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Distribution and geochemical behaviour of heavy metals (Cr, Cu, Ni and Pb) in Iloilo river estuarine sediments

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Abstract. Heavy metals released to the estuarine ecosystem usually bind and enriched in sediments by means of various processes. These metals can exist in various forms in sediments and are kept bound by different forces depending on the existing environmental conditions. It is essential to study the geochemical behaviour of metals in sediments because the accumulated metals may be subsequently released to the water column by various processes of remobilisation and in changing form can move up to the food chain manifesting toxic effects. In this study, sequential extraction was used to determine the geochemical forms and distribution of Cr, Cu, Ni and Pb in surface sediments of Iloilo river in Central Philippines. Iloilo river is a site of interest because of its great economic and environmental importance. Results show that most of the Cr present in sediments was associated with the residual fraction (66-74%), indicating that it is not likely to be released to the water column under normal conditions. The remaining 15-24% was found bound to Fe-Mn oxide (reducible fraction) and could be released to the water column under anoxic conditions. Only a small amount of the total Cr in the sediments was found bound to organic matter (8-13%) and exchangeable/carbonate (0-3%) fractions. Metals bound to organic matter fraction could be released under oxic conditions while those associated with exchangeable/carbonate fractions could be leached out by changes in the ionic composition and pH of the water. Cu was mainly associated to organic matter (36-52%) and residual (39-47%) fractions. Three to eleven percent (3-11%) of the total Cu was bound to Fe-Mn oxide while 0-17% was bound to exchangeable/carbonate fraction. The same geochemical association pattern was observed with Ni, which was found mainly bound to the organic fraction (43-57%), while 25-39% bound to residual fraction. Only 6-14% of the total Ni was bound to Fe-Mn oxide and 5-13% bound to exchangeable/carbonate fraction. Pb was mainly associated with the residual (48%) and organic matter (39%) fractions. Only 7% was found associated with Fe-Mn oxide fraction, and 6% with exchangeable/carbonate fraction. Overall, almost 50% of all the metals found in the Iloilo River sediment has the potential to be released to the water column and may become available to aquatic organisms under favorable environmental conditions.

Key Words: speciation, bioavailable metal, exchangeable fraction, reducible fraction.

Introduction. Iloilo river is an estuarine ecosystem in the southern portion of Iloilo City in the central islands of the Philippines between latitudes N 10°41’35” and 10º42’30” and longitudes E 122º30’ and 122º35’. Located along the 11-km stretch of the river are the domestic port of Iloilo City, fuel bulk depots, fuel-based electric power generator plant, fishponds, hospitals, private residential houses and several commercial and food establishments. Its major tributaries are the Calajunan and Dungon Creeks. These creeks also receive domestic and commercial wastes, leachates from garbage disposal sites, agricultural runoff, commercial and industrial wastes. All wastes are discharged directly into the river without treatment. As such, the Iloilo river estuary acts as a sink for various pollutants, including metals. Under favorable environmental conditions, metals could be released to the water column and become serious environmental and health concerns.

The behaviour and concentration of metals in sediments are among the major considerations in detecting sources, degree of pollution and distribution mechanism. In addition to the total metal concentration, the chemical form of the metal best describes its bioaccumulation, availability and mobility in the environment (Yang et al 2012; Arifin et al 2010; Harrison et al 1981). Sequential extraction has been successfully applied in determining sources, partitioning and potential hazards of metals in soil and sediments (Osakwe et al 2014; Venkatramanan et al 2013; Zhang et al 2012; Zhu et al 2012; Li & Thornton 2001; Henderson et al 1998; Adamo et al 1996; Hickey & Kittrick 1984). In the last thirty years following the sequential extraction scheme originally proposed by Tessier et al (1979), many studies on sequential extraction schemes have been carried out to describe the mobilization of metals in the environment (Zakir & Shikazono 2008; Lydia & Fabienne 2006; Hlavay et al 2004; Filgueiras et al 2002; Rauret et al 1999; Alabaster et al 1997; Warren 1981; Pilkington & Warren 1979). Tessier et al (1979) classified the metal fractions into: (1) exchangeable, (2) carbonate bound, (3) iron/manganese oxide bound, (4) organic bound, and (5) residual.

In this study, surface sediments collected from the Iloilo river estuary were analyzed using a modified Tessier's sequential extraction method to obtain the metal speciation (geochemical association and distribution) pattern. Speciation studies on sediments will help delineate the natural background levels from the anthropogenic input of metal pollutants and determine the likely behavior of metals in the environment. Chemical speciation studies such as this are valuable in describing the fate and transport of metals in aquatic environment. At present, no such data are available for aquatic environments in the Philippines, including the Iloilo river estuary.

Material and Method

Sample collection and preparation. Sediment samples were collected in 5 sites from the Iloilo river estuary in October 2004, prior to the dredging activities initiated by the local and national government. The sites were selected based on the previous study conducted in the Iloilo river sediments (Taberna & Wenclawiak 2005). The exact location of each sampling site (Table 1) was determined using a Global Positioning System (GPS) (GARMIN 12, USA). Samples were taken at about 11.5 cm in depth from 3 sampling points per site, transferred in a polyethylene plastic bag, mixed together, and kept 4°C until it reaches the Deparment of Chemistry laboratory of the University of the Philippines Visayas, where it is transferred to a freezer until analyzed. Prior to chemical analysis, samples were oven-dried at 50°C, sieved (24-mesh) and homogenized by grinding in an agate mortar.

Table 1

Coordinates of sampling sites within the Iloilo river estuary

Site	*Latitude N*	*Longitude E*
1	10°41.899'	122°31.652'
13	10°42.172'	122°33.173'
14	10°42.148'	122°33.602'
21	10°41.974'	122°34.187'
24	10°41.805'	122°34.303'

Sequential metal extraction. Dried sediment samples, 2.00 g, were also digested following US EPA Method 3050B (US EPA 1996) in order to determine total metal concentration. The geochemical association or the binding hosts of the metals, Cr, Cu, Ni and Pb, was determined using the method developed by Tessier et al (1979) with minor modification (Table 2). Aqua regia was used in the extraction of metals in the residual fraction instead of $HF:HClO_4$. All operations were carried out in a 60 mL polyethylene bottle with cap. Samples were left to stand for 24 hours to allow the separation of the solid and liquid phases. The solid residue was washed with 15 mL distilled water prior to the next extraction sequence. All analytical determination was carried out in 3 replicates. Blank was run simultaneously at all stages of the procedure.

Table 2

Modified Tessier's extraction conditions per two (2) grams of sediment sample

Fraction	*Extraction reagent*	*Conditions*
Exchangeable	$MgCl_2$	16 mL 1M $MgCl_2$ (pH 7), 24 hr, room temp., intermittent shaking
Carbonate	CH_3COONa	16 mL 1M CH_3COONa + CH_3COOH (pH 5), 48 hr, room temp., intermittent shaking
Reducible	$NH_4OH \cdot HCl$	40 mL 0.04M $NH_4OH \cdot HCl$ in 25% CH_3COOH, 6 hr, 96 ± 3°C, intermittent shaking
Oxidizable	H_2O_2	6 mL 0.02M HNO_3 + 4 mL 30% H_2O_2 (pH 2), 2 hr, 85 ± 3°C, intermittent shaking; 6 mL 30% H_2O_2 (pH 2), 3 hr, 85 ± 3°C, intermittent shaking; 10 mL 3.2M CH_3COONH_4 in 20% HNO_3 + 14 mL H_2O, 30 min, room temp.
Residual	Aqua regia	15 mL 37% HCl + 5 mL 65% HNO_3, near dryness

Chemical analysis. Metal concentrations were determined using Flame Atomic Absorption Spectrophotometry (FAAS) (SpectrAA 55B, Varian, Australia). Analytical performance was checked by measuring a standard solution after every 5 samples.

Results and Discussion

Total metal concentration. The mean total metal concentrations in sediment samples are presented in Table 3. All sediment samples indicated Cr, Cu, and Ni concentrations 2-3 times greater than the average concentrations previously determined in the Iloilo river estuary (Taberna & Wenclawiak 2005). These results suggest that Cr, Cu, and Ni containing wastes have been continuously discharged into the river. Comparing the levels of metals found in Iloilo river sediments with those reported for other urban rivers in the Philippines, higher levels of Cu were observed in Iloilo river sediments than in Marikina and Bulacan Rivers (Prudente et al 1994) (Table 3). Concentrations of Ni were also higher in the Iloilo river sediments compared to sediments collected from Marikina, Pasig and Bulacan rivers, while Pb levels were lower in Iloilo river than the aforementioned rivers (Table 3). Moreover, total Cr, Cu, and Ni concentrations in the Iloilo river sediments were all above the concentration range set for "uncontaminated" estuarine and marine sediments (50–100 $\mu g\ g^{-1}$ dry weight for Cr (Morrison 1989); 10–50 $\mu g\ g^{-1}$ dry weight for Cu (Salomons & Förstner 1984); and 50 $\mu g\ g^{-1}$ or less dry weight for Ni (Morrison 1989)). Pb was detected in only one sediment sample at 22.2 $\mu g\ g^{-1}$ dry weight. This level is within the range set for uncontaminated estuarine and near-shore marine sediments (5–30 $\mu g\ g^{-1}$ dry weight) as reported by Salomons & Förstner (1984).

Table 3

Total Cr, Cu, Ni, and Pb concentrations ($\mu g\ g^{-1}$ dry weight ± SD, n = 3) in sediments from Iloilo river estuary, and comparison with previous study and from other river sediments in the Philippines and with average shale value

Site	*Cr ($\mu g\ g^{-1}$)*	*Cu ($\mu g\ g^{-1}$)*	*Ni ($\mu g\ g^{-1}$)*	*Pb ($\mu g\ g^{-1}$)*
1	103.0 ± 1.8	73.2 ± 2.62	63.9 ± 8.23	< 0.05
13	102.0 ± 3.2	62.6 ± 1.26	53.4 ± 6.56	< 0.05
14	107.0 ± 1.9	80.9 ± 1.38	77.2 ± 4.01	< 0.05
21	151.0 ± 0.2	112 ± 4.10	76.6 ± 2.73	22.2 ± 1.99
24	115.0 ± 4.0	92.4 ± 2.17	86.9 ± 2.37	< 0.05
Mean	**116.0 ± 19.0**	**84.1 ± 18.9**	**71.6 ± 13.0**	**22.2**
Range from this study	102–151	62.6–112	53.4-86.9	< 0.05-22.2
Range from previous study (year 2000)[1]	19.2–65.1	10.3-82.6	15.6-39.5	3.64-38.1
Range from previous study (year 2002)[2]	42.6–88.1	13.0-72.2	25.9-41.5	3.22-35.9
Marikina river[3]	-	28-79	11-22	18-31
Pasig river[4]	-	110-189	14-27	66-137
Rivers in Bulacan[5]	100	36-98	12-23	11-220
Average shale[6]		50	52	20

[1,2]Taberna & Wenclawiak (2005); [3,4,5]Prudente et al (1994); [6]Turekian & Wedepohl (1961).

Metal speciation. Measurement of the total metal concentrations in sediments provides information on the estimate of the total metal burden in the sink. However, it provides limited information in terms of mobility, availability, uptake, and transport of metals in the environment. As such, knowledge on the distribution of metals in the sediment is very important in determining sources and potential risks posed by the mobilization of metals (Benson et al 2013; Li & Thornton 2001; Henderson et al 1998; Adamo et al 1996; Hickey & Kittrick 1984; Kuo et al 1983).

The geochemical association and distribution of Cr, Cu, Ni and Pb in Iloilo river sediments are presented in Figures 1–4.

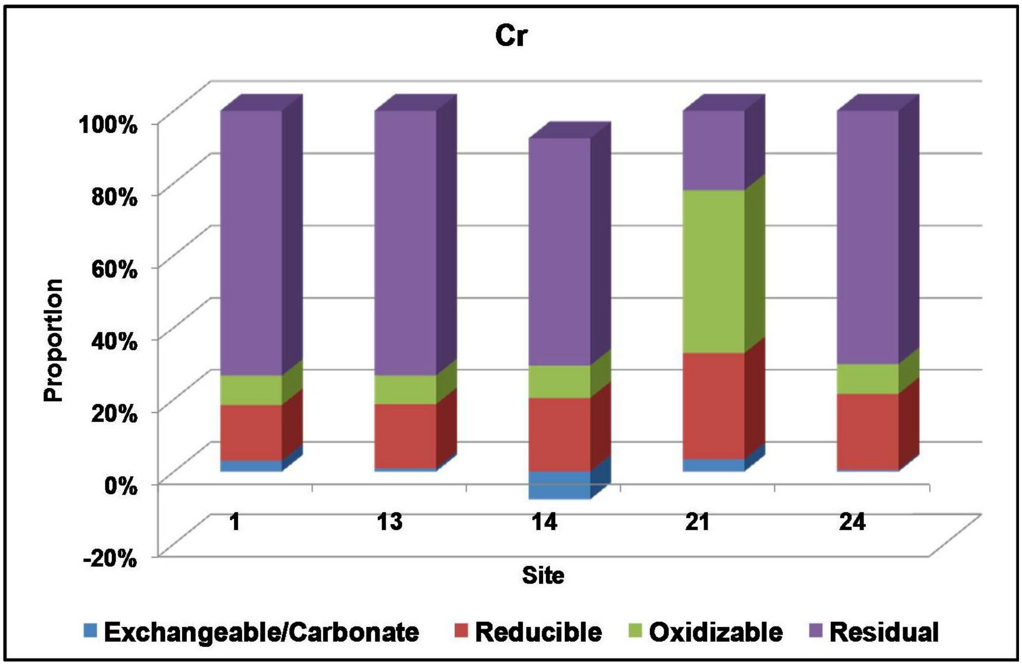

Figure 1. Chromium (Cr) distributions in Iloilo river sediments collected from 5 sites (1, 13, 14, 21 and 24) and determined by sequential extraction.

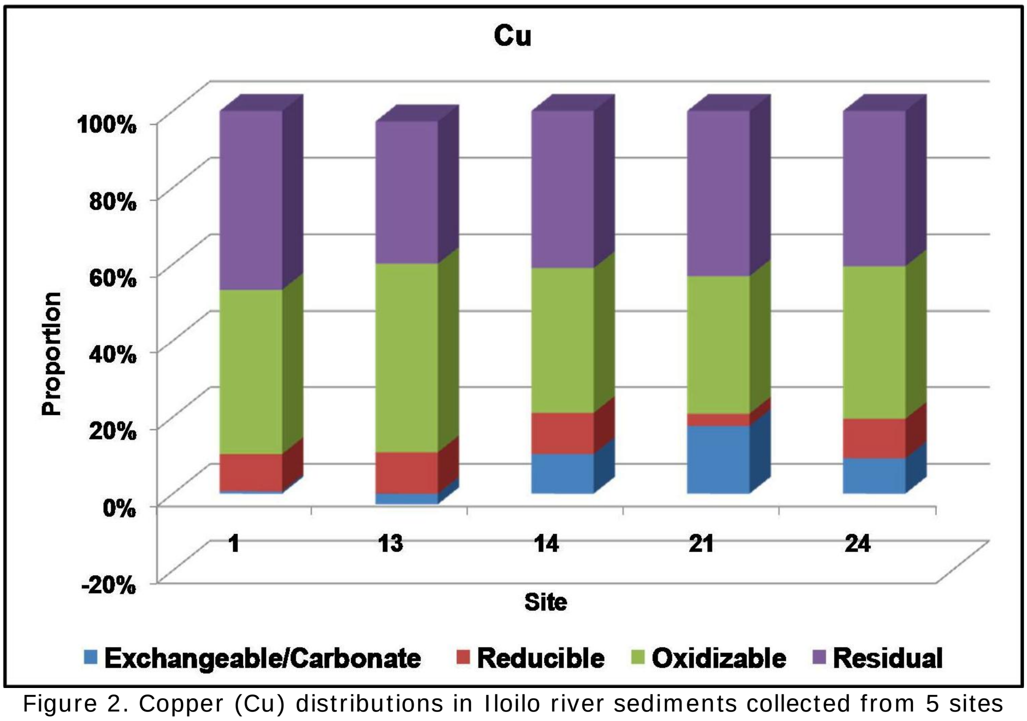

Figure 2. Copper (Cu) distributions in Iloilo river sediments collected from 5 sites (1, 13, 14, 21 and 24) and determined by sequential extraction.

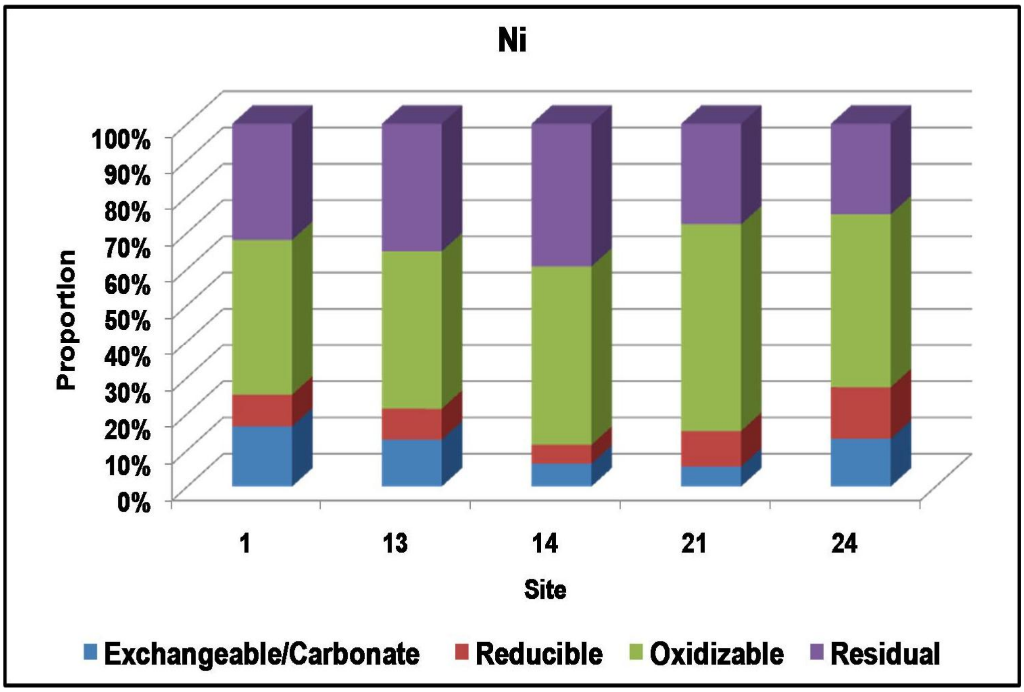

Figure 3. Nickel (Ni) distributions in Iloilo river sediments collected from 5 sites (1, 13, 14, 21 and 24) and determined by sequential extraction.

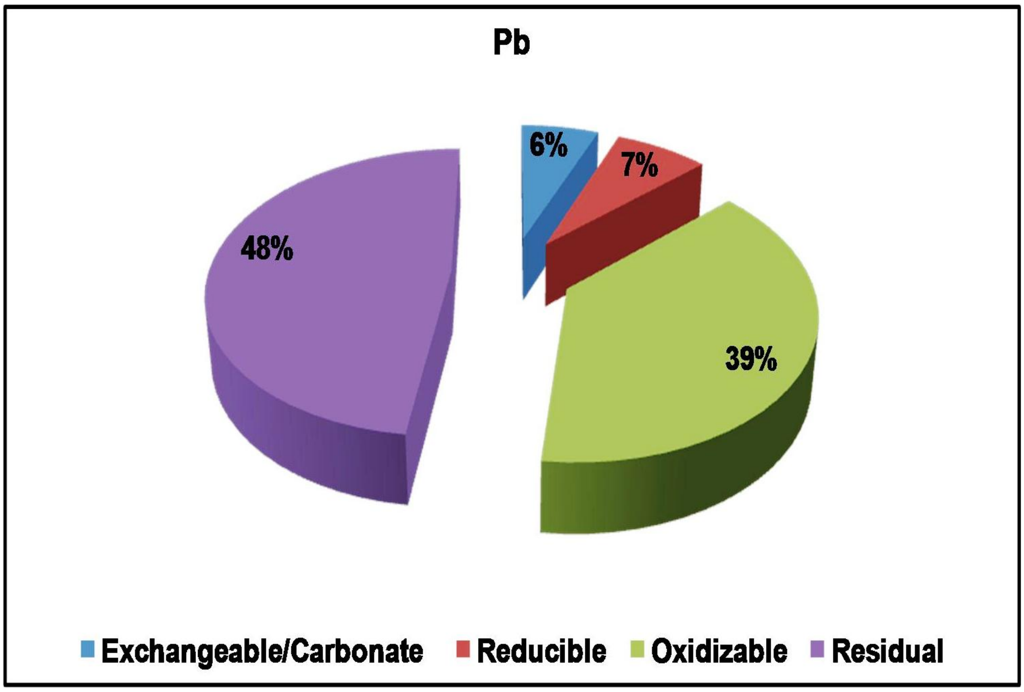

Figure 4. Lead (Pb) distributions in Iloilo river sediments collected from site 21 and determined by sequential extraction.

The distribution of Cr, the most abundant of the metals analyzed, was dominated by the residual (66–74%) and reducible phases (15–24%), with minor oxidizable phase (8–13%). The exchangeable and acid extractable fractions are less significant and accounts only for 0.5–2% of the total Cr contents in the sediments (Figure 1). The distributions of Cu and Ni (Figures 2 and 3) were similar to one another. These metals were largely associated with the oxidizable fraction, which accounts for 36–52% of total Cu and 43–57% of total Ni. The residual fraction also carries a significant proportion of Cu (39–47%) and Ni (25–39%). In contrast, only 3–11% and 6–14% of the total Cu and Ni concentrations, respectively, were associated with reducible fraction. Similarly, Pb was mainly associated with the residual (48%) and oxidizable (39%) phases. Moreover, the reducible and exchangeable/acid extractable phases account for only around 7% of the total Pb content in sediments (Figure 4).

Over-all, the residual fraction accounts for bulk of the Cr, Cu, Ni, and Pb concentration in the Iloilo river sediments. These metals are commonly associated with the silicate lattice of clays. Mean concentrations of Cr (82.1 µg g^{-1}), Cu (35.5 µg g^{-1}), and Pb (10 µg g^{-1}) are in accordance to the average shale values (Turekian & Wedepohl 1961).

The metal levels determined from the sequential extraction analysis represent the concentrations of metals bound to the different fractions in the sediments. The exchangeable fraction consists of metals that are readily leached by neutral salt. It represents the adsorbed metals and is affected by changes in water ionic composition (Tessier et al 1979). In soils and sediments, the exchangeable and acid extractable fractions are combined together (Tack & Verloo 1995). Metals associated with the acid extractable fraction, also known as the carbonate fraction, could be leached out using acetic acetate buffer solution at pH 5. This step dissolves carbonates and thereby releases the associated metals (Tessier et al 1979). In this study, only a small percentage of the total metals concentrations is associated with this fraction, suggesting that carbonate is not a significant binding host for Cr, Cu and Ni (Figures 1-3).

The residual fraction serves as the host of most of the Cr and Pb, and for significant amount of Cu and Ni in the Iloilo river sediments (Figures 1-4). Similar findings have been reported in various geochemical studies of sediments from other areas (Idriss & Ahmad 2012; Zhang et al 2012; Liu et al 2011; Arifin et al 2010; Tack & Verloo 1999; Perin et al 1997; Donazzolo et al 1984). It is likely that the concentrations of these metals in this fraction are largely governed by catchment geology and therefore could serve as the “natural background concentration” or the amount of metals present in sediment due to natural processes such as chemical weathering.

Metals in the residual fraction are considered part of the natural minerals that make up the sediment particles. They are retained within the silicate lattice of clays. The metals associated with fraction are considered immobile and therefore not expected to be released to the water column and become available to aquatic organisms under normal environmental conditions (Benson et al 2013; Tack & Verloo 1999; Tessier et al 1979).

Another important host for Cu, Ni and Pb in Iloilo river sediments is the organic matter. Organic matter-associated metals are considered anthropogenic in origin (Perin et al 1997). Metals tend to form complex with organic matter due to hydrological conditions and to the increase incoming nutrients from human activities in an area (Perin et al 1997). Sediments in Iloilo River estuary are essentially rich in nutrients and organic matter. Furthermore, significant amount of metals (Cu, Pb, Zn) were found in road-dust sediments along bridges overlying Iloilo river due to traffic-related activities (Taberna et al 2014).

Metals in the organic fraction could only be released upon degradation of the organic matter under oxidizing conditions (Tessier et al 1979). They are not considered very mobile or bioavailable since they are considered bound to the stable high molecular weight humic substances (Tack & Verloo 1999).

The surface of Fe and Mn oxides was previously found to have special affinity with the cations at natural pH (Martley et al 2004; Hall et al 1996; Lion et al 1982). Metals associated with reducible or the Fe-Mn oxides fractions are thermodynamically unstable under anoxic conditions (Tessier et al 1979). Reducible fraction is not an important host for Cu, Ni and Pb in Iloilo river sediments (Figures 2-4). Cr however was present in considerable amount in the reducible fraction (Figure 1). These results agree with findings reported in similar sequential studies on sediments (Tack & Verloo 1999; Lion et al 1982).

In some cases the sums of the extracted fractions were more than the independently determined total metal concentrations. Similar observations were previously reported (Perin et al 1997; Arunachalam et al 1996; Hall et al 1996; Belzile et al 1989; Tipping et al 1985), and could be due to the redistribution of metals among phases during the extraction process. This is not expected to influence the overall accuracy of the extraction procedure. The metal concentration in the exchangeable/acid extractable fractions of the sediments was determined by subtracting the total sequential concentration of the three fractions (reducible, oxidizable, and residual fractions) to the total metal concentration of the sediment samples.

Conclusions. The results of the present study indicate that 70% of Ni, 56% of Cu, 52% of Pb and 34% of Cr present in Iloilo river sediments can be attributed to anthropogenic sources. These sediment-bound metals could be released to the water column, under favorable conditions, and become bioavailable and can enter the food chain, thus posing danger not only to the aquatic life in the river but also to human health.

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