Heavy metal concentrations in marine sediments impacted by a mine-tailings spill, Marinduque Island, Philippines

C.P. David

Abstract A mine-tailings spill occurred on the island of Marinduque, Philippines, on 24 March 1996. Originating from the Marcopper Mine, tailings sludge flowed down the Boac River abruptly and during subsequent storm events. Most of the tailings material has since accumulated in the nearshore environment along the western coast of the island. Nineteen sediment cores were collected from this site and analyzed for heavy metals. Elevated concentrations of Cu (706–3,080 ppm), Mn (445–1,060 ppm), Pb (43–56 ppm), and Zn (131–276 ppm) are present in the tailings. Two horizons of high metal concentrations in the marine sediment profile are interpreted to correspond to two distinct tailings input events. The lower horizon corresponds to the original 1996 spill, whereas the spike near the surface is thought to be a combination of input due to dredging of the river in 1997 and reworking of sediments. A previous history of contamination is also deduced from the metal profiles. The volume of tailings material released into the marine environment due to the spill is estimated to be 180,000 to 260,000 m^3.

C.P. David (✉)
Department of Geological and Environmental Sciences,
Bldg. 320, Stanford University, Stanford, CA 94305-2115, USA
E-mail: cdavid@pangea.stanford.edu
Tel.: +1-650-7250075
Fax: +1-650-3294545

Permanent address: C.P. David
National Institute of Geological
Sciences, University of the Philippines Diliman
Quezon City 1101, Philippines
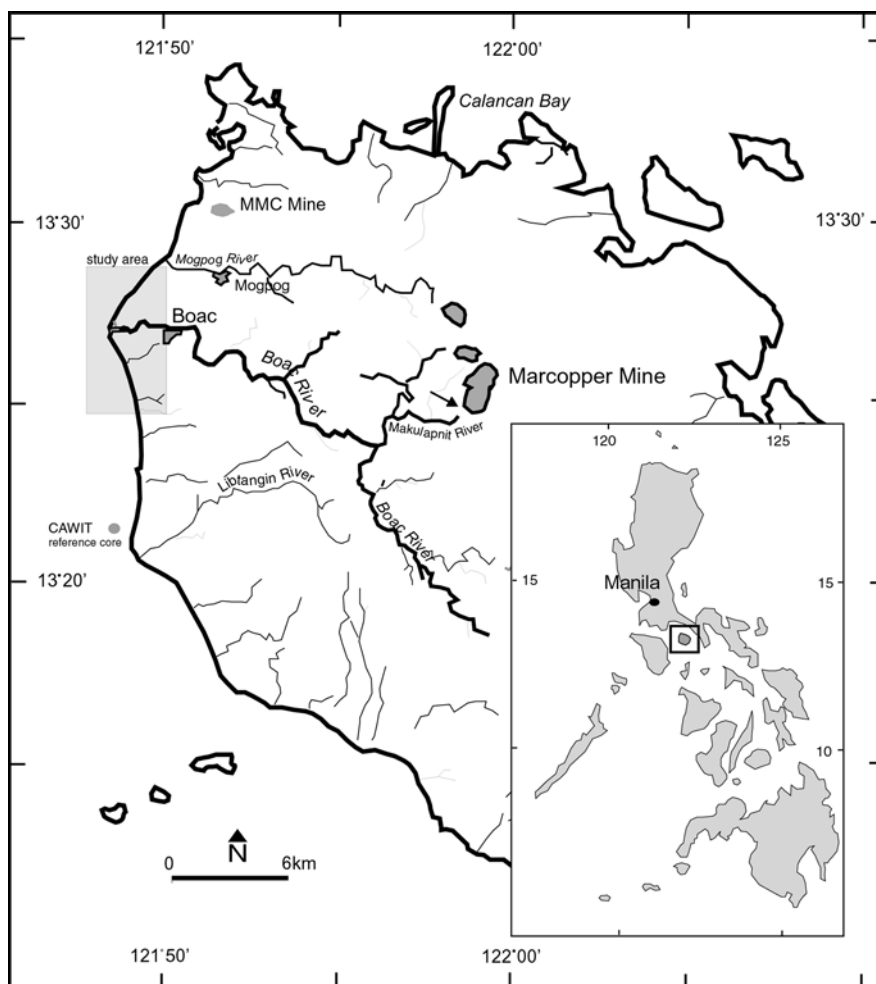e-mail: cpdavid@nigs.upd.edu.ph

Introduction

An important concern for any mining operation is the containment and/or disposal of hazardous waste generated during mining, milling, and smelting of ore minerals (Moore and Luoma 1990; Lambors 1994). Mine tailings (the byproduct of milling and ore flotation) pose a special problem not only because these comprise the bulk of the generated waste but also due to the characteristically high metal concentrations (Dold, unpublished data 1999). Their typical fine-grained nature also make tailings susceptible to transport. Metal contamination from mine tailings is further highlighted in instances in which a sudden event like a mine-tailings spill results in the instantaneous release of large amounts of this waste material. Recently, there have been two other major cases of mine spills which occurred besides the 1996 Marcopper Mine spill. In 1995, a ruptured tailings dam in the Omai Gold Mine, Guyana resulted in the contamination of the Omai and Essquibo rivers with 3×10^6 m^3 cyanide-laced tailings sludge (Jacobson 1998). In 1998, a similar mine-tailings pond collapse at the Los Frailes Zinc Mine in southern Spain resulted in the release of around 5×10^6 m^3 acid sludge into the Guadiamar River and the Doñana estuary (Van Geen and Chase 1998). In both cases, the impact on the surrounding environment was both sudden and persistent. On 24 March 1996, a large volume of mine waste was released from one of the largest copper mines in the Philippines when the tailings pond of Marcopper Mine on Marinduque Island (Fig. 1) was breached. Tailings material flowed down the Boac River system, as one of its headwaters (the Makulapnit River) directly drains the mine's waste pond. It was initially estimated that around 1.6×10^6 m^3 tailings material was deposited along the river, excluding an undetermined volume of material which reached the western shore of the island within a few days of the spill, according to Placer Dome Technical Services (PDTS, unpublished data 1997).

Few studies have been done in the area except for the monitoring and assessment work conducted by PDTS. The purpose of this research is to describe the impact of the spill by evaluating the extent of metal contamination of sediments in the area which later on may be related to contaminant uptake by aquatic organisms (David, unpublished data 2001). The specific goals of this work include the geochemical characterization, spatial distribution, and estimation of the volume of tailings material

Fig. 1
Map of the study area. The collapsed mine-tailings pond is at the southernmost tip of the mine's property. The *arrow* locates where the spill originated. The *shaded box* at the western coast of the island is where the offshore cores were taken (Fig. 2). Also indicated in the map is the CAWIT core site used for establishing regional metal background values

deposited in the marine environment. This study follows previous research at other nearshore sites with elevated heavy metals in sediments (Gonzales and Ramirez 1995; Hornberger and others 1999; Astrom and Nylund 2000; Baptista-Neto and others 2000). However, this study is different in that it presents a rare opportunity to study the impact of trace-metal contamination of a coastal region in which the introduction of contaminants occurred in a single voluminous event in a relatively short span of time. The sediment record is utilized to document the spatial coverage of the tailings and to provide constraints on the timing and evolution of the spill.

Methodology

Sampling

Sediment samples were collected in the Boac River channel and at 15 offshore sites (Fig. 2) using a 0.5-m-long gravity corer. Cores were collected either in August 1998 (BR prefix and dredged channel-DRG), in August of the following year (CX prefix), or in July 2001 (CAWIT). Typically, a core length of around 20–40 cm was recovered from each site. Each core was sampled onsite at 2.5-cm intervals except for cores BR-10, 11 and DRG which were

sampled at 5-cm intervals. Lastly, three sites (PDTS cores) within the dredged channel were cored by PDTS in 1999 for this author. Two samples (surface and 1–1.5 m beneath the surface) from each site were collected. All sediment samples were sieved using a 63-μm mesh to separate the silt-clay (<63 μm) size particles from the sand fraction. Only the <63-μm fraction was analyzed for metals. Sieving removes the most important grain-size biases which can affect intersample comparisons (Salomons and Forstner 1984; Axtmann and Luoma 1991). Both grain-size fractions were dried at 60 °C and weighed to calculate grain-size distribution.

For one of the cores (CX-2), porewater was also extracted on site from each sample by filtering the sediments through a 0.45-μm filter. Temperature and pH measurements were performed in situ with a portable pH/ISE meter (Orion 290A) fitted with a pH electrode (Orion pH/ATC probe).

Sediment analysis

Metal concentrations in the <63-μm fraction were determined after decomposition using concentrated nitric acid reflux as described by Luoma and Bryan (1981). Each sample (0.5–0.6 g) was digested in 10 ml of concentrated trace-element-grade nitric acid, capped with a reflux bulb and left overnight at room temperature. The
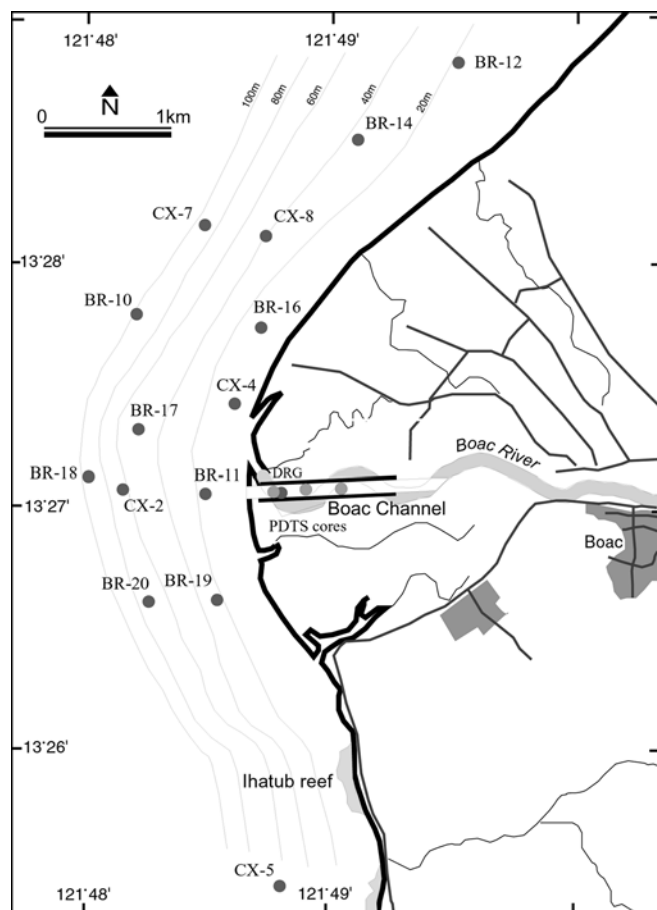
Fig. 2
Location of core samples. Cores were collected either in August 1998 (*BR* prefix, *DRG*) or the same month the following year (*CX* prefix) or in December 1999 (*PDTS* cores)

concentrations represent the average of three replicates with relative standard deviation less than 5%.
Metal recovery using the HNO_3 reflux method was between 90–100% for most metals – Co (100%), Cu (94.3%), Fe (93.5%), Pb (100%), and Zn (94.6%). Cd values are slightly higher than the reported value. Other metal recoveries are significantly lower than reported bulk concentrations – Al (46.4%), Cr (56.7%), Mn (85.2%), and Ni (81.3.0%). These recovery values were determined by employing an NIST standard reference material (SRM 2711) of similar geochemical composition (Table 1). It should be noted that the recovered fraction does not include metals bound in the silicate lattice of the particles which would likely be available for diagenesis or biological uptake (Luoma and Bryan 1981; Hornberger and others 1999).
Investigation of the mineralogy of mine tailings was also done using a Rigaku Geigerflex X-ray diffractometer (XRD). The <63-μm fractions of mine-tailings samples were scanned (0.25°/s) from 0 to 65° incident angle relative to the plane of the sample surface. Scanning electron microscopy (JEOL JSM-5600LV) also provided additional information on clay mineral geochemistry using a semi-quantitative energy dispersive system (EDS).

Modeling and volume estimates
Aid in generating isopach plots and volume estimates was gained by using Matlab v. 5.3 (Mathworks Inc.) and Surfer v. 5.0 (Golden Softwares Inc.). Contour lines were constructed using triangulation with linear the interpolation method. However, it should be noted that values along the coastline were inferred based on the nearest core. Volume estimates were carried out with the trapezoidal rule method in Surfer v. 5.0.

samples were then refluxed at 100 °C for 14 days, stirring the solution every day. The bulbs were then removed and the samples were evaporated to dryness. The residue was reconstituted in 0.6 N trace-metal-grade hydrochloric acid, and filtered through a 0.45-μm filter to extract an aliquot. Analyses of samples, duplicates, blanks and reference materials were accomplished using a Thermo Jarrell Ash IRIS inductively coupled plasma optical emission spectrometer (ICP-OES). Concentration standards and quality-control standards were prepared to closely match the sample matrix. All reported

Results and discussion

Marinduque Island consists mainly of Tertiary volcanic rocks, carbonate formations, and mineral-bearing diorite intrusives. The western coast consists mostly of basaltic flows and volcaniclastics, overlain by reefal carbonates. The mineralized regions of the island are in the central part (Marcopper Mine) and in the northwestern part of the island (abandoned MMC Mine). Both mineralizations are porphyry copper deposits, with pyrite and chalcopyrite occurring as disseminations in both source and host rocks

Table 1
Calculation of percent recovery of elements using the nitric acid reflux digestion method of Luoma and Bryan (1981). A standard reference material (SRM 2711 Montana Soil) of similar geochemical composition was used. Metals bound in the lattice of silicate minerals are not liberated using this digestion procedure

	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
No. of samples	12	12	12	12	12	12	12	12	12	12
Min	26,800	43.3	10	23.0	106	25,900	532	16.3	1,130	325
Max	31,800	45.4	11	27.8	110	27,300	557	17.3	1,190	338
Mean	30,300	44.4	10	26.6	107	27,000	544	16.7	1,160	331
Certified concentration	65,300	41.7	10	47	114	28,900	638	20.6	1,160	350
Recovery (%)	46.4	106.5	100.0	56.7	94.3	93.5	85.2	81.3	100.0	94.6

Table 2
Analysis of CX2 core porewater. Evident in these data is the confined, high trace-metal concentration observed in the 5–10 cm sample. All values are in ppm, <*D.L.* is less than detection limit which is 0.1 ppm for most elements

	Distance from the surface (cm)				
	0–2.5	2.5–5	5–10	10–15	15–20
T (°C)	25.0	28.2	29.7	29.1	28.8
pH	7.3	7.3	7.1	7.2	7.3
Ca	358	398	479	447	394
K	341	395	376	350	318
Mg	1,100	1,210	1,110	1,040	869
Na	9,460	10,500	9,450	9,140	7,940
Al	1.9	1.3	66	1.5	2.1
Cu	0.1	<D.L.	9.2	<D.L.	<D.L.
Co	<D.L.	<D.L.	0.3	<D.L.	<D.L.
Cr	<D.L.	<D.L.	0.1	<D.L.	<D.L.
Fe	0.7	0.2	181	10.8	0.4
Mn	1.3	1.2	8.7	2.7	1.6
Pb	0.2	0.2	0.7	0.1	0.1
Ni	<D.L.	<D.L.	0.1	<D.L.	<D.L.
Zn	<D.L.	<D.L.	1.4	0.4	0.4

(BMG 1981). The Marcopper Mine started operation in 1969. It was eventually shut down the day after the mine spill occurred.

The largest river on the island is the east-west Boac River system, with its headwaters splitting into the Boac upstream and the Makulapnit River. Downstream, prior to the dredging of the Boac River channel, the river opening was around 300 m to the north of the current, dredged channel opening. This geometry had a significant impact on the dispersal of tailings during the first few months before the river was finally dredged during October 1996. Construction of a 1-km-long channel at the mouth of the Boac River was undertaken to facilitate the removal of the tailings still deposited along the river. It was intended to trap most of the tailings which would soon be washed down during storm events, and to let the fine-grained fraction disperse in the open ocean. Completed in 1997, the dredged channel now holds an approximate volume of 530,000 m^3 of both coarse and fine-grained tailings material (PDTS, unpublished data 1997). The brackish water overlying the channel is only 1–2 m deep. Increased flow during the rainy season and storm events remobilize the top portion of the deposited materials in the channel and redeposit these in the nearshore area. PDTS estimated that most of the tailings material are now confined in the nearshore marine environment within 2 km of the Boac River opening, whereas beyond this radius only trace amounts (less than 1 cm) of the tailings have been deposited.

The bathymetric profile of the western coast of the island shows an ocean floor which gradually slopes to 20 m in depth, then steeply drops off to 150-m depth within 1.5 km from the shoreline. The longshore current is controlled by a southwest wind direction from May to September, and a stronger northeasterly wind direction from October to April (Philippine Atmospheric, Geophysical, and Astronomical Services Administration (PAGASA), unpublished data 2001). Acoustic doppler current profiler (ADCP)

measurements reveal that surface currents offshore of the Boac River area are relatively weak, rarely more than 50 cm/s; at 98-m water depth the current speed is only 5 cm/s (Hay and Co., unpublished data 1996). The annual mean discharge of the Boac River is estimated at 10.5 m^3/s based on a 10-year record (1959–1969; Siringan and Ringor, unpublished data 2001), with expected higher discharge occurring during the high-rainfall season (July to December) (PAGASA, unpublished data 2001). Still, the predominant north-northeast longshore current and the higher river discharge rate during the second half of the year should cause sediment deposition from the Boac River to be slightly skewed northwards.

The possibility of metal mobilization due to diagenetic and/or biologic processes after the tailings have been deposited was a major concern due to the fact that the cores were taken 2–3 years after the spill. Porewater analysis of the CX2 core collected in 1999 revealed a confined, metal-enriched zone 5–10 cm beneath the surface (Table 2) which also corresponded to high metal concentrations in the sediments. High trace-metal levels in the associated porewater in tailings either resulted from the dissolution of soluble phases or they were due to sulfide oxidation of minerals such as pyrite and chalcopyrite (Al and others 1994). Regardless of the origin of this associated water, it suggested little or no migration of metals within the sediment section at the time of sampling.

Establishing background trace-metal concentrations

Background trace-metal values were established using a sediment core taken from a site which reflects the regional geologic character of the island but lies beyond range of the Marcopper tailings spill. The CAWIT core site (50-m depth) is situated along the western coast of Marinduque Island 10 km south of the Boac River (Fig. 1). The nearest river to this core site is the Libtangin River which is 2.5 km farther south. This river drains the same mountain ridge as that of the upstream Boac River.

The 35-cm-long CAWIT core shows a flat metal-concentration profile downsection. Relatively narrow ranges in Al, Fe, Cd, Co, Cr, Mn, Ni, Pb, and Zn values typify this core, suggesting a uniform geochemical character for its sediment source(s). However, it did exhibit slight variability in Cu concentration, partly due to an enriched topmost layer (227 ppm Cu) which may still have derived tailings material from reworking of contaminated sediments. Excluding the topmost (0–2.5 cm) sample, the average Cu concentration in the core is 113 ppm. This value is consistent with previous Cu analyses of sediments in the Libtangin area which showed an average Cu concentration of 102 ppm (34–259 ppm range). Deep-sea sediment samples collected west of Marinduque also gave a range of 43–142 ppm Cu (Siringan and Ringor, unpublished data 2001). Furthermore, this value is close to the observed minimum values in some of the cores collected off the Boac River (cores CX-5, BR-14, CX-8, BR-10, and BR-20). This will be further discussed below.

Metal concentrations in tailings material

Mine-tailings samples collected from the Boac dredged channel revealed a material which is inherently heterogeneous in terms of grain-size distribution, mineral composition, and metal concentrations. Based on the three PDTS cores collected in 1999, the surface of the dredged channel has a coarser grain-size distribution, with the <63-μm fraction comprising only around 5–28% of the volume by weight. This contrasts with samples collected 1–1.5 m beneath the surface which have the finer fraction comprising 31–85%. The 40-cm DRG core collected in 1998 showed higher amounts of the <63-μm fraction (58–89%) but nevertheless has the same higher coarse grain-size distribution towards the surface. The color of the tailings also grades from light brown to very light gray, as opposed to the dark, greenish-gray color of sediments in the CAWIT core.

X-ray diffraction of samples revealed mineral proportions dominated by quartz, plagioclase, mica, and clay minerals. Iron oxide phases are also found to be abundant in the finer grain size fractions. Analysis of several tailings samples using EDS failed to detect any primary sulfide phases which may have contained copper and other metals. Instead, low copper concentrations were found in clay particles, particularly in chlorite minerals. This observation suggests that the metals also occurred as weakly bound phases in clay minerals. Sorbed metals on clay minerals have been previously documented in other sulfide tailings investigations (Lambors 1994; Dold, unpublished data 1999).

Metal concentrations were found to be generally higher in the <63-μm fraction compared to the coarser fraction of the samples. The fine-grained tailings material also showed a much wider range of metal concentrations. This was particularly evident for copper which had an average of 1,340 ppm but ranged from 706 to 3,080 ppm in the PDTS tailings samples. The DRG core showed higher metal concentrations (1,260–3,750 ppm) but was comparable with the surface PDTS samples. The variability in composition is probably a natural characteristic of the tailings materials, which not only have diverse source rocks but have also been subjected to variable environmental conditions (i.e., oxidation, pH of overlying water, T, etc.). Comparing the marine sediment baseline metal values with mine-tailings values (Table 3), metals can be classified into three groups: metals which show a similar range in concentration in both types of material (Al, Fe, and Co), metals which are depleted in the tailings (Cd, Cr, and Ni), and metals which evidently show enrichment in mine tailings (Cu, Mn, Pb, and Zn). Copper displayed the highest enrichment (11.9×) in the tailings, followed by Pb (4.7×), Zn (2.8×), and Mn (1.8×). As expected, metal values in the Boac offshore cores lie between the background and tailings values (Table 3), in as much as these sediments represent mixtures in varying proportions of tailings and marine sediments. The significant addition of Cu from mine tailings was used to trace the mine spill in terms of its extent and evolution of its deposition in the offshore region.

Metal concentrations in marine sediments

Figure 3 shows the metal tracer profiles for each of the cores. In terms of concentration ranges, copper showed the largest variation in the cores. Manganese, lead, and zinc concentrations varied only slightly within each core. However, the slight deviations from the average values of these elements were similar to the copper profile. Iron, which does not show a definite enrichment in contaminated sediments, was also investigated because it also showed a slight positive correlation with Cu in most cores. Flat metal profiles were observed in cores more than 3 km away from the Boac outlet (cores CX-5, BR-12, and BR-14). Both BR-14 and CX-5 cores exhibited a flat yet elevated Cu profile for at least the topmost 15 cm (averages of 616 and 456 ppm, respectively), and returned to near-baseline values in stratigraphically lower samples. Core BR-12 also had a relatively flat profile which slightly decreased downsection but did not reach the baseline value. On the other hand, a common feature in cores within 3 km of the Boac River outlet was a high copper concentration horizon at or near the surface, and another at 10–20 cm depth depending on core location. Cores CX-2 and CX-4 may have also shown the same profile if longer cores had been extracted. Within these horizons, Cu values reached more than 900 ppm, 100–200 ppm higher than the core average values. The highest Cu value recorded was from core CX-4 (1,530 ppm) which was only 500 m away from the original Boac outlet. As usual, the other metals, particularly Zn, closely mimicked the Cu profiles.

The two horizons are interpreted to correspond to distinct sedimentation events in the past. The lower horizon (15–20 cm depth) is due to the input of mine tailings during the spill in March 1996. March–June 1996 were high rainfall months, which may well have resulted in

Table 3

Comparison of metal concentrations in marine sediments (CAWIT core), mine tailings (PDTS samples), and in the Boac offshore cores. Given are average values as well as the concentration range for each element

| Metal	CAWIT baseline core	Mine tailings (PDTS cores)	Boac offshore cores
Al (wt%)	4.0 (3.6–4.3)	4.7 (3.9–5.6)	4.9 (2.8–7.6)
Fe (wt%)	4.3 (4.0–4.5)	3.9 (3.3–4.8)	4.8 (3.3–6.8)
Cd (ppm)	3.5 (3.2–3.7)	0.6 (0.1–0.9)	2.9 (1.9–4.4)
Co (ppm)	20.1 (18.2–21.1)	24.8 (16.7–36.1)	20.5 (12.9–34.0)
Cr (ppm)	67.9 (56.9–73.7)	32.1 (22.6–42.2)	40.6 (24.5–66.7)
Cu (ppm)	113 (53.8–161)	1,340 (706–3,080)	803 (136–1,530)
Mn (ppm)	421 (404–429)	741 (445–1,060)	566 (403–1,040)
Ni (ppm)	90.9 (76.8–102)	20.4 (11.1–32.4)	28.0 (14.1–42.7)
Pb (ppm)	10.7 (8.8–12.4)	50.1 (42.5–56.3)	25.2 (10.1–45)
Zn (ppm)	60.9 (50.0–67.0)	168 (120–276)	127 (80.8–203)
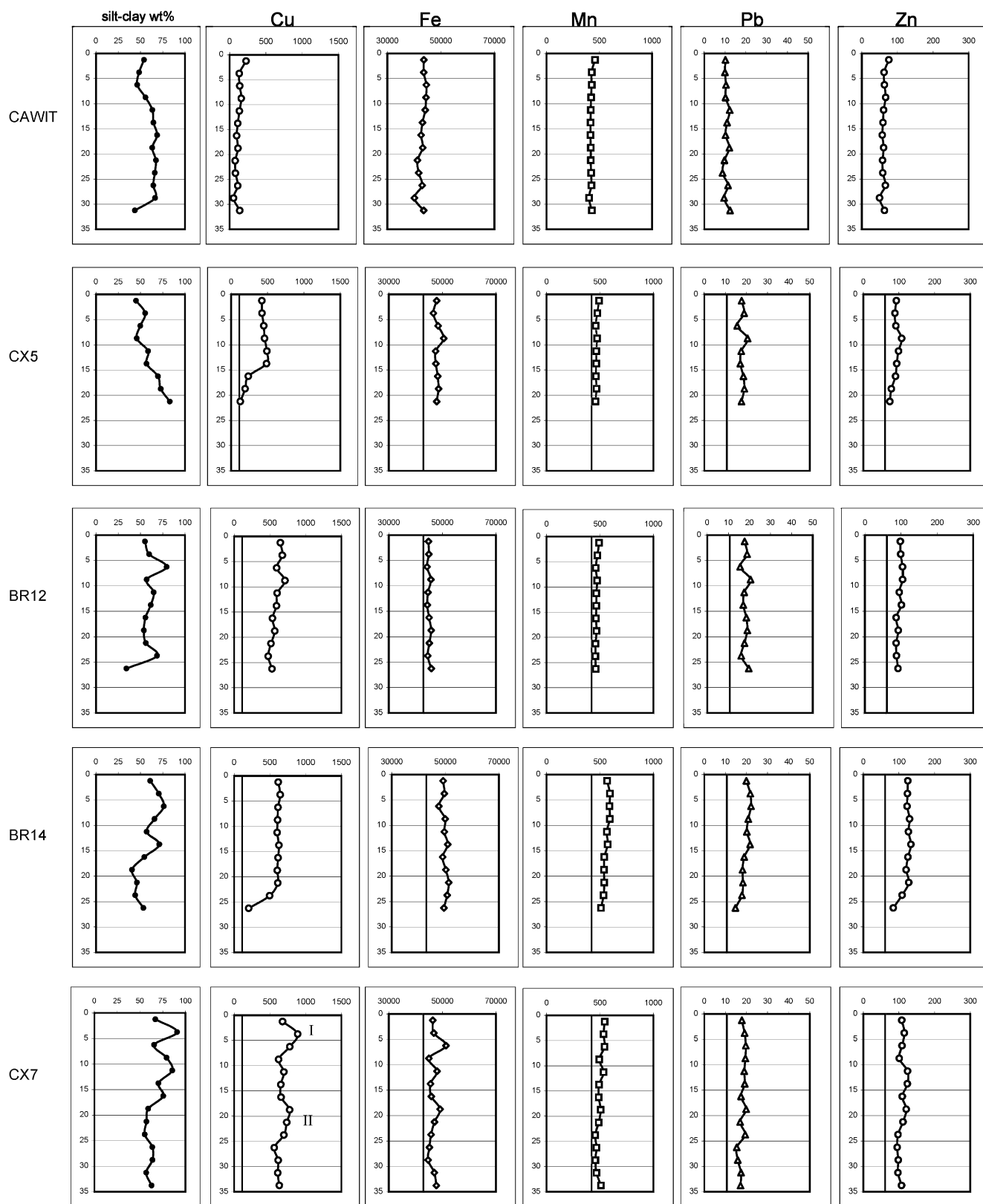
Fig. 3
Cu, Fe, Mn, Pb, and Zn concentrations (in ppm) in the cores. The y-axis for all plots represents depth (in cm) below the surface. The cores are arranged based on their distance from the original Boac River opening, starting with the farthest. The regional baseline value based on the CAWIT core is plotted for reference. Two Cu horizons are observed in most cores, one occurring at 0–7.5 cm (*I*) and a lower horizon at 10–20 cm depth (*II*)
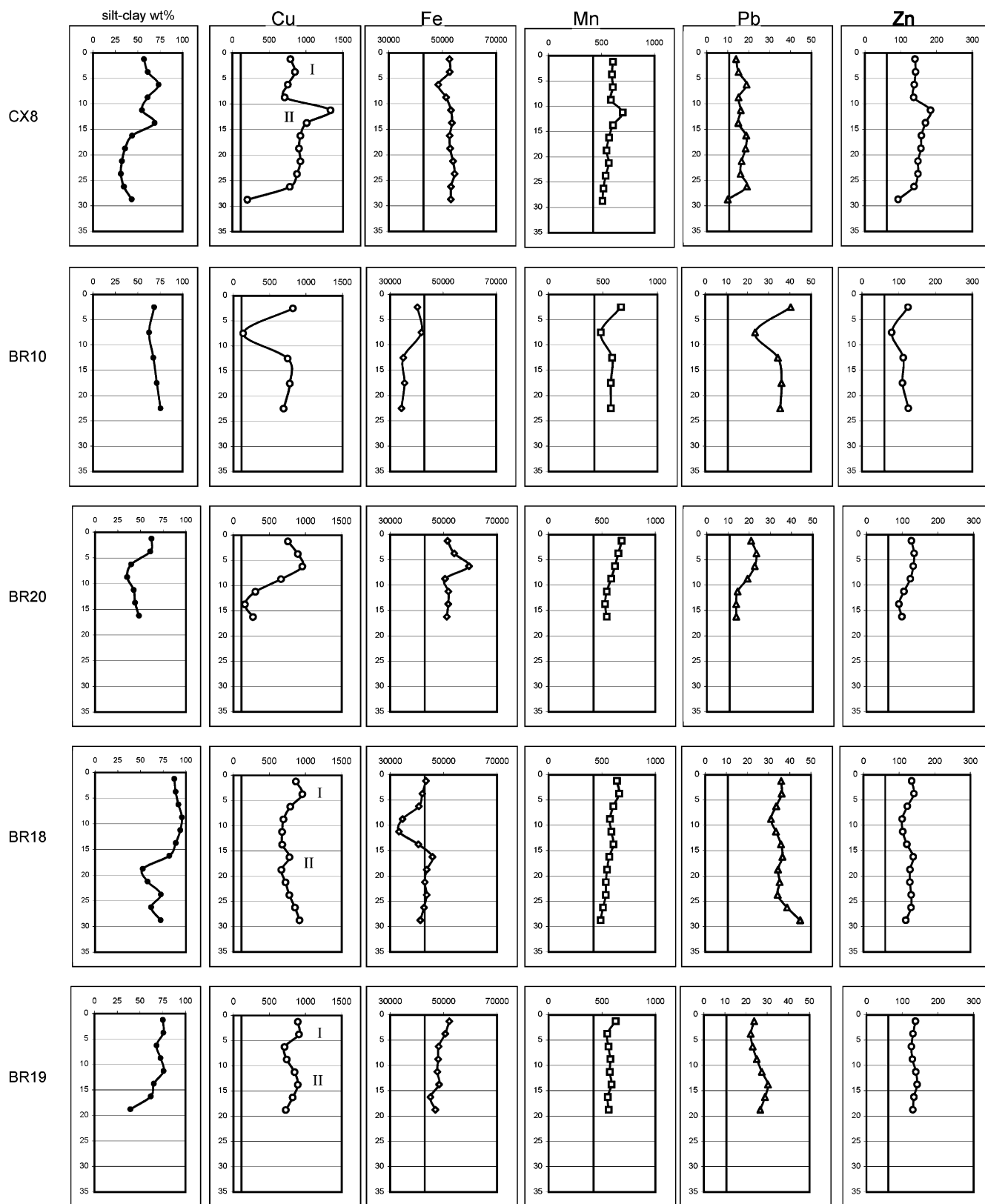
Fig. 3
(Contd.)

more materials being flushed out during a very short time period. The upper metal horizon was thought to be predominantly due to the new tailings input in 1997 as well as reworking of deposited materials. A probable cause for this latter input of materials was the dredging work performed at the mouth of the Boac River from October
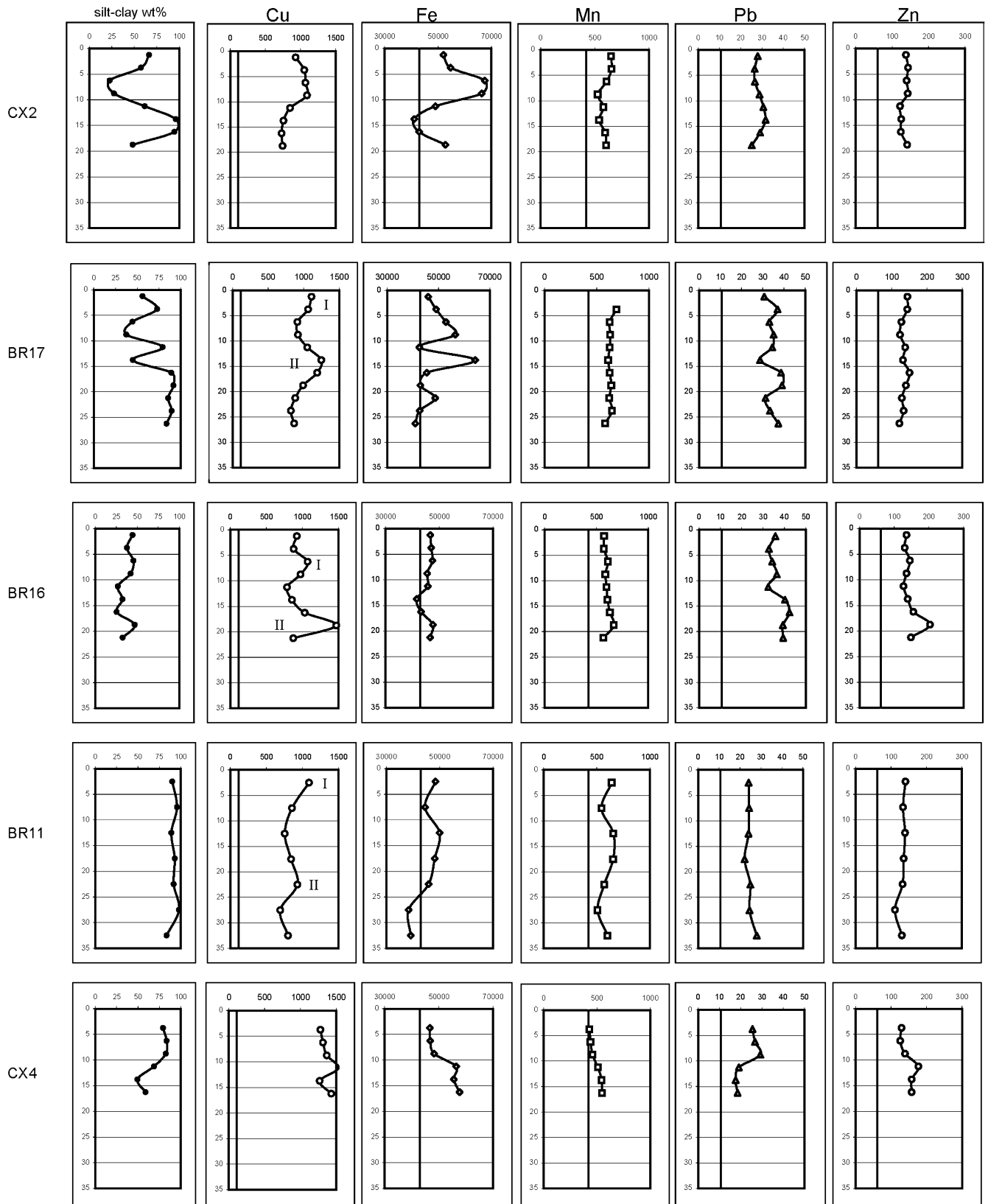
Fig. 3
(Contd.)

1996 to July 1997. Reworking of sediments cannot be discounted, as even cores collected in 1999 (CX-2, CX-4, and CX-8) showed high metal values near the surface. Furthermore, remobilization of materials within the dredged channel was also observed during storm events. The pervasive high metal concentrations in surface sediments imply that metal availability to benthic organisms may still be an important concern several years after the spill.

At most of the sites near the channel, the lowermost samples in cores have metal concentrations exceeding the perceived background metal values. This implied either that the core has not penetrated through pre-spill layers or that the sediments adjacent to the mouth of the river inherently had higher trace-metal levels prior to the spill. Cores which reached the established regional baseline concentration (cores CX-8, BR-14, CX-5) indicated a contaminated section of 15–27.5 cm. Considering the thickness of contaminated sediments and the distance from where these cores were collected, it is unlikely that this contaminated section may be attributed solely to the 1996 spill. It is probable that it had only overprinted onto a much older history of contamination.

Mine-tailings distribution in the offshore region

Figure 4 shows the average Cu, Fe, Mn, Pb, and Zn values for the topmost 20 cm of each core. An evident metal concentration gradient, particularly for Cu, is present away from the original Boac River channel. Iron, lead, and zinc also show this distribution to a certain extent. Manganese varied slightly (470–685 ppm), so any trend would not have been as distinct as for the other elements. The tailings distribution was slightly skewed northwards, with cores CX-8 and BR-16 showing average Cu concentrations of >900 ppm. A steeper gradient seawards in metal concentrations indicates dispersion of the tailings having a strong lateral (longshore) component.

The hypothesis that there was previous contamination of the area needs to be addressed to isolate the exclusive addition of mine tailings due to the 1996 spill. An apparent, local Cu baseline value for each core was deduced using the Cu concentration immediately below the lower Cu horizon (usually at >20 cm from the surface). In most cores, this value was similar to the one observed between the two Cu spikes. However, this baseline differed in each core, suggesting a local baseline which was not uniform but graded away from the Boac channel (Fig. 5). For cores
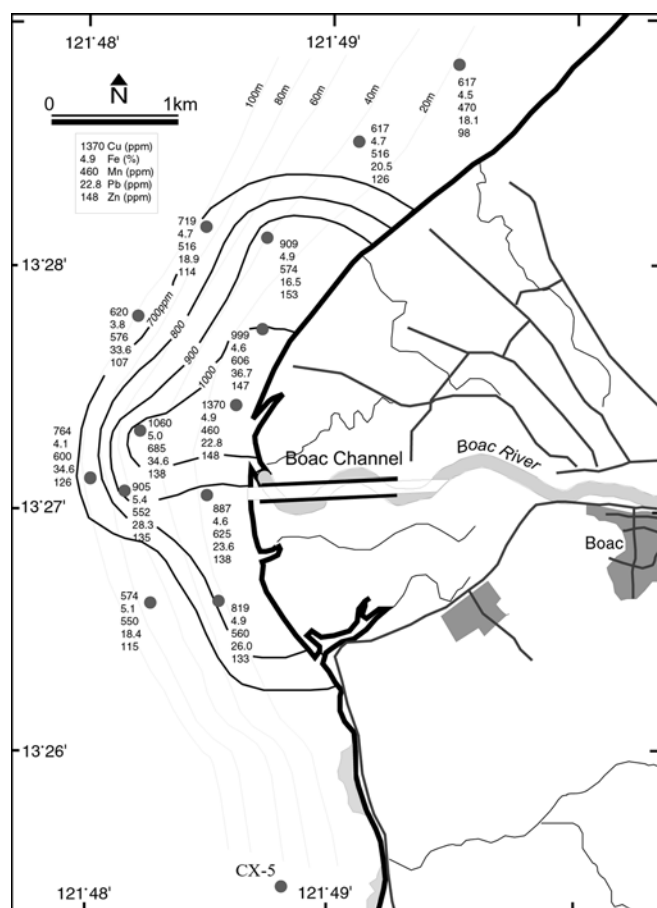

Fig. 4
Average concentrations of Cu, Fe, Pb, Mn, and Zn in the topmost 20 cm of each core. An evident gradient away from channel is observed, particularly for copper. The isopach lines plotted are for Cu
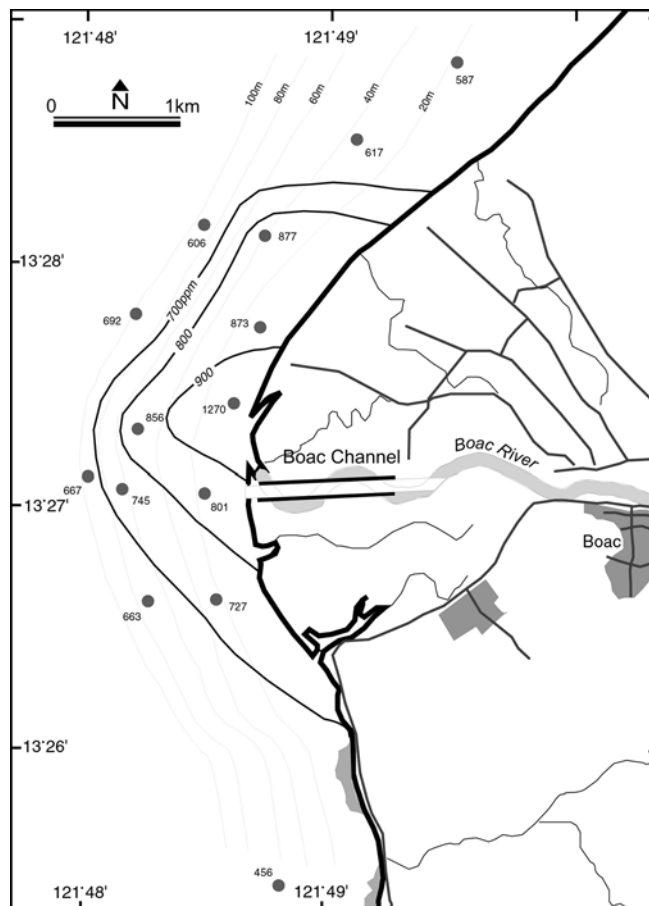

Fig. 5
Isopach map of local copper baseline values (in ppm). This is taken as the Cu concentration directly beneath the lower Cu horizon (usually at 20-cm depth). Evident in this map is a local baseline which decreases with distance from the Boac channel
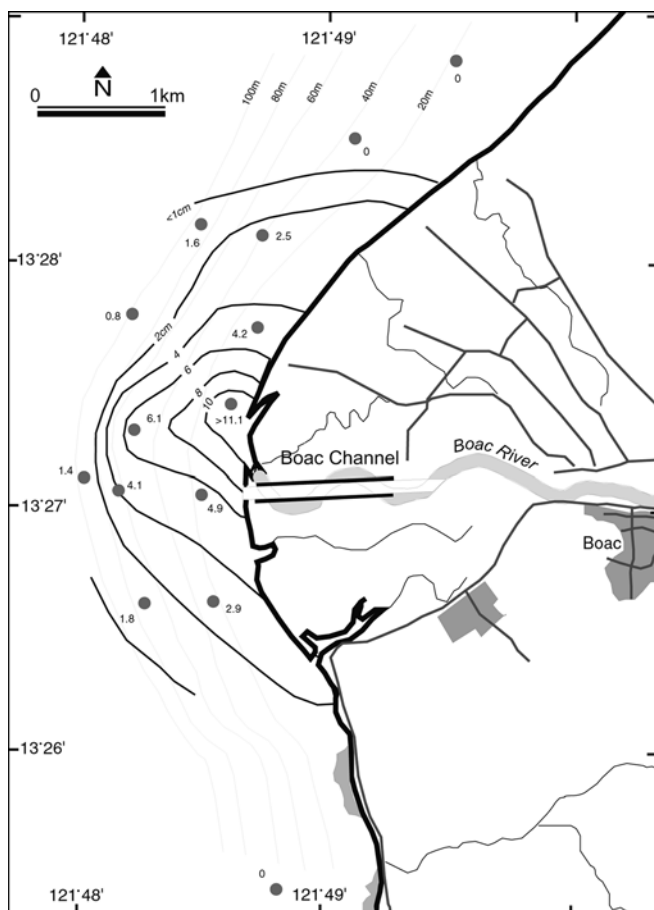
Fig. 6
Isopach map of calculated total tailings (in cm) deposited from the 1996 mine spill. This was done by normalizing Cu values in cores with the local Cu baseline and a Cu value representative of pure mine tailings (1,540 ppm)

Figure 6 shows the distribution of mine tailings in the study area as calculated with Eq. (1). As expected, a tailings thickness gradient away from the old channel was observed. A large amount of tailings seems to have been deposited within 1 km of the channel because at least 10 cm of tailings material was calculated in the CX-4 core. A slight shift in tailings distribution northwards is evident but deposition beyond 60-m depth rapidly decreases seawards. A volume estimate using these values indicated a total tailings volume of 180,000 m^3. Using a value of 1,340 ppm to characterize the pure tailings material, a new volume estimate of 260,000 m^3 was calculated. The larger estimate assumed that most of the 18-cm CX-4 core was composed of pure mine tailings.

Conclusions

Elevated concentrations of Cu, Mn, Pb, and Zn in marine sediments can be traced to the 1996 mine-tailings spill. Two high-Cu horizons in most offshore cores are attributed to distinct input events (actual spill and dredging/sediment reworking). However, a much older history of contamination in the area is perceived as reflected in cores some distance removed from the Boac channel (cores BR-14 and CX-5) as well as from the deduced, local baseline values at sites adjacent to the channel. This may be related to heightened mining activity in the early 1980s, although this hypothesis still needs to be confirmed by future work. Another important observation made was the persistence of contamination in surface sediments even several years after the spill. This should be an important concern when evaluating the overall impact of the spill. Further studies on the availability of these sediment-bound metals to aquatic organisms should also be undertaken.

The spatial analysis of metals in the sediment cores shows a gradient away from the original channel. A significant amount of the tailings has been deposited within a 1-km radius; however, considerable dispersion of the material northwards is also evident. This suggests a wider area affected by the spill, as reported in previous assessment work done by PDTS. The total mine tailings confined within the nearshore area was estimated to be 180,000–260,000 m^3. This excludes the thin tailings layer (<2 cm) which may have been deposited in a much wider area. The estimate was made possible by using the geochemical characteristics of mine tailings to trace its spatial/stratigraphic distribution and distinguish it from uncontaminated sedimentation in the region.

which showed flat metal profiles (cores CX-5, BR-12, and BR-14), the average concentration was taken as the local baseline value.

To normalize the copper concentrations observed, the local baseline value was subtracted from the Cu concentrations observed. A Cu value (1,530 ppm) representative of average Cu values in mine tailings was used to calculate the percent tailings in the marine sediments. This Cu concentration is the highest value found in offshore cores (core CX-4, 10–12.5 cm) and is also comparable to the average Cu concentration in the three PDTS cores (1,340 ppm). Below is the equation used to calculate the total tailings deposited at each core site:

$$T = \sum_{n=1} j \times \left(\frac{[X_{sample}] - [X_{baseline}]}{[X_{tailings}] - [X_{baseline}]} \right) \quad (1)$$

where T is the calculated total tailings thickness, j is sampling interval (2.5 or 5 cm), and n is the number of samples in each core. X_{sample} is Cu concentration in each sample, $X_{tailings}$ is the average Cu value in mine tailings (1,530 ppm), and $X_{baseline}$ is the local Cu baseline in each core.

References

Al TA, Blowes DW, Lambors JL (1994) A geochemical study of the mine tailings impoundment at the Falconbridge Limited, Kid Creek Division Metallurgical Site, Timmins, Ontario. In: Lambors JL, Blowes DW (eds) Environmental geochemistry of sulfide mine wastes. Mineral Assoc Can 22:323–364

Astrom M, Nylund K (2000) Impact of historical metalworks on the concentrations of major and trace elements in sediments: a case study in Finland. Appl Geochem 15:807–817

Axtmann EV, Luoma SN (1991) Large-scale distribution of metal contamination in the fine-grained sediments of the Clark Fork River, Montana, USA. Appl Geochem 5:75–88

Baptista-Neto JA, Smith BJ, McAllister JJ (2000) Heavy metal concentrations in surface sediments in nearshore environment, Jurujuba Sound, Southeast Brazil. Environ Pollut 109:1–9

BMG (1981) Geology and mineral resources of the Philippines, vols 1 and 2. Bureau of Mines and Geosciences Philippines Ministry of Natural Resources Publ, pp 60–65

Gonzales H, Ramirez M (1995) The effect of nickel mining and metallurgical activities on the distribution of heavy metals in Levisa Bay, Cuba. J Geochem Explor 52:183–192

Hornberger MI, Luoma SN, Van Geen, A, Fuller C, Anima R (1999) Historical trends of metals in the sediments of San Francisco Bay, California. Mar Chem 64:39–56

Jacobson M (1998) Guyana's gold standard. Nat History 9:12

Lambors JL (1994) Mineralogy of sulfide-rich tailings and their oxidation products. In: Jambors JL, Blowes DW (eds) Environmental geochemistry of sulfide mine wastes. Mineral Assoc Can 22:59–102

Luoma SN, Bryan GW (1981) A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. Sci Total Environ 17:167–196

Moore JN, Luoma SN (1990) Hazardous wastes from large scale metal extraction: A case study. Environ Sci Technol 24:1279–1285

Salomons W, Forstner U (1984) Metals in the hydrosphere. Springer, Berlin Heidelberg New York

Van Geen A, Chase Z (1998) Recent mine spill adds to contamination of Southern Spain. EOS Trans Am Geophys Union 79:449