CORRELATION OF IRON/IRON OXIDES AND TRACE HEAVY METALS IN SEDIMENTS OF FIVE RIVERS, IN SOUTHERN TAIWAN

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ABSTRACT
The main purpose of this study is to verify the correlations between iron element/iron oxides and the aqua-regia extractable heavy metal in depth profiles of river sediment cores. Sediments, sampled from five main rivers (the Yenshui, Tsengwen, Chishui, Potzu, and Peikang Rivers), contaminated with different level of heavy metals pollution located in southern Taiwan, were used to determine the average concentration ratio between each heavy metal and iron element. The influence of total anthropogenic heavy metal concentration on the average concentration ratio also can be assessed to realize the total binding capacity of iron element with heavy metals in high and moderate pollution level of river sediment. The correlation coefficients between Iron element and aqua-regia extractable heavy metals (Cu, Cr, Zn, Ni, Pb, Co, and Mn) are higher than those between Iron oxides and aqua-regia extractable heavy metals in sediments of five rivers. It indicated that the adsorption and coprecipitation of heavy metals on the iron oxides was not the only mechanism for the accumulation of heavy metals with iron element in sediment.
The average concentration ratio of heavy metal versus iron element was defined as the concentration (mg/kg) of each kind of aqua regia extractable heavy metals divided by iron element (%) in sediments. The values of the average concentration ratio for each heavy metal were found as the slope of the linear regressive line of heavy metals versus iron element and could be used as an indicator to score the pollution degree clearly in the river sediment. The coefficients of linear regression between the trace heavy metals and iron element in sediments of five rivers were mostly higher than 0.7, indicating that the importance of iron element in the accumulation of heavy metals in river sediments.
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KEYWORDS: Correlation coefficients, Heavy metals, Iron element, Iron oxides, River sediment.

INTRODUCTION
Sediment is known as traps or sources of chemical compounds and elements from the river water. The distribution of heavy metals in sediment can be separated as exchangeable, carbonates, oxidizing, organic matter and residual fractions (Tessier et al., 1979; Ryssen et al., 1999; Stephens et al., 2001). The percent of metals bound to five fractions were associated with kinds of metals (Stephens et al., 2001). The metals extracted from the oxidizing fraction including the destruction of physical (adsorption and absorption) and chemical actions (e.g. bound to iron oxides) (Donahoe, et al., 198).The metals in different sequential extraction can be used to realize the geochemical behavior regarding remobilization. However, the importance of iron element or iron oxides controlling the distribution of these aqua-regia extractable trace metals in the sediment need to be compared.
Iron element is an abundant and natural component in the sediment (Nolting et al., 1999). The main objective of this study is to investigate the metals relationship between iron element or iron oxides and aqua-regia in high or middle heavy metal polluted river, and to assess the availability of average concentration ratio in expression the pollution degree of metals.

MATERIALS AND METHODS
Study areas
The five main rivers (the Yenshui, Tsengwen, Chishui, Potzu, and Peikang Rivers) flow through the largest plain area of southern Taiwan. The catchments of the Yenshui River 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 and contained low concentration of heavy metals and middle concentration of organic matters.

Sediment core samples preparation
Sediment cores were sampled from the five main rivers with a hand-operated sediment corer (Wildco, U.S.A.) for investigation in this study. The sediment cores were held vertically in 4 ice-box when taking back to our laboratory and 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. Each sediment core segment was air-dried at room temperature before chemical analysis.

Chemical analysis
Geochemical components in the sediment were determined using the acid hydroxylamine method for Fe-oxides (Wang, 1987). Fe in hydroxylamine solution were analyzed by atomic absorption spectrometer and expressed in % of Fe_2O_3. The heavy metals in different depth of river sediment were released by microwave assisted strong acid digestion. 0.2-0.5 gram of air-dried sediments 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%) (Breder, 1982). This digestion process was performed by the Milestone MLS 1200 programmed microwave system. The temperature of the acid-sample mixture in the vessel was brought to 170±5 in 10 minutes and maintained at this temperature for 10 minutes. 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).

RESULTS AND DISCUSSIONS

Heavy metals pollution in river sediment

The different depth of sediments in Yenshui river were seriously polluted by trace heavy metals (Cu, Cr, Zn, Ni, Pb, and Co) accumulating from river water as shown in Table 1. The mostly highest concentrations of trace heavy metals were found in the top layer of sediment below the water sediment interface. Cu, Cr, Zn, Ni, Pb, and Co were as high as 1000, 820, 830, 430, 105, and 140 mg/kg. The concentrations of metals near the background level were also can be found in the sediment core segments, except Cu. The concentration variation of Cu, Co, Pb, and Ni were near background level in the four moderate heavy metal polluted river sediments, indicating that little amount of those metals were discharged in those catchments.

Table 1 Ranges of heavy metals Concentration in highly and moderately heavy-metal pollution river sediments

Heavy Metals Pollution Levels		
Metals	High pollution[a] (mg/kg)	Moderate pollution[b] (mg/kg)
Cu	80-1000	5-35
Cr	15-820	13-50
Zn	45-830	43-250
Ni	15-430	15-38
Pb	10-105	10-46
Co	8-140	8-26

a Sediment core segments sampled from the Yenshui River.
b Sediment core segments sampled from the Tsengwen, Chishui, Potzu, and Peikang Rivers.

Binding capacity of iron element

The average concentration ratios between aqua-regia extractable heavy metals versus iron element mg/kg vs. % can be used to express the binding capacity of iron element in sediment as shown in Table 2. The average concentration ratio values increase with the level of heavy metals pollution. Those values can be used as indicator for the express of metals pollution degree. The average concentration ratios of Cu, Cr, Ni, Pb, Co, and Zn were 298.6, 296.7, 121.9, 24.2, 16.8 and 289.7. Those values were significantly higher than the values found in the other four rivers.

Table 2 Summary of average concentration ratios for aqua-regia extractable heavy metals versus iron element,mg/kg vs. %.

Average Concentration Ratio							
Rivers	Cu	Cr	Zn	Ni	Pb	Co	Mn
The Yenshui River	298.6	296.7	289.7	121.9	24.2	16.8	89.5
The Tsengwen River	5.4	6.4	20.4	7.5	8.7	4.9	163.3
The Chishui River	10.1	6.9	33.8	6.6	8.3	4.5	96.6
The Potzu River	9.1	12.3	66.9	5.7	6.4	3.2	89.6
The Peikang River	9.1	7.1	49.5	5.7	12.3	5.8	131.3

Correlations of Iron element/Iron oxides and trace heavy metals

The aqua-regia extractable heavy metals (Cu, Cr, Zn, Ni, Pb, Co, Mn, and Fe) had significant linear correlation coefficients (mostly larger than 0.90) with iron element in sediments of five rivers as shown in Table 3 and Figure 1. The linear correlation coefficients for Ni, Pb, Co, and Mn in Yenshui River were larger than those found in the Tsengwen, Chishui, Potzu, and Peikang Rivers. Another correlation between aqua-regia extractable heavy metals and iron oxides had lower linear correlation coefficients than those of iron element for each metal.

Table 3. Summary of linear correlation coefficients between Iron element/Iron oxides and aqua-regia extractable heavy metals in sediments of five rivers

Rivers	Correlated Parameters	Aqua-regia Extractable Heavy Metals							
		Cu	Cr	Zn	Ni	Pb	Co	Mn	Fe
Yenshui R.	Iron Element	0.91	0.91	0.87	0.81	0.88	0.78	0.95	1.00
	Iron Oxides	0.72	0.78	0.77	0.75	0.80	0.73	0.66	0.93
Tsengwen R.	Iron Element	0.94	0.91	0.96	0.85	0.75	0.81	0.90	1.00
	Iron Oxides	0.81	0.80	0.79	0.72	0.57	0.63	0.65	0.81
Chishui R.	Iron Element	0.86	0.60	0.89	0.78	0.63	0.70	0.88	1.00
	Iron Oxides	0.77	0.49	0.75	0.32	0.27	0.67	0.64	0.74
Potzu R.	Iron Element	0.88	0.81	0.80	0.67	0.60	0.59	0.85	1.00
	Iron Oxides	0.43	0.52	0.57	0.59	0.36	0.30	0.61	0.69
Peikang R.	Iron Element	0.90	0.82	0.72	0.59	0.71	0.69	0.85	1.00
	Iron Oxides	0.68	0.43	0.34	0.41	0.42	0.58	0.75	0.72

CONCLUSION

The correlation coefficients between iron element and aqua-regia extractable heavy metals (Cu, Cr, Zn, Ni, Pb, Co, and Mn) are higher than those between iron oxides and aqua-regia extractable heavy metals in sediments of five rivers. The average concentration ratios of Cu, Cr, Zn, Ni, Pb, and Co derived from the four moderate heavy metal pollution river sediments were smaller than those derived from the high heavy metal contamination river sediments. It indicated the importance of the trace heavy metals binding capacity in the fixation of metals in sediment particle.

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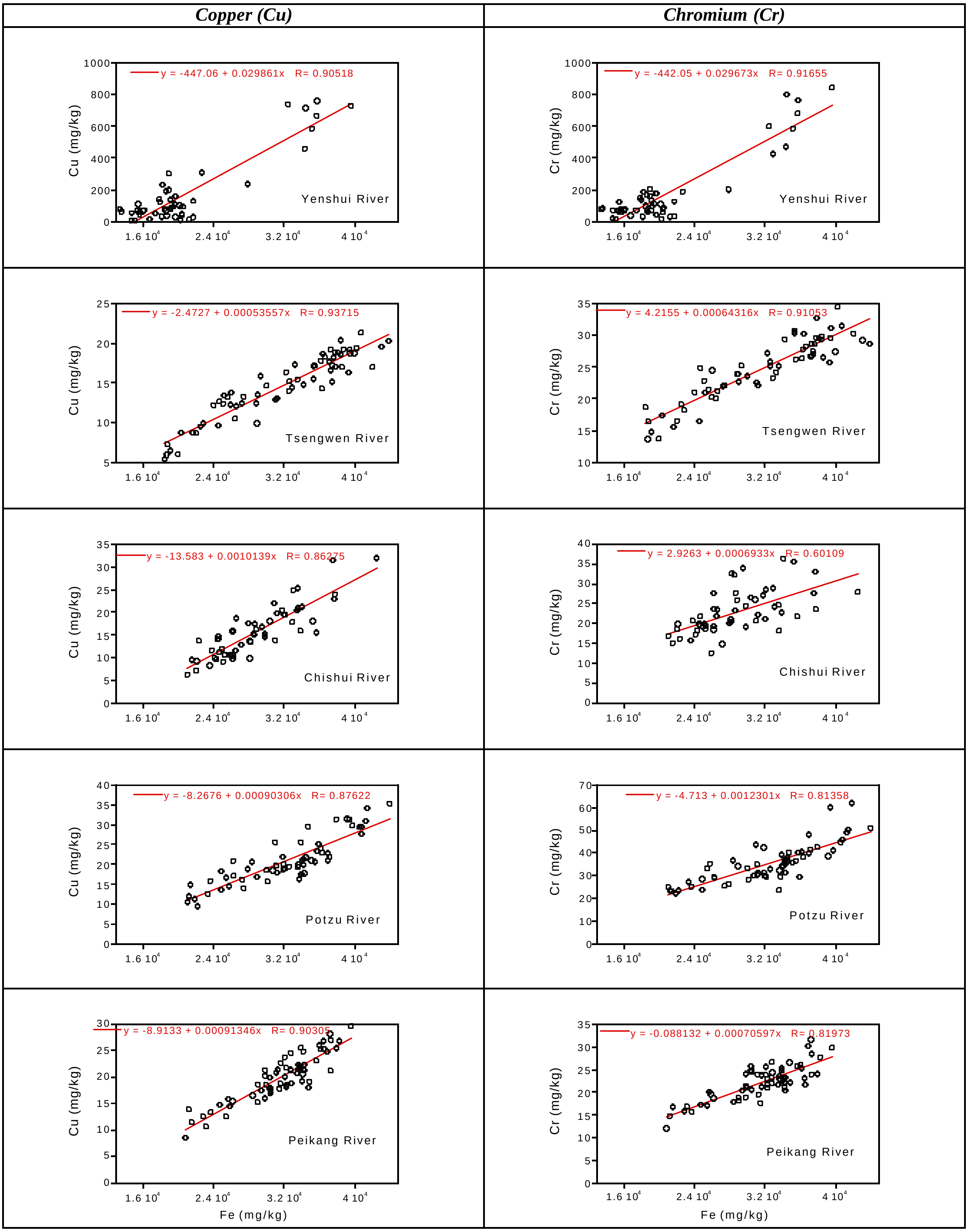


Fig. 1 (ab) *Linear correlation of iron element versus trace heavy metals in different depth of sediments from five rivers in southern Taiwan. (a) Cu; (b) Cr*

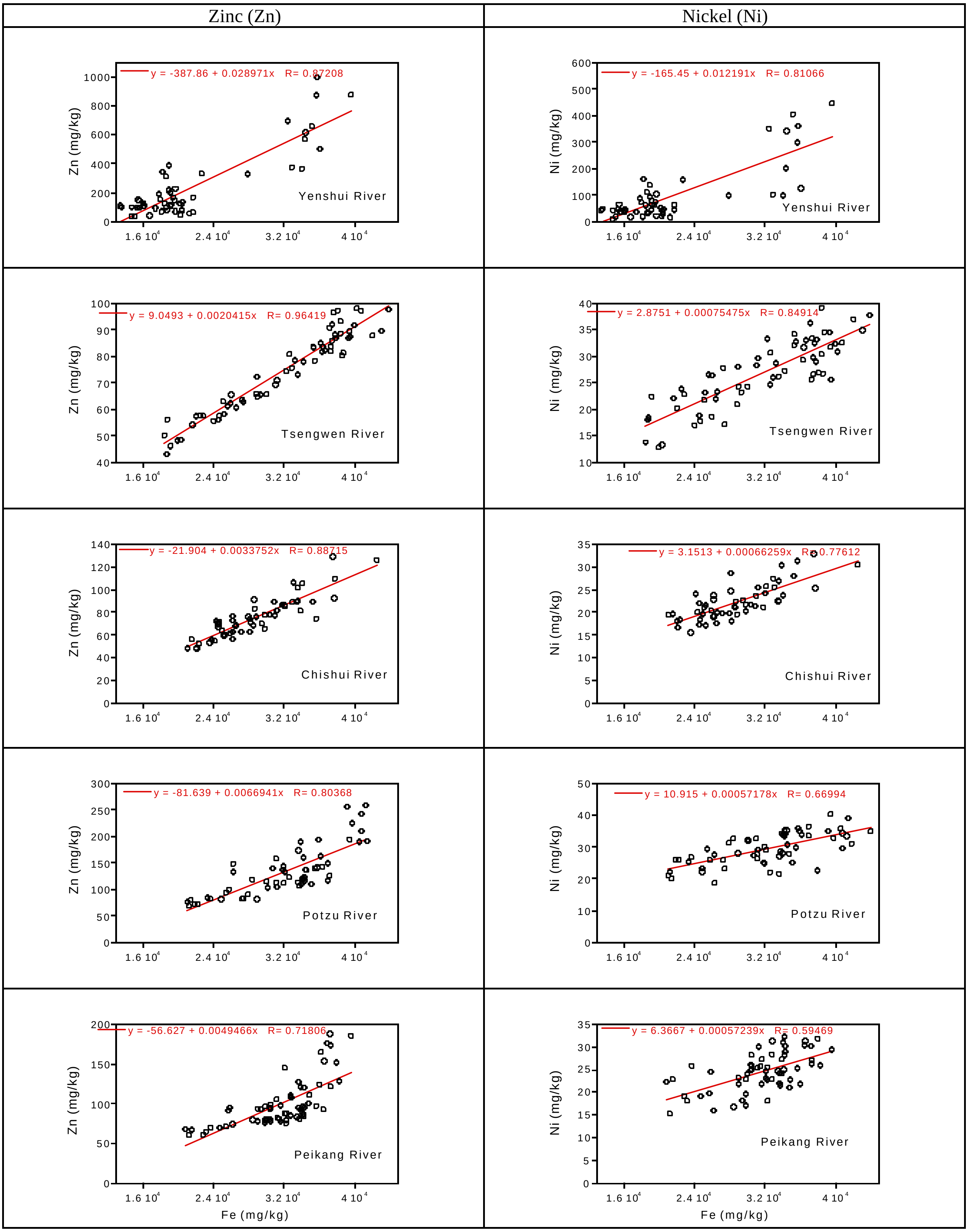


***Fig. 1 (cd)** Linear correlation of iron element versus trace heavy metals in different depth of sediments from five rivers in southern Taiwan. (c) Zn; (d) Ni*

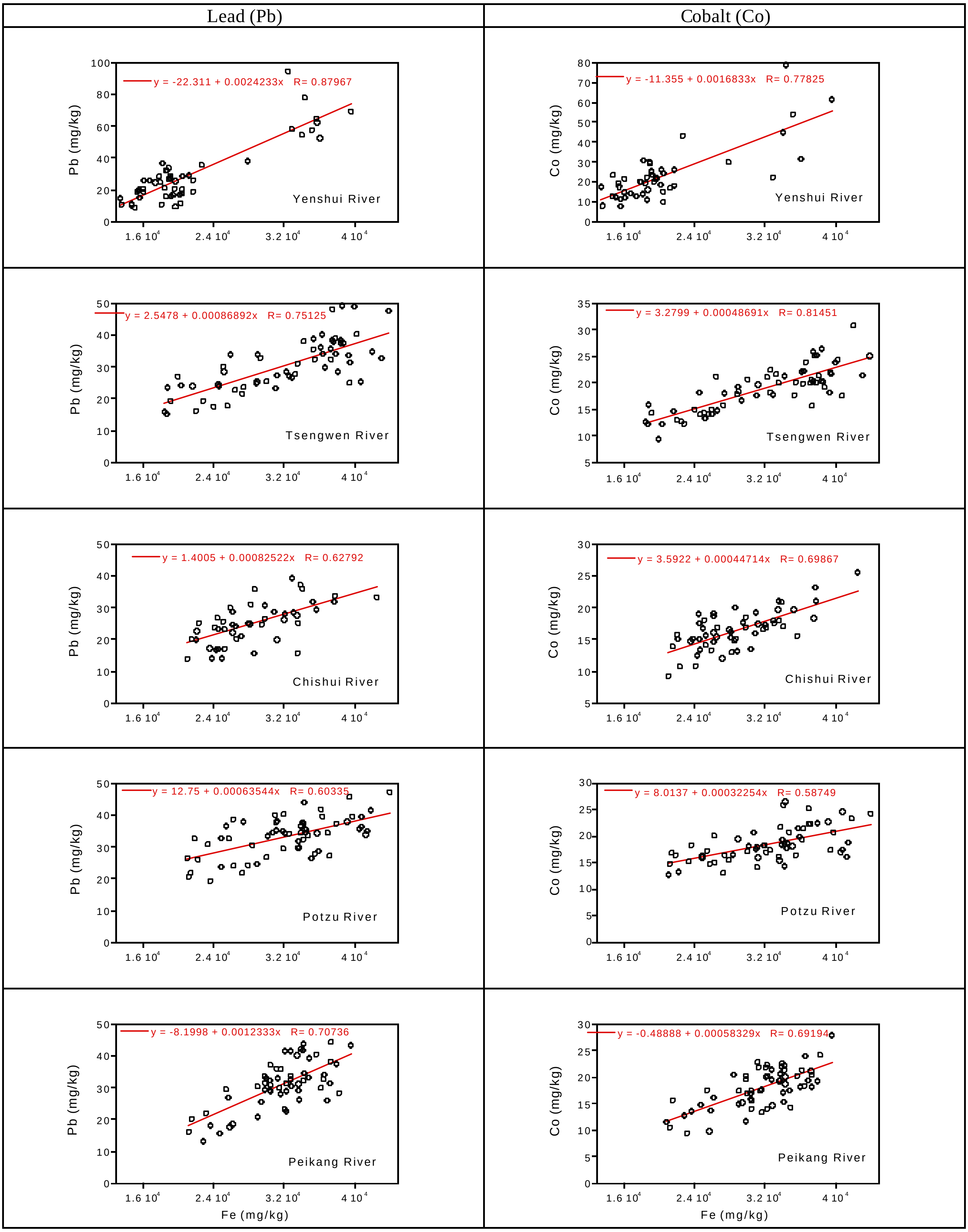
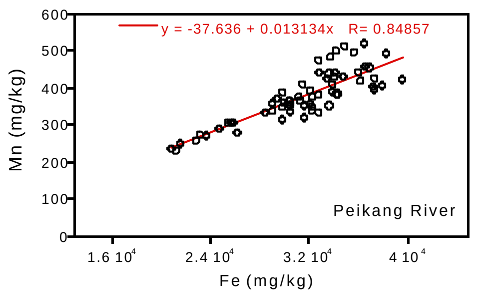
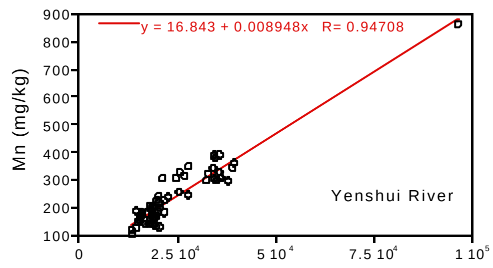
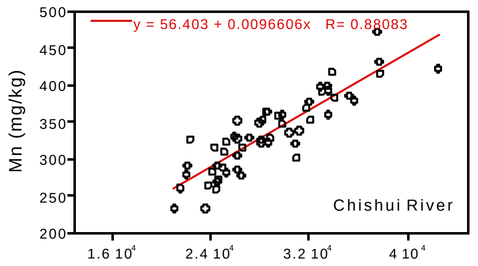


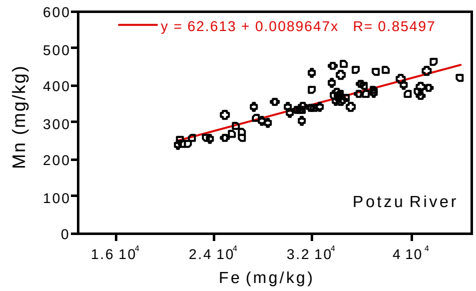
***Fig. 1 (ef)** Linear correlation of iron element versus trace heavy metals in different depth of sediments from five rivers in southern Taiwan. (e) Pb; (f) Co*

Manganese (Mn)









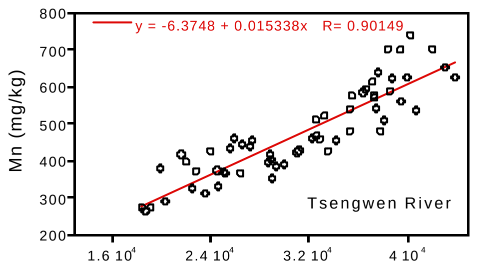


Fig. 1 (g) *Linear correlation of iron element versus trace heavy metals in different depth of sediments from five rivers in southern Taiwan. (g) Mn.*