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Journal of Hazardous Materials 148 (2007) 630–639
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Cadmium distribution in sediment profiles of the six main rivers in southern Taiwan

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Received 25 August 2006; received in revised form 7 January 2007; accepted 7 March 2007
Available online 12 March 2007

Abstract

Dynamic cadmium distribution has been studied in six main rivers flowing through the largest, most highly developed and polluted area of southern Taiwan. Sediment profile samples were also analyzed for Cu, Cr, Zn, Ni, Pb, Co, Mn, Fe, carbonates, Mn-oxides, Fe-oxides and organic matter in order to characterize the geochemical environment and to identify the pollutant sources. Higher Cd concentrations (about 3.5 mg/kg) at depths of 0–10 cm have been detected in the samples of Yenshui, Ell-ren and Potzu rivers, associated to the history of industrial activity in their catchments. According to the linear correlation coefficient (r) between Cd and the geochemical components, carbonates are the primary Cd binding phase in the Ell-ren river ($r = 0.85$), and Cd comes from the same pollutant sources of those containing Cr, Ni, Cu and Zn ($r > 0.80$). Cadmium concentration in the Potzu and Peikang river sediments is probably due to waste deposits rich in Cr and Cu ($0.54 < r < 0.65$). In the case of the Yenshui river, there is only a weak indication that cadmium derives from waste material containing Cr, Ni, Cu, Zn, and Pb (r around 0.40). On the other hand, in the Tsengwen and Chishui sediments cadmium concentrations seem to represent natural background. Generally, the Ell-ren and Yenshui rivers show strong heavy metal pollution, while no important heavy metal contamination has been found in the Tsengwen, Potzu, Chishui, and Peikang rivers.

Keywords: Cadmium; Heavy metals; Sediment profile; River; Taiwan

1. Introduction

Because of long residence time for contaminant in sediment, the study of river sediments plays an important role in proof of man-made contamination [1]. The measurements of heavy metals in water and suspended solid collected from river are not conclusive due to water discharge fluctuations and low residence time. The history of heavy metals distribution can be assessed by taking vertical sediment core samples from river-beds, as the makeup of sediment cores reflects the geochemical and contamination history of a given region, including any anthropogenic impact, and can act as a useful indicator of metal pollution flux [2–4]. Metals concentration in sediments usually exceeds those in overlying water by three to five orders of magnitude [5]. Sediment can accumulate and integrate the temporal variability of heavy metals in river water originating from anthropogenic activities into spatial river sediment [1]. Moreover, the vertical metal concentration profile in sediment from urban estuaries is a mixture of pollutants from different sources [1]. The vertical concentration profile of metals in sediment cores can be used to reveal the degree of metal pollution in recent decades [4,6,7].

The Ell-ren, Yenshui, Tsengwen, Chishui, Potzu, and Peikang rivers flow through the largest and most highly developed area of southern Taiwan, with a population of 4.6 million people. The distribution behavior of cadmium in high and low anthropogenic polluted area of Taiwan is not well understood, therefore, it's important to understand the distribution and fate of cadmium in river sediment.

The aim of this study was to realize the distribution of Cd in sediment cores, affected with other heavy metals, geochemical components, river depth and distance from the estuary, taken from the six main rivers in southern Taiwan. In order to identify the sources of cadmium, linear correlation between this metal and Cu, Cr, Zn, Ni, Pb, Co, Mn, Fe, and geochemical components (carbonates, organic matter, Fe-oxides, and Mn-oxides) were also investigated using a correlation matrix method.

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doi:10.1016/j.jhazmat.2007.03.024

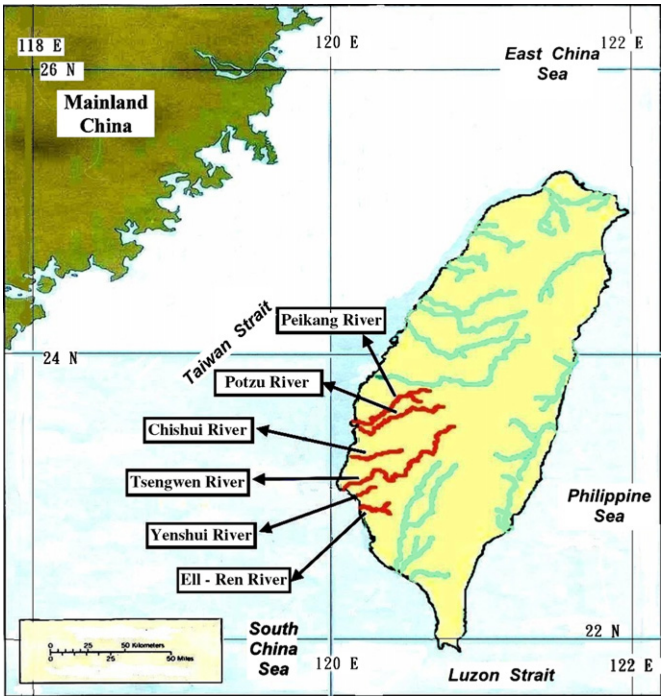

Fig. 1. The geographical map of six main rivers in southern Taiwan.

2. Materials and methods

2.1. Study areas

The Central Range forms the backbone ridge and is the main water divide between the eastern and the western slopes of Taiwan Island (Fig. 1). It separates Taiwan Island into two unequal parts, the western flank being about twice as wide as the eastern flank. The Central Range slopes westward into foothills and then into broad plains. A wide coastal plain extends southwest of this foothill region, bordering the Taiwan Strait on the east. The geologic province of the western foothills is the site of a Late Cenozoic sedimentary basin west of the Central Range. The western foothills gradually merge westward into the tablelands and coastal plains bordering the Taiwan Strait. This coastal plain has a north-south length of 240 km and a maximum east-west width of 45 km (Central Geological Survey, Ministry of Economic Affairs (MOEA)) [8], and the six main rivers: Ell-ren, Yenshui, Tsengwen, Chishui, Potzu, and Peikang flow through it. The annual river flows are concentrated between April and September with a predicted flood flows of 9200, 2730, 3240, 986, 1100 and 2023 $m^3 s^{-1}$ for Tsengwen, Yenshui, Ell-ren, Chishui, Potzu, and Peikang rivers, respectively. Most of them have gradients of approximately 1:300 flowing through hills and valleys and approximately 1:2000 flowing westward through flat plain in downstream near the estuary, while the average gradients for catchments of each river are ratios of 1:118 (Chishui), 1:78 (Tsengwen), 1:3000 (Yenshui), 1:142 (Ell-ren), 1:79 (Potzu) and, 1:248 (Peikang), respectively (2nd River Management Office Water Resource Agency, Ministry of economic affairs (MOEA)) [9]. The flow length, sampling time, drainage area, number of sampling sites, total depth of each sediment core sampled, and number of divided sediment core segments for each river are shown in Table 1. The total sum of the six rivers' drainage areas is about one-eighth the area of Taiwan (as shown in Fig. 1).

2.2. Sediment core samples

Sediment cores were taken from two rivers with higher heavy metal contamination (the Ell-ren and Yenshui) and from four rivers with lesser heavy metal contamination (the Tsengwen, Chishui, Potzu, and Peikang). Sediment samples were taken from section of river which was easy to have the silt and particulate suspended solid deposition using a hand-operated sediment corer (Wildco, U.S.A.). It consisted of hollow stainless-steel core barrel (5.3 cm in inner diameter, 50 cm in height), polycarbonate core tube, core catcher, core cutter to facilitate penetration of the sediment, and core valve to allow water to pass freely. The primary sources of pollutants were located and discharged into each river near the downstream. The polluted sediment in upstream and downstream could be flushed away in the concentrated rainy season (in July and August) and deposited near the estuarine with very low flow velocity of river water. The river sediment with the larger depth and more pollutants existed were selected as the sampling sites in each river. The total number of sampling sites near the estuarine of the Yenshui, Ell-ren, Potzu, Tsengwen, Chishui, and Peikang rivers were 7, 3, 6, 7, 6, and 6, respectively. The total depths of collected sediment core varied from 25 to 39, 14 to 36, 25 to 40, 25 to 45, 17 to 46, and from 33 to 41 cm for the Yenshui, Ell-ren, Potzu, Tsengwen, Chishui, and Peikang rivers, respectively (Table 1). The work of sampling was done between March and May of 2000 before the rainy season of that year. The sedimentation of particulate solid from river water was more active in the Yenshui and Tesengwen rivers, so the number of sampling sites were chosen as 7, respectively. The distances of sampling site pointed from the estuaries mouth and total depth of each sampled sediment core were 0.5 (30), 1.0 (34), 2.0 (27), 3.0 (25), 4.0 (30), 5.0 (25), and 10.0 (39) km (cm) along the Yenshui river (Table 1). Similarly, the distances and total depth sampled of sampling site pointed from the estuarine for Tsengwen river were 0.5 (30), 3.0 (25), 4.0 (30), 6.4 (36), 7.0 (39), 9.1 (30), and 11.1 (45) km (cm). The sediment cores were held vertically in ice boxes during transportation back to the laboratory, after which they were cut into core segments. From the water-sediment interface of the sampled sediment core to a depth of 10 cm, they were cut into 2-cm core segments and, at depths >10 cm, into 5-cm core segments, using a plastic blade. The total numbers of sediment core segments collected from the Yenshui, Ell-ren, Potzu, Tsengwen, Chishui, and Peikang rivers were 58, 18, 67, 63, 58, and 64, respectively (Table 1). Each sediment core segment was then air-dried at room temperature prior to chemical analysis.

2.3. Chemical analysis

Of the geochemical components, Fe-oxides and Mn-oxides were extracted using the acid hydroxylamine method [10], analyzed by atomic absorption spectrophotometer, and expressed as

Table 1
Rivers' length, drainage area, and sampling data

Rivers	Flow length (km)	Sampling day (d/m/y)	Drainage area (km^2)	Total no. of sampling sites	Distances and total depth sampled of sampling site pointed from the estuarine for each river (km (cm))	Total no. of core segments for each river
Yenshui river	87	12/3/2000	222	7	0.5 (30), 1.0 (34), 2.0 (27), 3.0 (25), 4.0 (30), 5.0 (25), 10.0 (39)	58
Ell-ren river	65	3/5/2000	350	3	0.3 (20), 1.0 (14), 1.5 (36)	18
Potzu river	76	12/4/2000	400	6	0.3 (25), 1.6 (40), 2.9 (38), 4.2 (33), 5.5 (37), 6.4 (40)	63
Tsengwen river	138	20/4/2000	1177	7	0.5 (30), 3.0 (25), 4.0 (30), 6.4 (36), 7.0 (39), 9.1 (30), 11.1 (45)	67
Chishui river	65	10/5/2000	379	6	0.9 (17), 2.0 (36), 2.5 (43), 3.0 (36), 3.6 (46), 4.4 (38)	58
Peikang river	82	20/3/2000	645	6	1.0 (34), 2.0 (36), 2.5 (43), 3.0 (34), 3.6 (41), 4.4 (33)	64

% of Fe_2O_3 or MnO_2. Determination of organic matter content (%) was made by oxidation with an excess of potassium dichromate and back titration with a standardized solution of ferrous sulfate, using the Walkley–Black method [11] and converted to a % figure [12], while carbonate content (%) was determined using the quantitative gravimetric method (U.S. department of agriculture soil conservation service)[13]. For heavy metal extraction, 0.2–0.5 g of air-dried sediment was taken from each sediment segment and added to a fluorocarbon polymer vessel with 3 mL of nitric acid (65%) and 9 mL of hydrochloric acid (37%) [14]. Digestion was then performed using the Milestone MLS 1200 programmed microwave system: the temperature of the strong acid-sediment mixture in the vessel was brought to $170 \pm 5^{\circ}$ in 10 min and maintained at this temperature for 20 min.

2.4. Accuracy and precision of analysis

For each extractable heavy metal (Co, Cr, Cu, Zn, Ni, Pb, Mn, and Fe), triplicate analysis of the samples was performed on a flame atomic absorption spectrophotometer (GBC, AA960, Australia), and Cd concentration on a graphite atomic absorption spectrophotometer (GBC, AA960, Australia). The detection limit for the analysis of metals was Co: 0.031 mg/L; Cr: 0.031 mg/L, Cu: 0.005 mg/L, Zn: 005 mg/L, Ni: 0.057 mg/L, Pb: 0.21 mg/L, Mn: 0.065 mg/L, Fe: 2.59 mg/L; and Cd: 0.00018 mg/L. The accuracy and precision of the AAS analysis were checked by testing repeatedly the certified river sediment reference material (BCR 320) from Community Bureau of Reference, European Commission, the recoveries were 88.2% for Co, 117.5% for Cr, 90.5% for Cu, 94.7% for Zn, 95.1% for Ni, 91.0% for Pb, 89.3% for Mn, 101.1% for Fe, and 83.6% for Cd. The coefficients of variation were for Co: 4.2%, for Cr: 3.0%, for Cu: 4.8%, for Zn: 13.5%, for Ni: 5.4%, for Pb: 9.0%, for Mn: 6.2%, for Fe: 2.4%, and for Cd: 22.7%.

3. Results and discussion

3.1. Vertical distribution of metals in sediments

Table 2 shows the distribution of heavy metals in different depths of river-bed sediment cores sampled from the six rivers. The maximum concentrations of Cu, Cr, Zn, Ni, and Co were found in the Yenshui River sediment, and were 1953, 1521, 1932, 885, and 191 mg/kg, respectively. The maximum Pb concentration, 588 mg/kg, was found in the Ell-ren River. These findings are consistent with the serious metals pollution history of these rivers connected with the industrial and agricultural activities of the last decade. According to the river water quality, quarterly monitoring results of the six main rivers, which includes 29 monitoring stations, the chronological accumulation of heavy metals (Cu, Cd, Pb, Cr, and Zn) pollution in each river sediment with depth should be associated with the historical heavy metals loads in river water quality data analyzed and collected from 1979 to 2005 as shown in Fig. 2 (data from Environmental Protection Administration of Taiwan [15]). The trend of Zn concentration variation in river water quality matched with the developed his-

Table 2
Summary statistics for each aqua-regia extractable heavy metal content in different sampling depth of sediment collected from six main rivers

Rivers	Sediment cores number in each river		Heavy metals in different depth of river sediment								
			Cu (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Co (mg/kg)	Mn (mg/kg)	Fe (%)	Cd (mg/kg)
Yenshui	58	Mean	184.7	189.4	248.3	102.2	31.2	33.1	233.7	2.4	0.26
		Minimum	5.2	10.3	34.5	10.3	8.6	7.5	104.0	1.3	N.D.
		Maximum	1953.0	1521.6	1932.0	885.6	111.8	191.7	862.3	9.6	3.57
		Standard deviation	305.2	266.7	313.7	143.8	23.2	37.4	114.3	1.2	0.57
		C.V.	*1.7*	*1.4*	*1.3*	*1.4*	*0.7*	*1.1*	*0.5*	*0.5*	***2.14***
Ell-ren	18	Mean	230.8	68.2	264.1	49.4	92.0	36.2	336.3	2.9	0.49
		Minimum	22.7	19.5	76.8	5.6	28.4	10.5	165.0	2.4	0.05
		Maximum	1487.2	318.7	1499.0	268.0	588.6	183.6	468.2	3.7	3.07
		Standard deviation	377.3	75.8	342.4	58.5	129.7	52.0	85.8	0.4	0.78
		C.V.	*1.6*	*1.1*	*1.3*	*1.2*	*1.4*	*1.4*	*0.3*	*0.1*	***1.59***
Tsengwen	67	Mean	14.5	24.7	74.0	26.5	29.3	18.9	508.9	3.2	0.07
		Minimum	5.4	13.6	43.1	12.8	9.2	9.4	224.1	1.8	N.D.
		Maximum	21.3	39.8	98.2	39.2	49.1	30.8	1180.3	4.4	0.16
		Standard deviation	4.0	5.3	15.2	6.3	9.0	4.3	199.4	0.7	0.04
		C.V.	*0.3*	*0.2*	*0.2*	*0.2*	*0.3*	*0.2*	*0.4*	*0.2*	***0.56***
Potzu	63	Mean	21.0	34.9	150.4	29.9	33.4	18.8	352.8	3.2	0.20
		Minimum	9.4	20.5	68.8	18.7	19.2	12.7	238.2	2.1	0.01
		Maximum	43.8	61.9	597.1	51.0	47.2	35.1	464.2	4.4	3.29
		Standard deviation	6.6	8.9	82.9	5.8	6.1	4.1	60.5	0.6	0.54
		C.V.	*0.3*	*0.3*	*0.6*	*0.2*	*0.2*	*0.2*	*0.2*	*0.2*	***2.64***
Chishui	58	Mean	16.0	22.6	76.7	21.8	27.2	16.7	335.1	2.9	0.10
		Minimum	6.2	2.1	47.8	10.2	11.2	9.2	232.8	2.1	N.D.
		Maximum	31.9	36.3	128.9	33.0	56.3	25.5	472.5	4.4	0.30
		Standard deviation	5.9	6.4	19.4	5.6	9.2	3.1	51.4	0.5	0.07
		C.V.	*0.4*	*0.3*	*0.3*	*0.3*	*0.3*	*0.2*	*0.2*	*0.2*	***0.67***
Peikang	64	Mean	19.9	22.2	99.6	24.8	31.1	17.9	377.2	3.2	0.09
		Minimum	8.6	12.0	60.0	8.5	10.9	5.9	231.8	2.1	N.D.
		Maximum	29.5	31.6	187.6	38.9	50.7	27.9	519.0	4.0	0.22
		Standard deviation	4.5	3.8	30.6	5.4	8.8	4.2	68.7	0.4	0.04
		C.V.	*0.2*	*0.2*	*0.3*	*0.2*	*0.3*	*0.2*	*0.2*	*0.1*	***0.44***

Note: N.D., Concentrations below the detection limits of the instrument; Bold values are the most significant C.V. (coefficient of variation) between metals in each river; Italic values denote the C.V. of each metal at river sediment with different depth.

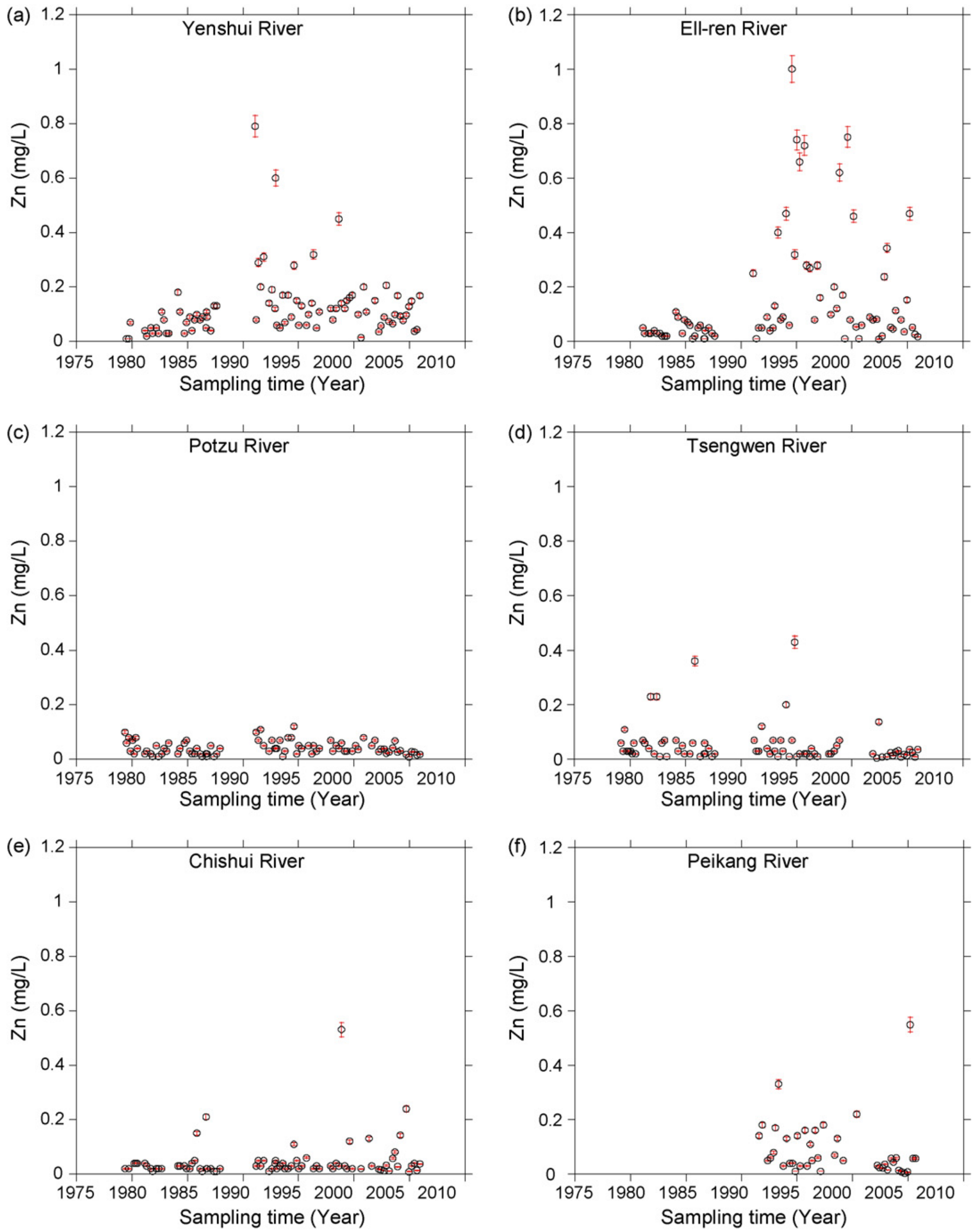

Fig. 2. Variation of Zn obtained from river water monitoring station near the sediment sampling sites of each river (data from EPA [15]).

tory of industrial activities and the gradually strict waste water discharge standard in Taiwan. The primary Zn loads in six river water quality were found in about 1995. The catchments of the Ell-ren and Yenshui rivers contain domestic and industrial plants which discharge large amounts of wastewater contaminated with high concentrations of organic matter which can be proved with the variation of chemical oxygen demand (COD) value obtained from the river water monitoring data ranging from 1976 to 2006 (Fig. 3a and b). The most serious pollution years expressed as COD was found in about 1977 and 1996. On the other hand, the major pollutant loads in the Potzu, Chishui, and Peikang rivers are from domestic and agricultural activities and founded in about 1990 (Fig. 3c, e, and f). These pollutant loads include low concentrations of heavy metals and moderate concentrations of organic matter. The accumulation and storage of heavy metals in the clay, clay-silt and silt size particles deposited in flat river-bed and also is environmental pollution evidence. However, the sediment cores from the Tsengwen, Chishui, Potzu, and Peikang rivers were only slightly polluted with heavy metals. The maximum concentrations of Cu, Cr, Ni, Pb, and Co for these rivers were all below 62 mg/kg, although Zn concentration was 597 mg/kg in sediment from the Potzu river (Table 2). These results are related to the developing history of agricultural activities in the Tsengwen, Chishui, Potzu, and Peikang catch-

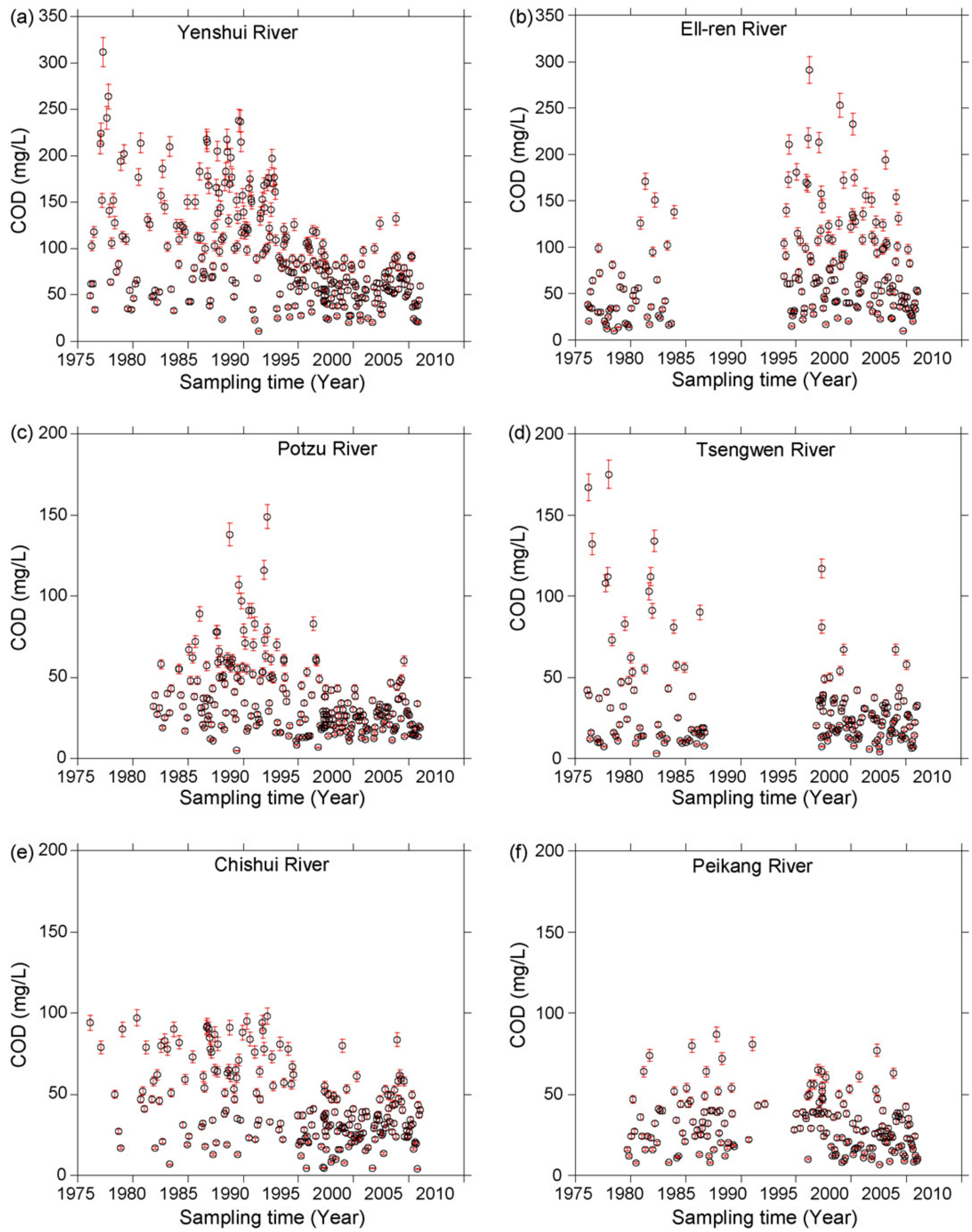

Fig. 3. Variation of chemical oxygen demand (COD) value obtained from river water monitoring station near the sediment sampling sites of each river (data from EPA [15]).

ments. The change in metal concentration with sediment depth was not regular. The variation of metal pollution in sediment of each river was expressed as a coefficient of variation (C.V.), and is shown in Table 2. The C.V. was defined as the standard deviation of the metals divided by the mean concentration in the core segments of each river. The C.V. value can be used to express the distribution of metals in vertical profile of sediment which varied with the metal concentration in river water discharged from domestic, industrial and agricultural activities in the past at river catchments. The higher C.V. value for Cu found in the Yenshui and Ell-ren rivers meant the higher variation of Cu concentration in vertical profile of sediment cores which were accumulated from the river water pollutant with different level of Cu concentration. The largest C.V. values for Cu, Cr, Zn, Ni, Pb, Co, Mn, and Fe were 1.65, 1.41, 1.30, 1.41, 1.41, 1.44, 0.49, and 0.5, respectively. These came from the seriously polluted sediment of the Yenshui or Ell-ren rivers and matched with the river water pollution history. However, in the remaining only slightly polluted river sediment, the C.V. of Cu, Cr, Ni, Pb, and Co mostly ranged from 0.28 to 0.17. The largest C.V., for Cd, was 2.64, from the Potzu river. There were 58, 18, 67, 63, 58, and 64 sediment segments in each river, and nine heavy metals concentration analyzed from each segment. It is difficult to express the heavy metal concentration distribution with depth in so many data using the enrichment factors and geo-accumulation indices. The C.V. value of each metal was tried to simplify the variation of heavy metal concentration which deposited from the river water every year in this study.

3.2. Cadmium distribution in river sediments

The variation of Cd concentration with sediment depth and distance pointed from the estuarine mouth of the river is shown in Fig. 4 For rivers with low levels of Cd pollution, the distribution pattern of Cd in the vertical concentration profile for each river was not regular and did not have good association with the distance pointed from the estuarine mouth (Fig. 4d, e, and f). The lowest concentration of Cd was found in the deepest sediment segment and was considered to be the background concentration of Cd in each river's sediment which was eroded from the native rock in the upstream. The highest concentrations of Cd were 3.57, 3.07, and 3.29 mg/kg, found at a sediment depth of 0–10 cm in the Yenshui, Ell-ren, and Potzu rivers, respectively (Fig. 4a, b, and c). This result indicates that Cd sourced from anthropogenic pollutant and that was discharged into the rivers in recent decades. The concentration of Cd in river sediments decreased gradually from the sediment-water interface to the deeper sediment, significantly in the Yenshui and Ell-ren river (Fig. 4a and b). This trend for Cd concentration variation with depth was similar to the variation format of COD and Zn^{2+} of river water quality sampled annually. The Cd concentration variation trend with sediment depth have similar pattern in Odiel

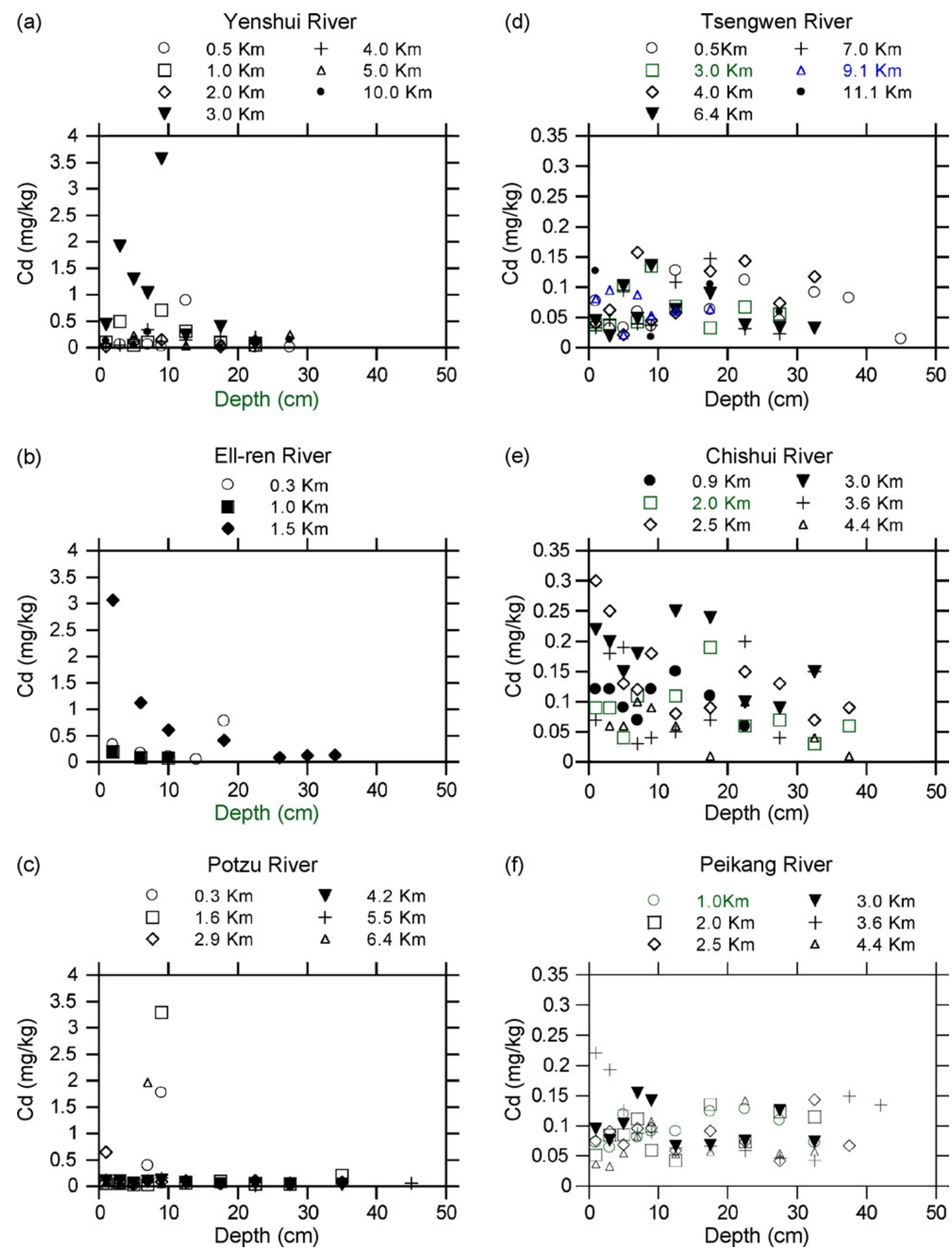

Fig. 4. Cadmium distribution in sediment core profiles at different distances from the estuarine mouth. (a) Yenshui, (b) Ell-ren, (c) Potzu, (d) Tsengwen, (e) Chishui, and (f) Peikang rivers.

river at southern Spain [16]. The Cd concentration in six main rivers sediment of Taiwan is very low if compared with the total mean Cd concentration of the whole Amazonian Guajará Estuary sediment samples (469 ± 164 mg/kg) [4]. But the purpose of this research was focused on the correlation and variation of Cd affected by other most seriously polluted heavy metals in river sediment of Taiwan.

In both high and low Cd-polluted rivers, the Cd concentration distribution in sediment was not associated with distance of sampling site pointed from the estuarine mouth (Fig. 4). Because Cd exists in lower concentrations than the other metals in sediment, and primarily exists in exchangeable and carbonate phases [17], Cd ions contained in discharged wastewater are absorbed into the sediment immediately, where discharged, and cannot transport long distances downstream. In the Yenshui river, for example, the highest Cd concentration, found 3.0 km from the estuarine mouth, is due to Cd ion discharge into the river near this sampling site. The same is true for Cd in the Ell-ren and Potzu rivers (Fig. 4a, b, and c). Because the concentration variation of Cd was similar for all sampling sites in the Tsengwen, Chishui, and Peikang, the Cd contamination can be assumed to be discharged from non-point sources.

3.3. Correlation of Cd with metals and geochemical components

The amount of heavy metals bound to sediment matrices is associated with the geochemical components of the sediment [17–20]. The contents of geochemical components in sediment matrices of the six rivers are shown in Table 3. The largest mean concentration of carbonates (8.81%) was found at the Ell-ren river. The largest concentrations of organic matter (3.80%) and Fe-oxides (3.33%) were found at the Yenshui and Ell-ren rivers. As for heavy metals, the degree of variation in geochemical components in each river between unpolluted age and pollution with human activity was expressed as C.V. values (as shown in Table 3). The carbonates, Mn-oxides, Fe-oxides and organic matters came from river water and deposited with pollutants like heavy metals and organics. The higher the C.V. value were, the larger variation of geochemical components existed in different depth of sediment matrices, indicating different pollution level happened in this river catchments at the past. There were high pollution industries, like metal surface processing, electrical-plating finishing, and dyeing manufacture, located in the Yenshui river catchments from 1978. The most significant variations in

Table 3
Summary statistics for each geochemical component in sediment matrices with different depth at six rivers

Rivers	Sediment cores number in each river		Geochemical components			
			Carbonates (%)	Mn-oxides (mg/kg)	Fe-oxides (%)	Organic Matter (%)
Yenshui river	58	Mean	2.19	251	0.86	1.39
		Minimum	0.54	97	0.46	0.53
		Maximum	9.18	529	2.01	3.80
		Standard deviation	1.43	112	0.43	0.93
		C.V.	**0.65**	**0.45**	**0.50**	**0.67**
Ell-ren river	18	Mean	8.81	415	2.73	1.57
		Minimum	5.69	229	1.99	0.93
		Maximum	11.83	750	3.33	2.75
		Standard deviation	1.97	101	0.32	0.48
		C.V.	**0.22**	**0.26**	**0.12**	**0.31**
Tsengwen river	67	Mean	4.62	722	0.72	1.04
		Minimum	2.58	328	0.35	0.50
		Maximum	7.49	1964	1.07	1.78
		Standard deviation	1.13	309	0.17	0.37
		C.V.	**0.24**	**0.43**	**0.24**	**0.36**
Potzu river	63	Mean	2.91	436	0.76	1.57
		Minimum	1.04	288	0.53	0.72
		Maximum	5.46	653	0.98	2.66
		Standard deviation	1.04	81	0.12	0.49
		C.V.	**0.36**	**0.19**	**0.15**	**0.31**
Chishui river	58	Mean	3.65	423	0.75	1.33
		Minimum	1.69	286	0.11	0.54
		Maximum	6.19	656	1.12	2.63
		Standard deviation	1.03	72	0.16	0.49
		C.V.	**0.28**	**0.17**	**0.22**	**0.37**
Peikang river	64	Mean	2.19	508	0.90	1.20
		Minimum	1.21	301	0.61	0.50
		Maximum	6.01	815	1.32	1.79
		Standard deviation	0.95	112	0.15	0.30
		C.V.	**0.43**	**0.22**	**0.17**	**0.25**

Note: Bold values predominantly denote C.V. for each geochemical component at each river sediment matrice.

Table 4
Linear correlation coefficients between cadmium and geochemical components and between cadmium and other metals in sediment

	Aqua-regia extractable cadmium					
	Yenshui river	Ell-ren river	Tsengwen river	Potzu river	Chishui river	Peikang river
Depth	−0.04	−0.35	−0.02	−0.29	−0.11	−0.08
Geochemical components						
Organic matter	0.28	−0.49	0.02	−0.17	−0.11	−0.14
Carbonates	0.44	0.85	0.05	0.63	−0.17	0.38
Fe-oxides	0.43	0.22	0.13	0.19	−0.10	0.28
Mn-oxides	0.30	0.20	0.00	0.34	−0.12	0.30
Aqua-regia extractable metals						
Fe	0.38	−0.45	0.10	0.52	−0.10	0.47
Mn	0.36	−0.68	0.03	0.47	−0.08	0.36
Cr	0.45	0.97	0.10	0.54	0.01	0.50
Co	0.35	−0.22	−0.04	0.28	−0.14	0.41
Ni	0.40	0.98	0.16	0.25	−0.09	0.12
Cu	0.44	0.95	0.10	0.64	−0.12	0.54
Zn	0.45	0.83	0.10	0.65	−0.04	0.46
Pb	0.43	0.46	0.09	0.34	0.37	0.39

carbonates, Mn-oxides, Fe-oxides and OM were found at the Yenshui river, with C.V.'s of 0.65, 0.45, 0.50, and 0.67, respectively.

The linear correlation coefficients between Cd and geochemical components and between Cd and the other metals in sediment from the six rivers are shown in Table 4. Extractable Cd did not show significant linear correlation with depth of sediment segment, as also shown in the results of Fig. 4. There was significant linear correlation ($r = 0.85$) between Cd and carbonates in sediment from Ell-ren river. This is because Cd is primarily bound to carbonates and exchangeable fractions [21], and because higher concentrations of Cd and carbonates existed in this river sediment than in that from the other rivers. Although the linear correlation coefficient between Cd and carbonates was less significant in other rivers, similar trends were identified in sediments from Potzu and Yenshui rivers, with $r = 0.63$ and 0.44, respectively, and those were larger than coefficients between Cd and other geochemical components in all rivers' sediment. There were no significant linear correlations between Cd and geochemical components of OM, Fe-oxides and Mn-oxides, because the amount of Cd bound to OM, Fe-oxides and Mn-oxides is less than that bound to carbonates [21]. Significant linear correlation coefficients existed between Cd and Cr, Ni, Cu, Zn, and Pb in the Ell-ren river (0.97, 0.98, 0.95, 0.83, and 0.46, respectively), indicating that these metals were discharged from the same pollution sources. However, in the Ell-ren river the coefficients between Cd and Fe, Mn, and Co were not significant. This is because Cd is an anthropogenic pollutant, while Fe, Mn, and Co primarily came from the native rock. The linear correlation coefficients between Cd and other metals ranged from 0.35 to 0.65 in the Yenshui, Peikang, and Potzu rivers, indicating that some of the Cd did not come from the same source as other metals. The similar coefficients found at the Chishui and Tsengwen were near zero, indicating that the sources of Cd were different from the other metals and with low concentration of loads in those river catchments.

4. Conclusions

Although the Cd pollution is not as serious as the other heavy metals in six main rivers sediment of southern Taiwan, the toxicity of Cd is larger than other heavy metals discussed. The fate and distribution of Cd in water environmental and biological system also should be concerned to realize the river water pollution history in Taiwan's industrial development. Variations of heavy metals concentration in the vertical profiles of sediment samples taken at different distances from the estuarine mouth of the six rivers were non-regular and caused from different pollutant sources. The C.V. value for each metal and geochemical component is a good proxy, instead of enrichment factors and geo-accumulation indices, to simply express the variation of metal pollution and geochemical component concentration in the sediment profiles at different depths and distances from the estuarine mouth for so many data collected. Of the geochemical components, Cd had the most significant linear correlation with carbonates ($r = 0.85$) in the Ell-ren river sediment. The Ell-ren river sediment was most seriously polluted with Cd and other metals. There were no significant linear correlations between Cd and organic matter, Fe-oxides, or Mn-oxides. The linear correlation coefficient between Cd and other metals can be used as an indicator to express the degree of similarity of pollutant source.

Acknowledgement

Financial support (research grant: NSC 90-2211-E-041-011) from the National Science Council of the Republic of China is greatly appreciated.

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