

Fluvial contamination associated with artisanal gold mining in the Ponce Enríquez, Portovelo-Zaruma and Nambija areas, Ecuador.

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Running Title: Contamination from gold mining in Ecuador.

Abstract

Artisanal gold mining in the Ponce Enríquez, Portovelo-Zaruma and Nambija areas of Ecuador has resulted in extensive contamination of the fluvial environment by mercury (Hg) and potentially toxic ore-related elements including arsenic (As), cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn). This occurs principally through the fluvial dispersion of contaminated mineral processing wastes and recycling of Hg sublimated during the burning of amalgam. Mercury concentrations in filtered (<0.45µm) surface waters do not exceed the WHO Drinking Water Guideline value and the USEPA Water Quality Criteria for the Protection of Aquatic Life. Criteria for other potentially harmful elements are, however, exceeded by a wide margin in the Ponce Enríquez (As, Cu, Zn) and Portovelo-Zaruma (Cd, Cu, Zn) districts, but not in the Nambija area. The Environment Canada sediment quality Hg

Toxic Effect Threshold for the Protection of Aquatic Life is exceeded in all three mining areas. As, Cd and Cu in many sediment samples from the Ponce Enríquez and Portovelo-Zaruma districts exceed Sediment Toxic Effects Thresholds by factors of 10 to >1000. The results highlight the need to ensure that contaminated sediment and water do not enter commercial banana plantations and shrimp ponds downstream of the Ponce Enríquez mining district.

1. Introduction

Environmental contamination by mercury is of particular concern in those countries of Latin America, South East Asia and sub-Saharan Africa which have witnessed an expansion of artisanal gold mining during the past three decades. Problems of mercury (Hg) contamination arising from gold mining in the Amazon River basin of Brazil have been widely documented (e.g. Lacerda and Salomons, 1998) yet there remain relatively few quantitative data for other major artisanal mining areas world-wide. The results are reported here of a study of the magnitude and extent of mining-related contamination of the fluvial environment in the Ponce Enríquez, Portovelo-Zaruma and Nambija artisanal gold mining areas in Ecuador. The potential toxicological significance to aquatic biota and humans of Hg and associated contaminants derived from mineral processing wastes is evaluated with reference to water and sediment quality guidelines for drinking water, aquatic biota and shellfish.

2. Artisanal gold mining in Ecuador

The gold rush in southern Ecuador started in the early 1980's when artisanal miners started to re-work old mines in the Portovelo-Zaruma area (Figure 1). This was followed by the re-discovery of the Nambija gold deposits where up to 20,000 people adopted relatively inefficient mining and mineral beneficiation processes, including the widespread use of mercury for amalgamation (Litherland et al., 1994). The Ponce Enríquez mining district was developed by artisanal miners during the mid-1980's, although the number of people involved and the social and environmental impacts are correspondingly less than at Nambija. More than 2,000 people live in the Ponce Enríquez mining settlements of which about 1000 are directly involved in mining the Bella Rica sector (Figure 2).

At Ponce Enríquez, gold in high temperature arsenopyrite-chalcopyrite hydrothermal veins is extracted from a series of adits, ground in Chilean mills (*trapiches*) and concentrated gravimetrically. Gold is recuperated from sluice box heavy mineral concentrates or tromol mills (James, 1994) by amalgamation. Cyanidation plants have recently been installed to treat gravity tailings. Large volumes of gravity tailings that contain very high concentrations of As and Cu, in addition to being contaminated with Hg, are stored on the steep slopes of the Bella Rica mining sector. The tailings dumps are prone to erosion by heavy rainfall which washes the material into the Río Siete and Estero Guanache drainage systems (Figure 2). There is some concern about the environmental impacts of Hg and other potentially toxic element pollution from artisanal gold mining with respect to the economically important coastal shellfish and banana production areas located about 20 km downstream of the Bella Rica mining sector.

The multiple phase mineralisation of the Portovelo-Zaruma mining area, incorporating discrete base-metal rich mesothermal and base-metal poor epithermal assemblages, has

yielded more than 120 tons of gold and about 250 tons of silver since exploitation started in the Spanish colonial era (Vanthournout et al., 1996). Some 40 grinding and gravity separation and 30 cyanidation plants currently operate in the Portovelo-Zaruma area. Mining-related contamination of the rivers Calera and Amarillo (Figure 3) include acid mine drainage with high concentrations of Cu, Cd and Zn; Hg derived from amalgamation, filtration and burning; and high suspended sediment loads derived from the mineral processing plants.

Artisanal mining in the Nambija area is primarily focused within the deeply incised Quebrada Calixto and Quebrada Cambana drainage basins, both of which form headwater tributaries of the Río Nambija (Figure 4). Gold occurs principally in quartz-carbonate veins and stringers that follow NE-trending faults within a N-S trending skarnfield of Jurassic age. Gold-bearing skarn pockets are worked via a series of adits. Beneficiation is carried out primarily within the major river valleys, where a series of sluices has been constructed to process milled ore. Smaller-scale alluvial mining operations have been developed at several locations downstream of the main artisanal settlement within the Quebrada Calixto and throughout the mid- and lower reaches of the Río Nambija. Gold is extracted from heavy mineral concentrates by amalgamation. Progressively falling production during the 1990's prompted a decline in the Nambija population that had contracted to c. 8,000 by 1997. Nambija residents have elevated blood mercury concentrations (mean 17.5 µg/l compared with 3.9 µg/l for a non-gold mining area) which probably result from exposure to methylmercury in contaminated food and mercury vapour inhaled during the burning of amalgam (Counter et al., 1998). There is also evidence that children employed as gold washers are exposed to abnormally high mercury levels (Harari et al., 1997).

Figure 1.

3. Sample collection and analysis

Sampling of the Ponce Enríquez area (Appleton *et al.*, 1996) and a reconnaissance study of the Portovelo-Zaruma area (BGS, unpublished data) were undertaken in July 1996 followed by a separate pilot-survey of the Nambija area in November 1996 (Williams and Orbea, 1997).

3.1 Water samples

Stream water pH, temperature, Eh and conductivity were determined in the field using temperature-compensated electrodes and meters. Water (W) samples for chemical analysis were filtered through 25 mm diameter, 0.45 µm MilliporeTM cellulose acetate membranes into 30 ml Sterilin tubes or into acid-washed 30 ml HPDE bottles (NalgeneTM). Coarse prefilters were used in conjunction with the normal 0.45 µm cellulose disks on all obviously turbid samples. At each site, the suite of water samples collected included: - (a) 30 ml preserved with 1% v/v HNO₃ (Analytical Grade) for determination of major and trace cations by inductively-coupled plasma emission spectrometry (ICP-ES), and, for the Ponce Enríquez samples, high precision hydride generation AAS analysis of As, (b) 30 ml unacidified water for SO₄²⁻, NO₃⁻ and Cl⁻ analysis by ion chromatography and (c) 30 ml preserved with 0.3 ml conc. HNO₃ + 0.3 ml 0.2 vol.% K₂CrO₇ for total Hg analysis by Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS) to a practical detection limit of 30 ng/l. Blank water samples, made using distilled water and acids/reagents used for preservation, were submitted

in blind fashion to the BGS ICP-ES and CVAFS laboratories in conjunction with field samples. Results for these blanks confirmed that there was no detectable background enhancement caused by the addition of acids/reagents to the field samples with respect to the elements of major interest to the present survey (As, Cd, Cu, and Hg).

3.2 Bottom sediment, suspended particulate matter and heavy mineral concentrate samples

Bottom sediment (BS) samples of 100-200 g mass were collected by wet-screening river or stream-bed detritus through a <150 µm sieve, using a minimal amount of water to avoid the loss of fine silt and clay fractions. Samples were sealed in securitainers to avoid evaporative losses and oxidation. In the Ponce Enríquez survey, suspended particulate matter (SPM) samples were obtained by filtering a fixed volume of stream water (250 or 500 ml depending upon the amount of SPM) through 45 mm diameter, 0.45 µm *Millipore*TM cellulose acetate membranes using a hand operated *MityvacII*TM vacuum pump. Filter membranes were carefully removed to avoid contamination and stored in 30 ml Sterilin tubes. Heavy mineral concentrate (HMC) samples were collected by screening approximately 2 kg of <2 mm stream bottom sediment, and removing the lighter fractions in a conventional prospecting pan. In the Nambija survey, heavy mineral concentrates were visually examined in the field to establish the presence of metallic Hg-Au amalgams but no quantitative analyses were performed on these samples. Hg analyses of BS and HMC samples were carried out by CVAFS, using 1 g milled sub-samples digested at <50°C in *aqua regia*. SPM samples were dried and the sediment digested with the cellulose filter membrane in *aqua regia* at <50°C and Hg determined by CVAFS. The practical CVAFS limit of determination for Hg in solid samples is 0.02 mg/kg. Multi-element analysis of BS and SPM samples from Ponce Enríquez and Portovelo-Zaruma was carried out by ICP-AES using an aliquot of the *aqua regia*

digestate. Major oxide and trace metal analysis were determined for the Nambija BS samples by X-ray fluorescence (XRF) analysis of 12 g pellets made following disaggregation, ignition of organic matter and milling of sediment to <63 μm .

4. Results and discussion

4.1 Contaminants in solution

In the Ponce Enríquez area, Hg exceeded the detection limit (0.02 $\mu\text{g/l}$) in only two filtered stream water samples from the Río Siete which drains the main mining and mineral processing area of Bella Rica and none exceed the background range for unpolluted freshwaters (0.005 to 0.05 $\mu\text{g/l}$). Recent working of alluvial gravels at one site in the headwaters of the Estero Guanache gave rise to the only high Hg value in filtered water (0.9 $\mu\text{g/l}$). Hg in stream water below this anomalous site decreases to <0.02 $\mu\text{g/l}$ within a distance of 2 km probably as a result of dilution and sorption by sediment. Generally low Hg concentrations in filtered river water also characterise the Portovelo-Zaruma and Nambija areas with occasional higher concentrations of up to 0.1 $\mu\text{g/l}$ reflecting local influx of contamination (Table I). Data published for gold mining impacted rivers of North and South America fall in the range 0.2 - 19.8 $\mu\text{g/l}$ (e.g. Pfeiffer *et al.*, 1989, 1991; Lacerda and Salomons, 1998) whereas much higher concentrations (up to 2900 $\mu\text{g/l}$) have been reported from the Diwalwal mining district on the island of Mindanao, the Philippines (Appleton *et al.*, 1999). At Ponce Enríquez, As in stream water ranges from 0.1 to 470 $\mu\text{g/l}$, with an erratic distribution of high concentrations (240-470 $\mu\text{g/l}$) in the upper and middle sections of the Río Siete declining to 77 $\mu\text{g/l}$ immediately above the shrimp farms (Figure 5). Cu in stream water ranges from <2 to 7277 $\mu\text{g/l}$, declining rather erratically from 3-4,000 $\mu\text{g/l}$ in the headwaters of the Río Siete to 17 $\mu\text{g/l}$ immediately

above the shrimp farms (Figure 5). There is an anomalous peak (7277 µg/l) in the downstream dispersion pattern approximately 9.5 km downstream of Bella Rica that may be caused by a temporally high flux of contaminated water from mineral processing plants located adjacent to the Río Siete (Figure 2). Iron (Fe) in stream water ranges from <0.004 to 6.0 mg/l with the highest concentrations associated with very acid waters (pH 3.7) in the headwaters of the Estero Guanache and a stream draining to the north of Bella Rica into the Río Tenguel (pH 3.9). Sulphate produced as a consequence of the oxidation of sulphide minerals associated with the gold mineralisation dominates the ionic balance. Elevated levels of NO₃ (40 mg/l above a background of 0.1 mg/l) in stream and river water collected close to the Bella Rica mining settlement reflect high inputs of organic material (sewage). The influence of the outflow from cyanidation plants adjacent to the Río Siete is indicated by enhanced stream water pH, Ca and Na (maxima of 9.7, 128 mg/l and 24 mg/l respectively; Appleton *et al.*, 1996). However, the concentrations recorded are not as high as in many other gold mining areas and are not, in themselves, indicative of the presence of cyanide in the stream waters. Factor analysis of the hydrochemical data (Table II) indicates two major factors. The first, accounting for 49% of the variance, comprises the strong positive grouping of Al, Co, Fe, Hg, Mn, Ni, Si, SO₄²⁻, Zn, and conductivity with negative grouping of pH and alkalinity. This reflects the influence of acid mine drainage and the oxidation of sulphides in tailings. The second factor (24% of the variance) comprises a strong positive association of As, Cu, Na, pH and alkalinity. Anomalously high concentrations of As, Cu and Na are associated with cyanidation plants in the headwaters and adjacent to the Río Siete implying that cyanometallic complexes in the high pH effluents from cyanidation plants may enhance the solubility of As and Cu. High concentrations of dissolved Cd, Cu and Zn (max. 41, 437 and 3354 µg/l, respectively) reflect the sulphide mineral assemblage associated with Au

mineralization in the Portovelo-Zaruma area. Factor analysis (Table II) indicates the strong influences of both sulphide mineral oxidation and cyano-metallic complexation on the concentrations of the major contaminants. Hydrogeochemical conditions downstream of Nambija reflect the low toxic trace element component within the mineralised assemblage (and hence the process waste) coupled with a strongly-buffered regime which inhibits mobilisation of metals such as Pb, Zn and Cu (Table I).

Figure 2. Figure 3. Figure 4. Figure 5.

Table I

Table II

4.2 Suspended particulate matter, bottom sediment and heavy mineral concentrates In the Ponce Enríquez area, Hg in SPM, BS and HMC ranges from 0.01 to 9.61 mg/kg, 0.1 to 13 mg/kg and 0.01 to 5.0 mg/kg, respectively. Particularly high concentrations occur close to ongoing or recent processing of alluvial gravels. Slightly higher concentrations characterise bottom sediments in the Nambija area (Figure 4) whereas lower Hg in both SPM (max. 1.3 µg/l) and BS (max. 3 µg/l; Figure 3) in rivers draining the Portovelo-Zaruma district (Table III) may reflect the greater reliance on cyanidation for gold extraction. Background concentrations in uncontaminated areas typically range from 0.1 - 0.4 mg/kg in bottom sediments whilst in other gold mining contaminated regions, Hg ranges up to 7.4 mg/kg in N. Carolina (Callahan et al., 1994), 32 mg/kg in Mindanao, the Philippines (Appleton et al., 1999) and 157 mg/kg in Brazil (Malm et al., 1990; Lacerda and Salomons, 1998). Extremely high concentrations of As and Cu characterise the drainage systems in the Ponce Enríquez area as a result of the large amounts of arsenopyrite and chalcopyrite associated with the gold mineralisation. SPM and BS in the Portovelo-Zaruma area are also highly contaminated with

Cd and Zn (Table III) which reflects the dominance of sphalerite in the mineralised assemblage. Concentrations of As, Cd, Cu, Pb and Zn in BS from the Nambija mining area are much lower (Table III).

Table III

4.3: Fluvial sediment dispersion trends and mechanisms Downstream variation of Hg in stream bottom sediments at Ponce Enríquez displays no coherent trend ranging from 3 mg/kg immediately below the main Bella Rica mining and mineral processing sector to 3 mg/kg some 15 km downstream of Bella Rica, at a site c. 2 km upstream of the eastern margin of the shrimp ponds (Figures 3 and 6). Over the same transect Hg concentrations in suspended sediments and heavy mineral concentrates decrease more progressively (Figures 6 and 7). Hg in suspended sediments decreases by a factor of nearly 100 over a distance of 15 km. The relatively high Hg concentration (3 mg/kg) in stream bottom sediment c.15 km below Bella Rica implies that the average level of contaminant transfer must have been higher in the past, presumably during periods of higher rainfall.

Sediment-bound Hg concentrations in surface drainage characteristically reflect contamination via a range of pathways including (i) deposition and inwash of Hg formerly mobilised as vapour during the burning of amalgams, (ii) particulate Hg inputs derived from the inwash of contaminated mineral processing tailings, (iii) Hg scavenged from solution by surface adsorption (Lacerda and Salomons, 1998). Mass transport of the contaminant Hg load is dominated by the SPM (by a factor of 1000 relative to dissolved Hg). HMC Hg is generally less than Hg in bottom sediment (Figure 6) suggesting that much of the Hg dispersed in the aquatic environment is adsorbed onto fine mineral particles derived from mineral processing rather than discrete particles of metallic mercury or amalgam. Hg dispersion is principally in an inorganic state, especially in the highly siliceous and aluminous, apparently low total

organic carbon (TOC), sediments of all three mining areas investigated (Appleton *et al.*, 1996; Williams and Orbea, 1997). Bottom sediments in these areas are dominated by recently deposited, finely ground tailings material from the mining operations which have been mechanically transported along the river bed or deposited from material transported in suspension (SPM). High concentrations of Hg in suspended particulate matter (SPM) indicate that Hg adsorbed onto mineral surfaces will make a significant contribution to the Hg load of bottom sediments.

In the Ponce Enríquez area, As, Cu, and Fe are all major components of the primary mineralisation and gravity tailings - principally occurring in chalcopyrite, pyrite, arsenopyrite, pyrrhotite and their alteration products. Erosion of tailing dumps during heavy rainfall and channelling of waste water from mineral processing activities directly into the streams and rivers has resulted in extensive contamination of river sediments (Figures 6 and 7). River water is frequently very turbid due to the high load of very fine grained gravity tailings, which is transported downstream in suspension. Suspended particulate matter loads of up to 6.2 g/l were recorded in the Río Siete during the present survey, decreasing to 0.02 g/l immediately above the shrimp ponds (Figure 7). Similar SPM loads in the range 0.1 to 5.8 g/l characterise the streams and rivers in the Portovelo-Zaruma area.

At Ponce Enríquez, copper in BS declines gradually from 9,134 mg/kg in the headwaters of the Río Siete to 2912 mg/kg at a site immediately above the shrimp farms (Figure 6) whereas in the corresponding SPM samples, copper concentrations decrease from 6437 mg/kg to 387 mg/kg (Figure 7). The progressive increase of the Hg BS/HMC ratio downstream from Bella Rica reflects sedimentation of high specific gravity metallic Hg, Au-Hg amalgam and Hg contaminated mineral grains close to the source of contamination (Figure 8). SPM Hg declines fairly rapidly downstream as the relatively heavy Hg contaminated particles are

preferentially deposited close to the source of contamination. In contrast, Hg, As, Cu and Fe in BS decline less rapidly reflecting the more extensive dispersion of contaminants during periods of maximum river flow and also the adsorption, over an extended period, of contaminants onto BS. Hence the BS/SPM ratio also increases progressively downstream from Bella Rica (Figure 8). It is likely that the BS/SPM ratio would not increase so rapidly downstream at times of maximum flow because the relatively heavy contaminant particles would be transported further in a more dynamic hydraulic regime. In the Río Siete, the BS/SPM ratio is significantly higher for Hg compared with As, Cu and Fe (Figure 8) reflecting the higher specific gravity of Hg. In addition, the amplitude of fluctuations in both element and ratio dispersion patterns is greatest for Hg, possibly as a consequence of low concentrations and the irregular distribution of Hg-rich particles within the river sediment.

Figure 6.

Figure 7.

Figure 8.

4.4 Within-site and temporal variation

Short-term temporal variation in the dissolved contaminant and suspended particulate load of water has been recognised in the Ponce Enríquez area. Sampling was executed over a period of six days so fluctuations in the load of suspended particulate matter reflect the variable rate of discharges from grinding and processing plants. These fluctuations are mirrored in contaminant concentrations in both the filtered river water and SPM. At 9.5 km below Bella Rica, for example, there is a subsidiary peak of SPM load which is also reflected by As, Cu, Fe, Na and SO_4^{2-} in water (Appleton *et al.*, 1996) and to a lesser extent by As, Cu, Fe and Hg

in SPM (Figure 7). As expected, the peak is not clearly reflected in the BS or HMC contaminant concentrations.

Concentrations of Cu in water samples tended to be lower in samples collected in a period of high rainfall and river flow (March-April) compared with samples collected in the drier month of July in the Ponce Enríquez area (Figure 9a) although other elements demonstrated a less consistent relationship reflecting the high temporal variance in contaminant fluxes in water. Cu and Hg in bottom sediments collected at the same sites for different sampling programmes correlate positively in Ponce Enríquez (Figure 9b) and Portovelo-Zaruma (Figure 10). However, (i) the variance is much higher at high concentrations of Cu (Figure 9b) and (ii) Hg concentrations were higher by a factor of about two in the 1995 survey (Figure 10). Other elements exhibit temporal variance that reflects fluctuations in the amount of finely ground sulphide minerals emitted from mineral processing plants. Within site variation is small compared with between-site variance (Appleton *et al.*, 1996). The greatest within-site variance was recorded for Hg in HMC, which reflects both the low Hg concentrations and the ‘nugget’ effect caused by the occurrence of Hg in discrete particles of Au-Hg amalgam.

Figure 9.

Figure 10.

4.5 Water quality

Hg in filtered river water samples collected from all three artisanal mining areas is below both the WHO Drinking Water Guideline value and the US-EPA Water Quality Criteria for the

Protection of Aquatic Life (Table I) so has no obvious toxicological significance. In the Ponce Enríquez area, the WHO Drinking Water Guideline (10 µg/l) and the EC Directive Maximum Admissible Concentration in Drinking Water (50 µg/l) for As are clearly exceeded in several instances, whereas the maximum water safety level for aquatic life (400 µg/l; Fergusson, 1990) is exceeded in only one sample. No samples exceed the value of 3000 µg/l As adopted by the UK-DOE (NRA, 1994) to comply with the EEC Shellfish Waters Directive (79/923/EEC) but the more stringent US-EPA Water Quality Criteria for fresh water (190 µg/l) is exceeded at five sites (Appleton *et al.*, 1996). Copper in nine water samples exceeds the EEC Directive Guide Level for Drinking water (100 µg/l) and five samples exceed the WHO Drinking Water Guideline (2000 µg/l). A sample taken approximately 4 km upstream of the shrimp farms on the Río Siete contained 809 µg/l Cu which significantly exceeds the UK-DOE standard (10 µg/l) adopted to comply with the EC Shellfish Waters Directive (79/923/EEC) and also the US-EPA Freshwater Criteria for the Protection of Aquatic Life (11 µg/l; Table I). This evaluation of water quality is based on samples collected over a short period of a few days. Water quality varies considerably with seasonal and short-term variations in rainfall and river flow (Figure 9a). If the temporal variations related to changes in contaminant fluxes and hydraulic regime are common then higher concentrations may sometimes occur in the vicinity of the shrimp farms. More detailed monitoring is required to verify the level, frequency and duration of high contaminant fluxes in stream water.

None of the filtered water samples from Portovelo-Zaruma and Nambija filtered water samples analysed in this study failed to meet WHO potable water standards (Table I) apart from Cd in one sample from the relatively acid waters of the Zaruma Urcu, a small tributary to the river Calera, in the Portovelo-Zaruma area. Dissolved Cu in Portovelo-Zaruma fluvial system generally exceeds the US-EPA Freshwater Criteria for the Protection of Aquatic Life by

a factor of 10 whereas the criteria for Zn was exceeded significantly in only one sample (3354 µg/l; Table I).

4.6 Sediment quality

Contaminant concentrations in this study were determined in the fine (<150µm) fraction of bottom sediment whereas Sediment Quality Criteria are based on concentrations in unsieved sediment. This difference may not be significant as most of the contaminants will tend to be concentrated in the fine fraction as a result of adsorption onto fine particles, clay minerals and organic material.

The Hg Toxic Effect Threshold for the Protection of Aquatic Life (MacDonald, 1994; Table III) is exceeded in bottom sediments in all three mining areas. The bioavailability and true toxicity of this Hg load is, however, not known. Such high sedimentary concentrations of Hg may constitute a long-term source of contamination, which is likely to become more widely dispersed during periods of high flow. With progressive methylation in the anoxic sediments that characterise the lower sections of the Río Siete, food chain translocation is likely (Lacerda and Salomons, 1998).

All As, Cd and Cu concentrations in BS samples from the Río Siete exceed Sediment Quality Criteria (Toxic Effects Threshold) for the Protection of Aquatic Life by factors of up to 2700, 16 and 106, respectively (Table III). It should be recognised that high As and Cu concentrations (possibly up to 1000 mg/kg) would occur naturally in this area prior to the initiation of mining activities. Bergey (1979) reported As values of up to 1000 mg/kg in sediments collected prior to the initiation of mining in the early 1980's. Pb and Zn in BS from the lower section of the Río Siete are either lower, or do not significantly exceed, the Sediment Quality Criteria for the Protection of Aquatic Life (Table III). Arsenic, Cd, Cu, Pb,

and Zn in all bottom sediment and suspended particulate matter samples from the Portovelo-Zaruma area exceed Sediment Quality Criteria (Toxic Effects Threshold) for the Protection of Aquatic Life by factors of 10 to >1000 (Table III). In strong contrast, base metal sulphide minerals are not a major component of the gold mineralisation in the Nambija area so only a few samples exceed the Toxic Effects Thresholds by a relatively small margin (Table III). It should be noted that the sediment quality criteria do not take into account the bioavailability of potentially harmful elements, which will be influenced by their chemical and mineral form (speciation).

4.7 Impacts of contamination on aquatic biota

Whereas the impacts of mining related contamination on aquatic biota were not investigated as part of the present study, there is clearly cause for concern that arsenic and mercury contaminated fish may present a health hazard to the local people. In the Ponce Enríquez area, no significant impact from the mining related contamination has been observed in the shrimps cultivated in shrimp ponds using seawater (Sangfors et al., 1998). Hg in shrimps was at or below the limit of detection and these low concentrations contrasted strongly with higher values in native shrimps in the rivers and streams impacted by mining contamination. The high sediment and contaminant load has led to the complete eradication of higher aquatic species in the Río Siete (Ponce Enríquez) although a few aquatic (principally marine) species reappear in the estuary (Sangfors et al., 1998).

Marine invertebrates and fish usually contain high concentrations of arsenic in the range of about 1 to 100 mg/kg dry weight (Neff, 1997) with wet weight concentrations for shrimps typically being in the range of 1 to 18 mg/kg (mean 5 mg/kg) - significantly higher concentrations being recorded for fresh compared with frozen shrimps (Sadiq *et al.*, 1995). These concentrations

exceed the general UK food limit of 1 mg/kg and the maximum permissible limit of 1 mg/kg for shrimp products in Saudia Arabia (Sadiq *et al.*, 1995). However, the arsenic in shrimps and other marine organisms is largely in the form of organoarsenic compounds of which arsenobetaine is the major component. Whereas organoarsenic compounds are bioaccumulated by human consumers of seafood, the arsenic is mostly excreted, mainly as arsenobetaine which is neither toxic nor carcinogenic to mammals (Neff, 1997). Consequently, arsenic in shrimps and other marine organisms is thought to represent a low risk to people who consume these fishery products. In addition, approximately 50% of total arsenic may be released in the defrost liquid from previously frozen marine organisms (Le *et al.*, 1994), further reducing any potential risk to humans if defrost water is not consumed. A detailed study of arsenic in the shrimps and fish both in the lower reaches of the Río Siete and adjacent shrimp ponds may help to determine the toxicological significance of the high concentrations of arsenic in the river-water, suspended particulate matter and bottom sediments.

5. Conclusions

- (1) This survey has highlighted the impact of artisanal gold mining on the flux of Hg in the fluvial environment in all three study areas and of ore mineral related potentially harmful elements (principally As, Cu and Zn) in the Ponce Enríquez and Portovelo-Zaruma mining districts. The bulk of the contaminant load in the aquatic environment has been transported in association with the suspended (SPM) load of the rivers. Water and SPM samples indicate the current flux of contamination to the drainage system but are very susceptible to temporal variations related to short term fluctuations in discharges from processing plants and to rainfall-related dilution

effects. Bottom sediment (BS) provides a more stable indication of the extent and magnitude of contamination whereas heavy mineral concentrate samples indicate the amount of particulate Hg metal and Au-Hg amalgam in the river sediment. More detailed monitoring is required to verify the level, frequency and duration of high contaminant fluxes in stream water and suspended particulate matter.

- (2) Although surface water contaminated by As, Cu, Hg and Zn may pose a hazard to aquatic biota and humans in all three areas, the major concern is the potential effect of this contamination on the commercial banana plantations and shrimp ponds in the Ponce Enríquez area. Mercury in water and SPM provide an indication of contaminant fluxes at the time of sampling and hence the potential hazards to biota and humans via this exposure route. Concentrations of potentially harmful elements in bottom sediment indicate the likely hazard to biota from remobilization as a result of methylation and other processes.
- (3) Whereas dissolved Hg concentrations in water do not exceed the WHO Drinking Water Guideline value and the USEPA Water Quality Criteria for the Protection of Aquatic Life, criteria for other potentially harmful elements are exceeded by a wide margin in the Ponce Enríquez (As, Cu, Zn) and Portovelo-Zaruma (Cd, Cu, Zn) districts but not in the Nambija area. Only dissolved Cu exceeds the criteria for Protection of Aquatic Life in samples taken immediately upstream of the commercial shrimp ponds at Ponce Enríquez. Arsenic and Cu in bottom sediment collected 2 km upstream of the shrimp farms exceed Sediment Quality Criteria (Toxic Effects Threshold) for the Protection of Aquatic Life by factors of about 400 and 30 respectively. This study was unable to collect samples from the banana plantations and shrimp ponds. Until such data become available, it is recommended that care

should be taken to ensure that contaminated sediment and water do not enter the banana plantations and shrimp ponds downstream of the Ponce Enríquez mining district.

- (4) In any aquatic system subject to inorganic As, Cu and Hg contamination, the attendant toxicological risk (with respect to magnitude and temporal duration) cannot readily be determined from data depicting total sedimentary loads. Additional geochemical and ecotoxicological studies are required to establish factors such as the rates of sedimentary Hg methylation and subsequent bioassimilation. The principal exposure route to Hg and As for local people is through the consumption of fish and shellfish. Detailed dietary data, epidemiological information, and body burden data would be critical precursors to any meaningful exposure assessment. Such studies are now required in the Ponce Enríquez, Portovelo-Zaruma and Nambija areas.

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Table I. Comparison of potentially harmful element concentrations in filtered water samples from 2 km (MA-28) and 4 km (MA-30) above the Río Siete shrimp farms (Ponce Enríquez) with maximum concentrations in the Ponce Enríquez, Portovelo-Zaruma and Nambija artisanal mining areas and Water Quality Criteria

| | Freshwater ¹ | | Saltwater ¹ | | Shellfish Directive (79/923/EEC) ⁴ | WHO Drinking Water | EC Drinking Water MAC | Ponce Enríquez | | Portovelo-Zaruma | Nambija | |
|----|-------------------------|--------------------------|-------------------------|--------------------------|---|--------------------|-----------------------|----------------|------|------------------|---------|------|
| | Max. Conc. ² | Cont. Conc. ³ | Max. Conc. ² | Cont. Conc. ³ | | | | MA28 | MA30 | | | Max. |
| As | 360 | 190 | 69 | 36 | 3000 | 10 | 50 | 77 | 109 | 470 | nd | nd |
| Cd | 3.7 | 1 | 42 | 9.3 | 330 | 5 | 5 | <4 | <4 | 9 | 41 | <4 |
| Cu | 17 | 11 | 2.4 | 2.4 | 10 | 2000 | 100 | 17 | 809 | 7277 | 437 | 3.5 |
| Pb | 65 | 2.5 | 210 | 8.1 | 100 | 50 | 50 | nd | nd | nd | nd | <40 |
| Hg | 2.1 | 0.012 ⁵ | 1.8 | 0.025 | 1 | 1 | 1 | <0.02 | 0.03 | 0.9 | 0.1 | 0.1 |
| Ni | 1400 | 160 | 74 | 8.2 | 100 | - | 50 | <10 | <10 | 165 | 35 | <10 |
| Zn | 110 | 100 | 90 | 81 | 10 | 5000 | - | 49 | 46 | 821 | 3354 | <5 |

Explanation:

¹ EPA Section 304 (a) Criteria for the Protection of Aquatic Life from Priority Toxic Pollutants (US Clean Water Act, February 5, 1993; Part 131-Water Quality Standards, Sec. 131.36 proposed amendment April 1995). The criteria refers to the inorganic form only. Freshwater aquatic life criteria vary with total hardness and pollutant's water effect ratio (WER). Values quoted here correspond to total hardness of 100 mg/l and a WER of 1.0 (abstracted from Haines et al. 1994, MacDonald, 1994)

² Criteria maximum concentration (CMC) = the highest concentration of a pollutant to which aquatic life can be exposed for a short period of time (1-hour average) without deleterious effects.

³ Criteria continuous concentration (CCC) = the highest concentration of a pollutant to which aquatic life can be exposed for an extended period of time (4 days) without deleterious effects

⁴ UK-DOE "I" (imperative) values recommended for compliance with EC Shellfish Waters Directive (79/923/EEC) (NRA, 1994)

⁵ If the CCC exceeds 0.012 µg/l more than once in a 3 year period in the ambient water, the edible portion of aquatic species of concern must be analysed to determine whether the concentration of methyl mercury exceeds the FDA action level of 1.0 mg/kg.

Table II. Factor analysis loadings for forced 3 factor principal components solution for Ponce Enríquez (n= 23) and Portovelo-Zaruma (n=5) filtered waters.

| Variable | Ponce Enriquez | | Portovel o- Zaruma | |
|-----------------|-------------------|----------|--------------------------|----------|
| | Factor 1 | Factor 2 | Factor 1 | Factor 2 |
| Al | 0.84 | 0.12 | 0.84 | 0.46 |
| As | -0.32 | 0.89 | -0.24 | 0.78 |
| Co | 0.98 | 0.12 | n.i. | n.i. |
| Cu | -0.15 | 0.86 | 0.71 | 0.66 |
| Fe | 0.62 | 0.09 | 0.98 | 0.19 |
| Hg | 0.83 | 0.13 | -0.45 | 0.72 |
| Mn | 0.91 | 0.03 | n.i. | n.i. |
| Na | 0.27 | 0.94 | 0.87 | 0.48 |
| Ni | 0.97 | 0.21 | n.i. | n.i. |
| NO ₃ | 0.11 | 0.03 | -0.53 | 0.24 |
| Si | 0.73 | -0.32 | 1.00 | 0.01 |
| SO ₄ | 0.80 | 0.36 | 0.99 | 0.05 |
| Zn | 0.80 | 0.38 | 0.99 | 0.04 |
| pH | -0.79 | 0.52 | -0.89 | 0.44 |
| Eh | 0.45 | -0.67 | -0.52 | 0.60 |
| Conductivity | 0.75 | 0.42 | 0.99 | 0.10 |
| Alkalinity | -0.62 | 0.67 | -0.72 | 0.58 |
| Variance | 49% | 25% | 68% | 19% |

n.i. = not included in factor analysis

Table III. Comparison of potentially harmful element concentrations in suspended particulate matter (SPM) and stream bottom sediments (BS) from above the Río Siete shrimp farms (MA-28) at Ponce Enríquez with maximum concentrations in the Ponce Enríquez, Portovelo-Zaruma and Nambija and Sediment Quality Criteria for the Protection of Aquatic Life (concentrations in mg/kg).

| | Sediment Quality Criteria ¹ | | | Ponce Enríquez | | Portovelo-Zaruma | | Nambija | | |
|----|--|---------------------------------|-------------------------------|----------------|-------|------------------|-------|-------------|------------|------------|
| | No effects threshold | Minimal effects threshold | Toxic effects threshold | SPM | | BS | | SPM Max. | BS Max. | BS Max. |
| | | | | MA28 | Max. | MA28 | Max. | | | |
| As | 3 | 7 | 17 | 957 | 22626 | 7258 | 46049 | 1564 | 7493 | 34 |
| Cd | 0.2 | 0.9 | 3 | 2 | 18 | 12 | 24 | 23 | 104 | 3 |
| Cu | 28 | 28 | 86 | 387 | 6437 | 2912 | 9134 | 2912 | 8750 | 409 |
| Pb | 23 | 53 | 170 | 123 | 1061 | 175 | 666 | 1997 | 10524 | 42 |
| Hg | 0.05 | 0.2 | 1 | 0.1 | 9.61 | 3 | 13 | 1.3 | 3.0 | 34 |
| Zn | 100 | 150 | 540 | 108 | 743 | 347 | 924 | 2567 | 9792 | 231 |

Note: SPM = suspended particulate matter; BS = bottom sediment; ¹ Sediment Quality Criteria for Protection of Aquatic Life (Environment Canada, 1992 quoted in MacDonald, 1994).

Figures

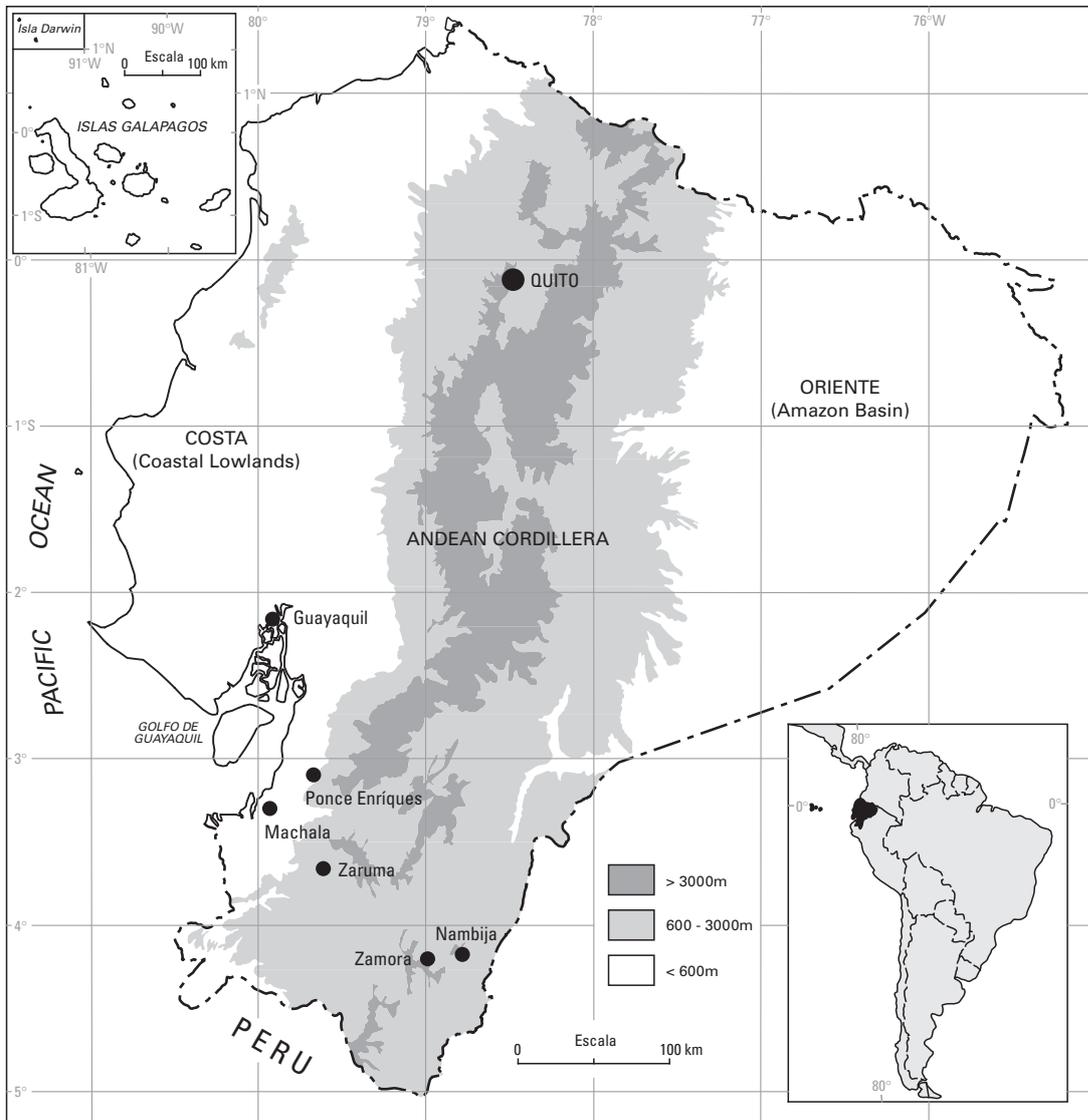


Figure 1. Location of the Ponce Enríquez, Portovelo-Zaruma and Nambija artisanal gold mining areas, Ecuador.

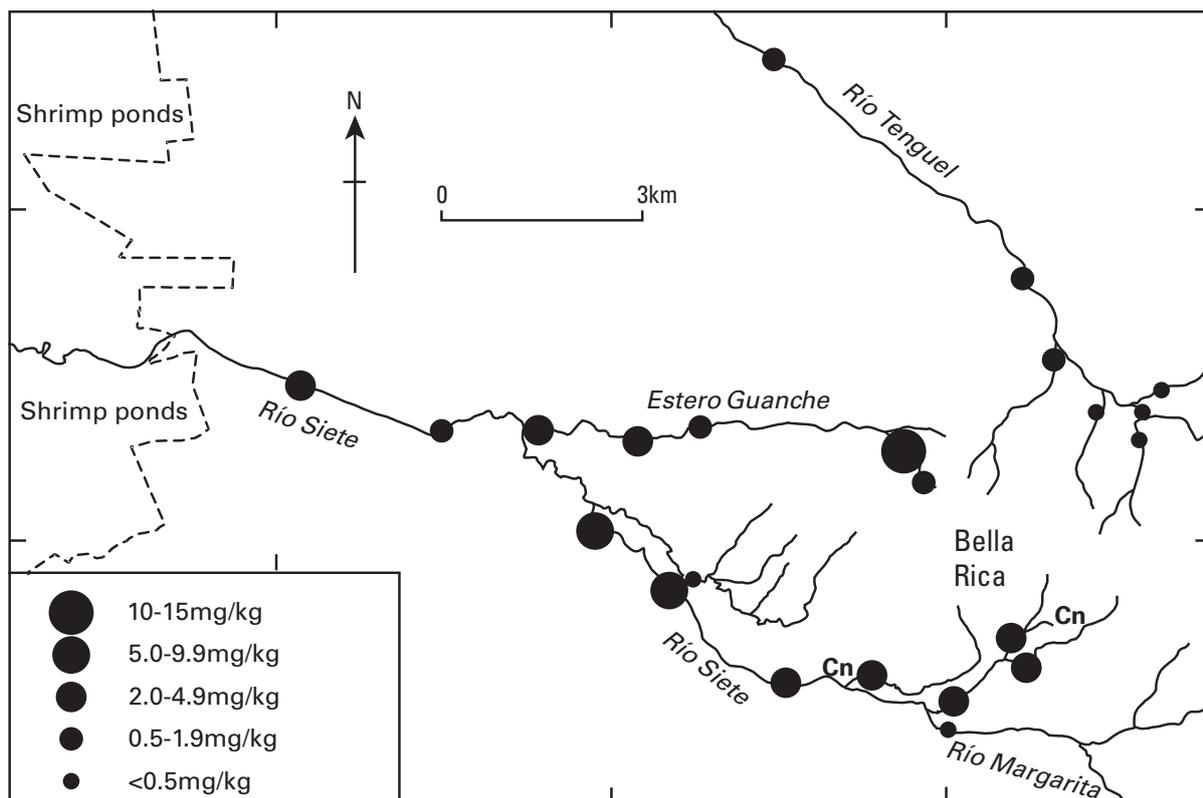


Figure 2. Distribution of Hg in bottom sediment in rivers draining the Ponce Enríquez (Bella Rica) artisanal gold mining area, Ecuador (Cn = approx. location of cyanidation plants).

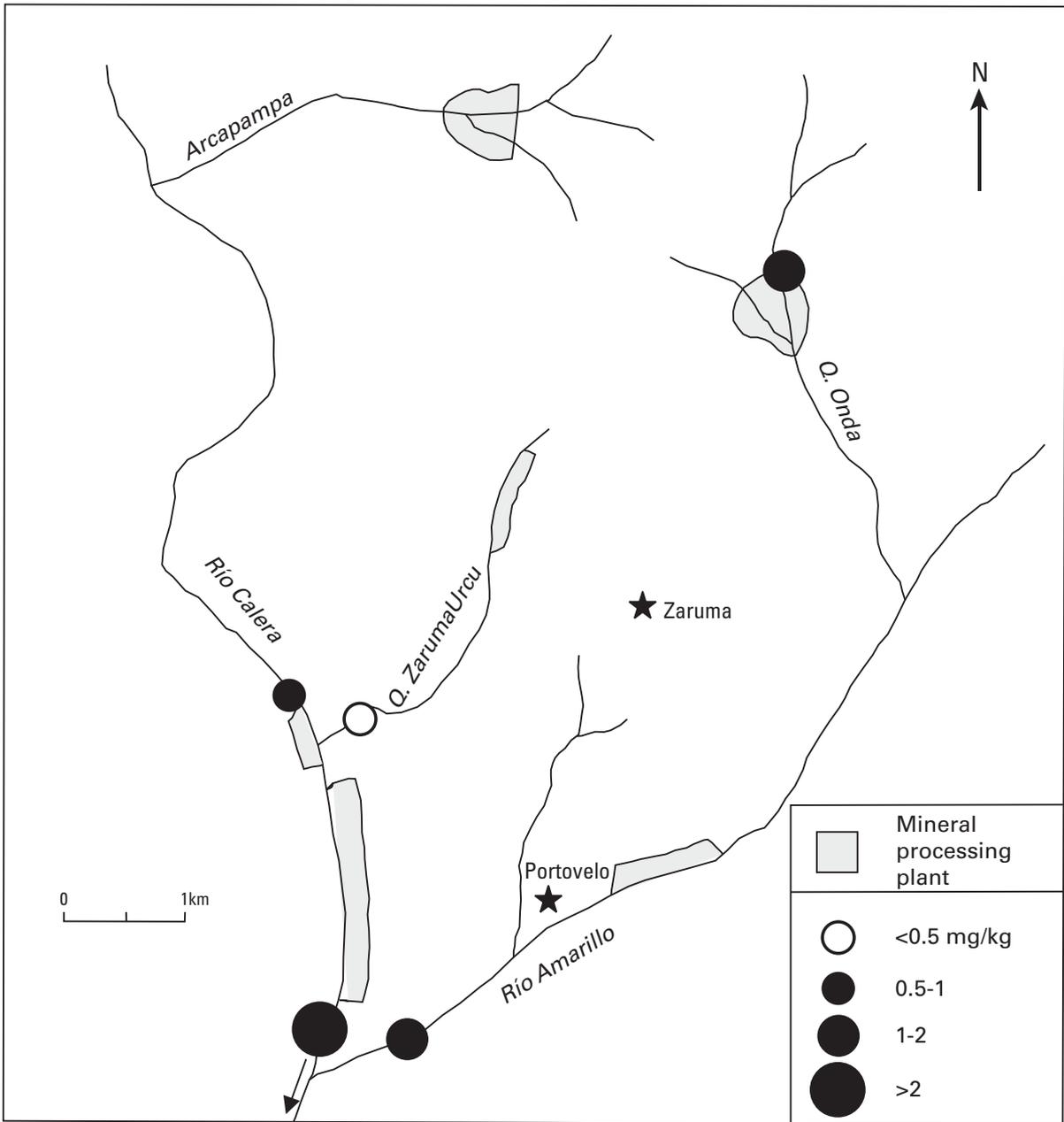


Figure 3. Distribution of Hg in bottom sediment in rivers draining the Portovelo-Zaruma gold mining area, Ecuador.

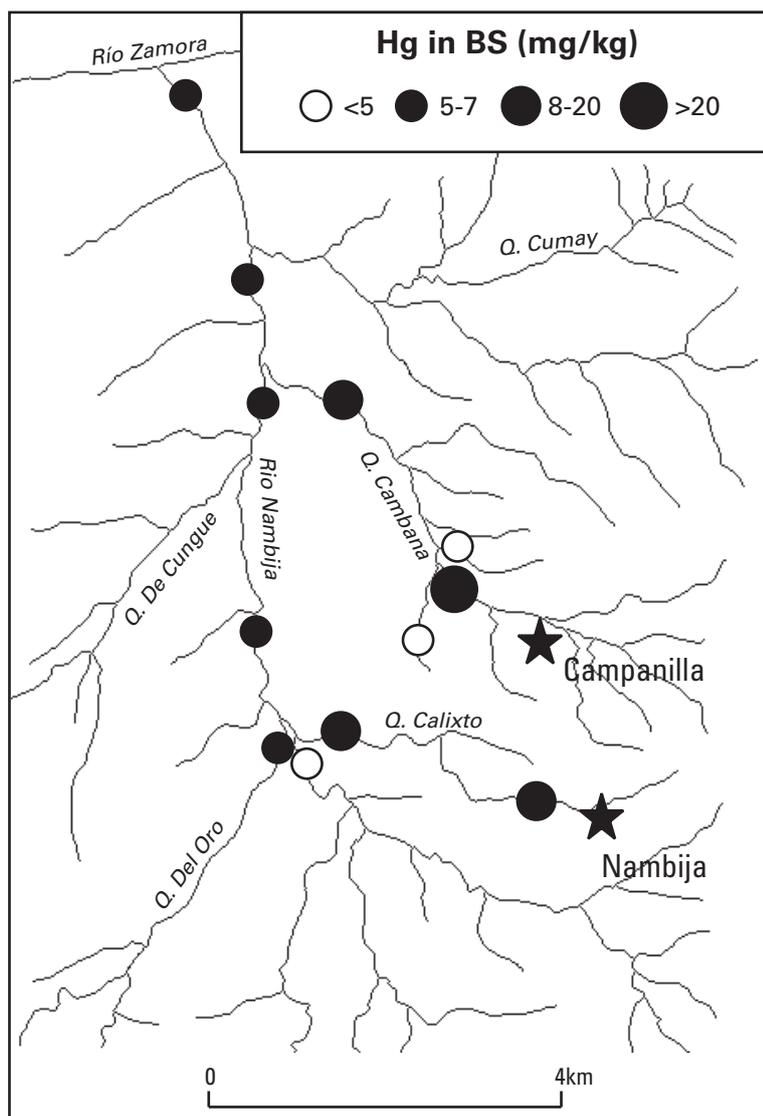


Figure 4. Distribution of Hg in bottom sediment (BS) in rivers draining the Nambija artisanal gold mining area, Ecuador.

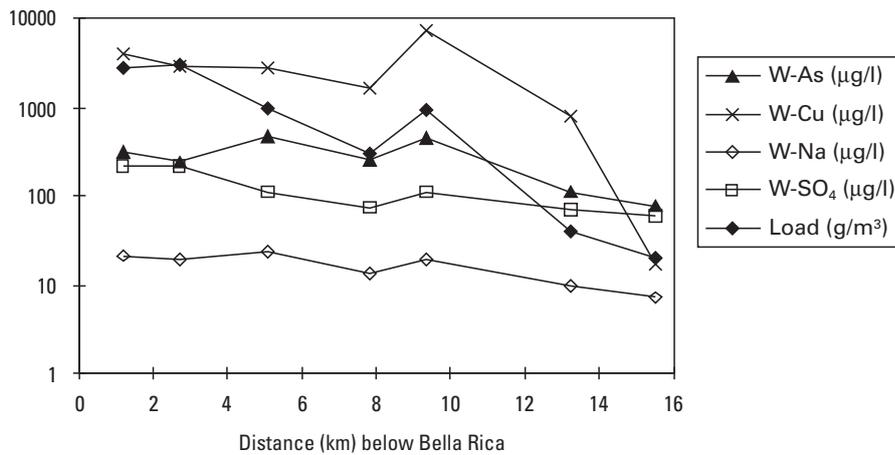


Figure 5. Downstream dispersion of contaminants in filtered water samples (W), Río Siete, Ponce Enríquez.

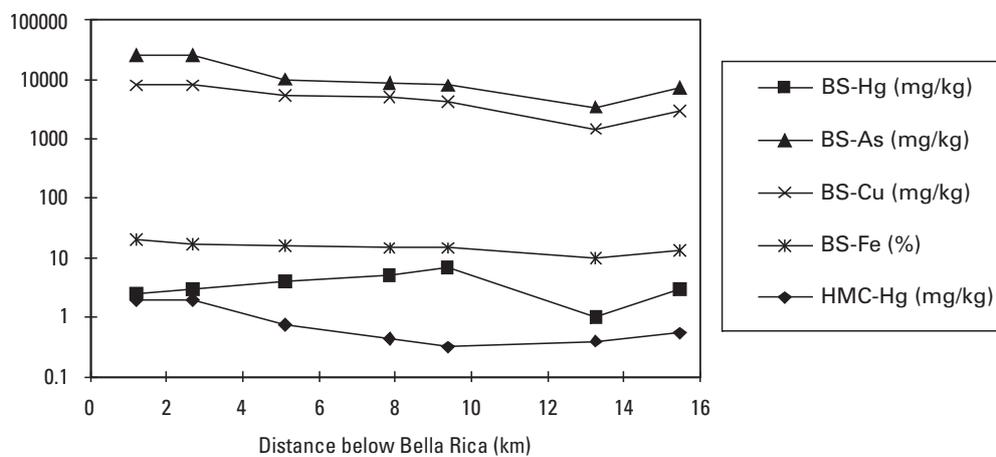


Figure 6. Downstream dispersion of contaminants in bottom sediment (BS) and heavy mineral concentrates (HMC), Río Siete, Ponce Enríquez.

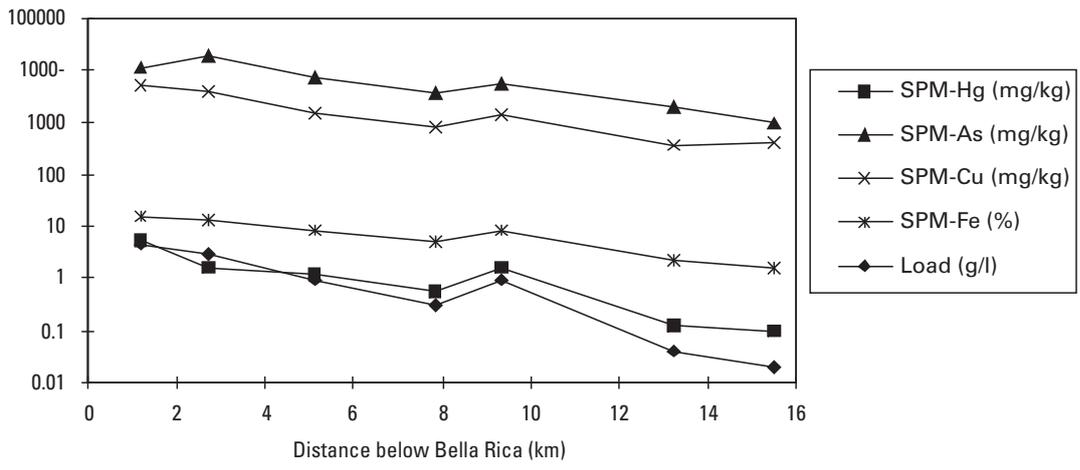


Figure 7. Downstream dispersion of contaminants in suspended particulate matter (SPM), Río Siete, Ponce Enríquez.

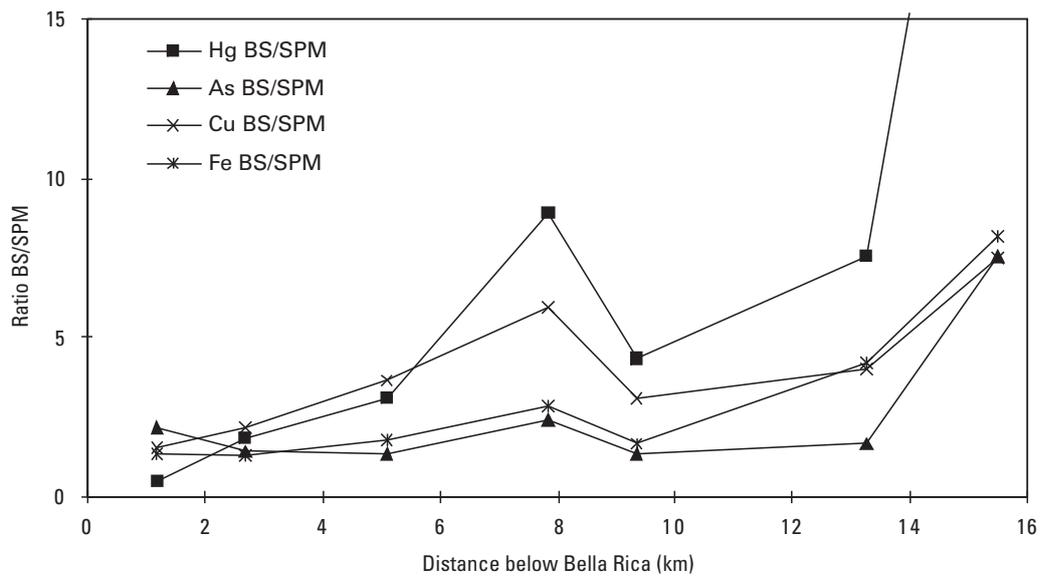


Figure 8. Relative concentrations of Hg, As, Cu and Fe in bottom sediment (BS) and suspended particulate matter (SPM) samples from the Río Siete, Ponce Enríquez area.

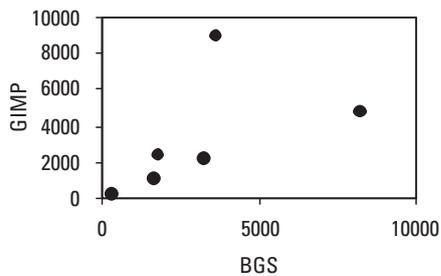
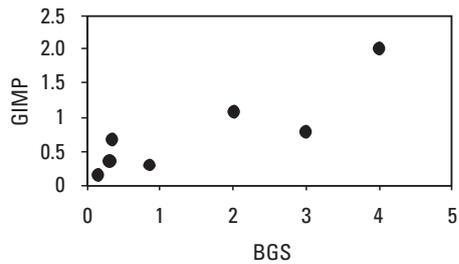


Figure 9. (a) Cu ($\mu\text{g/l}$) in filtered river water and (b) Cu (mg/kg) in bottom sediments collected at the same sites in the Ponce Enrquez area. (**GIMP** = unpublished data from 1995 BGS-PRODEMINTCA regional stream sediment survey; **BGS** = this study, July 1996 samples).

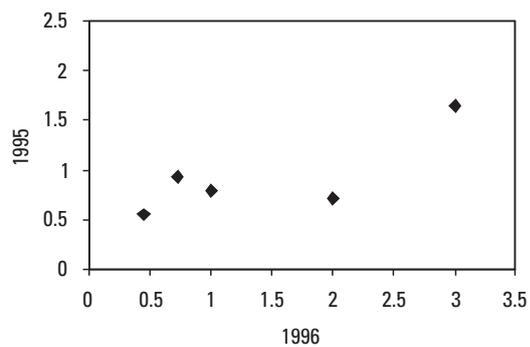


Figure 10. Hg (mg/kg) in bottom sediments collected at the same sites in the Portovelo-Zaruma area. (**1995** = unpublished data, January-February 1995 samples (Maldonado, 1996); **1996** = this study, July 1996 samples (Appleton *et al.*, 1996)).