DDDC) followed by freon (1, 1, 2-trichloro-1, 2, 2-trifluorethane) extraction, and the metals were then back-extracted into a final 10 ml dilute nitric acid solution. Manganese, however, was preconcentrated by the C18 SEP-PAK Catridge (Water Associates; Milford, USA). In most cases concentrated Zn was high enough to be determined by flame-AA, whereas other metals were determined by GFAA. Riverine and coastal seawater reference materials (SLRS-1/CASS-1, National Research

Table 1. Accuracy and precision of trace metal analyses in river and sea waters

Element	Method[*]	Spike[**]	% Recovery n=6	CASS-1 seawater		SLRS river water	
				Certified conc. (μg/L)	Measured conc. (mean, n=2) μg/L	Certified conc. (μg/L)	Measured conc. (mean, n=2) μg/L
Fe	a	60 μg	98	0.873 ± 0.076	0.794 (9)[#]	31.5 ± 2.1	28.0 (11)[#]
Mn	b	60 μg	104	2.27 ± 0.17	2.09 (8)	1.77 ± 0.23	1.61 (9)
Cu	a	20 μg	96	0.291 ± 0.027	0.300 (3)	3.58 ± 0.30	3.40 (5)
Cd	a	10 μg	92	0.026 ± 0.005	0.0247(5)	0.015 ± 0.002	0.0135(10)
Pb	a	20 μg	101	0.251 ± 0.027	0.271 (8)	0.106 ± 0.011	0.109 (3)
Zn	a	40 μg	103	0.98 ± 0.099	0.999 (2)	1.34 ± 0.20	1.42 (6)
Ni	a	20 μg	91	0.290 ± 0.031	0.255(12)	1.07 ± 0.06	0.995 (7)

* a: APDC/DDDC-freon preconcentration - GFAA determination
  b: SEP-PAK C18 preconcentration - GFAA determination

** Metals were spiked in the coastal seawater off southwestern Taiwan

Values in parentheses are % deviations of measured conc. from certified conc.

Council of Canada) were analyzed with the same procedures. The precision and accuracy of the analyses are better than 89 % and 91 %, respectively for the river and the sea waters (Table 1).

Trace metals in soils, suspended and bottom sediments including their clay fractions, were determined by decomposing materials with an acid mixture (HNO_3, $HClO_4$ and HF) in Teflon lined acid digestion bombs, followed by the flame AA/GFAA measurement. Trace metal species in the suspended particulates were determined by a method of selective extraction/GFAA determination. Fractions of exchangeable, carbonate, Fe-Mn oxides, organic and crystalline forms were separated and determined. Detailed procedures for determining the total number and species of particulate metals has been decribed elsewhere (Hung, 1988).

3. RESULTS AND DISCUSSION

The Tsengwen river is one of the major river in Taiwan. It has a length of 138.5 km and a drainage area of 1176.6 km^2. The river originates from the Wanshui mountain of the Central Range, flowing through the Chai-I and Tainan counties, toward southwest to reach sea in the Chiku area.

The average annual discharge of the river for the period of 1972-1981 was $1.40 \times 10^9 \ m^3 \ yr^{-1}$ for water and $1.43 \times 10^6 \ ton \ yr^{-1}$ for solid (hydrological yearbook of Taiwan, R.O.C.). The flow rate is slightly reduced by the Tsengwen resvoir in the upper basin, but in general it is higher in the wet season (May-October) than in the dry season (November-April). The middle and down stream portions of the river have been polluted by either domestic or industrial wastewater, and the situation is getting worse, especially during the dry season.

a. Dissolved metals in the river and the estuary

Dissolved metals in the Tsengwen river and estuary are displayed in Fig. 3. The concentrations of metals was plotted as a function of salinity in the estuary and as a function of the landward distance with reference to the salt intrusion point in the river portion. Data for the river were obtained from the averaged concentrations of two cruises in 1986 and 1987, respectively, for the high-flow and low-flow, whereas data for the estuary were the results of cruises in June (high-flow) and December (low-flow), 1987. Estuary data from the cruises in September, 1986, and January, 1987, were not presented and discussed because of inadequate data, particularly in the low salinity range (0-9 %) where we did not collect any samples. Meanwhile, the salinity of a sampling location in the estuary was not the same for any two cruises, therefore the data obtained from the similar flow conditions but different cruises were not suitable to be
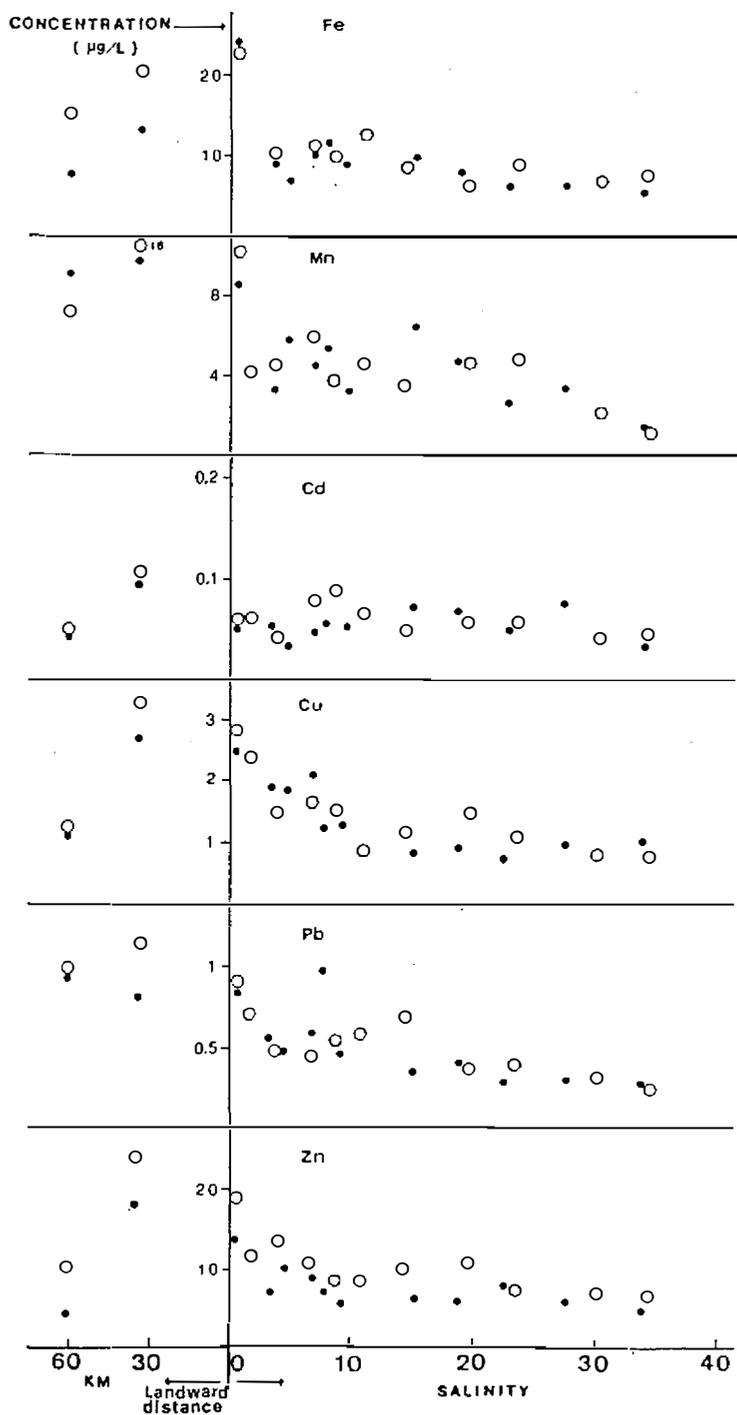
Fig. 3. Concentrations of dissolved metals in the Tsengwen river and estuary;
(•) is during high flow; (o) is during low flow.

Table 2. Concentrations of dissolved metals in riverwaters, $\mu g/L$

River	Fe	Mn	Cd	Cu	Pb	Zn
Tsengwen (this study)	8.2-23.3	7.1-16	0.04-0.11	1.09-3.3	0.82-1.14	4.4-24.4
Kaoping [a]	7-24	1.3-4.8	0.03-0.055	1.02-2.3	0.32-0.5	6.4-16.2
Background [b]	55	6	0.02	1	0.2	10
Mississippi [c]	5	10	0.1	2	0.2	10
St. Lawrence [d]	55	6.3	0.11	2.5	-	8.6
Amazon [e]	34	19	--	1.77	--	-
Yukon [e]	50	20	-	2.0	-	--
Raritan [f]	25.8-76.5	4.7-34.7	0.4-0.9	2.4-4.1	0.5-1.9	30.1-109
Rhine [g]	35	5.2	5.5	34	57	330

a Hung and Huang (1990)

b Salomons and Forstner (1984)

c Trefry and Presley (1976)

d Yeats and Bewers (1982)

e Gibbs (1977)

f Maest (1984)

g Anon (1982) and Heinrichs (1975), after Salomons and
     Forstner (1984)

combined for this discussion.

From Fig. 3 we found that all metals generally have higher concentrations in the middle and down streams than in the upper stream of the river. This is ascribed to the fact that the middle and lower sections of the river have been contaminated with metals. Compared to other rivers in the world, concentrations of metals in the Tsengwen riverwater are somewhat higher than those in the rivers without pollution (backgrounds), but they are much lower than those in the severely polluted river (Rhine) (Table 2). As the Tsengwen riverwater mixed with seawater in the estuary, dissolved river-borne metals with the exception of cadmium behaved non-conservatively, removals of metals from a solution over the low salinity range (0-10 %) were found. Cadmium, however, did not display a significant removal or addition throughout the estuary. These geochemical reactions were judged from the comparison of concentrations of

metals that were positive or negative deviations from mixing lines between the riverine and oceanic end members.

The geochemical processes involved in non-conservative removals are complicated. Nevertheless, several publications reported that flocculation as well as adsorption and coprecipitation could be reponsible for removals of geochemically reactive metals, while complexation with chloride or desorption from particulates may cause an increase of Cd in the estuary (Sholkovitz, 1978; Galloway,1979; Eaton, 1979; Klinkhammer and Bender, 1981; Li *et al.*, 1984; Waslenchuck and Windom, 1987). Overall for dissolved metals, the concentration was higher in the dry seasons than in the wet seasons in the river but there was no significant difference in the estuary. Apparently the distributions of dissolved metals in both river and estuary were dominated by the processes of pollutant inputs, estuarine physical-chemical reactions, and flow conditions, presuming that biological effects can be neglected.

b. Metals in sediments

Metal distributions in the suspended particulates and bottom sediments are shown in Fig. 4. Metal concentrations are expressed in terms of total sediment/particulate and clay fractions of sediment/particulate. Metals in the clay fractions of the sediments are higher than those in the total sediments because metals are usually concentrated in small particles. However, metal distributions have similar trends for both total and clay fractions of sediments in the Tsengwen river and estuary. In general, metals are little different in the Tsengwen river and estuary except for Cd in the middle river where it could have been polluted by the Cd associated phosphorus fertilizers. Overall, metals in the Tsengwen estuary are comparable to those in the relatively unpolluted *St.* Lawrence estuary (Loring, 1978; Cu: 24-25 ppm, Zn: 84-115 ppm, Pb: 21-30 ppm, Cd: 0.22-0.26 ppm), but they are much lower than those in the polluted Rhine-Meuse estuary (Salomons and Mook, 1977; Cu: 99 ppm, Zn: 870 ppm, Pb: 213 ppm, Cd: 5 ppm). Variations of Fe and Mn distributions were probably due to their lithological characteristics. Forstner and Wittmann (1979) have found that in the less contaminated material a general decrease of metal concentration is found with increasing particle diameter, whereas in the polluted material there is a typical increase of metal concentrations in the clay and silt fractions. Therefore, it is usually necessary to compare metal distribution on the basis of a standard with regard to particle size.

Metal distributions in total and clay fractions of suspended particulates also showed a similar trend, this is due to the fact that suspended particulates contain mainly fine particles, predominantly in silt, clay minerals and organic materials. As a result, metal concentrations in the suspended particulates were
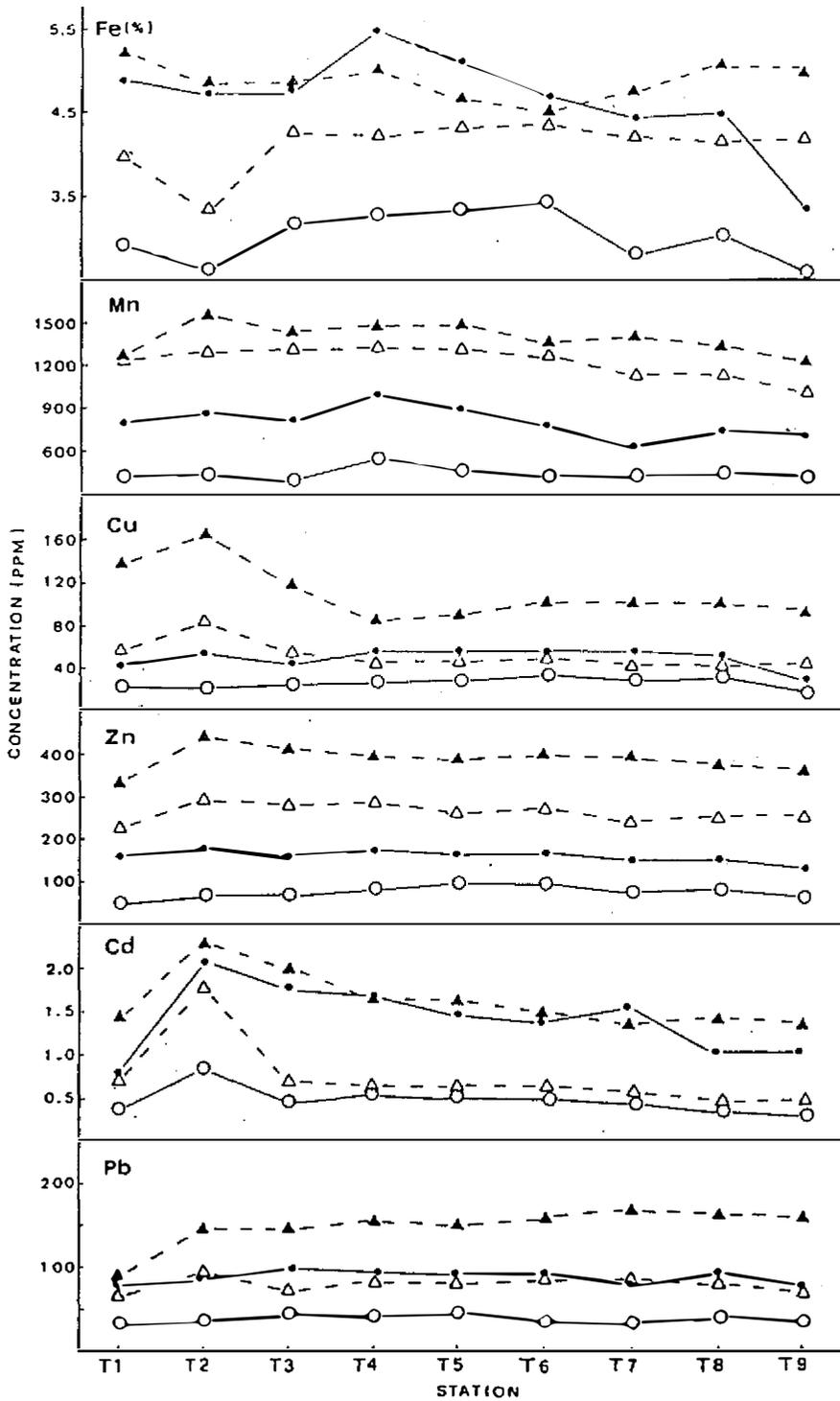
Fig. 4. Concentrations of metals in suspended particulates and bottom sediments of the Tsengwen river and estuary; (o) is the average conc. of total sediments; (•) is conc. in $< 2 \ \mu m$ sediments; (△) is the average conc. of total suspended particulates; (▲) is the conc. in $< 2 \ \mu m$ suspended particulates.

Table 3. Geoaccumulation indices for metals in the bottom sediments and suspended particulates from the Tsengwen river and estuary.

I_{geo}	$I_{geo-class}$	Suspended particulate				Bottom sediment			
		U	M	L	E	U	M	L	E
2 - 3	3	Cd	CdPb	CdPb	Cd		Cd	Cd	CdPb
1 - 2	2	CuPb Zn	CuZn	Zn	CdZn	CdPb	Pb	Pb	CdPb
0 - 1	1	Mn	Mn	CuMn	CuMn	Zn	Zn	Zn	Zn
< 0	0	Fe	Fe	Fe	FeMn	FeMn Cu	FeMn Cu	FeMn Cu	FeMn CuZn

U: Upper river; M: Middle river; L: Lower river; E: Estuary, covering a range of sampling stations.

always higher than those in the bottom sediments.

In order to know the degree of metal accumulation in particulates and sediments with respect to the background levels, we applied an "index of geoaccumulation (Igeo)", which was proposed by Muller (1979), to estimate metal accumulation in river basins. According to the Muller's equation,

$$Igeo = log_2 \ Cn/1.5 \ Bn,$$

in which Cn is the measured concentration of the element "n" in the pelitic sediment fraction ($< 2 \ \mu m$) and Bn is the geochemical background value in the fossilized argillaceous sediment (average shale); the factor 1.5 is used because of possible variations of the background data due to lithogenic effects. The results of estimated indices for metals in sediments and particulates from the Tsengwen river basin are shown in Table 3. It is evident that Cd and Pb were relatively enriched either in sediments or in particulates, while Zn showed one class order behind the Cd and Pb, whereas Fe and most of Mn and Cu showed no enrichment with respect to the background values. Spatial variations of metal pollution in the river basin can be revealed from the values of Igeo at different river locations as shown in Table 3. Because Igeo is free of the lithogenic effect, It can clearly reflect the effects of post-industry on metal accumulation. Consequently, the enriched sequence ($Cd, \ Pb > Zn, \ Cu > Fe, \ Mn$) corresponds somewhat to the accumulation of metals in fossil residue (Salomons and Forstner, 1984) which may act as a mirror for the cultural effects.

c. Mechanisms of metal transports

Table 4 represents the metal contents in the particulates of the Tsengwen river, mean metal contents in the particulates of world rivers, metal contents of soils in the river basin, and typical metal contents of world soils. We found that particulate *Fe*, *Mn*, *Cd* and *Cu* in the Tsengwen river fall in the ranges close to the mean values of those in the world rivers; particulate *Pb* and *Zn*, however, are much lower than those in the world rivers. Nevertheless, particulate metals are much higher than those in the respective soils of the drainage basin. Obviously, riverine particulate metals were enriched with respect to the soil metals in the drainage basin. According to the viewpoints of Martin and Meybeck (1979), in the tropical areas the suspended matter of rivers mainly originates from weathered soil materials rather than from rock debris, and in this type of river the contents of particulate Al, *Fe* and Ti are usually the highest, while the contents of particulate Ca and Na are the lowest. In our study the content ratios of metals between riverine particulate and drainage soils are 1.69 for *Fe*, 3.55 for *Mn*, 9.57 for *Cd*, 3.99 for *Cu*, 6.39 for *Pb*, and 3.86 for *Zn*. This indicates an anthropogenic impact on the metal runoff pathways from drainage basin to the river.

Table 4. Comparison of metal concentration between suspended particulates in the river and soils of the basin.

Metal	Particulates of Tsengwen river (range, ppm)	Soils of Tsengwen basin (range, ppm)	Particulates[+] of world rivers (average, ppm)	World soils[#] (typical, ppm)
Fe	3.37-4.22 %	2.02-2.47 %	4.8 %	3.2 %
Mn	1245-1318	340-382	1050	760
Cd	0.70-1.79	0.071-0.13	(1)	0.6
Cu	52.1-81.9	15.0-18.6	100	26
Pb	67.3-70.5	9.82-11.7	150	29
Zn	224-293	62-72	350	60

+ Martin and Meybeck (1979)

Ure and Berrow (1982)

In considering the fact that the metals transported by suspended matter may exist in different chemical forms with various strength for biota availability, particulate metal speciation through the transport en route was investigated. Fig. 5 displays the metal species distributions from the sampling stations on the Tsengwen river. Overall, the particulate metal speciation is rather dependent
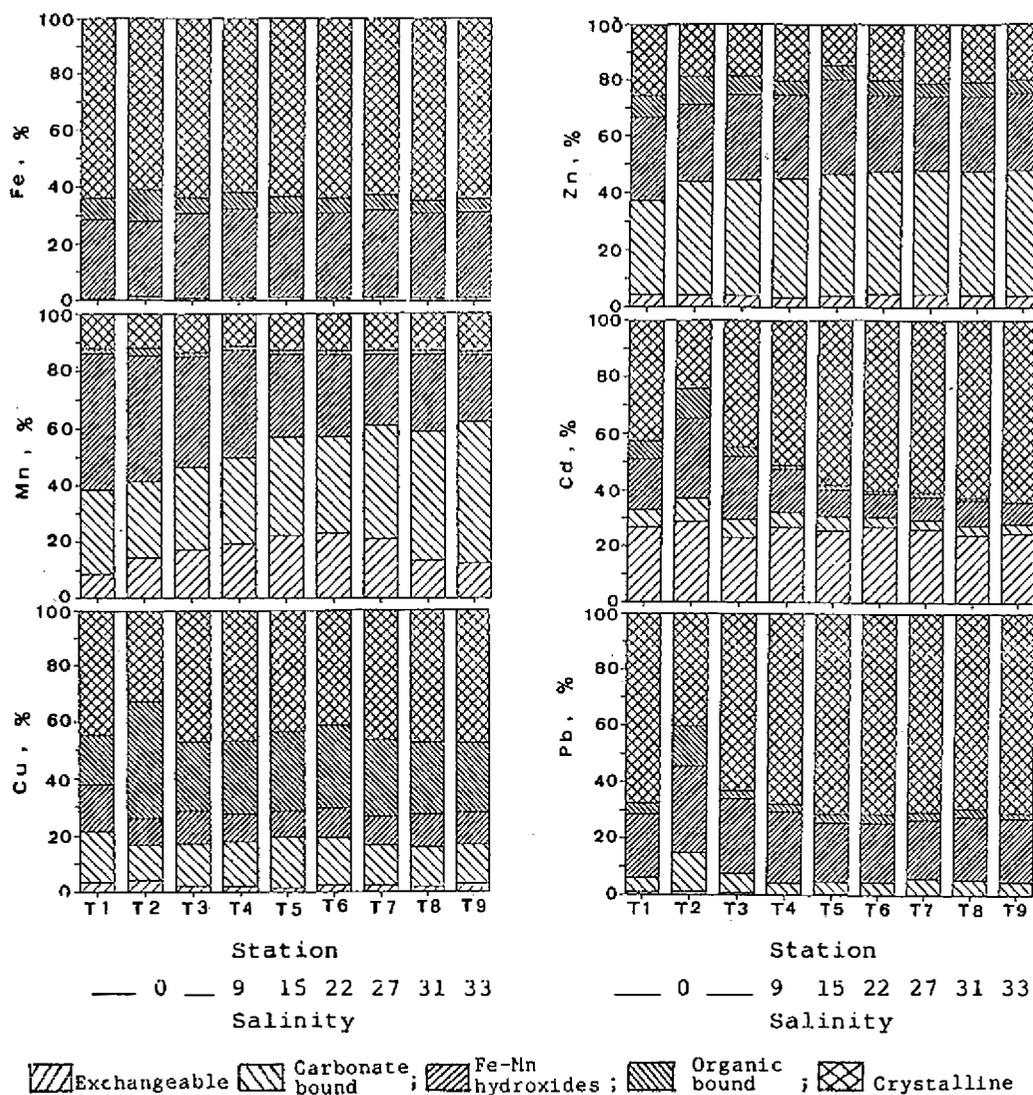
Fig. 5. Distribution of metal species in suspended particulates for the Tsengwen river and estuary.

on the metal type. Particulate Fe and Pb are mostly concentrated in the Fe-Mn hydroxides and crystalline fractions. Particulate Mn, Cu, Zn and Cd distribute rather significantly, in addition to Fe-Mn hydroxides and crystalline fractions, in exchangeable and carbonate phases, carbonate and organic phases, the carbonate phase and exchangeable phase, respectively. The particulate metal speciation is little different between riverwater and estuarine water. In general, metals in exchangeable, carbonate, Fe-Mn hydroxides and organic phases are of both natural and anthropogenic origins; they are considered as

potentially available, while metals incorporated in the structures of crystalline materials are essentially of geological origin and are usually inert toward the biota (Calmano and Forstner, 1983; Gibbs, 1977, Tessier *et al.*, 1979).

Particulate metal species may be subject to alteration as suspended matter enters the estuary. Exchangeable metals may be released into the water if salt concentrations and organic complexing agents increase and pH decrease. Metals in *Fe-Mn* hydroxides may be released if estuarine water becomes acidic or reduced. Organically-bound metals may become available to the biota through the decay of organic matter. Among the environmental factors examined in this system, pH and redox potential would contribute little to the alteration of metal speciation, because there is no significant change of pH (7.6-8.2) and dissolved oxygen content (4.6-6.5 $mg\ L^{-1}$) in the river system. Consequently, the increase of ionic strength (salt concentration), decay of organic matter, and increase of ligand concentration should be responsible for the shift in speciation.

Table 5. Riverine fluxes of metals from the Tsengwen river.

Metals	Dissolved [*]	Suspended [**] particulate	Total
Fe	33.6(0.06)[@]	60,346(99.94)[@]	60,380
Mn	13.2(0.71)	1,854(99.29)	1,867
Cd	0.07(6.60)	0.99(93.40)	1.06
Cu	3.72(4.76)	74.5(95.24)	78.2
Pb	1.20(1.18)	101(98.82)	102
Zn	23.1(5.49)	398(94.51)	421

[*] Dissolved load (ton/yr) = (Concentration of dissolved metal)
       X(Annual discharge)[#]
[**] Suspended load (ton/yr) = (Concentration of suspended metal)
       X(Annual load of suspended particulate)[+]
[#] Annual discharge: 1.40×10^9 m^3/yr (Ave., 1972-1981)
[+] Annual suspended load: 1.43×10^6 ton/yr (Ave., 1972-1981)
[@] Values in parentheses are the percentages of total concentrations

The annual discharge (gross fluxes) of metals from the Tsengwen river were estimated. They were calculated as the sum of dissolved and particulate metals averaged from high and low flows. From Table 5 we found that over 93 % of the total fluxed metals were transported by the particulate phase. Gibbs (1977)

has claimed that suspended sediments transport over 97 % of the total mass of transition metals to the world's oceans. Martin and Meybeck (1979) have also found that the dissolved transport index in rivers only accounted for 0.1-10 % of most transition and rare earth elements in the world's rivers. Yeats and Bewers (1982), however, have estimated dissolved fluxes in less than 10 % for Al, *Fe*, *Cu* and *Cd*, but up to 28 % for *Mn*, 48 % for Co, 66 % for *Zn*, and 74 % for Ni, in the St. Lawrence river in Canada. The difference was ascribed to the lower content of suspended matter and relative lack of pollution in the St. Lawrence river. The Tsengwen river discharged total metals approximately 0.004-0.01 % of those from other global rivers, but it discharged only 0.004 % of the global amount in water discharge. Apparently trace metals transported by suspended matter are relatively important, and this could be relevant to the rapid denudation and erosion of rocks and soils in Taiwan.

d. Mass-balance in the estuary

An estuary can be a sink or a source for river borne materials. In order to understand the net fluxes of metals into the coast, we shall use a box model (Fig. 6) to decribe the mass-balance of metals in the Tsengwen estuary. The boundary between the river and theestuary is the Kuosheng bridge, and the boundary between the estuary and the Taiwan Strait is the river mouth. Water flowing in and out the estuary is defined as Q_R, from the river, and Q_E, from the estuary, Q_O, is bottom water exchange from the Taiwan Strait.
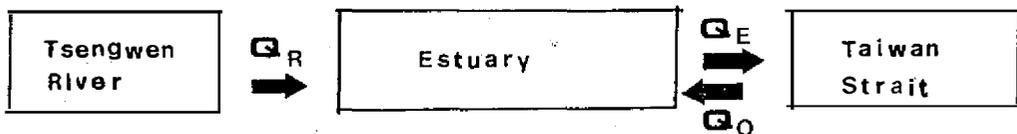

Fig. 6. A box model of metal transport in the Tsengwen estuary.

Because salinity is generally thought of as a conservative parameter (Klinkhammer and Bender, 1981), we apply the requirement of salt balance (equation 1) to derive a mass-balance condition. We calculated the mean salinity in the estuary (S_E) from the salinity profile in Fig. 2 ($S_E = \sum Si \times Vi / \sum Vi$, where Si is one of the salinity values in Fig. 2 and Vi is the water volume of that salinity) and use sea-end salinity as the mean salinity in the box of the Taiwan Strait.

$$Q_E S_E = Q_O S_O \tag{1}$$

$$Q_E = Q_O S_O / S_E \tag{2}$$

$$Q_E = Q_R + Q_O \tag{3}$$

Combining equations 2 and 3, we obtain

$$Q_O = \frac{Q_R}{(S_O/S_E - 1)} \qquad (4)$$

Table 6. Chemical balance of metals in the Tsengwen estuary.

Element	Influx (ton/yr)		Outflux (ton/yr)	
	Dissolved	Particulate	Dissolved	Particulate
Fe	40.7	60,432	22.6(56%)*	20,966(35%)*
Mn	14.5	1,856	11.0(76%)	598(32%)
Cd	0.11	0.99	0.126(114%)	0.28(28%)
Cu	4.70	74.6	3.13(67%)	22.0(29%)
Pb	1.49	101	1.25(84%)	38.9(39%)
Zn	29.4	399	21.4(73%)	199(50%)

* Values in parentheses are percentages of outflux:influx.

The S_O is taken as 34.5 0/00 and S_E is calculated to be 15.5 0/00. The Q_R is 1.40×10^9 m^3 yr^{-1}. The Q_O is then calculated to be 1.14×10^9 m^3 yr^{-1}. Therefore, we can use the data listed in Figs. 3 and 4 and Table 5 to estimate the metal fluxes into and out of the Tsengwen estuary. From Table 6, we can see that about 56 %, 76 %, 114 %, 67 %, 84 % and 73 % of dissolved influxes as well as 35 %, 32 %, 28 %, 29 %, 39 % and 50 % of particulate influxes, respectively for *Fe*, *Mn*, *Cd*, *Cu*, *Pb* and *Zn*, are transported across the Tsengwen estuary. It seems that little of the particulate metals has been converted into the dissolved phase. Apparently, the imbalance of metals between the dissolved and particulate phases could be attributed to the deposition of metals in the estuary.

4. CONCLUSION

This comprehensive study provides data for understanding the transport mechanisms and hehaviors of trace metals in the Tsengwen river and its estuary. The data shows that the Tsengwen riverwater has been slightly contaminated with anthropogenic metals in the middle and down streams. The riverborne dissolved metals with the exception of *Cd* behaved non- conservatively in the estuary. Dissolved *Fe*, *Mn*, *Cu*, *Pb* and *Zn* exhibited significant removals in

the initial mixing zone; Cd, however, did not display a signal of removal or addition over the estuary. Concentrations of particulate and sediment metals, similar to those of dissolved metals, were higher in the middle river than in the adjacent stations, but there was little difference over the estuarine locations. The accumulated particulate and sediment metals with reference to baselines follow a sequence of $Pb, Cd > Zn, Cu > Fe, Mn$.

We also found that trace metals were mainly transported by suspended particulates, accounting for over 93 % of total gross fluxes. The human impacts on this metal transport are clear. Particulate metal speciation is characteristic of metal geochemical properties and it is closely related to metal bioavailability. The net fluxes of metals out of the estuary are modeled as approximately 56 %, 76 %, 114 %, 67 %, 84 % and 73 % of the dissolved influxes as well as 35 %, 32 %, 28 %, 29 %, 39 % and 50 % of the particulate influxes, respectively for Fe, Mn, Cd, Cu, Pb and Zn. The imbalance of metals between the dissolved and particulate phases is thought to result from metal deposition in the estuary. The net fluxes of metals may provide important clues for evaluating the effects of terrestrial sources on the quality and productivity of coastal water.

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曾文河川及河口地區微量金屬
之輸送及行為研究

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摘 要

本研究係探討鐵、錳、鎘、銅、鉛、鋅等微量元素在曾文河川及河口地區之地化行為與輸送機制。曾文溪河川溶解態金屬，均在中游或下游有較高的分佈。一般而言，微量金屬濃度均比世界河川背景值稍高，但比污染嚴重之河川為低。溶解態鐵、錳、銅、鉛、鋅在河口地區均有移除現象發生，而鎘則未有顯移除或添加現象。懸浮顆粒與沉積物金屬在河川中游亦有較高的濃度，但在河口各站中均未有明顯的分佈差異。由地化累積指數可以看出懸浮顆粒與沉積物金屬之富集程度依序為Pb、Cd > Cu、Zn > Fe、Mn。

曾文河川中微量金屬元素主要經由懸浮顆粒之輸送，約佔總輸送量之93%以上，且在輸送過程中已受到人為污染之影響。顆粒性微量金屬元素之物種分佈取決於元素種類。鐵及鉛主要存在於鐵錳氧化物及礦物晶體中。錳、銅、鋅、鎘則除了分佈於鐵錳氧化物及礦物晶體外，亦分別在交換性及碳酸鹽相、碳酸鹽及有機相、碳酸鹽相、及交換性相有明顯的分佈。利用箱型模式估算結果發現，對輸入河口的鐵、錳、鎘、銅、鉛、鋅而言，分別有56%，76%，114%，67%，84%及73%的溶解態以及35%，32%，28%，29%，39%，及50%之顆粒態通過河口進入台灣海峽。因此河口中溶解相與顆粒相中金屬元素之質量差異部份相信已沈積於河口之沈積物中。