

嘉南藥理科技大學專題研究計畫成果報告

計畫編號：CNEE94-02 子計畫(3)

計畫名稱：河川底泥中重金屬與有機物鍵結之相關性研究

執行期間：94 年 1 月 1 日至 94 年 12 月 31 日

■整合型計畫

計畫總主持人：余光昌

子計畫主持人：蔡利局

□個別型計畫

計畫主持人：

中華民國 95 年 2 月 24 日

整合型計畫：受污染河川底泥中重金屬與各鍵結物之相關性研究

總主持人：余光昌

CNEE94-02 子計畫(3) 河川底泥中重金屬與有機物鍵結之相關性研究

計畫主持人：蔡利局

嘉南藥理科技大學環境工程與衛生系

摘要

河川底泥基質蓄積經由空氣、水、土壤傳送之天然及人為重金屬及有機污染物。河川底泥中重金屬(Cu, Cr, Co, Ni, Pb and Zn) 有機物含量及鍵結於有機態重金屬之複雜化學反應機制發現可以簡單之數學模式表示其相關性。二仁溪、鹽水溪、曾文溪、急水溪、朴子溪及北港溪分別受到不同程度之重金屬及有機物污染，二仁溪底泥中重金屬(Zn, Cr, Pb, Cu, and Ni)與單位重量有機物鍵結之重金屬具有明顯之指數型態正相關，而鹽水溪底泥中重金屬(Co, Cr, Pb, Cu, and Ni)與單位重量有機物鍵結之重金屬呈現明顯之指數型態正相關，且相關係數分別為 0.92、0.84、0.77、0.72、及 0.63。受高濃度重金屬及有機物污染之二仁溪、鹽水溪重金屬與單位重量有機物鍵結之重金屬可以下述半對數方程式描述

$$\ln M = A + B \times (\text{Metal bound to OM/OM})$$

複合物形成常數 B 可用於描述重金屬與有機物之鍵結能力。B 值越大，重金屬與有機物之鍵結能力越小。然而於受輕度污染之河川底泥中，重金屬與單位重量有機物鍵結之重金屬模式則符合線性方程式。

關鍵詞：數學模式、重金屬、有機物。

Abstract

River sediment matrices accumulate and collect pollutant from water, soil, and air including organic and inorganic material, coming from natural and anthropogenic sources. Simply empirical mathematic models were demonstrated to realize and predict the correlation among aqua-regia extractable heavy metals (Cu, Cr, Co, Ni, Pb and Zn), metals bound to organic matters (OM), and OM for the complicated chemical reactions existing in the river sediment matrices. Six main rivers, the Yenshui, Ell-ren, Tsengwen, Chishui, Potzu, and Peikang Rivers, located in southern Taiwan, were contaminated with heavy metals and OM in different level from industry, domestic, and agricultural wastewater. Significant exponential correlations among aqua-regia extractable heavy metals (Zn, Cr, Pb, Cu, and Ni), OM, and metals bound to OM were found in different depth of Ell-ren river sediment. The exponential correlation coefficient between aqua-regia extractable heavy metals (Co, Cr, Pb, Cu, and Ni) and metals bound to OM in per unit weight of OM in the Yenshui river sediment were 0.92, 0.84, 0.77, 0.72, and 0.63, respectively. The correlations between aqua-regia extractable heavy metals and metal bound to OM in per unit weight OM at serious metal contamination river sediment can be defined in empirical mathematic

model as below

$$\ln M = A + B \times (\text{Metal bound to OM/OM})$$

By usage of the model, the amount of each heavy metal forming complex with unit weight of OM can be predicted with concentration of aqua-regia extractable metal in sediment. The calculated results for complex formation constant (B) between aqua-regia extractable metals and metals-OM/OM from experimental data can be used as an index to compare the binding capacity of metal with OM. The larger the complex formation constant B existed, the weaker binding force of metal and OM was. However, in slightly polluted river sediment matrices with heavy metals, the empirical mathematic model was as below:

$$M = A + B \times (\text{Metal bound to OM/OM})$$

Where A and B have different values for each heavy metal.

Keywords: mathematic model, heavy metal, organic matters.

一、前言

水體環境中重金屬可依據粒徑大小來區分重金屬的型態，將樣品以 $0.45\text{ }\mu\text{m}$ 孔徑濾紙區分，通過者稱為溶解態金屬(dissolved metal)，被截留在濾紙上的稱為顆粒態金屬(particulate metal)。水體環境中的顆粒態金屬，係指與懸浮物質和底泥結合之金屬(陳氏，1992)。當水體呈現靜止狀態無擾動時，懸浮物質將會逐漸沈降及累積在湖泊或河川中的底泥(Ryssen *et al.*, 1999)。底泥中的重金屬，一部份來自於自然界中自然形成，源自於岩石及礦物風化的碎屑產物；一部份則為水體中溶解態金屬或顆粒態金屬因吸附、沈澱等作用而形成的。

(一) 底泥中重金屬鍵結機制

底泥所含之化學組成，如黏土質、有機物、與鐵錳水合之氧化物，以及底泥之其他特性，如顆粒尺寸、pH 值、氧化還原的狀態，及水體中氯鹽的濃度皆會影響底泥顆粒和污染物質之間的相互作用。底泥中的有機碳的含量將會影響污染物質的吸附能力，例如多氯聯苯(PCBs)。底泥顆粒尺寸也會影響底泥與污染物質的結合作用和污染物移動的可能性，小粒徑的顆粒經常能容納高濃度的污染物(U.S. EPA, 1993)，此現象主要乃是由於小粒徑之底泥顆粒具有較大之表面積。

底泥中重金屬的鍵結機制主要分為：1.吸附作用。2.與鐵錳水合氧化物共沈澱作用。3.與有機物分子錯合作用。4.結合於礦物的結晶格中。其水體環境中金屬與底泥之鍵結機制如表 1 所示。Boothman (1988) 指出微量金屬在底泥中與不

同型態物質結合係經由不同反應，如離子交換、與有機物質錯合或結合於底泥中。

表 1 水體環境中重金屬與底泥之鍵結機制

	碎屑產物 有機物碎屑 (腐植酸、瀝青)	有機質 物、碳酸鹽與硫化物	微量金屬、氫氧化鐵錳水合 物、碳酸鈣		
結合於晶格中	XX	(X)			
表面吸附	X	X	(X)	(X)	(X)
離子交換	X	X	(X)	X	(X)
沈澱			XX		
共沈澱				XXX	X
錯合、凝聚		XXX			

註：XXX—主要機制；XX—重要機制；X—一般機制；(X)—可能機制

資料來源：陳靜生(1992)

底泥中重金屬各種鍵結型態之分佈可能會受到 pH、氧化還原電位、離子強度、化學及生物氧化還原反應和複合的氧化還原反應影響，因而導致各種鍵結型態重新分佈(Gunn *et al.*, 1988)。Kabata-Pendias (1992) 發現土壤 pH 值、有機物、碳酸鹽、黏土及氧化物含量會影響金屬物種形成與其移動性。Calmano *et al.* (1993) 也指出當厭氧之底泥暴露在大氣中時，其氧化還原條件會發生改變(由厭氧態轉變為好氧態時)，底泥中重金屬之鍵結形態將重新分佈與發生轉換。

底泥中重金屬鍵結型態的轉換(transformation)的形態包括下列主要程序：

1. 吸附與脫附作用
2. 碳酸鹽鍵結之重金屬的形成與溶解
3. 可溶解性與非溶解性金屬有機複合物的形成與分解
4. 氢氧化物與氫氧化水合氧化物的形成與溶解
5. 鐵錳金屬氧化物的吸附與共沉澱作用(尤其在好氧環境中性 pH 值下)
6. 在強大的還原環境中金屬硫化物的沉澱作用及在好氧條件下硫酸鹽的溶解

(二) 金屬在底泥中鍵結型態

土壤和底泥中的微量金屬以不同的化學型態或鍵結方式存在(Rauret, 1998)。逐步萃取法(sequential extraction procedure, SEP)，經常被用在河川、港灣或海水中底泥重金屬的各種鍵結型態之分析(Tessier *et al.*, 1979；

Belzunce-Segarra *et al.*, 1997；Singh *et al.*, 1998；Tsai *et al.*, 1998)。Mulligan *et al.* (2001) 指出使用萃取法可決定土壤中之金屬型態，而使用不同的萃取劑則可溶解出不同型態之金屬。因此，底泥中重金屬的存在形態可依萃取法的不同而區分出不同之金屬型態。文獻中金屬常見的區分型態如表 2 所示。

Tessier *et al.* (1979) 將重金屬在底泥中型態以操作上之定義區分為可交換態、碳酸鹽態、鐵錳氧化物態、有機物與硫化物鍵結態及殘餘態等五種型態；Calmano *et al.* (1993) 則將之區分為可交換態、碳酸鹽態、易還原態、中度還原態及有機物與硫化物鍵結態，其中再將還原態之金屬細分為與錳氧化物鍵結之金屬稱為易還原態(easily reducible)，而與非結晶形的鐵氧化物鍵結之金屬稱為中度還原態(moderately reducible)。而 He *et al.* (1995) 更將之區分為六種型態，分別為水溶解態、可交換態、有機複合態、有機鍵結態、固體顆粒態及殘餘態；此外，Community Bureau of Reference (BCR) 則僅將其區分為酸可溶解態、可還原態及可氧化態(Perez-Cid *et al.*, 1998)。

表 2 文獻中有關金屬鍵結型態之區分

參考文獻	鍵結型態
Tessier <i>et al.</i> (1979)	可交換態、碳酸鹽態、鐵錳氧化物態、有機物與硫化物鍵結態、殘餘態
Calmano <i>et al.</i> (1993)	可交換態、碳酸鹽態、易還原態、中度還原態、有機物與硫化物鍵結態
He <i>et al.</i> (1995)	水溶解態、可交換態、有機複合態、有機鍵結態、固體顆粒態、殘餘態
Perez-Cid <i>et al.</i> (1998)	酸可溶解態、可還原態、可氧化態

四個文獻中對於底泥中重金屬之型態區分大致上差異不大，各相之間會有些重疊，但主要還是以五種鍵結型態為主，分別為可交換態、碳酸鹽鍵結態、可還原鍵結態、可氧化鍵結態與殘餘態，五種型態的個別意義將詳加說明如下：

1. 可交換態

係指底泥中離子交換之重金屬，主要鍵結為靜電吸引力(Mulligan *et al.*, 2001)。利用交換特性，將表面吸附之污染物離子交換出來。當水中離子成分改

變時，可能對此型態重金屬發生吸附-脫附作用(Tessier *et al.*, 1979)。

2. 碳酸鹽鍵結態

係指以醋酸鈉溶液在 pH 值為 5.0 的條件下，將碳酸鹽溶解而釋出碳酸鹽所結合之金屬(Mulligan *et al.*, 2001)。Tessier *et al.* (1979) 指出此型態極易受到 pH 值改變的影響。

3. 可還原鍵結態

即為鐵錳氧化物鍵結態，係指以還原劑在 pH 值為 2.0 的條件下，可被萃取之金屬。使用羥胺鹽酸化合物當萃取劑把含鐵和錳的氫氧化物還原成可溶解形式(Mulligan *et al.*, 2001)。

4. 可氧化鍵結態

即為與有機物與硫化物鍵結態，係指以過氧化氫及硝酸之萃取劑在氧化條件下，可被萃取之金屬(Mulligan *et al.*, 2001)。以氧化劑破壞有機物並氧化硫化物形成硫酸鹽(Rauret, 1998)。

5. 殘餘態

即為經由上述之逐步萃取後殘留在原生與次生礦物結晶晶格中穩定的存在，在自然界中不易釋出(Tessier *et al.*, 1979)；需在高溫強酸的條件下，矽酸鹽與其他物質被溶解後，所被萃取出之金屬(Mulligan *et al.*, 2001)。

Rauret (1998) 指出一般應用於逐步萃取法之萃取劑規劃通常根據下面的次序：無緩衝性之鹽類、弱酸、還原劑、氧化劑與強酸。

從文獻中不同的研究中可發現各種重金屬在不同水體底泥或土壤中各鍵結態之含量均不同，如 Ryssen *et al.* (1999) 在比利時 Bovenschelde 及 Dommel 河段底泥中重金屬之鍵結型態分析中發現，Bovenschelde 河川中厭氧性底泥，除了錳以可交換態和碳酸鹽態鍵結外，其餘元素(鐵、銅、鋅、鎘與鉛)幾乎無鍵結。然而所有金屬皆與殘餘態之鍵結約在 50 到 90 % 之間。相對地，在 Dommel 河川沙質底泥中，其銅、鋅與鎘之鍵結結果則為完全不同，鋅主要與碳酸鹽鍵結，銅則完全以可氧化態鍵結，鎘除了不以殘餘態鍵結外，其餘鍵結態皆有；鐵與鉛主要以殘餘態鍵結。Tessier *et al.* (1979) 分析加拿大魁北克 Yamaska 與 Saint-Francois 河川下游河段 Saint-Marcel 與 Pierreville 底泥之鍵結型態，發現矽與鋁皆大部分主要以殘餘態鍵結；鈣則主要以殘餘態鍵結，其次為以可交換態形式存在。Kabata-Pendias (1992) 曾對土壤中微量金屬進行鍵結型態分佈之研究，

發現鋅與鎘主要以有機物鍵結態、可交換態及水溶解態存在，銅則主要以有機物鍵結態及可交換態存在，然而，鉛則僅具有稍微之移動性，主要以殘餘態鍵結。

(三) 底泥中鍵結型態之來源及其移動性

底泥中重金屬之型態主要以五種鍵結型態為主，分別為可交換態、碳酸鹽鍵結態、可還原鍵結態、可氧化鍵結態與殘餘態。在本研究中，將可還原鍵結態細分為錳氧化物鍵結態與鐵氧化物鍵結態兩種型態。因此，將底泥中重金屬之鍵結型態分為六種，分別為可交換態、與碳酸鹽鍵結態、與錳氧化物鍵結態、與鐵氧化物鍵結態、與有機物及硫化物鍵結態及殘餘態。其不同鍵結型態之來源及其移動性與生物可利用性如表 3 所示，其來源分為人為污染與天然形成，於表中，前五種鍵結型態主要為人為污染所造成，而殘餘態則主要為自然存在於礦物晶格中；然而以水體環境中金屬之移動性與生物可利用性而言，以可交換態為最容易於水體中移動，以殘餘態之移動性最低。

因此，在本研究中，僅針對底泥中之可交換態、與碳酸鹽鍵結態、與錳氧化物鍵結態、與鐵氧化物鍵結態及與有機物鍵結態之金屬生物溶出量進行研究，而不加以探討底泥中自然存在於礦物晶格中的殘餘態鍵結之金屬含量。且將各重金屬之五種鍵結型態(不包括自然存在於晶格中之殘餘態)之含量總合稱為重金屬之總可萃取量(total extractable heavy metals, TEHMs)。

表 3 重金屬不同鍵結型態的來源及其移動性與生物可利用性

金屬鍵結型態	形成來源		金屬移動性 (生物可利用性)
	人為污染	自然形成	
可交換態	++++	+	++++
碳酸鹽態	++++	++	+++
錳氧化物態	++++	++	++
鐵氧化物態	++++	++	++
有機物與硫化物	++++	++	+

態

殘餘態

—

+++

—

註：++++:非常顯著；+++:顯著；++:稍顯著；+:不顯著； -:不可能

(四) 金屬鍵結型態在環境上的意義

當環境條件改變時，分佈在這些型態中的重金屬將有各別之再移動性。土壤或底泥中重金屬之化學型態將影響其溶解度，而溶解度直接影響之生物可利用性。因此，測定污染底泥中重金屬之總量將不足以評估對環境之影響。因為，在環境中決定重金屬之行為及移動性的是重金屬之化學型態而不是總量。

Rauret (1998) 指出微量金屬不同鍵結型態的測定可在其移動性及生物可利用性或生物之致毒性上給予更多的資訊。且鍵結在底泥中的重金屬之類型及穩定性為金屬移動性與生物可利用性之潛在可能的決定因子。金屬的不同化學型態在生態系統中其轉移能力與生物可利用性上大大地不同(Calmano *et al.*, 1993)。

在過去十多年間，以底泥中重金屬之不同鍵結型態來探討重金屬的移動性機制和生物可利用性之研究相當多 (Förstner, 1989 ; Pardo *et al.*, 1990 ; Boughriet *et al.*, 1992 ; Warran and Zimmerman, 1993 ; Tsai *et al.*, 1998)。了解重金屬在底泥中存在之型態，將有助於評估重金屬對於水生動植物或人體可能造成之危害。就以底泥中重金屬之移動性而言，在未受污染的底泥中重金屬主要與矽酸鹽及原生礦物鍵結且相對地較不具有移動性；反之，在受污染的底泥中，重金屬則與其他型態有較多鍵結且通常較具有移動性(Rauret, 1998)。在生物可利用性上，以溶解或弱吸附性的金屬可能容易被植物與水中生物體所利用；而鍵結在主要與次要礦物結晶架構晶格之金屬則較不為生物所利用，除非這些礦物受過地球化學的風化作用(Calmano *et al.*, 1993)。對於底泥中各鍵結型態重金屬之毒性而言，可交換態金屬離子的毒性大於有機物鍵結態之金屬，更大於結合於原生礦物中之金屬。He *et al.* (1995) 指出水溶態的重金屬在環境中易溶出且易受生物利用；可交換態和有機複合態的重金屬是不穩定的且可能受生物所利用；重金屬的有機鍵結態和固粒態是相當穩定且不易受生物利用的；而殘餘態中的重金屬在自然情況下是不會釋出的。

Ramos *et al.* (1994) 針對受污染之土壤以逐步萃取法評估鎘、鋅、鉛與銅之

金屬移動性，發現鎘是最具有移動性及很可能被生物可利用之金屬。

(五) 本研究之目的

為了釐清重金屬與各鍵結物間鍵結之相關性，本整合型研究計畫乃針對臺灣地區南部六條受污染河川底泥中重金屬及地質化學成分進行分析並以統計方法討論重金屬、地質化學成分與重金屬在各鍵結物型態中含量之相關性，並評估受污染底泥中重金屬在與何種鍵結物鍵結時其自底泥釋出之難易度。因此，本整合型計畫分三個子計畫，分別針對子計畫(1)河川底泥中重金屬與碳酸鹽、子計畫(2)河川底泥中重金屬與鐵錳化物、子計畫(3)河川底泥中重金屬與有機物之鍵結相關性進行為期一年之研究。

二、研究方法及步驟

1. 實驗材料及分析方法：

(一) 底泥樣品的收集及前處理：

- (1) 重金屬及有機物含量高底泥：利用 sediment core sampler 於二仁溪及鹽水溪下游，採集二仁溪及鹽水溪流域受工業廢水和家庭污水污染最嚴重的底泥，採集的樣品垂直放置並存於 4°C 冰箱中帶回實驗室，先置於負溫冰櫃使底泥柱將近結凍狀態，以塑膠刀片將與水交界表面向下 10cm 內每隔 2cm 切成片狀，10cm 以下深度之底泥柱每隔 5cm 切成片狀，置於塑膠盤於室溫下乾燥後磨成細粉狀，進行底泥基質中各種物理化學特性分析。
- (2) 重金屬及有機物含量低底泥：利用 sediment core sampler 於曾文溪、急水溪、朴子溪及北港溪下游，採集流域內只受輕度工業廢水和家庭污水污染的底泥，採集的樣品垂直放置並存於 4°C 冰箱中帶回實驗室，先置於負溫冰櫃使底泥柱將近結凍狀態，以塑膠刀片將與水交界表面向下 10cm 內每隔 2cm 切成片狀，10cm 以下深度之底泥柱每隔 5cm 切成片狀，置於塑膠盤於室溫下乾燥後磨成細粉狀，進行底泥基質中各種物理化學特性分析。

(二) 底泥中各種物理化學特性分析：

- (1) 有機物含量：以 Walkley-Black method (Gerhard, 1993) 測定顆粒中有機物含量。並以 Sims et al.(1991)等提出之公式轉化成%表示
- (2) 重金屬含量分析：以火焰式或石墨爐式原子吸收光譜儀（GBC, AA960, Australia）分析經微波萃取溶出液中及經連續萃取步驟得到之各階段上澄液中重金屬含量。

2. 實驗步驟

(一) 河川底泥中各種重金屬含量分析（強酸萃取法）：

取 0.5~1.0 克經空氣乾燥之六條（二仁溪、鹽水溪、曾文溪、急水溪、朴子溪及北港溪）河川之不同深度及採樣位置之底泥，置入高壓微波消化瓶中，加入 3ml 濃硝酸，9ml 濃鹽酸，置於抽氣櫃中約 20min，先讓有機物分解產氣，加蓋鎖緊高壓微波消化瓶，於 180°C 經 600W 微波條件進行分解 10min，待冷卻後倒入離心管中，以 10000rpm，離心 2min 處理後，取上澄液經 0.45μm 濾紙過濾後，以原子吸收光譜儀測底泥中 Cu, Zn, Ni, Pb, Co, Cr, Fe 及 Mn 之個別總量(Breder, 1981)。

(二) 與有機物鍵結態金屬之連續萃取步驟：

本研究將分析各種重金屬在底泥中與有機物鍵結量。

首先需將 3g 取自六條（二仁溪、鹽水溪、曾文溪、急水溪、朴子溪及北港溪）河川中，不同深度及採樣位置之乾底泥以 Tessier A, et al (1997) 發表的 Sequential Extraction Procedure (SEP) 萃取法將有機物鍵結態之重金屬萃取至萃取液中，於 11,000 rpm 下，離心 20 min 後之上澄液，先經 0.45 μm 薄膜(Nucleopore polycarbonate membrane filter)過濾後(Ma et al. 1997)，再以石墨爐式原子吸收光譜儀(GFAAS)來測有機物鍵結態中各重金屬含量。改良型之 SEP 之分析步驟如圖 1 所示。

(三) 河川底泥中有機物含量分析：

將 3g 取自六條（二仁溪、鹽水溪、曾文溪、急水溪、朴子溪及北港溪）河川中，不同深度及採樣位置之乾底泥以 Walkley-Black method (Gerhard, 1993) 測定顆粒中有機物含量，並以 Sims et al.(1991)等提出之公式轉化成%表示。

(四) 底泥分析數據之統計分析：

以線性迴歸軟體求出有機物含量、與有機物鍵結態重金屬量及重金屬總量間之線性相關經驗公式，並比較不同河川、不同金屬間存在之線性相關係數 R 及 A、B 常數之差異。

三、結果與討論

1. 底泥中有機物對重金屬之鍵結能力

受高濃度重金屬污染之河川底泥(如鹽水溪及二仁溪)中重金屬與單位重量有機物鍵結之金屬量間之關係不同於受低濃度重金屬污染之河川底泥(如曾文溪、急水溪、朴子溪及北港溪)中重金屬與單位重量有機物鍵結之金屬量間之關係。

鹽水溪距出海口不同距離及深度底泥中重金屬(Cr, Cu, Co, Pb 及 Ni)、有機物含量、及與有機物鍵結之重金屬量間存在很顯著之指數迴歸關係(如圖 2)，實驗數據經指數迴歸整理之相關係數分別為 0.84(Cr)、0.72(Cu)、0.929(Co)、0.77(Pb)、及 0.63(Ni)，但鹽水溪底泥中 Zn、有機物含量及與有機物鍵結之 Zn

量間指數迴歸相關性則不明顯，只有 0.36(如表 4)。推究原因可能為 Zn 在底泥中主要鍵結型態為鐵及錳氧化態(Tsai *et al.*, 2002; Borovec, 1996)。二仁溪底泥中重金屬(Cr, Cu, Zn, Pb 及 Ni)與單位重量有機物鍵結重金屬間存有很明顯之指數關係，指數迴歸係數分別為 0.9(Cr), 0.97(Cu), 0.9(Zn), 0.89(Pb)及 0.96(Ni) (如圖 3)，但二仁溪底泥中無明顯增加之 Co 污染量，因此 Co 總量則與單位重量有機物鍵結 Co 量間無相關性存在。

受高濃度重金屬污染之河川底泥中各種重金屬總量與單位重量有機物鍵結重金屬之能力可以指數相關數學經驗式表達為：

$$\ln M = A + B \times (\text{Metal bound to OM/OM})$$

其中 M 代表底泥中強酸可萃取之個別金屬總量(Cr, Cu, Co, Pb, Zn 及 Ni)，單位為(mg/kg)，Metal bound to OM/OM 代表與單位重量有機物鍵結重金屬，單位為(mg/g)。A 代表 Y 半對數座標圖中之截距，B 代表重金屬與有機態之鍵結能力指標，B 值愈大底泥中重金屬與有機物之鍵結能力愈弱，Cu 之 B 值最小(0.2161)顯示其有最大之有機態鍵結能力，文獻顯示底泥中 Cu 主要鍵結於有機態(Tsai *et al.*, 2002; Silva *et al.*, 2002)。其他金屬之 B 實驗值分別為 Cr(1.1195)、Ni(1.7212)、Co(2.306)、及 Pb(3.1782)。

曾文溪、急水溪、朴子溪及北港溪底泥中重金屬與單位重量有機物鍵結之金屬量間之線性相關係數並不明顯，較趨向線性關係如圖 4 至圖 7。

受低濃度重金屬污染之河川底泥中各種重金屬總量與單位重量有機物鍵結重金屬之能力亦可以線性相關數學經驗式表達為：

$$M = A + B \times (\text{Metal bound to OM/OM})$$

常數 A、係數 B 及線性相關係數 R 如表 5 所示。

表 4. Empirical model coefficients existing among aqua-regia extractable metals, metals bound to OM, and OM in sediment matrices seriously contaminated with heavy metals and OM.

$$\ln M = A + B \times (\text{Metal bound to OM/OM})$$

Rivers	Aqua-regia extracted	Constans	Coefficient	Exponential correlation
	heavy metals (M)	(A)	constant (B)	coefficient (R)
Yenshui	Cr	2.65	1.1195	0.84
	Cu	3.24	0.2161	0.72
	Co	2.43	2.3060	0.92
	Zn	4.49	0.5208	0.36
	Pb	2.46	3.1782	0.77

	Ni	2.61	1.7212	0.63
Ell-ren	Cr	-2.27	0.0126	0.9
	Cu	0.47	0.0091	0.97
	Co	-2.25	0.0035	0.05
	Zn	0.15	0.0008	0.9
	Pb	-0.94	0.0036	0.89
	Ni	-1.27	0.0076	0.96

表 5. Empirical model coefficients existing among aqua-regia extractable metals, metals bound to OM, and OM in sediment matrices slightly contaminated with heavy metals and OM.

$M = A + B \times (\text{Metal bound to OM}/\text{OM})$					
Rivers	Aqua-regia extracted heavy metals (M)	Constants (A)	Coefficient constant (B)	Linear correlation coefficient (R)	
Tsengwen	Cr	0.61	-0.0117	0.37	
	Cu	0.43	0.0085	0.26	
	Co	0.33	-0.0079	0.41	
	Zn	2	-0.0084	0.33	
	Pb	0.21	0.0035	0.28	
	Ni	0.61	-0.0086	0.32	
Chishui	Cr	0.49	-0.0006	0.02	
	Cu	0.63	0.0062	0.17	
	Co	0.41	-0.0099	0.34	
	Zn	2.88	-0.0141	0.45	
	Pb	0.34	0.0036	0.3	
	Ni	0.61	-0.0049	0.12	
Potzu	Cr	0.79	0.0036	0.19	
	Cu	1.02	-0.0051	0.21	
	Co	0.34	-0.0034	0.19	
	Zn	3	-0.0022	0.26	
	Pb	0.88	0.0012	0.07	
	Ni	1.11	-0.0114	0.28	
Peikang	Cr	0.93	-0.0168	0.39	
	Cu	1	0.0041	0.13	
	Co	0.37	-0.0057	0.34	
	Zn	2.43	-0.0017	0.09	
	Pb	0.84	-0.0052	0.19	
	Ni	0.96	-0.0091	0.24	

2. 單位重量有機物鍵結重金屬之比值

鹽水溪底泥中平均每克有機物對與有機物鍵結之不同種類重金屬(Cr, Cu, Co, Pb, Zn 及 Ni)量之平均比值分別為 0.54、6.04、0.11、0.78、1.51、及 0.48。而二仁溪底泥中之平均比值分別為 1.74、5.27、0.29、0.23、1.03、及 0.86(如表 6)。因為每條河川之採樣為不同深度及距河口距離，收集到之底泥樣本已包括未受重金屬污染之背景泥樣及受人為重金屬嚴重污染之底泥，因此單位重量有機物鍵結重金屬之比值正比於河川遭受污染之嚴重程度，六條河川中，受高濃度重金屬污染之鹽水溪底泥中，每克有機物對與有機物鍵結之不同種類重金屬(Cr, Cu, Co, Pb, Zn 及 Ni)量之最高值分別為 19.95、1.26、3.88、5.70、0.72、及 2.47。而受輕度污染之曾文溪、急水溪、朴子溪及北港溪底泥中，每克有機物對與有機物鍵結之不同種類重金屬(Cr, Cu, Co, Pb, Zn 及 Ni)量之比值則較小如表 6 所示。

表 6. Statistical results of complexation ratio between metals-OM and OM in sediment segments of six rivers

Rivers	Samples	Complexation ratio of metals-OM vs OM (mg of metals bound to OM/g of OM in sediment matrices)						
		Cu	Co	Cr	Zn	Pb	Ni	
Ell-ren R.	18	Mean	6.04	0.11	0.54	1.51	0.78	0.48
		Min.	0.96	0.07	0.05	0.96	0.06	0.21
		Max.	14.83	0.18	2.26	3.42	3.61	1.86
		C.V.	0.96	0.75	0.39	0.26	0.78	1.04
Yenshui R.	61	Mean	5.27	0.29	1.74	1.03	0.23	0.86
		Min.	0.06	0.05	0.26	0.61	0.01	0.25
		Max.	19.95	1.26	3.88	5.70	0.72	2.47
		C.V.	1.01	0.68	0.53	0.23	0.64	0.50
Tsengwen R.	67	Mean	0.57	0.18	0.32	1.53	0.31	0.38
		Min.	0.11	0.09	0.12	0.65	0.08	0.16
		Max.	1.18	0.60	0.96	2.96	0.62	0.91
		C.V.	0.29	0.45	0.52	0.45	0.35	0.44
Chishui R.	58	Mean	0.73	0.24	0.48	1.80	0.44	0.51
		Min.	0.28	0.11	0.15	0.71	0.21	0.15
		Max.	1.39	0.51	1.02	3.31	0.93	1.09
		C.V.	0.30	0.38	0.38	0.33	0.26	0.43
Potzu R.	63	Mean	0.91	0.27	0.91	2.69	0.92	0.77
		Min.	0.55	0.15	0.47	1.54	0.61	0.33
		Max.	1.62	0.48	1.29	2.91	1.23	1.43
		C.V.	0.18	0.27	0.18	0.19	0.12	0.31
Peikang R.	64	Mean	1.08	0.27	0.56	2.27	0.67	0.73
		Min.	0.69	0.11	0.27	1.04	0.25	0.36
		Max.	1.59	0.48	1.06	1.74	1.42	1.42
		C.V.	0.13	0.26	0.29	0.24	0.35	0.28

四、結論

受高濃度重金屬污染鹽水溪底泥中，平均每克有機物對與有機物鍵結之不同種類重金屬(Cr, Cu, Co, Pb 及 Ni)量之比值和底泥中個別重金屬總量成明顯之指數型正相關，但因 Zn 之人為污染量比例不高，故相關性較不明顯。相似的，受高濃度重金屬污染二仁溪底泥中，平均每克有機物對與有機物鍵結之不同種類重金屬(Cr, Cu, Zn, Pb 及 Ni)量之比值和底泥中個別重金屬總量成明顯之指數型正相關，但因 Co 之人為污染量比例不高，故相關性較不明顯。相反的，受低濃度重金屬污染之河川(曾文溪、急水溪、朴子溪及北港溪)底泥中各種重金屬總量與單位重量有機物鍵結重金屬量間之相關性則趨向於線性相關但不明顯。本研究推導出個別河川之專一性經驗方程式，可應用於快速簡潔推測底泥中與有機物鍵結之重金屬含量，只需分析重金屬總量及有機物含量即可代入公式中求與有機物鍵結之金屬量，而不需藉由複雜之逐步萃取步驟進行分析。

伍、誌謝

本研究承蒙嘉南藥理科技大學經費補助才得以完成，在此致上謝意，經費補助編號 CNEE94-02。

六、參考文獻

- Adams W.J., Kimerle R.A. and Barnett Jr. J.W. "Sediment quality and Aquatic Life Assessment", Environ. Sci. Technol., 26, pp.1864-1875, 1992.
- Ahonen L., Tuovinen O.H. "Temperature effects on bacterial leaching of sulfide minerals in shake flask experiments", Appl. Environ. Microbiol., 57, pp. 38-145, 1991.
- Anderson B.C., Brown A.T.F., Watt W.E. and Marsalek J. "Biological leaching of trace metals from stormwater sediments: influential variables and continuous reactor operation", Wat. Sci. Technol., 38, pp.73-81, 1998.
- Belzile n., Lecomte P. and Tessier A. "Testing readsortion of trace elements during partial chemical extractions of bottom sediment", Environ. Sci. Tech., 23, pp.1015-1020, 1989.
- Belzunce-Segarra M.J., Bacon J.R., Prego R. and Wilson M.J. "Chemical forms of heavy metals in surface sediments of the San Simon inlet, Ria de Vigo, Galicia", J. Environ. Sci. Health (A), 32, pp.1271-1292, 1997.
- Blais J.F., Tyagi R.D., Auclair J.C. and Lavoie M.C. "Indicator bacteria reduction in sewage sludge by a metal bioleaching process", Wat. Res., 26, pp.487-495, 1992a.
- Blais J. F., Tyagi R.D., Auclair J.C. "Bioleaching of metals from sewage sludge by sulfur-oxidizing bacteria", J. Environ. Eng., 118, pp.690-707, 1992b.
- Blais J.F., Tyagi R.D., Auclair J.C. and Huang C.P. "Comparison of acid and microbial leaching for metal removal from municipal sludge", Wat. Sci. Technol., 26, pp.197-206, 1992c.
- Blais J.F., Tyagi R.D. and Auclair J.C. "Bioleaching of metals from sewage sludge: effects of

- temperature " , Wat. Res., 27, pp.111-120, 1993a.
- Blais J.F., Tyagi R.D. and Auclair J.C. " Bioleaching of metals from sewage sludge: micro-organisms and growth kinetic " , Wat. Res., 27, pp.101-110, 1993b.
- Bloomfield C. and Pruden G. " The effects of aerobic and anaerobic incubation on extractability of heavy metals in digested sludge " , Environ. Pollut., 8, pp.217-232, 1975.
- Boothman W.S. " Characterization of trace metal associations with polluted marine sediment by selective extraction " , In : Chemical and Biological Characterization of Sludges, Sediment, Dredge Spoils, and Dredging Muds, eds Lichenberg J. J., Winter F. A., Weber C. I. and Fradheim L., American Society Test. Mater. Spec. Tech. Publ., USA, pp.81-92, 1988.
- Boughriet A., Ouddane B., Fischer J.C., Wartel M. and Leman G. " Variability of dissolved Mn and Zn in the Seine estuary and chemical speciation of these metals in suspended " , Wat. Res., 26, pp.1359-1378, 1992.
- Breder R., 1981. Optimization studies for reliable trace metal analysis in sediments by atomic absorption spectrometric methods. *Fresenius' Z. Anal. Chem.*, 313, 395-402.
- Borovec Z. (1996). Evaluation of the concentrations of trace elements in stream sediments by factor and cluster analysis and the sequential extraction procedure. *Sci. Total Environ.* **177**, 237-250.
- Campbell P.G., Lewis A.G., Chapman P.M., Crowder A.A., Fletcher N.K., Imber B., Louma S.N., Stokes P.M. and Winfrey M. " Biological available metals in sediment " , In : National Research Council of Canada, NRCC27694, Québec, Canada, pp.298, 1988.
- Calmano W., Hong J. and Förstner U. " Binding and mobilization of heavy metals in contaminated sediment affected by pH and redox potential " , Wat. Sci. Technol., 28, pp.223-235, 1993.
- Chartier M. " Development of a process to remove metals from sediment, Master Thesis. INRS-Eau, Université du Québec, Sainte-Foy, QC, Canada, pp.272, 1992.
- Chartier M. and Couillard D. " Biological process: the effect of initial pH, percentage inoculum and nutrient enrichment on the solubilization of sediment bound metals " , Wat. Air Soil Pollut., 96, pp.249-267, 1997.
- Chartier M., Mercier G. and Blais J. F. " Partitioning of trace metals before and after biological removal of metals from sediment " , Wat. Res., 35, pp. 1435-1444, 2001.
- Chen S.Y. and Lin J.G. " Factors affecting bioleaching of metal contaminated sediment with sulfur-oxidizing bacteria " , Wat. Sci. Technol., 41, pp.263-270, 2000.
- Chen S.Y. and Lin J.G. " Bioleaching of heavy metals from sediment: significance of pH " , Chemosphere, 44, pp.1093-1102, 2001.
- Chen S.Y., Chiu Y.C., Chang P.L. and Lin J.G. " Assessment of recoverable forms of sulfur particles used in bioleaching of contaminated sediments " , Wat. Res., 37, pp.450-458, 2003.
- Cornwell D.A., Westermoff G.P. and Cline G.C. " Batch feasibility testing of heavy metals removal from wastewater sludge with liquid-ion exchange " , Proc. Mid. Atlantic Waste Conf., 12 Tm Bucknell Univ., Lewisburg, PA, July13-15, pp.111-119, 1980.

- Couillard D. and Mercier G. "Bacterial leaching of heavy metals from sewage sludge-bioreactors comparasion ", Environ. Pollut., 66, pp.237-253, 1990.
- Couillard D. and Chartier M. " Removal of metals from aerobic sludges by Biological solubilization in batch reactors ", J. Biotech., 20, pp.163-180, 1991.
- Couillard D. and Chartier M. " Biological removal of metals from sediment: the influence of the energy substrate, the solid content and the temperature ", Environ. Technol., 14, pp.919-930, 1993.
- Couillard D., Chartier M and Mercier G. " Removal of Cd, Cu, Mn and Zn from metal laden sediments by biological solubilization, Rev. Sci. Eau., 7, pp.251-268, 1994.
- Couillard D. and Mercier G. " Optimal residence time (in CSTR and Airlift Reactor) for bacterial leaching of metals from sewage sludge, Wat. Res., 25, pp.211-218, 1991.
- Damian S. " Developing National Sediment Quality Criteria ", Environ. Sci. Technol., 22, pp.1256-1261, 1988
- Environment Canada. " Plan d'utilisation des matériaux dragués dans le fleuve St-Lauret ", Annexe no 6. Rapport soumis au comité d'étude sur le fleuve St-Laurent par la direction générale des eaux intérieures, p173, 1978.
- Elzeky M. and Attia Y.A. " Effect of bacterial adaptation on kinetics and mechanisms of bioleaching ferrous sulfides ", Chem. Eng. J., 56, pp. 115-124, 1995.
- Förstner U. " Chemical forms and reactivities of metals in sediment ", In : Chemical Methods for Assessing Bioavailable Metals in Sludges and Soils, R. Leschhber *et al.* (eds), Elsevier, London, pp.1-10,1985.
- Förstner U. " Contaminated sdeiment ", In lecture Notes in Earth Sciences, eds. Bhattacharij, *et al.*, pp.1-157,1989.
- Förstner U., Ahlf W., Calmano W. and Kersten M. " Sediment criteria development ", In: Heling D., Rothe P., Förstner U. and Stoffers P. (Eds.) Sediment and Environmental Chemistry. Springer, Berlin, pp.311-338, 1990.
- Förstner U., Ahlf W. and Calmano W. " Sediment quality Objectives and Criteria Development in Germany ", Wat. Sci. Tech., 28, pp.307-314, 1993.
- Fuller C.C., Davis J.A., Cain D.J., Lamothe P. J., Fernandez G., Vargas J. A. and Murillo M. M. " Distribution and transport of sediment-bound metal contaminations in the Rio Grande de Tarcoles, Costa Rioca (Central America) ", Wat. Res., 24, pp.805-812, 1990.
- Gerhardt A., (1993), Review of Impact of Heavy Metals on Stream Invertebrates with Special Emphasis on Acid Conditions, Water, Air and Soil Pollution, Vol.66, pp.289-314.
- Gunn A.M., Winnard D.A. and Hunt D.T.E. " Trace metal speciation in sediment and soil: an overview from a water industry perspective ", In Metal Speciation; Theory, Analysis and Application, eds J. Kramer and H. E. Allen, Lewis Publishers, Chelsea, MI, USA, pp.263-264, 1988.
- Hayes T.D., Jewell W.J. and Kabrick R.M. " Heavy metals removal from sludges using combined biological/chemical treatment ", Proc. 34th Ind. Waste Conf., Purdue Univ., West Lafayette,

- Indiana, pp.529-543, 1980.
- He X.T., Logan T.J. and Traina S.J. " Physical and chemical characteristics of selected U.S. municipal solid waste composts, J. Environ. Qual., 24, pp. 543-552,1995.
- Hiromitsu S., Yotaka K. and Kazuo S. " Distribution of heavy metals in water and sieved sediment in the Toyohira river " , Wat. Res., 20, pp.559-567, 1986.
- Janssen A.J.H., Sleyster R., Van Der Kaa C., Jochemsen A., Bontsema J., Lettinga G. "Biological sulfide oxidation in a fed-batch reactor", Biotechnol. Bioeng., 47, pp.327-333, 1995.
- Jain D.K. and Tyagi R.D. "Leaching of heavy metals from anaerobic sewage sludge by sulfur-oxidizing bacteria" , Enzyme Microb. Technol., 14, pp. 376-383, 1992.
- Jenkins R. L., Benjamin J. S., Marvin L. S. Rodger B., Lo M. P. and Huang R. T. " Metal removal and recovery from municipal sludge " , J. Wat. Pollut. Control Fed., 53, pp.25-32,1981.
- Juan G.M. and Sosa A.M. " Trace metals in Valencia lake (Venezuela) sediment " , Wat. Air Soil pollut., 77, pp.141-150,1994.
- Kabata-Pendias A. " Trace metals in soils in Poland-occurrence and behaviour", Trace Subst. Environ. Health, 25, pp.53-70, 1992.
- Karavaiko G.I., Rossi G., Agates A.D., Groudev S.N. and Avakyan Z.A. " Biogeotechnology of Metals: Manual for International Project GKNT", Moscow, Soviet Union, 1988.
- Keraten M. and Förstner U. " Geochemical characterization of the potential trace metal mobility in cohesive sediments " , Geo-Marine Letters, 11, pp. 184-187, 1991.
- Kiff R.J. and Brown S. " The development of an oxidative acid hydrolysis process for sewage sludge detoxification " Proc. Int. Conf. Heavy Metals in the Environment, Amsterdam, September, pp.159, 1981.
- Kitada K., Ito A., Yamada K., Aizawa J. and Umita T. " Biological leaching of heavy metals from anaerobically digested sewage sludge using indigeneous sulfur-oxidizing bacteria and sulfur waste in a closed system " , Proceeding of 1st World Water Congress of the International Water Association, pp.359-366, 2000.
- Leving C. D. " The ecologival consequences of dredging and dredge spoil disposal in Canadian Waters. NRCC # 18130 " , pp.140, 1982.
- Literathy P., Nasser Ali L., Zarba M.A. and Ali M.A. " The role and problems of monitoring bottom sediment for pollution assessment in the coastal marine environment", Wat. Sci. Technol., 19, pp. 781-792,1987.
- Lo S.L. and Chen Y. H. " Extracting heavy metals from municipal and industrial sludges " , Sci. Total Environ., 90, pp.99-116, 1990.
- Lombardi A. T. and Garcia O. Jr. "Biological leaching of Mn, Al, Zn, Cu and Ti in an anaerobic sewage sludge effectuated by *Thiobacillus ferrooxidans* and its effect on metal partitioning", Wat. Res., 36, pp.3193-3202, 2002.
- Luoma S.N. " Can we determine the biological availability of sediment-bound trace element ? " , Hydrobiology, 176/177, pp.379-396, 1989.

- Ma L. Q., Rao G. N., 1997, Effects of phosphate Rock on Sequential Chemical Extraction of Lead in Contaminated Soils, J. Environ Qual., Vol.26, 788-794.
- Marquenie J.M. " Bioavailability of micropollutants ", Environ. Technol. Lett., 6, pp.351-358, 1985.
- Mercier G., Chartier M. and Couillard D. " Strategies to maximize the microbial leaching of lead from metal-contaminated aquatic sediment ", Wat. Res. , 30, pp.2452-2464, 1996.
- Mcintosh A. " Trace metals in freshwater sediment: a review of the literature and an assessment of research needs ", In: Metal Ecotoxicology: Concepts and Application, Lewis Publishers, Chelsea, Michigan, USA, pp.243-260, 1991.
- Murrell M.C., and Hollibaugh J.T. (2000). Distribution and composition of dissolved and particulate organic carbon in northern San Francisco Bay during low flow conditions. Estuar. Coast. Shelf Sci. 51, 75-90.
- Mulligan C.N., Yong R.N. and Gibbs B.F. " Remediation technologies for metal-contaminated soils and groundwater: an evaluation ", Eng. Geol., 60, pp.193-207,2001.
- Nelson D.W. and Sommer L.E. " Total carbon, organic carbon and organic matter ", In: Page, A.L. (Eds.). Methods of Soil Analysis, Part 2, Chemical and Microbiological properties. American Society of Agronomy, Madison, Wisconsin, U.S.A., pp.538-580, 1982.
- Noel R. Krieg, John G. Hol, bacteria, " Bergy's Manual of Systematic Bacteriology ", pp.1845, 1984.
- Olver J.W., Kreye W.C. and King P.H. " Heavy metal release by chlorine oxidation of sludge ", J. Wat. Pollut. Control Fed, 47, pp.2490-2497, 1975.
- Pardo R., Barrado E., Perez L. and Vega M. " Determination and speciation of heavy metal in sediment of the Pisuerga river ", Wat. Res., 24, pp. 337-343, 1990.
- Perez-Cid B., Lavilla I. and Bendicho C. " Speeding up of a three-stage sequential extraction method for metal speciation using focused ultrasound ", Analytica Chimica Acta, 360, pp.35-41, 1998.
- Raad A.A. " Manual on soil sampling and methods of analysis ", in J. A. McKeague (ed). Soc. Soil Sci., Ottawa. ON., 1978.
- Ramos L., Hernandez L.M. and Gonzalez M.J. " Sequential fractionation of copper, lead, cadmium and zinc in soils or near Donana National Park ",J. Environ. Qual., 23, pp.50-57, 1994.
- Richard L. Jenkins, Benjamin J. Scheybeler, Marvin L. Smith, Rodger Baird, Mingon P. Lo and Roger T. Haug " Metal removal and recovery from municipal sludge ", J. Wat. Pollut. Control Fed., 53, pp.25-32, 1981.
- van Ryssen R., Leermakers M.and Baeyens W. " The mobilization potential of trac metals in aquatic sediments as a tool for sediment quality classification ", Environ. Sci. Policy , 2, pp.75-86,1999.
- Rauret G. " Extraction procedures for the determination of heavy metals in contaminated soil and sediment ", Talanta, 46, pp.449-455, 1998.
- Schönborn W. and Hartmann H. " Bacterial leaching of metals from sewage sludge ", Eur. J. appl. Microbiol. Biotechnol., 5, pp.305-313, 1978.
- Seidel H., Ondrusch K. J., Morgenstern P. and Stottmeister U. " Bioleaching of heavy metals from

- contaminated aquatic sediments using indigenous sulfur-oxidizing bacteria : a feasibility study
“ International Conference on Contaminated Sediments, Preprints, Vol. I, pp.420-427, 1997.
- Seidel A., Zimmels Y. and Armon R. “ Mechanism of bioleaching of coal fly ash by *Thiobacillus thiooxidants* ” , Chem. Eng. J., 837, pp.123-130, 2001.
- Shea D. “ Developing national sediment quality criteria ” , Environ. Sci. Technol., 102, pp.313-328, 1988.
- Silva I.S., Abate G., Lichtig J., and Masini J.C.(2002). Heavy metal distribution in recent sediments of the Tiete-Pinheiros river system in Sao Paulo state, Brazil. *Appl. Geochem.* **17**, 105-116.
- Sims J.T., S.E. Heckendorn, 1991, Methods of Soil Analysis, University of Delaware, College of Agricultural Sciences. Soil Testing Laboratory.
- Singh S.P., Tack F.M. and Verloo M.G. “ Heavy metal fractionation and extractability in dredged sediment derived surface soils ” , Wat. Air Soil Pollut., 22, pp.1256-1261, 1998.
- Sreekrishnan T.R., Tyagi R.D., Blais J.F. and Campbell P.G.C. “ Kinetics of heavy metal bioleaching from sewage sludge - I. effects of process parameters ” , Wat. Res., 27, pp.1641-1651, 1993.
- Sreekrishnan T.R. and Tyagi R.D. “ Sensitivity of metal-bioleaching operation to process variables ” , Proc. Biochem., 30, pp.69-80, 1995.
- Sreekrishnan T.R., Tyagi R.D., Blais J.F., Meunier N. and Campbell P.G.C. “ Effect of sulfur concentration on sludge acification during the SSDML process s ” , Wat. Res., 30, pp.2278-2738, 1996.
- Tsai L. J., Yu K.C., Chang J.S. and Ho S.T. “ Fractionation of heavy metals in sediment cores from the Ell-Ren river, Taiwan ” Wat. Sci. Technol., 37, pp. 217-224, 1998.
- Tsai L.J., Yu K.C., Huang J.S., and Ho S.T. (2002). Distribution of heavy metals in contaminated river sediments. *J. Environ. Sci. and Health. Part A Toxic/Hazardous Substances & Environmental Engineering*, **A37(8)**,1421-1439.
- Tessier A., Gampbell P., and Bisson M. “ Sequential Extraction Procedure for the Speciation of Particulate Trace Metals ” , Anal. Chem., 51, pp. 844-851, 1979.
- Tessier A., Rapin F. and Carignan R. “Trace metals in oxic lake sediments: possible adsorption onto iron oxyhydroxides”, Geochim. Cosmochim. Acta., 47, pp.1091 -1098, 1985.
- Tessier A. and Campbell P.G.C. “Partitioning of trace metals in sediment and it relationship to their accumulation in benthic organisms”, In metal speciation in the Environment, eds Broekaert J. A. C., Gucer S. and Adams F., Springer, Berlin, Germany, pp.545 -563, 1990.
- Tyagi R.D. and Couillard D. “Bacterial leaching of metals from digested sewage sludge”, Proc. Biochem., 22, pp.114 -117, 1987.
- Tyagi R.D., Couillard D. and Tran F.T. “Heavy metals removal from anaerobically digested sludge by chemical and microbiological methods”, Environ. Pollut., 50, pp.295 -316, 1988.
- Tyagi R.D. and Couillard D. “Bacterial leaching of metals from sludge” , In Encyclopedia of

Environmental Control Technology. (Edited by Cheremisinoff P. E.). Library of environmental Pollution control Technology, Gulf Publishing Co., Texas, Vol. 3, pp. 557-591, 1989.

Tyagi R.D., Couillard D. and Tran F.T. " Studies on microbial leaching of heavy metals from municipal sludge " , Wat. Sci. Technol., 22, pp.229-238, 1990.

Tyagi R.D., Couillard D. and Grenier Y. " Effects of medium composition on the bacterial leaching of metals from digested sludge " , Environ. Pollut., 71, pp.57-67, 1991.

Tyagi R.D. and Tran F.T. " Microbial leaching of metals from digested sewage sludge in continuous system " , Environ. Technol. Letters, 12, pp.303-312, 1991.

Tyagi R.D., Blais J.F., Auclair J.C. and Meunier N. " Bacterial leaching of toxic metals from municipal sludge: influence of sludge characteristics " , Wat. Environ. Res., 65, pp.196-204, 1993.

Tyagi R.D., Sreekrishnan T.R., Blais J.F. and Campbell P.G.C. " Kinetics of heavy metal bioleaching from sewage sludge - III. temperature effects " , Wat. Res., 28, pp. 2367-2375, 1994.

Tyagi R.D., Meunier N. and Blais J.F. " Simultaneous sewage sludge digestion and metal leaching - effect of temperature " , Appl. Microbiol. Biotechnol., 46, pp.422-431, 1996.

Tyagi R.D., Blais J.F., Meunier N., and Benmoussa H. " Simultaneous sewage sludge digestion and metal leaching - effect of sludge solids concentration " , Wat. Res., 31, pp.105-118, 1997.

U.S. EPA, " Guide to Disposal of Chemically Stabilized and Solidified Wastes " , SW-872 Office of Solid Waste and Emergency Response , Washington, DC, 1982.

U.S. EPA, " Selecting Remediation Techniques for Contaminated Sediment " , EPA-823-B93-001 U.S. Environmental Protection Agency, 1993.

U.S. EPA, " EPA ' s Contaminated Sediment Management Strategy " , EPA-823-R-98-001 U.S. Environmental Protection Agency, 1998.

Warran L.A. and Zimmerman A.P. " Trace metal-suspended particulate matter associations in a fluvial system: physical and chemical influences " ,In : Particulate Matter and Aquatic Contaminants, ed. S. S. Rao, Lewis Publishers, Chelsea, MI, USA, pp.127-155,1993.

Wong L. and Henry J.G. " Bacterial leaching of heavy metals from anaerobically digested sludge " , Wat. Pollut. Res. J. Can., 18, pp.151-162, 1983.

Wong L. and Henry J.G. " Decontaminating biological sludge for agricultural use " , Wat. Sci. Technol., 17, pp.575-586, 1984.

Wong L. and Henry J.G. " Bacterial leaching of heavy metals from anaerobically digested sludge " , In Biotreatment Systems (Edited by Wise, D.L.) CRC Press Inc., Bocca Raton, Florida, pp.125-169, 1988.

Xiang L., Chan L.C. and Wong J.W.C. " Removal of heavy metals from anaerobically digested sewage sludge by isolated indigenous iron-oxidizing bacteria " ,Chemosphere, 41, pp.283-287, 2000.

Yu K.C., Ho S.T., Chang J.K. and Lai S.D. " Multivariate correlation of water quality, sediment and benthic bio-community components in Ell-Ren river system, Taiwan " , Wat. Air and Soil Pollut., 84, pp.31-49, 1995.

- Yu K.C., Ho S.T., Tasi L.J., Chang J.S. and Lee S.Z. " Remobilization of zinc from Ell-Ren river sediment fractions affected by EDTA, DTPA and EGTA " ,Wat. Sci. Tech., 34, pp.125-132, 1996.
- Yu K.C., Ho S.T., Chang J.S. and Tasi L.J. " Remobilizations of lead, nickel and copper from Ell-Ren river sediment fractions affected by EDTA, DTPA and EGTA " ,Toxicol. and Environ. Chem., 58, pp.85-101, 1997.
- Yu K.C., Ho S.T., Tsai L.J., Hong M.Y., Chang J.S., and Chang J.K. " Assessing the toxicity of heavy metals in the ELL-REN river sediment by using acid volatile sulfide and simultaneously extracted metal " , 3rd IWA Specialized Conference on Hazard Assessment and Control of Environments, Otsu, Japan, 1999.



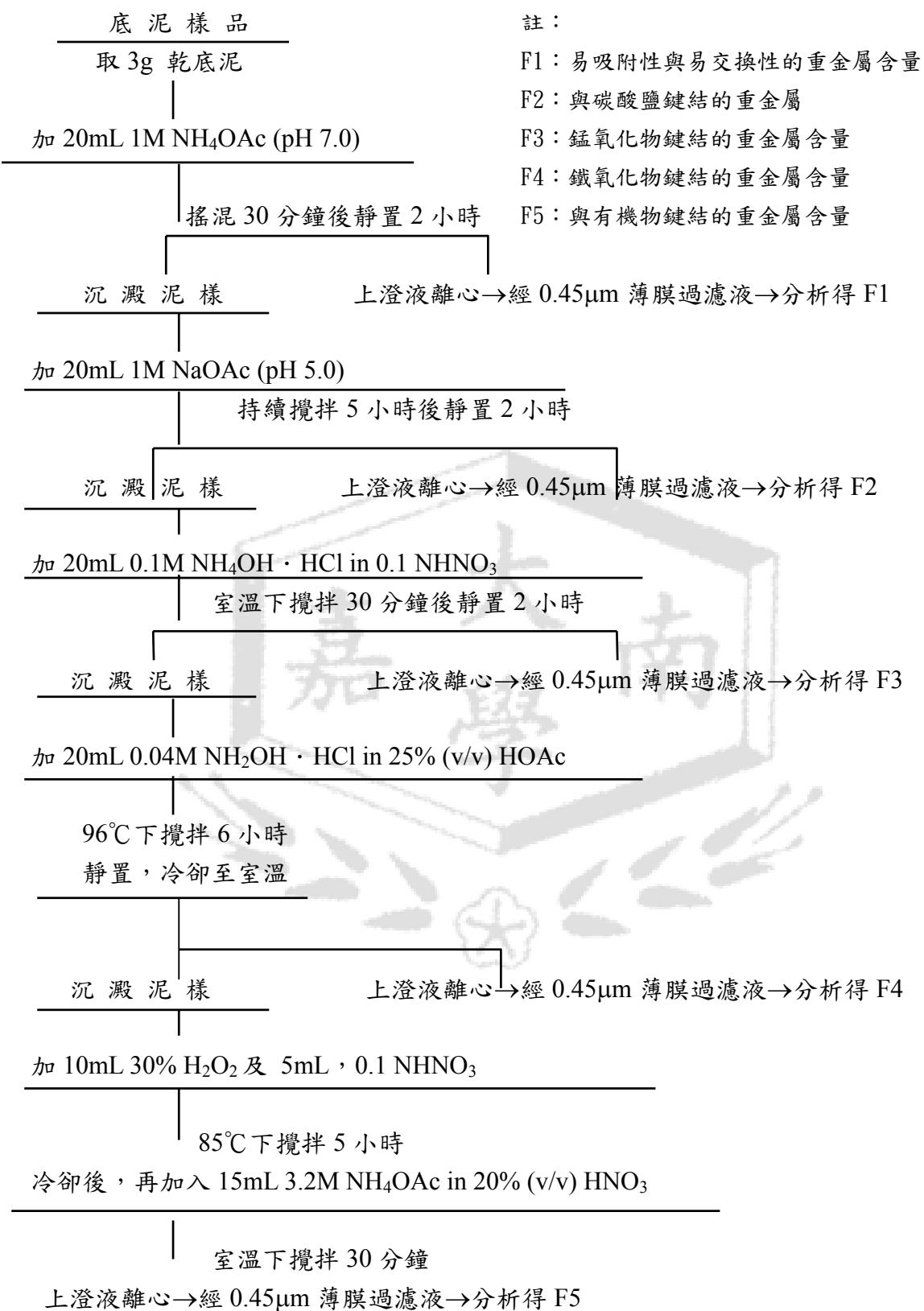


圖 1 逐步萃取法(SEP)

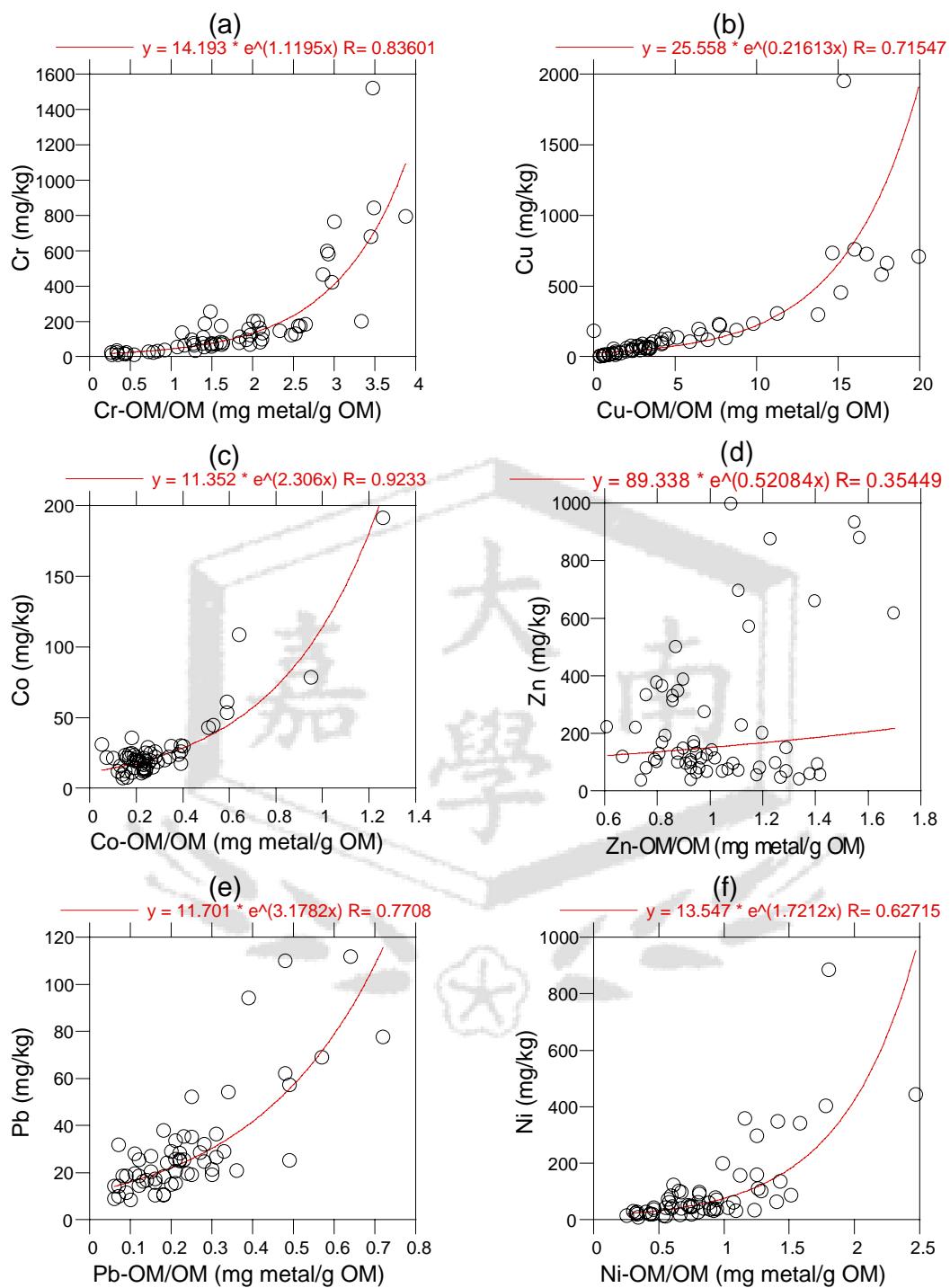


圖 2. Correlations between aqua-regia extractable heavy metals and metal bound to OM in per unit weight OM at sediment matrices from the Yenshui River (a) Cr, (b) Cu, (c) Co, (d) Zn, (e) Pb, and (f) Ni.

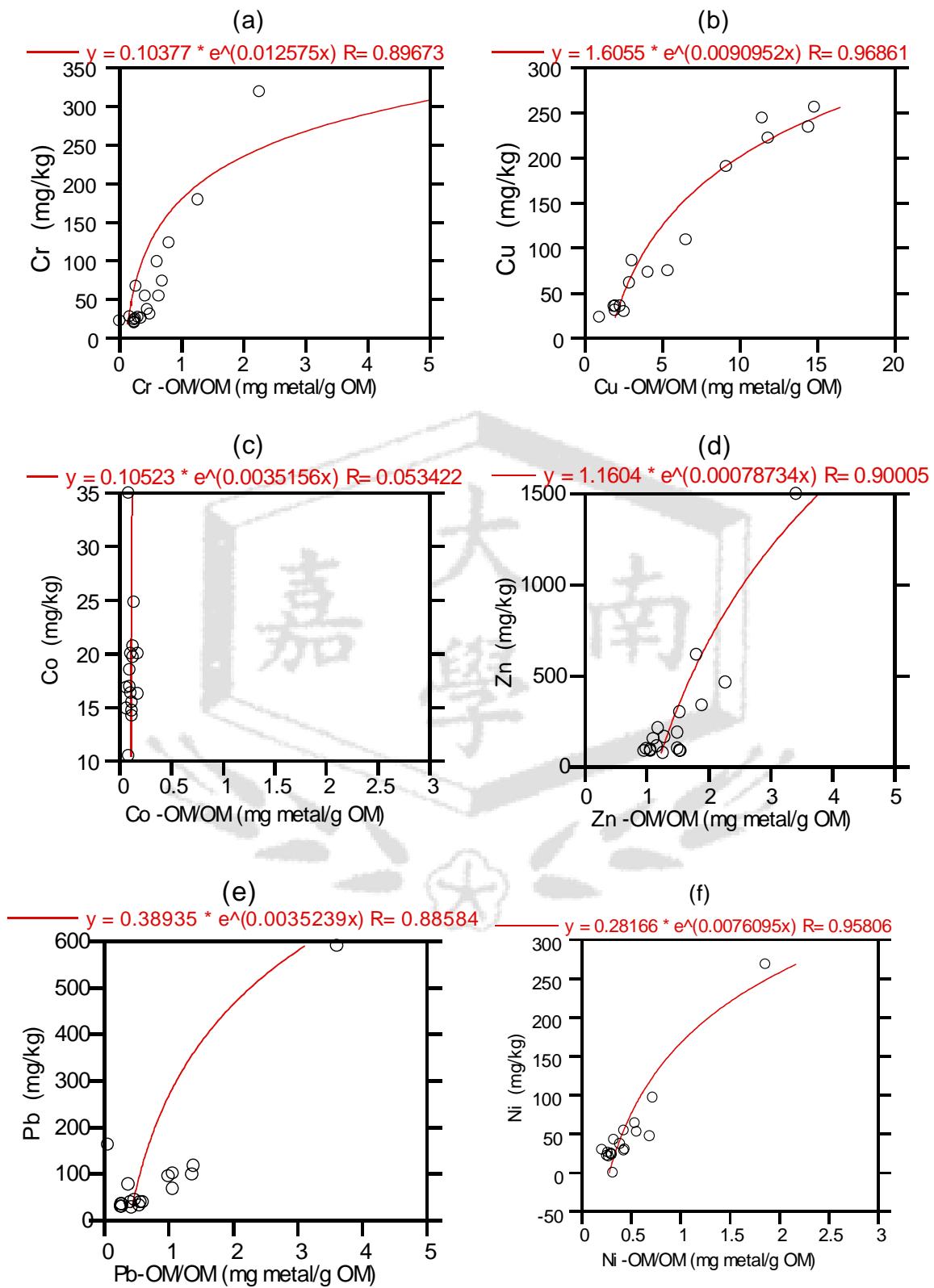


圖 3. Correlations between aqua-regia extractable heavy metals and metal bound to OM in per unit weight OM at sediment matrices from the Ell-ren River (a) Cr, (b) Cu, (c) Co, (d) Zn, (e) Pb, and (f) Ni.

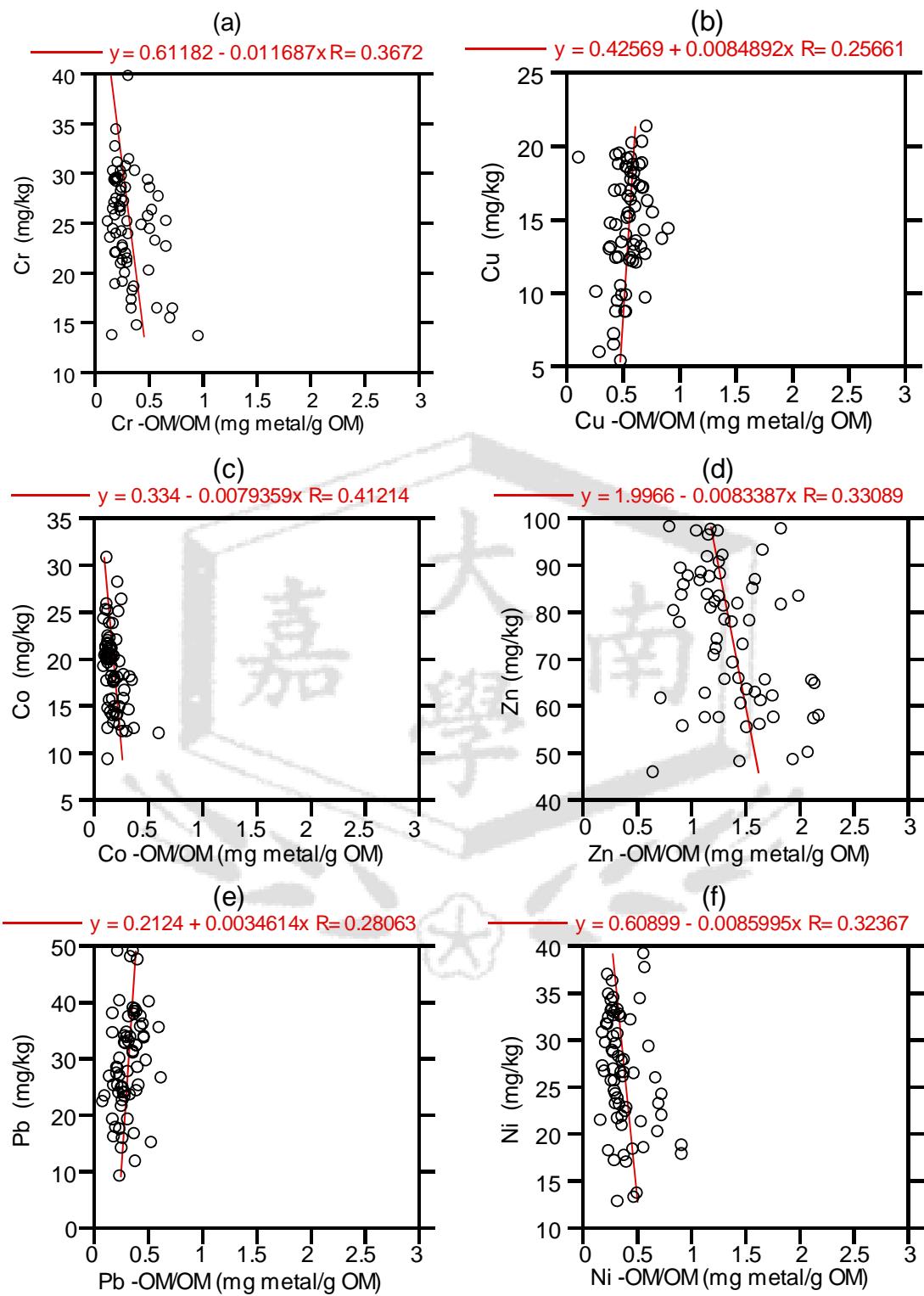


圖 4. Correlations between aqua-regia extractable heavy metals and metal bound to OM in per unit weight OM at sediment matrices from the Tsengwen River
(a) Cr, (b) Cu, (c) Co, (d) Zn, (e) Pb, and (f) Ni.

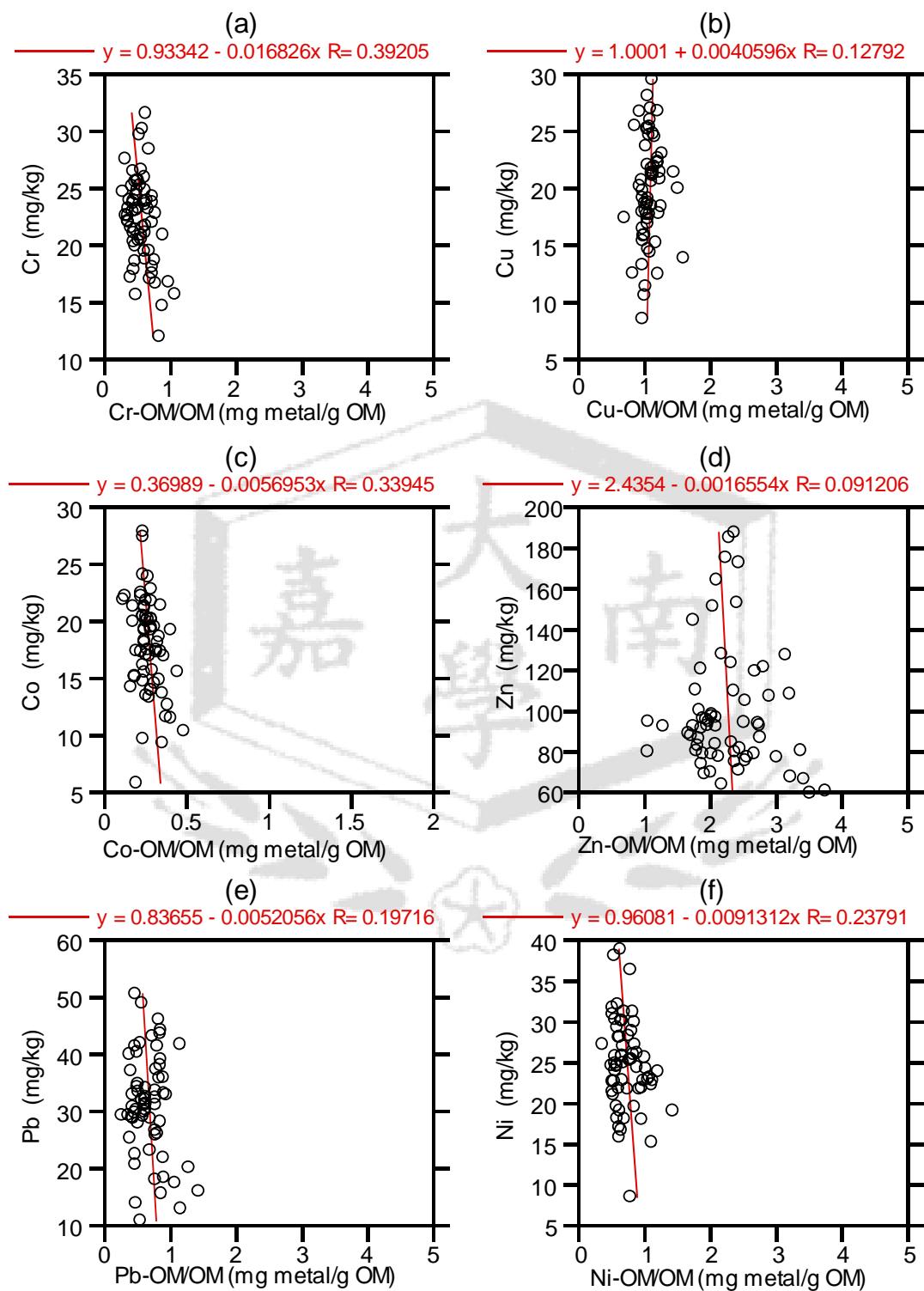


圖 5. Correlations between aqua-regia extractable heavy metals and metal bound to OM in per unit weight OM at sediment matrices from the Peikang River (a) Cr, (b) Cu, (c) Co, (d) Zn, (e) Pb, and (f) Ni.

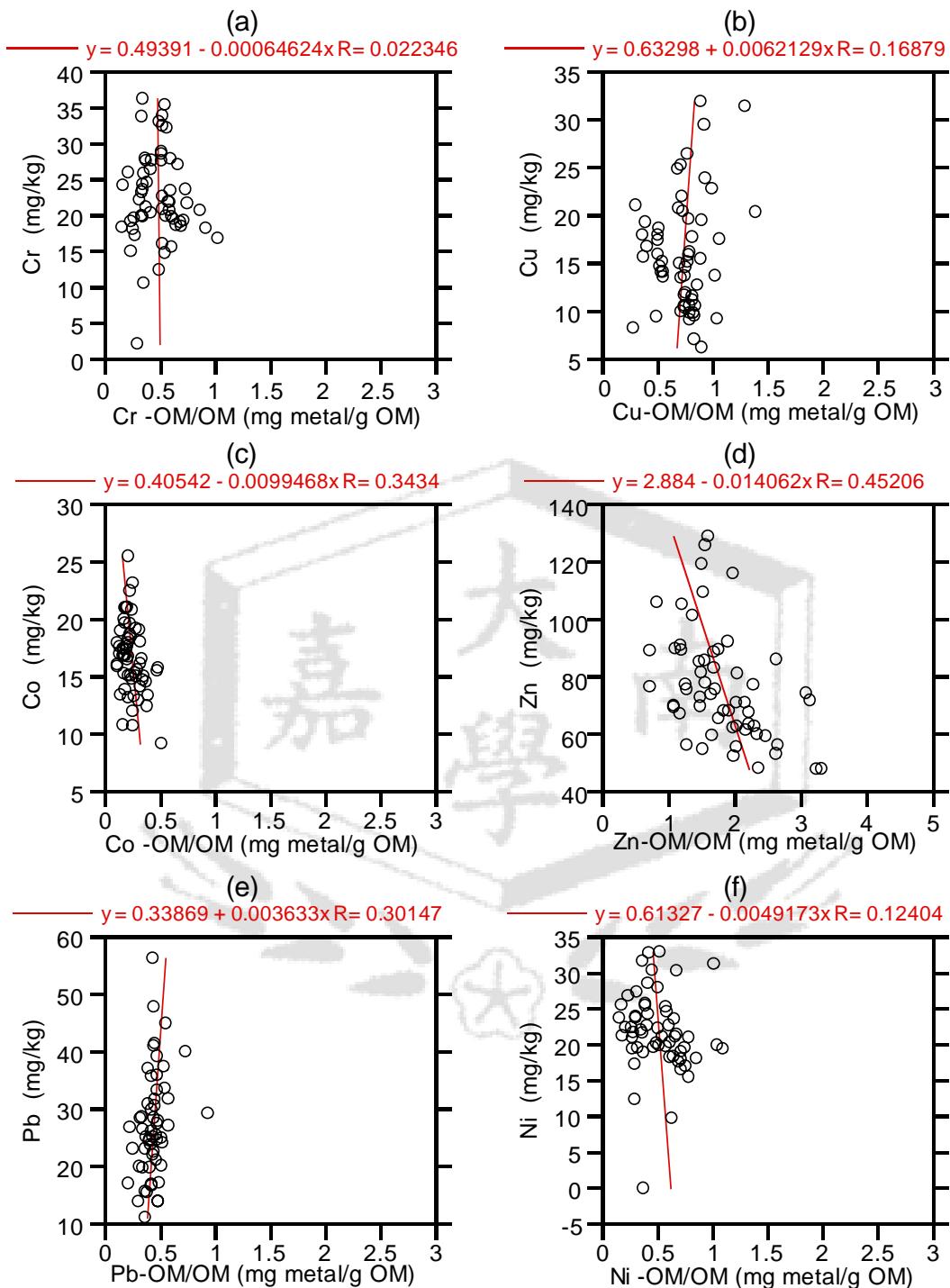


圖 6. Correlations between aqua-regia extractable heavy metals and metal bound to OM in per unit weight OM at sediment matrices from the Chishui River (a) Cr, (b) Cu, (c) Co, (d) Zn, (e) Pb, and (f) Ni.

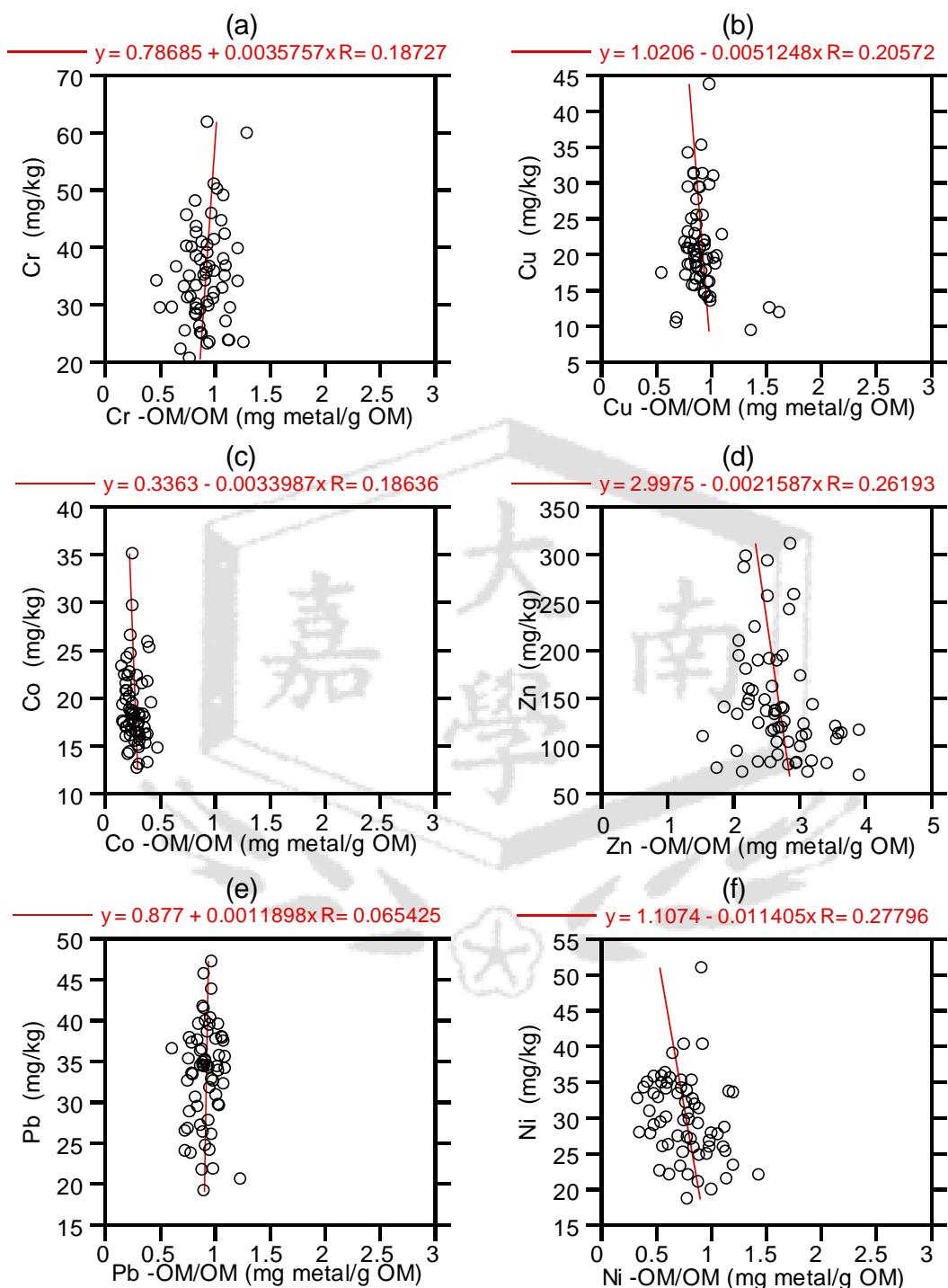


圖 7. Correlations between aqua-regia extractable heavy metals and metal bound to OM in per unit weight OM at sediment matrices from the Potzu River (a) Cr, (b) Cu, (c) Co, (d) Zn, (e) Pb, and (f) Ni.