

## **Anthropogenic effects on sediment quality offshore southwestern Taiwan: Assessing the sediment core geochemical record**

Kandasamy Selvaraj<sup>a, b\*</sup>, Gopal Partiban<sup>b, c</sup>, Chen-Tung Arthur Chen<sup>b</sup>, Jiann-Yuh Lou<sup>d</sup>

<sup>a</sup> Research Center for Environmental Changes, Academia Sinica, Taipei 115, Taiwan

<sup>b</sup> Institute of Marine Geology and Chemistry, National Sun Yat-sen University, Kaohsiung 804, Taiwan

<sup>c</sup> National Institute of Oceanography, Dona Paula, Goa, India

<sup>d</sup> Department of Marine Science, Naval Academy, P.O.Box 90175, Kaohsiung, Taiwan

\*Corresponding author. Tel.: +886-2-2653-9885 ext. 280; fax: +886-2-2783-3584.

E-mail addresses: ksraj@gate.sinica.edu.tw; kselva8@yahoo.com

### **ABSTRACT**

Slag material was dumped in two sites off southwestern Taiwan by the China Steel Corporation during 1984-1995. By geochemically analyzing four sediment cores, we investigate the impact of slag on the sediment chemistry. Elemental profiles from the dumping sites show a strong depletion in detrital elements and enrichment in alkaline and redox-sensitive elements, especially for the top ~20 cm of sediments. The relative enrichment factor ( $EF_{rel}$ ) exhibits wider range for Ca (0.73-13.33), Fe (0.88-3.03), Mg (0.94-9.58), and Mn (1.22-33.30) due to contamination of sediments by slag. Sediment weathering indicators also show a distinct change with lower values in sediments influenced by dumping due to Ca and Sr addition. Higher  $EF_{rel}$  for As, Cd and Pb in the top sections of the cores indicate an additional modern/industrial input of these elements since ~1950. Our study suggests that slag dumping may have a localized effect on biogeochemical processes by inducing the diagenetic remobilization of certain elements.

*Keywords:* Sediment quality, Detrital dilution, Metal enrichment, Industrial slag, Waste dumping, Southwestern Taiwan

## 1. Introduction

The geochemical composition of estuarine and coastal marine sediments is largely governed by the physicochemical characteristics (pH,  $E_h$ ,  $O_2$ , etc.) of the depositional environment and associated natural biogeochemical processes such as diagenesis, adsorption/desorption on/from organic matter, and precipitation-dissolution of Fe-Mn oxyhydroxides (e.g. Berner, 1980). Nevertheless, since the 1950s, elemental concentrations in sediments deposited near major cities and harbor areas have been significantly influenced by various contaminants/wastes produced through modern human and industrial activities. Determination of anthropogenic impact from those of natural processes on sedimentary composition is essential for environmental monitoring studies because sediments are very sensitive and reliable recorders of both natural and anthropogenic source contributions at accurately detectable levels (Förstner and Wittmann, 1981; Szefer, 2002). The spatial and temporal geochemical records of sediments are thus deemed to be vital to evaluate recent contamination levels and pollution histories within estuarine, coastal and shelf regions world-wide (Szefer et al., 1995; Zwolsman et al., 1996; Nolting et al., 1999; Selvaraj et al., 2004).

Coastal and offshore regions of southwestern Taiwan (Fig. 1) annually receive  $\sim 35$  million tons ( $Mt\ yr^{-1}$ ) of chemically weathered sediments from the high mountains of Taiwan and the upper crust of the Yangtze Craton (UC-YC, China), mainly through river input and substantially by aeolian pathways. With nearly  $36,000\ km^2$  of land and a population over  $\sim 23$  million, Taiwan generated  $\sim 1.6$  Mt of domestic and industrial wastes in the year 2000, primarily from factories, farming activities, hospitals and other major business organizations, which increased the heavy metals and organics loads in natural environments (Tsai and Chou, 2004). The steel industries, in particular, play an important role in the island's economic development and are equally responsible for producing an appreciable quantity of solid waste, i.e.,  $\sim 420\ kg\ ton^{-1}$  of steel production (Topkaya et al., 2004). The China Steel Corporation, the largest producer of steel in Taiwan, used the offshore region of southwestern Taiwan as their solid waste disposal site from 1984 to 1995 (Fig. 1). During this time period,  $\sim 2$  Mt of slag were dumped in the old dumping site (Fig. 1) located approximately 14 km from Kaohsiung Harbor (Chou et al., 2002). Since 1988, in the establishment of the island's strict Environmental Pollution Prevention regulations, dumping activities were shifted to a new site (documentation data are not available for this site), located  $\sim 14$  km from the old one (Fig. 1). Marine waste disposals induce water column turbidity changes, seabed smothering effects and sediment contamination, which all in turn affect the habitat

characteristics, food chain integrity and ultimately fishery resources (e.g. Johnson and Frid, 1995). Most importantly, the bed sediment is disturbed and brought from anoxic to oxic conditions by dumping of higher density materials such as steel slag. Such a disturbance can alter the sediment characteristics by affecting the ongoing biogeochemical processes; as a result, sediment can act either as a sink or a pollutant source for the overlying water column (Standing et al., 2002).

In order to investigate the impact of slag material on the sediment chemistry, extensive seabed monitoring surveys at a high spatial resolution were conducted in and around slag dumping sites as well as in the region near Kaohsiung Harbor during 1995. This work was done based on the assumption that the dumped material is characterized by a higher density than the surrounding sediment dominated by mud (silt + clay) and helped us to follow the sediment layers in the topmost tens of cm of the sediment column for selecting suitable core sampling locations. During the program, twelve short gravity sediment cores were raised from the seabed in the former region. Here, we present the results of a detailed geochemical evaluation of four sediment cores, CS12, CS14, CS19 and CS21. Among them, core CS19 was dated by the  $^{210}\text{Pb}$  method to infer the recent history of contamination with respect to pre-industrialization in Taiwan, i.e., before 1950. The analyzed dataset was used to investigate (a) the anthropogenic contribution from the provenance contribution; (b) the contaminant inventory compared to the regional background; (c) the geochemical processes responsible for the mobility of elements and/or dispersion of contaminants; and (d) the geochemical factors responsible for the interrelationships among chemical parameters studied through a statistical approach.

## **2. Materials and methods**

### *2.1. Study area and sampling*

The study area off of southwestern Taiwan occupies 70 km<sup>2</sup> east of Kaohsiung Harbor at water depths of ca. 100-400 m (Fig. 1). During 1995, on the basis of high resolution sediment acoustic profiling, 12 stations were sampled from the region with the help of a 2-m single-tube gravity corer available onboard the *R/V Ocean Researcher 3* (Cruise No. 274). The collected cores were capped, sealed airtight and frozen before they were brought back to the shore laboratory for further investigation. Four of the cores (CS12, CS14, CS19 and CS21; see Fig. 1 for sampled locations) were selected site-specifically for detailed grain size and geochemical analyses of major and trace elements. All cores were sliced at 1-2 cm intervals down to 10 cm depth and 2, 5 and 10 cm intervals were applied for the

remaining length of the cores. Details of the investigated cores, including the number of sub-samples in each core, are given in Table 1.

## 2.2. *Grain size and elemental analyses*

Prior to the detailed laboratory work, all 77 sub-samples were freeze-dried for 24-h to achieve a constant weight and homogenized (removal of particles >2 mm). Grain size analysis was carried out on a part of each homogenized sample using a Coulter LS-100 laser particle size analyzer after removal of carbonate with 1 N HCl and organic matter using 30% H<sub>2</sub>O<sub>2</sub>. Another portion of each sediment sample was finely ground to ~200-mesh in an agate mortar and pestle for elemental (C and N) and geochemical analyses. For elemental analysis, the sub-samples of bulk sediments (<2 mm) were oven-dried at 60°C, homogenized and finely powdered by using an agate mortar. Total carbon (TC) and nitrogen (TN) were determined by using a LECO CHN-932 elemental analyzer. The instrument was calibrated with reference standards, BCSS-1 and NIST-2704, and triplicate analyses of standards as well as samples yielded a precision better than 5%. Inorganic carbon (IC) was measured after liberating CO<sub>2</sub> with 1N HCl and measuring its concentration with a UIC Coulometer. The analytical accuracy and precision were better than 5%. The IC was converted to calcium carbonate by multiplying its value by 8.333. Organic carbon (OC) was calculated as the difference between TC and IC.

## 2.3. *Geochemical analysis of sediments*

The total concentrations of 22 major and trace elements (Al, As, Ca, Cd, Cl, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Rb, S, Si, Sr, Ti, V and Zn) were determined using an X-ray fluorescence (XRF) spectrometer (Rigaku RIX2000) equipped with an Rh tube. For this study, 2-3 grams of each sediment powder were compacted into a round disc (30 mm diameter) under appropriate pressure with cellulose as the backing. These pellets were X-rayed with the measurement was carried out at an acceleration voltage of 50 kV and a current of 50 mA. The accuracy of the analytical method was established with the standard reference materials (SRMs) MAG-1, BCSS-1, PACS-1, NIES-2, and GBW 07314. Based on the analyses of SRMs, the ranges of recoveries in percentage of all the elements analyzed are as follows: Al (97-105), As (77-110), Ca (97-105), Cd (91-110), Cl (90-105), Cr (95-103), Cu (95-105), Fe (96-102), K (97-105), Mg (95-98), Mn (98-106), Na (91-105), Ni (95-105), P (92-103), Pb (93-108), S (95-107), Si (94-100), Ti (96-106), V (91-110) and Zn (99-105). Three replicates of one sample were run and the following coefficient of variation obtained in percentage: Al, 0.44; As, 2.04; Ca, 0.76; Cd,

7.02; Cl, 0.38; Cr, 5.97; Cu, 0.95; Fe, 0.43; K, 0.58; Mg, 0.84; Mn, 0.60; Na, 4.97; Ni, 1.86; P, 0.29; Pb, 3.04; S, 0.34, Si, 0.58; Ti, 0.39; V, 6.13 and Zn, 2.22. The detection limits of XRF for major and trace elements obtained in the present work are as follows: Al, 0.07%; As, 4  $\mu\text{g g}^{-1}$ ; Ca, 0.06%; Cd, 5  $\mu\text{g g}^{-1}$ ; Cl, 0.01%; Cr, 2.6  $\mu\text{g g}^{-1}$ ; Cu, 2.7  $\mu\text{g g}^{-1}$ ; Fe, 0.06%; K, 0.03%; Mg, 0.02%; Mn, 39  $\mu\text{g g}^{-1}$ ; Na, 0.02%; Ni, 3.5  $\mu\text{g g}^{-1}$ ; P, 131  $\mu\text{g g}^{-1}$ ; Pb, 6  $\mu\text{g g}^{-1}$ ; Rb, 2.1  $\mu\text{g g}^{-1}$ ; S, 0.01%; Si, 0.13%; Sr, 4.6  $\mu\text{g g}^{-1}$ ; Ti, 0.01%; V, 8.8  $\mu\text{g g}^{-1}$  and Zn, 8.2  $\mu\text{g g}^{-1}$

Since the accuracies of the elements of sufficient anthropogenic input such as As, Cd and Pb with XRF are not enough to discriminate the contaminant inventory because their concentrations in sediments studied were mostly below the detection limits of XRF, these three elements were also measured with an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS; PE-SCIEX ELAN 5000). For each bulk sediment sample, 0.3 g of powder were reacted with 20 ml of 1.6 N  $\text{HNO}_3$  for 24 h and centrifuged to obtain the clear supernatant. These leachates were analyzed for As, Cd and Pb with an ICP-MS and these values are used for further discussion. The ranges of recovery and RSD for MAG-1, BCSS-1, PACS-1, MESS-2, NIES-2 and GBW07314 reference materials analysis of As, Cd and Pb were determined to be 90-110% and 5% for As, 94-106% and 5% for Cd, and 91-109% and 5% for Pb.

#### 2.4. $^{210}\text{Pb}$ geochronology

The age-depth relationship in core CS19 was calculated using the short-lived isotope  $^{210}\text{Pb}$  ( $t_{1/2} = 22.3$  years), a natural radionuclide byproduct of the  $^{238}\text{U}$  decay series that is supplied to the environment via atmospheric precipitation. This is an ideal tracer for dating the modern sediments deposited during the last 100 years, a period of time during which detectable geochemical changes occurred due to modern industrial and human activities (Ruiz-Fernández and Hillaire-Marcel, 2009).  $^{210}\text{Pb}$  measurements were carried out on sediment samples by beta counting of the ingrown  $^{210}\text{Bi}$ , the energetic beta emitter of  $^{210}\text{Pb}$  daughter, as described in Chung and Craig (1983). Sediment samples were digested with appropriate combination  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HF}$  and  $\text{HClO}_4$ , instead of  $\text{HNO}_3$  alone. The digested aliquot was purified for Pb isotopes through an anion exchange column and finally precipitated as  $\text{PbSO}_4$  onto an aluminum disc and stored for 1 month before beta counting of the ingrown  $^{210}\text{Bi}$ . The counter used was Tennelec  $\alpha/\beta$  LB 51200-2800-II low-background beta counting system which was calibrated against a  $^{210}\text{Pb}$  standard. The sedimentation rate was calculated to be 0.74  $\text{cm yr}^{-1}$  in the top 8.5 cm section of the core CS19 (Fig. 2), which corresponds to a short period of 11 years from 1985 to 1995 and brackets

the time period of dumping activity at the old dumping site from which this core was retrieved. From 8.5 and up to 52.5 cm, the core CS19 shows a low background sedimentation rate of  $0.19 \text{ cm yr}^{-1}$ . This supports the idea that the top portion of the core was significantly influenced by slag materials and therefore had a higher sedimentation rate. In the active continental margins such as southwestern Taiwan, the dynamics of high mountain erosion coupled with the huge export of full spectrum of critical zone components at least during typhoon season as well as the prevailing strong current patterns, one cannot expect a constant sedimentation pattern. However, the limited downcore variations of major and trace elements of detrital nature permit us to assume the constant sedimentation rates for older sections over 100 years. In that case, the 52.5 cm core CS19 roughly corresponds to the period of sedimentation from 1753 to 1995, which also covers the time of modern industrial establishment in Taiwan (i.e., 1950s).

### 2.5. *Enrichment factor and statistical analysis*

In order to accurately reconstruct the history of trace elements deposition and metal contamination, down-core elemental values should be normalized for natural variability caused by provenance weathering. Geochemical normalization of estuarine and coastal sediments can be achieved from depth-equivalent concentrations of crustal reference elements such as Al (Windom et al., 1989), Li (Loring, 1991) and Yb (Szefer et al., 1999; Szefer, 2002). Among these, Al is a conservative element that can compensate for variations in both grain size and composition as it characterizes the detrital metal-bearing sedimentary matrix such as silt and clay. Since sediments investigated composed chiefly of silt and clay, and anthropogenic input of Al are never reported in the study region, in order to identify trace element enrichment in southwestern Taiwan, we calculated a relative enrichment factor ( $EF_{rel}$ ) using Al as a normalization tracer employing the formula:  $EF = [Z/Al]_{sample}/[Z/Al]_{BCL}$ , where  $[Z/Al]_{sample}$  is the ratio of the concentration of the element Z to the concentration of Al in the sample at a given depth, and  $[Z/Al]_{BCL}$  is the ratio of background concentration level (BCL - mean value taken from the bottom three sub-samples of the respective cores) of elements Z and Al in the studied cores.

In the present study, the metal concentration levels vary widely due to multiple sources contribution. Therefore, statistical methods such as correlation analysis and principal component analysis (PCA) were performed in order to obtain information about the interrelationships and behavior of major and trace elements, as well as to identify the associations among 28 variables in all sediment

cores studied to corroborate the element/metal provenance. The computer package SPSS (version 7.5) was employed to perform the statistical analyses. The rotation of the principal component was carried out by the Varimax normalized method and only the variables that showed loadings  $\geq 0.7$  were considered for provenance interpretation.

### **3. Results and discussion**

#### *3.1. Sediment characteristics*

Mean sediment grain sizes ( $M_z$ ) of all four cores (CS12: 8.05-44.8  $\mu\text{m}$ ; CS-14: 5.05-10.2  $\mu\text{m}$ ; CS-19: 8.9-30.8  $\mu\text{m}$ ; and CS21: 12.2-36.3  $\mu\text{m}$ ) fall under the fine, medium and coarse silts categories of Wentworth (1922) size classification. The corresponding phi values (7-4  $\phi$ ) indicate very poorly to extremely poorly sorted sediments due to quick removal and deposition of sediments from the source to the sink. Characteristically, four samples from 2.5 to 5.5 cm in core CS19 and one sample at 9.5 cm in core CS12 show abnormally high  $M_z$  (265-377 and 114  $\mu\text{m}$ ). Since both cores were from dumping sites, these larger mean grain sizes suggest the influence of medium to coarse sand-sized slag tailings rather than real sediments. The mean  $\text{CaCO}_3$  contents of all four cores range from 2.23 to 5.69%, with higher carbonate contents associated with the top few samples in dumping site cores CS12 and CS19, as well as the surface sediment of core CS21. The mean contents of OC and TN in the studied cores are low and vary from 0.30 to 0.60% and from 0.02 to 0.07%, respectively. The calculated molar organic carbon to total nitrogen (C/N) ratio varies from 8 to 22 with a mean of 12 (n=61), although sixteen samples exhibit extremely high C/N ratios due to very low TN contents that are very close and/or even lower than the instrument detection limit (0.02%). The overall mean values of OC, TN and C/N ratio (0.46%, 0.04% and 12, respectively) suggest a mixed origin, terrestrial and marine, for organic matter, with the dominance of the former.

#### *3.2. Major element geochemistry*

Supplementary Table S1 provides a complete set of geochemical data, including mean grain size,  $\text{CaCO}_3$  and OC, for all four sediment cores studied. Also included are elemental data for the upper continental crust (UCC; Taylor and McLennan, 1985), the upper crusts of the Yangtze Craton (UC-YC; Gao et al., 1998) and Kaohsiung offshore sediments (KH-OSS; Chen and Selvaraj, 2008) for comparison. In general, the mean concentrations and element/Al ratios of almost all elements studied agree well with the reference compositions such as UCC, UC-YC and KH-OSS. The major element/Al

ratios of surface sediments in this region are consistent with this, indicating that the upper crust of the Yangtze Craton and sedimentary rocks of Taiwan are major sources for these sediments (Chen and Selvaraj, 2008). X-ray diffraction (XRD) scanning of surface slices of all 12 core sediments showed that sediment particles were mainly composed of a quartz-feldspar-calcite-illite-chlorite-kaolinite assemblage (Chen, 1997). This further implies the dominance of physical erosion and thus very poor sorting of grains.

Depth profiles of representative individual elements show considerable variations (Figs. 3 and 4); for instance, lower values for detrital elements but higher values for authigenic/diagenetic elements in sediments affected exclusively by dumped slag materials in the study area. The detrital elements Al and Ti exhibit a strong positive correlation ( $r = 0.96$ ,  $P < 0.01$ ) to each other as well as other elements such as Si, Na and K, indicating their source as detrital aluminosilicates. Al and Ti are believed to be index elements for the terrigenous source and are extremely immobile in the marine environment (Nath et al., 1989), and both are negatively correlated with authigenic/diagenetic elements (Fe, Mg, Ca, Mn and P), suggesting a strong dilution of the detrital source in the study area (discussed in detail below). Interestingly, in core CS12 from the new dumping site, the sediment at 8.5 cm records the highest Ca concentration (9.87%; Fig. 4) as well as the highest Ca/Al ratio (2.1; not shown). Likewise, Ca exhibits higher concentrations and high element/Al ratios in the top ~10 cm section of core CS19 from the old dumping site (Figs. 3 and 4).

### 3.3. *Detrital dilution and diagenetic enrichment*

Coastal and offshore sediments are mixtures of land-derived aluminosilicates, biogenic components, and authigenic oxyhydroxides precipitates (Calvert et al., 1993). The latter two components, in general, dilute the proportion of land-derived terrigenous material and therefore obliterate the detrital signals primarily produced by them. Figure 4 displays depth profiles of selected detrital (Si, Ti, Al and K) and alkaline elements (Ca and Mg) in sediment cores CS12, CS14, CS19 and CS21. The cores from the reference sites (CS12 and CS14) did show some variations throughout, but strong fluctuations are evident in the top ~20 cm. Elemental fluctuations were strong in core CS21, which was retrieved from deeper water than core CS14, which was raised from a shallow water depth (Table 1). In these cores, decreasing Si and increasing Al and K values from ~70 up to 20 cm suggest the dominance of fine sediment delivery during this interval in the study area. Increasing concentrations



of Mn, P, S, Cu, Cr, Ni and Zn evident in the top ~10-20 cm are concurrent with OC fluctuations, implying the precipitation of Fe-Mn oxyhydroxides and/or metal sulfides and co-precipitation of Cu, Cr, Ni and Zn in the top sections of the core that were in contact with oxygenated bottom waters. In CS14, Cr, Fe, P, Ni, S and Zn all seem to be involved in the above process, but Mn and Cu do not show any such involvement. These elemental associations show that early diagenetic processes are more active at site CS21 than at site CS14.

Nevertheless, the downcore profiles of detrital elements (Si, Ti, Al and K) in sediment core CS19 from the old dumping site display a decreasing trend in sediments deposited between ~9.5 and 3.5 cm, and since then an increasing trend towards the core top is obvious (Fig. 3). There is also a clear strong depletion of all of these detrital elements between 5.5 and 3.5 cm. This reveals that detrital dilution essentially attributed to dumped slag materials at this site. A similar detrital dilution was observed in core CS12 from the new dumping site, where the top ~8 cm consists mainly of slag rather than sediments (Fig. 3). Strikingly, the Cu, Ni and Zn profiles in both cores show a dilution trend (Fig. 3) very similar to the detrital elements, further confirming their silicate lattice association in the study region. It is apparent from Fig. 4 that the alkaline elements (Ca and Mg) in cores from reference sites behave very similarly to the detrital elements, but these elements show abnormal enrichment in the cores from dumping sites, indicating the addition of Ca and Mg through slag dumping. Furthermore, Fig. 4 displays abnormal enrichment in authigenic/diagenetic elements (Mn, P, and S), including trace elements (Cd, Cr, Sr and Zr) in cores from dumping sites. The association of Sr could be explained by the Ca in this group. Characteristically, the association of typical immobile detrital element (Zr) with alkaline and diagenetic elements suggests slag-induced enrichment of Zr, a refractory mineral perhaps used in steel-making processes. ‘Detrital dilution’ and consistent ‘diagenetic enrichment’ are attributed to dumped slag materials because chemical data of recovered slag from core CS12 reveal that slag contains a significant percentage of lime flux with a high CaO content (25.02%; see Supplementary Table 1). Furthermore, higher Ca/Al ratios and a strong positive association of Ca with Fe, Mg, Mn and P (see sub-section 3.7 for correlation values) indicate the contamination of sediments through dumping, which is also responsible for detrital dilution.

### 3.4. *Relative enrichment factors ( $EF_{rel}$ )*

The calculation of  $EF_{rel}$  gives an estimate of sediment enrichment due to either local pollution or changing patterns of atmospheric deposition (Ruiz-Fernández et al., 2004; Selvaraj et al., 2004). Table 2 shows summary statistics of  $EF_{rel}$  values calculated in this study. The  $EF_{rel}$  values obtained in cores from the reference sites are  $>2$  for Cr, Ni, V and Zn in core CS14 and As, Cd, Cr, Cu, Pb, V and Zn in core CS21, suggesting modern and industrial input for these elements. Interestingly, abnormal enrichments in a few top sub-samples show  $EF_{rel}$  values of  $>2$  to 10 for Mn, Mg, Ca, P, S, As, Cr, Sr, V and Zr in the old dumping site core CS19, indicating authigenic mineral formation and coprecipitation of certain trace elements attributed to dumping materials rich in lime flux. Very similar behaviors of Fe and Cd in core CS12 from the new dumping site substantiate the above inference. A recent study indicates that liming of lakes causes increased sequestration of many elements in sediments, including Al, As, Cd, Fe, Mn, Ni and Zn (Wällstedt et al., 2008). A wide range of  $EF_{rel}$  values along with the higher standard deviations shown in Table 2 for these elements in contaminated samples support that they were essentially from an anthropogenic source, i.e., slag dumping.

### 3.5. *Modern chemical weathering*

A recent investigation on sediment yield to the ocean shows that the suspended sediment load ( $17,800 \times 10^{12} \text{ g yr}^{-1}$ ) from high-standing islands (Taiwan, the Philippines, Papua New Guinea and New Zealand) of South Asia-Oceania contributes over 40% (Syvitski et al., 2005). This amount may increase due to the acceleration of erosion and weathering in these islands by modern human and land use practices. Considering the high physical erosion rate of Taiwan ( $1365 \text{ mg cm}^{-2} \text{ y}^{-1}$ ; Li, 1975), one would expect some changes in the rate of chemical weathering, although the chemical weathering trend of this island was moderate, except in the high-alpine regions, for the past few thousand years (Selvaraj and Chen, 2006). It is also important to know the pattern of modern weathering before the reappraisal of sediment quality in terms of dumping and industrialization. To check these aspects, we applied silicate weathering indicators such as the chemical index of alteration (CIA) and the elemental ratios K/Si and Rb/Sr. The CIA was calculated using the major oxides compositions of sediments using the formula:  $CIA = 100 \times Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)$  in molar proportions, where  $CaO^*$  is the CaO associated with only the silicate fraction (Selvaraj and Chen, 2006, and references therein).

According to the  $^{210}\text{Pb}$  chronology, the entire 52.5 cm sedimentation in core CS19 collected from the old dumping site corresponds to the period from ~1753 to 1995, covering the time intervals of both modern industrial growth in Taiwan (~1950-present) and dumping activities in the present study area (1984-1995). The CIA values of all sediments, excluding the sediments affected by dumping, vary narrowly from 73 to 77 (n=65). The depth profile of CIA in core CS19 does not show any distinct change for the last ~225 years of sedimentation, except for the samples between 1969 and 1985 (Fig. 5). The CIA started to decrease in ~1969 and reached the lowest value (32) in ~1977, essentially due to the dominance of slag and thus the dilution of detrital components. Since then, the CIA has increased and attained a value (76) equal to that in the sediments formed pre-1969. In fact, dumping was done between 1984 and 1995, but the  $^{210}\text{Pb}$  chronology of core CS19 reveals the presence of slag-affected sediments at slightly deeper depths between 1969 and 1984, likely due to the sinking of higher density slag a few centimeters deeper in the unconsolidated surface sediments. Given the fact that the dumped materials contain a significant amount of CaO (max. 25.02%), sediment-slag interaction seems to bring down the CIA value to its lowest, as the increase in CaO always estimates lower CIA values.

Similar to the CIA, the K/Si and Rb/Sr ratios are highly depleted in sediments deposited between 1969 and 1985, supporting the effect of slag materials on the chemistry of sediments that contain significant amounts of Sr along with CaO. Increasing trends of all of these indicators in core CS19 from 1977 to 1994, however, suggest a recovery of sediment composition from the effect of slag dumping rather than an actual increase in the chemical weathering of provenance rocks (Fig. 5). All weathering indicators show inconsistent trends in the top ~15 cm, corresponding to the last ~45 years in the sediments of the reference site cores. For instance, the CIA shows an increasing trend, but K/Si decreases since ~1950 in core CS14. Such changes are obvious in ratios of K/Si and Rb/Sr in core CS21 since ~1900, although downcore profiles of these ratios show a slightly increasing trend from ca. 1600 (Fig. 5). Such pattern indicates the combined effect of changes in sediment delivery and early diagenetic processes in the surface unconsolidated sediments in these cores. Especially, sediment delivery which is mostly event-dominated such as typhoon and landslides in Taiwan that probably masks the chemical weathering trend at shorter (decadal-centennial) timescales. For example, Kaoping River, the second largest river in Taiwan (Fig.1), annually discharges ~17 Mt yr<sup>-1</sup> of suspended sediment load, resulting in high sediment accumulation ranging from 0.08 to 1.44 g cm<sup>-2</sup> yr<sup>-1</sup> in the continental margin of southwestern Taiwan (Kao et al., 2006).

### 3.6. *Modern industrial impact*

Dated sediment cores were used to reconstruct the historical metal input in coastal sediments. Here we use well-known elements (As, Cd and Pb) of anthropogenic origin to reconstruct the modern industrial effect on sediment quality. The highest values of As ( $3.83 \mu\text{g g}^{-1}$ ), Cd ( $0.399 \mu\text{g g}^{-1}$ ) and Pb ( $61 \mu\text{g g}^{-1}$ ) are associated with sediments immediately below the slag materials, i.e., the subsample at a depth of 8.5 cm (for As, 11.5 cm) in core CS12 from the old dumping site. In this core, depth profiles of these three elements mimic other secondary/authigenic elements such as Ca, Mg, P, Mn and S (Figs. 4 and 5). This suggests dumping-induced diagenetic enrichment of these elements in surface samples that were in contact with the slag. However, such a slag influence on these elements in core CS19 from the old dumping site is not seen (Fig. 5), although most of the surface samples show fluctuating values. In addition, this core shows relatively higher As, Cd, and Pb contents in sediments between ~1900 and 1935, followed by decreasing trends (Fig. 6), but the values are lower than their concentrations in other cores. Interestingly, these three elements show high values in the top ~20 cm of core CS21 and their depth profiles are very similar to Cu, Cr, Mn, P, S and Zn, suggesting that surface enrichment of these elements is due to their diagenetic mobilization at the deeper water depth.

The calculated  $EF_{\text{rel}}$  with respect to BCL in core CS14 retrieved from a water depth of 293.8 m are invariably  $<2$  for all trace elements studied, suggesting that the offshore region of southwestern Taiwan ( $\geq 300$  m water depth) has probably not been affected by modern anthropogenic activities. The highest  $EF_{\text{rel}}$  values for As (2.12) and Cd (1.57) found in sediment deposited in ~1978 with respect to the background sedimentation rate (0.19 cm/yr), however, seem to coincide with the modern intense industrial phase (1970s) in Taiwan. By contrast, the other reference site core CS21 raised from a relatively deeper water depth (453.2 m) shows  $EF_{\text{rel}} >2$  for Cd, with a wide, abnormal range (2.54-22.07) in sediments deposited from 1978 onwards, indicating the influence of modern activities/industrial input. As and Pb exhibit slight enrichments ( $\sim 2$ ) during these intervals, but Zn shows  $EF_{\text{rel}} >2$  only in surface sediment, corresponding to an age of ~1993. We note here that, in core CS21, three consecutive subsamples deposited at 29.5, 24.5 and 19.5 cm contain high  $EF_{\text{rel}}$  for Cd, varying from 2.05 to 2.78. The exact cause for this Cd enrichment is not known because no such Cd enrichment was found in the other long cores, CS14 or CS12 around this time interval, even though the latter two cores come from shallower water depths (Table 1). Such Cd enrichment at deeper depths however implies the precipitation of CdS under reducing conditions in core CS21 where sulfur concentrations

also show relatively higher values. Consistent to this inference, solubility calculations and field studies suggest that authigenic Cd removal via CdS precipitation in suboxic sediments in the presence of trace levels of H<sub>2</sub>S (e.g. Rosenthal et al., 1995).

### 3.7. *Elemental provenance*

Three principal components were found (eigenvalues >2; Table 3) to explain the 79% of the total variance (49%, 20% and 10% for factors 1, 2 and 3, respectively). The PC1 (terrigenous input and detrital dilution) had positive loadings for Al, Cu, Ga, K, Na, Ni, Rb, Si and Ti, the assemblage of elements that characterizes the detrital mineral matrix. Among these, Al and Ti are extremely immobile in marine environment and are thus considered to be refractory elements. The significant correlation ( $P < 0.01$ ) found between Al and K, Si and Ti ( $r = 0.97, 0.77$  and  $0.96$ , respectively) indicates their detrital origin and suggests that Cu, Ni and Rb variability in the sediments can mainly be attributed to terrigenous input. The PC1 had negative loadings for Ca, Mg, Mn, S, Sr, Zr and mean grain size that, however, represents the anthropogenic contribution of slag materials, which act as a dilution factor for the detrital input.

The PC2 (diagenetic enrichment) accounted for 20% of the total variance and had positive loadings for Cd, Cr, Fe, P, V and Zn without any significant negative loadings for the variables included in the dataset. This association represents redox-sensitive elements and related diagenetic remobilization of Cd, Cr, V, and Zn with Fe-oxyhydroxides precipitation. The significant correlation ( $P < 0.01$ ) between Fe and Cd, Cr, V and Zn ( $r = 0.51, 0.63, 0.90$  and  $0.66$ , respectively) suggests that Fe-oxyhydroxides are likely the most important metal carrier phase controlling the accumulation of these elements in the study area. Although sediment grain size and physical absorption on particulate organic matter are most important in controlling these trace metal concentrations in coastal sediments, the absence of such an association here suggests a weak control of organic carbon and grain size on metal enrichment in the studied samples. The PC3 (industrial input) accounted for 10% of the variance and included positive loadings for As, Pb (although it had a low but significant loading of 0.5) and CaCO<sub>3</sub> and a negative loading for OC content, most likely indicating the accumulation of As and Pb in shell materials and thus authigenic input, as a dilutor of the organic materials represented by OC content at the site. Depth profiles of As, Cd and Pb in the acid-leached fractions, which generally do not account for the fraction associated with the residual silicate phase (Loring and Rantala, 1992), further points to

an anthropogenic source contribution of As, Cd and Pb. Their statistically insignificant association with other studied variables such as Al, Ti, OC, S and mean grain size also favors the idea that they might have been contributed by external sources.

### 3.8. *Sediment-slag interactions: an overview*

Steel-producing industrial units generate ~420 kg of solid waste in the production of a ton of steel in the form of furnace slag, flue dust, sludge and refractory material in their oxide forms, which is also rich in various trace elements, including toxic heavy metals (Dutra et al., 2006). While ~65% of the furnace slag (Kawatra and Ripke, 2002; Motz and Geiseler, 2001) and ~74% of the dust (Dutra et al., 2006) is recycled/reused, excess slag, gaseous emanations and other ~150 kg of wastes produced during steel-making processes end up as potential environmental contaminants (Hagni et al., 1991). Slag materials dominated by limestone ( $\text{CaCO}_3$ ) and iron ore impurities collected at the top of the molten iron make up the largest portion of the waste. Ca, Si, Mg, Mn and P are the major constituents reported in slag materials (Alanyali et al., 2006; Dutra et al., 2006). The bulk composition of slag sometimes exceed 40% Ca and also contains trace elements (Cu, Cr, Co, Mo, Ni, Ti and V) of varying levels depending upon the type of steel produced. The metal dusts produced by electric arch furnaces are known for their Cd, Pb and Zn enrichment and are sometimes extracted and further reused. The large quantity of waste dumping offshore enriched in major and trace elements can therefore act as potential contaminants for the top 10 cm of sediments in the region. Biogeochemical interactions between dissolved and particulate matter through authigenic processes during deposition and post-depositional conditions alter the elemental chemistry of the original sediments. Since the major elements, such as Ca, Fe, Mn, and P, are susceptible to both authigenic and diagenetic changes, their concentrations might have increased due to slag-induced early diagenesis in the sediments of dumping sites.

Steel slag composite generated as a waste byproduct is mildly alkaline with a solution pH generally in the range of 8 to 11. High pH values (8.61 and 8.12) and low Eh values (96 mV and 88 mV) recorded in the old and new dumping sites and very high S content suggest temporary oxygen-depleted conditions only in dumping sites. Such values were possible as a result of the production of hydroxide ions during the partial dissolution of carbonate and iron sulfides in slag materials according to the equations:  $\text{CaCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^-$  and  $\text{H}_2\text{O} + \text{FeS} \leftrightarrow \text{Fe}^{2+} + \text{HS}^- + \text{OH}^-$ . Such dissolution was possible due to the relative solubility of iron sulfides (e.g., pyrrhotite- $\text{Fe}_{1-x}\text{S}$  and mackinawite- $\text{FeS}_{1-x}$ ) present in the slag when it sinks a few centimeters below the sediment-water interface due to its

higher density to the zone of low oxygen. Due to concentration gradients, liberated reduced  $\text{Fe}^{2+}$  along with  $\text{Mn}^{2+}$ , which migrated upward in the sediment column's interstitial waters as dissolved species and oxidized to  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$ , is precipitated either as Fe-Mn oxyhydroxides in the presence of free  $\text{OH}^-$  or metal sulfides because of  $\text{HS}^-$ . These processes result in Fe and Mn enrichment at the surface as well as in subsurface sediment layers, very similar to the role of early diagenesis in unpolluted sediments (Shaw et al., 1990; and Gobeil et al., 1987). Vdović et al. (2006) reported a partial dissolution of slag resulting in Pb, Zn and Cu release due to sediment-slag interactions within the fresh water medium. They also observed a high metal absorption and retention capacity for sediments and suggested an oxyhydroxide or sulfide coprecipitation mechanism for the removal of these elements. Interestingly, Mn, P, and S enrichments within the top ~ 10 cm surface sections are associated with chemically very mobile Ca, Mg, and Sr as well as immobile Cr and Zr further strongly supporting the above inference.

Very high concentrations of many elements (Ca-25.02%; Cr-640  $\mu\text{g g}^{-1}$ ; Fe-11.55%; Mn-14350  $\mu\text{g g}^{-1}$ ; P-5840  $\mu\text{g g}^{-1}$  and S-6060  $\mu\text{g g}^{-1}$ ) in slag recovered from core CS12 indicate these as a major source of contamination/pollution (see Supplementary Table 1). Abnormal Mn values (1650, 1930, 4200, 4930 and 5650  $\mu\text{g g}^{-1}$ ; Supplementary Table 1) in five subsamples between 2.5 and 6.5 cm in core CS19 from the old dumping site and two subsamples (7780 and 4420  $\mu\text{g g}^{-1}$ ) in core CS12 from the new dumping site clearly indicate the influence of dumped materials. This is also supported by the very high concentration of Mn (14350  $\mu\text{g g}^{-1}$ ) in slag recovered from the latter core. Relatively low Mn values in sediments from the old dumping site compared to those in from the new dumping site suggest that the Mn and other contaminants were likely diluted by recent sediments through natural attenuation. This is consistent with the dilution of chemical elements observed at a historical dumping site in the Baltic Sea (Leipe et al., 2005).

#### **4. Conclusions**

Detailed geochemical studies of sediment cores raised from slag dumping sites off of southwestern Taiwan indicate that sediment, slag waste, and seawater interactions probably resulted in the initial dissolution, remobilization of dissolved chemical constituents within sediment subsurface levels and re-precipitation at favorable conditions. Our study suggests that anthropogenic input such as slag dumping into the coastal sediments would induce the diagenetic remobilization of certain elements and can thus alter the original characteristics of downcore elemental behaviors of both detrital (Si, Ti, Al

and K) and secondary/diagenetic elements (Ca, P, Mn, S and Cr). Recovery of the sediment composition from the effect of dumping to its original concentration seems to be attained at the old dumping site within less than a decade. Such a recovery suggests that slag dumping may produce a local rather than regional effect on biogeochemical processes. This also implies that sediment efficiency in trapping released contaminants from slag-sediment interactions may take a few years (about 5 or more) after dumping. Therefore, caution should be taken in dumping slag waste in other fragile ecosystems such as reef formations, mangroves and estuarine ecosystems harboring diverse marine and freshwater biota, although the effect of buried sediment rich in slag contaminants on the benthic biotic abundance and structure is beyond the scope of our present study. Furthermore, sediments of considerable thickness (~4-5 cm) with greatly reduced contents of detrital elements (Si, Ti, Al and K) may possibly be used as an indicator zone for future environmental monitoring studies in this region.

### **Acknowledgements**

Financial supports from the China Steel Corporation (84-Y93-003), the National Science Council of Taiwan (NSC 97-2611-M-110-002 and 97-2811-M-110-026) and the Aim for the Top University Program are greatly appreciated. GP thanks the Director, NIO (Goa, India), for his encouragement and BJ Wang for her analytical help. We gratefully acknowledge Miguel A. Goni and anonymous reviewers for their helpful comments and critiques of the original manuscript.



## References

- Alanyali, H., Col, M., Yilmaz, M., Karagoz, S., 2006. Application of magnetic separation to steelmaking slags for reclamation. *Waste Management* 26, 1133-1139.
- Berner, R.A., 1980. *Early Diagenesis*. Princeton Univ. Press, Princeton, New Jersey.
- Calvert, S.E., Pederson, T.F., Thunell, R.C., 1993. Geochemistry of the surface sediments of the Sulu and South China Seas. *Marine Geology* 114, 207-231.
- Chen, C.T.A., 1997. Research report on phytoplankton, benthos, fishery resources and sediment quality in and around the slag disposal area of the China Steel Company, off SW Taiwan. No. 31, Institute of Marine Geology and Chemistry, National Sun Yat-Sen University, Taiwan [in Chinese]
- Chen, C.T.A., Selvaraj, K., 2008. Evaluation of elemental enrichments in surface sediments off southwestern Taiwan. *Environmental Geology* 54, 1333-1346.
- Chou, W.R., Tew, K.S., Fang, L.S., 2002. Long-term monitoring of the demersal fish community in a steel-slag disposal area in the coastal waters of Kaohsiung, Taiwan. *ICES Journal of Marine Science* 59, S238-S242.
- Chung, Y., Craig, H., 1983.  $^{210}\text{Pb}$  in the Pacific: the GEOSECS measurements of particulate and dissolved concentrations. *Earth and Planetary Science Letters* 65, 406-432.
- Dutra, A.J.B., Paiva, P.R.P., Tavares, L.M., 2006. Alkaline leaching of zinc from electric arc furnace steel dust. *Minerals Engineering* 19, 478-485.
- Förstner, U., Wittmann, G.T.W., 1981. *Metal Pollution in Aquatic Environment*. Springer-Verlag, Berlin.
- Johnson, L.J., Frid, C.L.J., 1995. The recovery of benthic communities along the county Durham coast after cessation of colliery spoil dumping. *Marine Pollution Bulletin* 30, 215-220.
- Gao, S., Luo, T.C., Zhang, B.R., Zhang, H.F., Han, Y.W., Zhao, Z.D., Hu, Y.K., 1998. Chemical composition of the continental crust as revealed by studies in East China. *Geochimica et Cosmochimica Acta* 62, 1959-1975.
- Gobeil, C., Silverberg, N., Sundby, B., Cossa, D., 1987. Cadmium diagenesis in Laurentian trough sediments. *Geochimica et Cosmochimica Acta* 51, 589-596.
- Hagni, A.M., Hagni, R.D., Demars, C., 1991. Mineralogical characteristics of electric arc furnace dusts. *JOM* 43, 28-30.
- Kao, S.J., Shiah, F.K., Wang, C.H., Liu, K.K., 2006. Efficient trapping of organic carbon in sediments n the continental margin with high fluvial sediment input off southwestern Taiwan. *Continental Shelf Research* 26, 2520-2537.

- Kawatra, S.K., Ripke, S.J., 2002. Pelletizing steel mill desulfurization slag. *International Journal of Mineral Processing* 65, 165-175.
- Li, Y.H., 1975. Denudation of Taiwan island since the Pliocene epoch. *Geology* 4, 105-107.
- Leipe, T., Kersten, M., Heise, S., Pohl, C., Witt, G., Liehr, G., Zettler, M., Tauber, F., 2005. Ecotoxicity assessment of natural attenuation effects at a historical dumping site in the western Baltic Sea. *Marine Pollution Bulletin* 50, 446-459.
- Loring, D.H., 1991. Normalization of heavy-metal data from estuarine and coastal sediments. *ICES Journal of Marine Science* 48, 101-115.
- Loring, D.H., Rantala, R.T.T., 1992. Manual for geochemical analyses of marine sediments and suspended particulate matter. *Earth Science Reviews* 32, 235-283.
- Motz, H., Geiseler, J., 2001. Products of steel slags an opportunity to save natural resources. *Waste Management* 21, 285-293.
- Nath, B.N., Rao, V.P., Becker, K.P., 1989. Geochemical evidence of terrigenous influence in deep-sea sediments up to 8°S in the Central Indian Basin. *Marine Geology* 87, 301-313.
- Nolting, R.F., Ramkema, A., Everaats, J.M., 1999. The geochemistry of Cu, Cd, Zn, Ni and Pb in sediment cores from the continental slope of the Banc d'Arguin (Mauritania). *Continental Shelf Research* 19, 665-691.
- Rosenthal, Y., Lam, P., Boyle, E.A., Thompson, J., 1995. Authigenic cadmium enrichments in suboxic sediments: Precipitation and postdepositional mobility. *Earth and Planetary Science Letters* 132, 99-111.
- Ruiz-Fernández, A.C., Páez-Osuna, F., Urrutia-Fucugauchi, J., Preda, M., Rehault, I., 2004. Historical trace metal fluxes in the Mexico City Metropolitan Zone as evidenced by a sedimentary record from the Espejo de los Lirios lake. *Journal of Environmental Monitoring* 6, 473-480.
- Ruiz-Fernández, A.C., Hillaire-Marcel, C., 2009. <sup>210</sup>Pb-derived ages for the reconstruction of terrestrial contaminant history into the Mexican Pacific coast: Potential and limitations. *Marine Pollution Bulletin* 59, 134-145.
- Shaw, T.J., Gieskes, J.M., Jahnke, R.A., 1990. Early diagenesis in differing depositional environments. The responses of transition metals in pore water. *Geochimica et Cosmochimica Acta* 54, 1233-1246.
- Selvaraj, K., Chen C.T.A., 2006. Moderate chemical weathering of subtropical Taiwan: Constraints from solid-phase geochemistry of sediments and sedimentary rocks. *The Journal of Geology* 114, 101-116.
- Selvaraj, K., Ram Mohan, V., Szefer, P., 2004. Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: geochemical and statistical approaches. *Marine Pollution Bulletin* 49, 174-185.

- Standring, W.J.F., Oughton, D.H., Salbu, B., 2002. Remobilization of Cd, Zn and Mn from freshwater-labelled river sediments when mixed with seawater. *Environment International* 28, 185-195.
- Syvitski, J.P.M., Vörösmarty, C.J., Kettner, A.J., Green, P., 2005. Impact of humans on the flux of terrestrial sediment to the global coastal ocean. *Science* 308, 376-380.
- Szefer, P., 2002. *Metals, Metalloids and Radionuclides in the Baltic Sea Ecosystem*. Elsevier Science B.V., Amsterdam.
- Szefer, P., Glasby, G.P., Pempkowiak, J., Kaliszan, R., 1995. Extraction studies of heavy-metal pollutants in surficial sediments from the southern Baltic Sea off Poland. *Chemical Geology* 120, 111-126.
- Szefer, P., Glasby, G.P., Stüben, D., Kusak, A., Geldon, J., Berner, Z., Neumann, T., Warzocha, J., 1999. Distribution of selected heavy metals and rare earth elements in surficial sediments from the Polish sector of the Vistula Lagoon. *Chemosphere* 39, 2785-2798.
- Topkaya, Y., Sevinc, N., Günaydin, A., 2004. Slag treatment at Kardemir integrated iron and steel works. *International Journal of Mineral Processing* 74, 31-39.
- Tsai, W.T., Chou, Y.H., 2004. A review of environmental economic regulations for promoting industrial waste recycling in Taiwan. *Waste Management* 24, 1061-1069.
- Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust: Its Composition and Evolution*. Blackwell, London.
- Vdović, N., Billon, G., Gabelle, C., Potdevin, J., 2006. Remobilization of metals from slag and polluted sediments (Case Study: The canal of the Deûle River, northern France). *Environmental Pollution* 141, 359-369.
- Wällstedt, T., Borg, H., Meili, M., Mörth, C.-M., 2008. Influence of liming on metal sequestration in lake sediments over recent decades. *Science of the Total Environment* 407, 405-417.
- Wentworth, C.K., 1922. A scale of grade and class terms of clastic sediments. *The Journal of Geology* 30, 377-392.
- Windom, H.L., Schropp, S.J., Calder, F.D., Ryan, J.D., Smith, J.R.G., Burney, L.C., Lewis, F.G., Rawlinsons, C.H., 1989. Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern United States. *Environmental Science and Technology* 23, 314-320.
- Zwolsman, J.J.G., van Eck, G.T.M., Burger, G., 1996. Spatial and temporal distribution of trace metals in sediments from the Scheldt estuary, south-west Netherlands. *Estuarine Coastal Shelf Science* 43, 55-79.

## Figure Legends

**Figure 1** Map showing the study area off southwestern Taiwan. The locations of core samples used in this study, including the old and new dumping sites, are also shown as an enlargement. Core CS8 is not included in this study because of its short length (9 cm).

**Figure 2**  $^{210}\text{Pb}_{\text{excess}}$  variations for the sediment core CS19 from old dumping site. Sedimentation rate (SR) obtained are also indicated.

**Figure 3** Depth profiles of selected detrital elements in cores CS12, CS14, CS19 and CS21.

**Figure 4** Depth profiles of diagenetic elements, including calcium carbonate ( $\text{CaCO}_3$ ) and organic carbon (OC), in cores CS12, CS14, CS19 and CS21.

**Figure 5** Downcore profiles of silicate weathering indicators illustrating recent weathering trends in cores CS12, CS14, CS19 and CS21.

**Figure 6** Downcore profiles of As, Cd and Pb depicting modern anthropogenic influence in cores CS12, CS14, CS19 and CS21 from off southwestern Taiwan.

Figure 1

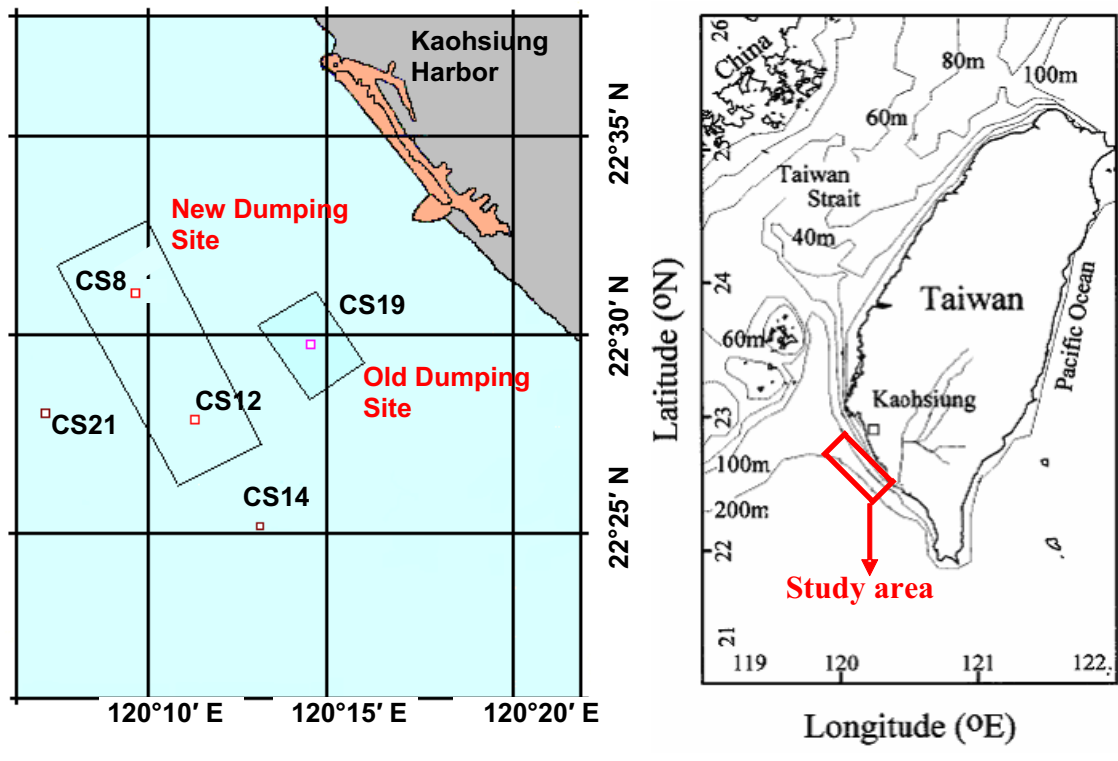


Figure 2

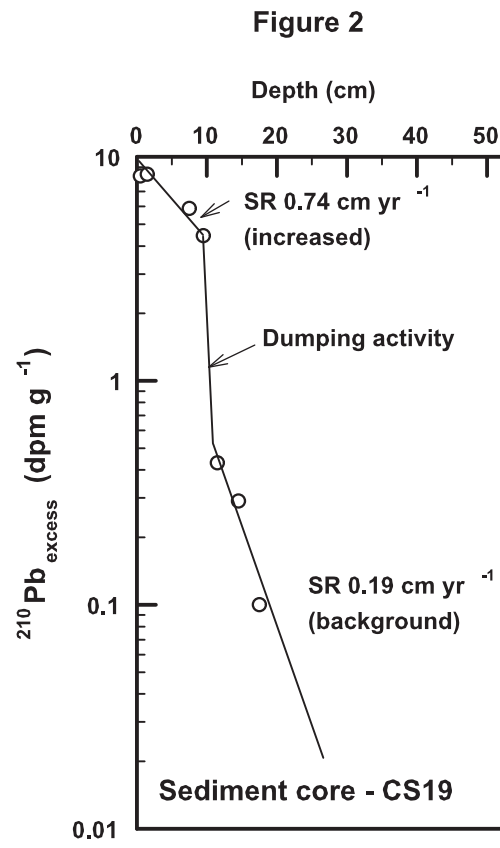


Figure 3

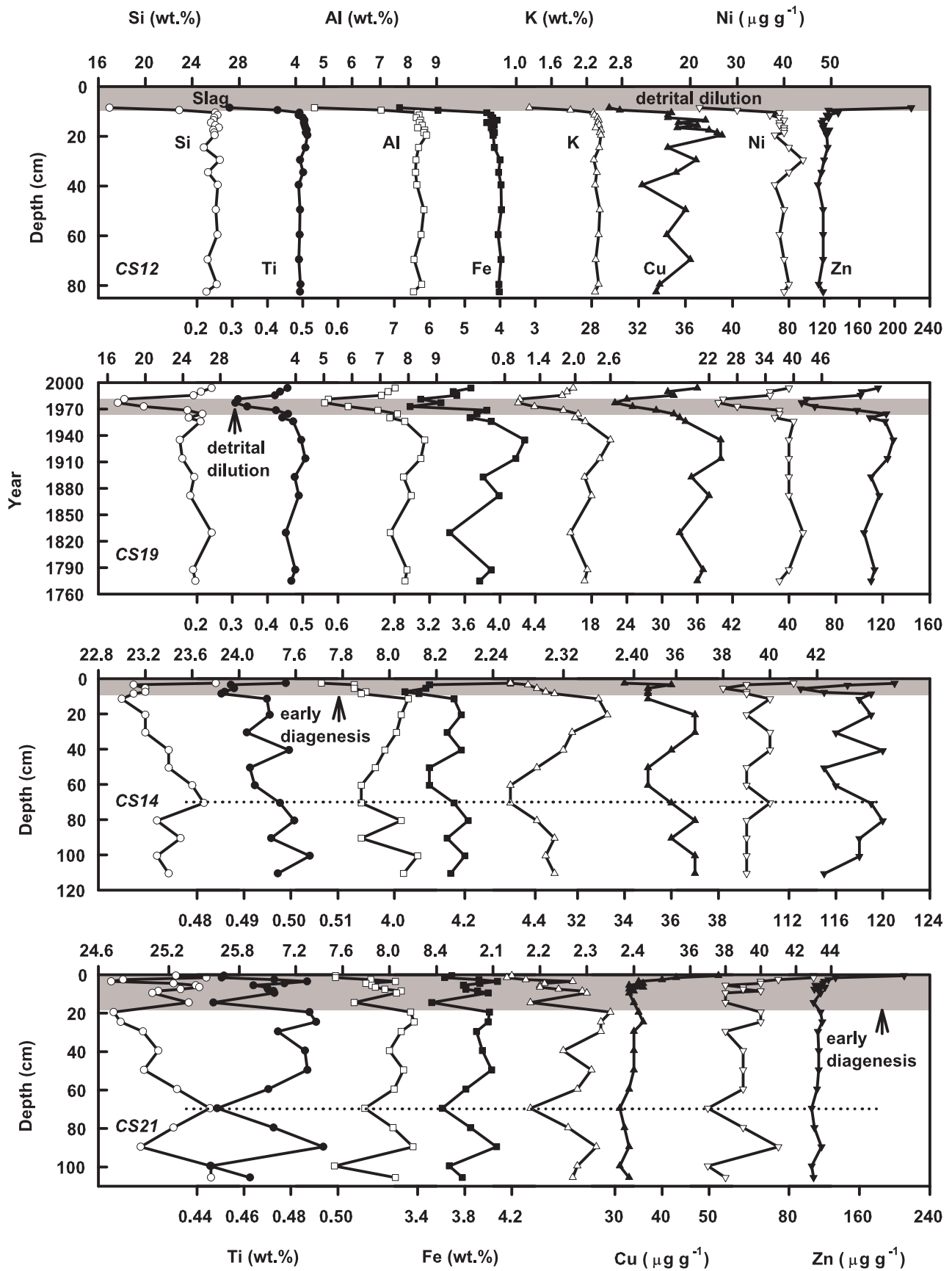


Figure 4

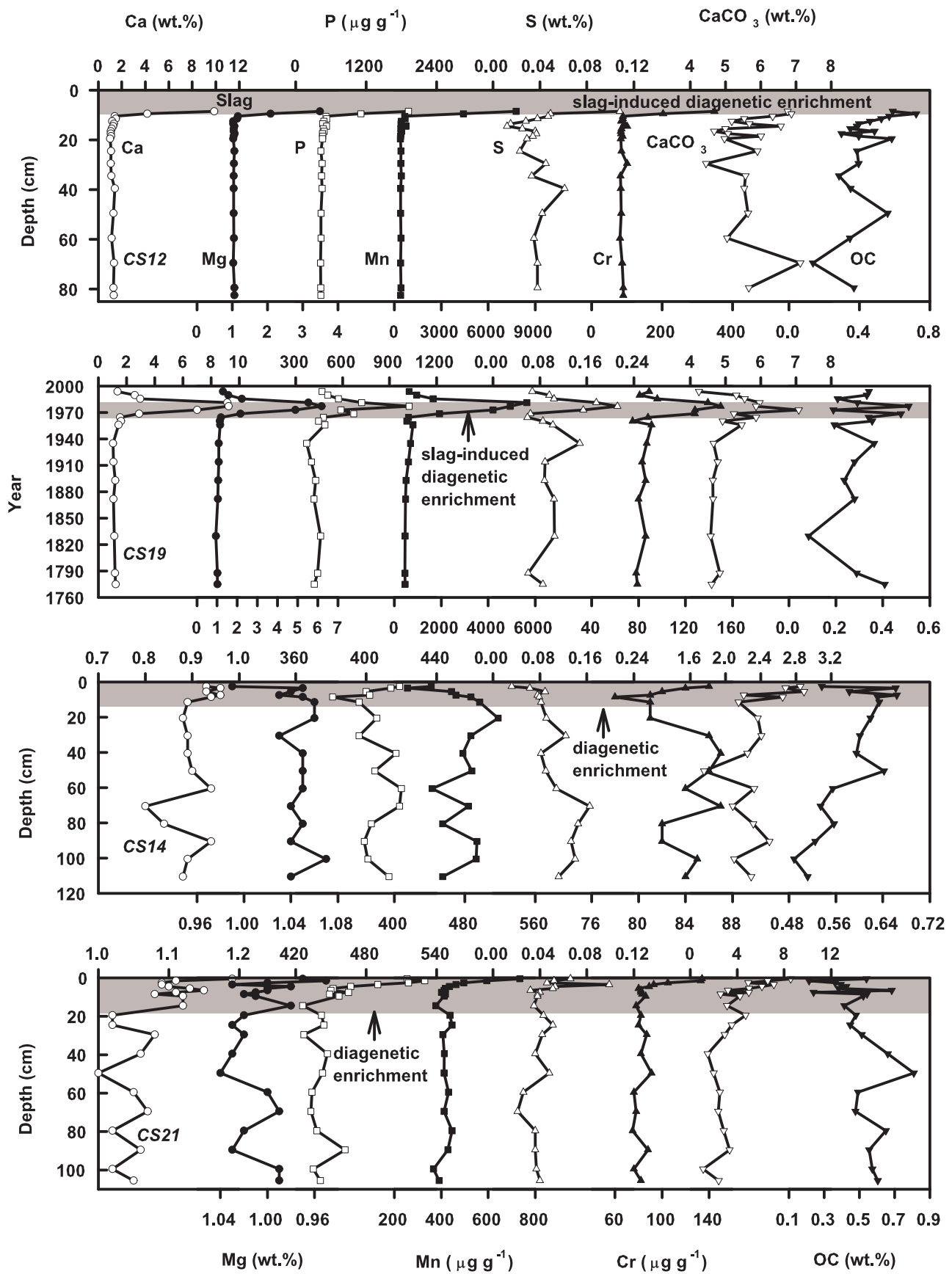




Figure 5

Figure 5

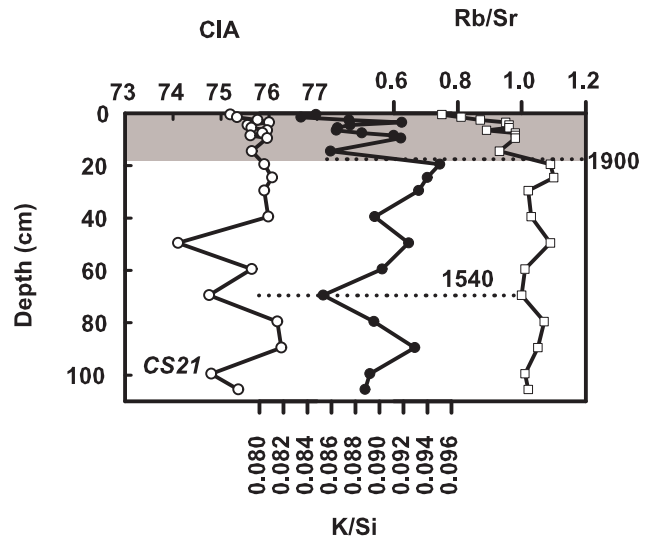
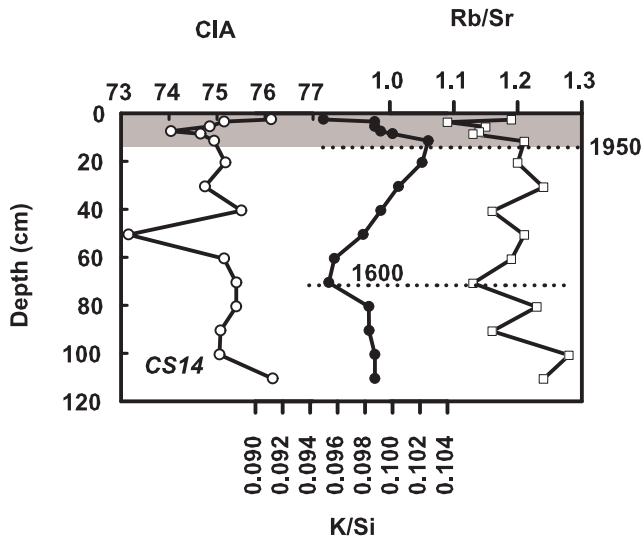
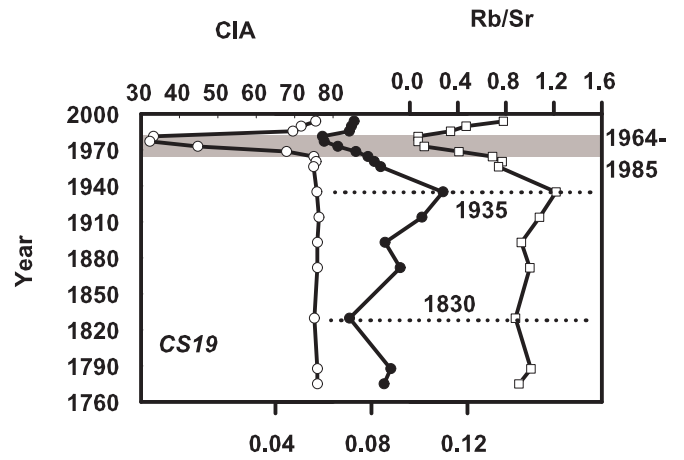
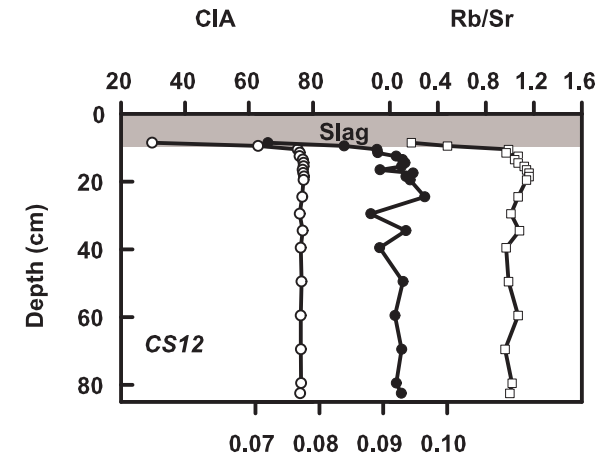
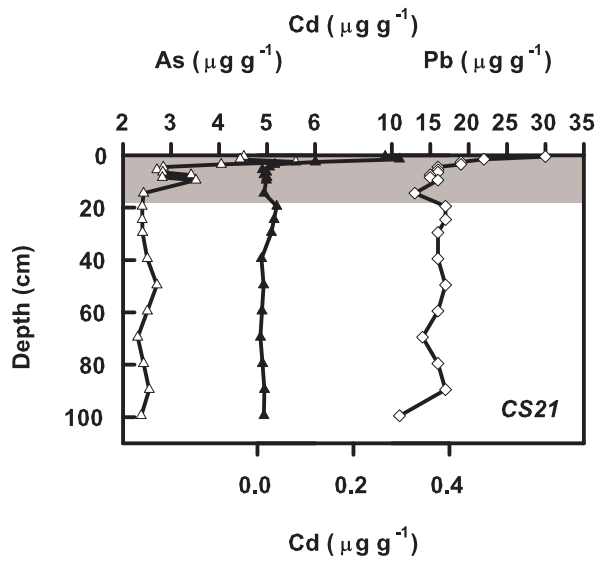
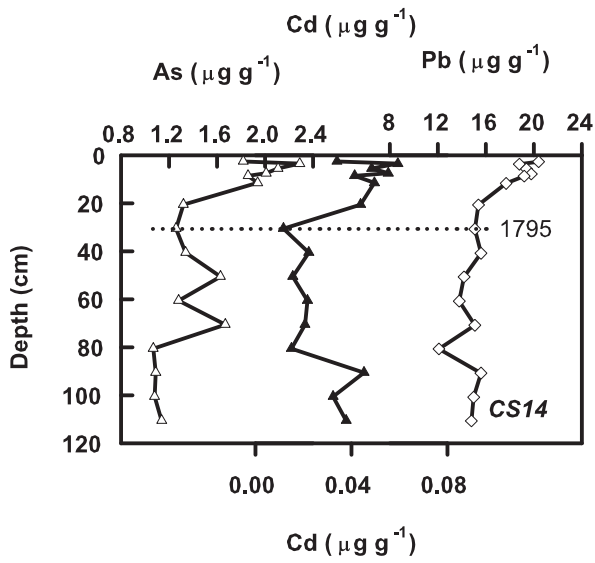
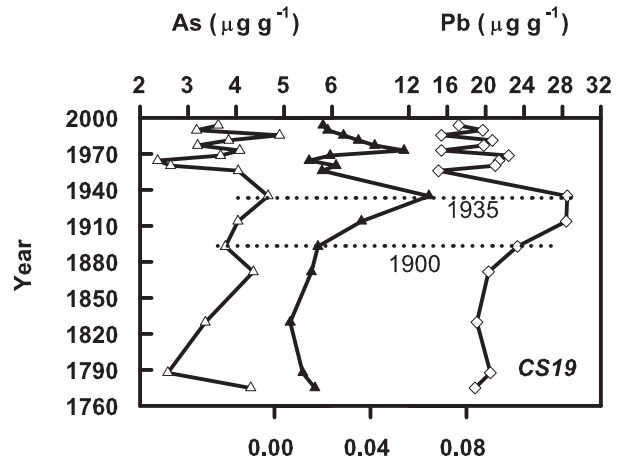
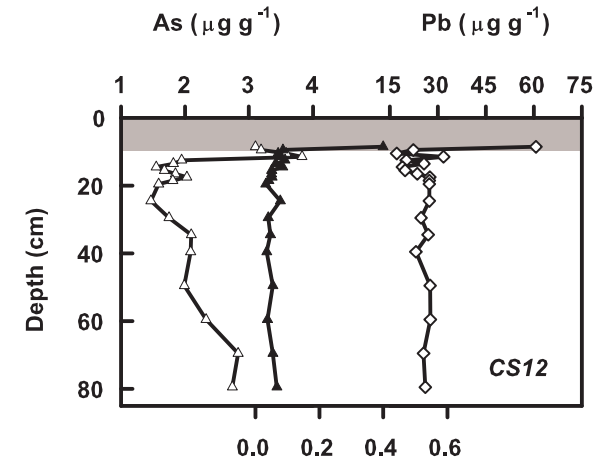


Figure 6



**Table 1**  
 Details of sediment cores selected for environmental impact assessment study off Kaohsiung Harbor, southwestern Taiwan.

Core Number	Site Name	Latitude (°N)	Longitude (°E)	Water depth (m)	Core length (cm)	No. of subsamples
CS12	New dumping site	22°28.70'	120°10.71'	315.8	79	22
CS14	Reference site 1	22°25.59'	120°12.11'	293.8	117	16
CS19	Old dumping site	22°29.82'	120°13.88'	105.2	53	17
CS21	Reference site 2	22°28.43'	120°06.82'	453.2	106	22

**Table 2**

Summary statistics of relative enrichment factors (REF) with respect to background concentration level (BCL) of cores studied from off southwestern Taiwan.

Elements	Ca	Fe	Mg	Mn	P	S	As	Cd	Cr	Cu	Ni	Pb	Sr	V	Zn	Zr
<b>All samples (N = 77)</b>																
Min	0.73	0.88	0.94	0.88	0.76	0.53	0.53	0.30	0.89	0.92	0.88	0.68	0.87	0.89	0.72	0.73
Max	13.33	3.03	9.58	33.30	7.95	13.28	2.32	22.07	6.96	1.69	1.17	10.82	4.59	3.20	3.31	6.98
Mean	1.63	1.05	1.42	2.33	1.23	1.42	1.17	2.13	1.19	1.03	0.99	1.30	1.17	1.07	1.06	1.19
SD	144	24	107	204	72	127	35	169	64	11	5	88	54	26	28	76
<b>Contaminated samples (N = 12)</b>																
Min	1.18	1.00	1.14	1.22	1.07	1.05	0.70	1.25	0.98	0.92	0.88	0.75	1.04	0.91	0.72	0.87
Max	13.33	3.03	9.58	33.30	7.95	13.28	1.99	11.23	6.96	1.53	1.05	10.82	4.59	3.20	3.31	6.98
Mean	5.13	1.31	3.68	9.08	2.29	3.91	1.30	3.55	2.13	1.02	0.97	2.05	2.12	1.41	1.18	2.32
SD	92	44	83	109	86	97	29	81	78	17	5	137	59	44	58	86
<b>Background samples (N = 65)</b>																
Min	0.73	0.88	0.94	0.88	0.76	0.53	0.53	0.30	0.89	0.92	0.89	0.68	0.87	0.89	0.85	0.73
Max	1.36	1.09	1.10	1.95	1.42	1.66	2.32	22.07	1.72	1.69	1.17	2.43	1.16	1.16	2.01	1.18
Mean	0.99	1.01	1.00	1.09	1.03	0.96	1.14	1.87	1.02	1.03	1.00	1.16	0.99	1.01	1.03	0.98
SD	11	3	2	19	9	20	36	194	14	10	5	25	6	6	13	8
<b>New Dumping Site – Core CS12 (N = 22)</b>																
Min	0.73	0.96	0.94	0.90	0.98	0.53	0.53	0.50	0.89	0.92	0.88	0.87	0.87	0.91	0.95	0.91
Max	13.33	3.03	5.90	33.30	7.95	13.28	1.99	11.23	6.96	1.53	1.09	10.82	2.49	3.20	3.31	1.96
Mean	1.64	1.15	1.29	3.20	1.49	1.62	0.87	1.44	1.34	1.04	0.97	1.66	1.03	1.15	1.14	1.04
SD	168	40	85	230	104	172	42	158	100	12	5	129	33	43	44	22

Reference Site 1 – Core CS14 (N = 16)

Min	0.90	0.88	0.98	0.88	0.96	0.58	0.97	0.30	0.91	0.95	0.97	0.68	0.98	0.89	0.85	0.97
Max	1.36	1.08	1.02	1.40	1.42	1.18	2.12	1.57	1.07	1.01	1.09	1.36	1.10	1.04	1.08	1.18
Mean	1.03	1.00	1.00	1.02	1.04	0.94	1.43	0.91	1.00	0.98	1.01	1.06	1.04	0.96	1.00	1.03
SD	10	4	1	11	10	18	26	43	4	2	3	18	3	5	5	5

Old Dumping Site – Core CS19 (N = 17)

Min	0.79	0.97	0.98	0.96	0.76	0.85	0.70	0.59	0.94	0.92	0.89	0.75	0.89	0.89	0.72	0.73
Max	12.03	1.38	9.58	18.28	3.58	7.86	1.69	6.04	2.85	1.05	1.12	1.60	4.59	1.76	1.15	6.98
Mean	3.00	1.07	2.52	4.15	1.35	2.17	1.17	2.55	1.34	0.98	0.97	1.11	1.67	1.12	0.99	1.82
SD	124	10	110	136	53	99	24	65	45	4	6	21	70	18	13	99

Reference Site 2 – Core CS21 (N = 22)

Min	0.94	0.94	0.97	0.97	0.94	0.81	0.95	0.48	0.90	0.98	0.96	0.83	0.94	0.92	0.96	0.89
Max	1.20	1.05	1.04	1.95	1.25	1.66	2.32	22.07	1.72	1.69	1.17	2.43	1.16	1.16	2.01	1.12
Mean	1.03	1.00	1.00	1.12	1.03	1.03	1.24	3.43	1.08	1.09	1.02	1.28	1.01	1.03	1.08	0.98
SD	6	3	1	20	8	18	31	173	20	15	5	25	6	5	20	7

---

**Table 3**

PCA for geochemical data (Varimax normalized) from sediment cores, CS12, CS14, CS19 and CS21, off southwestern Taiwan.

Variable	Factor 1 (Terrigenous input)	Factor 2 (Diagenesis)	Factor 3 (Industrial input)
Si	<b>0.75</b>	-0.25	0.21
Ti	<b>0.90</b>	-0.16	-0.23
Al	<b>0.89</b>	-0.18	-0.16
Fe	0.00	<b>0.89</b>	-0.31
Ca	<b>-0.95</b>	0.28	0.11
Mg	<b>-0.98</b>	0.00	0.00
Na	<b>0.78</b>	-0.26	0.00
K	<b>0.92</b>	0.00	-0.23
P	-0.63	<b>0.73</b>	0.00
Cl	-0.15	0.00	-0.27
S	<b>-0.92</b>	0.26	0.15
As	-0.21	0.00	<b>0.79</b>
Ba	0.55	-0.35	-0.25
Cd	-0.10	<b>0.80</b>	0.34
Cr	-0.56	<b>0.79</b>	0.12
Cu	<b>0.77</b>	0.22	0.22
Ga	<b>0.91</b>	-0.16	-0.17
Mn	<b>-0.88</b>	0.45	0.00
Ni	<b>0.91</b>	-0.24	0.00
Pb	-0.30	0.64	0.23
Rb	<b>0.86</b>	-0.13	-0.38
Sr	<b>-0.94</b>	-0.15	0.19
V	-0.11	<b>0.87</b>	-0.30
Zn	0.45	<b>0.80</b>	0.16
Zr	<b>-0.85</b>	-0.30	0.17
Mz	<b>-0.80</b>	-0.29	0.26
C <sub>org</sub>	0.00	0.21	<b>-0.75</b>
CaCO <sub>3</sub>	-0.22	0.30	<b>0.73</b>
Eigenvalues	13.79	5.56	2.84
Variance %	49.23	19.85	10.15

Significant loadings (>0.7) are in bold.