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ORIGINAL ARTICLE

Mineralogy and trace element relative solubility patterns of shallow marine sediments affected by submarine tailings disposal and artisanal gold mining, Buyat-Ratototok district, North Sulawesi, Indonesia

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Abstract Shallow marine sediments of the Buyat-Ratototok district of North Sulawesi, Indonesia, are affected by submarine disposal of industrial gold mine tailings and small-scale gold mining using mercury amalgamation. Industrial mine tailings contained 590–660 ppm arsenic, 490–580 ppm antimony, and 0.8–5.8 ppm mercury. Electron microprobe survey found both colloidal iron–arsenic-phases without sulphur and arsenian pyrite in tailings and sites to which tailings had dispersed, but only arsenopyrite in sediments affected by artisanal mining. Antimony in tailings was present as antimony oxides, colloidal iron–antimony phases, colloidal iron–antimony phases, and stibnite in sediments affected by both types of mining. A sequential extraction found that 2% of arsenic held in tailings and tailings-contaminated sediments was exchangeable, 20–30% was labile, including weakly adsorbed, carbonate- and arsenate bound, 20–30% was metastable, probably incorporated into iron or manganese oxyhydroxides, or strongly adsorbed to silicate minerals, and 40–48% was relatively insoluble, probably incorporated into sulphides or silicates. Arsenic in sediments affected by artisanal gold mining was 75–95% relatively insoluble. Antimony in all sediments was >90% relatively insoluble. Relative solubility patterns of most other metals did not differ between industrial tailings-affected, artisanal-mining affected areas, and fluvial sediments. Results suggest that submarine tailings disposal is not suitable for refractory Carlin-like gold deposits because ore processing converts arsenic to forms unstable in anoxic marine sediments.

Keywords Submarine mine tailings · Artisanal mining · Arsenic · Sequential extraction · Indonesia

Introduction

Trace element 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). Relatively few studies have focused on submarine tailings disposal (STD), the tailings management technique used by the industrial mine in this case (e.g. Ellis et al. 1995; Jones and Ellis 1995; Johnson et al. 1998; Blanchette et al. 2001). A critical question for STD is the geochemical stability of mine tailings in the receiving environment (Ellis et al. 1995). The reactivity of mine tailings in marine environments is controlled by tailings mineralogy, which results from ore deposit geology, ore processing techniques utilized, and a variety of oceanographic condi-

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tions, especially the pH and redox conditions of sediments (Rochette et al. 1998; Blanchette et al. 2001; Salzsauler et al. 2005; Walker et al. 2005).

This study compares the mineralogy and relative solubility of metal(oids) in marine sediments affected by industrial gold mine tailings deposited using a submarine disposal system, and sediments affected by artisanal mining. The study characterizes mineral composition of mine tailings, river sediments (both affected and not affected by small-scale mining), and marine sediments receiving metal(oid)s from both of these sources. Finally, trace element relative solubility patterns associated with both types of mining are examined using a sequential extraction. Dispersal of industrial mine tailings and mercury from artisanal mining is described in a companion paper (Edinger et al. 2006). Related research on mercury methylation and bioaccumulation (Lasut et al., in preparation), and the record of metal contamination in coral skeletons (Edinger et al. 2003, in preparation), will be published separately.

Regional geology and mining history

North Sulawesi is composed of a Tertiary and Quaternary island arc and associated back-arc basins, including andesite volcanic rocks and associated volcaniclastic, siliciclastic, and carbonate sedimentary rocks. North Sulawesi contains significant gold mineralization in several mining districts. The Buyat-Ratototok district (Fig. 1) has experienced gold mining activity since the 1920s, with extensive renewed activity beginning in the early to mid-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 that it occurs 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, mostly 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. The principal ore body exploited by the industrial mine, the Mesel deposit, is >80% refractory gold, such that recovery can only be achieved by oxidative treatment (Turner et al. 1994). By contrast, gold in the adjacent Totok watershed is present as native gold, and is mined by artisanal miners using mercury amalgamation (Turner et al. 1994).

Whole ore from the Mesel deposit, with an average grade of 6.90 g/ton (Weeks et al. 1997) was roasted at

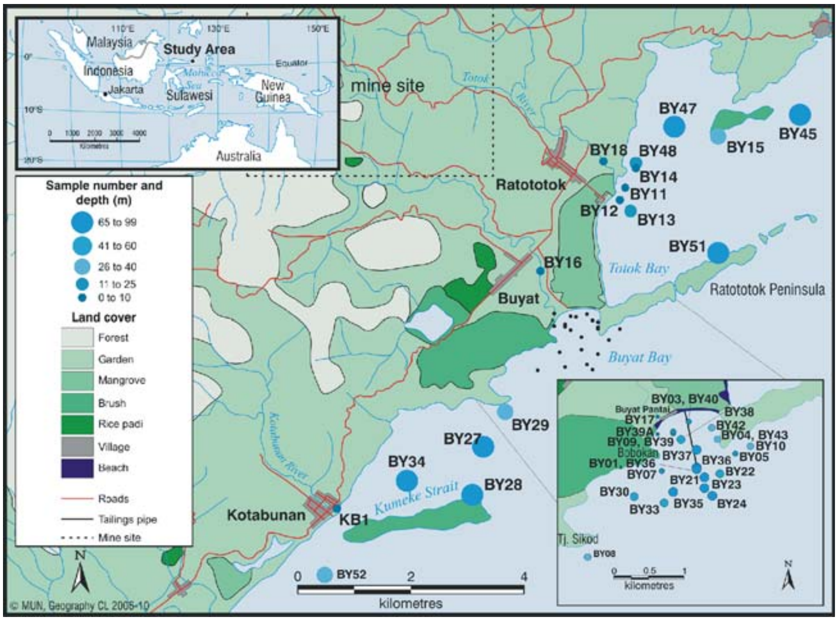


Fig. 1 Location and depth of sample sites. *Black line* through inset map indicates location of tailings pipe. Artisanal mining occurs in Totok watershed. Samples analysed for mineralogy and relative solubility were BY01-BY18, all collected in 2002

550–580°C. Whole ore, rather than concentrate, was roasted in the presence of limestone and dolomite from host rock, with the intent of capturing some arsenic as magnesium arsenate (Weeks and Wan 2000). After cyanidation at pH 9–9.2 to extract gold, tailings were treated with ferrous sulfate 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. Remaining mercury in solution was captured in the ferrous sulfate treatment stage as mercuric sulphide. Mining operations closed in 2001, and milling operations ceased in late August 2004.

Following treatment, tailings were pumped approximately 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 approximately 2,000 tons/day. The tailings pipe burst in 1998, approximately 100 m from shore in about 25 m water depth, close to the position of samples BY03 and BY40 (PTNMR 1998). The mining company commenced a monitoring program upon the opening of the mine in 1996. Mining company monitoring data showed high concentrations of arsenic, antimony, and mercury in mine tailings, but low dissolved concentrations of these metals 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 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 both 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 tons/year for the entire province (James 1994) to 110 tons/year for the Talawaan, Tatelu and Ratototok regions (Aspinall 2001). Within the last 10 years, most 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 approximately 1989. A reduced scale of artisanal gold mining continues, including lode and placer mining in the Totok watershed, 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 30–120 kg Hg/month, most of which was lost to tailings, wastewater, or to the atmosphere on burning amalgam (Aspinall 2001). Tailings are no longer dumped directly into the Totok river, but on-going Hg flux by wastewater dumping into the Totok River was estimated at 0.2 kg Hg/year (Aspinall 2001).

Materials and methods

Sampling areas

Field sampling was concentrated in two bays along the Molucca Sea coast of North Sulawesi province, Indonesia (Fig. 1). Buyat Bay is exposed to wave action from the Molucca Sea. The Buyat River debouches at the northwest corner of the bay. The village of Buyat Pantai is built on a coarse sand tombolo that separates Buyat Bay from Totok Bay. The east side of Buyat Bay hosts fringing coral reefs. Reefs also occur along the Ratototok Peninsula, and to the west of Buyat Bay (Fig. 1). Maximum depth in the bay is approximately 90 m. The mouth of the mine tailings disposal pipe lies 900 m from shore in 82 m of water. The shelf remains relatively flat until reaching the shelf break at about 120 m depth, roughly 8 km from shore (PTNMR 1994). The shape of the Buyat River mouth, visible plumes of sediment from the Buyat River, and PTNMR current meter data suggest that 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 is Miocene limestone of the same formation that hosts the Mesel deposit. Coastlines are mangroves along the protected side of the tombolo separating Totok Bay from Buyat Bay and along the northern margins of the bay, fringing coral reefs along the inner side of the Ratototok Peninsula and the islands in the bay, and cleared mangrove area in front of Ratototok village, and adjacent to the mouth of the Totok River. Maximum depth 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 approximately 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, 2006). Sediment sampling sought to characterize three primary sources of sediment in the system: artisanal gold mining (Totok River), industrial gold mine tailings disposed in Buyat Bay, and the Buyat river, which drains the mine site and has similar bedrock geology to the Totok River watershed. Many samples were collected close to coral reefs, to provide information on reef sediments, for comparison with heavy metal concentrations in coral skeletons (Edinger et al. 2003; E.N. Edinger et al., in preparation). Background sediment composition was determined from two sources: the sites furthest to sea in Totok Bay (BY15 and 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. 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 vs. siliciclastic) were recorded in the field, with subsequent measurement of grain size distribution, carbonate content, and organic content in the lab. All samples were frozen immediately upon return to shore and kept frozen until analysis.

Grain size, carbonate content, and organic 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. Partitioning of the <63 μm fraction in five samples that contained >50% mud was determined by sedigraph analysis using a Micrometrics Sedigraph 5100 particle size analyzer. Grain size distribution of 2002 samples was determined by wet sieving through standard graduated sieves (see electronic supplemental material).

Carbonate content was measured by dissolution of the acid-soluble fraction in 10% HCl. Two gram subsamples of each sediment sample were dried, weighed, 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.

Organic content of samples was estimated by loss-on-ignition (Berglund 1986). Two gram subsamples were dried for 12–24 h at 105°C, then cooled and weighed. Dried samples were ground in an agate mortar and ignited in pre-weighed porcelain crucibles for 2 h in a muffle furnace at 550°C. Samples were allowed to cool in a desiccator; the ash weight was subtracted from the dry sample weight to determine the organic content.

Mineralogy

Mineralogy of samples was assessed by visual petrography and electron microprobe analysis of polished thin sections. Thin sections were prepared by embedding sediments in epoxy resin, cutting and polishing to 30 μm thickness. Using the point counting method, 20–400 grains were selected for mineralogical identification in each thin section.

Very fine-grained sediments were characterized mineralogically by electron microprobe (EMP) analysis using a Cameca SX-50 scanning electron microprobe, with a beam current of 20 nano-amperes and an accelerating voltage of 15 keV, and approximately 1 μm beam diameter. Mineral identifications in electron microprobe examinations were made by energy-dispersive X-ray (EDX) microanalysis and the grey levels in backscattered electron images. Candidate silt-sized grains were selected based on their greater brightness (e.g. higher atomic number) relative to the surrounding groundmass of silicates and carbonates. The standard used for all elements was the Kakanui Hornblende (KaHb).

To assess the concentrations of metals in the sand, silt, and clay-sized fractions of the industrial mine tailings, metal concentrations were measured in sand grains (>63 µm, *n* = 20), silt-sized grains (4–63 µm, *n* = 50) and aphanitic ground mass (<4 µm, *n* = 50) of two polished thin sections of tailings embedded in epoxy resin using X-ray dispersion analysis on the electron microprobe. Because only 1 standard was used, elemental concentrations from the electron microprobe are best considered semi-quantitative. Elemental concentrations in grains from the electron microprobe are accurate for measuring major element composition and mineralogy to approximately 1%, but not reliable for concentrations below 1%.

Relative solubility of metals

Relative solubility of metals in sediment samples was assessed using the sequential extraction procedure of Fitzgerald et al. (1987). This sequential extraction procedure was designed for marine sediments containing a variety of trace elements from different sources in a wide range of amorphous and mineral forms (Fitzgerald et al. 1987). Small (0.5 g) dry subsamples were treated with six leaches, as described in Table 1. Because the acetic acid leach is capable of dissolving exchangeable metals, metals weakly adsorbed to mineral particles and metals incorporated into carbonates, fresh 1 g subsamples were treated with 8 ml 1 M magnesium chloride ($MgCl_2$) for 1 h at room temperature to measure exchangeable metals (Tessier et al. 1979). Reported metal concentrations for the acetic acid leach were calculated as the initial acetic acid leach concentration less the magnesium chloride leach concentration. To assess organically-bound metals, fresh 2 g subsamples were dissolved in 20 ml of solution composed of 25% acetic acid and 10% hydrogen peroxide at pH 2 for 24 h at room temperature. The organic fraction was measured as the concentration of each metal in the hydrogen peroxide–acetic acid leach less the concentration of that metal in the acetic acid leach (Buckley and Winters 1992). Resultant solutions from all sequential extraction phases were analyzed by ICP-MS, referenced to the USGS solution standards t143, t145, t153, t155, and t171 (see electronic supplementary material Table S1). Relative solubility of metals released in the various phases of the sequential extraction procedure was defined operationally, as described in Table 1.

Duplicate sequential extraction analyses were conducted of two samples from the 2002 suite (Table 2). Duplicate subsamples of muddy tailings sample BY01 generally yielded results within 30% of each other for

Table 1 Sequential Extraction leaches, procedures, common metal forms and mineral types dissolved (Fitzgerald et al. 1987), and interpretations (Chester and Hughes 1967; Tessier et al. 1979; Fitzgerald et al 1987; Buckley and Winters 1992)

Leach	Concentration	Quantity (ml)	pH	Duration (h)	Metal forms and minerals dissolved	Interpretation
Magnesium chloride	1 M	8	8.0	1	Weakly adsorbed metals	Exchangeable
Hydrogen peroxide–acetic acid	10% H_2O_2 25% $C_2H_4O_2$	20	2.0	24	Organically bound metals and oxidizable sulphides	Organically bound
Acetic acid	25%	20	2.0	16	Weakly adsorbed metals, metals bound in carbonates, readily oxidizable hydrated sulphides (Buckley and Winters 1992)	Labile
Hydroxylamine hydrochloride	1 M	20	5–6	16	Potentially reducible metals (Chester and Hughes 1967)	Meta-stable
Hot hydroxylamine hydrochloride (80°C)	0.04 M	10	2.0	6	Metals incorporated into Fe- and Mn-oxyhydroxides, and metals (Buckley and Winters 1992) strongly adsorbed to silicate minerals (Tessier et al. 1979)	Meta-stable
Hot Hydroflouric acid–nitric acid	Concentrated HF, 8 N HNO_3	2	2.0	72	Metals incorporated into refractory silicate minerals, metal oxides, and sulphides	Insoluble

Table 2 Percent variation between duplicate sequential extraction results of two samples

Sample	Leach	Cr	Fe	Mn	Co	Cu	Zn	As	Sb
Tailings (BY01)	Magnesium chloride	0	14.98	3.17	5.44	11.99	100	10.77	25.83
	Hydrogen peroxide–acetic acid	4.36	26.61	0	36.30	100	100	0	45.83
	Acetic acid	1.03	3.73	4.93	4.41	5.56	37.07	1.09	8.83
	Hydroxylamine hydrochloride	100	25.91	26.65	100	14.53	100	17.76	0.53
	Hot hydroxylamine hydrochloride (80°C)	1.35	0.16	14.33	1.86	3.79	27.80	1.24	15.53
	Hydroflouric acid–nitric acid	1.67	6.64	1.34	0.50	1.45	1.34	1.05	2.37
Totok River (BY18)	Magnesium chloride	1.00	25.98	4.46	1.88	21.28	0	16.54	74.11
	Hydrogen peroxide–acetic acid	0	56.14	50.06	51.94	41.00	100	100	2.22
	Acetic acid	100	3.67	2.53	17.76	8.08	100	100	100
	Hydroxylamine hydrochloride	100	10.71	1.45	7.74	3.09	100	100	100
	Hot hydroxylamine hydrochloride (80°C)	8.39	8.60	1.43	6.05	10.08	8.38	6.85	8.68
	Hydroflouric acid–nitric acid	1.47	89.65	5.36	1.33	9.84	2.51	9.85	12.70
All	Percent deviation from MESS-2 standard	–44.17	–27.97	–35.67	–26.45	–38.04	–39.84	–31.50	–13.76

Because the two samples for which duplicates were analyzed were quite different in nature, both are reported, rather than the average of the two. Zero (0) indicates that no concentration for that element in that leach was detected in either duplicate, while 100 indicates that a concentration was detected in one duplicate, but not in the other

most elements except Zn, with lowest variation in the magnesium chloride, acetic acid leach and total dissolution leaches. Duplicate subsamples of sandy Totok River sample BY18 were more variable, and had lowest variation in the two hydroxylamine hydrochloride leaches. Percent deviation from published values for the MESS-2 (National Research Council of Canada) sediment standard were calculated by summing the concentrations for the various extractions, and calculating the percent difference between this sum and the published concentration of each element in the MESS standard.

Results

Mud content, carbonate concent, loss-on-ignition, and mineralogy

Most samples were >70% siliciclastic, except reef samples BY05, BY07, BY08, BY10, BY15 (Fig. 2). Most of the siliciclastic samples were dominantly mud, except for shallow nearshore samples BY07, BY09, BY11, collected near the mouths of the Buyat and Totok rivers, and samples BY16, 17, and 18, collected in the Buyat and Totok rivers (full grain size data are presented in supplementary material).

The samples collected near the end of the tailings pipe were fine silts. Tailings sample BY01 was composed of approximately 73% silt and 13% sand, with a median grain size of 15 μm (Table 3). Carbonate content was approximately 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, while carbonates in fluvial and non-reefal sediments were subangular crystalline detrital carbonates.

Organic content, estimated by loss-on-ignition (LOI), was generally low, ranging from 0.6% in tailings sample BY01 to 1.8 % in the marine muds (Fig. 2). When only Totok Bay sediments, uninfluenced by fine grained arsenic–antimony rich tailings were considered, there were no significant positive or negative correlations between mud content and metal concentrations (correlation coefficient range –0.22 to 0.75, $n = 6$, As, $r = 0.156$ Sb, $r = 0.50$), but mud content and LOI were very strongly correlated ($r = 0.93$, $P = 0.008$, $n = 6$). Arsenic and antimony concentrations in Totok Bay muddy sediments (BY13, 14) were nearly identical with those in adjacent sands (BY11–12; Edinger et al. 2006).

Mineralogy of sediments affected by artisanal mining

Sediments collected from the Buyat (BY16, BY17) and Totok rivers (BY18), river mouths (BY09, 09A, BY11), and from further offshore in Totok Bay (BY12, BY13, BY14) were consistent in their mineralogy (Fig. 3). Fluvial and nearshore sand and muddy sand were characterized by poorly-sorted, angular, dominantly fine-grained plagioclase (fresh and extensively altered), detrital carbonate grains, quartz, andesite lithoclasts, pyroxene, heavily weathered amphiboles and opaque phases (dominantly oxides). Rare sulphide grains were recognized, including one arsenopyrite grain each in Totok Bay samples BY11 and BY14, and

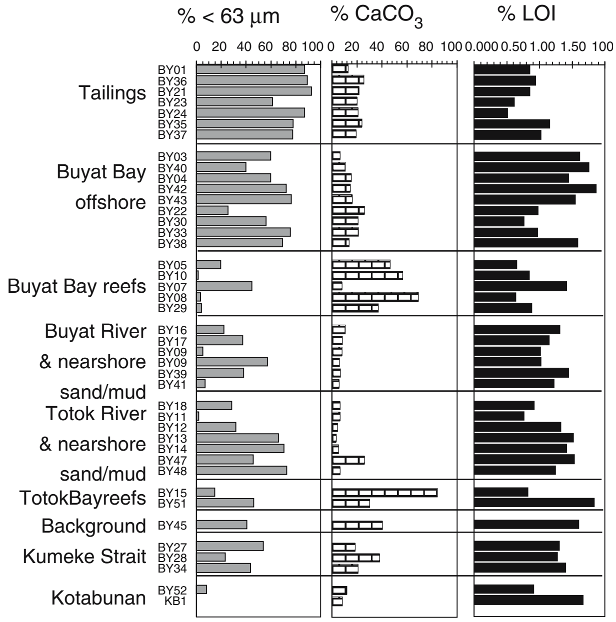


Fig. 2 Mud content, carbonate content and organic content estimated as Loss on ignition (*LOI*) of sediment samples. Mud content (% < 63 µm): *grey bars*; carbonate content: brickwork; LOI: *black*. Samples analysed for mineralogy and relative solubility were BY01-BY18, all collected in 2002. See electronic supplementary material Table S2 for full grain size data

in Buyat River sample BY16 (thought not counted in point-counts).

Mineralogy 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; Fig. 3). Among the dominant elements in the tailings, Si, Al, Ca, and Fe, the relative abundance of Si and Al was similar in sand, silt, and clay-sized particles, but Ca was less abundant in the ground mass than in silt and sand-sized material, and Fe was most abundant in the clay-sized ground mass (Fig. 4). Arsenic was found mostly as fine-grained colloids of arsenic and iron, without sulphur (Fig. 5a), and in grains of pyrite with arsenic-rich rims (Fig. 5b). The fine-grained colloids of arsenic and iron appeared to include both clumps of discrete particles and grain coatings forming cements between other grains. Because these colloids apparently contained no sulphur, they likely included some ferric arsenate from roaster byproducts and authigenic formation of Fe–(As)–OOH preciptates from dissolved Fe and As on mixing with seawater in the tailings pipe or near the sediment–water interface on the seafloor (cf. Murray 1979).

Antimony occurred primarily as silt-sized grains of antimony oxide (Fig. 5c). The large majority of potentially metal(oid)-bearing grains sampled were iron oxide compounds (69%, likely magnetite, maghemite, or hematite; Fig. 6a). Other metal(oid)-bearing phases in the tailings were antimony oxide (8 %), ilmenite (7.5%), barite (4.8%), pyrite (4.3%), and chromite and sphalerite (~1% each) iron–arsenic oxide phases (1.2%), iron–antimony phases (1.5%), and arsenian pyrite (0.8%; Fig. 6).

The majority of metal(oid)-bearing grains identified in Buyat Bay tailings-affected sediments were iron oxide (36–45%), ilmenite, (28–52%) and non-arsenical pyrite (0–27%) (Fig. 6b). Rare grains of iron–arsenic or iron–antimony phases, arsenical pyrite and antimony oxide, as observed in tailings sample BY01, were detected in BY03, BY04 and BY05, but not in any of the fluvial or nearshore marine samples from either Buyat Bay or Totok Bay.

Sequential extraction results

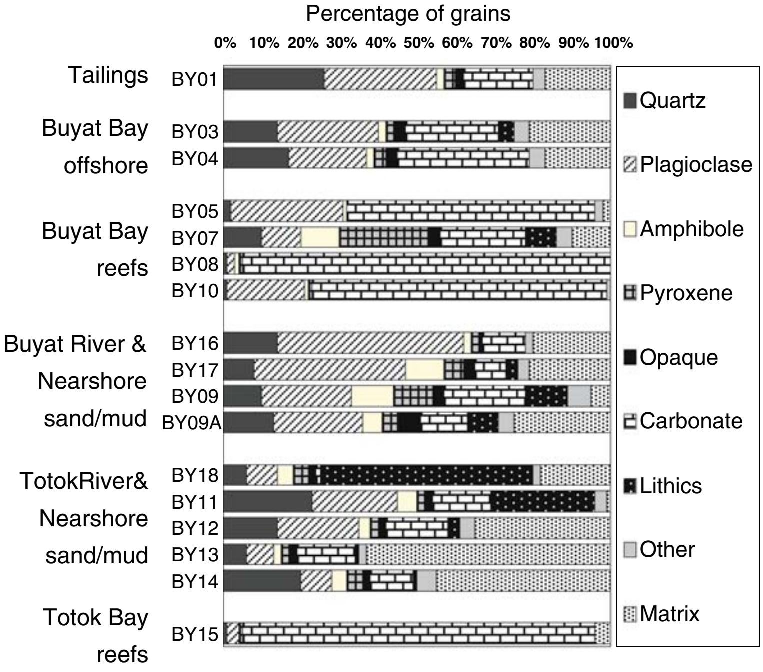
Arsenic

Sequential extraction of the 2002 tailings sample BY01 found 2% (13–15 ppm) of the arsenic to be soluble in

Table 3 Partitioning of <63 µm grain sizes in fine-grained 2002 samples, as determine by Sedigraph analysis

Sample	Grain size (µm)						
	Gravel%	Sand%	Silt%				Clay%
	>2,000	63–2,000	31.0–63.0	15.5–31.0	7.8–15.5	3.9–7.8	<3.90
BY01	0	12.98	13.06	24.79	20.02	15.10	14.05
BY03	0	31.31	8.81	17.95	13.51	9.87	18.55
BY04	0	42.88	8.53	15.17	11.60	7.53	14.29
BY09A	0	48.51	13.59	15.18	7.91	6.11	8.70
BY13	0	28.02	6.01	18.63	16.46	10.01	20.87

Fig. 3 Dominant minerals represented. Samples BY01, BY03, and BY04 analysed by electron microprobe survey, matrix = material < 4 μm. Remaining samples analysed by optical petrography, matrix = material < 63 μm



MgCl$_2$, and 30% (184 ppm) soluble in acetic acid, while 48% was released only by total dissolution (Fig. 7a). The balance of the arsenic was released by the two strong acid fractions intermediate between weak acid extraction and near-total dissolution. Tailings sample BY01 contained no organically bound arsenic. At the tailings pipe burst site (BY03), 12% of the arsenic was in the weak-acid soluble fraction, with none in the organic fraction. Similarly, at the reefs inside and immediately northeast of Buyat Bay (BY04, BY05), 18% of the arsenic present was in the weak-acid soluble fraction. 11% of the arsenic in southwest Buyat Bay reef sediment BY07 was weak-acid soluble.

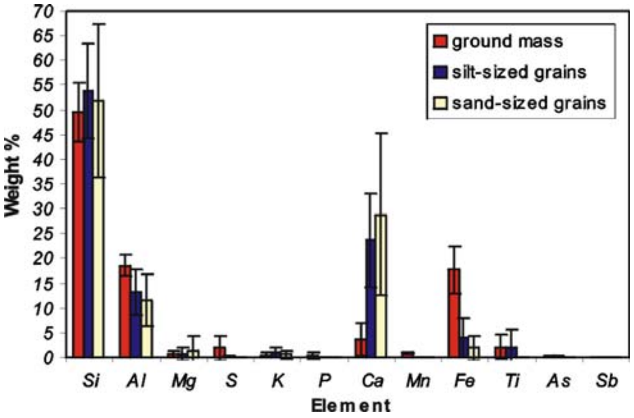


Fig. 4 Concentrations of major elements in sand, silt, and clay-size fractions of mine tailings sample BY01, analyzed by EDX unit on Electron Microprobe. Average As and Sb concentrations were less than 1% in clay-sized ground mass, and below detection limits in silt-sized and sand-sized particles

By contrast, arsenic in the Totok River and Totok Bay samples (BY11–14, BY18) was 85–95% insoluble. Arsenic in the Buyat River and river mouth samples (BY09, BY09A, BY16, BY17) was 70–75% insoluble, with <10% of the arsenic soluble in the weak acid leach. In the carbonate-dominated reef samples, approximately 20% of arsenic was soluble in the weak acid leach, and 45–60% was insoluble.

Antimony

Antimony was >85% insoluble in all siliciclastic-dominated samples, with less than 10% found in more soluble fractions in all but two cases (Fig. 7b). At the pipe burst site (BY03) and the Buyat River mouth sample (BY09), 9.5% of the antimony was bound to organic matter. Carbonate dominated samples all showed lower proportions of insoluble antimony than siliciclastic samples.

Copper, cobalt, chromium, zinc, iron, and manganese

Copper was >65% insoluble in samples from the rivers, river mouths, and fluvially-derived sediments in Buyat and Totok Bays (Fig. 7c). The only exceptions to this pattern were the tailings sample BY01 and the Buyat Bay reef samples BY05, BY08, and BY10: copper was >40% weak acid soluble or exchangeable in the tailings, and 40–60% weak-acid soluble or exchangeable in the Buyat Bay reef samples. A higher proportion of cobalt was insoluble in the fluvial and nearshore mar-

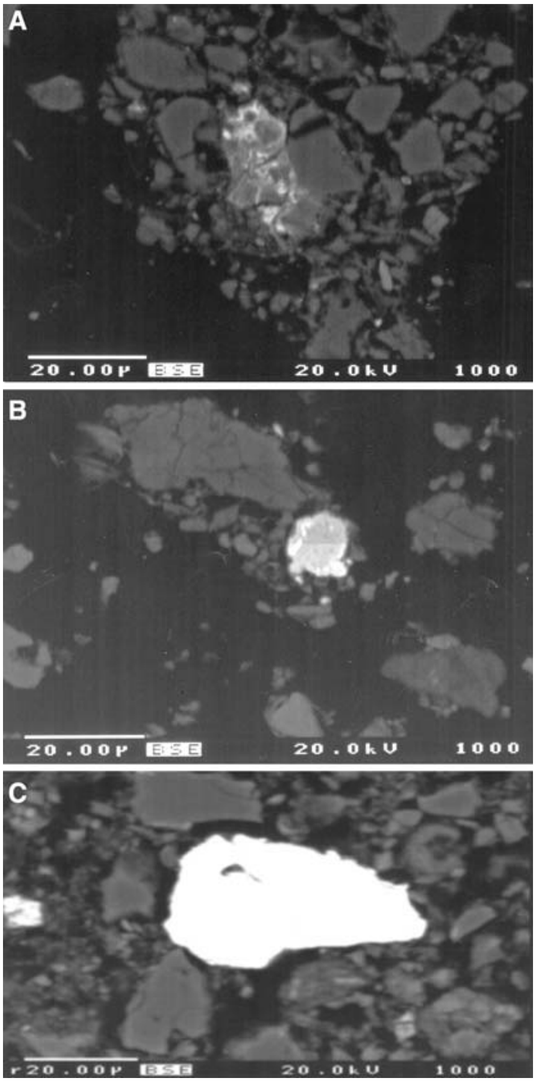


Fig. 5 Electron microprobe backscattered electron images of arsenic- and antimony-bearing phases in mine tailings thin section BY01. **a** arsenic–iron phase, probably ferric arsenate, binding together silt-sized grains of silica and andesite lithic fragments. This As–Fe phase was 36 wt% As, 28 wt% Fe, and contained no sulphur. **b** Weathered arsenic-rimmed pyrite grain, probably representing unreacted ore. **c** Angular antimony-oxide grain

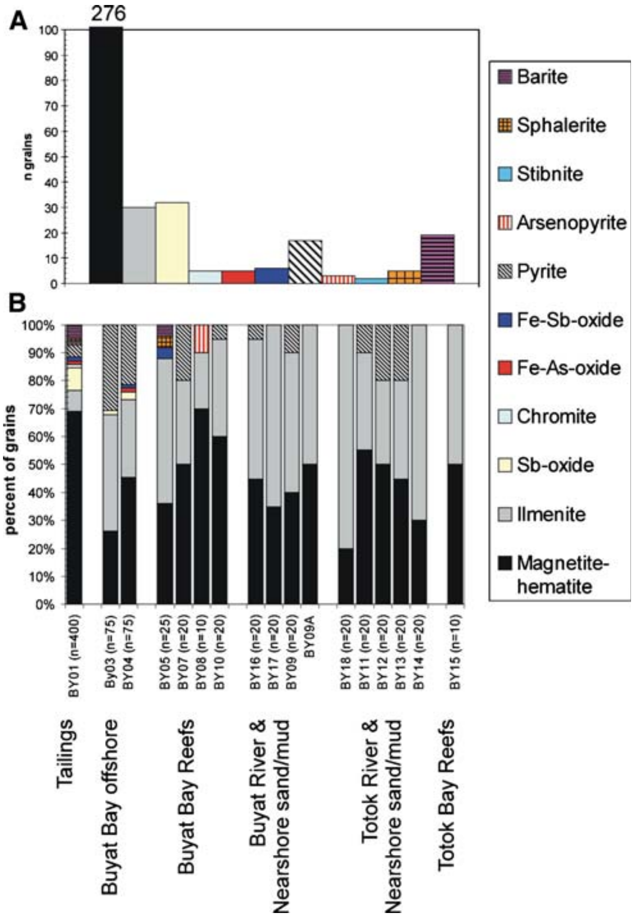


Fig. 6 **a** Relative abundance of opaque minerals represented as bright mineral grains in tailings sample BY01. n = 400. **b** Percent abundance of opaque minerals represented as bright mineral grains in all samples collected in 2002. Number of points indicated for each sample in x-axis. See electronic supplementary material Table S3 for full data table

ine sand and mud samples than in the tailings (Fig. 7d). Chromium relative solubility patterns were fairly consistent among all siliciclastic-dominated samples, but showed higher degrees of relative solubility in finer-grained samples and in carbonate-dominated samples (Fig. 7e).

Zinc was >70% weak-acid soluble in tailings sample BY01, in striking contrast to all the other samples (Fig. 7f). The high proportion of weak-acid soluble zinc may result from oxidation of zinc in the roaster phase; the concentration of zinc in the tailings was not unusually high, and there is no record of zinc addition during the cyanidation stage of ore treatment (Weeks and Wan 2000). The proportion of weak-acid soluble zinc was slightly higher in carbonate-dominated samples than in siliciclastic samples. Iron in all samples was dominantly insoluble, and the relative importance of the six fractions was nearly constant among all samples (Fig. 7g). Manganese was dominantly acetic-acid soluble or strong-acid soluble in all samples except the Buyat river mouth sandy sample (BY09, Fig. 7h). Manganese was >75% acetic-acid soluble in tailings sample BY01.

Discussion

Relationships between mineralogy and relative solubility of metals in mine tailings

For the present study, trace elements dissolved in the $MgCl_2$-soluble phase are described as weakly

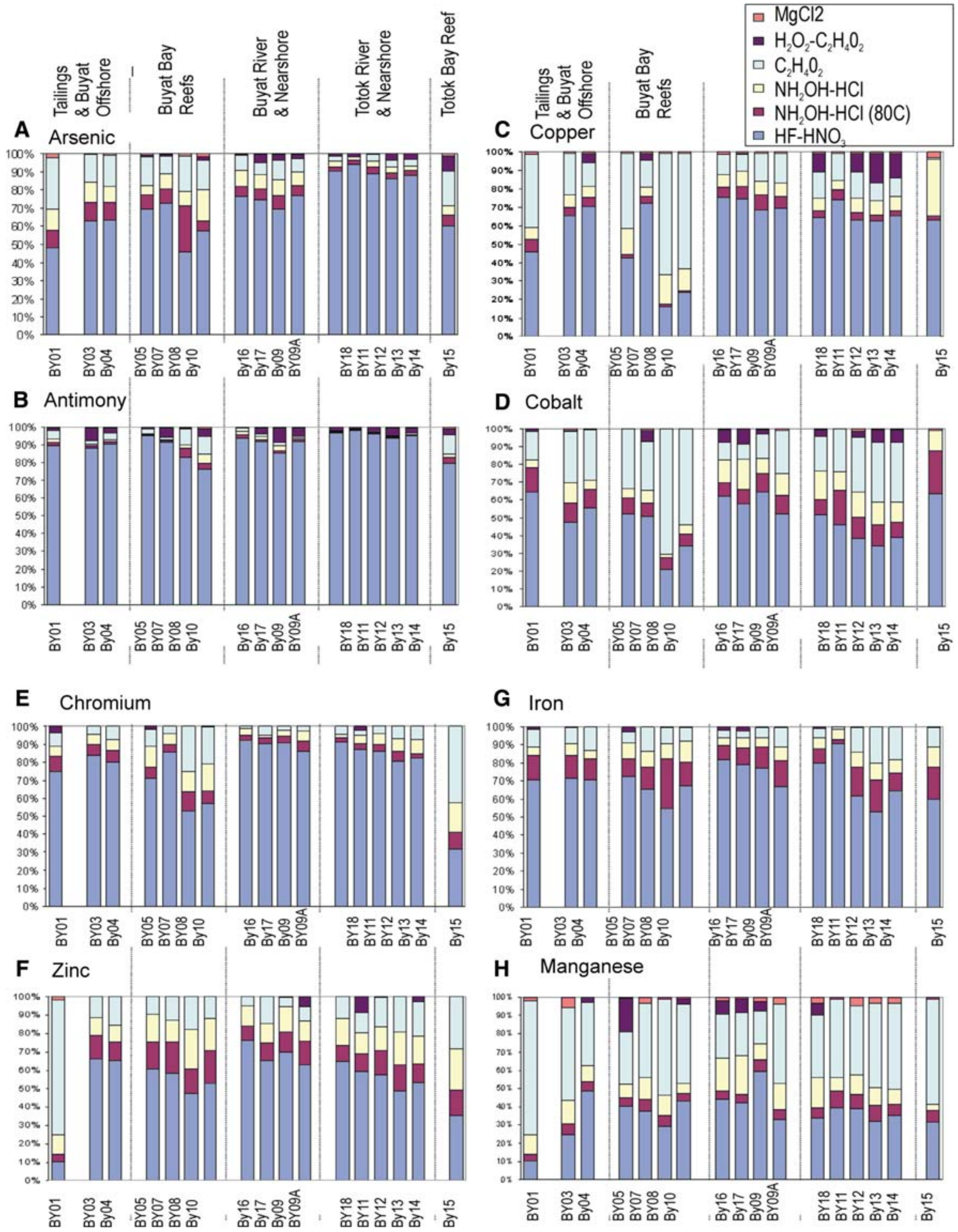


Fig. 7 Relative solubilities of metals of concern. **a** Arsenic. **b** Antimony. **c** Copper. **d** Cobalt. **e** Chromium. **f** Zinc. **g** Iron. **h** Manganese. Interpretation of fractions: $MgCl_2$: exchangeable; H_2O_2–$C_2H_4O_2$: organic, $C_2H_4O_2$: labile; NH_2OH–HCl: metastable 1; NH_2OH–HCl 80C: metastable 2; HF–HNO_3: insoluble. See electronic supplementary material Table S4 for concentrations of each metal in each leach in each sample

adsorbed, and interpreted as exchangeable (Tessier et al. 1979). Trace elements in the acetic-acid soluble phase are described as weakly adsorbed and carbonate bound; and interpreted as labile (Buckley and Winters 1992). Elements in the two hydroxylamine hydrochloride-soluble phases are described as metal(oid)s incorporated into reducible minerals such as iron or manganese oxy-hydroxides and elements strongly adsorbed to silicate mineral surfaces (Buckley and Winters 1992). The hydroxylamine hydrochloride stages are also likely to dissolve some portion of the metal(oid) sulphides present in anoxic sediments (Peltier et al. 2005). Because the hydroxylamine hydrochloride stage may over-represent metal(oid) solubility in certain environments, the results of these phases are conservatively interpreted as meta-stable, rather than labile (cf. Buckley and Winters 1992).

Interpretation of sequential extraction results can be challenging, because no extraction exactly duplicates natural conditions. Furthermore, sequential extractions affect all minerals present, rather than attacking specific minerals individually, such that sequential extractions in general do not yield a 1:1 correspondence between extraction phase and mineral forms (Mihaljevic et al. 2003). Drying may induce oxidation of some minerals, and the generally lower solid/liquid ratios in the lab than under natural conditions in marine sediment may also affect sequential extraction results. Some researchers have questioned the value of sequential extractions in general, given their labour-intensive nature and the ambiguity surrounding their interpretation (e.g. Cook and Parker 2006). Nonetheless, because arsenic is an important environmental toxin whose toxicity and solubility is strongly affected by chemical and mineral form (e.g. Magalhaes 2002), speciation studies of arsenic using sequential extractions remain an important avenue of research (Mihaljevic et al. 2003). Differences in results depending on sample treatment, including drying temperature, solid–liquid ratios, and different reagents emphasize the need for universal standard techniques and certified reference materials for analysis of arsenic speciation using sequential extraction techniques (Hudson-Edwards et al. 2004).

The sequential extraction procedure used here (Fitzgerald et al. 1987) was designed for marine sediments containing metal(oid)s from a variety of sources in a range of adsorbed and mineral forms, but was not intended to separate the mineralogical sources of metals in particular extraction phases. The Tessier et al. (1979) method is most appropriate for soils, i.e. dry aerobic sediments (Cook and Parker 2006). Several other sequential extraction procedures have been developed that may assess the individual contributions of particular mineral phases (e.g. Borovec et al. 1993; Hall et al. 1996; Zhang and Moore 1997; Blanchette et al. 2001; but see Mihaljevic et al. 2003) or are precisely designed for specific types of mine tailings (Dold 2003). In general, sequential extractions using an acetic acid leach followed by hydroxylamine hydrochloride phases underestimate arsenic in the exchangeable-adsorbed-carbonate bound phase and overestimate arsenic in the residual phase (Mihaljevic et al. 2003). The procedure used in this study was most similar to the Hall et al. (1996) sequential extraction procedure, determined to be the most effective of four sequential extractions compared for assessing arsenic speciation (Mihaljevic et al. 2003). Furthermore, the method used in this study assesses organically-bound metal(oid)s in a separate oxidizing leach using hydrogen peroxide and acetic acid, which is subtracted from the acetic acid leach itself, thus removing the ambiguity in the interpretation of the final two leaches of the Tessier et al. (1979), Borovec et al. (1993) or Hall et al. (1996) methods. Because of the uncertainties surrounding interpretation of sequential extractions in general, the sequential extraction results are interpreted with caution, especially the hydroxylamine hydrochloride leaches.

Relative solubilities of most metals were similar between tailings, tailings contaminated sediments in Buyat Bay, and fluvially derived marine sediments in both Buyat and Totok Bays. Relative solubility of most trace elements was generally greater in mud than in sand, and greater in carbonate-dominated reef sediments than in siliciclastic sediments, but arsenic did not follow the general pattern with respect to grain size. The higher proportion of weak-acid soluble metals in reef sediments than in siliciclastic sediments is likely an artifact of the acetic acid digestion, which also dissolved metals associated with carbonates (cf. Blanchette et al. 2001). Because arsenic was one of the principal contaminants of concern identified by the industrial mine (PTNMR 1994, 2002a, b), discussion of the sequential extraction results focuses mostly on arsenic.

Several factors that could limit the validity of the sequential extraction results probably do not have major effects on this research. First, the sample size of industrial mine tailings and tailings-affected samples analyzed for mineralogy and relative solubility was limited. The total arsenic, antimony, iron, manganese, copper, chromium, cobalt, and zinc concentrations in the samples analyzed for mineralogy and relative solubility are nearly identical with total metal(oid) concentrations in a larger suite of tailings and tailings-affected samples from Buyat Bay (Edinger et al. 2006). The larger suite of samples showed very low variability in total metal(oid) composition within the tailings and tailings-affected sediments, suggesting that the small sample size analyzed here does not limit the mineralogy and sequential extraction results. Second, the deviation between the trace element concentrations in the sum of fractions and the published values for the MESS-2 standard exceeded 15% for all metals except antimony (Table 2). Nonetheless, the sum of the arsenic sequential extraction fractions was within 10% of the total arsenic concentration as determined by whole sediment dissolution of separate subsamples in all cases (Edinger et al. 2006), as was true for antimony. While total concentrations for the other elements had variable agreement with the MESS-2 standard, the partitioning of metal(oid)s into relative solubility classes is probably fairly reliable. Finally, sequential extractions using the hydroxylamine hydrochloride leaches (Tessier et al. 1979) may overestimate the solubility of sulphide phases, particularly fine-grained sulphides (Mihaljevic et al. 2003; Peltier et al. 2005). Accordingly, most attention is focused on the magnesium chloride and acetic acid leaches.

Arsenic

The predicted arsenic reaction products of the ore roasting, leaching, and detoxification at the PTNMR site are magnesium arsenate, ferric arsenate, and arsenical ferrihydrite (Weeks and Wan 2000). Solubility of calcium, magnesium, and iron arsenates is highly variable, depending on exact composition, grain size, pH, and redox conditions (Rochette et al. 1998; Magalhães 2002; Paktunc et al. 2004; Walker et al. 2005; Zhang et al. 2005; Zhu et al. 2005). Although these reaction products have low to intermediate solubility under subaerial and normal oxygenated seawater conditions (as in the $MgCl_2$ leach), the Mg–arsenate and Fe–arsenate would probably dissolve in the acetic acid leach, particularly the colloidal Fe–As-oxide phase observed under electron microprobe analysis. While the arsenical ferrihydrite would probably dissolve in the two hydroxylamine hydrochloride phases (Mihaljevic et al. 2003), thus liberating arsenic bound into those oxyhydroxides, free ions adsorbed to these oxyhydroxides and colloidal iron–arsenic-phases adhered to them would dissolve in the magnesium chloride and acetic acid leaches, respectively. Thus arsenic associated with the arsenical ferrihydrite might be dissolved in several leaches. Although unaltered arsenopyrite, as observed in some fluvial and Totok Bay samples, would dissolve mostly in the HF–HNO_3 dissolution, fine-grained sulphides exposed to dissolved oxygen on the seafloor would slowly oxidize to more reactive forms, particularly if transported into better aerated shallow water reef environments Some portion of the arsenian pyrite present in the tailings under anoxic conditions may have dissolved in the hydroxylamine hydrochloride leaches (cf. Peltier et al. 2005).

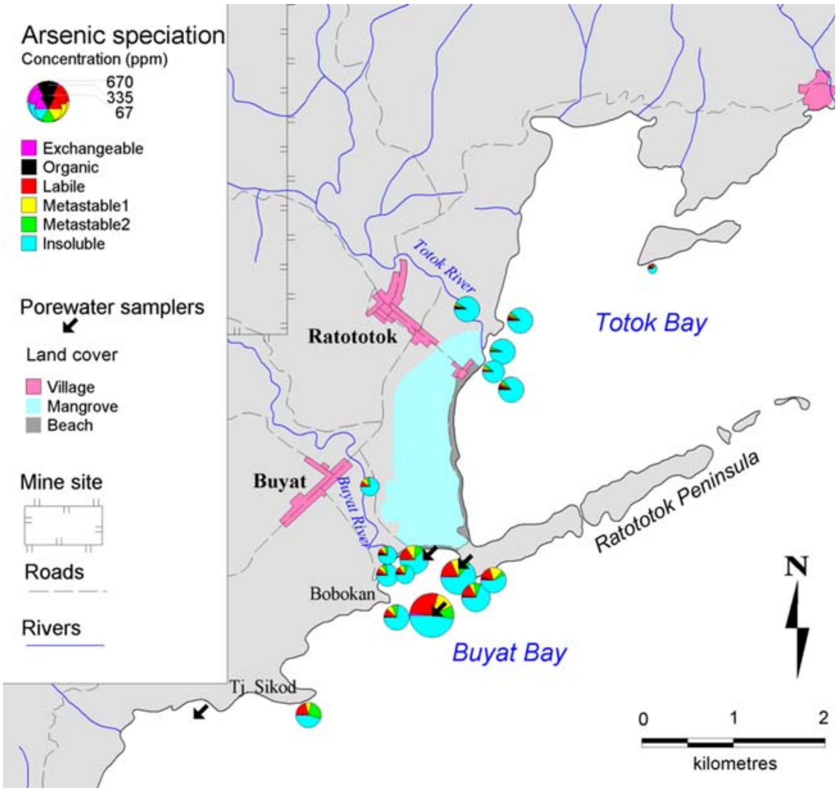


Fig. 8 Concentrations and relative solubility of arsenic. *Black arrows* indicate locations of PTNMR sediment porewater samplers (PTNMR 2002b). Size of pie diagrams (logarithmic scale) indicates total concentration, determined as the sum of all sequential extraction fractions

The most striking difference in mineralogy between the samples affected by industrial mine tailings and those affected by small-scale mining was in the forms of arsenic. Industrial tailings-affected samples included both fine-grained amorphous non-sulfurous Fe–As phases and crystalline sulphide forms (arsenian pyrite and arsenopyrite), in which the amorphous Fe–As phases were consistent with the predicted reaction products of the mine (Fig. 6a). Arsenic-bearing minerals observed in fluvial and small-scale mining-affected samples were exclusively arsenian pyrite and arsenopyrite. The sequential extraction data indicated that approximately 20–30% of the arsenic contained in the mine tailings (BY01) and tailings-contaminated sediments (BY03–BY04) was found in the labile phase. Proportions of exchangeable and labile arsenic were considerably higher in the tailings and tailings-influenced sediments of Buyat Bay than in the fluvial sediments and small-scale mining-influenced sediments of Totok Bay, regardless of grain size. High proportions of labile arsenic in carbonate-dominated Buyat Bay reef samples (BY05, BY08, BY10) likely show the effects of tailings dispersal to those sites (Edinger et al. 2006), but may also reflect an artifact of high carbonate content, similar to Totok Bay reef BY15. The total concentrations of arsenic in BY05, BY08, and BY10 were approximately 10 times that of BY15 (Fig. 8, and Edinger et al. 2006, see supplementary material), despite similar carbonate contents (Fig. 2). The magnesium chloride extraction (exchangeable fraction) replicated short-term dissolution into seawater. Only trace elements in the exchangeable fraction are likely to dissolve directly into the water column overlying the mine tailings (Tessier et al. 1979). All other extractions do not replicate natural conditions, complicating their interpretation. Labile arsenic (i.e. arsenic in the weak-acid soluble fraction, 184 ppm in tailings) is likely to undergo dissolution under the appropriate conditions of Eh and pH (Buckley and Winters 1992; Rochette et al. 1998; Mihaljevic et al. 2003). Ferric arsenate, which probably dissolved in the weak-acid phase (Mihaljevic et al. 2003), is relatively insoluble under aerobic conditions, but dissolves readily under reducing conditions (Rochette et al. 1998). Concentration of labile arsenic in the tailings sample was approximately 4.4 times greater than the Canadian probable effect level (PEL) for total arsenic in marine sediments, at which >47% of test fish showed negative biological effects (41.6 mg kg^{-1}, CCME 2001). Because the Canadian PEL results from toxicological tests, it should be readily applicable to other regions of the world.

Arsenic solubility, sediment porewater and potential biotic effects

Sediment pore-water samplers deployed by the mining company close to site BY04–BY43 (see Fig. 8 for porewater sampler locations) found maximum concentrations of dissolved arsenic in sediment pore water of 2,000 μg/l about 20 cm below the sediment water interface, declining toward the sediment surface, and remaining low in the water column above the sediment (PTNMR 2002b). Concentration of exchangeable + labile arsenic in sample BY04, collected at the sediment surface, was 28 ppm. Sediment pore water dissolved arsenic concentrations close to the end of the tailings pipe reached a maximum of 300 μg/l at 20 cm, the greatest depth of sampler insertion; the maximum concentration occurring at the end of the tailings pipe is not known. Sediment porewater dissolved arsenic concentrations at a reference site southwest of Tj. Sikod reached a maximum of 150 μg/l at 15 cm depth. Modeling based on the sediment porewater data at the sediment–water interface predicted a maximum concentration of dissolved arsenic of 11 μg/l in the water column above the tailings, consistent with most of the monitoring data (PTNMR 2002b), matching observed dissolved arsenic concentrations in the water column immediately above the tailings pile (PTNMR 2002b; Apte et al 2004).

Two possible processes could explain the sediment porewater dissolved arsenic patterns in the context of the sequential extraction results reported here. First, slow flux of dissolved arsenic from the exchangeable fraction could diffuse from sediment porewater into the overlying water column, where it would be diluted as water circulated under the influence of tidal currents or internal waves on the seasonal thermocline (Shepherd-Miller 2001; PTNMR 2002b). Second, labile arsenic from magnesium and ferric arsenates could dissolve under anoxic conditions at moderate depth (>10 cm) within the sediment, migrate upward toward the sediment–water interface, and re-precipitate under more oxygenated conditions close to the sediment surface. Because organic matter concentrations, as measured by LOI, were higher in most Buyat Bay sediments than in the tailings themselves, Eh is likely to have decreased more rapidly with depth in the sediment at the site close to BY04–BY43 than on the tailings pile itself, possibly promoting a shallower maximum in sediment porewater dissolved arsenic concentrations.

The second explanation is more conservative, and implies greater chemical stability of the tailings material. Vertical dissolution-precipitation cycles driven by changes in Eh and pH have been described for a variety of heavy metals in shallow marine conditions (e.g. Buckley and Winters 1992) and in As-rich mine tailings in fresh water impoundments (e.g. Salzsauler et al. 2005), and imply greatest dissolved arsenic exposure among benthic infauna (cf. Larsen et al. 2001), and nektobenthic fish (cf. Johnson et al. 1998). For example, the maximum sediment porewater arsenic concentrations at the site closest to samples BY04 and BY43 are higher than those from a Nova Scotia estuary contaminated with early twentieth century gold mine tailings (Daniels et al. 2005). This estuary was recently closed to clam digging by Canadian regulators, because clams excavated from tailings-contaminated sediments had flesh arsenic concentrations determined to be unsafe by toxicological assessment (Parsons et al. 2005). Arsenic at this Canadian site appears to be derived mainly from contaminated freshwater inputs, with a secondary contribution from tailings in the estuary (M. Parsons, personal communication, 2006).

Deposit-feeding benthos may contribute to metal dissolution within sediments. The chemical conditions inside the gut tract of deposit feeding invertebrates are acidic (pH ~5.6) and reducing (Eh < 0; Ahrens and Lopez 2001). Activities of deposit-feeding benthos can alter the mineralogy of clays within marine sands (Needham et al. 2004), and may be capable of converting heavy metal bearing compounds from less soluble to more soluble forms. Mg- and Fe-arsenates, and Fe- and Mn-oxyhydroxides such as the arsenical ferrihydrite, considered one of the meta-stable phases in this study, would be the most likely arsenic-bearing forms affected by possible biologically-driven dissolution. Regardless of pathway, the sequential extraction data suggest that arsenic from the industrial mine tailings may enter the benthic food chain, even though the modelled flux of dissolved arsenic from tailings to the water column is apparently low.

Trace element concentrations in a range of benthic invertebrates (cf. Larsen et al. 2001) have not been measured at this site, but trace elements have been measured in several fish species. Fish flesh arsenic, antimony, and mercury concentrations were all higher in sand- or mud-bottom fish than in reef fish or pelagic fish (Shepherd-Miller 2001). Interpretations of fish tissue trace element concentrations are contradictory: PTNMR monitoring concluded that fish tissue trace element concentrations are within international guidelines, but Indonesian Ministry of Environment testing suggested that fish consumption at current rates was hazardous to the health of women and children (Indonesian Ministry of Environment 2004).

Other trace elements

Weak-acid soluble copper and zinc were proportionally higher in the tailings than in other siliciclastic-dominated samples, but this pattern did not hold for chromium or cobalt. Most iron in all samples was insoluble, as expected for iron oxides and ilmenite, which were both abundant in all the sediments. Labile iron in the industrial mine tailings most likely represents ferric arsenate or iron bound into detrital carbonates, while meta-stable iron in the tailings probably came from a variety of iron oxy-hydroxides, including arsenical ferrihydrite. Labile and meta-stable iron in non-tailings samples was probably present as goethite, lepidocrocite, and other iron oxy-hydroxides, which are common in a wide variety of siliciclastic marine sediments (Murray 1979).

Manganese was almost equally abundant in all the samples analyzed (Edinger et al. 2006). Manganese was >40% weak-acid soluble in all sediments analyzed, and >70% weak-acid soluble in the mine tailings themselves. Manganese oxides and oxy-hydroxides are common readily-soluble cements in siliciclastic environments. A variety of trace elements can adsorb to or be incorporated into Mn oxides and oxy-hydroxides (Burns and Burns 1979). Many of the labile and meta-stable metal(oid)s observed in all the samples may have been adsorbed to or incorporated into Fe- and Mn-oxides and oxy-hydroxides.

Sediments affected by small-scale mining had higher metal(oid) concentrations than pre-mining background sediments, implying fluvial erosion of metal(oid)-bearing sediments by erosion (Appleton et al. 2001; Edinger et al. 2006). Nonetheless, the mineralogy and sequential extraction results from fluvial, Buyat river mouth, and Totok Bay samples suggest that small-scale mining had no effect on relative solubility of metals.

Management implications

Some scientists have advocated submarine tailings disposal (STD) a priori for sulfide ores in coastal regions as a way to avoid acid mine drainage (e.g. Pedersen 2001) or as a lowest-risk option in seismically active regions or where rainfall exceeds evaporation, both conditions that apply in North Sulawesi (Ellis et al. 1995). The apparent reactivity of the tailings, coupled with the lateral dispersal of tailings toward shore and onto local coral reefs (Edinger et al. 2006), and the recolonisation of the tailings by benthic organisms documented by the mining company monitoring (PTNMR 2002b) suggest the possibility that arsenic may be transferred from the tailings into the benthic food chain. Submarine tailings disposal at this mine was conducted in shallower depths and on gentler slopes than is generally recommended (IIED 2002).

Mineralogy and sequential extraction results in this study suggest that submarine tailings disposal is not appropriate for Carlin-like refractory sulfide gold ore deposits with As–Sb–Hg–Tl anomalies, because commonly used ore processing techniques convert arsenic from relatively insoluble arsenian pyrite to relatively reactive arsenic phases that are unstable in marine settings, particularly where sediments can become anoxic. Submarine tailings disposal of refractory sulfide gold ore tailings is particularly unacceptable in shallow waters from which tailings can disperse onto adjacent fishing grounds.

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