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ORIGINAL ARTICLE

Heavy metal concentrations in shallow marine sediments affected by submarine tailings disposal and artisanal gold mining, Buyat-Ratototok district, North Sulawesi, Indonesia

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Abstract Trace element concentrations in shallow marine sediments of the Buyat-Ratototok district of North Sulawesi, Indonesia, are affected by submarine disposal of industrial gold mine tailings and unregulated dumping of tailings and wastewater from small-scale gold mining using mercury amalgamation. Industrial mine tailings contained 590–690 ppm arsenic, 490–580 ppm antimony, and 0.8–5.8 ppm mercury. Tailings-affected sediment As and Sb concentrations were 20–30 times higher than in muddy sediments not contaminated with tailings, and 50–60 times higher than pre-mining average. Highest mercury concentrations were observed in sediments affected by small-scale mining using mercury amalgamation (5–29 ppm). Concentrations of most other trace elements were comparable in sediments affected by both types of mining and were slightly higher than regional averages for sediments collected before the onset of industrial mining. Elevated concentrations of both As and Sb in approximately equal proportions suggest tailings dispersal of at least 3.5 km. Mercury released from artisanal gold mining dispersed up to 4 km from river mouths. Slight increases in concentrations of non-mercury trace elements in areas affected by artisanal mining over pre-industrial mining concentrations were probably caused by increased rates of erosion.

Keywords Mine tailings · Coastal contamination · Heavy metals

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Introduction

Heavy metal contamination associated with gold mining is one of the principal environmental concerns in the Indonesian province of North Sulawesi. Gold mining activities in North Sulawesi include widespread unregulated artisanal mining using mercury amalgamation (James 1994; Limbong et al. 2003), and intensive industrial mining of refractory sediment-hosted gold deposits (Turner et al. 1994). Environmental concern about mercury contamination from small-scale mining is long-standing and widespread through many parts of the developing world (De Lacerda 2003). Mercury release from small-scale gold mining in North Sulawesi has been studied (Kambey et al. 2001; Limbong et al. 2003), but not the effects of small-scale mining on concentrations of other metals (cf. Appleton et al. 2001). Heavy metal contamination from industrial mine tailings and tailings spills has been studied extensively in both temperate terrestrial (e.g. various papers in Jambors et al. 2003) and tropical coastal environments (e.g. David 2002), but relatively few studies have focused on submarine tailings disposal (STD), the tailings management technique

used by the industrial mine in this case (Ellis et al. 1995; Jones and Ellis 1995; Johnson et al. 1998; Blanchette et al. 2001). A crucial question in STD is the mobility of tailings. If tailings remain in their intended repository, the environmental conditions to which they are subject can be predicted. In contrast, if tailings disperse into adjacent depositional environments, particularly those used by humans for fishing or other activities, then the risk of unintended effects increases (Ellis et al. 1995). Similarly, the areal extent of mercury contamination from small-scale mining is an important consideration in assessing its impact on coastal marine environments.

This study compares the concentrations and dispersal of trace elements in shallow marine sediments affected by industrial mining using STD and small-scale mining using mercury amalgamation in the Buyat-Ratototok district of North Sulawesi, Indonesia. The study characterizes metal composition of mine tailings, river sediments both affected and not affected by mercury amalgamation, and marine sediments influenced by these sources, and assesses lateral dispersal of trace elements associated with each type of mining.

Regional geology and mining history

North Sulawesi is composed of a Tertiary and Quaternary island arc and associated back-arc basins, including andesite volcanic and associated volcaniclastic, siliciclastic, and carbonate sedimentary rocks. The region contains significant gold mineralization in several mining districts. The Buyat-Ratototok mining district (Fig. 1) has experienced mining activity since the 1920s, with renewed activity beginning in the 1980s (Turner et al. 1994). Artisanal gold mining reached its peak in this district in the 1980s, but continues at a low level in both the Totok and Kotabunan watersheds (Aspinall 2001).

Industrial mine geology, ore processing and tailings disposal

The Newmont Minahasa Raya (PTNMR) gold mine exploited a refractory replacement style sediment hosted deposit with As-Sb-Hg-Tl anomalies typical of Carlin-type deposits (Turner et al. 1994). This deposit differs from most Carlin-type deposits in being found within a back-arc basin setting rather than a continental environment. Gold within the refractory deposit is found mostly within fine-grained (<10 μm) arsenian pyrite, typically in the form of pyrite crystals with arsenic-rich rims. Stibnite and cinnabar are also associated with the ore. The ore-bearing minerals occur in solution cavities within partially silicified vuggy fine-grained Miocene muddy limestones, surrounded and capped by coeval andesitic volcanic breccias that constitute most of the bedrock in the region. Because the principal ore body exploited by the industrial mine is >80% refractory gold, gold recovery requires oxidative treatment (Turner et al. 1994). In contrast, gold in the adjacent Kotabunan and Totok watersheds is present as native gold, and is mined by artisanal miners using mercury amalgamation (Turner et al. 1994; Aspinall 2001; Limbong et al. 2003).

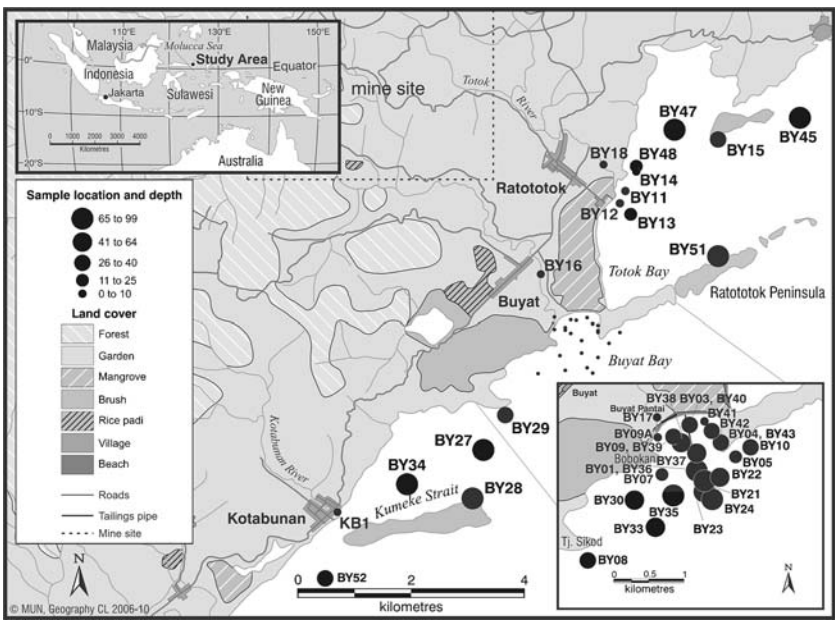

Fig. 1 Location and depth of sample sites. *Black line* through inset map indicates location of tailings pipe. Artisanal mining occurs in Totok and Kotabunan watersheds. Repeat sample pairs in approximately identical locations include BY01 (2002)–BY36 (2004), BY03 (2002)–BY40 (2004), BY04 (2002)–BY43 (2004), BY08 (2002)–BY29 (2004), BY09 (2002)–BY39 (2004), and BY14 (2002)–BY48 (2004)

Whole refractory ore, with an average grade of 6.90 g/t (Weeks et al. 1997), was roasted at 550–580°C. Ore was roasted in the presence of limestone and dolomite from host rock with the intent of capturing some arsenic as magnesium arsenate. After cyanidation at pH 9–9.2 to extract gold, tailings were treated with ferrous sulphate to produce two arsenic-bearing iron phases: ferric arsenate and arsenical ferrihydrite (Weeks and Wan 2000). Mercury in the ore was mostly volatilized during roasting, and was supposed to have been captured by scrubbers. The remaining mercury in solution was captured as mercuric sulphide. Mining operations closed in 2001, and milling operations ceased in late August 2004.

Following treatment, tailings were pumped ~5 km from the mine and processing site to Buyat Bay, deaerated, mixed with seawater, and deposited via pipe 900 m from shore at 82 m depth. While the mill operated, tailings were deposited at ~2,000 t/day. The mining company commenced a monitoring programme upon the opening of the mine in 1996, and modelled the tailings mound as covering an area of ~0.32 km^2, all at depths >70 m (PTNMR 2002a). Mining company-monitoring data showed high concentrations of arsenic, antimony, and mercury in mine tailings, but low-dissolved concentrations of these elements in seawater above the tailings mound. Tailings were interpreted to pose little environmental danger on the basis of the low-dissolved metal concentrations (PTNMR 2002b). Local villagers, however, reported mine tailings accumulation on corals in the bay, fish with tumours on reefs near the tailings outfall, fish kills, and a variety of health complaints consistent with arsenic or mercury poisoning (Glynn 2002).

Small-scale mining techniques

Small-scale or artisanal mining expanded dramatically around the world beginning in the 1970s, including widespread activity in North Sulawesi since the early 1980s (De Lacerda and Salomons 1998; Aspinall 2001; Limbong et al. 2003). Artisanal gold mining in Sulawesi mostly uses the tromol mill, a hand-operated ball mill made from a 45-gallon drum, in which crushed ore or gold-bearing sediment is mixed with elemental mercury (James 1994). Following several hours of milling, the material is removed from the tromol, the gold-mercury amalgam is separated from the remaining sediment, and mercury is removed by open-air roasting. Large fluxes of mercury are released to air and water, some of which is incorporated into fish consumed by humans (Kambey et al. 2001; Limbong et al. 2003). Estimates of mercury loss to the environment in North Sulawesi range from 15 t/year for the entire province (James 1994) to 110 t/year for the Talawaan, Tatelu, and Ratototok regions combined (Aspinall 2001). Within the last 10 years, some artisanal miners have attempted to capture some of the volatilized mercury using retorts, but mercury loss remains high.

In the region of this study, artisanal gold miners operated extensively in the Totok watershed (Fig. 1) until ~1989. Artisanal gold mining continues to a much lesser extent in both the Totok and Kotabunan watersheds. Activities include lode and placer mining in the Totok and Kotabunan watersheds, and backyard mills in Ratototok village. No small-scale mining has occurred in the Buyat River watershed (Turner et al. 1994).

Approximately 47 small-scale miners operated in the Totok watershed in 2000, mostly in lode deposits. These small-scale miners purchased 30–20 kg Hg/month, most of which was lost to the atmosphere on burning amalgam, to tailings, or to tailings wastewater (Aspinall 2001). Tailings are no longer dumped directly into the Totok River, but small-scale mining wastewater containing mercury is dumped into the river. Ongoing Hg flux from small-scale mining wastewater is estimated at 0.2 kg Hg/year (Aspinall 2001).

Materials and methods

Sampling areas

Buyat Bay is exposed to wave action from the Molucca Sea. The east side of Buyat Bay hosts fringing coral reefs, and reefs occur along both sides of the Ratototok Peninsula, and to the west of Buyat Bay. Maximum depth in the bay is ~90 m. The shelf remains relatively flat until reaching the shelf break at about 120 m depth, roughly 8 km from shore (PTNMR 1994). Both surface and bottom currents generally flow counter-clockwise around the bay (PTNMR 1994).

Totok Bay is protected from wave action by the Ratototok Peninsula, which is composed of Mio-Pliocene andesitic volcanic breccia. Bedrock along the north side of Totok Bay and the large island in the bay is Miocene limestone of the same formation that hosts the Mesel deposit. Bedrock on both sides of Kumeke Strait is Mio-Pliocene andesitic volcanic breccia (Effendi 1976). The maximum depth in Totok Bay is about 100 m. The shape of sand spits suggests that currents in Totok Bay generally flow in a counter-clockwise direction around the bay. Tides in the region are mixed semi-diurnal and microtidal, with an average tidal range of ~0.5 m. The climate is monsoonal, with a

rainy season November–April, and dry season May–October. General surface currents and sediment drift are from southwest to northeast (PTNMR 1994).

Sampling methods

Field sampling took place in June 2002 (17 samples) and August 2004 (25 samples), and was coupled with reef surveys and coral collections (Edinger et al. 2003, 2005). Three primary sources of sediment were characterized: (1) artisanal gold mining (the Totok River and Kotabunan River), (2) industrial gold mine tailings disposed in Buyat Bay, and (3) the Buyat River, which drains the mine site and has similar bedrock geology to the Totok River watershed (Effendi 1976). Many samples were collected close to coral reefs to provide information on reef sediments, and for comparison to trace element concentrations in coral skeletons (Edinger et al. 2003). Background sediment composition was determined from two sources: the site furthest to sea in Totok Bay (BY45), and the description of Buyat Bay marine sediments in the Environmental Impact Assessment for the industrial gold mine (PTNMR 1994).

Sediment samples were collected using a hand-operated stainless steel Petit-Ponar grab sampler deployed from a motorized outrigger canoe or fishing boat. The position of sampling stations was recorded using a hand-held GPS. Depth was determined by the length of grab sampler rope; depth measurements associated with grab samples are therefore maximum depth estimates. Visual descriptions of sediment colour, grain size, and bulk composition (carbonate versus siliciclastic) were recorded in the field, with subsequent measurement of mud fraction and carbonate content in the lab. All samples were frozen immediately upon return to shore and kept frozen until analysis.

Mud fraction and carbonate content

Weight percentage of sediment <63 μm in each sample was determined by dry sieving 3 g subsamples through 0.0625 mm polyurethane mesh, and weighing both the fraction that passed through the sieve and the fraction that did not.

Carbonate content was determined by dissolution of the acid-soluble fraction in 10% HCl. Two-gram subsamples of each sediment sample were dried, weighed, and then dissolved in an excess of acid for 48 h. The resulting solution was filtered through pre-weighed acid-washed 0.45 μm glass microfibre filters, which were dried and re-weighed. Because 10% HCl dissolution of the sediment samples often appeared to dissolve other constituents of the sediments, $CaCO_3$ content was also estimated directly from ICPMS results, according to the relationship:

$$\%\ CaCO_3 = \text{ppm Ca} \times 10^{-4} \times (1/0.40), \quad (1)$$

where 0.40 is the weight per cent Ca in $CaCO_3$.

Trace element concentrations

Whole-sediment concentrations of all trace elements except mercury were determined using total dissolution in HF-HNO_3, measured by inductively coupled plasma mass spectrometry (ICP-MS), and referenced to the PACS-1, MESS-1, and MESS-2 standards. Sediment subsamples were homogenized, dried, ground to <10 μm, and homogenized again for analysis. Approximately 0.2 g dry subsamples were dissolved in 2 ml of concentrated hydrofluoric acid and 8 N nitric acid in 1:1 proportions. Solutions were heated on hot-plates for 72 h, then evaporated to incipient dryness, and diluted to 60 ml with nano-pure distilled water. Whole sediment analysis rather than analysis of the <63 μm fraction allowed direct comparison with Canadian marine sediment quality standards (CCME 2001), which are based on whole-sediment concentrations. Pre-mining sediment chemistry is reported as the average of 31 marine sediment samples from Buyat Bay and environs, as reported in the mining company's original environmental impact assessment (PTNMR 1994).

Mercury concentrations were determined by cold-vapour atomic absorption spectroscopy (cv-AAS) at an external certified laboratory. About 0.5 g subsamples were digested with aqua regia at 90°C. The Hg in the resulting solution was oxidized to the stable divalent form, and then reduced to the volatile free atomic state using stannous chloride. Argon gas was bubbled through the mixture of sample and reductant solutions to liberate and to transport the Hg atoms into an absorption cell, and the cell was analysed at 253.7 nm on a Perkin Elmer FIMS 100 cold vapour Hg analyser.

Analytical accuracy and precision

Duplicate analyses of identical samples for whole sediment metal concentrations ($n = 9$ pairs) yielded results differing by <2–27% of signal, depending on the element in question, with variation among pairs mostly below 10% (Table 1). Analysis of PACS-1 and MESS-2 standards generally yielded values within 10% of the published valued for one of both standards for all elements except Ag (MESS-2 standard, range 90–120%).

Table 1 Percent variation between duplicate samples, and deviation from published standards, in whole sediment dissolution analyses

Year	Standard	Measure	Ca	Ti	V	Cr	^{57}Fe	Mn	Co	Ni	Cu	Zn	As	Ag	Cd	Sn	Sb	Pb
2002		Variation among duplicates (n = 5) (%)	10.70	8.89	10.45	10.05	13.11	10.39	16.14	15.55	12.91	27.30	15.71	20.55	28.49	16.18	9.44	13.30
	MESS-2	Deviation from published value (%)			6.99	4.38	20.69	20.85	6.47	10.44	8.67	5.90	6.95	119.81	34.80	15.96	11.70	1.87
	PACS-1	Deviation from published value (%)	7.01	10.50	4.54	0.51	24.73	8.31	1.08	11.65	7.48	1.63	14.92		5.35	3.97	4.75	1.66
2004		Variation among duplicates (n = 4) (%)	4.28	1.71	3.34	2.31	2.70	3.00	3.27	5.08	1.55	21.27	2.04	7.04	17.87	2.58	1.85	31.82
	MESS-2	Deviation from published value (%)			16.44		16.52	11.47	10.89	1.50	21.08	9.35	9.56	90.87	23.01	32.38	22.54	3.07
	PACS-1	Deviation from published value (%)	0.63	10.68	10.05		17.56	10.32	8.77	3.85	14.41	0.65	16.66		7.21	5.15	6.51	12.79

Data analysis

Because the sample suite included carbonate-dominated, siliciclastic dominated, and mixed carbonate-siliciclastic sediments, metal concentrations were normalized for carbonate content assuming that the carbonate fraction of the sediment contained negligible heavy metals, particularly As, Sb, and Hg, the principle elements of concern identified by previous studies in the region. Trace element concentrations were normalized to carbonate content by multiplying concentrations by the inverse of carbonate content, according to:

$$(\text{Metal})_{\text{CaCO}_3-\text{normalized}} = \{(\text{Metal})_{\text{total}} \times [1/(1 - \%\text{CaCO}_3)]\}. \quad (2)$$

Dispersal distances and relationship between distance from source and metal concentration were assessed using linear and exponential regression. Distance between each sample location and the relevant point source (tailings outfall or river mouth) was measured using the ruler function in MapInfo®. Both linear and exponential regressions were calculated; the regression that explained the greatest amount of variance in metal concentration was reported. Correlations among metals were calculated using bivariate linear correlation of ln-transformed whole sediment trace element concentrations, then repeated for ln-transformed $CaCO_3$-normalized trace element concentrations.

Results

Mud fraction, Carbonate content and mineralogy

Most samples were >70% siliciclastic, except reef samples BY05, BY07, BY08, BY10, BY15, BY29, and BY51 (Fig. 2). Most of the siliciclastic samples were dominantly mud, except for shallow nearshore samples BY07, BY09, BY11, BY39, BY41, and BY52, collected near the mouths of the Buyat, Totok, and Kotabunan rivers, and samples BY16, 17, and 18, collected in the Buyat and Totok rivers.

The samples collected near the end of the tailings pipe (BY01, BY21, BY23, BY24, BY35–38) were fine silts; sample BY01 had a median grain size of 15 μm (Blackwood 2006). Carbonate content was ~10–15% in fluvial and river-mouth sandy sediments, 14–26% in other marine sediments, including the tailings, and 15–70% in reef sediments (Fig. 2). Carbonates in reef sediments were poorly sorted, angular, very coarse-grained bioclasts from corals, calcareous algae, and molluscs,

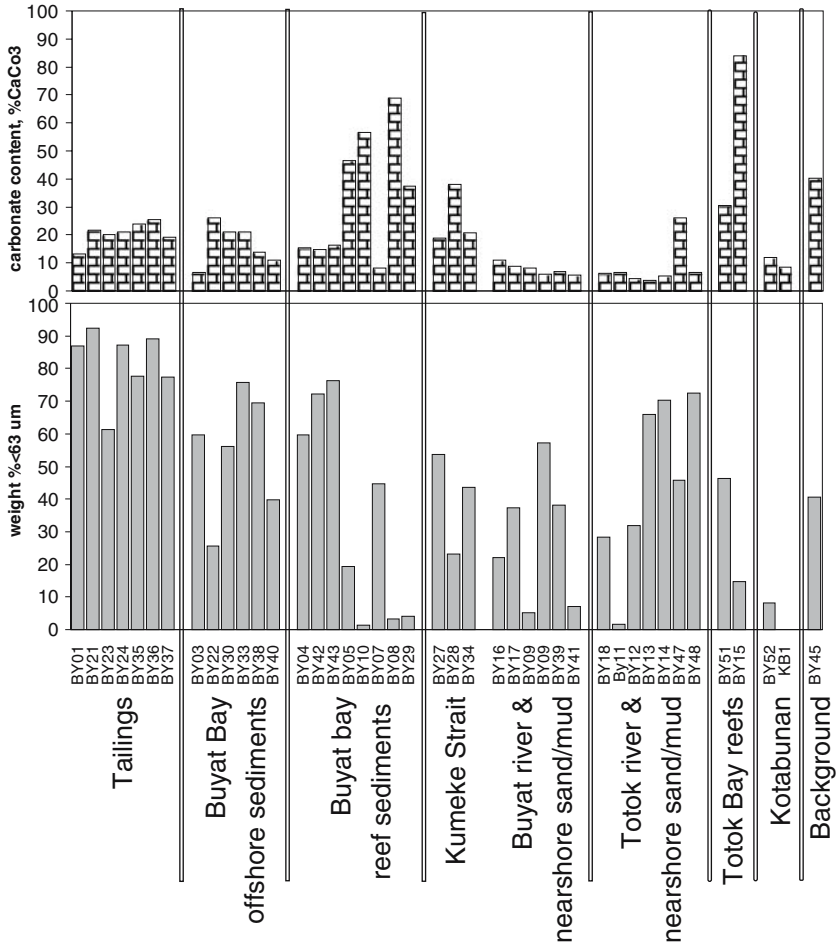

Fig. 2 Mud fraction and carbonate content of sediment samples. Mud fraction (% <63 μm): *grey bars*; carbonate content: *brickwork*

while carbonates in fluvial and non-reefal sediments were subangular crystalline detrital carbonates.

Mud content (%<63 μm) was negatively correlated with carbonate content (r = –0.33, p = 0.012, n = 41). Most trace elements were not significantly correlated with mud content, except for arsenic, antimony, chromium, and manganese (As: r = 0.71, Sb: r = 0.57, Cr: r = 0.53, Mn: r = 0.48). When only Totok Bay sediments, uninfluenced by fine grained arsenic-antimony rich tailings, were considered; however, there were no significant positive or negative correlations between mud content and metal concentrations (correlation coefficient range –0.22–0.75, n = 10, As: r = 0.22; Sb: r = 0.26). Arsenic and antimony concentrations in Totok Bay muddy sediments (BY13, 14, and 48) were nearly identical with those in adjacent sands (BY11–12).

Composition of tailings-derived sediments on the sea floor

Tailings were red–brown fine silt composed of moderately poorly sorted, angular, and very fine-grained plagioclase feldspar (~29%), quartz (~26%), and detrital carbonate (16%), with lesser amounts of pyroxene, amphibole, and opaque phases (e.g. oxides and sulphides; Blackwood 2006). Arsenic was found mostly as fine-grained colloids of arsenic and iron, without sulphur, and grains of pyrite with arsenic-rich rims. Antimony occurred primarily as silt-sized grains of antimony oxide (Blackwood 2006).

Rare grains of iron-arsenic or iron-antimony phases, arsenical pyrite, and antimony oxide, as observed in tailings sample BY01, were observed in Buyat Bay offshore sediment and reef samples BY03, BY04, and BY05, but not in any of the fluvial or nearshore marine samples from either Buyat Bay or Totok Bay (Blackwood 2006).

Trace element concentrations and spatial distributions

Highest arsenic concentrations were observed in the samples collected closest to the end of the tailings pipe, especially samples BY36 and BY01 (Fig. 3a). Arsenic concentrations in tailings samples ranged from 409 to 695 ppm; in other Buyat Bay muddy sediments, from

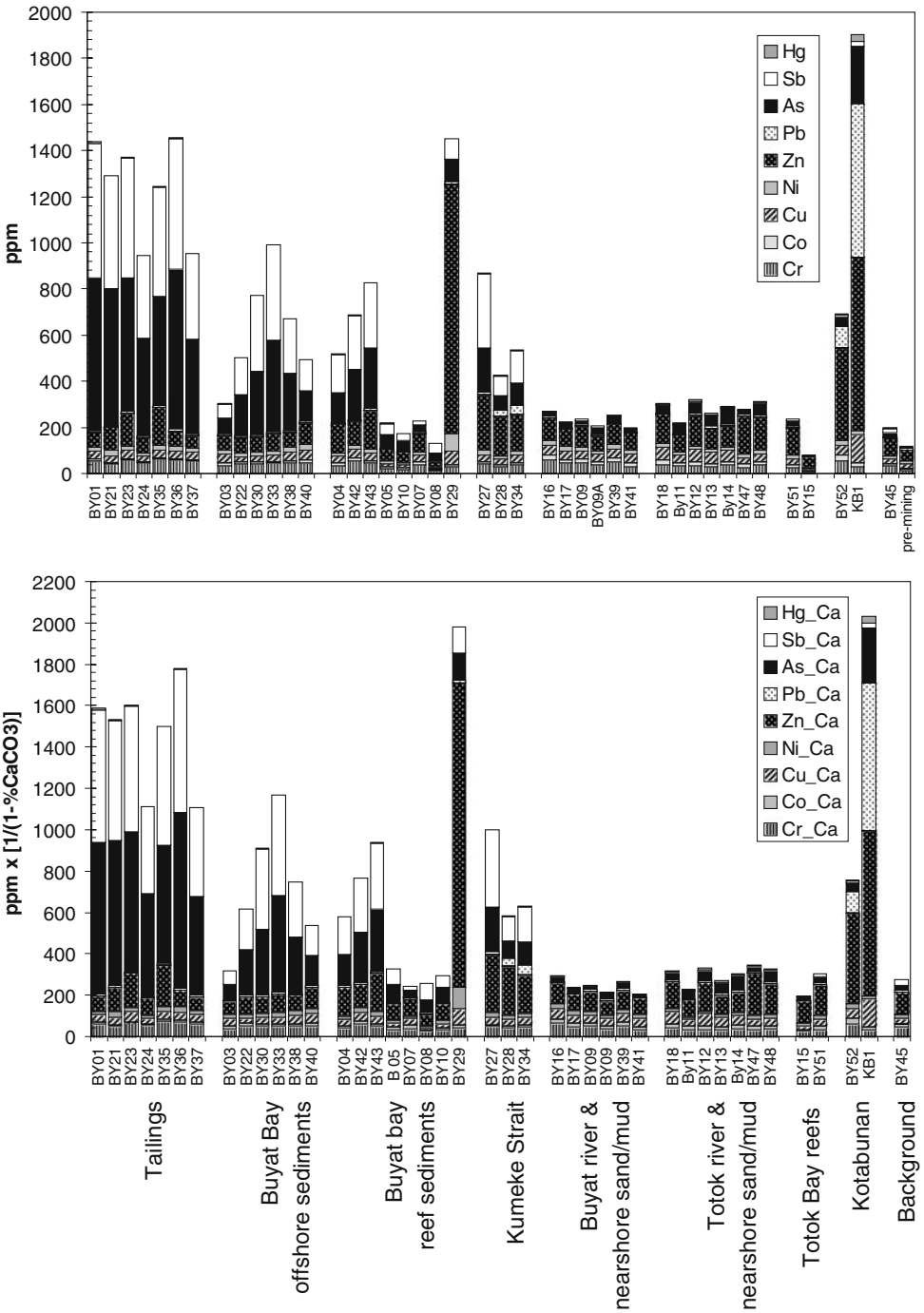

Fig. 3 Concentrations of Cr, Co, Ni, Cu, Zn, Pb, As, Sb, and Hg, in all samples, as measured by ICP-MS, grouped by sampling region and depth. Pre-mining data are average of 31 marine sediment samples from Buyat Bay and vicinity, as reported in PTNMR environmental impact assessment. Sb was below detection limits in pre-mining samples. **a** Concentrations. **b** Concentrations normalized to $CaCO_3$ content. $CaCO_3$ content calculated from %CaO in ICPMS results

69 to 397 ppm; and in Buyat Bay reef sediments, from 30 to 262 ppm. Arsenic concentrations in Buyat Bay and Kumeke Strait sediments decreased linearly with distance from the end of the pipe ($r^2 = 0.24$, $p < 0.009$, $n = 24$, Fig. 4a). Arsenic concentrations were lowest in sandy and muddy fluvial and nearshore siliciclastic sediments of Totok Bay and Buyat Bay (range 20–64 ppm), including both sands and muds, and Totok Bay reef samples. Analysis of trace element concentrations normalized to carbonate content reduced variation among samples within carbonate-rich groups (e.g. Buyat Bay reef sediments, Totok Bay reef reference samples BY15 and BY51), but did not change overall patterns (Fig. 3b).

Highest antimony concentrations were observed in the samples collected near the end of the tailings pipe, especially samples BY01 and BY36. Antimony concentrations in Buyat Bay and Kumeke Strait sediments

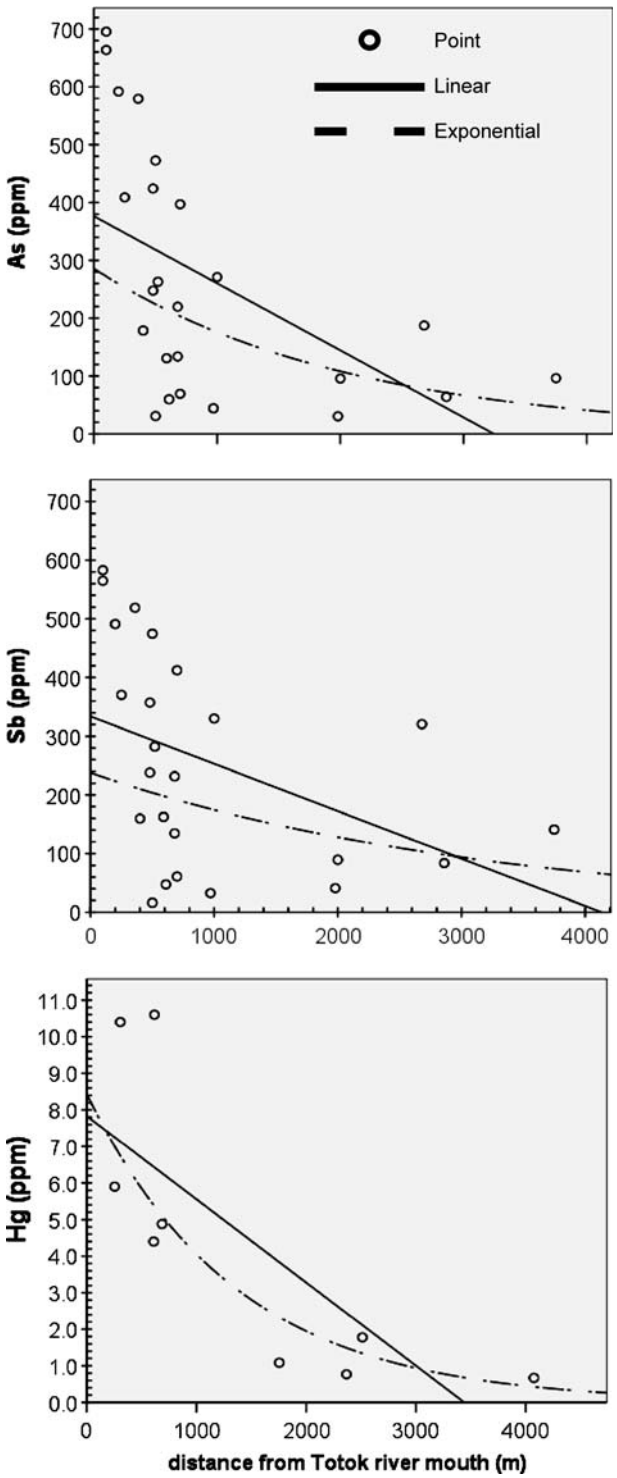

Fig. 4 Relationship between distance from source and trace element concentration. **a** Arsenic in Buyat Bay and Kumeke Strait. **b** Antimony in Buyat Bay and Kumeke Strait; *X*-axis represents distance from tailings outfall. **c** Mercury in Totok Bay; *X*-axis represents distance from Totok River mouth

decreased linearly with distance from the end of the pipe ($r^2 = 0.14$, $p < 0.05$, $n = 24$, Fig. 4b). Antimony concentrations were lowest in fluvial and nearshore marine sands and muds of Buyat Bay and Totok Bay. Arsenic and antimony concentrations were strongly correlated with each other ($r = 0.96$, $p < 0.0001$, $n = 42$) and were approximately equal to each other in tailings samples, offshore Buyat Bay samples, Buyat Bay reef samples, and some Kumeke Strait samples. In contrast, arsenic concentrations were generally 5–10 times greater than antimony concentrations in fluvial sediments from the Buyat, Totok, and Kotabunan rivers and nearshore sands and muds from those bays (Fig. 3).

Chromium, cobalt, nickel, copper, and zinc concentrations were generally consistent in all samples, with the exception of high zinc concentrations in samples from Kotabunan [KB1, BY52 and samples from Kumeke Strait (BY27, 28, 29, and 34)]. Lead concentrations were generally low and consistent in all samples except the Kotabunan samples and Kumeke Strait.

Highest mercury concentrations were observed in Totok Bay muddy samples and the Kotabunan River sample (Fig. 5). Secondary Hg peaks were observed associated with 2002 tailings pipe sample (BY01) and 2002 nearby reef (BY04), and in 2004 samples from Kumeke Strait (BY27 and BY34) and Kotabunan Bay (BY52). Mercury concentrations in the tailings samples from 2004 were all lower than those from 2002. Mercury concentrations in Totok Bay 2002 sample BY14, re-sampled in 2004 (BY48), remained unchanged. Mercury concentrations declined linearly and exponentially with distance from the Totok River mouth (exponential $r^2 = 0.78$, $p = 0.002$, $n = 8$, Fig. 4c). There were no significant relationships between mercury concentrations and distance from the tailings outfall in either 2002 ($r^2 = 0.27$, $p = 0.23$, $n = 6$) or 2004 data ($r^2 = 0.13$, $p = 0.224$, $n = 12$).

Correlation analysis

Correlations of metal concentrations in all samples distinguished two distinct groups of metals. (1) Arsenic and antimony were very strongly correlated to one another ($r = 0.96$), and were positively correlated with manganese and chromium ($r = 0.60$–0.66), and negatively correlated with cobalt ($r = -0.59$–0.65). (2) Iron, titanium, vanadium, and cobalt were all highly correlated to each other, $r > 0.95$ (Table 2a). Mercury was not strongly correlated to any of the metals in either of these groups, but was weakly correlated with lead, copper, and arsenic. Correlation patterns of trace element concentrations normalized to carbonate content were nearly identical with those for non-normalized data (Table 2b).

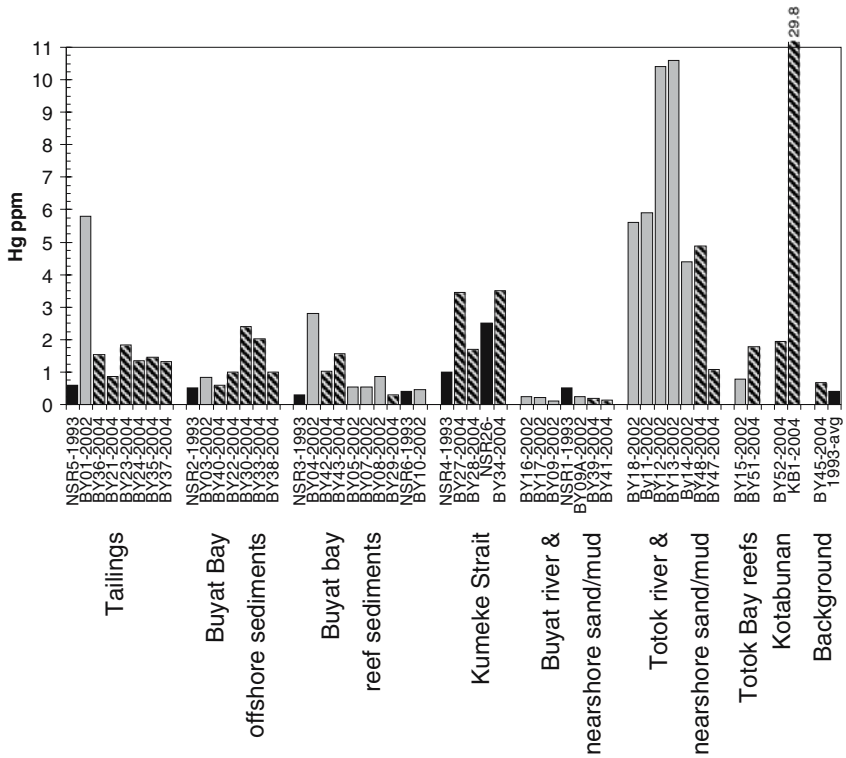

Fig. 5 Concentrations of Hg in all samples, as measured by cv-AAS, grouped by sampling region and depth. Date of collection indicated after each sample number. *Black* Pre-mining data, sample numbers NSR(n)-1993, from PTNMR (1994); *Grey* 2002 samples; *cross-hatched* 2004 samples

Table 2a Correlation matrix among ln-transformed elemental concentrations

	%<63 μm	$\%CaCO_3$	Mn	Cr	Co	Ni	Cu	Zn	As	Sb	Hg	Pb	Fe	Ti	V
%<63 μm	1														
$\%CaCO_3$	–0.33*	1													
Mn	0.48**	–0.68**	1												
Cr	0.53**	–0.70**	0.87**	1											
Co	–0.29*	–0.65**	0.23	0.24	1										
Ni	0.17	–0.37*	0.55**	0.58**	0.30	1									
Cu	0.28	–0.83**	0.65**	0.59**	0.60**	0.59**	1								
Zn	–0.08	–0.26	0.29	0.20	0.33*	0.61**	0.63**	1							
As	0.71**	–0.17	0.63**	0.57**	–0.42**	0.33*	0.23	0.13	1						
Sb	0.57**	0.08	0.41**	0.44**	–0.45**	0.29	–0.06	0.03	0.91**	1					
Hg	0.36	–0.19	0.17	0.01	–0.01	–0.19	0.31*	0.29	0.36*	0.14	1				
Pb	–0.05	–0.31*	0.36*	0.19	0.33*	0.24	0.59**	0.72**	0.22	0.05	0.55**	1			
Fe	–0.23	–0.71**	0.36*	0.35*	0.98**	0.36*	0.67**	0.43**	–0.29	–0.44**	0.05	0.45**	1		
Ti	–0.24	–0.71**	0.32*	0.33*	0.98**	0.31*	0.66**	0.38*	–0.34*	–0.50**	0.04	0.42**	0.98**	1	
V	–0.28	–0.69**	0.33*	0.31*	0.98**	0.31*	0.66**	0.39*	–0.34*	–0.51**	0.05	0.44**	0.98**	0.99**	1

$n = 42$ in all cases, except $n = 41$ for %<63 μm

*$p < 0.05$

**$p < 0.01$

Discussion

Trace element concentrations, correlations and sources

Concentrations of arsenic, antimony, and mercury in the mine tailings samples were consistent with previous reports (Shepherd-Miller 2001; PTNMR 2002b; Apte et al. 2004; Indonesian Ministry of Environment 2004). Pre-mining arsenic concentrations in deep portions of Buyat Bay, including the end of the tailings pipe, ranged from 10 to 25 ppm (PTNMR 1994), consistent with the concentrations reported here for background sample in Totok Bay (sample BY45), although the average arsenic concentration of 31 pre-mining samples was lower than observed in sample BY45. Anti-

Table 2b Correlation matrix among elemental concentrations normalized to %$CaCO_3$, ln-transformed

	%<63 μm	Mn	Cr	Co	Ni	Cu	Zn	As	Sb	Hg	Pb	Fe	Ti	V
%<63 μm	1													
Mn	0.29	1												
Cr	0.33*	0.71**	1											
Co	–0.63**	–0.44**	–0.45**	1										
Ni	–0.12	0.34*	0.43**	–0.01	1									
Cu	0.08	0.12	–0.109	0.22	0.26	1								
Zn	–0.27	0.11	–0.01	0.19	0.58**	0.59**	1							
As	0.64**	0.65**	0.56**	—0.78**	0.22	0.01	0.05	1						
Sb	0.51**	0.53**	0.59**	–0.75**	0.31*	—0.21	0.03	0.92**	1					
Hg	0.26	0.08	–0.16	–0.15	–0.25	0.25	0.27	0.33*	0.14	1				
Pb	–0.15	0.17	–0.11	0.16	–0.10	0.53**	0.69**	0.14	0.03	0.53**	1			
Fe	–0.69**	–0.33*	–0.37*	0.96**	0.07	0.23	0.33*	–0.71**	–0.67**	–0.10	0.32*	1		
Ti	–0.57**	–0.38*	–0.42**	0.96**	–0.08	0.32*	0.20	–0.73**	–0.75**	–0.13	0.26	0.94**	1	
V	–0.62**	–0.32*	–0.39**	0.95**	–0.06	0.32*	0.23	–0.71**	–0.74**	–0.10	0.30	0.95**	0.99**	1

$n = 42$ in all cases, except $n = 41$ for %<63 μm

*$p < 0.05$

**$p < 0.01$

mony was below detection limits in the pre-mining samples (PTNMR 1994). Arsenic concentrations in tailings were ~90 times higher than the Canadian interim marine sediment quality standard for arsenic (7.24 ppm) and ~12 times higher than the probable effect level (PEL, 41.6 ppm), the threshold above which > 40% impact on test organisms was observed (CCME 2001). Mercury in marine sediments affected by artisanal gold mining was 20–85 times higher than the Canadian marine sediment quality standard for mercury (0.13 ppm, PEL = 0.70 ppm).

Metal correlations suggest three principle sources of heavy metals. (1) The high correlation between arsenic and antimony suggests tailings. (2) Titanium, vanadium, iron, and cobalt were all highly correlated and dominated fluvial and nearshore marine sediments, including both sands and muds, from Buyat Bay and Totok Bay. (3) Mercury was not strongly correlated with any other trace element, indicating its primary source as release from small-scale mining operations. Mercury was weakly correlated with arsenic, probably because of the secondary peak in mercury associated with the industrial mine tailings; Lead and zinc were highly correlated; although concentrations of these elements were generally low, concentrations were highest in samples from Kotabunan River, Kotabunan bay, and Kumeke Strait, with secondary peaks in the Totok River and Bay. Lead and zinc in these areas may derive from epithermal Pb-Zn-Ag-Au deposits mined in the Kotabunan area, similar to those mined in Mindanao, southern Philippines (cf. Giles and Nelson 1982; White 2002).

Distribution of tailings-derived sediment and heavy metals

Industrial mine tailings contained nearly equal concentrations of arsenic and antimony, but arsenic concentrations in fluvially influenced sediments were 5–10 higher than antimony concentrations. The relative abundance of arsenic and antimony, therefore, was useful in mapping tailings dispersal. Elevated arsenic and antimony concentrations in approximately equal proportions suggest that tailings-derived material dominated by arsenic and antimony reached sampling locations up to 3.5 km southwest, and at least 1 km northeast, of the end of the tailings pipe (Fig. 6). Reef sediments with apparent tailings contamination were collected in water depths ranging from 20 to 38 m, indicating that tailings-derived material had shoaled considerably from the depth of the tailings pile itself at 82 m. Sediments with high As and Sb concentrations, and with texture and colour identical to that of the tailings, were found throughout Buyat Bay in waters as shallow as 40 m, and as little as 100 m from the beach at Buyat Pantai, indicating significant shoreward dispersal of tailings. Lateral tailings dispersal ranges are consistent with dispersal patterns following mine tailings spills (e.g. David 2002) or other STD operations (Jones and Ellis 1995; Ellis 2000). Tailings are probably transported from the tailings mound by tidal currents, or by tidally induced internal waves on the seasonally variable thermocline at 50–100 m (PTNMR 1994; Shepherd-Miller 2001). Experimental studies of nickel mine tailings suggest that waves as small as 0.13 m

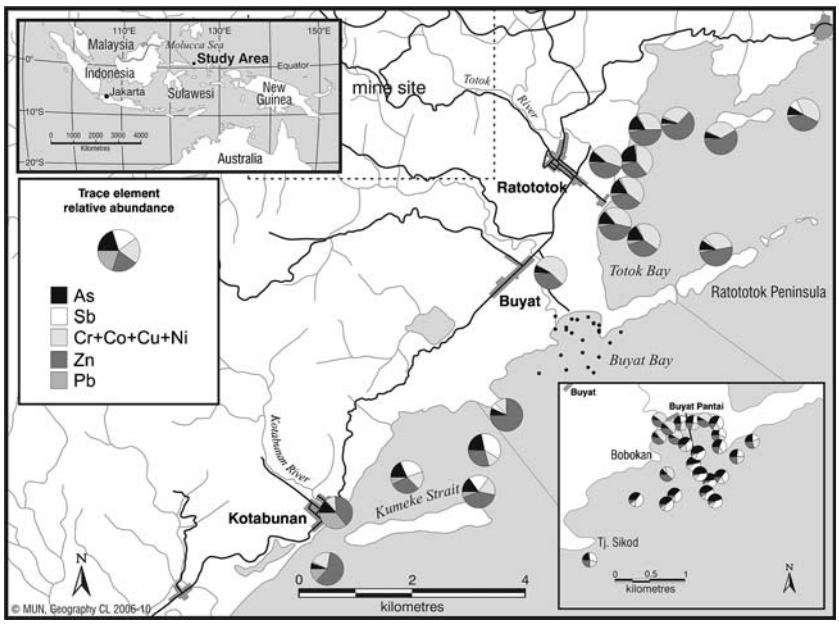

Fig. 6 Map showing relative abundance of trace elements in all samples. Tailings influence indicated by high-relative abundance of As and Sb in ~1:1 ratio. *Black line* through inset map indicates location of tailings pipe

significant wave height applying critical shear stress of 0.20 N/m^2 can mobilize fine grained mine tailings (Davé et al. 2003).

Arsenic concentrations in Kumeke Strait sample BY34 were ~3.2 times higher than arsenic concentrations in the <63 μm fraction of the pre-mining sample taken in approximately the same location (PTNMR 1994), and had an ~1:1 ratio of arsenic : antimony, suggesting tailings influence. In contrast, mercury concentrations in sample BY34 were only slightly elevated from the pre-mining Hg concentration reported by the mining company (Fig. 5). Mercury in Kumeke Strait samples is probably derived from artisanal gold mining in the Kotabunan watershed.

The relatively high Pb and Zn concentrations that Kumeke Strait samples BY28, BY29, and BY34 share with the Kotabunan river (KB1) and bay (BY52) samples suggest influence from the Kotabunan region, as would be expected from regional current and sediment drift patterns. Mercury, arsenic, and silver concentrations in Kotabunan river sample were very high, and may reflect dumping of artisanal gold mine tailings into the Kotabunan River. No antimony anomaly was detected in the Kotabunan River or Bay samples.

Tailings contamination within shallow water sediments was detected primarily within Buyat Bay. Siliciclastic sediments on northeast Buyat Bay reefs, observed in thin section between carbonate bioclasts in thin section, were similar in colour and texture to the tailings, and iron-arsenic phases, arsenian pyrite, and iron-antimony oxides similar to those described in the tailings were observed on sediments from Buyat Bay reefs BY04 and BY05 (Blackwood 2006). SCUBA observations of the reefs adjacent to stations BY42 and BY04-BY43 found red–brown silt resembling the mine tailings coating dead corals in water as shallow as 3 m on these reefs. Siliciclastic sediments on these reefs also contained andesite lithoclasts, probably derived from the nearby bedrock. Some portion of the arsenic observed in Buyat Bay reef sediments may have been derived from detrital arsenopyrite, as observed in Totok Bay, but detrital arsenopyrite cannot not account for the 1:1 ratio of arsenic : antimony observed in sediments from BY04, BY05, BY08, and BY10. In contrast, sediments from reef BY07, on the west side of Buyat Bay, were much more similar in mineralogical and chemical composition to the sandy muds from the Buyat River mouth (e.g. BY09A), even though Reef BY07 is quite close to the end of the tailings pipe. Tailings dispersal into shallow water on coral reefs brings tailings into the principal fishing grounds for inshore fisheries based in Buyat Pantai.

The mining company tailings modelling study predicted that tailings would be confined to the small canyon in which the tailings pipe sits, and would eventually flow down slope from the end-of-pipe depth of 82 m to the 4–5 km wide shelf at 100–120 m (PTNMR 2002a). These predictions assumed that a seasonally stable thermocline at 50–100 m would prevent tailings advection into shallow water (PTNMR 1994). The slope of the canyon at the end of the tailings pipe site is ~2°, but the recommended minimum slope for STD outfalls is 12° (IIED 2002). This slope is recommended to ensure that tailings are transported down slope as density currents. While lateral and shoreward transport of tailings has been documented

here, the proportion of the tailings that have dispersed upwards into shallow water is unknown.

Mercury sources and dispersal

Mercury from artisanal gold mining was apparently more widespread, had higher concentrations, and less temporally variable than mercury from the STD. The Kotabunan River sample, which contained 29.8 ppm Hg, also had high concentrations of As, Zn, and Pb, but not Sb. This sample was likely influenced by tailings from artisanal gold mining, rather than wash water, as has been described for the Totok River (Aspinall 2001). High mercury concentrations in the Kumeke Strait samples suggest transport of Hg from the Kotabunan River to the Kumeke Strait, and the western parts of Buyat Bay, close to Tj. Sikod. Mercury concentrations reported from Kumeke Strait in 2004 were unchanged from those documented in the early 1990s (PTNMR 1994). Mercury concentrations in Totok Bay background sample BY45 were higher than those in average pre-mining samples from the region, but were on par with individual pre-mining samples from Buyat Bay. The apparent increase in mercury concentrations reflected in sample BY45 may reflect a small degree of contamination from artisanal gold mining, suggesting possible mercury dispersal of up to 4 km from the river mouth (Fig. 4c).

Mercury concentrations from Buyat Bay tailings—influenced samples collected in 2004 were considerably lower than those in tailings and tailings-contaminated samples from Buyat Bay collected in 2002 (BY01 versus BY21 and BY36, BY03 versus BY40, or BY04 versus BY43, respectively). This change probably reflects a change in the ore grade being fed through the mill. The mine reached peak production in 2000, and the principle refractory deposit was mostly mined out by the end of 2001. Ore feed in the last 2 years of mill operation may have included lower grade material from elsewhere in the mine site. An additional source of mercury was airborne emissions from the mill. Although the mill was equipped with mercury scrubbers, it operated without scrubbers for much of its lifetime. The fate of mercury released to the atmosphere has not been studied.

Management implications

The Newmont Minahasa Raya mine was among the shallowest of a new generation of mines using deep submarine tailings disposal (DSTP), with the tailings outfall in shallower water and on less of a slope than the recommended minimum depth and slope for DSTP. This study documented shoreward movement and shoaling of industrial gold mine tailings, including movement onto fringing coral reefs that constituted the primary fishing grounds in the region. Tailings dispersal documented here emphasizes the danger of tailings dispersal in STD operations and reinforces the need to follow minimum depth and slope recommendations in DSTP operations (IIED 2002).

Artisanal mining using mercury amalgamation represents a serious environmental threat in this region. Trace element concentrations reported in our Totok Bay samples were slightly elevated above average pre-mining samples in Buyat Bay and could indicate release of other metals associated with small-scale mining. Such increases likely result from increased rates of physical erosion caused by the direct activities of small-scale miners (Appleton et al. 2001). The degree of apparent increase in trace element concentrations in Totok Bay above regional pre-industrial mining levels is consistent with that found in placer mining regions of Ethiopia (Getaneh and Alemayehu 2006), but is considerably lower than that described from Ecuador (Appleton et al. 2001). Mercury loading probably results more from dumping of small-scale mining waste rock into rivers (e.g. Kotabunan River and prior activities in the Totok River) than from small-scale mining wash-water (e.g. current activities in the Totok River, Aspinall 2001).

Use of mercury amalgamation in small-scale mining should be discouraged or eliminated. The government of North Sulawesi is exploring possibilities of establishing cyanidation facilities in areas of intense small-scale mining to reduce the loss of mercury to the environment. Promoting the use of cyanide in an industry that defies licensing and regulation seems risky, even more so in a country where use of cyanide in ornamental fishing and the live food fish trade is an on-going problem (Edinger and Browne 2000). Nonetheless, the risks to the environment and to human health from small-scale mining using mercury amalgamation are high, pervasive, and well-understood, and require attention.

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