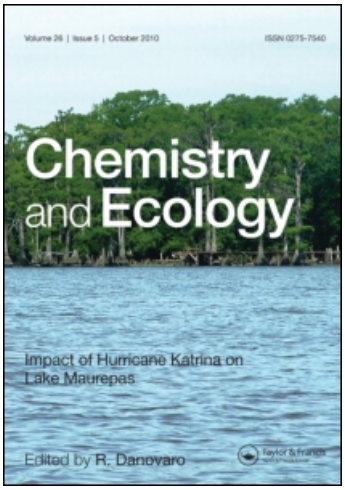

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Fluxes and Transport of Organic Carbon and Trace Metals in the Tropical Tsengwen Estuary, Southwestern Taiwan

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FLUXES AND TRANSPORT OF ORGANIC CARBON AND TRACE METALS IN THE TROPICAL TSENGWEN ESTUARY, SOUTHWESTERN TAIWAN

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Distributions of organic carbon and trace metals were investigated in the tropical Tsengwen river end-member and in the estuary to better understand thoroughly the riverine fluxes and estuarine transports of constituents into the sea. Experimental results indicated that riverine fluxes of organic carbon and trace metals possessed a highly temporal variability, attributed primarily to temporal variation in river water discharge and suspended load. More than 70% of annual fluxes of dissolved constituents and >90% of particulate constituents arose from river floods caused by summer typhoons. The flushing time of fresh water in the estuary varied from a half month in the dry season to a half day in the flood period. Dissolved organic carbon (DOC) and nutrient-type metals (Cd, Cu, Zn) were conservatively transported through the estuary. Dissolved particle-reactive metals (Mn, Pb), however, were apparently transported non-conservatively through the estuary. Particulate organic carbon (POC) and trace metals (PTM) were transported non-conservatively by following the transport mode of total suspended matter (TSM) in the estuary. DOC slightly dominates the transport of organic carbon while particle-reactive PTM predominates the transport of trace metals through the estuary. Total organic carbon (TOC) in estuarine sediment was progressively enriched with ^{13}C downstream, as derived by mixing the overlying TSM between terrestrial and marine end-members. Distributions of trace metals in sediment were subsequently controlled by sedimentary TOC and particle size. Based on results presented here, we believe that enrichments of trace metals in the estuary are attributed primarily to the natural processes of transport and sedimentation of fluvial TSM.

Keywords: Fluxes; transport; organic carbon; trace metals; Tsengwen Estuary

INTRODUCTION

Estuarine and coastal zones, the most productive areas in the ocean, comprise only 8% of ocean surface but account for about 26% of ocean production (International Geosphere-Biosphere Programme, (IGBP), 1994). However, the coastal areas are also subject to human impact through exploitation of coastal resources, economic growth and social activities. The LOICZ (Land-Ocean Interactions in the Coastal Zone) research programmes have recently been promulgated to enhance our understanding of the roles of coastal systems in determining regional or global environmental change (LOICZ, 1996).

The southwestern coastal environment in Taiwan has dramatically changed during recent decades owing primarily to changes in land use and inputs of pollutants from contaminated rivers (Hung, 1995). The Tsengwen River is a tropical and mountainous river in southwestern Taiwan. The river, although less polluted than others in southwestern Taiwan, has an estuary and coast that may incur unforseeable changes in the future, owing to the planned petrochemical and steel industries around the watershed of its estuary. The detrimental change in Tsengwen Estuary may also endanger certain biological species including blackface spoonbills which use the Tsengwen Estuary as their winter shelter. As anticipated, additional organic carbon and trace metals will be discharged into the Tsengwen Estuary after the petrochemical and steel industries are established. The human intervention may alter the environmental quality of estuary and give a severe change for biological inhabitants. However, the future change cannot be perceived without understanding thoroughly the current estuarine environment.

The fluxes of materials from land to sea are an important focus in LOICZ (IGBP, 1994). The extent of fluxes, however, relies heavily on the change of external forcing or boundary conditions in the study regime. The tropical Tsengwen River water discharge shows a distinct dry and wet (or flood) seasonal pattern and has been dammed since 1973. The fluxes of organic carbon and trace metals are expected to follow the seasonal patterns of water discharge, and may influence their behaviour in the Tsengwen Estuary as well. This study, a part of global LOICZ research, is performed to examine the variabilities of fluxes for organic carbon and nutrients as well as to investigate the

biogeochemical transport and distribution of organic carbon and trace metals in the Tsengwen Estuary.

MATERIALS AND METHODS

Study Area

The Tsengwen River is a mountainous river in southwestern Taiwan. The river drains through the Tainan and Chai-I counties with a total area of 1177 km^2 and a total length of 138.5 km (Hydrological Year Book of Taiwan, 1995). The sea water intrusion zone ranges approximately from 10 km to 25 km from the river mouth depending on the discharge volume of river water. Figure 1 depicts the study area of the Tsengwen Estuary, which is seasonally variable. As Figure 2 indicates, two contrasting seasons, wet (May-September) and dry (October-April) seasons, induce high and low river water discharges. During the wet season, accumulated river water discharge after episodic storm floods caused mainly by typhoons may contribute up to

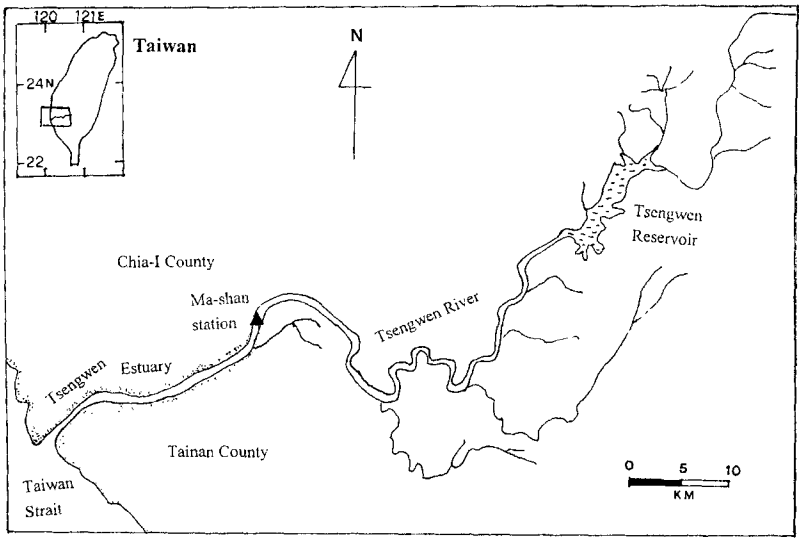

FIGURE 1 Schematic diagram of the study area.

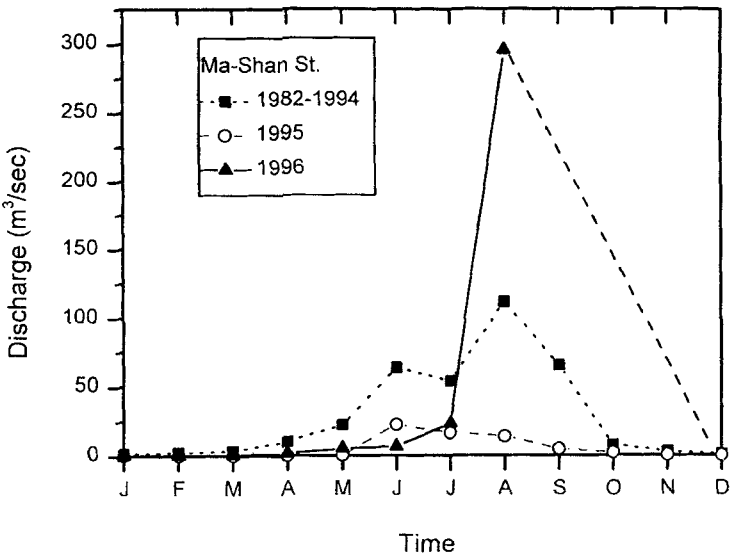

FIGURE 2 Monthly discharge of the Tsengwen river water at the Ma-shan Station (data available from Hydrological Year Book of Taiwan before 1995; data in 1996 are calculated from the water level of river recorded by the Taiwan Provincial Water Conservancy Bureau).

90% of annual river water discharge. In this study, the estuary covers a watershed with a salinity exceeding 0.2 per mil.

Sampling and Analytical Methods

Water samples were taken at the Tsengwen River end-member station at least bimonthly, and at the Tsengwen Estuary during the dry season (January 10, 1995), flooding period (June 14, 1995) and wet season (September 30, 1995). Estuarine water samples were collected upstream from the river mouth on board a small vessel. At each sampling station, the water samples were collected sequentially at desired depths using a home-made sampling system consisting of a manual peristaltic pump and a silicon tube. Contamination was carefully avoided. Salinity, pH and dissolved oxygen (DO) were measured *in situ* with a salinometer (Hydro-Bios), a pH meter (Orion Research) and a DO-meter (YSI model 58), with a reproducibility generally exceeding 5%, 2% and 7%, respectively. Salinity was determined via an Autosal

salinometer (Guildline 8400B) in the laboratory again to gain more precise salinity values. Four litres of each sample was stored in a polyethylene bottle and brought back the laboratory. Next, water was filtered through an acid-cleaned, dried and pre-weighed Nucleopore membrane filter to determine the concentrations of total suspended matter (TSM) and dissolved and particulate trace metals.

Sediment samples were collected from the bed surface in the estuary. A portion of the sediment sample was used to determine the grain size distribution with a particle size counter (Coulter LS particle Size Analyzer). Another portion of the sediment was washed with distilled-deionized water (DDW) to remove any remaining sea salt and then dried in an oven at 60°C. The dried sediment was ground to powder using an agate mortar and pestle before further analyzing the contents of organic carbon and trace metals.

Immediately after the samples were brought to the laboratory, samples for dissolved organic carbon (DOC) and nitrogen (DON) as well as particulate organic carbon (POC) and nitrogen (PON) were filtered through pre-combusted GF/F filters (at 450 °C, 4 hr). DOC was measured with the high temperature catalytic oxidation method (Shimadzu TOC 5000) (Hung and Chang, 1992; Hung and Lin, 1994). DON was determined from the difference between total dissolved nitrogen (TDN) and dissolved inorganic nitrogen ($NO_3 + N$-$O_2 + NH_4$). TDN was measured with the high temperature oxidation method (Antek N/S analyzer), while the inorganic nitrogen was determined with flow injection analysis (FIA) methods (Pai *et al.*, 1990). Particulate organic carbon (POC) and nitrogen (PON) as well as sedimentary organic carbon (SOC) and nitrogen (SON) were then determined with a C/N/S analyzer (Fisons NCS 1500) after removing the inorganic carbon with hydrochloric acid. Finally, stable carbon isotope (^{13}C) was determined with a C/N mass spectrometer (Tracermass, ANCA-MS).

For trace metal analyses, dissolved metals were preconcentrated with chelation back extraction method (APDC/DDDC-freon-diluted HNO_3) modified from Danielsson *et al.* (1982) and Statham (1985). Dissolved manganese, however, was preconcentrated with C18 Sep-Pak cartridges (Waters Association, Milford, USA) detailed in Sturgeon *et al.* (1985) and Hung and Shy (1995). Particulate metals were analyzed by digesting the filtration residue with mixed super-pure

acids (HNO_3: HCl: HF = 3:3:4) heated by a microwave oven (CEM 2000). The digested solution was then diluted with DDW before metal measurements. Trace metals in sediments were analyzed with the same procedures as those for particulate trace metals. Pretreated dissolved and particulate metals were then determined either with a flame or a flameless atomic absorption spectrophotometer (Perkin-Elmer 5100 PC, HGA 600). Matrix modifiers and Zeeman background corrector were applied throughout the flameless measurement. Analytical precision generally exceeded 90% reproducibility (Hung, 1988; 1995).

RESULTS AND DISCUSSION

Temporal Variability of River Discharge and Flux

The long-term distribution of rainfall in this tropical Tsengwen drainage basin displays a contrasting pattern between dry and wet seasons. More than 80% of annual precipitation falls from May through September, with a major portion provided by monsoon rain or typhoons (Hydrological Year Book of Taiwan, 1995). The temporal variations of river water discharge closely coincide with the rainfall pattern. The river water discharge generally increases from May to August and then decreases to near zero after October (Fig. 2). The river water discharges of recent years (1995 to 1996) are apparently lower than that of the long-term average (1982–1994), with the exception of August 1996, due to an unusual typhoon. The Gloria and Herb typhoons brought in enormous rainfall during July-August 1996. As a result, a river water discharge of historical proportions by the Typhoon Herb was recorded (Fig. 3). The total river water discharge of July and August accounts for 84% of the annual discharge. Consequently, typhoons heavily influenced the annual discharge of Tsengwen river water. Meanwhile, the suspended load was also concentrated between May and September (Fig. 4) because rainfall intensity determines soil erosion. The total suspended load between July and August 1996 accounts approximately for 99% of the annual load.

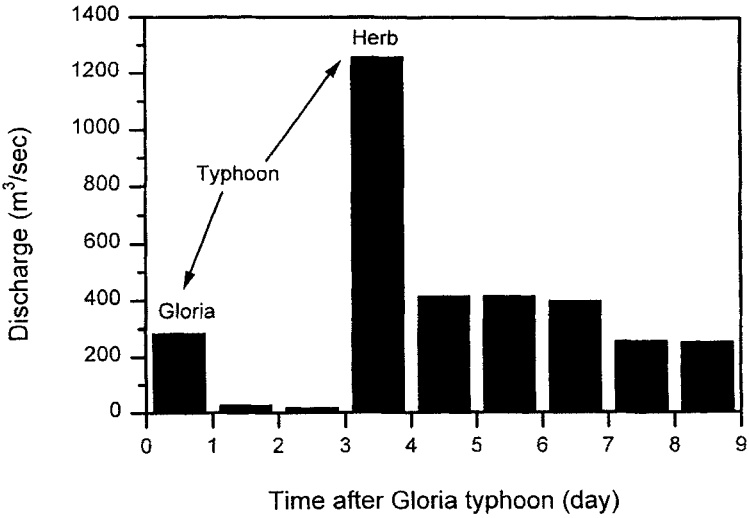

FIGURE 3 Discharge of Tsengwen river water at the Ma-shan Station during the typhoon periods. Data are calculated from the water level of river recorded by the Taiwan Provincial Water Conservancy Bureau.

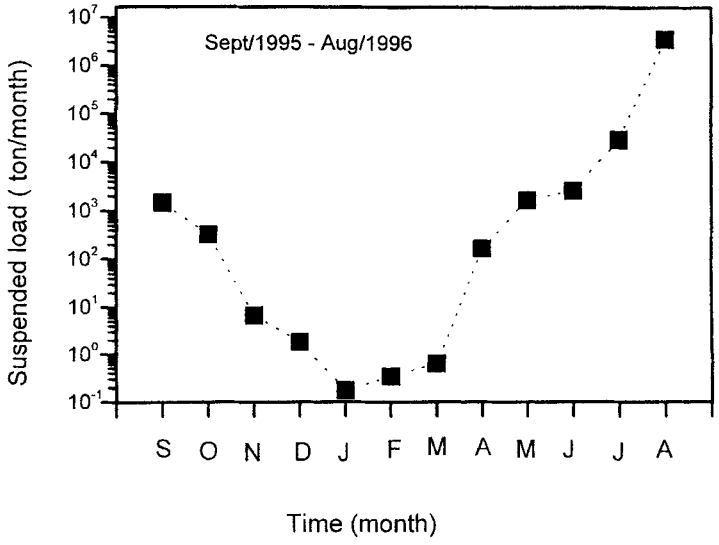

FIGURE 4 Monthly variation of suspended load from the Tsengwen River at the Ma-shan Station.

Annual fluxes of measured constituents are estimated from the annual river water discharge and elemental concentrations. Both river water discharges (Fig. 2) and elemental concentrations (Fig. 5) vary with time. Each constituent concentration varied monthly even during the same season, indicating that the input of a constituent from the watershed to the river was temporally variable. Figure 6 presents the calculated monthly fluxes of constituents. Apparently, the fluxes of dissolved constituents depended heavily on river water discharge rather than on their concentration although the greater river water discharge frequently reduces the concentration. Meanwhile, the fluxes of particulate constituents were primarily determined by the total suspended load which was then determined by the concentrations of TSM and river water discharge. For an annual cycle, the fluxes of constituents decreased from September to minimum at January and then increased to a maximum at August.

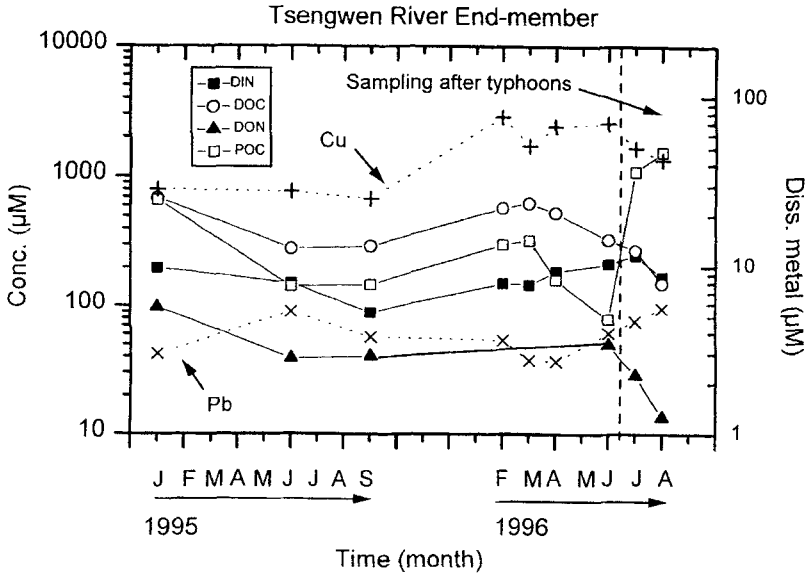

FIGURE 5 Temporal distributions of constituents in the river end-member of Tsengwen River.

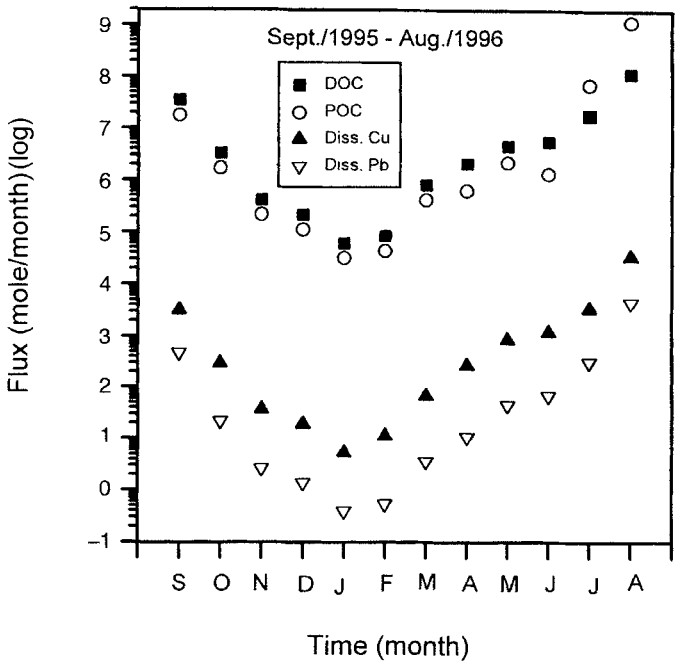

FIGURE 6 Temporal variations of constituent fluxes in the end-member of Tsengwen River.

Hydrochemistry of the Estuary

Figures 7a–c depict the distributions of salinity in the Tsengwen Estuary during the dry, flooding and wet seasons, respectively. Sea water intrusion reached approximately 22 km from the estuarine mouth upstream during the dry season. This distance was roughly two times than in the flooding season when sea water was pushed downstream and confined to a lower portion of the water column. River water mixed fairly well with sea water in the estuary during the dry season, but was only partially mixed during the flooding period and wet season. Therefore, the flushing time of river water in the estuary, derived from the fraction of fresh water method (Asselin and Spraulding, 1993), was significantly longer in the dry season (150 day) than in the flooding season (< 1 day) and wet season (2.5 day). The estuary was generally in an oxygenated condition with dissolved

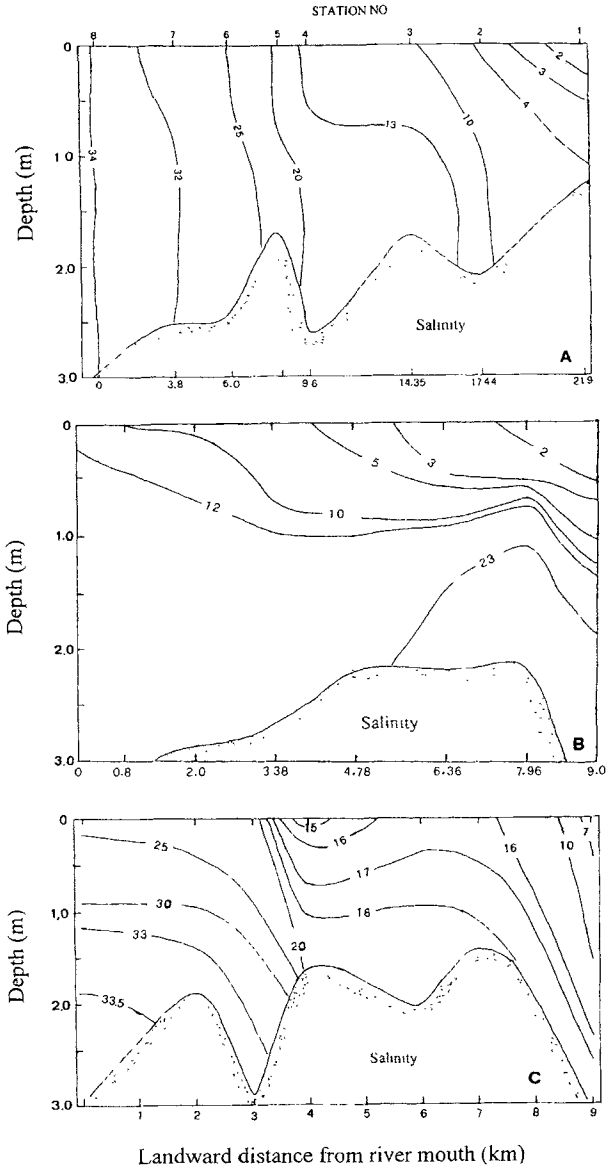

FIGURE 7a–c Salinity profiles of the Tsengwen Estuary during the various seasons. A, dry season; B, flood period; C, wet season.

oxygen exceeding 150 μM. Distributions of total suspended matter (TSM) also display contrasting patterns among the seasons. The horizontal concentration gradient increases toward the turbidity maximum from upstream and then decreases away from it towards the river mouth during the dry season (Fig. 8a). The longitudinal TSM distributions, however, do not indicate that turbidity maximum occurs during the flood (Fig. 8b) and wet (Fig. 8c) seasons. The TSM generally decreases first downstream and then increases again towards the river mouth. As a result, the fluxes of organic carbon and trace metals differ between seasons in the estuary.

Organic Carbon in the Estuary

Figure 9 plots the distribution of dissolved organic carbon (DOC) against salinity. DOC behaved quite conservatively in the estuary during different seasons. This behaviour resembles those found in other estuaries in Taiwan (Hung, 1995) and those found in other estuaries (Sharp *et al.*, 1982; Mantoura and Woodward, 1983; Norredin and Courtot, 1989). This finding suggests that the mixing process primarily controls DOC in the Tsengwen Estuary and, to a lesser extent, is controlled by biological utilization/regeneration processes. DOC concentrations range from 680 to 100 μM in the dry season, which were markedly greater than those during flooding and wet seasons (298 – 150 μM). The concentration near the river end-member in the low-flow period always exceeded that in the high-flow period (Fig. 5), implying that a large portion of DOC was released from phytoplankton and periphyton after localized production during the dry season, when the flushing time of river water was substantially longer and more appropriate for biological development. DON was also conservative in the estuary during the dry season, but apparently non-conservative during flooding and wet seasons (not shown here). The ratio of DOC/DON in the estuary varied only slightly over each season, ranging from ca. 9.10 at river end-member to ca. 6.40 at the river mouth, reflecting the characteristics of estuarine DOC owing to mixing between riverine and marine DOC.

Particulate organic carbon (POC) was transported non-conservatively in the estuary during the various seasons (Fig. 10a) because the heterogeneous distribution of TSM determine the distribution of POC.

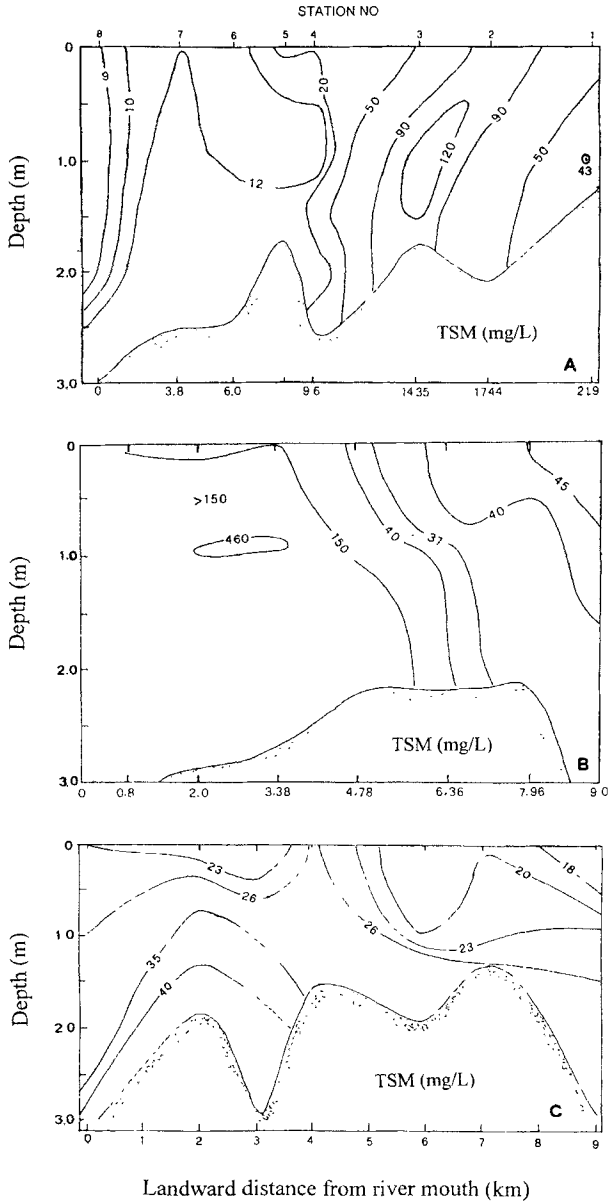

FIGURE 8a–c TSM profiles of the Tsengwen Estuary during the various seasons. A, dry season; B, flood period; C, wet season.

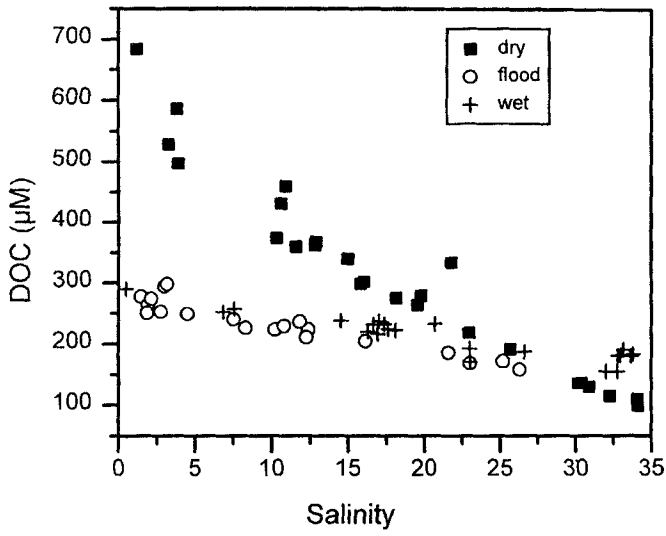

FIGURE 9 Distribution of DOC in the Tsengwen Estuary during various seasons.

Estuarine POC concentrations markedly exceed those in the coastal ocean, ranging from 660 to 30 μM in the dry season, from 200 to 60 μM in the flood period, and from 150 to 50 μM in the wet season. Perhaps, a large portion of estuarine POC deposited and/or decayed before export out of the estuary. In addition, the POC concentration correlated well ($R = 0.8878$, $p < 0.0001$) with that of DOC, implying that both may be largely determined by terrestrial inputs. Moreover, POC was systematically lower than that of DOC in the estuary with the exception of that in the upper estuary near the river end-member. This distribution pattern differs from those in coastal and open oceans where DOC exceeds POC (Burney, 1994). The source of POC in the Tsengwen Estuary can be assessed from the enrichment of stable isotope (^{13}C) in TSM. The fraction of POC (f_t) derived from terrestrial source, ranged from 80–100% in the upper estuary, to 40% in the lower estuary (Fig. 10b), assuming that $\delta\ ^{13}C$ value is 29 in the terrestrial end-member and 19.5 in the marine end-member. The carbon isotope (^{13}C) was also progressively enriched in sediment from upper to lower estuaries (Fig. 14), reflecting that estuarine sediment was derived from overlying TSM as mixed from riverine and marine TSM.

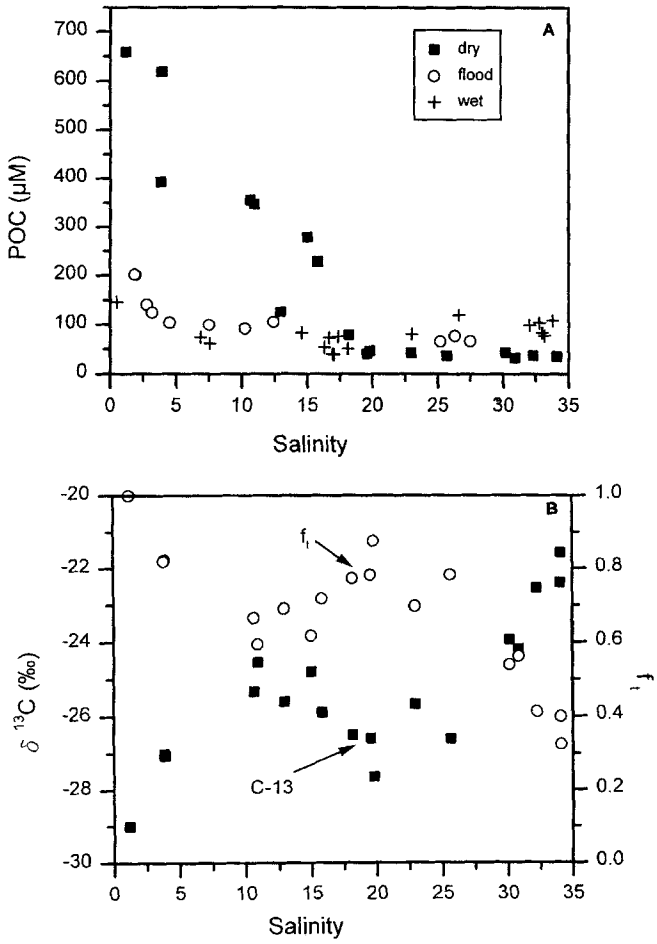

FIGURE 10 Abundance of POC in the Tsengwen Estuary during various seasons (A) as well as distributions of $\delta^{13}C$ and terrestrial fraction (f_t = terrigenous POC/ total POC) for POC in the dry season (B). The f_t was derived from measured, riverine and marine end-member $\delta^{13}C$ values ($\delta^{13}C_{measured} = [\delta^{13}C_{river} \times f_t] + [\delta^{13}C_{marine} \times (1-f_t)]$).

Distribution and Transport of Trace Metals in the Estuary

Figure 11 displays distributions of dissolved trace metals in the Tsengwen Estuary during the different seasons. As this figure reveals, concentrations generally decreased with increasing salinity. Distributions of dissolved cadmium, copper and zinc were likely to be

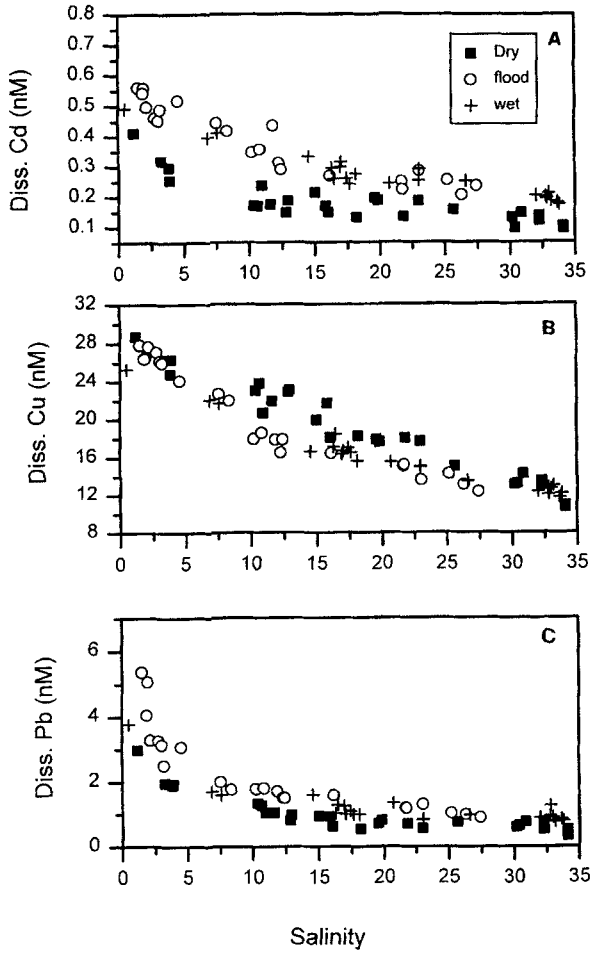

FIGURE 11 Distributions of dissolved trace metals in the Tsengwen Estuary. A, cadmium; B, copper; C, lead; D, manganese; E, zinc.

conservative with only a slight removal, if any, in the estuary. A relatively lower cadmium concentration was found in the dry season, likely attributed to biological utilization. Otherwise, the distributions of these nutrient-type metals only differed slightly among seasons. Dissolved lead and manganese behaved non-conservatively and were obviously removed in the estuary. This observation may be owing to flocculation and scavenge of particle-reactive metals (Mn, Pb) in the

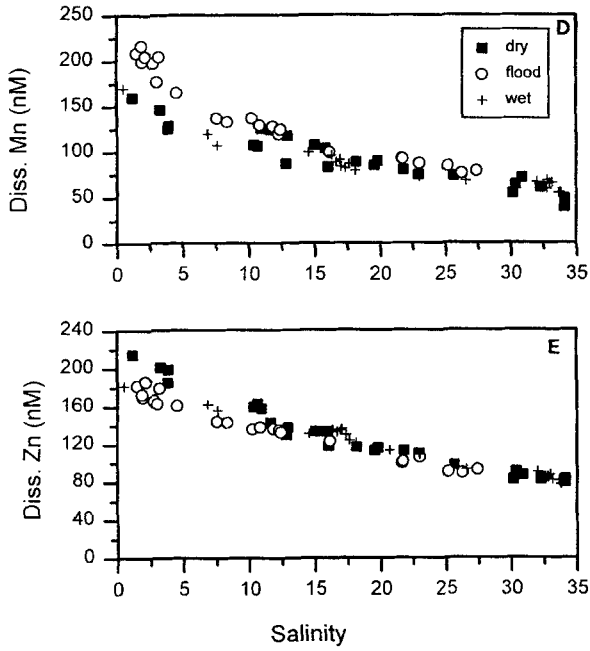

FIGURE 11 (Continued).

estuary (Sholkovitz, 1978; Chester, 1990). The removal process can be supported by the distribution of distribution coefficients [k_d(1/kg) = (moles particulate metal/mass solid)/(moles dissolved metal/volume solution)] of lead in the estuary. The magnitude of K_d simply expresses the affinity of a metal on particles. The K_d of lead generally increases with salinity in various seasons (Fig. 12a), indicating the elevated adsorption of dissolved lead on to particles with increasing salinity (Li *et al.*, 1984). Meanwhile, K_d(Pb) decreases with an increasing TSM (Fig. 12b), indicating the role of colloids in scavenging the dissolved lead. Particulate trace metals (PTM) are transported non-conservatively by following the transport mode of TSM (Fig. 13). Therefore, PTM is the major transport mode for most trace metals throughout this estuary. Trace metals, although enriched in TSM with respect to those distributions in crust (data not shown here), cannot be solely ascribed to anthropogenic influence. Naturally enriched processes may be responsible for this, since TSM is mostly fine-grained and POC

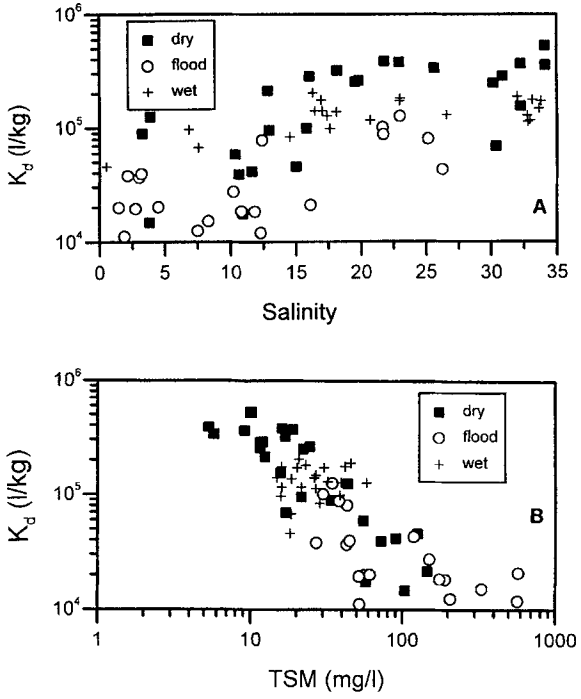

FIGURE 12 Relationships between K_d and salinity (A) as well as between K_d and TSM (B).

enriched which are a medium for metal adsorption. On the other hand, distributions of trace metals in estuarine sediments may be a better indicator of pollution because sediment represents the relatively long-term record of distribution.

Trace Metals in Estuarine Sediment

Trace metals are generally transported by TSM from rivers to the ocean (Gibbs, 1973, 1977; Salomons and Forstner, 1984; Martin and Meybeck, 1979, Keeney-Kennicutt and Presley, 1986). The fluvial TSM can be significantly trapped in the estuary (Chester, 1990), thus the abundance of trace metals in estuarine surface sediments is a good indicator of recent human perturbation. Metal abundance in sediment not only relies on anthropogenic inputs, but is also determined by

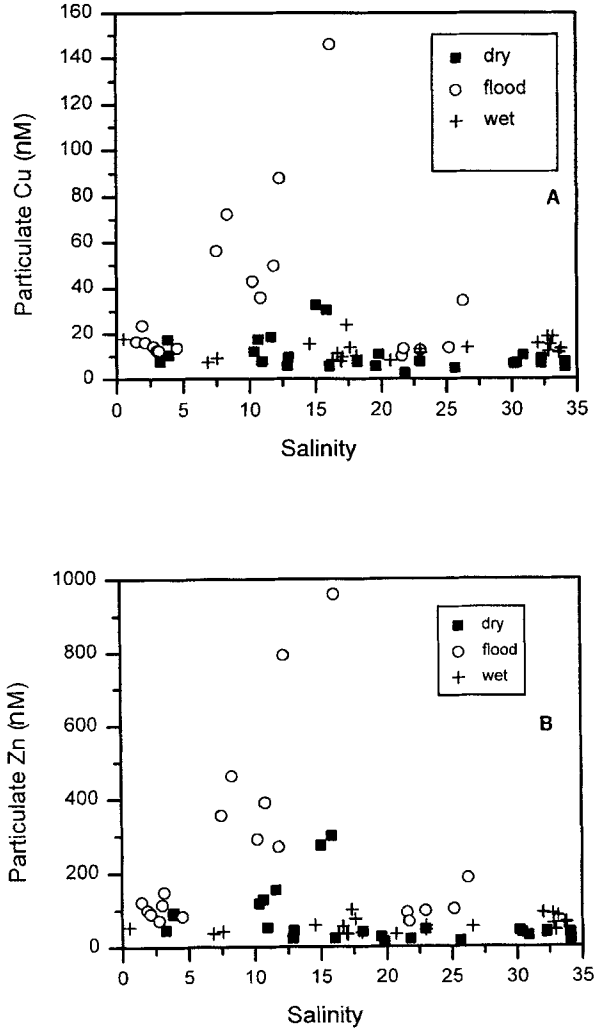

FIGURE 13 Distributions of particulate copper (A) and zinc (B) in the Tsengwen Estuary.

natural sedimentation processes. Figure 14 demonstrates that the contents of trace metals, organic matter and mud increase landward from sediments in the river mouth to sediments in the upper estuary. Consequently, metals and organic carbon are normally concentrated in mud and the distribution patterns of these constituents closely

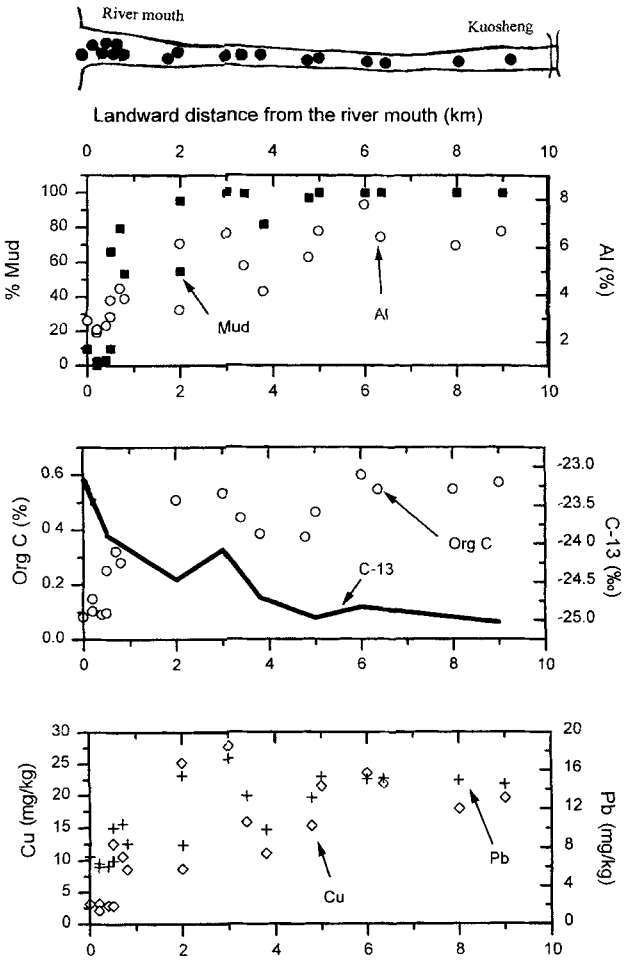

FIGURE 14 Distributions of mud, organic matter and trace metals in estuarine sediments.

coincide with each other in the estuary. In addition, concentrations of trace metals (Cu, Zn, Pb and Cd) including aluminium, iron and manganese correlate highly ($p < 0.01$) with each other and also closely correspond to the contents of mud and organic matter. The metal enrichment factors, as deduced from the crustal metal/Al ratio, indicate that most trace metals, except for zinc, accumulated in

estuarine sediments, may not be attributed primarily to anthropogenic inputs, that is, if the enrichment value 0.5–2.0, is regarded as a natural variability (Fig. 15). In contrast, estuarine transport and sedimentation of fluvial TSM primarily determine the current abundance of trace metals in sediments.

SUMMARY

The riverine fluxes of constituents depend heavily on the changes of external forcing. More than 70% of annual river water discharge and > 90% of annual suspended load occurred during the short periods of floods induced mostly from summer typhoons. Also, the fluxes of dissolved and particulate constituents in and out of the estuary adhere to the pattern and degree of annual river water discharge and suspended load. Moreover, the hydrochemistry of estuarine water differed among the dry, flooding and wet seasons. DOC and nutrient-type metals were transported conservatively and apparently conservative. POC, TSM, particle-reactive DTM and PTM, however, were transported non-conservatively in the estuary, but DOC slightly dominates the

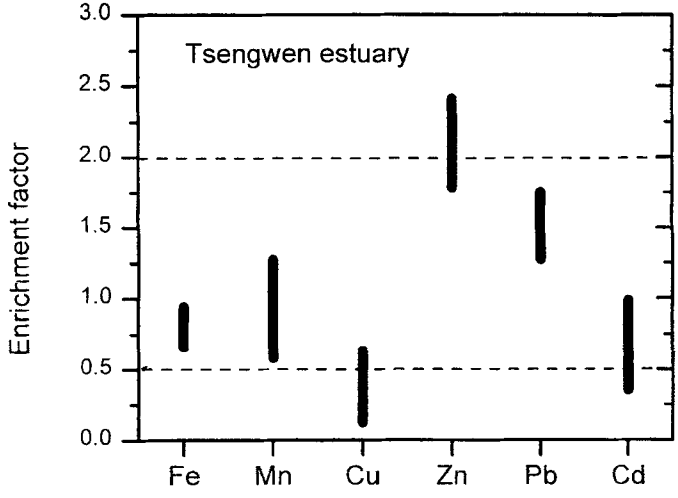

FIGURE 15 Enrichments of trace metals in estuarine sediments.

transport of organic carbon and particle-reactive PTM predominates the transport of trace metals. The riverine inputs of TSM control primarily distributions of trace metals in estuarine sediments. Although trace metals in the estuary derived mainly from the Tsengwen river, anthropogenic contributions may be smaller than those metals in the other estuaries of southwestern Taiwan.

Acknowledgements

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