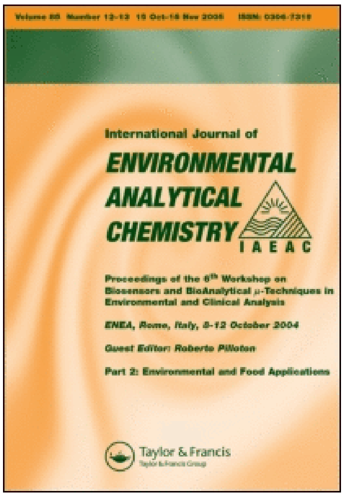

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Levels and Distribution of Trace Metals in Sediments of Laguna Lake (Philippines) and its Tributary Rivers

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LEVELS AND DISTRIBUTION OF TRACE METALS IN SEDIMENTS OF LAGUNA LAKE (PHILIPPINES) AND ITS TRIBUTARY RIVERS

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Trace metal levels in bottom sediments of Laguna Lake (Luzon, Philippines) and of five of its tributary rivers, and in lakeshore samples were compared. Total metal analyses by flame atomic absorption spectrophotometry indicate relatively low (Cu, Zn, and Pb) to moderate (Fe, Mn, Hg, and Cd) metal contamination in the sediments.

Using the Tessier *et al.* sequential chemical extraction scheme, the order of remobilizability was Mn > Cu > Zn ≫ Fe for lake sediments; similar trends were observed in tributary river sediments and lakeshore soil samples, except that Zn was more extractable than Cu. Organic matter bound significant amounts of Cu, Zn, and Fe in lake sediments and of Cu in river sediments. Mn was distributed rather evenly across all fractions in all samples. The largest fraction of all metals in lakeshore soil was associated with reducible Fe/Mn oxides. The non-available or residual fraction (relative to the total metal content) in all samples ranged as follows: Fe, 85–94%; Zn, 40–81%; Cu, 39–78%; Mn, 9–74%.

KEY WORDS: Laguna Lake (Philippines), metal levels in lake and river sediments, metal distribution in sediments/soil, metal speciation in sediments/soil, remobilizability of metals from sediments/soil

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INTRODUCTION

Man's activities are continuously increasing the levels of various pollutants (e.g., trace metals, pesticides, and other hazardous substances) in natural water systems, thus posing threats to both aquatic organisms and users of water resources. Bottom sediments represent an important indicator of contamination because they tend to accumulate pollutants in aquatic systems. They therefore help identify areas which have become contaminated and reveal spread patterns from sources, and, through analyses of core samples, contaminant input history. They show much less temporal and spatial variation than the water column and thus provide more reliable time-integrated information than water column data. In addition, metal levels in sediments are generally one to two orders of magnitude higher than the amount of dissolved forms in water and, hence, may be determined more accurately by existing analytical techniques in conventional (i.e., not classified as 'clean') laboratory facilities.

Studies have demonstrated that the ecotoxicity or bioavailability of a metal not only varies with biological species[1] but also depends on the chemical form ('species') of the metal[2]. Soils and sediments are heterogeneous mixtures of bedrock mineral fragments and weathering and decomposition products. Trace metals may be distribued or partitioned between many components of the soil or sediment and may be bonded to them in different ways. The nature of these associations in the sediment or soil structure has often been referred to as 'speciation' and determines the capacity of the sediment/soil to resupply the water column with the metal when physicochemical conditions are favourable.

The impact of contaminated sediments on the aqueous environment is more realistically estimated by sediment speciation than by the total metal content[3]. This approach helps differentiate between contributions from natural (which are mainly found in the inert lithogenic fraction) and from anthropogenic (which are relatively remobilizable) sources.

Pickering[4] has reviewed the numerous soil and sediment speciation schemes in the literature. Generally, these schemes use reagents that selectively release trace metals, which are held in the soil or sediment by different chemical bonds, or dissolve certain mineral phases. Although these reagents are not highly specific in extracting metals from different phases[5–7], they provide a useful means for estimating potentially 'available' metal concentrations and for comparing different sediment/soil samples with regard to the remobilizability of incorporated metals under different environmental conditions.

This study assesses the extent of metal pollution in Laguna Lake (Philippines), southeast Asia's largest (surface area ca. 90,000 hectares) freshwater lake and a vital resource of Laguna province and neighbouring regions, including Metropolitan Manila. There have been a few scattered studies on the general state of pollution in the lake. The most comprehensive study[8] was commissioned in 1975–1978 by the Laguna Lake Development Authority (LLDA), which manages the use of the lake. Reyes[9] recently reported 1984 mercury levels in lake sediments and in some fish and macroinvertebrates thriving in the lake.

This paper also reports the first attempt to determine the distribution of some trace metals in the lake sediments, in some tributary rivers' sediments, and in soil samples from sites along the lakeshore (which often become pseudo-lacustrine sediments during the rainy season, typically between June to October, when the lake volume rises).

EXPERIMENTAL

Description of the test sites Laguna Lake (locally known as Laguna de Bay) is located in Laguna province on Luzon island and is about 25 km southeast of Manila. Its basin (ca. 382,000 hectares) includes 20 towns in five surrounding provinces (Laguna, Rizal, Cavite, Batangas, and Quezon) and about 1000 industries[10], the majority located in the northwestern side of the lake (cf. Figure 1).

The lake has three branches: the West, Central, and East Bays. It has a shoreline of about 220 km, an average depth of about 3 m, and an average water elevation of 11.5 m. The deepest part (known as Diablo Pass and located at the northern tip of Talim Island) is at least 15 m during the wet/monsoon season (June–October). Details of the geology, mineralogy, and soil profile of the lake basin are available elsewhere[11,12].

There are 21 tributary rivers to the lake, but only one outlet (the Napindan Channel, at the northern end of West Bay), which drains into the Pasig River–Manila Bay estuary. Two recently constructed major infrastructures may dramatically affect the lake's ecosystem: an hydraulic control structure (operating since 1983) closed off the Napindan Channel to minimize backflow of saline water (from Manila Bay) into the lake during the summer months, when the lakewater level may become relatively low; and the Mangahan floodway (operating since 1988) which serves to divert to the lake overflows from Marikina River (northeast of West Bay) during the rainy season.

The current uses of the lake include: (1) aquaculture (mainly fish farming) production, which involves about 25% of the lake, and open fishing (about 25 varieties of fish are known[13]); (2) irrigation water for Laguna rice farms (mainly located south and east of the lake); (3) power generation: two oil-fired power plants (at Sucat and Jala-jala) utilize the lakewater for cooling purposes, while an hydroelectric plant (Kalayaan) pumps lakewater into Lake Caliraya (a man-made lake situated some 170 m above Laguna Lake and to the east of East Bay), and supplements the peak needs of the Luzon power grid; (4) transportation, which include barging operations (for the power plants, an oil refinery, and a cement plant), and motorized boats to ferry residents of Talim Island; (5) duckfarming, largely in the northern area; and (6) recreation (mainly swimming) for local inhabitants.

The lake is generally turbid and eutrophic, with frequent abundant growth of water hyacinths[10].

Sampling and sample pretreatment Bottom (0–15 cm deep) sediments were obtained (using an Eckman dredge grab) from the eight regular LLDA sampling stations (marked A and I–VII in Figure 1) in July 1985. Soil samples (0–15 cm deep) were

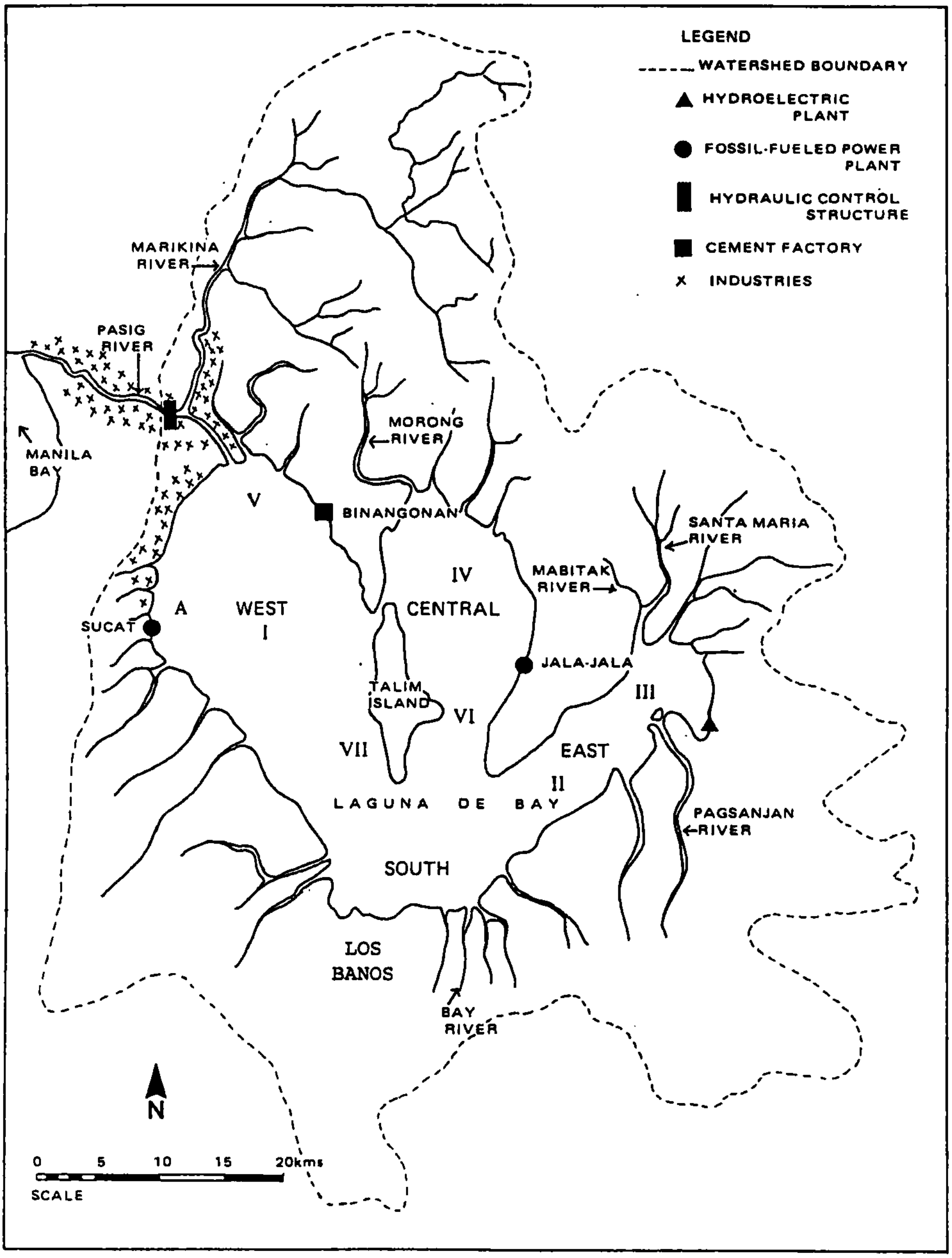

Figure 1 Laguna Lake: the watershed area, tributary rivers, and sampling stations.

taken along the lakeshore at Binangonan, Jala-jala, Los Banos, and Sucat (cf. Figure 1) in June 1986. Bottom sediments from five of the lake's tributary rivers (Bay, Mabitak, Morong, Pagsanjan, and Santa Maria Rivers; see Figure 1), which account for about 40% of the total flow into the lake[8], were sampled in January 1987. The distance of the river sampling sites varied from 200 m to 7 km from the lake, where water depths ranged from 40 to 400 cm deep.

The sediment samples were centrifuged to remove entrained water, air-dried, and then passed through a 20-μm nylon sieve. Sediment/soil analyses were performed on the fine fraction (<20 μm) only, since preliminary work indicated that this fraction concentrated more trace metals, and grain-size effects[14] on the analyses would be minimized. The supernatant water was preserved with concentrated nitric acid (5 ml per liter of sample).

Particle analysis and mineralogy A Shimadzu RS-11 recording sedimenter was used to determine the particle size distribution of the lake sediments according to Jackson's sedimentation velocity method[15]. X-ray diffraction (Rigaku d max II diffractometer) was used for mineralogical analysis of the sediments. The surface area of the sediment particles was estimated by nitrogen adsorption (QUANTASORB) at 88°K.

Organic matter content Ball's loss-on-ignition (380°C for 16 h) method[16] was used to determine organic matter content. Alternatively, it was determined by loss-in-weight after the sample was treated with hydrogen peroxide at 40°C to destroy organic matter, which gave results that agreed within 6% with the former method. Organic carbon content was determined using Wilde's spectrophotometric procedure[17], which involved the oxidation of organic matter by potassium dichromate.

Metal analyses Total metal contents of sediments or soil was determined on 2-g (oven-dried at 60°C) samples using a single extraction[18] with a mixture of concentrated hydrochloric (5 ml) and nitric (10 ml) acids; the digested sample was filtered (Whatman no. 42) and diluted to 100.0 ml. Mercury analysis[19] used a 1-g (oven-dried at 60°C) sample digested in 5% (v/v) nitric acid solution at 90°C in the presence of excess 5% potassium permanganate and 2 ml 5% potassium persulfate, filtered, and diluted to 100.0 ml.

500 ml of sediment supernatant water were digested in two 3-ml portions of concentrated nitric acid, evaporated to near dryness, taken up with 5 ml of 1:1 hydrochloric acid, filtered, and diluted to 100.0 ml[20].

Fe, Mn, Zn, Cu, Pb, Hg, and Cd were analyzed by flame atomic absorption spectrophotometry (Shimadzu AA-600). Concentrations were determined using calibration graphs, except where matrix effects appeared to be significant (i.e., total Cd and Pb content of lake sediments, and Fe content of the fractions in speciation analysis), when the standard addition technique was employed. The accuracy of both methods as checked against three European soil reference samples[21], which were kindly provided by the Institute of Soil Science, University of Hamburg (Federal Republic of Germany).

Speciation analysis Determination of metal speciation or distribution in sediment or soil employed the Tessier *et al.*[22] sequential chemical extraction scheme (cf. Figure 2). 1-g air-dried samples were used and extractions were carried out directly in 40-ml polyethylene centrifuge tubes to minimize losses. Residues were separated from the supernatant by 15-min centrifugation (KUBOTA KR-2000 S refrigerated ultracentrifuge) at 10,000 rpm. Washings of the residue were combined with the supernatant and the total volume of each fraction was made up to 25.0 ml with 0.008 M nitric acid to preserve the solution.

All solutions were prepared from reagent-grade chemicals and doubly-distilled deionized waters. Duplicate trials were performed in all analyses.

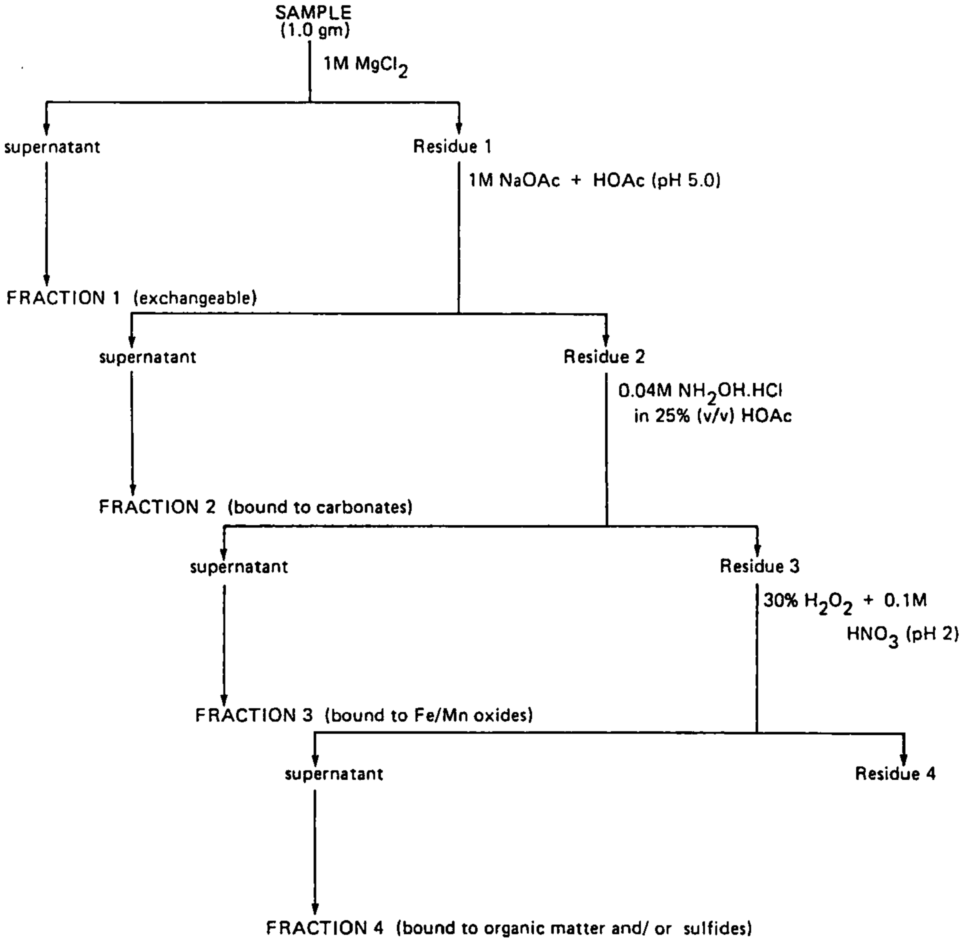

Figure 2 Tessier *et al.* sequential chemical extraction scheme for sediments/soil speciation.

RESULTS AND DISCUSSION

Physicochemical analyses of sediments and lakeshore soil

The lake sediments had a greyish appearance with a fine clayey consistency. The particle size distribution was quite narrow and showed little variation between samples: approx. 50% of the particles were less than 1 μm, about 70% less than 2 μm, almost 90% were less than 5 μm, and 100% were less than 20 μm. The average surface area of the particles was 17.3 ± 1.4 m^2/g. In contrast, the river sediments had a very heterogeneous particle size distribution, with a significant proportion having silty and sandy texture. The lakeshore soil samples likewise had a much higher proportion of coarser particles (> 100 μm).

The average lake surface temperature and dissolved oxygen content on the day of sampling was 29.0 ± 0.5°C and 7.0 ± 0.6 mg/l, respectively, while the lake bottom conditions were 27.4 ± 0.5°C and 5.1 ± 0.6 mg/l, respectively. These correspond to oxygen saturation[23] levels of 93% and 66% at the surface and bottom of the lake, respectively. The water quality standard[24] for dissolved oxygen in waters for fish farming is a minimum of 5 mg/l. During this month, maximum algal growth is said to occur, with the lake water pH rising to about 9.6[9], compared to a typical pH range of 7.4–8.5[8].

X-ray diffraction analyses revealed that the lake sediments from all sampling stations had very similar mineralogy in spite of the huge watershed area. The following minerals were found: quartz, plagioclase, kaolinite, chlorite, and traces of goethite. Lake sediments are allogenic minerals which reflect the mineralogy of the lake surroundings; goethite, however, may also be of authigenic and endogenic origin[25].

The average organic carbon content of the lake sediments from all sampling stations was 4.0 ± 0.2% (range, 3.5–4.4%), while the mean organic matter content was 7.5 ± 0.4% (range, 6.5–7.9%), i.e. a ratio of organic carbon to organic matter content of 0.53, which is similar to that obtained in humic substances[26]. The mean organic matter contents of the river sediments and the lakeshore soil samples were slightly lower at 5.5 ± 1.6% (range, 4.2–7.4%) and 5.9 ± 1.5% (range, 4.0–7.5%), respectively. Humic acids were extracted from the lake sediments and characterized in separate studies[26,27]; these are of special interest because they can form complexes with trace metals and consequently modify the metal's ecotoxicity[28,29].

The average moisture contents were: lake sediments, 6.1 ± 1.1% (range, 5.2–8.8%); river sediments, 2.7 ± 0.5% (range, 2.2–3.4%); and lakeshore soil, 2.3 ± 0.7% (range, 1.6–3.5%). In a separate study using the same samples, Pfeiffer *et al.*[30] found that the average pH of a suspension of the lake sediment in 0.01 M $CaCl_2$ (ratio, 1:2.5) was 6.1 ± 0.3 (range, 5.6–6.4).

The lake is vulnerable to emissions from the densely populated (ca. 8 million) and highly urbanized Metropolitan Manila area. Although there are no data available on atmospheric metal concentrations in the region during the period of the study, evidence for atmospheric trace metal emissions was obtained by Pfeiffer *et al.*[30], who observed that metal levels in vegetation grown in contaminated soils (both plants and soils sampled in September 1985) of Metro Manila in many cases did not correlate directly with the soil content; instead, a significant proportion of the data indicated foliar uptake, rather than absorption through the plant roots.

Analyses of the supernatant water samples from lake and river sediments revealed that Cu and Zn levels were below 0.04 ppm; Hg, Pb, and Cd levels were below the AAS limits of detection for water analyses (0.4 ppb, 0.2 ppm, and 0.02 ppm, respectively). The water quality apparently conformed to the national standards[24] set to sustain fishery and aquatic life.

Table 1 summarizes the total Zn, Cu, Fe, Mn, Hg, Pb, and Cd contents in sediment/soil samples. The total metal analyses of the lake sediments are seen to be in fair agreement with X-ray fluorescence spectroscopic and graphite-furnace AAS data of Pfeiffer *et al.*[30] on the same samples. The relative standard deviations (RSD) of the data in this study were generally 10% or better, except in some Hg, Pb, and Cd results, where poor reproducibility was observed due to the levels approaching

Table 1 Total metal content of sediments/soil in ppm.

Sediment/soil sample		*Zn*	*Cu*	*Mn*	*Fe*	*Hg*	*Cd*	*Pb*
A. LAGUNA LAKE								
Station I		83	99	1758	70103	0.78	0.35	3.9
Station II		79	93	1540	73311	3.33	0.12	4.2
Station III		95	102	1492	70312	1.48	0.12	6.1
Station IV		94	95	1729	77873	2.06	0.11	5.9
Station V		116	108	2158	71851	2.44	0.09	9.3
Station VI		72	89	1568	70363	0.30	0.08	6.2
Station VII		90	89	1538	57999	2.27	0.20	7.4
Station A		93	111	962	74005	0.44	0.17	3.2
Pfeiffer *et al.*[a]	Mean	114	100	1861	83088	0.106	0.27	10.4
	Min	107	94	962	79300	0.07	0.23	9.0
	Max	137	115	2265	87400	0.143	0.33	12.0
LLDA study[b]		446	115	1600	51000	1	—	37
B. TRIBUTARY RIVERS								
Bay (BAY)		109	80	1426	40774	<0.1	0.64	11.8
Mabitak (MAB)		126	69	1249	63236	<0.1	1.83	5.4
Morong (MOR)		130	67	793	40323	<0.1	0.53	13.7
Pagsanjan (PAG)		160	120	1030	51150	<0.2	1.67	12.4
Santa Maria (SAN)		145	68	1308	54720	<0.1	2.24	—
LLDA study[c]	Min	115	59	1100[d]	30000	0.2	—	17
	Max	421	130	—	47000	6	—	70
C. LAGUNA LAKESHORE								
Binangonan (BIN)		53	70	774	58010	<0.04	0.33	—
Jala-jala (JAL)		53	73	620	31012	<0.04	0.52	2.7
Los Banos (LOS)		95	65	630	33410	<0.04	1.14	9.4
Sucat (SUC)		60	51	996	35036	<0.04	1.60	—

[a] XRF data, except for Hg and Cd which were analyzed by graphite furnace-AAS; taken from ref. 30.

[b] Flame-AAS data on 23 sediments (mostly 10 cm deep) from sites I-V; taken from ref. 8.

[c] Flame-AAS data on river (San Pedro, San Cristobal, San Juan, and Santa Cruz rivers) sediments; taken from ref. 8.

[d] Only San Pedro river was analyzed.

the limits of detection for sediment/soil analyses (0.04, 0.2 and 0.02 ppm, respectively). For comparison, 1975–1978 data from the LLDA report[8] are also included in Table 1.

Table 2 presents some literature values for background, core, or baseline metal levels in sediments/soils. Since many parts of Luzon island are geologically characterized[35] by basaltic and pyroclastic volcanic rock materials, as well as shales and limestone, the metal levels in igneous rocks and shales are relevant. Because of limited resources, the present study was not able to analyze any core sediment/soil samples.

In general, a comparison of the data from Tables 1 and 2 indicate that there appears to be low to moderate metal pollution in the lake and its tributary rivers. Specific observations for each metal are given below.

Iron The LLDA study[8] reported that core (30–60 cm deep) sediments at five sites of the lake contained an average 5.1% Fe, compared with an average of 7.1% for surface (0–15 cm) sediments found in this study. The former study also reported a mean content of 3.62% Fe from sediments of four tributary rivers, compared to an average of 5.0% in five other tributary rivers (see Table 1) in the present study. From these results, it appears that an appreciable elevation in Fe content in the lake and river sediments has occurred over the past several years.

Manganese The LLDA study[8] reported 1600 ppm Mn in lake sediments and 1100 ppm in one river sediment. Pfeiffer *et al.*[30] and the present study found comparable levels of Mn in lake sediments, which were roughly twice the levels found in river sediments.

Copper An average of 115 and 98 ppm Cu in lake and river sediments, respectively, were reported by the LLDA study[8]; in addition, 30–60 cm core sediments from the lake over six sites gave an average content (cf. Table 2) of 85 ppm (range, 57–134 ppm). Data from the present study suggest that Cu levels in the lake have remained

Table 2 Literature values of metal levels on sediments/soils (in ppm)

	Fe	*Mn*	*Cu*	*Zn*	*Pb*	*Hg*	*Cd*	*Ref.*
Mean sediment	41000	770	33	95	19	0.19	0.17	31
Shallow water sediment	65000	850	56	92	22	—	—	31
Laguna Lake 30–60 cm	4000	—	57	44	16	—	—	8
core sediments[a]	65500	—	134	376	52			
Luzon sediments[b]	62000	1230	60	56	25	0.15	0.16	32
Mean crust	41000	950	50	75	14	0.05	0.11	31
Average shale	47000	850	45	95	20	0.18	0.22	31
Igneous rocks[c]	14000	—	15	40	1	<0.1	0.2	33
	94000		90	110	18			
Laguna rice farm	34150	1007	81	59	16	<0.06	<1	34
Paranaque, Metro Manila	82900	1420	155	87	13	0.08	0.06	30
30–100 cm core soil[c]	98700	2280	176	94	25	0.09	0.12	

[a] Minimum and maximum values of core samples (analyzed at 10-cm intervals) from sites I–VI.

[b] Baseline levels in freshwater sediments from natural waters in Luzon Island, Philippines.

[c] Minimum and maximum values are quoted.

relatively constant, while levels were apparently slightly lower in the more recent river sediments.

Zinc This study found that the mean lake sediment content was 90 ppm Zn, in contrast to the 446 ppm reported by LLDA[8]. Fairly comparable levels were found in river sediments: a mean of 118 ppm from three river sediments in the earlier study (although a fourth river yielded 421 ppm), compared to a mean of 134 ppm from the five rivers in this study. The earlier report also indicated that the average Zn content of 30–60 cm core sediment from six sites was 123 ppm (range, 44–368 ppm). It would seem that the lake at that time received tremendous Zn emissions (possibly from combined domestic, agricultural and industrial sources), especially at site I, where most of the high Zn analyses occurred. Zn contamination during analyses is a frequent threat, since Zn occurs in many common reagents; however, the LLDA study did not indicate whether this possibility was ruled out.

Lead Leaded gasoline and diesel fuel are still largely used by motor vehicles, motorized boats and barges. These are diffuse sources of Pb in the atmosphere, which would eventually enter water systems.

The LLDA study[8] reported 37 ppm Pb in lake sediments and an average of 38 ppm in four tributary rivers; 30–60 cm core sediments had an average content of 31 ppm. These levels are all higher than the mean value found in this study and by Pfeiffer *et al.*[30] Reyes[9] reported a mean level of 14 ppm for a 12-month monitoring period in 1984.

Mercury Recent lake sediments contained an average of 1.6 ppm Hg, while tributary river sediments had <0.1 ppm (cf. Table 1). Reyes[9] reported a mean Hg content of 0.64 (range, 0.070–2.86) ppm for lake sediments sampled in 1984. In contrast, the LLDA study[8] reported an average of 1 ppm and 2.2 ppm for lake and river sediments, respectively. Moreover, lake sediments close to one power station (at Sucat) reportedly contained 42 ppm Hg. Although combustion of fossil fuels releases Hg and other trace metal[36], this level seems incredibly high; however, the possible source of the contamination was not identified.

Cadmium Lake sediments gave an average Cd content of 0.16 ppm, which compares quite well with the value quoted for mean sediments (Table 2). However, much higher levels occurred in some river sediments, which suggests industrial pollution sources.

The considerable and temporal variability observed in trace metal concentrations over the relatively short time interval between this study and that sponsored by LLDA in 1975–1978 may be evidence that the lake is a very dynamic system with rapid transport, deposition, and remobilzation processes. This may be promoted by the lake's relative shallowness and its long reaches; thus, wind-induced resuspension of the sediment would be expected to increase mixing of pollutant-enriched sediment in the lake. The monsoonal climate may cause a build-up of pollutants during the dry season, when there is virtually no flow out of the lake, followed by a fairly rapid flushing during the wet season. The average water residence time has been estimated to be 0.93 year[8]. More work is needed to understand the pollution transport and deposition processes involved.

Metal distribution (speciation)

It will be gleaned from the speciation scheme (Figure 2) that extractability of the metal decreases, i.e., the metal association in the sediment becomes increasingly stronger, as one progresses through the sequence of extractions. The first four extractions (Fractions 1–4) may be taken to represent the remobilizable or potentially available metal levels, which may be attributed mainly to anthropogenic sources. The fifth or inert fraction (Residue 4) represents detrital lithogenic minerals; this fraction has been shown to have the highest relative metal content only in unpolluted water systems[3]. Due to limited resources, this last fraction was estimated indirectly in this study by taking the difference between the total metal content (as given in Table 1) and the sum of the metal levels in Fractions 1–4.

It is observed from Table 1 that the total content of the various samples cover a wide range. Hence, for easier comparison of the samples, the distribution of metals in the various fractions are shown in relative amounts in Figs. 3–6 below. Although Fe, Mn, Cu, and Zn are essential to living organisms, they may become toxic when present in excess[37]. For instance, an *in vitro* study of the cytotoxicity of metals found that large doses of these metals led to toxicity in the order Zn > Cu > Mn > Fe[38]. Speciation analyses for Pb, Cd, and Hg were not performed because of the limited sensitivity of the flame-AAS technique.

Specific observations on the partitioning of the metals in sediments/soil are given below.

Iron Figure 3 shows the distribution of Fe in the sediments/soil. Fe was found to be the least extractable among the four metals. Essentially negligible amounts were exchangeable (Fraction 1) or bound to carbonates (Fraction 2). The amount present in the reducible fraction which is bound to Fe/Mn oxides (Fraction 3) was also quite low; more substantial amounts occurred in the oxidizable fraction, which is bound to organics/sulfides (Fraction 4). In contrast, more Fe occurred in Fraction 3 in the case of river sediments and lakeshore soil. The sum of Fractions 1–4 gave an average value which was less than 12% of the total Fe for all sample types; 85–94% Fe remained in the inert or residual fraction in all samples.

Manganese In agreement with other studies[31,39], this was found to be the most extractable metal and quite evenly spread among the fractions (see Figure 4). Up to 30% of the total Mn in the lake sediments was found associated with the reducible oxide phase (Fraction 3) and somewhat similar amounts (21–23%) in Fractions 2 and 4. However, up to 45% occurred in the carbonate phase (Fraction 2) of the river sediments, while similar amounts (38%) were present in Fractions 2 and 3 of the lakeshore samples. The lake sediments generally gave the lowest residual fraction (26–40%). The average potentially available Mn (sum of Fractions 1–4) for all samples ranged from 43 to 66%.

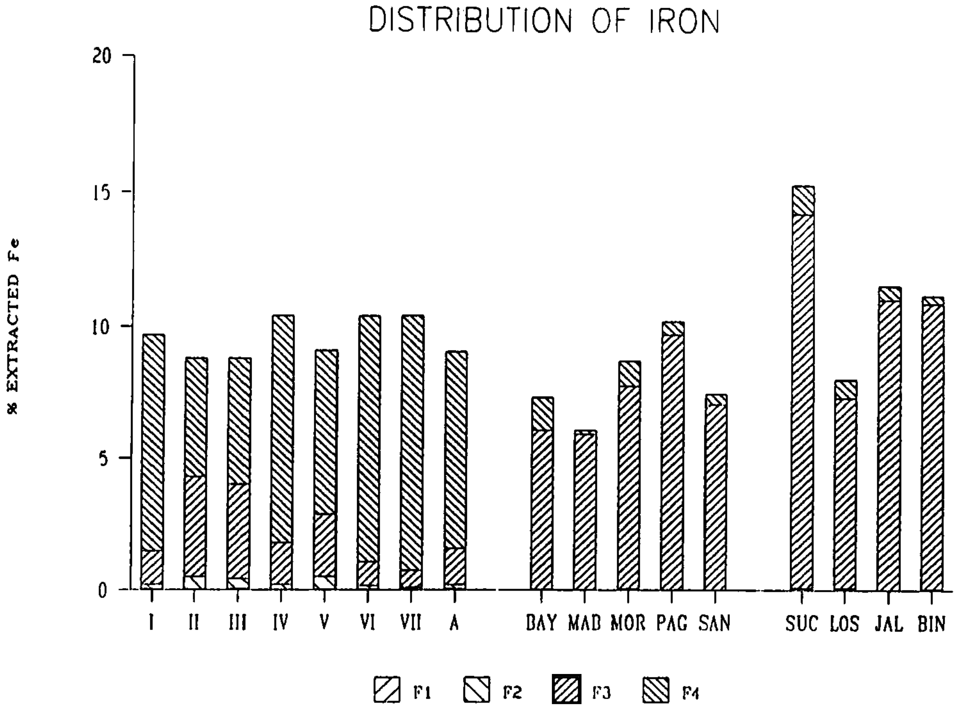

Figure 3 Distribution of Fe in lake and river sediments and in lakeshore soil. Lake sampling stations are I–VII and A; rivers and lakeshore sites are identified by the first three letters of their names. The fraction (F) extracted (in %) is relative to the total metal content given in Table 1.

Copper It may be observed from Figure 5 that the organically bound fraction (Fraction 4) contained the largest amount in both lake (up to 47%) and river (up to 25%) sediments. However, in the lakeshore samples, slightly more was found in Fraction 3 than in Fraction 4, suggesting some scavenging mechanism possibly by adsorption and coprecipitation of Cu with precipitated Fe/Mn oxides. The residual fraction ranged from 39 to 78% for all samples, with the lake sediments giving the highest per cent remobilizable Cu (sum of Fractions 1–4).

Zinc Figure 6 shows that for the lake sediments, the amount of Zn in each fraction increased steadily from Fraction 1 (ca. 1%) to Fraction 4 (10–19%). This order was different in the river and lakeshore samples, wherein Fraction 3 contained substantially higher Zn levels than Fraction 4. Up to 40% of the Zn was found associated with the reducible Fe/Mn oxides (Fraction 3) in the lakeshore soil.

It is evident from Figs. 3–6 that there is a fair degree of variability in the distribution of the metals in the different samples. The variation is least pronounced in lake sediments, suggesting a much more homogeneous nature of the particles compared to the river sediments or lakeshore soil samples. The RSD of the mean percent remobilizable metal (sum of Fractions 1–4) across all sample types were: 6–12% for lake sediments, 12–56% for river sediments, and 18–29% for lakeshore soil. The

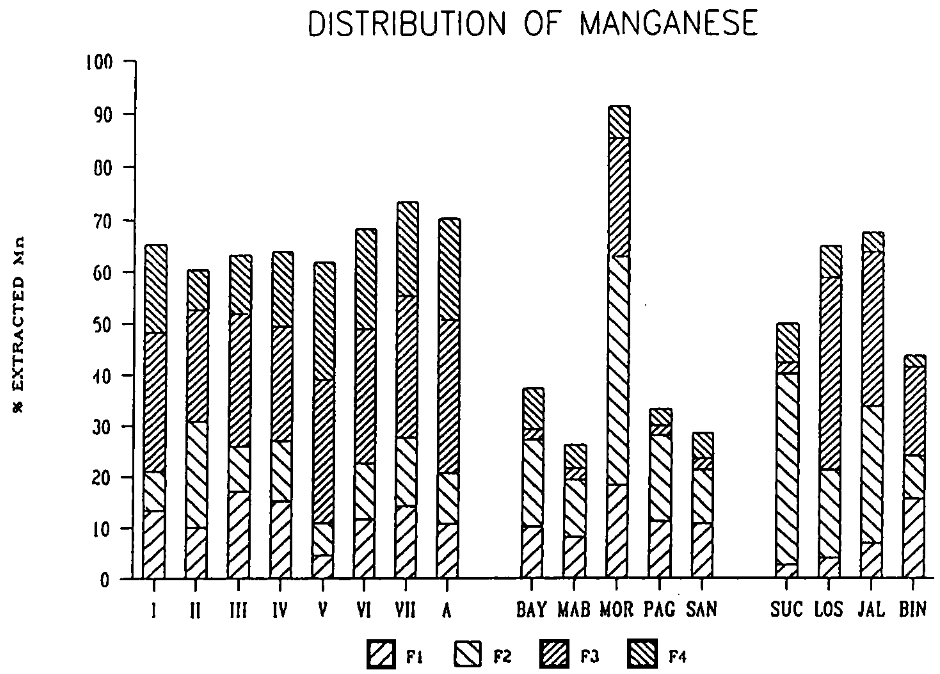

Figure 4 Distribution of Mn in sediments and soil.

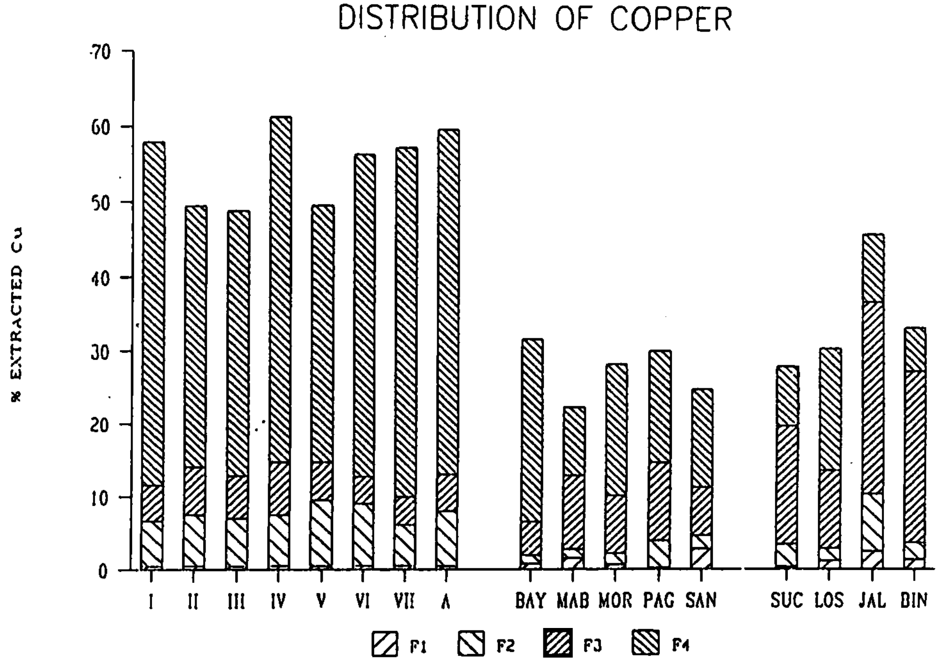

Figure 5 Distribution of Cu in sediments and soil.

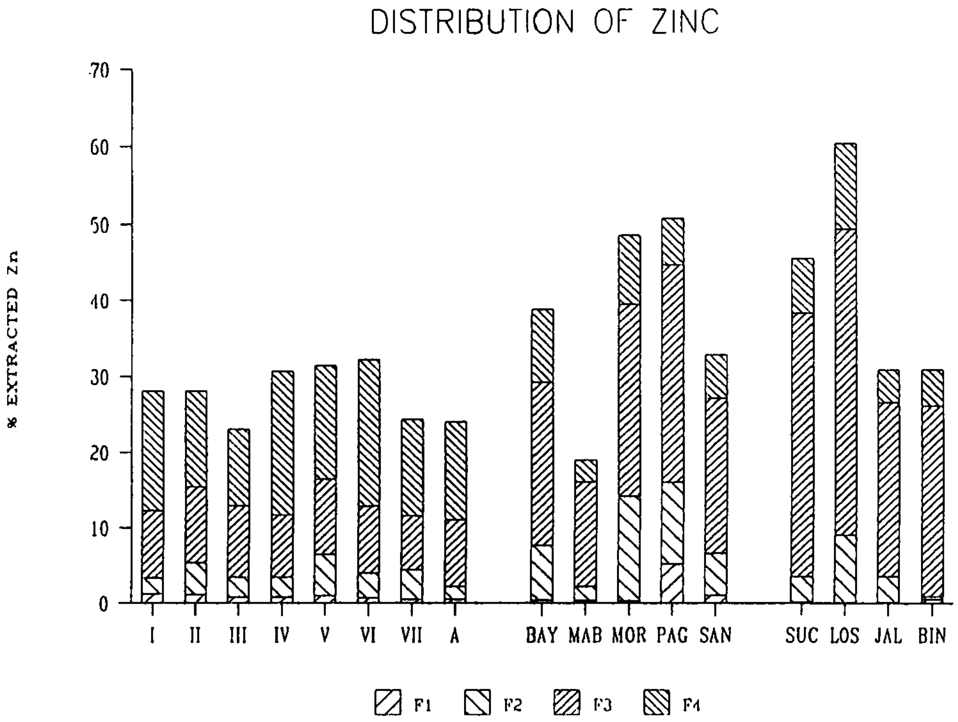

Figure 6 Distribution of Zn in sediments and soil.

analytical operations involved in the sequential extraction procedure undoubtedly contribute to some loss of precision. Other studies[40,41] have noted that the extent of pollution or stress on the water system may also contribute to variability in analyses. Under these circumstances, Rauret *et al.*[40] suggested that the extractant-to-sediment ratio may be very critical and should be validated.

SUMMARY AND CONCLUSIONS

Total metal analyses of the sediments reveal relatively low (specifically, Cu, Zn, and Pb) to moderate (Mn, Fe, Hg and Cd) pollution in Laguna Lake and its tributary rivers, and in the lakeshore soil. Recent lake sediments showed much lower total Pb and Zn contents than found in an earlier study conducted in 1975–1978[8]. There is some indication of increased Hg and Cd levels in these waters; this aspect should be further investigated or monitored in the future.

The exchangeable metal fraction in all cases was practically negligible. Organic matter bound the largest fraction of Cu, Zn, and Fe in lake sediment, and of Cu in river sediments. The largest fraction of Mn in lake sediments was associated with reducible Fe/Mn oxides with lesser but roughly equal amounts distributed in the other fractions. In the lakeshore soil samples, the four metals occurred mainly in the reducible fraction, although nearly equal relative amounts of Mn were also found in the carbonate fraction. More Zn was associated with the carbonate and reducible phases in the case of river sediments and lakeshore soil.

In agreement with other studies, the amount of remobilizable or potentially available metal (as estimated by its chemical extractability) was shown to differ considerably from the total metal content (generally estimated by a single extraction with a strong-acid mixture) of the sediment or soil.

The results show that the order of extractability in the lake sediments is $Mn > Cu > Zn \gg Fe$. The order for Cu and Zn is reversed in the case of river sediments and lakeshore soil, i.e., $Mn > Zn > Cu \gg Fe$. The residual (non-available) fraction in all sample types was 9–74% for Mn, 39–78% for Cu, 40–81% for Zn, and 85–94% for Fe.

The results indicate that some metal forms (i.e., exchangeable Fe, Cu, and Zn; carbonate-bound Fe) occur only to a very small extent. Hence, the pertinent analytical steps may be omitted in the extraction scheme, if the investigation aims to determine potentially available metal content.

The extraction conditions used in this study may not simulate the natural biogeochemical exchange processes. Further studies are needed to correlate actual biological uptake levels to the chemical extraction data; both satisfactory and unsatisfactory correlations have been reported in the literature[5] using different types of sediment samples.

Finally, information on water quality and comparison of different water systems with respect to heavy metal contamination are more easily achieved in conventional laboratories using sediment rather than water samples. Shea[42] has proposed recently that sediment quality criteria, in addition to water quality criteria, be adopted for regulatory purposes.

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