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ORIGINAL ARTICLE

Metal distribution and fractionation in surface sediments of coastal Tema Harbour (Ghana) and its ecological implications

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Abstract This study investigated the distribution and fractionation of metals (Mn, Ni, Pb, Cr, Cu, Zn, As, Cd, Hg and Sn) in surface sediments of Tema Harbour (Greater Accra, Ghana) as well as its ecological implications. Significant differences in sediment concentrations of Mn, Ni, Cr, Cu, Zn, As and Sn were observed across the Tema Harbour. Geochemical indices indicate that Cd, Hg, Pb, Cu, Zn, As and Sn in the Tema Harbour sediments derived mainly from anthropogenic sources, while Mn, Ni and Cr were mainly of lithogenic origin. Metal fractionation revealed a predominance of Al, Mn, Ni, Pb, Cr, Cu, As and Sn in the residual phase. In contrast, Cd and Hg were mainly present in the exchangeable phase, while Zn was mainly associated with the reducible phase. Based on the metal fractionation in the Tema Harbour sediments, the potential risks of metal bioavailability were high for Cd and Hg, low–medium for Mn, Ni, Zn, As and Sn and low for Pb, Cr and Cu. A screening-level ecotoxicological assessment revealed high potential toxicity of Hg and moderate potential toxicities of Pb, Cu, Zn, As and Cd in the Tema Harbour sediments. The potential influence of the buffer intensity, silt–clay, total organic carbon and carbonate content on the metal distribution in the Tema Harbour sediments was also inferred from their correlations. Comparison with previous studies did not reveal a progressive increase in metal contamination at the Tema Harbour since the year 2000.

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Introduction

Harbour sediments are often contaminated with a wide range of pollutants including metals (Casado-Martínez et al. 2006; Di Palma and Mecozzi 2007), which derive from anthropogenic activities associated with harbours such as shipping, fishing as well as industrial and urban wastewater discharges (Lepland et al. 2010; Schipper et al. 2010; Nyarko et al. 2014; Botwe et al. 2017a). Polluted sediments are potential secondary sources of chemical pollutants to benthic organisms living in contact with sediments and ultimately to other organisms within the food chain (Burton 2002; Kelderman and Osman 2007; Nyarko et al. 2011; Botwe et al. 2017a). Metals such as Ni, Pb, Cr, Cu, Zn, As, Cd and Hg are hazardous to marine organisms (Casado-Martínez et al. 2006; Schipper et al. 2010), and their contamination in the environment has adverse human health, socioeconomic and food security implications (Birch and Hutson 2009; Lepland et al. 2010; Botwe et al. 2017a). Contaminated harbour sediments may adversely impact other coastal marine and terrestrial ecosystems via the disposal of dredged materials (Caille et al. 2003; Schipper et al. 2010; Ho et al. 2012a; Botwe et al. 2017a).

Considering the threat contaminated sediments may pose to aquatic and terrestrial ecosystems, remediation of

contaminated sediments is a priority for environmental management in harbours (Pozza et al. 2004). Remediation of harbour sediments requires a prior screening of the sediments for their potential ecotoxicity and environmental risks in order to obtain information on (1) pollutants of prime concern, (2) the potential to cause adverse biological effects in benthic organisms and (3) identify the most impacted areas that deserve priority attention (Burton 2002; Long et al. 2006; Birch and Hutson 2009; Botwe et al. 2017a). A screening-level ecotoxicological assessment of sediments involves comparisons of measured pollutant concentrations in the sediment with established biological effect-based sediment quality guidelines (SQGs) (Long et al. 1995; Burton 2002; Botwe et al. 2017a). Two SQGs which have been widely used around the world for ecotoxicological screening of sediments are the effects-range low (ERL) and effects-range median (ERM) SQGs (Long et al. 1995; Burton 2002; Botwe et al. 2017a).

Sediment-bound metals may associate with different geochemical phases present in sediments, e.g. carbonate, Fe–Mn oxides and hydroxides, organic matter and sulphides. The phase association (fractionation) of metals in sediments determines their binding strength and consequently, their potential mobility and bioavailability (Calmano et al. 1993; Pueyo et al. 2001; Kelderman and Osman 2007; Ho et al. 2012b; Hamzeh et al. 2014). Investigation of the metal distribution over different geochemical phases (metal fractionation) in sediments is, therefore, relevant when screening the sediments for their potential environmental risks. A standardised procedure widely used for metal fractionation in sediments is the Community Bureau of Reference (BCR) three-step sequential extraction technique, which yields four metal fractions, namely the acid-soluble (exchangeable and bound to carbonate), reducible (bound to Fe–Mn oxides and hydroxides), oxidisable (bound to organic matter and sulphides) and residual (bound within the crystal lattice of minerals) fractions (Quevauviller et al. 1997; Pueyo et al. 2001; Ho et al. 2012a). Since metal fractionation and potential mobility in sediments are influenced by environmental factors such as pH, buffer intensity and redox potential (Calmano et al. 1993; Kelderman and Osman 2007; Di Palma and Mecozzi 2007; Ho et al. 2012a; Hamzeh et al. 2014), these factors should be considered in characterising the potential environmental risk of metal-contaminated sediments.

The coastal marine Tema Harbour in Greater Accra (Ghana) was constructed in 1960 and commissioned in 1962 to facilitate international trade and boost industrial development in Ghana. Thus, the Tema Harbour was sited at the seacoast of the industrial city of Tema, Greater Accra in Ghana and its commissioning marked the beginning of Ghana's industrial era. With over 180 industries in Tema, as well as shipping and fishing activities at the Tema

Harbour, the Tema Harbour is susceptible to metal pollution (Lepland et al. 2010; Schipper et al. 2010; Nyarko et al. 2014). Previous studies in 2000 (http://open_jicareport.jica.go.jp/pdf/11681632_03.pdf) and 2011 (Nyarko et al. 2014) characterised metal contamination levels in the Tema Harbour. However, the above studies focused on total metal concentrations without examining metal fractionation in the Tema Harbour sediments. Moreover, the Tema Harbour sediments have not been characterised for their buffer intensity against acidification, which determines metal leachability and associated environmental risk (Calmano et al. 1993; Jain 2004; Iqbal et al. 2013; Ho et al. 2012a). The objective of this study was, therefore, to investigate the distribution and fractionation of metals (Mn, Ni, Pb, Cr, Cu, Zn, As, Cd, Hg and Sn) in surface sediments from the Tema Harbour as well as its ecological implications.

Materials and methods

Sediment sampling and sample analyses

Surface sediment samples were collected in November 2014 with a stainless steel Ekman grab (3.5 L) from 21 stations across the different compartments of the Tema Harbour, which were previously monitored for organic (Botwe et al. 2017a) and radioactivity (Botwe et al. 2017b) contamination. Thus, sediment samples were collected from fourteen stations in the Main Harbour, two stations each in the Inner Fishing Harbour and the Outer Fishing Harbour, and three stations in the Canoe Basin (Fig. 1). The Main Harbour is where ships call at the Tema Harbour, and has a total of 14 berths. The Inner Fishing Harbour and the Outer Fishing Harbour provide handling facilities for semi-industrial and industrial fishing vessels, while the Canoe Basin serves as an artisanal canoe fishing landing site. Adopting the sampling strategy by Botwe et al. (2017a), three grab samples were collected at each station. Only grabs that arrived on the deck firmly closed without water leakage and were not filled with sediment to the lid were sampled to ensure that the fine particles were not lost and the surface layer was intact (Aloupi and Angelidis 2001; Botwe et al. 2017b).

From each grab, two subsamples each of about 200 g wet weight were taken with acid-washed plastic spoons from the upper 0–2 cm layer, which is representative of recently deposited sediments (Phillips 2007; Botwe et al. 2017a), into acid-washed FoodSaver® zipper bags. One subsample was for the analyses of metals, total organic carbon (TOC), carbonate, pH (and subsequently buffer intensity) and the other for grain size analysis. Samples for metal analysis were vacuum-sealed to minimise oxidation.
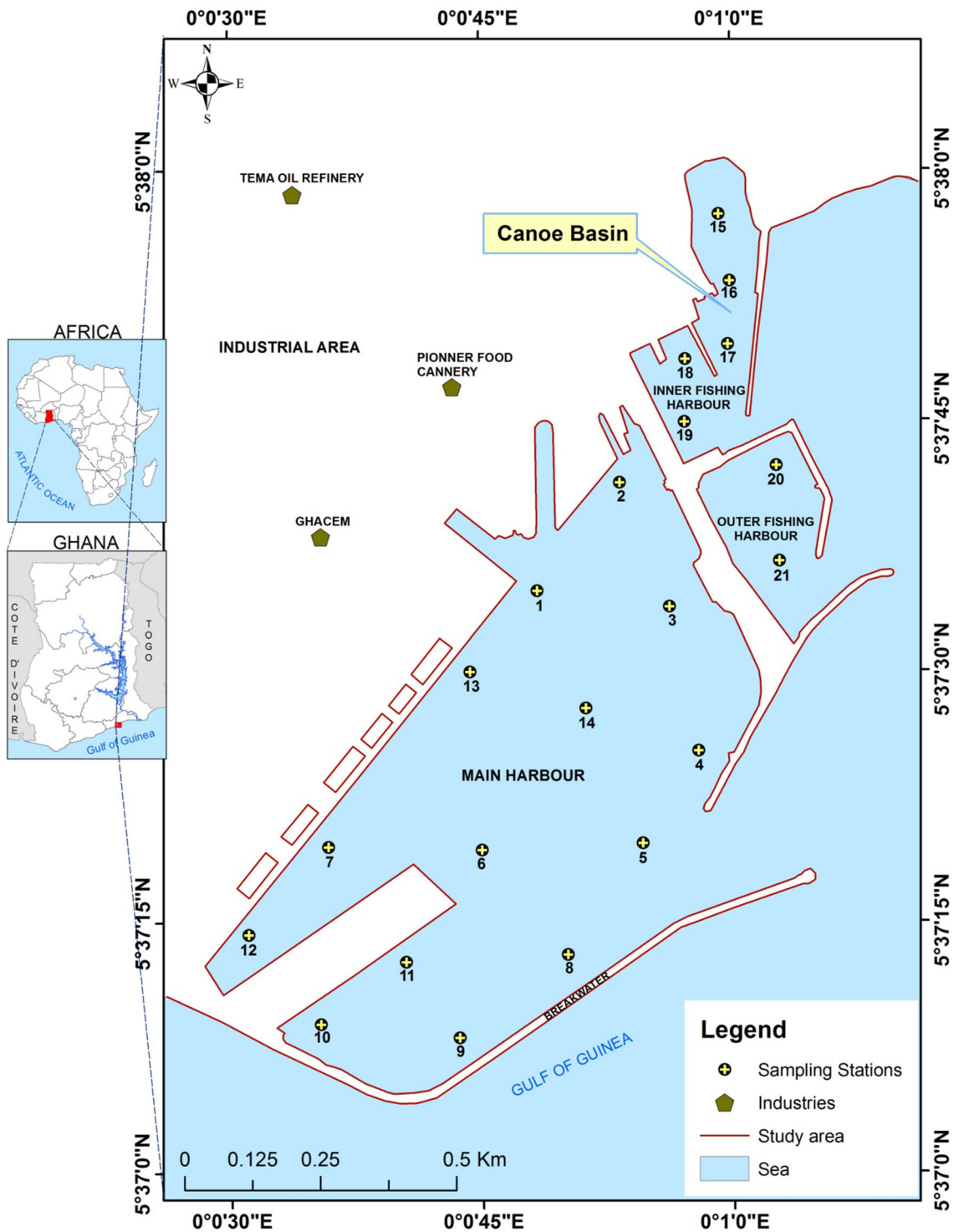
Fig. 1 Map of Tema Harbour showing sediment sampling stations within the different compartments: stations 1–14 in the Main Harbour; stations 15–17 in the Canoe Basin; stations 18–19 in the Inner Fishing Harbour; and stations 20–21 in the Outer Fishing Harbour

To avoid contamination, sediments in direct contact with the grab were not sampled (Botwe et al. 2017b). Redox potential was measured in situ near the sediment–water interface using a Hanna multiparameter probe (HI 9829) following Botwe et al. (2017b). All sediment samples were

kept on ice and transported to the University of Ghana laboratory for further analysis.

In the laboratory, the silt–clay ($<63\ \mu m$) and sand ($63–2000\ \mu m$) fractions in the sediment samples were determined on wet samples by the wet sieving method

following the method by Wang et al. (2001). Sediment samples for metal, total organic carbon (TOC), carbonate and pH analyses were freeze-dried and then homogenised using a Fritsch Pulveriser. Total metal concentrations and metal fractionation were determined on about 0.2 g portions of freeze-dried homogenised sediment samples by adopting the harmonised Community Bureau of Reference (BCR) 3-step sequential extraction and *aqua regia* extraction techniques, respectively, following Pueyo et al. (2001). Metal concentrations were assayed using an Atomic Absorption Spectrometer (Varian AA 240FS). The detection limits for the measured metals were: 0.10 for Al, Hg and As; 0.20 for Cd; 0.50 for Mn, Ni, Pb, Cr, Zn, Cd and Sn; and 1.0 for Cu. The TOC content was determined on 1 g of dry homogenised sediment sample using the Walkley–Black wet oxidation method after decarbonisation of the sediment with excess HCl (Schumacher 2002; Botwe et al. 2017a). The carbonate content was analysed by treating sediment samples with excess HCl (1 M), followed by titration with 0.5 M NaOH (Kelderman and Osman 2007). The sediment pH was determined on 10 g portions of homogenised sediment samples after the addition of 25 mL deionised water following Di Palma and Mecozzi (2007).

To characterise stability of the Tema Harbour sediment against small changes in pH, the buffer intensities of the sediments were evaluated following the procedure described by Calmano (1988). Briefly, 5-g portions of sediment were suspended in 50 mL deionised water (10% sediment suspensions) in acid-washed 50-mL polypropylene tubes and shaken on an end-to-end shaker for 1 h, after which the pH of the supernatant solutions (pH_o) were measured. This procedure was repeated using 50 mL of 0.1 M HCl, and the corresponding pH (pH_x) measured. The buffer intensity (δpH) was determined using Eq. (1) (Calmano 1988):

$$\delta pH = pH_o - pH_x \qquad (1)$$

The buffer intensities of the sediments were characterised as follows: $\delta pH < 2$ (strongly buffered), $\delta pH = 2-4$ (intermediate), and $\delta pH > 4$ (poorly buffered) (Calmano 1988).

For quality assurance and control, chemicals, solvents and reagents used in the extraction were of trace metal analysis grade. All containers used were either new or thoroughly cleaned by washing with detergent, soaking in 10% HNO_3 solution overnight and rinsing with deionised water. A sediment certified reference material (BCR-701) and blanks were analysed with the sediment samples. Sediment samples were analysed in triplicate. Metal recoveries ranged from 69.2 to 109% for the investigated metals, with relative standard deviations (RSD) in the range of 2.2–12.5%. The reported metal concentrations were corrected for recoveries, using their respective mean recoveries from the certified reference materials.

Metal enrichment and pollution level

Metal enrichment factors (EFs) were derived for the measured metals to characterise their enrichment in the Tema Harbour sediments based on Eq. (2) (Dung et al. 2013; Mahu et al. 2015):

$$EF = [M/Al]_{Sample} \Big/ [M/Al]_{Crust} \qquad (2)$$

where $(M/Al)_{Sample}$ is the metal–aluminium ratio for the Tema Harbour sediment sample and $(M/Al)_{Crust}$ is the metal–aluminium ratio for the continental crust.

Geo-accumulation indices (I_{geo}) were evaluated to assess the extent of metal contamination in the Tema Harbour sediments using Eq. (3) (Dung et al. 2013; Mahu et al. 2015):

$$I_{geo} = Log_2(M_s/1.5M_b) \qquad (3)$$

where M_s is the metal concentration in the Tema Harbour sediment, M_b is its average crustal concentration and 1.5 is introduced as a background matrix correction due to lithogenic effects (Addo et al. 2011; Iqbal et al. 2013; Mahu et al. 2015). In the evaluation of the EFs and I_{geo}, the average crustal concentrations of the metals (Taylor 1964) were used as proxies for the background concentration (Table 1), since pre-impacted or deep-core metal concentration data are not available for the Tema Harbour.

Data treatment

Pearson's product-moment correlations were performed to determine linear relationships between the measured sediment parameters using the Statistical Package for Social Sciences (SPSS 16.0) software. Descriptive statistics (means, standard deviations and coefficients of variation) were performed in Microsoft Excel 2007 for Windows at the 95% confidence interval. The spatial distribution patterns of metal concentrations in the Tema Harbour sediments were mapped in ArcGIS 10.2.2. One-way analysis of variance (ANOVA) with multiple comparison (Holm–Sidak and Kruskal–Wallis) tests was performed in SigmaPlot 11.0 to determine spatial differences in sediment metal concentrations in the Tema Harbour.

Results

Physicochemical characteristics of the Tema Harbour sediments

The sediment physicochemical parameters and in situ redox potential (E_h) at the sediment–water interface in the Tema Harbour are shown in Table 1. The Tema Harbour sediments were composed mainly of the silt–clay

Table 1 Sediment metal concentrations and physicochemical parameters measured in the Tema Harbour, Ghana

Harbour compartment	Sampling station	Metal concentration (mg kg⁻¹ dry weight)											Physicochemical parameters					
		Al	Mn	Ni	Pb	Cr	Cu	Zn	As	Cd	Hg	Sn	Silt–clay (%)	TOC (%)	CaCO$_3$ (%)	pH	Buffer intensity	E$_h$ (mV)
Main Harbour	1	17,980	194	21.0	30.5	69.2	81.1	205	14.9	7.5	2.6	23.9	67	4.5	9.5	8.0	1.9	−110
	2	14,170	165	21.3	49.3	57.8	77.2	160	10.0	5.1	2.1	28.8	67	5.4	9.4	8.0	1.4	−130
	3	14,100	160	21.1	45.3	56.6	75.1	155	9.6	7.5	1.4	10.6	67	4.7	9.7	7.7	1.6	−100
	4	27,500	270	26.2	36.3	73.9	79.4	185	15.0	8.7	1.9	12.7	68	5.8	9.0	7.6	1.0	−90
	5	19,280	210	22.8	38.1	66.3	43.3	124	14.5	8.1	0.4	0.8	39	6.0	9.0	8.0	1.0	−90
	6	17,640	195	21.6	40.0	63.0	44.8	128	14.2	17.7	0.4	0.6	70	2.4	10.6	8.0	1.3	−90
	7	14,170	183	21.4	57.6	58.9	42.5	164	10.0	4.3	0.4	0.7	53	1.1	9.8	7.6	1.3	−80
	8	17,890	177	24.7	33.1	63.3	34.2	77	14.0	8.0	0.3	0.5	57	2.2	9.7	7.3	1.4	−90
	9	19,070	187	23.2	56.8	60.9	46.5	110	9.8	9.2	0.6	0.7	84	5.4	9.5	8.0	1.3	−80
	10	16,730	198	20.0	68.4	58.8	44.5	89	14.9	6.0	0.3	0.7	62	2.2	9.3	8.1	1.3	−70
	11	16,220	198	21.9	63.3	70.2	30.9	137	14.1	5.4	0.4	0.6	52	4.7	9.5	7.8	1.3	−80
	12	18,100	187	26.1	57.8	55.8	36.2	123	12.6	7.7	0.8	0.9	71	4.1	9.2	7.6	1.3	−90
	13	20,260	223	35.9	79.9	77.6	78.7	208	15.6	5.8	0.9	14.7	66	5.8	9.6	7.8	1.4	−90
	14	16,840	250	27.6	73.5	71.6	66.3	170	15.3	9.4	0.7	11.3	80	4.5	9.2	8.3	1.3	−90
Canoe Basin	15	15,810	240	18.7	230	71.3	196	576	17.0	6.9	0.8	7.8	85	4.7	9.4	8.2	2.7	−350
	16	15,420	230	20.9	206	77.3	180	561	14.0	8.2	4.3	6.8	80	4.2	8.8	7.6	2.1	−260
	17	13,870	210	20.1	216	65.6	168	532	15.8	5.9	4.5	9.0	82	4.0	9.4	7.5	2.7	−240
IFH	18	19,050	270	22.6	130	110	264	518	21.3	9.2	1.6	12.9	89	5.8	9.0	7.8	1.8	−130
	19	26,710	260	30.4	122	106	220	500	18.7	12.7	2.2	14.0	87	5.4	9.8	7.6	1.7	−140
OFH	20	18,780	250	21.9	107	89.4	170	395	15.1	8.7	2.6	7.9	92	5.3	9.4	7.9	2.3	−150
	21	16,970	220	19.9	97.6	95.4	163	240	13.7	7.1	2.2	6.4	93	5.5	9.2	7.8	1.7	−160
	Mean	17,930	210	23	88	72	102	260	14.2	8.1	1.5	8.2	70	4.5	9.4	–	1.6	–
	ACC	82,300	950	75	12.5	100	55	70	1.8	0.2	0.08	2						
	Year 2000ᵃ	–	–	–	51.5	209	–	–	9.2	0.2	4.4	–						
	Year 2010–2011ᵇ	–	41.7	34.2	–	nd	25.8	28.5	1.5	13.4	–	–						

Average crustal concentrations of the measured metals as well as metal concentrations in Tema Harbour sediments from previous studies in 2000 and 2010–2011 are also presented for comparison

Buffer intensity < 2 indicates strongly buffered sediment; 2–4 indicates intermediate buffered sediment; >4 indicates poorly buffered sediment (Calmano 1988)

IFH inner fishing harbour, *OFH* outer fishing harbour, *ACC* average crustal concentration (Taylor 1964), *nd* not detected; '-' not applicable or not measured

ᵃ JICA (http://open_jicareport.jica.go.jp/pdf/11681632_03.pdf)

ᵇ Nyarko et al. (2014)

(<63 μm) fraction with a mean composition of 70 (±4) %. The sediment TOC and carbonate contents were in the ranges of 1.1–6.0 and 8.8–10.6%, respectively. The Tema Harbour sediments were slightly alkaline (pH range of 7.3–8.3) with buffer intensities in the range of 1.0–2.7, while the bottom water was anoxic with E_h values ranging from −70 to −350 mV. Sediments from the Canoe Basin were mostly anoxic. The silt–clay content, E_h and buffer intensity varied significantly across the Tema Harbour compartments. On the contrary, the pH, TOC and carbonate contents did not vary significantly across the Tema Harbour compartments. Table 2 shows that the silt–clay content correlated significantly with the Mn ($r = 0.52$, $p < 0.05$), Ni ($r = 0.52$, $p < 0.05$), Cr ($r = 0.58$, $p < 0.01$), Cu ($r = 0.60$, $p < 0.01$), Zn ($r = 0.75$, $p < 0.01$), As ($r = 0.64$, $p < 0.01$) and Sn ($r = 0.50$, $p < 0.05$) concentrations in the Tema Harbour sediments. The TOC content correlated with the Mn ($r = 0.48$, $p < 0.05$), Ni ($r = 0.46$, $p < 0.05$) and Cu ($r = 0.49$, $p < 0.05$) concentrations. The carbonate content correlated with the Hg concentration ($r = 0.47$, $p < 0.05$). The buffer intensity correlated with the Cr ($r = 0.85$, $p < 0.01$), Zn ($r = 0.71$, $p < 0.01$), As ($r = 0.83$, $p < 0.01$) and Sn ($r = 0.65$, $p < 0.01$) concentrations as well as with the silt–clay content ($r = 0.55$, $p < 0.01$). Sediment pH did not correlate significantly with the metal concentrations in the Tema Harbour sediments.

Metal concentrations and distribution patterns in sediments of Tema Harbour

The total metal concentrations in the Tema Harbour sediments are presented in Table 1. Overall, the mean sediment metal concentrations were: Al ($17{,}930 \pm 780$ mg kg^{-1} dw), Mn (210 ± 7 mg kg^{-1} dw), Ni (23 ± 1 mg kg^{-1} dw), Cr (72 ± 3 mg kg^{-1} dw), Pb (88 ± 13 mg kg^{-1} dw), Cu (102 ± 16 mg kg^{-1} dw), Zn (260 ± 40 mg kg^{-1} dw), As (14.2 ± 0.6 mg kg^{-1} dw), Cd (8.1 ± 0.6 mg kg^{-1} dw), Hg (1.5 ± 0.3 mg kg^{-1} dw) and Sn (8.2 ± 1.7 mg kg^{-1} dw). Significant positive correlations were observed among most of the sediment metal concentrations (Table 2). The Mn and Ni concentrations showed a perfect correlation ($r = 1.00$, $p < 0.01$), and both correlated significantly with all the other metals, except Pb, Hg and Sn. Cd exhibited significant correlations with all the metals except Cr. Pb exhibited a significant correlation with only Al ($r = 0.60$, $p < 0.01$), whereas Hg did not exhibit any significant correlation with all the other metals investigated.

The spatial distribution patterns of the metals are shown in Fig. 2. Sediment Al concentrations were relatively higher in the Inner Fishing Harbour and the Main Harbour entrance stations. Mn concentrations were relatively higher in the Fishing Harbour, Canoe Basin, and the entrance and mid-section of the Main Harbour. Relatively higher Ni concentrations occurred in the north-eastern corner of the Main Harbour. Sediments from the Fishing Harbour and the Canoe Basin contained relatively higher Cr concentrations. Sediment concentrations of As were relatively higher in the Inner Fishing Harbour and the Canoe Basin. Relatively higher sediment Cd concentrations occurred in the Inner Fishing Harbour. Sediments from the Canoe Basin and the Fishing Harbour contained relatively higher concentrations of Pb, Cu, Zn and Hg, while sediments from the north-eastern corner of the Main Harbour contained higher concentrations of Sn. Analysis of variance (ANOVA) revealed that the Mn, Ni, Cr, Cu, Zn, As and Sn concentrations differed significantly ($p < 0.05$) among the Main Harbour, the Inner Fishing Harbour, the Outer Fishing Harbour and the Canoe Basin.

Metal fractionation, enrichment and pollution in Tema Harbour sediments

The distribution of metals over the acid-soluble, reducible, oxidisable and residual phases of sediments from the Tema Harbour is shown in Fig. 3. At all the sampling stations, Cd occurred predominantly in the acid-soluble phase (70–85%) and was divided nearly equally among the reducible (5–10%), oxidisable (5–12%) and residual (5–10%) phases. Hg also occurred mainly in the acid-soluble phase (52–67%) with relatively higher fractions in the residual phase (15–42%) than in the reducible (0–15%) and oxidisable (0–14%) phases. At all the sampling stations, Al (73–83%), Mn (70–80%), Ni (62–72%), Pb (50–65%), Cr (60–76%), Cu (57–72%), As (52–63%) and Sn (50–100%) were mainly present in the residual phase. For most of these metals, the fractions in the acid-soluble phase were low, i.e. Al (4–8%), Mn (8–17%), Ni (8–15%), Pb (5–10%), Cr (3–7%), Cu (3–7%) and As (8–15%). In the case of Sn, no appreciable fraction was present in the acid-soluble phase at stations 5–12 in the Main Harbour, although their fraction was appreciable (17–28%) at the remaining sampling stations. For Zn, both the reducible (38–45%) and residual (35–42%) phases were the most important at all the sampling stations, while the oxidisable phase was the least important. Appreciable fractions of Zn (12–18%) were also present in the acid-soluble phase.

Table 3 shows the enrichment factors (EFs) of the investigated metals in the Tema Harbour sediments. The results show relatively higher enrichment of Cd over the other metals. The Cd concentrations in the Tema Harbour surface sediments exceeded the average crustal concentration by over an order of magnitude. The concentrations of Cd, Hg, Pb and As in the Tema Harbour sediments were 12–41, 2–33, 1–10 and 2–5 times their average crustal

Table 2 Correlation matrix of measured metals and physicochemical characteristics of surface sediments from Tema Harbour, Ghana (2-tailed; $n = 21$)

	Al	Mn	Ni	Pb	Cr	Cu	Zn	As	Cd	Hg	Sn	Silt–clay	TOC	Carbonate	pH
Mn	0.61**														
Ni	0.61**	1.00**													
Pb	0.60**	0.30	0.30												
Cr	−0.20	0.44*	0.44*	−0.22											
Cu	0.48*	0.78**	0.78**	0.23	0.36										
Zn	0.16	0.67**	0.67**	0.09	0.76**	0.81**									
As	0.04	0.61**	0.61**	−0.12	0.91**	0.61**	0.92**								
Cd	0.44*	0.79**	0.79**	0.23	0.45*	0.74**	0.69**	0.61**							
Hg	0.42	0.27	0.27	0.15	−0.10	0.26	0.12	0.06	0.28						
Sn	−0.05	0.27	0.27	−0.19	0.58**	0.32	0.61**	0.67**	0.18	−0.08					
Silt–clay	0.12	0.52*	0.52*	−0.03	0.58**	0.60**	0.75**	0.64**	0.36	0.27	0.50*				
TOC	0.42	0.48*	0.46*	0.29	0.12	0.49*	0.40	0.27	0.27	−0.01	0.27	0.34			
Carbonate	−0.07	−0.40	−0.40	0.07	−0.29	−0.23	−0.29	−0.27	−0.20	0.47*	−0.34	−0.13	−0.48		
pH	−0.16	0.10	0.10	−0.17	−0.05	−0.08	−0.08	−0.10	−0.04	0.11	−0.31	0.10	0.20	−0.02	
BI	−0.31	0.25	0.25	−0.37	0.85**	0.29	0.71**	0.83**	0.35	−0.11	0.65**	0.60**	0.07	−0.09	−0.03

* Correlation is significant at the 0.05 level; ** Correlation is significant at the 0.01 level

Fig. 2 Spatial distribution patterns of **a** Pb, **b** Cu, **c** Zn, **d** Hg, **e** Sn, **f** Al, **g** Mn, **h** Ni, **i** Cr, **j** As and **k** Cd in surface sediments of Tema Harbour
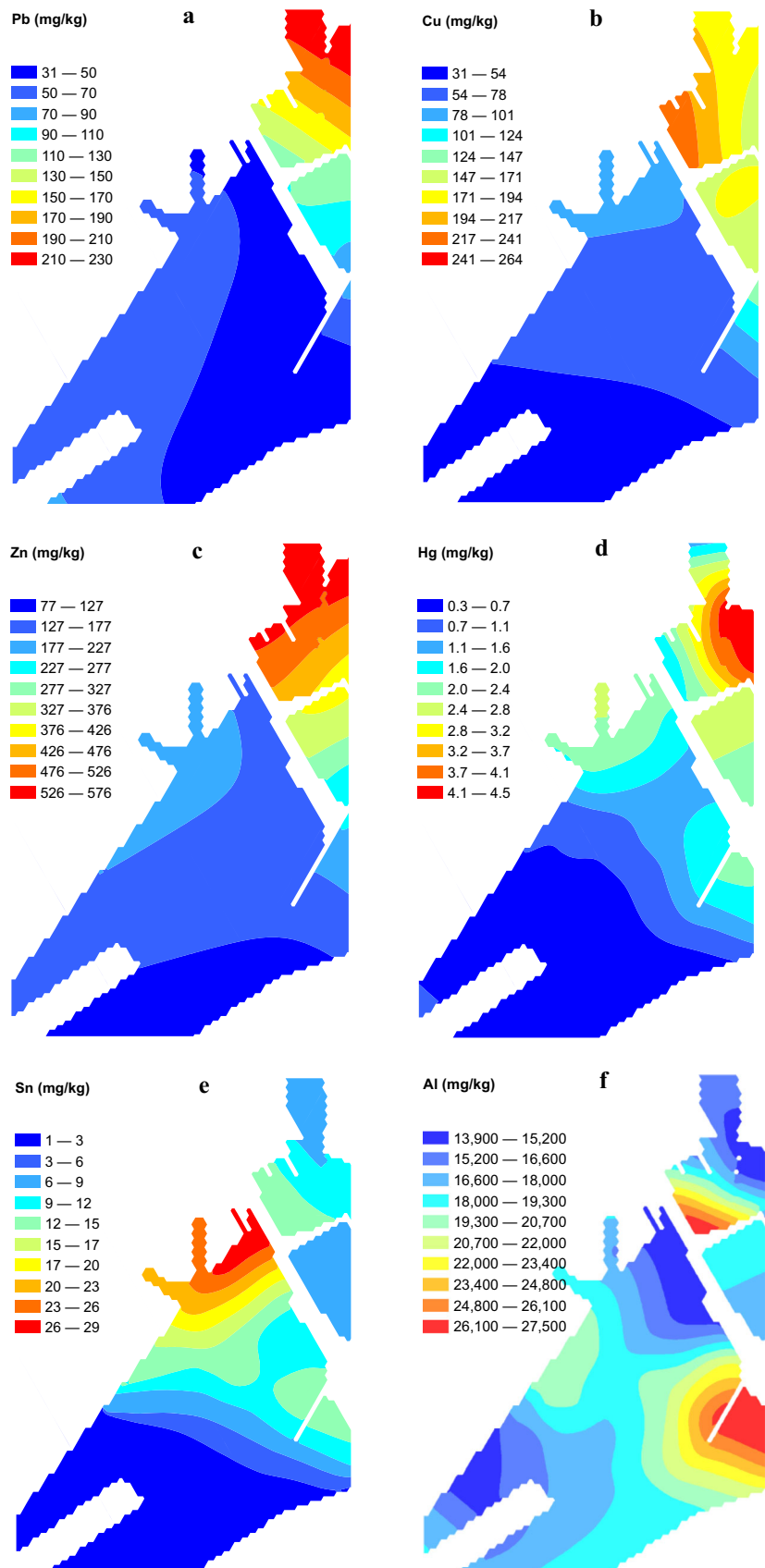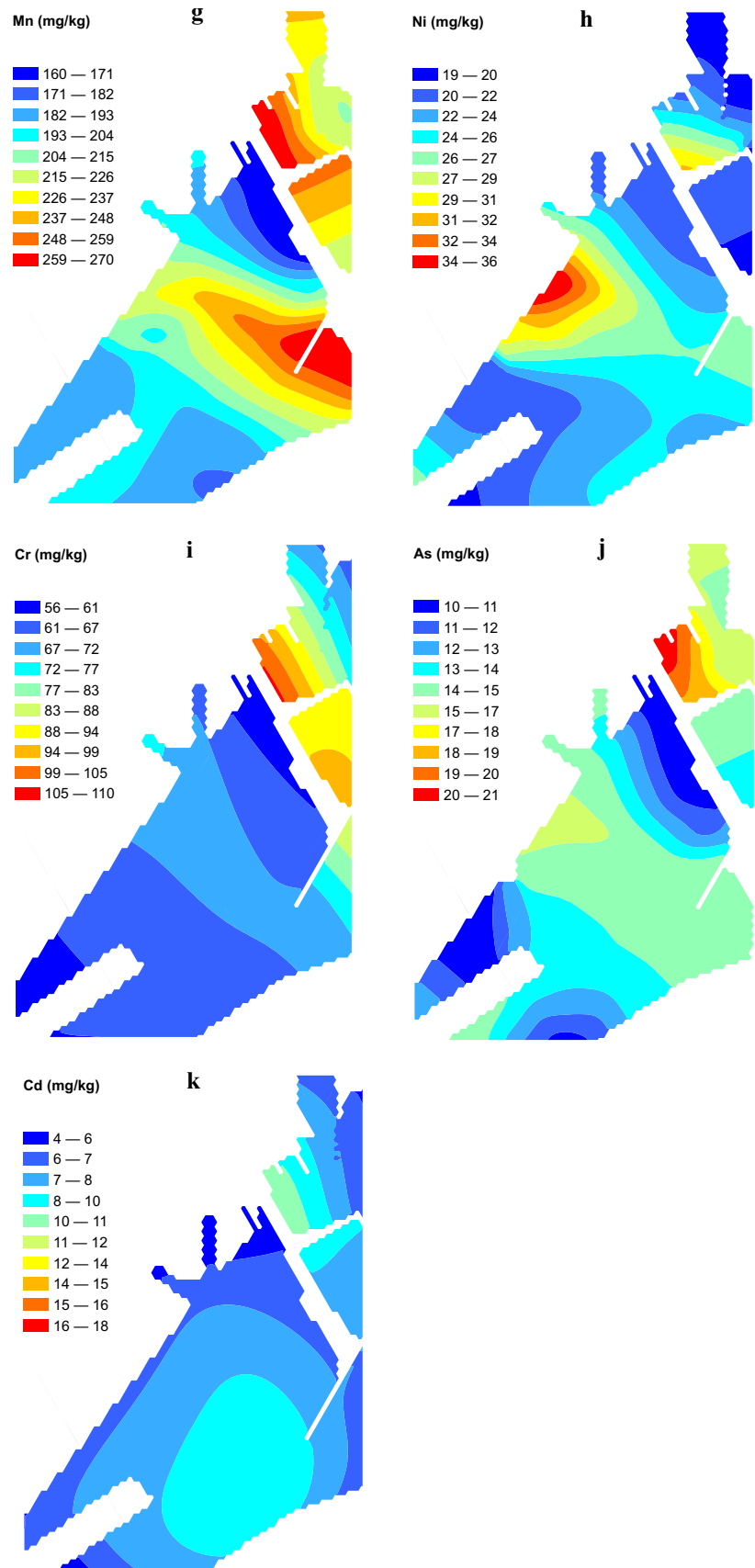
Fig. 2 continued

Table 3 Enrichment factors and geo-accumulation indices of measured metals in surface sediments from Tema Harbour, Ghana

Sampling station	Enrichment factors (EFs)										Geo-accumulation indices (I_{geo})									
	Mn	Ni	Pb	Cr	Cu	Zn	As	Cd	Hg	Sn	Mn	Ni	Pb	Cr	Cu	Zn	As	Cd	Hg	Sn
1	0.9	1.3	11.2	3.2	6.7	13.4	37.9	172	149	54.7	−2.9	−2.4	0.7	−1.1	0.0	1.0	2.5	4.6	4.4	3.0
2	1.0	1.6	22.9	3.4	8.2	13.3	32.3	148	153	83.6	−3.1	−2.4	1.4	−1.4	−0.1	0.6	1.9	4.1	4.1	3.3
3	1.0	1.6	21.2	3.3	8.0	12.9	31.1	219	102	30.9	−3.2	−2.4	1.3	−1.4	−0.1	0.6	1.8	4.6	3.5	1.8
4	0.9	1.0	8.7	2.2	4.3	7.9	24.9	130	71.1	19.0	−2.4	−2.1	1.0	−1.0	−0.1	0.8	2.5	4.9	4.0	2.1
5	0.9	1.3	13.0	2.8	3.4	7.6	34.4	173	21.3	1.7	−2.8	−2.3	1.0	−1.2	−0.9	0.2	2.4	4.8	1.7	−1.9
6	1.0	1.3	14.9	2.9	3.8	8.5	36.8	413	23.3	1.4	−2.9	−2.4	1.1	−1.3	−0.9	0.3	2.4	5.9	1.7	−2.3
7	1.1	1.7	26.8	3.4	4.5	13.6	32.3	125	29.0	2.0	−3.0	−2.4	1.6	−1.3	−1.0	0.6	1.9	3.8	1.7	−2.1
8	0.9	1.5	12.2	2.9	2.9	5.1	35.8	184	17.3	1.2	−3.0	−2.2	0.8	−1.2	−1.3	−0.4	2.4	4.7	1.3	−2.6
9	0.8	1.3	19.6	2.6	3.6	6.8	23.5	199	32.4	1.5	−2.9	−2.3	1.6	−1.3	−0.8	0.1	1.9	4.9	2.3	−2.1
10	1.0	1.3	26.9	2.9	4.0	6.2	40.7	148	18.4	1.7	−2.8	−2.5	1.9	−1.4	−0.9	−0.2	2.5	4.3	1.3	−2.1
11	1.1	1.5	25.7	3.6	2.9	9.9	39.7	137	25.4	1.5	−2.8	−2.4	1.8	−1.1	−1.4	0.4	2.4	4.2	1.7	−2.3
12	0.9	1.6	21.0	2.5	3.0	8.0	31.8	175	45.5	2.0	−2.9	−2.1	1.6	−1.4	−1.2	0.2	2.2	4.7	2.7	−1.7
13	1.0	1.9	26.0	3.2	5.8	12.1	35.2	118	45.7	29.9	−2.7	−1.6	2.1	−1.0	−0.1	1.0	2.5	4.3	2.9	2.3
14	1.3	1.8	28.7	3.5	5.9	11.9	41.5	230	42.8	27.6	−2.5	−2.0	2.0	−1.1	−0.3	0.7	2.5	5.0	2.5	1.9
15	1.3	1.3	95.8	3.7	18.6	42.8	49.2	180	52.1	20.3	−2.6	−2.6	3.6	−1.1	1.2	2.5	2.7	4.5	2.7	1.4
16	1.3	1.5	88.0	4.1	17.5	42.8	41.5	219	287	18.1	−2.6	−2.4	3.5	−1.0	1.1	2.4	2.4	4.8	5.2	1.2
17	1.3	1.6	103	3.9	18.1	45.1	52.1	175	334	26.7	−2.8	−2.5	3.5	−1.2	1.0	2.3	2.5	4.3	5.2	1.6
18	0.2	1.3	44.9	4.8	20.7	32.0	51.1	199	86.4	27.9	−2.4	−2.3	2.8	−0.4	1.7	2.3	3.0	4.9	3.7	2.1
19	0.8	1.2	30.1	3.3	12.3	22.0	32.0	196	84.7	21.6	−2.5	−1.9	2.7	−0.5	1.4	2.3	2.8	5.4	4.2	2.2
20	1.2	1.3	37.5	3.9	13.5	24.7	36.8	191	142	17.3	−2.5	−2.4	2.5	−0.7	1.0	1.9	2.5	4.9	4.4	1.4
21	1.1	1.3	37.9	4.6	14.4	16.6	36.9	172	133	15.5	−2.7	−2.5	2.4	−0.7	1.0	1.2	2.3	4.6	4.2	1.1

Main Harbour (stations 1–14); Canoe Basin (stations 15–17); Inner Fishing Harbour (stations 18 and 19); Outer Fishing Harbour (stations 20 and 21); Interpretations: EF ≤ 1 indicates no enrichment, 1 < EF ≤ 3: minor enrichment, 3 < EF ≤ 5: moderate enrichment, 5 < EF ≤ 10: moderately severe enrichment, 10 < EF ≤ 25: severe enrichment, 25 < EF ≤ 50: very severe enrichment, and EF > 50: extremely severe enrichment; I_{geo} < 0: unpolluted; 0 ≤ I_{geo} < 1: unpolluted to moderately polluted; 1 ≤ I_{geo} < 2: moderately polluted; 2 ≤ I_{geo} 3: moderately to highly polluted; 3 ≤ I_{geo} < 4: heavily polluted; 4 ≤ I_{geo} < 5: highly to very highly polluted; I_{geo} ≥ 5: very heavily polluted (Dung et al. 2013)

concentrations, respectively. The concentrations of Cu and Zn in the Tema Harbour sediments were elevated above their average crustal concentrations only in the Canoe Basin and the Fishing Harbour, while the sediment Sn concentrations exceeded the average crustal concentration only at stations 1–4, 13 and 14 in the north-eastern corner of the Main Harbour, the Canoe Basin and the Fishing Harbour. The concentrations of Mn, Ni and Cr in the Tema Harbour sediments were about an order of magnitude lower than their average crustal concentrations.

The potential elevation of metal concentrations in the Tema Harbour sediments was confirmed by the geo-accumulation indices (Table 3). The geo-accumulation indices categorised all the Tema Harbour sediments as heavily polluted with respect to Cd, but unpolluted with respect to the Mn, Ni and Cr concentrations. Sediments of the Canoe Basin (stations 15–17) were categorised, based on the geo-accumulation index, as polluted with respect to the Pb and Zn concentrations, those of the Fishing Harbours (stations 18–21) as polluted with respect to the Hg and Cu concentrations, and those of stations 1–4 in the north-eastern corner of the Main Harbour as polluted with respect to the Hg concentrations.

Discussion

Distribution and potential sources of metals in Tema Harbour surface sediments

This study showed high enrichment of Cd, Hg and As in the Tema Harbour surface sediments (EFs > 10), which indicates that Cd, Hg and As contamination in the Tema Harbour sediments is mainly of anthropogenic origin (Chatterjee et al. 2007; Addo et al. 2011; Mahu et al. 2015). Similarly, the high Pb enrichment in all the sediment samples (except for station 4) suggests significant anthropogenic inputs of Pb in the Tema Harbour sediments. The EFs of Cu, Zn and Sn also point to anthropogenic contributions of these metals in various parts of the Tema

Harbour (Table 3). The low enrichment of Mn, Ni and Cr in the sediment samples (EFs < 10) indicate that the sources of these metals in the Tema Harbour sediments were mainly from natural or lithogenic sources, such as weathering and chemical leaching of the bedrock. The metal enrichment in the Tema Harbour sediments is supported by the geo-accumulation indices (I_{geo}) (Table 3), which indicate that the Tema Harbour sediments are potentially polluted with respect to their Pb, Cu, Zn, As, Cd, Hg and Sn concentrations, while they are potentially unpolluted with respect to the Mn, Ni and Cr concentrations.

Potential anthropogenic sources of Pb, Cu, Zn, As, Hg and Sn contamination in the Tema Harbour sediments are varied and may relate to bunkering, fuelling, discharge of bilge, and scraping and painting of vessels as well as vehicular traffic, industrial and urban effluent discharges (Lepland et al. 2010; Mestres et al. 2010; Schipper et al. 2010; Nyarko et al. 2014). The use of antifouling paints on ships and fishing vessels, for example, is an important source of Cu and Sn in harbour sediments (Castro et al. 2012; Nyarko et al. 2011). There were significant correlations among the metals (Table 2), which can be attributed to common sources (Nyarko et al. 2014; Qu and Kelderman 2001) or similar distribution patterns (Aloupi and Angelidis 2001) of the metals in the Tema Harbour sediments.

Different proximities of sampling stations to local contamination sources in the Tema Harbour may account for the differences in the sediment metal concentrations across the harbour. For example, the Tema Harbour has two dry docks located close to stations 1 and 2, where activities such as sandblasting, high-pressure water cleaning, scraping and painting are carried out. Moreover, station 4 is close to the Oil Berth, where oil tankers berth and carry out bunkering activities. Thus, the proximity of the northeastern stations to the dry docks and the Oil Berth in the Main Harbour may have resulted in the relatively higher Cu, Hg and Sn concentrations present in the sediments from this area. Higher concentrations of Pb, Cu, Zn and Hg occurred in the Canoe Basin and the Fishing Harbour, which could be due to oil spills during refuelling of fishing vessels in these areas.

Moreover, the Main Harbour is frequently dredged, whereas the Fishing Harbour and Canoe Basin are not. Dredging in the Main Harbour may potentially remove contaminated surficial sediments and result in reduced metal levels, whereas the accumulation of sediments in the Canoe Basin and the Fishing Harbour may result in elevated concentrations of associated metals. The resuspension and redistribution of bottom sediment due to, for example, tidal currents, dredging and ship movements (Lepland et al. 2010) may also contribute to the spatial variations in the sediment metal concentrations in the Tema Harbour.

Since bulk sediments were analysed in this study, a correlation analysis was performed to examine the associations between the metal concentrations and sediment characteristics. Significant correlations were observed between the silt–clay content and the Cu, Zn, Sn, Mn, Ni, Cr and As concentrations in the Tema Harbour sediments (Table 2), which can be attributed to the high affinity of metals for the fine fractions of sediments owing to their large surface areas (Aloupi and Angelidis 2001; Kelderman and Osman 2007; Lepland et al. 2010; Nyarko et al. 2011). The distribution patterns of Cu, Zn, Sn, Mn, Ni, Cr and As in the Tema Harbour sediments (Fig. 2) may, therefore, be influenced by the differences in their silt–clay content. As a geochemical substrate for metals (Aloupi and Angelidis 2001), TOC may also play a role in the metal distribution, which may explain its correlations with Mn, Ni and Cu (Table 2).

Carbonate generally has a low capacity to adsorb and retain metals and is, therefore, considered as a diluent of metal concentrations in sediments (Horowitz 1985; Aloupi and Angelidis 2001). Thus, Aloupi and Angelidis (2001) found an inverse relationship between the metal and carbonate concentration of the Mytilene Harbour sediments. The Tema Harbour sediments had a nearly uniform carbonate content (Table 1), exhibiting generally poor correlations with the metal concentrations in the harbour sediments (Table 2). Al is known to distribute nearly equally between the fine and coarse fractions of a sediment (Aloupi and Angelidis 2001), which may explain the observed poor correlation between the Al concentration and the silt–clay fraction of the harbour sediments (Table 2).

The mean metal concentrations from this study were compared with previous studies in 2000 by JICA (2000) and 2010–2011 by Nyarko et al. (2014) (Table 1). Table 1 shows that the current mean Pb, As and Cd concentrations are higher than the levels in 2000, whereas the current concentrations of Cr and Hg are lower than the 2000 levels. Moreover, the current mean levels of Mn, Cr, Cu, Zn and As are higher than the levels in 2010–2011. The mean reported concentrations of Ni and Cd in 2010–2011 were, however, higher than the current levels. These comparisons did not reveal a progressive increase in metal contamination of Tema Harbour sediments since the year 2000.

Metal fractionation in the Tema Harbour sediments

The negative E_h values of the bottom water (Table 1) indicate anoxic bottom conditions in the Tema Harbour

(Matijević et al. 2007), which has also been observed in previous studies (Botwe et al. 2017a, b). Metal fractionation in the Tema Harbour sediments (Fig. 3) showed that most of the metals (Al, Mn, Ni, Pb, Cr, Cu, As and Sn) were predominantly present in the residual phase, where they are incorporated into the crystal lattice (Calmano et al. 1993; Kelderman and Osman 2007). Among the non-residual fractions, the oxidisable phase was most important for Pb, Cr, Cu and As. This indicates that complexation with organic matter and precipitation with sulphides were the main mechanisms for the immobilisation of Pb, Cr, Cu and As into the Tema Harbour sediments, which is the case for most metals under anoxic conditions (Caille et al. 2003; Ho et al. 2012a).

Mn and Sn were mainly present in the acid-soluble phase, while Al and Ni were distributed nearly equally between the non-residual phases. The fractionation of Zn showed that the reducible phase was most important. This suggests that co-precipitation with oxides or hydroxides of Fe and Mn was a main mechanism for Zn immobilisation into the Tema Harbour sediments. Cd (70–85%) and Hg (52–67%) were predominantly associated with the acid-soluble phase. In this phase, Hg may associate with carbonates, which may partly explain the observed correlation between Hg and carbonate (Table 2).

Ecological implications of metal contamination in Tema Harbour sediments

Ecotoxicological implications

Metal contamination in sediments may cause toxicity in sediment-dwelling organisms (Long et al. 1995, 2006). The effects-range low (ERL) and effects-range median (ERM) sediment quality guidelines (Long et al. 1995) were used to characterise the potential toxicity of the Tema Harbour sediments due to their metal (Ni, Pb, Cr, Cu, Zn, As, Cd and Hg) contamination. Metal concentrations below the ERL, at or above the ERL but below the ERM, and at or above the ERM are associated with, respectively, rare, occasional, and frequent occurrence of toxic effects (Long et al. 1995). For each metal, two quotients namely the effects-range low quotient (ERLQ) and effects-range median quotient (ERMQ) were derived by dividing the measured metal concentration by its corresponding ERL and ERM concentrations, respectively (Long et al. 2006). Within this approach, an ERLQ < 1 indicates toxic effects will rarely occur; an ERLQ $\geq$ 1 but ERMQ < 1 indicates toxic effects will occur occasionally; whereas an ERMQ $\geq$ 1 indicates toxic effects will occur frequently.

The ERLQ and ERMQ values (Table 4) indicate that Hg concentrations at most (67%) of the sampling stations may potentially cause frequent occurrence of toxic effects.

Thus, Hg is of potential concern in the Tema Harbour, particularly in the north-eastern corner of the Main Harbour, the Canoe Basin and the Fishing Harbour. Frequent occurrence of toxic effects is also expected as a result of the sediment Zn concentrations in the Canoe Basin and the Fishing Harbour. There are also isolated areas in the Tema Harbour where the concentrations of Pb and Cd in the sediments may be associated with frequent occurrence of toxic effects. At most of the stations, however, there is a potential for occasional occurrence of toxic effects as a result of Ni, Pb, Cu, As and Cd concentrations in the sediments, while the Cr concentrations are not likely to cause toxic effects based on the ERLQ and ERMQ values (Table 4).

To characterise the overall potential sediment toxicity due to a mixture of metals, mean ERM quotients (mERMQs) were calculated by averaging the different metal ERMQs with the assumptions that (1) the different metals contribute additively to the overall toxicity without being antagonistic or synergistic and (2) samples with the same mERMQ exhibit similar toxic effects (Long et al. 2006; Birch and Hutson 2009). The overall potential toxicity is classified as minimal if the mERMQ < 0.1, low if 0.1 $\leq$ mERMQ < 0.5, moderate if 0.5 $\leq$ mERMQ < 1.5 and high if mERMQ > 1.5 (Birch and Hutson 2009). The mERMQ values of the Tema Harbour sediments (Table 4) indicate that metal concentrations of the sediments from the north-eastern stations in the Main Harbour, the Canoe Basin and the Fishing Harbour may cause moderate toxicity to benthic organisms, while sediments from the remaining areas may be associated with low toxicity.

Ecological risk implications

Metal fractionation in sediments significantly determines their potential mobility and availability for uptake by benthic organisms (Calmano et al. 1993; Jain 2004; Pini et al. 2015). Metals associated with the acid-soluble phase have the greatest mobility and bioavailability potential and pose the greatest ecological risk, whereas those in the residual phase have the least mobility and bioavailability potential and pose the least ecological risk (Calmano et al. 1993; Jain 2004; Kelderman and Osman 2007; Iqbal et al. 2013; Ho et al. 2012a). A risk assessment code (RAC) has therefore been developed based on the fraction (%) of metal associated with the acid-soluble phase to characterise the potential risk of sediment-associated metals entering the food chain as follows (Jain 2004): acid-soluble fraction <1% indicates no risk, 1–10% indicates low risk, 11–30% indicates medium risk, 31–50% indicates high risk, and >50% indicates very high risk.

The phase distributions of the investigated metals in the Tema Harbour sediments (Fig. 3) show large fractions of

Fig. 3 Distribution of metals over the acid-soluble, reducible, oxidisable and residual phases of Tema Harbour sediments: **a** Al, **b** Mn, **c** Ni, **d** Pb, **e** Cr, **f** Cu, **g** Zn, **h** As, **i** Cd, **j** Hg, and **k** Sn
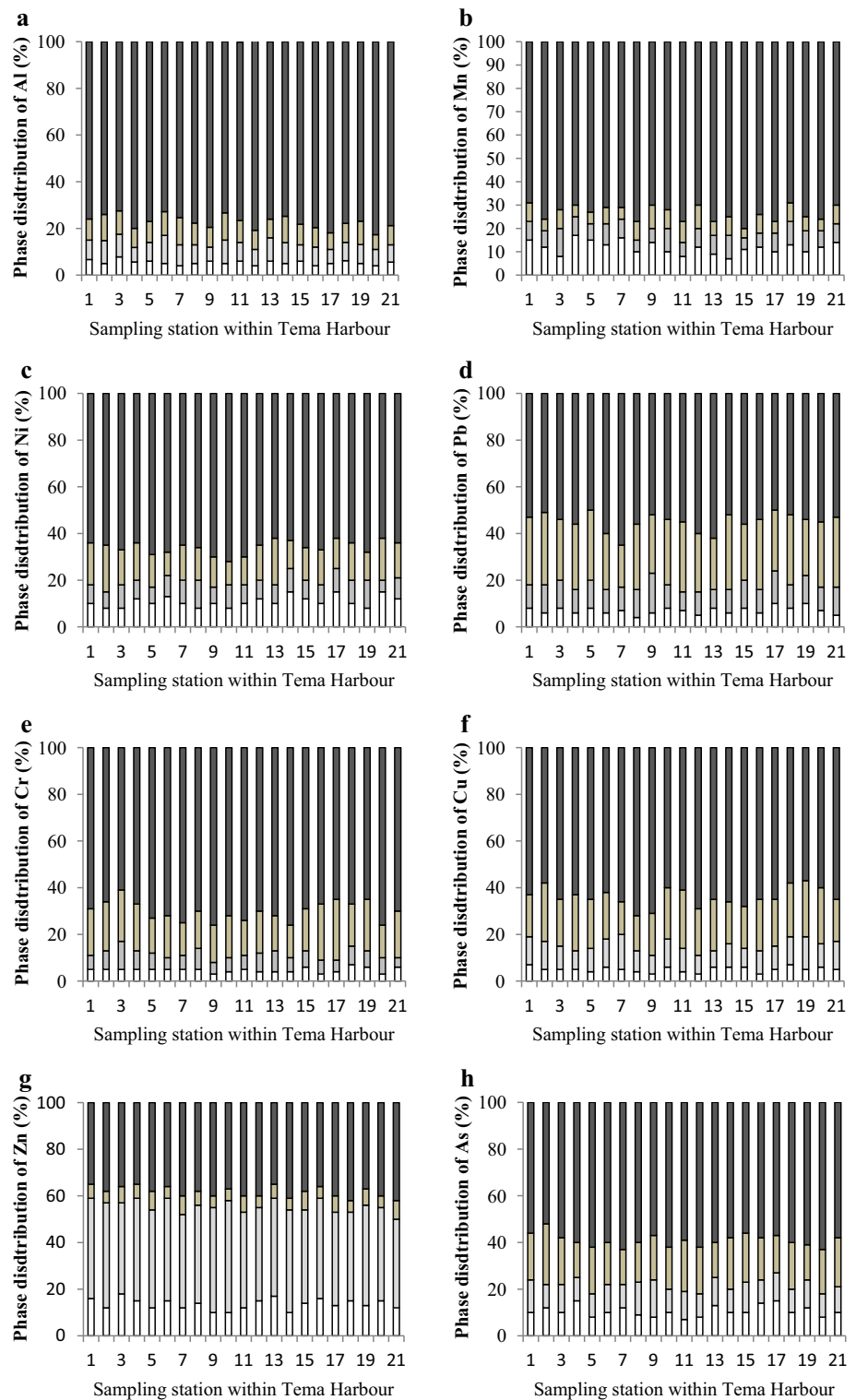
Cd (70–85%) and Hg (52–67%) in the acid-soluble phase, indicating that Cd and Hg contamination in the Tema Harbour sediments may pose very high ecological risks. Sn may pose medium risk at stations 1–4 in the Main Harbour, the Canoe Basin (stations 15–17) and the Fishing Harbour (stations 18–21), where the acid-soluble fraction ranged between 17 and 28%, but poses no risk at the remaining stations. The fractions of Mn (8–17%), Ni (8–15%), Zn (12–18%) and As (8–15%) in the acid-soluble phase indicate these metals pose low–medium risks, while those of

Fig. 3 continued
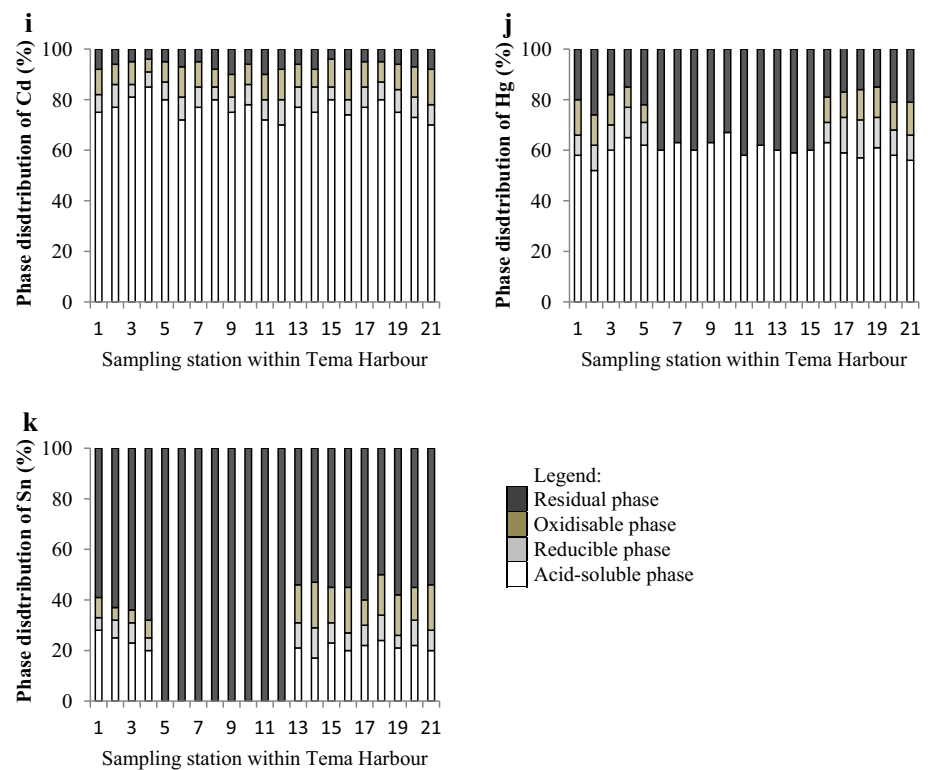
Pb (5–10%), Cr (3–7%) and Cu (3–7%) present low risk. The non-residual or labile (i.e. acid-soluble + reducible + oxidisable) fractions, however, constitute a pool of potentially bioavailable metals due to their potential to undergo changes under varying environmental conditions such as pH, E_h and resuspension of bottom sediments (Calmano et al. 1993; Kelderman and Osman 2007; De Jonge et al. 2012; Dung et al. 2013; Hamzeh et al. 2014; Pini et al. 2015). The considerable fractions of Mn (20–30%), Ni (28–38%), Pb (35–50%), Cr (24–40%), Cu (28–43%), As (37–48%) and Sn (0–50%) present in the labile phase and therefore have implications for their potential ecological risks.

Chemical stability of Tema Harbour sediment

The pH range of the Tema Harbour sediments (7.3–8.3; Table 1) indicates that all the investigated sediments were slightly alkaline. The buffer intensities of the Tema Harbour sediments ranged from intermediate to strong (Table 1). Thus, in general, the Tema Harbour sediments are potentially stable against small changes in pH, with the potential to lower the risk of metal remobilisation and exposure due to acidification. A reduction in pH (acidification) can substantially increase the risk of metal exposure to organisms via remobilisation of sediment-associated metals (Calmano 1988; Calmano et al. 1993; Kelderman and Osman 2007; Ho et al. 2012a). The potential ecological

risk of metal remobilisation due to acidification may be more pronounced in weakly buffered sediments, since they have a low capacity to resist slight changes in pH.

The carbonate content is a major determinant of the buffer intensity of sediments: sediments with carbonate contents > 10% are well buffered against acidification over a wide range (Calmano 1988). The carbonate contents of the Tema Harbour sediments were close to 10 (Table 1) and exhibited no significant correlation with the buffer intensity (Table 2). The observed significant correlations between buffer intensity and Cr, Zn, As and Sn concentrations in the Tema Harbour sediments indicate that increasing buffer intensity enhances the immobilisation and accumulation of these metals in the harbour sediments. The significant correlation between buffer intensity and silt–clay content (Table 2) suggests that the silt–clay content has a positive influence on the buffer intensity of the Tema Harbour sediments, possibly due to the effect of aluminosilicates, which are another major determinant of the sediment buffer intensity (Calmano 1988).

Conclusions

The metal (Al, Mn, Ni, Pb, Cr, Cu, Zn, As, Cd, Hg and Sn) distribution, fractionation and their ecological implications of surface sediments from the Tema Harbour (Greater Accra, Ghana) have been investigated. Sediment

Table 4 Calculated effects-range low quotients (ERLQ), effects-range median quotients (ERMQs) and mean ERM quotients (mERMQs) for measured metals in surface sediments from Tema Harbour, Ghana

Harbour compartment	Sampling station	ERLQ								ERMQ								mERMQ
		Ni	Pb	Cr	Cu	Zn	As	Cd	Hg	Ni	Pb	Cr	Cu	Zn	As	Cd	Hg	
Main Harbour	1	1.0	0.7	0.9	2.4	1.4	1.8	6.3	17.3	0.4	0.1	0.2	0.3	0.5	0.2	0.8	3.7	0.8
	2	1.0	1.1	0.7	2.3	1.1	1.2	4.3	14.0	0.4	0.2	0.2	0.3	0.4	0.1	0.5	3.0	0.6
	3	1.0	1.0	0.7	2.2	1.0	1.2	6.3	9.3	0.4	0.2	0.2	0.3	0.4	0.1	0.8	2.0	0.5
	4	1.3	0.8	0.9	2.3	1.2	1.8	7.3	12.7	0.5	0.2	0.2	0.3	0.5	0.2	0.9	2.7	0.7
	5	1.1	0.8	0.8	1.3	0.8	1.8	6.8	2.7	0.4	0.2	0.2	0.2	0.3	0.2	0.8	0.6	0.4
	6	1.0	0.9	0.8	1.3	0.9	1.7	14.8	2.7	0.4	0.2	0.2	0.2	0.3	0.2	1.8	0.6	0.5
	7	1.0	1.2	0.7	1.3	1.1	1.2	3.6	2.7	0.4	0.3	0.2	0.2	0.4	0.1	0.4	0.6	0.3
	8	1.2	0.7	0.8	1.0	0.5	1.7	6.7	2.0	0.5	0.2	0.2	0.1	0.2	0.2	0.8	0.4	0.3
	9	1.1	1.2	0.8	1.4	0.7	1.2	7.7	4.0	0.4	0.3	0.2	0.2	0.3	0.1	1.0	0.8	0.4
	10	1.0	1.5	0.7	1.3	0.6	1.8	5.0	2.0	0.4	0.3	0.2	0.2	0.2	0.2	0.6	0.4	0.3
	11	1.0	1.4	0.9	0.9	0.9	1.7	4.5	2.7	0.4	0.3	0.2	0.1	0.3	0.2	0.6	0.6	0.3
	12	1.2	1.2	0.7	1.1	0.8	1.5	6.4	5.3	0.5	0.3	0.2	0.1	0.3	0.2	0.8	1.1	0.4
	13	1.7	1.7	1.0	2.3	1.4	1.9	4.8	6.0	0.7	0.4	0.2	0.3	0.5	0.2	0.6	1.3	0.5
	14	1.3	1.6	0.9	2.0	1.1	1.9	7.8	4.7	0.5	0.3	0.2	0.2	0.4	0.2	1.0	1.0	0.5
Canoe Basin	15	0.9	4.9	0.9	5.8	3.8	2.1	5.8	5.3	0.4	1.1	0.2	0.7	1.4	0.2	0.7	1.1	0.7
	16	1.0	4.4	1.0	5.3	3.7	1.7	6.8	28.7	0.4	0.9	0.2	0.7	1.4	0.2	0.9	6.1	1.3
	17	1.0	4.6	0.8	4.9	3.5	1.9	4.9	30.0	0.4	1.0	0.2	0.6	1.3	0.2	0.6	6.3	1.3
IFH	18	1.1	2.8	1.4	7.8	3.5	2.6	7.7	10.7	0.4	0.6	0.3	1.0	1.3	0.3	1.0	2.3	0.9
	19	1.5	2.6	1.3	6.5	3.3	2.3	10.6	14.7	0.6	0.6	0.3	0.8	1.2	0.3	1.3	3.1	1.0
OFH	20	1.0	2.3	1.1	5.0	2.6	1.8	7.3	17.3	0.4	0.5	0.2	0.6	1.0	0.2	0.9	3.7	0.9
	21	1.0	2.1	1.2	4.8	1.6	1.7	5.9	14.7	0.4	0.4	0.3	0.6	0.6	0.2	0.7	3.1	0.8
	ERL*	20.9	46.7	81	34	150	8.2	1.2	0.15	–	–	–	–	–	–	–	–	–
	ERM*	51.6	218	370	270	410	70	9.6	0.71	–	–	–	–	–	–	–	–	–

The ERL and ERM values for the measured metals are also presented

ERLQ < 1 indicates toxic effects will rarely occur; ERLQ > 1 but ERMQ < 1 indicates toxic effects will occur occasionally; ERMQ > 1 indicates toxic effects will occur frequent. Overall sediment toxicity is minimal if the mERMQ < 0.1, low if $0.1 \leq$ mERMQ < 0.5, moderate if $0.5 \leq$ mERMQ < 1.5 and high if mERMQ > 1.5 (Birch & Hutson 2009). ERLQ and ERMQ for Mn and Sn not derived since their ERL and ERM are not available

IFH inner fishing harbour, *OFH* outer fishing harbour; **ERL/ERM* effects-range low/effects-range median (Long et al. 1995)

concentrations of Mn, Ni, Cr, Cu, Zn, As and Sn differed significantly across the Tema Harbour. Cd, Hg, Pb, Cu, Zn, As and Sn were enriched in the Tema Harbour sediments and may have been derived mainly from anthropogenic sources. As the Tema Harbour is located in an industrial area, potential anthropogenic sources of metals in the harbour include industrial effluent discharges as well as vehicular emissions. Moreover, metal contamination in the Tema Harbour may originate from shipping and fishing activities such as the use of antifouling paints on ships and fishing vessels, oil spills, discharge of bilge, and scraping and painting of vessels. On the other hand, Mn, Ni and Cr were not enriched in the Team Harbour sediments and may, therefore, be of lithogenic origin. Al, Mn, Ni, Pb, Cr, Cu, As and Sn were present mainly in the residual phase, Cd and Hg associated mainly with the exchangeable phase,

while the reducible phase was most important for Zn. Based on the metal fractionation in the sediments, Cd and Hg may pose high potential risks of entering the food chain; Mn, Ni, Zn, As and Sn may pose low–medium potential risks of entering the food chain, while Pb, Cr and Cu pose low potential risks of entering the food chain. A screening-level ecotoxicological evaluation of the sediment metal concentrations with reference to biological effect-based sediment quality guidelines indicated that Hg may be associated with high toxicity and should, therefore, be of potential concern. Pb, Cu, Zn, As and Cd concentrations may also induce appreciable toxicity.

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