CORRELATIONS AMONG AQUA-REGIA EXTRACTABLE HEAVY METALS IN VERTICAL RIVER SEDIMENTS

Ho S.T.[1], *Tsai L. J.[2], Yu K.C.[2],

[1]*Department of Industrial Safety and Hygiene, Chia-Nan University of Pharmacy and Science, Tainan 717, Taiwan, ROC*
[2]*Department of Environmental Engineering and Health, Chia-Nan University of Pharmacy and Science, Taiwan 717, Taiwan, ROC*

ABSTRACT
The historic anthropogenic heavy metals pollution in river water can be recorded by concentration of heavy metals in different depth of the river sediment core. Sediment cores collected from six rivers (the Ell-ren, Yenshui, Tsengwen, Chishui, Potzu, and Peikang), located in southern Taiwan were used to realize the spatial distribution of aqua-regia extractable heavy metals with sediment depth, and to assess the correlations among heavy metals. Sediments were sampled and analyzed from six rivers to compare the linear correlation coefficients and spatial distribution of metals in sediment with the effects of high or low anthropogenic heavy-metal pollution levels. Concentrations of trace heavy metals (Cu, Cr, Zn, Ni, Pb, Co), Mn, and Fe from 369 sediment segments were extracted with aqua-regia strong acid solution and determined by atomic absorption spectrometer. Results show that concentrations of trace heavy metals in sediments of the Ell-ren and Yenshui Rivers showed spatially large variation, indicating that significant anthropogenic heavy metals pollution had happened in recent years. However, the concentrations of trace heavy metals in sediments from the other four rivers showed non-significant spatial variation and reflected low level of anthropogenic heavy-metal pollution.
From the statistic analysis of correlation matrix, more significant correlation coefficients among trace heavy metal (Cu, Cr, Zn, Ni, and Pb) were found larger (0.83) in highly contaminated river sediments than those in low contaminated river sediments, indicating that the trace heavy metals in highly polluted rivers come from the same pollution sources. The higher the correlation coefficients existed, the higher the same predominant anthropogenic sources were. Whether in high or low pollution level of river sediment, the spatial distribution of heavy metal contaminants did not have linear correlation with sediment depth (the linear correlation coefficients near zero), indicating that the strong variation of pollution strength, eddy flow, and sediment mobility existed in the river system. In Ell-ren River sediment, the correlation coefficients among Fe, Mn, Co and trace heavy metals (Cu, Cr, Zn, Ni, and Pb) were not significant, and were different from those obtained from the other five rivers. It means that the concentration variation of Co Mn, and Fe in sediment of the Ell-ren River was the least, when compared with the other heavy metals. It means that anthropogenic pollution of Co, Fe and Mn in the Ell-ren River sediment was not as significant as the other metals had.

KEYWORDS: Correlation coefficients, Correlation matrix, Heavy metals, River sediment.

INTRODUCTION
Heavy metals are anthropogenic pollutants discharged from industrial, domestic and agricultural wastewater into the river water system (Guo et al., 1997; Ho et al., 2001). Sediment served as sinks for most of the metals in aqueous phase (Klavins, et al., 1995). Monitoring of the sediment with the determination of heavy metals is fundamental to the realization of toxic pollutants in the river sediment (Hlavay, et al., 1998). The variation of metals concentration with depth of sediment can be used as the historical of metals pollution (Ryssen, et al., 1999). The metals existing in some depth can be thought as coming from the same sources. In this study, the sediment cores sampled from two high heavy-metals contaminated rivers (the Ell-ren and Yenshui Rivers) and from four low heavy-metals contaminated rivers (the Tsengwen, Chishui, Potzu, and Peikang Rivers) were analyzed to explore the correlations of heavy metals (Cr, Co, Ni, Cu, Zn, Pb, Mn, and Fe) existing in different sediment with depth, and to realize the variation of metal concentration about sediment depth.

MATERIAL AND METHODS
Study areas and samples preparation
The six main rivers (the Ell-Ren, Yenshui, Tsengwen, Chishui, Potzu, and Peikang Rivers) flow through the largest plain area of southern Taiwan. The catchments of the Ell-Ren and Yenshui Rivers have many industrial plants which discharge large amount of wastewater contaminated with high concentration of heavy metals and organic matters. The major pollutions in the catchments of the other four rivers were due to domestic and agricultural activities. The catchments of the six rivers are highly developed area in southern Taiwan (Table 1).
The sediment cores sampled by hand-operated sediment corer (Wildco, U.S.A.) was cut downwards from the water-sediment interface (by plastic blades) to divide the cores into several 2-cm (between 0-10 cm depth of sediment core) and 5-cm (deeper under 10 cm depth of sediment core) segments.

Table 1. Description of catchments and sampling sites for six main rivers in southern Taiwan

Rivers	Flow Length km	Drainage Area km^2	Sampling Sites	No of* Segments
The Ell-Ren River	64.25	350.4	3	18
The Yenshui River	87.34	221.7	7	58
The Tsengwen River	138.47	1176.6	7	67
The Chishui River	65.12	378.8	6	58
The Potzu River	75.67	400.4	6	63
The Peikang River	82.25	645.2	6	64

- *Each sediment core was sliced into several segments with 2 cm length in 0-10 cm vertical depth*
- *and with 5 cm length in sediment core deeper than 10 cm.*

Chemical analysis

The concentrations of aqua regia extractable heavy metals were released by 3 mL of nitric acid (65%) and 6 mL of hydrochloric acid (37%) (Breder, 1982). The concentrations of each extractable heavy metal (Co, Cr, Cu, Zn, Ni, Pb, Mn, and Fe) were measured by flame atomic absorption spectrophotometer (GBC, AA960, Australia). Sum of aqua-regia extractable heavy metals (Cr, Co, Ni, Cu, Zn and Pb) in sediment is defined as total heavy metal (THM).

RESULTS AND DISCUSSIONS

Variation of aqua-regia extractable heavy metals in sediment profiles

The ranges of heavy metals concentration in seriously polluted sediment of the Ell-ren and Yenshui rivers were (Cu 1953 – 5 mg/kg; Cr 1521 – 10 mg/kg; Zn 1932 – 34 mg/kg; Ni 885 – 10 mg/kg; Pb 581 – 18 mg/kg; Co 191 – 8 mg/kg) (Figures 1a-1f). The variation between aqua-regia extractable heavy metals concentration and depth in the Ell-ren and Yenshui rivers sediment was more significant than the other four rivers (Tsengwen, Chishui, Potzu, and Peikang Rivers). The concentration of heavy metals (Cu, Cr, Zn, Ni, Pb, and Co) decreased with increasing of sediment depth of the Ell-ren River. The correlation between heavy metals (Cu, Cr, Zn, Ni, Pb, and Co) concentration and sediment depth of the Yenshui River was similar, except the highest concentration at 5 cm below water sediment interface. It means that the most serious heavy metal pollution happened in recent years. The concentrations of trace heavy metals in sediments from the other four rivers (which were not seriously polluted by heavy metals) showed non-significant spatial variation and reflected low level of anthropogenic heavy-metal pollution. Those were (Cu 33 – 10 mg/kg; Cr 145 – 15 mg/kg; Zn 298 – 69 mg/kg; Ni 39 – 17 mg/kg; Pb 49 – 11 mg/kg; Co 27 – 9 mg/kg), as shown in Figures 1a-1f. The concentration of Mn and Fe increased with the increasing of sediment depth in the Ell-ren River (Figures 1g, 1h). In figure 1g-1h, the variation of Mn and Fe concentrations was not significant with sediment depth of the four rivers (Tsengwen, Chishui, Potzu, and Peikang Rivers).

Correlation of heavy metals in the seriously polluted rivers

The linear correlations among aqua-regia extractable heavy metals from seriously heavy-metal polluted sediments of the Ell-ren and Yenshui Rivers were shown at Table 1a-1b. The linear correlation coefficients between Ni, Cr, Cu, Pb, and Zn were larger than 0.81 (mostly larger than 0.95), indicating that those metals were binding to the sediment in the same period. The linear correlation coefficients between Fe and Mn as well as trace metals (Ni, Cr, Cu, Co, Pb, and Zn) were larger than 0.60 (mostly larger than 0.80), indicating that the Fe and Mn oxides binding phase was the primary trace heavy metals fractions and discharged from the same pollution source in the Yenshui Rivers. However, this phenomenon did not found in the sediment of the Ell-ren River. It means that Fe, Mn, and Co were not the metal pollutant from the discharge of wastewater. This result coincided with the higher concentrations of Fe, Co, and Mn found at sediment of the Yenshui River (Figures 1f, 1g, 1h).

Correlation of heavy metals in the middle polluted rivers

From Table 1c-1f, the correlation matrix of aqua-regia extractable heavy metals from sediments of middle polluted river sediment (the Tsengwen, Chishui, Potzu, and Peikang Rivers) was found. The correlation coefficients among metals (Fe and Mn) and trace heavy metals (Cu, Cr, Ni, Pb, Zn, and Co) mostly ranged between 0.56-0.91, except the correlation coefficient between Co and the other metals. The concentrations of heavy metals were in small degree larger than the background metal concentration in this four river sediment. It means that Fe Mn, and trace metals could be thought as coming from the same sources, e.g. the agricultural and domestic water. Co is also used in those catchments scarcely.

CONCLUSION

The depth of sediment can be used as the record of heavy metals pollution of water in this catchment. The concentration of metals decreased with the increasing of sediment depth in seriously heavy metal polluted rivers. The concentration of metals varied irregular with depth in middle metals pollution river. More significant correlation coefficients among trace heavy metals (Cu, Cr, Zn, Ni, and Pb) were found larger (0.83) in highly contaminated river sediments than those in low contaminated river sediments, indicating that the trace heavy metals in highly polluted rivers coming from the same pollution sources.

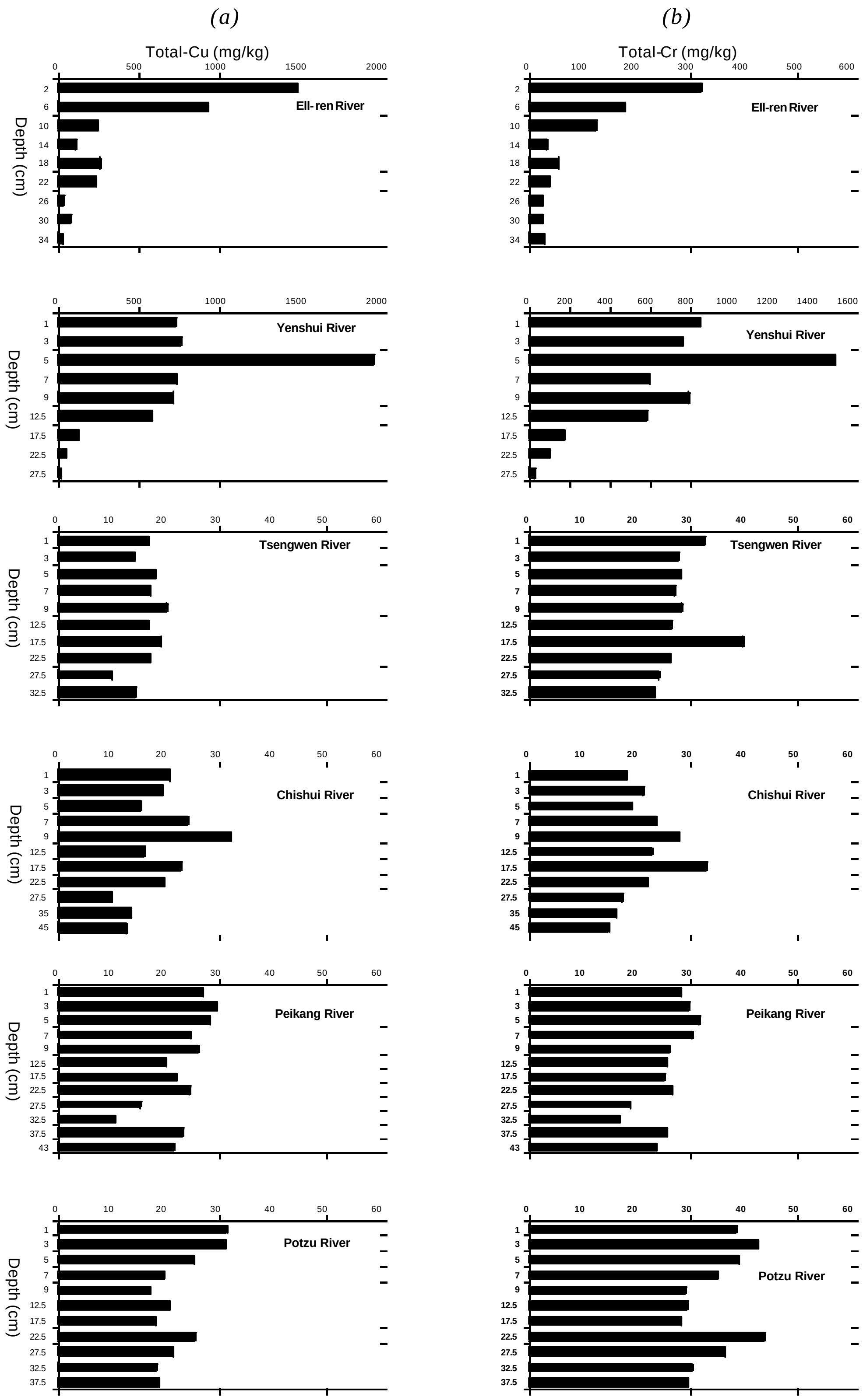

Fig. 1 *Spatial distribution of heavy metals at most seriously contaminated site for each river in southern Taiwan. (a) Cu; (b) Cr; (c) Zn; (d) Ni; (e) Pb; (f) Co; (g) Mn; and (h) Fe.*

(c) *(d)*

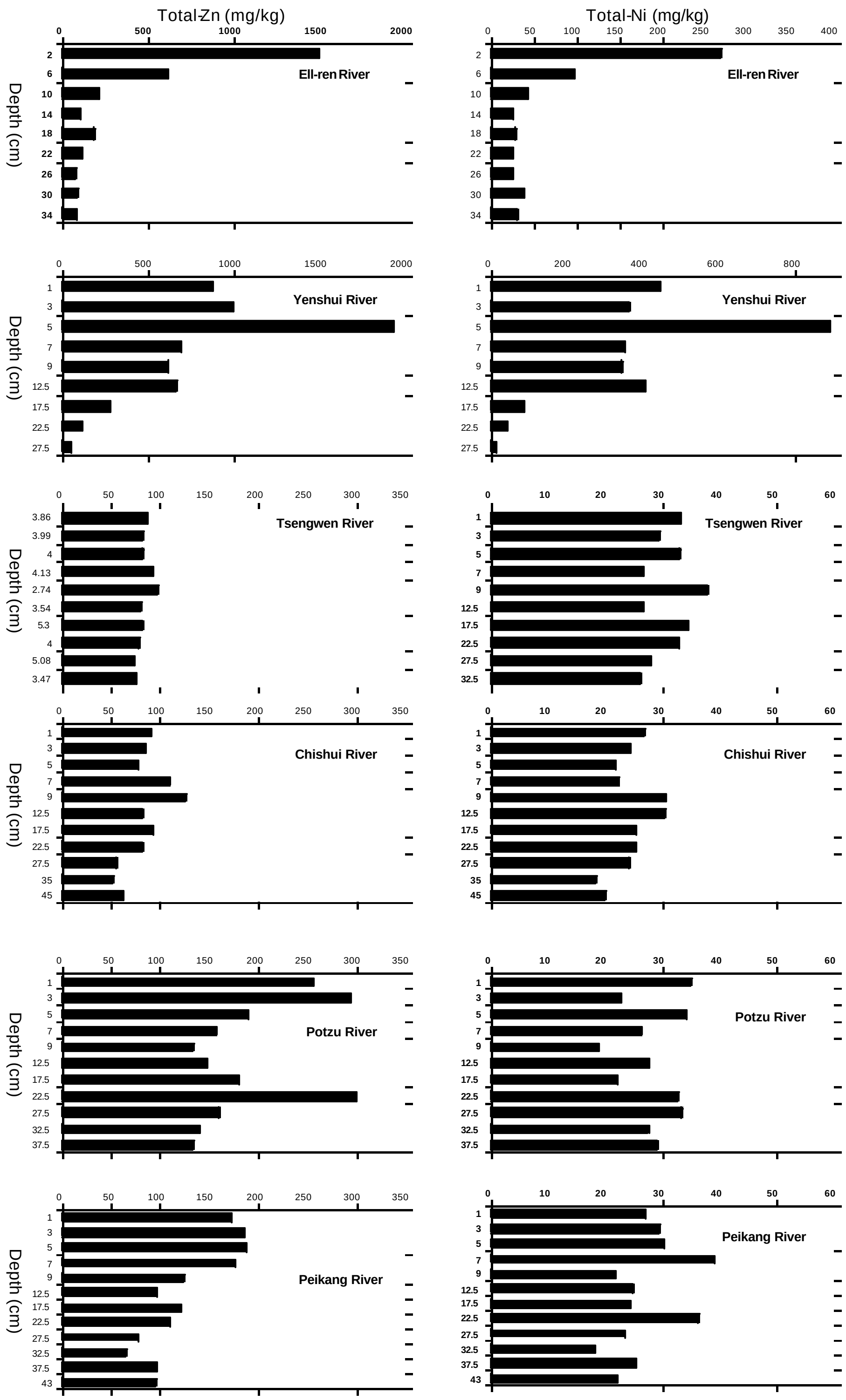

Fig. 1 *Continued. (c) Zn; (d) Ni*

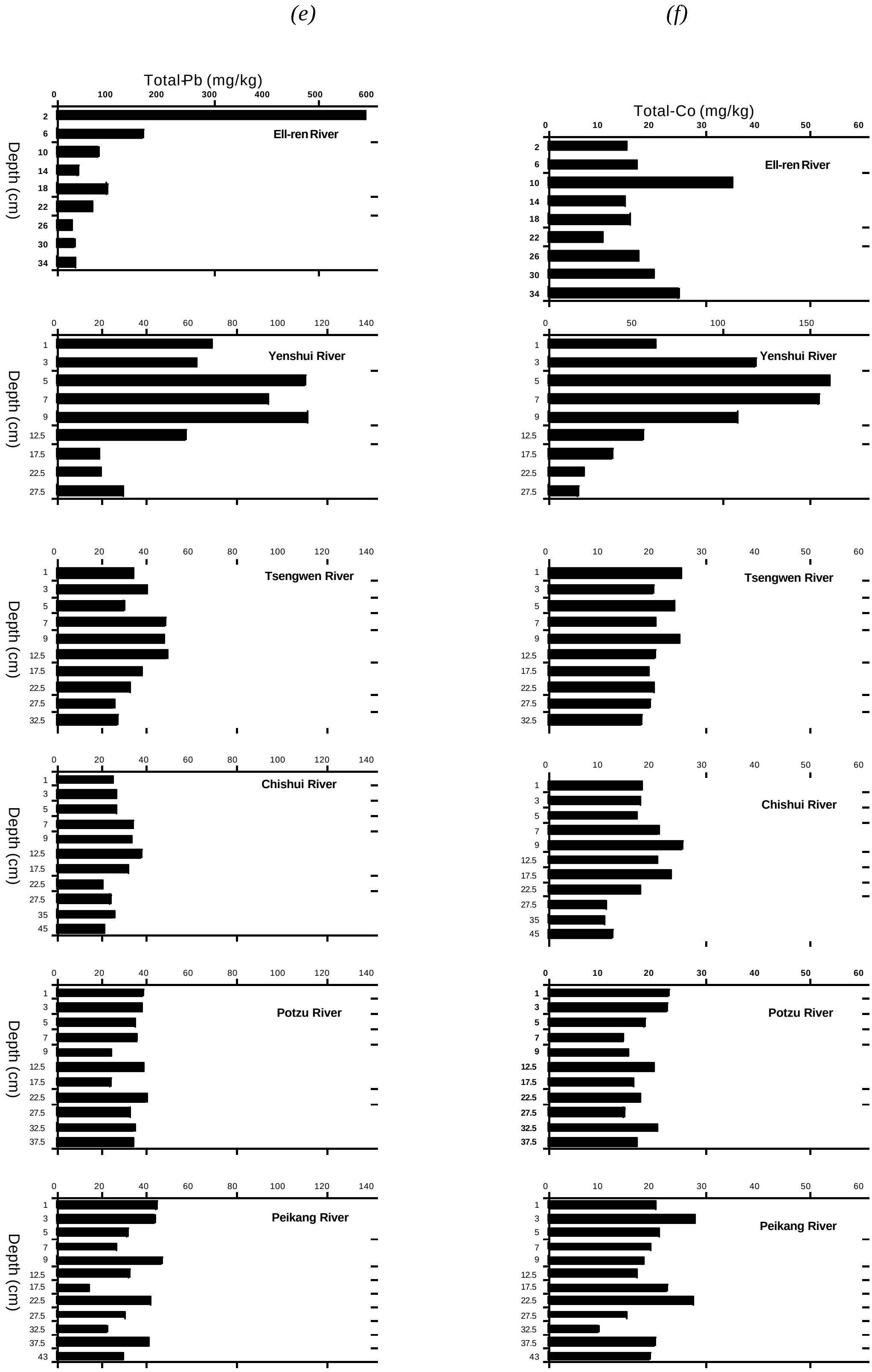

Fig. 1 *Continued. (e) Pb; (f) Co.*

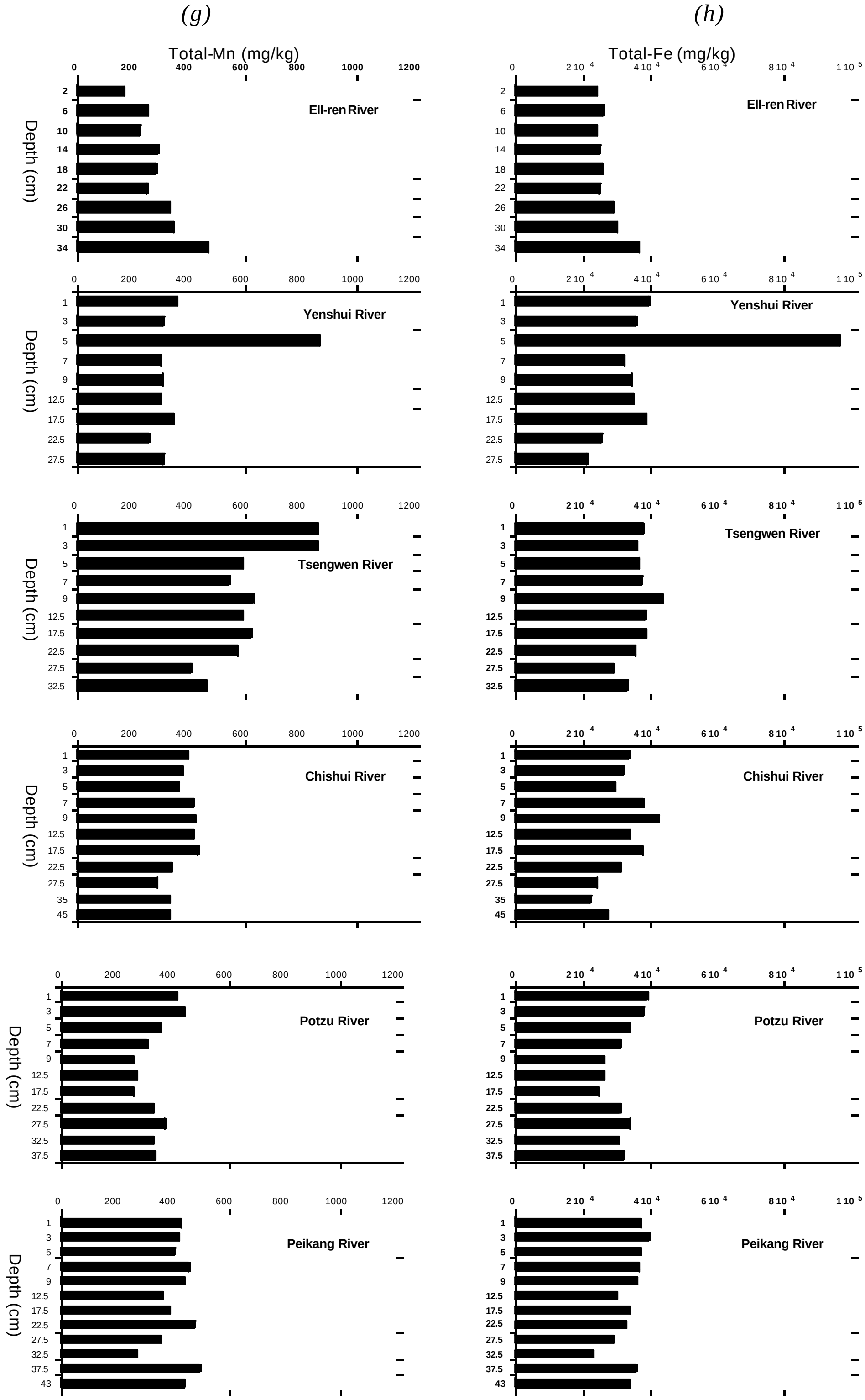

Fig. 1 *Continued. (g) Mn; (h) Fe*

REFERENCES

Breder R. Optimization studies for reliable trace metal analysis in sediments by atomic absorption spectrometric methods. Fresenius' Z. Anal. Chem., 313, 395-402.

Guo, T., Delaune R.D., Patrick, Jr. W.H. (1997). The influence if sediment redox chemistry on chemically active forms of arsenic, cadmium, chromium, and zinc in the estuarine sediment. Environmental International, 23(3), 305-316.

Hlavay, J., Polyak, P. (1998). Chemical speciation of elements in sediment samples collected at lake Baiaton. Microchemical J., 58, 281-290.

Ho, K.C., Hui, K.C.C. (2001). Chemical contamination of the east river (Dongjiang) and its implication on sustainable development in the Pear River delta. Environmental International, 26, 303-308.

Klavins, M., Briede, A., Klavins, I., Rodinov, V. (1995). Metals in sediment of lakes in Latvia. Environmental International, 21(4), 451-458.

Ryssen, R.; Leermarkers, M., Baeyens, W. (1999). The mobilization potential of trace metals in aquatic sediments as a tool for sediment quality classification. Environmental Science & Policy, 2, 75-86.

Table 1 Correlation matrix of aqua-regia extractable heavy metals from sediments of six rivers in southern Taiwan. (a) the Ell-Ren River, (b) the Yenshui River, (c) the Tsengwen River, (d) the Chishui River, (e) the Potzu River, and (f) the Peikang River. THM is the sum of aqua-regia extractable heavy metals from sediment (Cr, Co, Ni, Cu, Zn and Pb).

	Fe	Mn	Cr	Co	Ni	Cu	Zn	Pb	THM
(a)	*Ell-Ren R.*	*n=58*							
Depth	0.33	0.34	-0.40	0.09	-0.37	-0.38	-0.40	-0.35	-0.39
Fe		0.82	-0.35	-0.03	-0.25	-0.46	-0.28	-0.34	-0.37
Mn			-0.60	0.12	-0.51	-0.68	-0.52	-0.56	-0.60
Cr				-0.22	0.94	0.95	0.96	0.93	0.97
Co					-0.19	-0.20	-0.20	-0.19	-0.15
Ni						0.93	0.98	0.98	0.98
Cu							0.94	0.93	0.98
Zn								0.98	0.99
Pb									0.98
(b)	*Yenshui R.*	*n=61*							
Depth	-0.04	0.07	-0.23	-0.15	-0.23	-0.23	-0.22	-0.13	-0.22
Fe		0.95	0.81	0.67	0.82	0.82	0.84	0.71	0.83
Mn			0.69	0.60	0.70	0.71	0.73	0.65	0.72
Cr				0.85	0.98	0.97	0.98	0.88	0.99
Co					0.81	0.85	0.85	0.83	0.86
Ni						0.99	0.97	0.84	0.99
Cu							0.98	0.84	0.99
Zn								0.84	0.99
Pb									0.87
(c)	*Tsengwen R.*	*n=67*							
Depth	0.06	-0.24	0.08	-0.08	0.05	0.04	0.05	-0.03	0.03
Fe		0.72	0.89	0.78	0.84	0.94	0.94	0.71	0.97
Mn			0.58	0.60	0.56	0.60	0.68	0.58	0.69
Cr				0.71	0.76	0.90	0.85	0.63	0.90
Co					0.69	0.71	0.76	0.62	0.83
Ni						0.78	0.80	0.48	0.84
Cu							0.89	0.63	0.92
Zn								0.66	0.96
Pb									0.78
(d)	*Chishui R.*	*n=56*							
Depth	-0.18	-0.10	-0.06	-0.28	-0.17	-0.15	-0.29	-0.15	-0.26
Fe		0.82	0.57	0.73	0.56	0.88	0.91	0.43	0.92
Mn			0.50	0.56	0.47	0.74	0.75	0.44	0.78
Cr				0.35	0.38	0.50	0.51	0.39	0.67
Co					0.31	0.68	0.70	0.19	0.67
Ni						0.45	0.47	0.33	0.61
Cu							0.94	0.37	0.91
Zn								0.42	0.94
Pb									0.62
(e)	*Potzu R.*	*n=63*							
Depth	-0.40	-0.25	-0.50	-0.24	-0.26	-0.39	-0.27	-0.54	-0.34
Fe		0.85	0.81	0.48	0.63	0.85	0.63	0.60	0.73
Mn			0.60	0.44	0.52	0.66	0.52	0.50	0.59
Cr				0.34	0.59	0.86	0.74	0.60	0.83
Co					0.42	0.31	0.29	0.38	0.37
Ni						0.47	0.24	0.40	0.38
Cu							0.87	0.54	0.92
Zn								0.46	0.99
Pb									0.56
(f)	*Peikang R.*	*n=64*							
Depth	-0.02	0.20	-0.22	-0.03	-0.10	-0.06	-0.42	0.00	-0.31
Fe		0.85	0.82	0.60	0.60	0.90	0.72	0.60	0.85
Mn			0.68	0.51	0.54	0.76	0.49	0.51	0.64
Cr				0.58	0.53	0.81	0.77	0.43	0.84
Co					0.40	0.70	0.53	0.24	0.63
Ni						0.61	0.56	0.45	0.69
Cu							0.75	0.53	0.87
Zn								0.35	0.95
Pb									0.57