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**Assessment of mercury contamination in
the Ponce Enríquez artisanal gold mining
area, Ecuador**

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Cover illustration: Geochemical sampling in mining-contaminated stream,
Ponce Enríquez area, Ecuador.

Table 2: Mercury in stream water (W), suspended sediment (SS), stream bottom sediment (C) and heavy mineral concentrate (P); Ponce Enríquez gold mining district, Ecuador.

Sample	W-Hg($\mu\text{g/l}$)	SS-Hg(mg/kg)	C-Hg(mg/kg)	P-Hg(mg/kg)
1	0.01	ns	0.44	2.00
2	0.01	0.59	3.00	1.00
3	0.90	1.19	13.00	5.00
5	0.01	9.61	2.00	1.00
6	0.02	1.09	3.00	3.00
7	0.01	1.38	3.00	3.00
8	0.01	1.59	3.00	2.00
9	0.01	3.57	2.00	0.73
10	0.01	ns	0.15	0.01
11	0.01	ns	0.25	0.18
12	0.01	0.01	0.69	1.00
13	0.01	0.02	0.83	0.09
14	0.01	0.02	0.84	0.03
15	0.04	1.28	4.00	0.73
17	0.01	ns	0.10	0.13
18	0.02	0.56	5.00	0.42
19	0.01	0.32	0.85	0.11
20	0.01	0.26	1.00	0.16
21	0.01	0.41	4.00	0.12
28	0.01	0.10	3.00	0.53
29	0.01	0.07	3.00	0.59
30	0.03	0.13	1.00	0.39
31	0.02	1.61	7.00	0.32
32	0.02	1.39	8.00	0.94
33	0.01	ns	0.30	0.13
34	0.01	0.01	0.33	0.12
35	0.01	0.32	0.86	0.14
36	0.01	0.48	0.58	0.08

ns = no sample

Field duplicates in **bold**

Typical concentrations of Hg in waters polluted by mining and mineral processing activities in North and South America fall in the range 0.2 to 10 $\mu\text{g/l}$ (Pfeiffer et al., 1989, 1991). There was evidence of recent working of alluvial gravels at one site in the headwaters of the Estero Guanache and this gave rise to the only high Hg value in filtered water (MA3 0.9 $\mu\text{g/l}$). The use of mercury

EXECUTIVE SUMMARY

Mobilisation of Hg through the activities of small-scale gold miners exerts a major influence on the global pollutant Hg budget. A Technology Development and Research (TDR) programme (R6226) funded by the UK Government Overseas Development Administration (ODA), Engineering Division seeks to address the adverse impacts of mining-related Hg contamination. The project objectives are:-

1. Provision of a generic protocol for monitoring the sources and fates of contaminant mercury in gold mining regions.
2. Assessment of human and ecotoxicological impacts of mercury pollution and calculation of human/environmental risk thresholds.
3. Promotion of improved methods of gold recovery with applicability to the artisanal sector.
4. Design and implementation of practical legislation for abatement of mining-related mercury contamination.

Initial geochemical surveys carried out in the Philippines (Williams et al., 1995, 1996a, 1996b) have led to the development of protocols for monitoring the sources and fates of contaminant mercury in gold mining regions. In order to test the applicability of these protocols in other topographic, climatic and geological settings, a systematic assessment of the distribution of Hg and other contaminants in the Ponce Enriquez artisanal gold mining area of Ecuador was carried out in July 1996 in collaboration with CODIGEM, DINAPA, DINAMI and Swedish Consultants working with the World Bank funded "Proyecto Desarrollo Minero y su Control Ambiental" (PRODEMINCA).

A major environmental concern in the Ponce Enriquez mining district is the potential exposure of workers to mercury as a result of its use in the recovery of gold. There is also concern regarding mercury contamination of soil, stream water, stream sediment and vegetation, particularly in downstream areas hosting economically important banana plantations and shrimp farms. In addition to the Hg hazard, large volumes of gravity tailings holding high concentrations of potentially harmful elements (copper and arsenic) are stored on the steep slopes of the Bella Rica mining sector. At the time of the BGS survey, no comprehensive information existed on the level and spatial extent of degradation caused to the aquatic environment by mining and mineral processing in the Ponce Enriquez area.

Filtered water, suspended sediment, stream bottom sediment and heavy mineral (panned) concentrate samples were collected at c. 30 sites. Mercury and a range of other elements were determined in these samples by a combination of CV-AFS and ICP-AES methods. In this report, multi-element geochemical data are presented and their significance is discussed.

Mercury exceeded the detection limit (0.02 µg/l) in only two filtered stream water samples (0.03-0.04 µg/l) from the Rio Siete which drains the main mining and mineral processing area of Bella Rica. The background range for fresh (unpolluted) waters is 0.005 to 0.05 µg/l. Hence none of the water samples from the Rio Siete exceed this range. The WHO Guideline Value and CEC Directive Maximum Admissible Concentration for Hg in drinking water, together with the UK-DOE standard recommended for compliance with the EC Shellfish Waters Directive (79/923/EEC) are all 1.0 µg/l. The more stringent USEPA Water Quality Criteria for the Protection of Aquatic Life is 0.012µg/l. Typical concentrations of Hg in waters polluted by mining and mineral processing activities in Brazil fall in the range 0.2 to 10 µg/l. There was evidence of recent working of alluvial gravels at one site on the Estero Guanache, and this gave rise to the only high Hg value in filtered water (0.9 µg/l). Heavy mineral concentrates from this locality also contain elevated levels of Hg. Dissolved Hg concentrations downstream of this anomalous site decrease to <0.02 µg/l within a distance of 2 km, probably as a

result of dilution and sorption. The concentration of Hg in stream water draining through the banana plantations and shrimp farms located 10-15 km downstream of Bella Rica is $<0.02 \mu\text{g/l}$ and has no toxicological significance.

Mercury in suspended sediments, stream bottom sediments and heavy mineral concentrates range from 0.01 to 9.61 mg/kg, 0.1 to 13 mg/kg and 0.01 to 5.0 mg/kg, respectively. The level of Hg contamination is generally much lower than recorded during the BGS survey of the Eastern Mindanao (Philippines) gold mining area, where maximum values of 1539 $\mu\text{g/l}$ and 40 mg/kg occur in stream water and suspended sediment (Williams et al., 1995). Background concentrations in uncontaminated areas typically range from 0.1 - 0.4 mg/kg in stream sediments, whereas in mining contaminated regions Hg ranges up to 7.4 mg/kg (N. Carolina) and 25 mg/kg (Madeira river, Brazil).

Hg in Rio Siete stream sediment increases from 3 mg/kg in the headwaters to 7 mg/kg approximately 10 km down stream of Bella Rica before declining to 3 mg/kg at a site 2 km upstream of the eastern margin of the shrimp ponds. Over the same transect, Hg in suspended sediments decreases from 9.6 mg/kg to 0.1 mg/kg. The relatively high Hg concentration (3 mg/kg) in stream bottom sediment immediately above the shrimp farms suggests that the average level of contaminant transfer may have been higher historically. Hg exceeds the Sediment Quality Toxic Effect Threshold for the Protection of Aquatic Life (1 mg/kg) so the bioavailability and toxicological significance of Hg in stream bottom sediments in the lower reaches of the Rio Siete merits further investigation.

Arsenic, copper, iron and sulphur are all major components of the mineralisation at Bella Rica (mainly chalcopyrite, pyrite, arsenopyrite, pyrrhotite) and are thus likely to be enriched in stream water as a result of mining and mineral processing activities.

Arsenic 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 Rio Siete above the Panamericana highway declining to 77 $\mu\text{g/l}$ immediately above the shrimp farms. Samples from the Estero Guamnache and Rio Tenguel do not exceed 50 $\mu\text{g/l}$ As. The WHO Drinking Water Guideline (10 $\mu\text{g/l}$) and CEC Directive Maximum Admissible Concentration in Drinking Water (50 $\mu\text{g/l}$) are exceeded in eleven samples although the maximum water safety level for aquatic life (400 $\mu\text{g/l}$; Fergusson, 1990) is exceeded in only one case and no samples exceeded the value of 3000 $\mu\text{g/l}$ As adopted by the UK-DOE to comply with the EC Shellfish Waters Directive (79/923/EEC). The more stringent USEPA Water Quality Criteria for fresh water (190 $\mu\text{g/l}$) is exceeded at six sites. Of greater concern, perhaps, is the potential human health risk associated with the consumption of fish or shrimps living in waters with As concentrations exceeding the USEPA Human Health value (0.14 $\mu\text{g/l}$). This level is clearly exceeded in the lower reaches of the Rio Siete immediately above the shrimp farms where an As concentration of 77 $\mu\text{g/l}$ was recorded.

Arsenic in stream bottom sediment ranges from 29 to 46,049 mg/kg declining steeply from 46,000 mg/kg in the headwaters of the Rio Siete to about 10,000 mg/kg over a distance of 4 km then more gradually to 7258 mg/kg at a site immediately above the shrimp ponds. All arsenic concentrations in stream bottom sediments in the Rio Siete exceed Sediment Quality Criteria (Toxic effects threshold) for the Protection of Aquatic Life (17 mg/kg).

Copper 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 Rio Siete to 17 $\mu\text{g/l}$ immediately above the shrimp farms. Concentrations exceed the CEC Directive Guide Level for Drinking water (100 $\mu\text{g/l}$) in 9 cases, and 5 samples exceed the WHO Drinking Water Guideline (2000 $\mu\text{g/l}$). A sample taken 3.5 km upstream of the shrimp farms on the Rio Siete contained 807 $\mu\text{g/l}$, significantly exceeding the UK-DOE standard (10 $\mu\text{g/l}$) adopted to

comply with the EC Shellfish Waters Directive (79/923/EEC) and also the USEPA Freshwater Criteria for the Protection of Aquatic Life (11 µg/l).

Copper in stream bottom sediment ranges from 65 to 9134 mg/kg declining gradually from 9,134 mg/kg in the headwaters of the Rio Siete to 2912 mg/kg at a site immediately above the shrimp ponds where the Sediment Quality Criteria (Toxic Effects Threshold) for the Protection of Aquatic Life (86 mg/kg) is exceeded by a factor of 33.

Sediment loads of up to 6.2 g/l were recorded during the present survey decreasing to 1.0 g/l in the Rio Siete at the Panamericana highway and 0.02 g/l immediately above the shrimp farms. Most of the surface drainage water in the area, especially the Rio Siete, is very turbid due to the high load of very fine grained gravity tailings. Correlation and Principal Components Analysis confirm the close association of As, Cd, Fe, Zn in both stream bottom sediments and suspended sediments. These elements are also closely correlated with the quantity of suspended sediment (g/l) confirming that the major source of contamination is the effluent from the mineral processing activities. Hg is less strongly correlated with the other major contaminants, probably because Hg contamination is at much lower level and thus tends to be much more irregular.

Although both As, Cu and Hg in stream bottom sediment from the Rio Siete immediately above the shrimp farms exceed Sediment Quality Criteria for the Protection of Aquatic Life by factors of about 400, 30, and 3 respectively, this does not necessarily imply that sediment in the shrimp farm ponds is contaminated or that these contaminants are either affecting the development of shrimps or being absorbed by the shrimps and thus a potential human health hazard. It does suggest, however, that the composition of sediment and water in the shrimp ponds, together with the shrimps and fish in the Rio Siete, should be carefully assessed. Considerable care should be taken to ensure that contaminated sediment does not enter the shrimp ponds as the high concentrations of As and Cu, as well as Hg, may negatively affect both the productivity and quality of the shrimps.

The Ponce Enríquez survey has confirmed the utility of the BGS monitoring protocol established in the Philippines under this TDR project. Longer term monitoring of this area is planned under the World Bank funded PRODEMİNCA project (*Monitoreo de los impactos ambientales, socio-económicos y sobre la salud, relacionados con las actividades mineras*) and the Fundación CENDA-COSUDE (*Proyecto Minería Sin Contaminación*) project. More detailed monitoring is required to verify the level, frequency and duration of high As and Cu fluxes in stream water and sediment. There is probably little justification for major BGS involvement in additional Hg contamination studies in the Ponce Enríquez area under the auspices of this TDR project. Data collated through the World Bank PRODEMİNCA project and the *Proyecto Minería Sin Contaminación* should provide a comprehensive picture of the influence of Hg, As and Cu contamination on biota downstream of Ponce Enríquez. This should provide supporting information for work carried out in the Philippines directed towards the other main objectives of the current project (i.e. assessment of human and ecotoxicological impacts and the promotion of improved methods of gold recovery with applicability to the artisanal sector).

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1. INTRODUCTION

The adverse human and ecotoxicological consequences of mercury (Hg) pollution in terrestrial and aquatic systems are well documented (Fergusson, 1990). Whereas most mercury pollution previously resulted from hydrocarbon combustion and manufacturing processes in industrialised regions, significant quantities of mercury are now released into the environment as a result of its use for amalgamation by small scale gold producers. The amalgamation process requires the use of about 2 tons of mercury for each ton of gold recovered. Small-scale gold miners produce thousands of tons per annum. Environmental contamination by mercury release is thus of concern especially in the countries of Latin America, South East Asia and sub-Saharan Africa which have witnessed an expansion of artisanal mining during the past two decades..

A Technology Development and Research (TDR) programme to address the adverse impacts of mining-related Hg contamination was initiated by the British Geological Survey in April 1995 under funding from the UK Government Overseas Development Administration (ODA), Engineering Division (contract R6226). The project objectives are:-

1. Provision of a generic protocol for monitoring the sources and fates of contaminant mercury in gold mining regions.
2. Assessment of human and ecotoxicological impacts of mercury pollution and calculation of human/environmental risk thresholds.
3. Promotion of improved methods of gold recovery with applicability to the artisanal sector.
4. Design and implementation of practical legislation for abatement of mining-related mercury contamination.

In 1995 and 1996, surveys were undertaken in Mindanao and Palawan in the Philippines, to assess protocols for monitoring the sources and fates of contaminant mercury in gold mining regions (Williams et al. 1995, 1996a,b). In order to test whether the monitoring protocols recommended by Williams et al. (1996b) are applicable in other topographic, climatic and

geological environments, a systematic assessment of the distribution of contaminant Hg in the Ponce Enríquez area of Ecuador was made in July 1996 (Figure I). The survey was carried out in Dr J D Appleton (BGS) in collaboration with Ing. Hugo Orbea of CODIGEM (*Corporación de Desarrollo e Investigación Geológico-Minero Metalúrgica*), Ing. Milton Carrasco of DINAPA (*Departamento Nacional de Protección Ambiental*) and Ing. Roque Maldonado of DINAMI (*Dirección Nacional de Minería*) in Machala.



Figure I: Location of the Ponce Enríquez artisanal gold mining area, Ecuador

Due to the excellent logistic support provided by CODIGEM, DINAPA and DINAMI, the sampling programme was carried out very efficiently with a total of about 30 stations visited during a 7 day period. Filtered water, suspended sediment, stream sediment and heavy mineral (panned) concentrate samples were collected at each site and approximately 150 samples analysed for Hg and associated trace and major elements.

In this report, multi-element geochemical data for stream waters, stream bottom sediment, suspended sediment and heavy mineral concentrate samples are presented and their significance discussed.

2. MERCURY GEOCHEMISTRY AND TOXICOLOGY

Hg in uncontaminated freshwater systems ranges from 5 to 50 ng/l rising to 0.1-60 µg/l in geothermal waters (Fergusson, 1990) and 0.2 to 10.0 µg/l in mining contaminated surface waters (Pfeiffer et al., 1989; 1991). At moderate or high redox potentials, inorganic Hg is predominantly stabilised as $\text{Hg}(\text{OH})_2$ at $\text{pH} > 6$, while at lower pH, HgOH^+ or chloro-complexes predominate depending on the ambient concentration of chloride. Free Hg^{2+} forms a stable dissolved phase in acid waters at redox potentials of around 0.5V whilst free Hg and HgS phases are stabilised at redox potentials of $< 0.3\text{V}$ across a wide pH range.

Inorganic Hg in sediments is usually strongly adsorbed onto mineral particles and is not readily bioavailable. Methylation of inorganic Hg in lake, river and stream sediments is a key stage in the transfer of Hg into aquatic biota. Aerobic or anaerobic bacteria present in sediments are commonly involved in the methylation process with the highest rates of methylation occurring at relatively low redox potentials of +100 - -200 mV. The methyl species formed is strongly pH dependent, with methyl mercury ($(\text{CH}_3)\text{Hg}$) most common under acid conditions and dimethyl mercury ($(\text{CH}_3)_2\text{Hg}$) in alkaline systems. The alkyl/methyl species of Hg commonly constitute 0.5-3% of the total dissolved Hg in natural waters.

Mercury adversely effects physiological and neurological processes in humans. The toxicity of Hg generally increases through the sequence:- phenyl Hg salts > Hg²⁺ salts > free Hg vapour > alkyl/methyl species. Methyl mercury is considered to be 100-1000 times more toxic than inorganic Hg so the rate and extent of methylation is clearly important. Methyl mercury, which is considerably more toxic than dimethyl mercury, causes marked degeneration of the central nervous system.

Methyl mercury is more readily taken up by biota and less slowly released than inorganic mercury. Thus bioconcentration factors for methyl mercury are 30 to 900 times greater than for inorganic mercury (WHO, 1989). Bioconcentration is likely to be further enhanced at the high ambient temperatures prevailing in hot tropical regions, such as the Ponce Enríquez area.

Humans may ingest high levels of Hg through occupational practices, such as the amalgamation process used by artisanal gold producers. Humans may also be exposed through the ingestion of Hg contaminated food. Whereas Hg is generally low in grain (5 - 20 ng/g) and vegetables (1-40 µg/g; Fergusson, 1990), methyl mercury tends to accumulate in aquatic biota. Hg in fish may be more than 20,000 times the concentration of Hg in lake waters (Craig, 1982). Consumption of Hg contaminated shellfish and fish is especially hazardous because more than 80% of the total Hg occurs as the highly toxic methyl species. Additional information on the geochemistry and toxicology of mercury is presented by Fergusson (1990).

3 MERCURY AND MINE WASTE CONTAMINATION IN THE PONCE ENRÍQUEZ AREA

The mining sector in Ecuador provides employment for a large number of people, the majority of whom are artisanal miners. The major development of the informal mining sector in southern Ecuador took place in the 1980's in Nambija where up to 20,000 people adopted relatively inefficient mining and mineral beneficiation processes. This resulted in extensive environmental degradation.

The Ponce Enríquez mining district (Figure I) 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. It has been estimated that more than 2,000 people live in the Ponce Enríquez mining settlements of which about 1000 are involved in mining the Bella Rica sector (Fig. 1).

Most of the gold and associated minerals in the high temperature hydrothermal vein mineralisation is extracted by hard rock mining methods and the gold is concentrated gravimetrically following grinding in Chilean mills (*trapiches*). Gold is recuperated from heavy mineral concentrates by amalgamation. Cyanidation plants have recently been installed to treat gravity tailings, both below Bella Rica, in the headwaters of the Rio Siete, and also adjacent to the Rio Siete near the village of La Lopez (grid reference 6424 96582).

A major environmental concern in both the Nambija and Ponce Enríquez mining districts is the potential exposure of workers to mercury as a result of its use in the recovery of gold. Mercury vapour lost during the amalgamation process presents a health risk to workers and also contaminates soils and vegetation. It has been estimated that about 2 tonnes of Hg is released to the environment each year in the Ponce Enríquez area (Landner, 1991; CODIGEM & DINAPA, pers. comm.). Part of this mercury (estimated to be about 100 kg per year) may directly contaminate streams and rivers leading to a gradual increase in Hg concentrations in the aquatic environment. Methylation of inorganic Hg in organic rich stream sediments would

magnify the environmental hazard for reasons outlined in section 2 above. Methyl mercury is readily absorbed by aquatic organisms so the potential risk to the economically important shrimp farms located downstream from the Ponce Enríquez mining district is of particular concern. Although only a very limited amount of data is available, there are indications that fish from the estuary of the Rio Siete have Hg concentrations in the range 0.31-0.36 mg/kg (wet weight) whereas the few samples of shrimps examined from shrimp farms adjacent to the Rio Siete contained lower Hg concentrations (0.01-0.04 mg/kg, wet weight; unpublished data). These Hg concentrations in fish do not exceed the human health safety threshold value for marketed fish in the USA (0.5 mg/kg; USEPA) and may fall close to the average concentrations for marine fish in the Pacific (0.16-0.30 mg/kg in tuna and mackerel; 0.07-0.09 mg/kg for other non-predatory fish; IRPTC, 1980, quoted in Williams et al., 1996a). Additional sampling and analysis of both fish and shrimps is planned as part of the World bank funded PRODEMINCA (Sub-components 3.1, 3.2) project.

Large volumes of gravity tailings which contain very high concentrations of copper (chalcopyrite) and arsenic (arsenopyrite), in addition to being contaminated with mercury, are stored on the steep slopes of the Bella Rica mining sector (Fig. 1). The tailings dumps are prone to erosion by heavy rainfall which washes the material into the Rio Siete and Estero Guanache drainage systems. Most of the surface drainage water in the area, including the Rio Siete, is turbid due to the high load of very fine grained gravity tailings. Suspended sediment loads of up to 6.2 g/l (site MA 5 ; Fig. 1) were recorded during the present survey, decreasing to 1.0 g/l in the Rio Siete at the Panamericana highway and 0.02 g/l immediately above the shrimp farms (site MA 28). This suspended material is carried downstream to the coastal plain where commercially important banana plantations and shrimp farms are located. Concern has been expressed regarding the potential damage to these economic activities caused by contaminants such as mercury, arsenic and copper contained in the gravity tailings. Conflicting reports were received during the survey regarding the use of water from the Rio Siete for irrigation of the banana plantations and for pumping into the shrimp ponds.

At the time the current survey was carried out, no comprehensive information existed on the level and spatial extent of environmental degradation caused to the drainage systems by mining and mineral processing in the Ponce Enríquez area. Preliminary monitoring of drainage water had been carried out as part of the World Bank PRODEMİNCA project (subcomponents 3.1, 3.2) but stream and suspended sediments had not been systematically monitored. Stream sediment sampling was carried out over the upland sector of the Ponce Enríquez area in 1995 as part of the CODIGEM-BGS mapping and mineral exploration project (PRODEMİNCA Subcomponent 3.3) but this programme neither extended downstream onto the coastal plain nor incorporated the full range of geochemical sample media used in the present survey (i.e. suspended sediments, stream waters and heavy mineral concentrates in addition to stream bottom sediments).

4 GEOCHEMICAL SURVEY

4.1 Sampling and analytical procedures

The locations of sample sites are indicated in Figure 1. Sample sites were selected to obtain information on the level and downstream dispersion of Hg and other contaminants derived from mining and mineral processing activities in the Ponce Enríquez area. Filtered stream water, suspended sediment, stream bottom sediment and heavy mineral concentrate samples were collected at each site apart from sites 10, 11, 17 and 33 where the amount of suspended sediment was negligible. Stream water pH, temperature, Eh and conductivity were determined in the field using appropriate temperature-compensated electrodes and Hanna Instruments meters. Calibration of the electrodes was undertaken each day using commercial buffer solutions (pH 4, 7 and 9), a Zobell Eh standard (230 mV) and a 14.86 mS KCl solution. Water samples for chemical analysis were filtered through 0.45 µm Millipore cellulose acetate membranes into 30 ml Sterilin tubes. At each site, the suite of water samples collected included:- (a) 30 ml spiked with 1% v/v HNO₃ (Baker Analytical Grade) for multi-element analysis by ICP-AES and high precision hydride generation AAS analysis of As, (b) 30 ml

unacidified water for SO₄, NO₃ and Cl analysis by ion chromatography and (c) 30 ml spiked with 0.3 ml conc. HNO₃ + 0.3 ml 0.2 vol.% K₂CrO₇ for total Hg analysis by Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS). Practical detection limits for major and trace determinands are given in Table 1.

Table 1: Practical CVAFS, ICP-AES hydride generation AAS detection limits for all elements determined in Ponce Enríquez waters (mg/l).

Hg	0.00002	As	0.0001
Na	0.012	Mg	0.018
K	0.038	Al	0.014
P	0.061	Sr	0.001
B	0.011	V	0.006
Ca	0.013	Cr	0.016
Mn	0.001	Fe	0.004
Co	0.012	Ni	0.009
Cu	0.002	Zn	0.005
Pb	0.025	Mo	0.009
Cd	0.004	Ba	0.002
Si	0.010	Be	0.0003
La	0.007	Y	0.001

Blank water samples, made using distilled water (provided by the BGS) and field acids/reagents, 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.

Sediment samples of 100-200 g mass were collected by wet-screening active stream-bed sediment through a -100 BSI mesh (-150 µm) sieve, using a minimal amount of water to avoid the loss of fine silt and clay fractions. Samples were then sealed in securitainers to avoid evaporative losses. Suspended sediment samples were obtained by filtering a fixed volume of stream water (250 or 500 ml depending upon the amount of suspended sediment) through 45 mm diameter, 0.45 µm Millipore cellulose acetate membranes using a hand operated *MityvacII* vacuum pump. Filter membranes were carefully removed to avoid contamination and stored in 30 ml Sterilin tubes. Heavy mineral concentrates (HMC) were collected by screening around 2 kg of <2mm stream alluvium, and removing the lighter fractions in a conventional prospecting pan. Mercury analyses of stream sediments and HMC were carried out by CVAFS, using 1 g milled sub-samples digested at <50°C in *aqua regia*. Suspended sediments were dried and the sediment + cellulose filter membrane digested in *aqua regia* at <50°C. Practical CVAFS digestion limit for Hg in solid samples is 0.02 mg/kg. Multi-element analysis of stream sediment and suspended sediment samples was carried out by ICP-AES using an aliquot of the *aqua regia* digestate.

4.2 Results

Concentrations of anions, cations and trace elements in filtered stream water samples are presented in Appendix 1 together with pH, Eh, conductivity and alkalinity data. Mercury concentrations in waters and other sample media are presented in Table 2.

4.2.1 Mercury

Mercury exceeded the detection limit (0.02 µg/l) in only two filtered stream water samples from the Rio Siete (MA15 0.04 µg/l and MA30 0.03 µg/l; Figures 1 and 2) which drains the main mining and mineral processing area of Bella Rica. The background range for fresh (unpolluted) waters is 0.005 to 0.05 µg/l, thus none of the water samples from the Rio Siete exceed this range.

for amalgamation at this site, is strongly inferred from the high concentrations of Hg in both stream sediment and heavy mineral concentrate (Figs. 1, 4, 5 and Table 2). 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.

The concentration of Hg in stream water draining through the banana plantations and shrimp farms located 10-15 km downstream of Bella Rica is $<0.02 \mu\text{g/l}$ and has no toxicological significance. Hg concentrations in the lower course of the Rio Siete do not exceed the stringent USEPA Water Quality Criteria for the Protection of Aquatic Life and are well below the Human Health Criteria (carcinogenic risk from consumption of aquatic organisms), and the EC Shellfish Waters Directive "P" value (Table 3). No Hg concentrations in filtered water in the Ponce Enríquez area exceeded the WHO Drinking Water Guideline value or the EEC Directive Maximum Admissible Concentration for Hg in drinking water (Table 3).

Hg in suspended sediments, stream bottom sediments and heavy mineral concentrates range from 0.01 to 9.61 mg/kg, 0.1 to 13 mg/kg and 0.01 to 5.0 mg/kg, respectively. The level of Hg contamination is generally much lower than recorded by the BGS survey of an artisanal gold mining areas in Eastern Mindanao (Philippines) where maximum values of 1539 $\mu\text{g/l}$ and 40 mg/kg have been recorded in stream water and suspended sediment (Williams et al. 1995, 1996a,b). Background concentrations in uncontaminated areas typically range from 0.1 - 0.4 mg/kg in stream sediments whereas in mining contaminated regions Hg ranges up to 7.4 mg/kg (N. Carolina; Callaghan et al., 1994) and 25 mg/kg (Madeira river, Brasil; Reuther, 1994).

Downstream variation of Hg in Rio Siete stream sediments is erratic ranging from 3 mg/kg immediately below the main Bella Rica mining and mineral processing area to 3 mg/kg some 15 km downstream of Bella Rica, at a site which is only 2 km upstream of the eastern margin of the commercially important shrimp ponds (Figure 4). Over the same transect, Hg in suspended sediments decreases from 9.6 mg/kg to 0.1 mg/kg (Figure 3). Hg in suspended sediments decreases by a factor of nearly 100 over a distance of 15 km, suggesting that the

contaminant load at the time of sampling was low. However, the relatively high Hg concentration (3 mg/kg) in stream bottom sediment 15 km below Bella Rica suggests that the average level of contaminant transfer may have been higher historically. The bioavailability of Hg in stream bottom sediments in the lower reaches of the Rio Siete merits further investigation as Hg at site MA28 exceeds the Toxic Effect Threshold for the Protection of Aquatic Life (Table 4).

Table 3. Comparison of potentially harmful element concentrations in filtered water samples from above the Rio Siete shrimp farms (MA-28 and 30, see Fig. 1) with maximum concentrations in the Ponce Enríquez area and Water Quality Criteria

	Freshwater ¹		Saltwater ¹		Shellfish Directive (79/923/EEC) ⁴	Human health ^{1,5}	WHO Drinking Water	EEC Drinking Water MAC	Ponce Enríquez		
	Max. Conc. ²	Cont. Conc. ³	Max. Conc. ²	Cont. Conc. ³					MA28	MA30	Max.
As	360	190	69	36	3000	0.14	10	50	77	109	470
Cd	3.7	1	42	9.3	330	-	5	5	<4	<4	9
Cu	17	11	2.4	2.4	10	-	2000	100	17	809	7277
Pb	65	2.5	210	8.1	100	-	50	50	na	na	na
Hg	2.1	0.012 ⁶	1.8	0.025	1	0.15	1	1	<0.02	0.03	0.9
Ni	1400	160	74	8.2	100	4600	-	50	<10	<10	165
Zn	110	100	90	81	10	-	5000	-	49	46	821

Footnotes:

¹ EPA Section 304 (a) Criteria for the Protection of Aquatic Life from Priority Toxic Pollutants (US CleanWater 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

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 Human health (10⁻⁶ risk for carcinogens) for consumption of aquatic organisms living in waters. For 10⁻⁵ risk, move decimal point one place to the right.

⁶ 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 4. Comparison of potentially harmful element concentrations in suspended sediments (SS) and stream bottom sediments (C) from above the Rio Siete shrimp farms (MA-28 and 30, see Fig. 1) with maximum concentrations in the Ponce Enríquez area and Sediment Quality Criteria for Protection of Aquatic Life (concentrations in mg/kg).

	Sediment Quality Criteria ¹			Ponce Enríquez					
	No effects threshold	Minimal effects threshold	Toxic effects threshold	MA28-SS	MA30-SS	Max.-SS	MA28-C	MA30-C	Max.-C
As	3	7	17	957	1997	22626	7258	3392	46049
Cd	0.2	0.9	3	2	1	18	12	9	24
Cu	28	28	86	387	352	6437	2912	1428	9134
Pb	23	53	170	123	333	1061	175	85	666
Hg	0.05	0.2	1	0.1	0.13	9.61	3	1	13
Zn	100	150	540	108	172	743	347	177	924

¹ Sediment Quality Criteria for Protection of Aquatic Life (Environment Canada, 1992 quoted in MacDonald, 1994).

4.2.2 Arsenic, Cadmium, Copper, Iron, Lead, Sodium, Sulphate and Zinc

As, Cd, Cu, Fe, Pb, Zn and sulphur are all major or minor components of the mineralisation at Bella Rica (chalcopyrite, pyrite, arsenopyrite, pyrrhotite). Thus these elements are likely to be inherently enriched in stream water with concentrations further enhanced by mining and mineral processing activities. Sodium (Na) is a component of the principal compound used in gold cyanidation. It is thus commonly enriched in discharge effluents but its presence in stream waters need not necessarily indicate that cyanide concentrations are also elevated. The main cyanidation plants are located below Bella Rica in the headwaters of the Rio Siete and close to La Lopez (grid reference 6424 96582; Fig. 1).

4.2.2.1 Filtered Water

High precision (hydride generation AAS to 0.1 µg/l LoD) analysis of As in the Ponce Enríquez stream waters indicate that the highest concentrations occur in the Rio Siete reaching a maximum of 470 µg/l (Appendix 1 and Figure 6). Arsenic in stream water ranges from 0.1 to 470 µg/l, with an erratic distribution of high concentrations (240-470 µg/l) in the Rio Siete above the

Panamericana highway declining to 77 µg/l immediately above the shrimp farms (MA 18, Figure 6). There are anomalous peaks in the downstream dispersion pattern at sites MA15 and MA 31 which may be caused by temporally high release of contaminated water from mineral processing plants located adjacent to the Rio Siete. Water samples were collected on different days and may thus be subject to temporal variations. Concentrations of As in the Estero Guanache and Rio Tenguel do not exceed 40 µg/l and are generally less than 10 µg/l. Whereas the WHO Drinking Water Guideline (10 µg/l) and the EC Directive Maximum Admissible Concentration in Drinking Water (50 µg/l) are clearly exceeded in several instances, the maximum water safety level for aquatic life (400 µg/l; Fergusson, 1990) is exceeded in only one sample (MA 15, Figure 6). No samples exceed the value of 3000 µg/l As adopted by the UK-DOE to comply with the EEC Shellfish Waters Directive (79/923/EEC) but the more stringent USEPA Water Quality Criteria for fresh water (190 µg/l) is exceeded at five sites (Appendix 1 and Figure 6). Of greater concern, perhaps, is the potential human health risk (based on 10⁻⁶ risk for carcinogens) associated with the consumption of fish or shrimps living in waters with As concentrations >0.14 µg/l (Table 3). This level is clearly exceeded in the lower reaches of the Rio Siete immediately above the shrimp farms.

Copper in stream water ranges from <2 to 7277 µg/l (Appendix 1 and Figure 6), declining rather erratically from 3-4,000 µg/l in the headwaters of the Rio Siete to 17 µg/l immediately above the shrimp farms (MA 18, Figure 6). There is an anomalous peak in the downstream dispersion pattern at site MA 31 (7277 µg/l) which may be caused by a temporally high release of contaminated water from mineral processing plants located adjacent to the Rio Siete. Water samples were collected on different days and may thus be subject to temporal variations which should not affect stream sediment concentrations, for example. Copper in nine water samples exceeds the EEC Directive Guide Level for Drinking water (100 µg/l) and 5 samples exceed the WHO Drinking Water Guideline (2000 µg/l). A sample taken about 3.5 km upstream of the shrimp farms on the Rio Siete contained 807 µg/l 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 USEPA Freshwater Criteria for the Protection of Aquatic Life (11 µg/l; Table 3). If the temporal variation indicated by the very high Cu concentration in MA 31 are common, higher

concentrations may occur in the vicinity of the shrimp farms as a result of the release of contaminants. More detailed monitoring is required to verify the level, frequency and duration of high contaminant fluxes in stream water.

Iron (Fe) in stream water ranges from <0.004 to 6.0 mg/l (Appendix 1) with the highest concentrations associated with very acid waters in the headwaters of the Estero Guanache and a stream draining to the north of Bella Rica into the Rio Tenguel (site MA35). The fourth relatively high Fe concentration is in the headwaters of the Rio Siete which is somewhat unusual as the pH is very high (9.7). This could infer the presence of ferrous/ferric cyanide complexes, or uncomplexed Fe²⁺ in reducing waters. Only four values exceed the WHO Drinking Water Guideline (300 µg/l) and the EEC Maximum Admissible Concentration (MAC, 200 µg/l). Fe concentration immediately above the shrimp farms is only 12 µg/l (Appendix 1).

Sulphate concentrations in filtered stream waters reflect contamination derived from sulphide oxidation products from gravity tailings. Only two samples exceed the WHO Drinking Water Guideline (400 mg/l) and 5 samples the EEC MAC (250 mg/l). Such concentrations are not exceptional for streams draining sulphide mining and mineral processing districts.

The influence of the outflow from cyanidation plants adjacent to the Rio Siete is indicated by enhanced stream water pH, Ca and Na (Appendix 1 and Fig. 9) although the values 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.

The relationship between major cations, ions and trace elements, pH, Eh, conductivity and alkalinity in filtered stream waters is indicated in the Spearman Correlation Matrix (Appendix 2).

4.2.2.2 Stream bottom sediment and suspended sediment

Concentrations of As, Cd, Cu, Fe, Hg, Mn, Pb and Zn in stream bottom sediments (-150 μ m fraction) and suspended sediments are indicated in Appendices 2 and 3. As, Cu, and Fe are all major components of the primary mineralisation and gravity tailings at Bella Rica (principally occurring in chalcopyrite, pyrite, arsenopyrite, pyrrhotite and their alteration products). Erosion of tailing dumps during heavy rainfall and channeling of waste water from mineral processing activities directly into the surface drainage system has resulted in extensive contamination of the drainage systems in the Ponce Enriquez area. Suspended sediment loads of up to 6.2 g/l (site MA 5 ; Fig. 1) were recorded during the present survey decreasing to 1.0 g/l in the Rio Siete at the Panamericana highway and 0.02 g/l immediately above the shrimp farms (site MA 28). This suspended material is carried downstream to the coastal plain where the commercially important banana plantations and shrimp farms are located.

It is not, therefore, surprising that As and Cu are highly anomalous in stream sediments and suspended sediments from the Rio Siete, Estero Guanache and Rio Tenguel. Maximum contaminated stream sediment:background ratios are about 1000 for As, 150 for Cu, 8 for Cd, 10 for Hg, 25 for Pb and 12 for Zn. *Correlation and Principal Components Analysis confirm the close association of As, Cd, Fe, Zn in both stream bottom sediments and suspended sediments. These elements are also closely correlated with the quantity of suspended sediment (g/l) confirming that the major source of contamination is the gravity tailings and effluent from the mineral processing activities.* Hg, Pb, and Mn are less strongly correlated with the other major contaminants, either because they are relatively minor components of the mineralisation or, in the case of Hg, because Hg contamination is at much lower concentrations and thus tends to be much more irregular.

Arsenic in the -150 μ m fraction of stream bottom sediment ranges from 29 to 46,049 mg/kg (Appendix 2 and Figure 11) declining steeply from 46,000 mg/kg in the headwaters of the Rio Siete to about 10,000 mg/kg over a distance of 4 km then more gradually to 7258 mg/kg at a site immediately above the shrimp farms (MA 18, Figure 11). In the corresponding suspended sediment samples, arsenic concentrations decrease from 22,626 mg/kg to 957 mg/kg. All

arsenic concentrations in stream bottom sediments in the Rio Siete exceed Sediment Quality Criteria (Toxic Effects Threshold) for the Protection of Aquatic Life by a factor of up to 2700 (Table 4).

Copper in the $-150\mu\text{m}$ fraction of stream bottom sediment ranges from 65 to 9134 mg/kg (Appendix 2 and Figure 13) declining gradually from 9,134 mg/kg in the headwaters of the Rio Siete to about 1500 mg/kg at site MA30 before rising to 2912 mg/kg at a site immediately above the shrimp farms (MA 18, Figure 13). In the corresponding suspended sediment samples, copper concentrations decrease from 6437 mg/kg to 387 mg/kg. All copper concentrations in stream bottom sediments in the Rio Siete exceed Sediment Quality Criteria (Toxic Effects Threshold) for the Protection of Aquatic Life by a factor of up to 106 (Table 4). The anomalous peak in the downstream dispersion pattern at site MA 31 seen in water Cu is also reflected in the suspended sediment Cu (Appendix 3, Figure 14). This is probably caused by a temporally high release of contaminated sediment from mineral processing plants.

Cadmium in stream sediment at site MA28 exceeds Sediment Quality Criteria (Toxic Effects Threshold) for the Protection of Aquatic Life by a factor of 4 reaching a maximum of 16 in the headwaters of the Rio Siete (Table 4). Pb and Zn in stream sediment from the lower section of the Rio Siete (sites MA28 and 30) are either lower, or do not significantly exceed, the Sediment Quality Criteria for the Protection of Aquatic Life (Table 4).

Although both As and Cu in stream bottom sediment from the Rio Siete immediately above 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 does not necessarily imply that sediment in the shrimp farm ponds is contaminated or that these contaminants are either affecting the development of shrimps or being absorbed by the shrimps. It does suggest, however, that the composition of sediment and water in the shrimp ponds, and the shrimps themselves, should be carefully assessed. Considerable care should be taken to ensure that contaminated sediment does not enter the shrimp ponds as the high

concentrations of As and Cu, as well as Hg, may negatively affect both the productivity and quality of the shrimps.

5. CONCLUSIONS AND RECOMMENDATIONS

The results of the Ponce Enríquez (Ecuador) survey confirm that mining-related Hg contamination is of limited and rather sporadic significance. Dispersion of Hg in solution is very restricted. The main transfer of Hg appears to occur in association with stream sediment, carried either as metallic Hg, Hg amalgamated with Au or adsorbed onto particulate surfaces. Preliminary data indicate that As and Cu contamination derived from mine spoil may have greater environmental significance. The toxicological impact of As, Cd, Cu and Hg on commercially important shrimp farms and banana plantations located downstream of the Bella Rica mining area is urgently needed and is currently being assessed by PRODEMINCA. The investigation, design and implementation of alternative processing technologies involving Hg, as outlined in the original project memorandum, should be considered in this area and more efficient methods of restricting the dispersion of mining and mineral processing spoil should be investigated and implemented.

The Ponce Enríquez survey has confirmed the utility of the monitoring protocol established in the Philippines. Longer term monitoring of this area is planned under the World Bank funded PRODEMINCA project (*Monitoreo de los impactos ambientales, socio-económicos y sobre la salud, relacionados con las actividades mineras*) and the Fundación CENDA - COSUDE (*Proyecto Minería Sin Contaminación*). There is thus little justification for major BGS involvement in additional Hg contamination studies in the Ponce Enríquez area under the auspices of the current TDR project. Data collated through the World Bank PRODEMINCA project and the *Proyecto Minería Sin Contaminación* should provide a comprehensive picture of the influence of Hg, As and Cu contamination on biota downstream from the Ponce Enríquez mining district. This should provide supporting information for work carried out in the Philippines directed towards the other main objectives of the current project (i.e.

assessment of human and ecotoxicological impacts and the promotion of improved methods of gold recovery with applicability to the artisanal sector).

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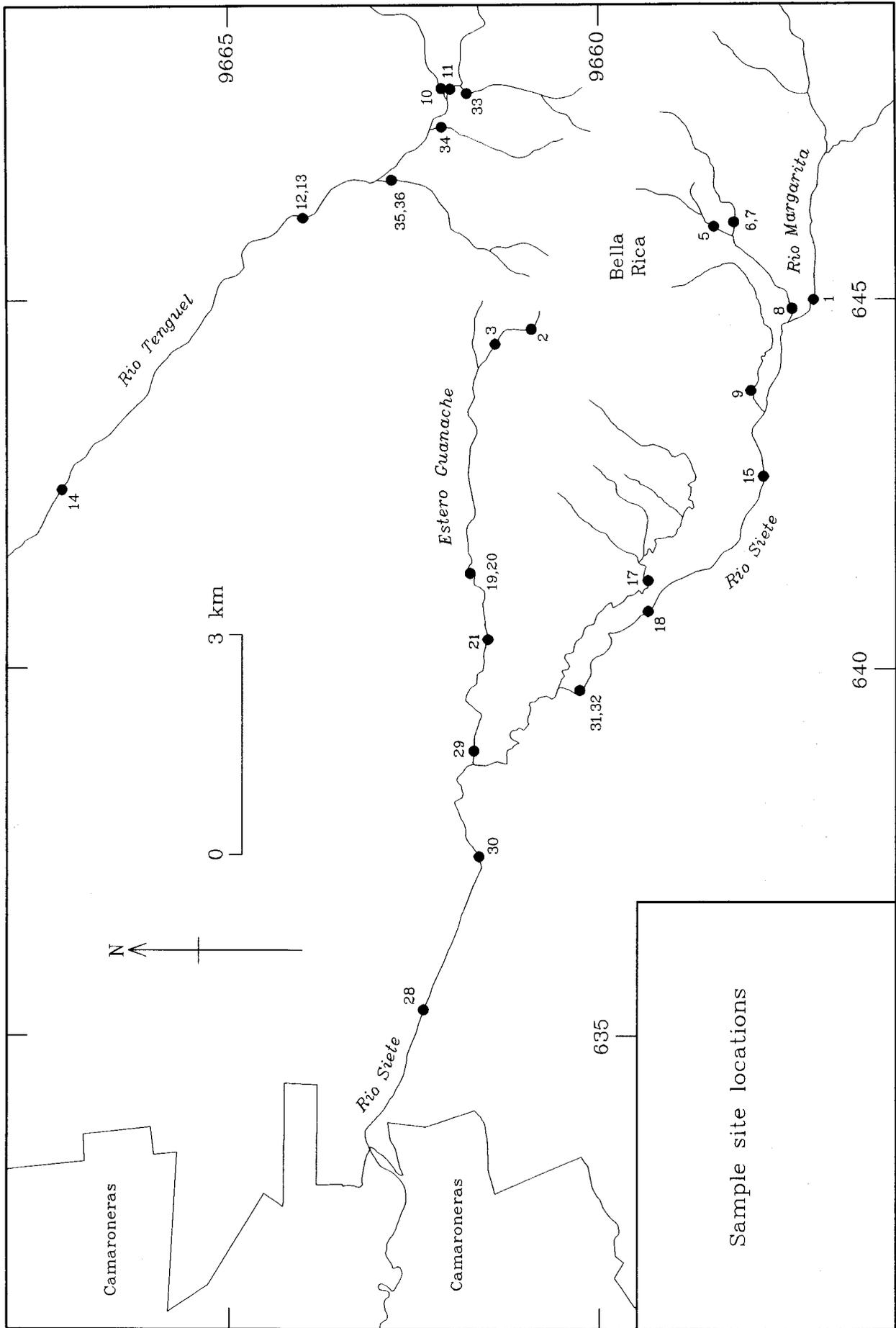


Figure 1: Sample site locations: Ponce Enríquez district, Ecuador

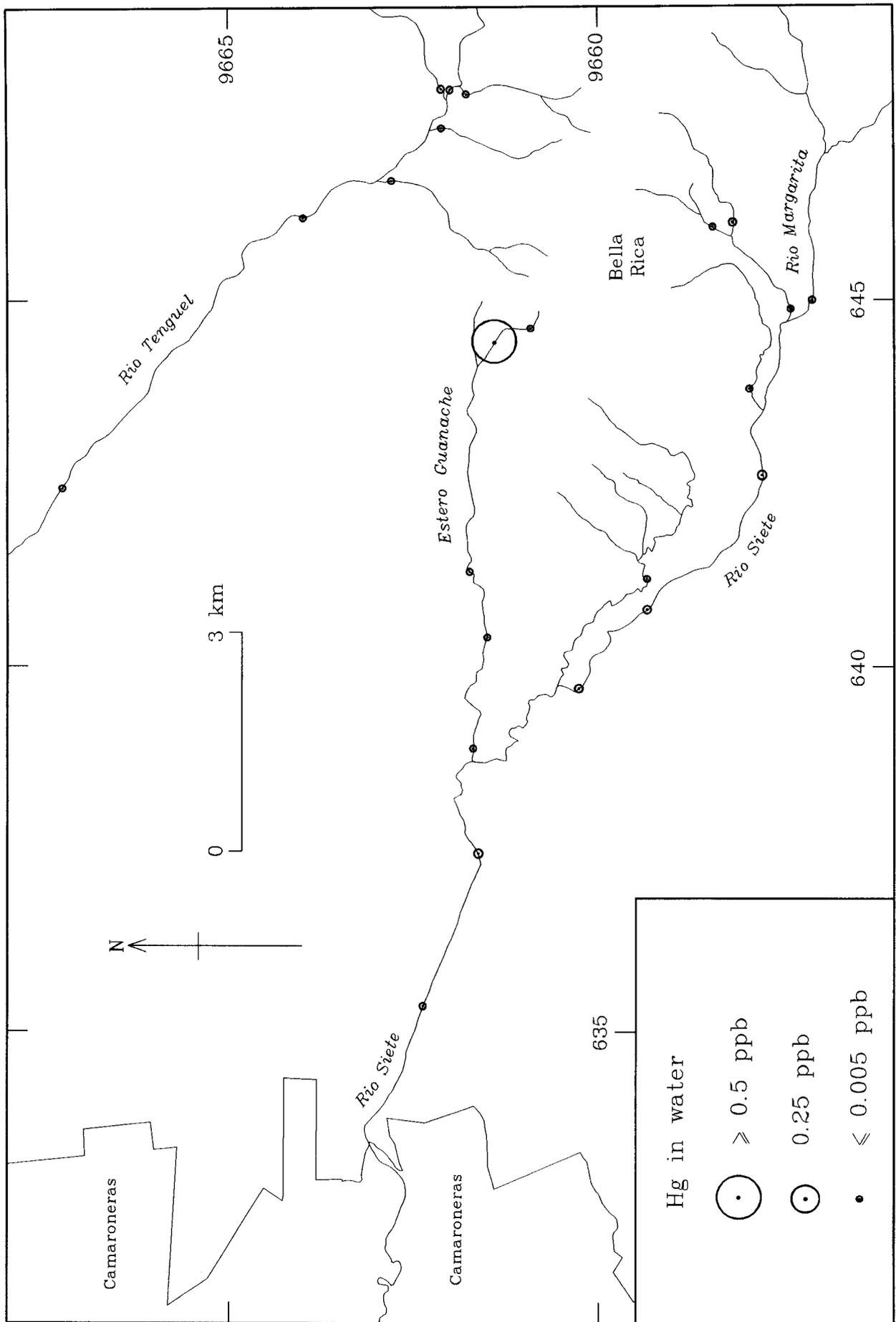


Figure 2: Hg in stream water: Ponce Enriquez district, Ecuador

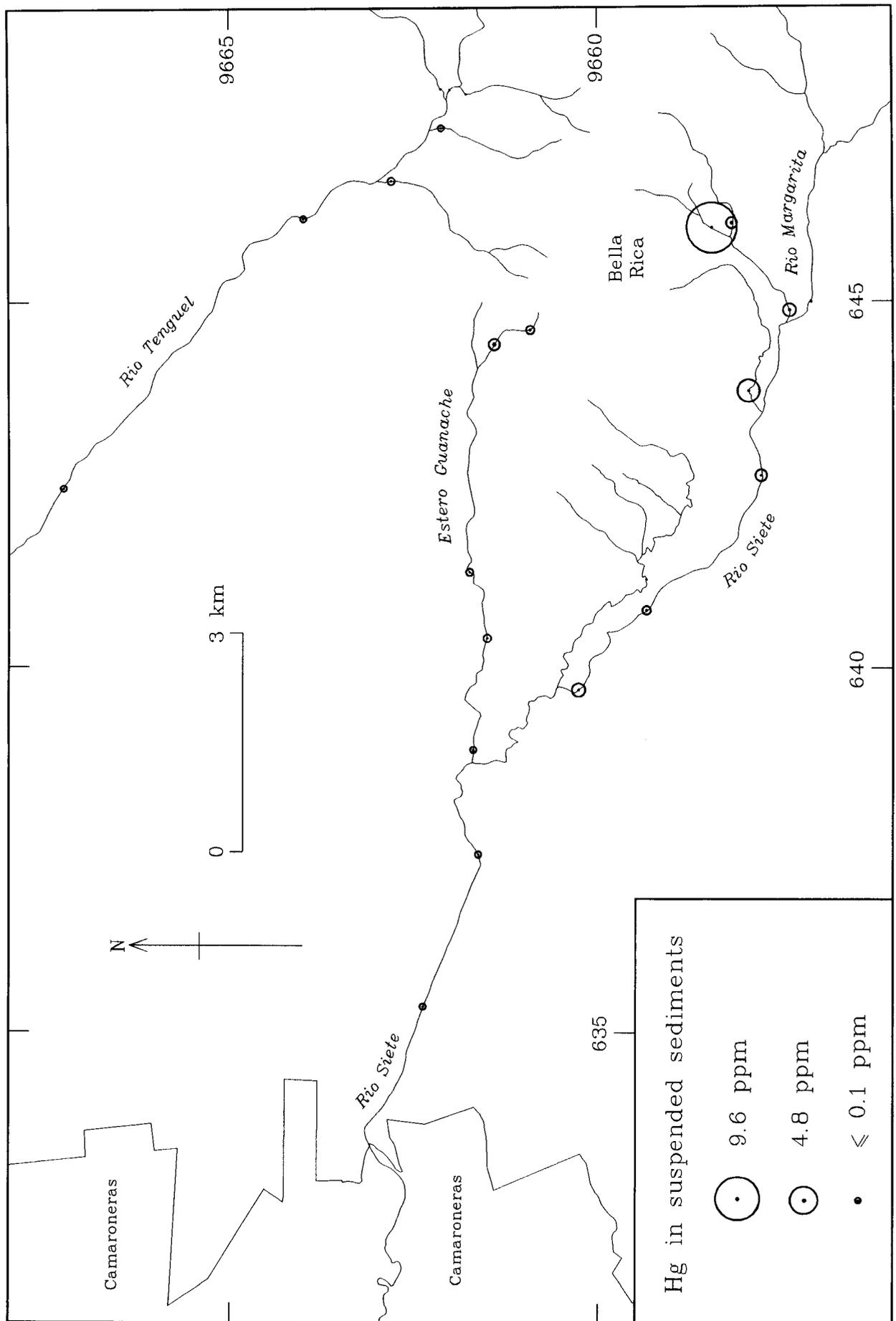


Figure 3: Hg in suspended sediments: Ponce Enríquez district, Ecuador

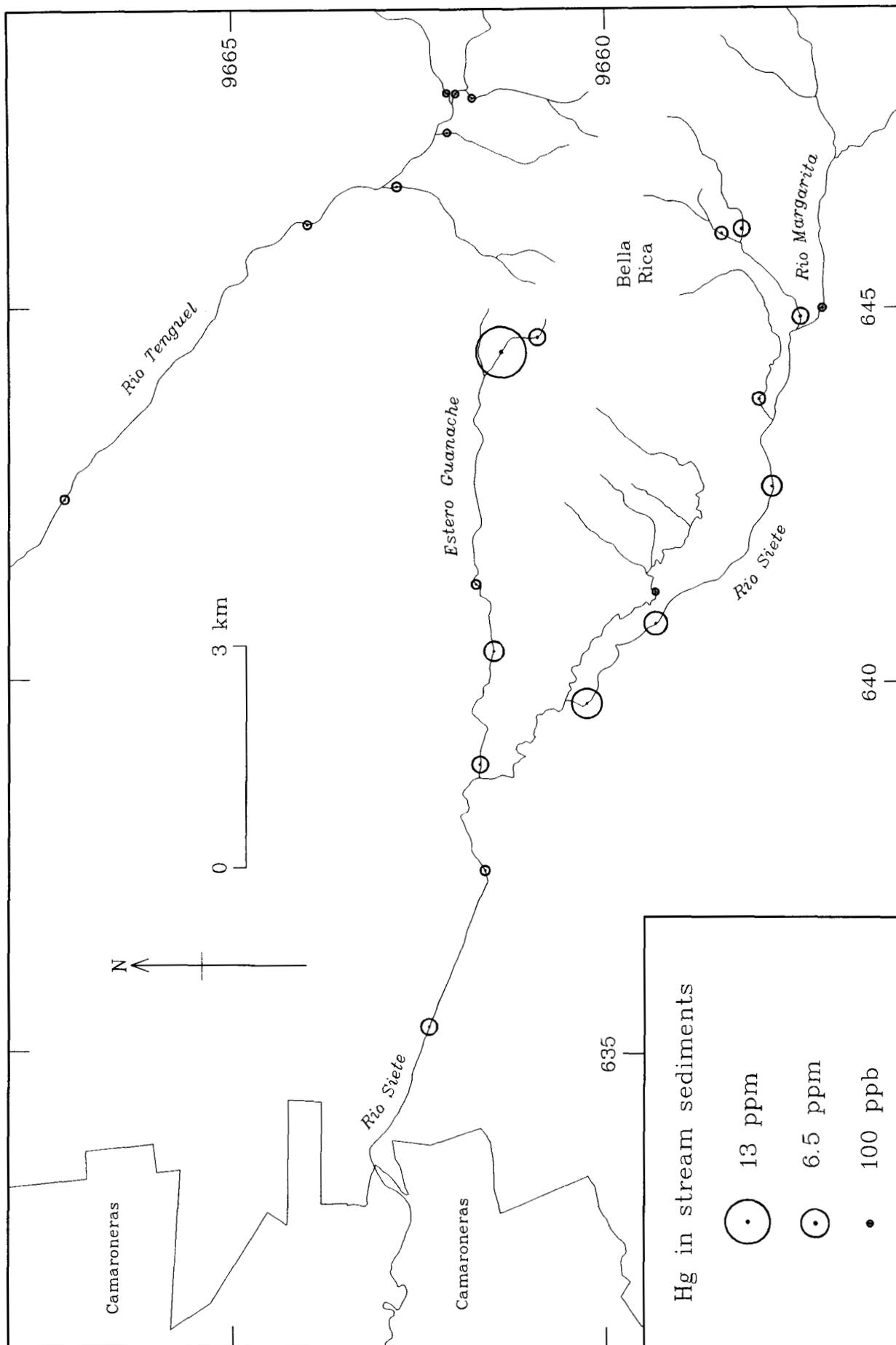


Figure 4: Hg in stream sediments (-150 μ m fraction) : Ponce Enríquez district, Ecuador

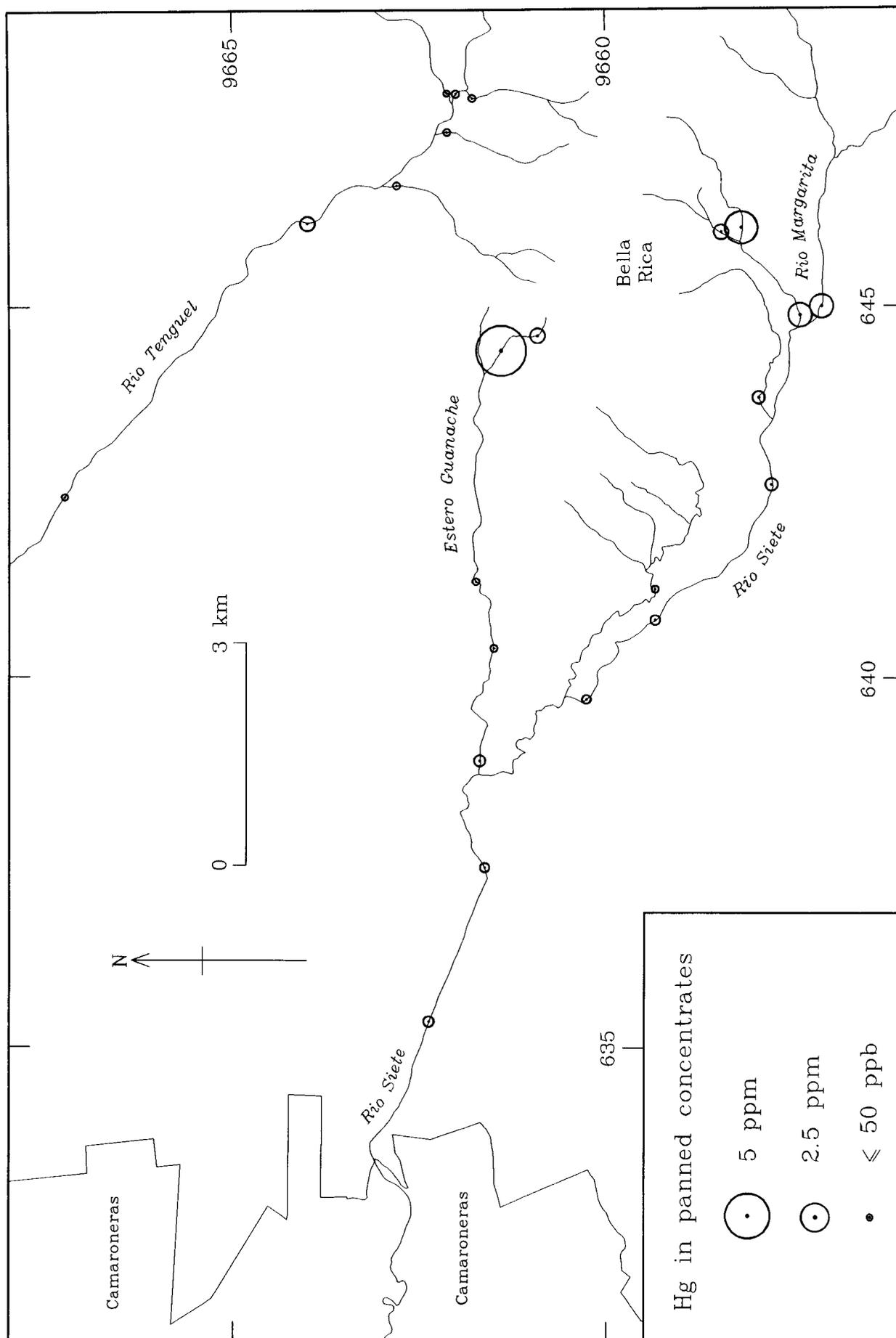


Figure 5: Hg in heavy mineral (panned) concentrates : Ponce Enríquez district, Ecuador

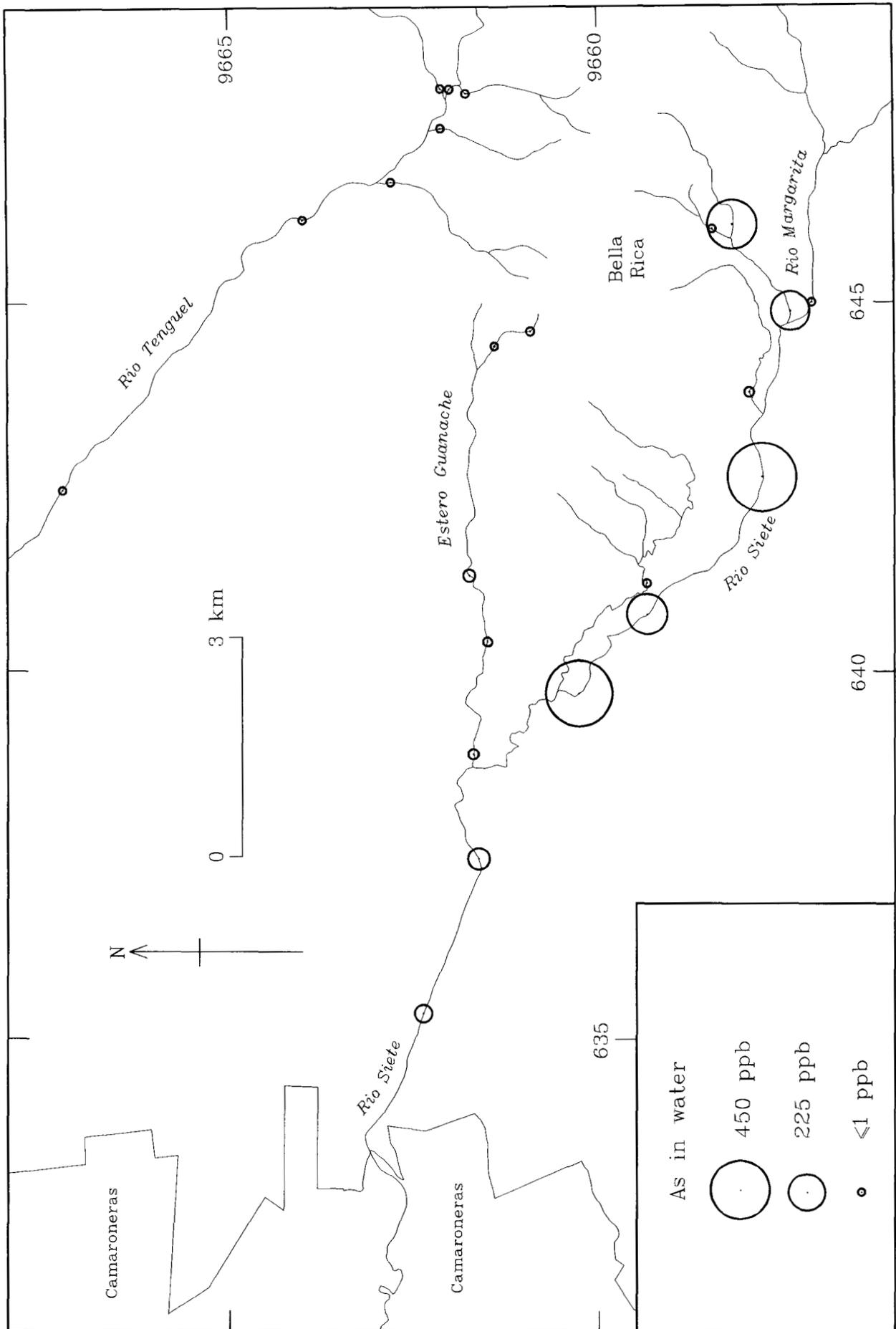


Figure 6: As in filtered stream water : Ponce Enríquez district, Ecuador

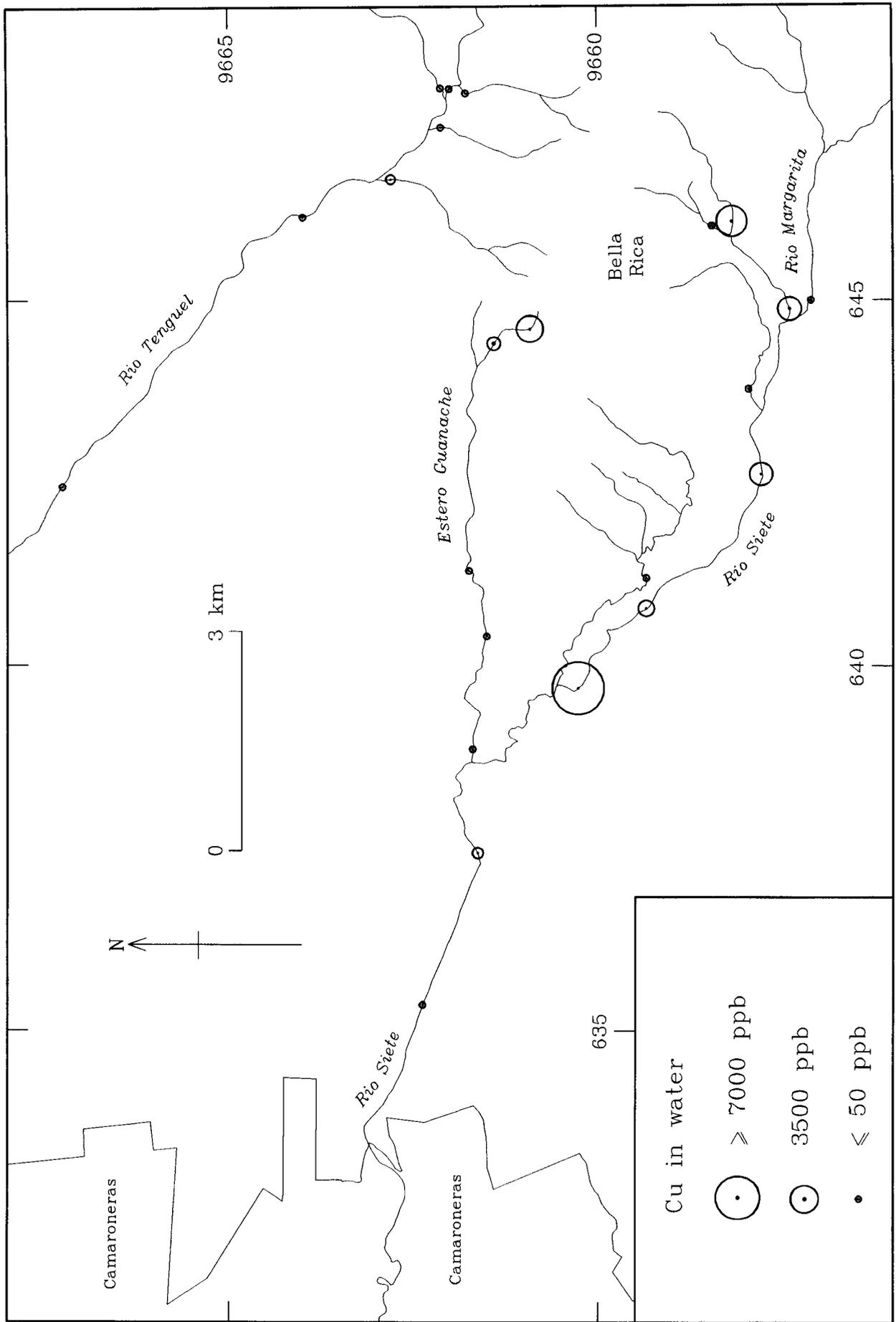


Figure 7: Cu in filtered stream water : Ponce Enríquez district, Ecuador

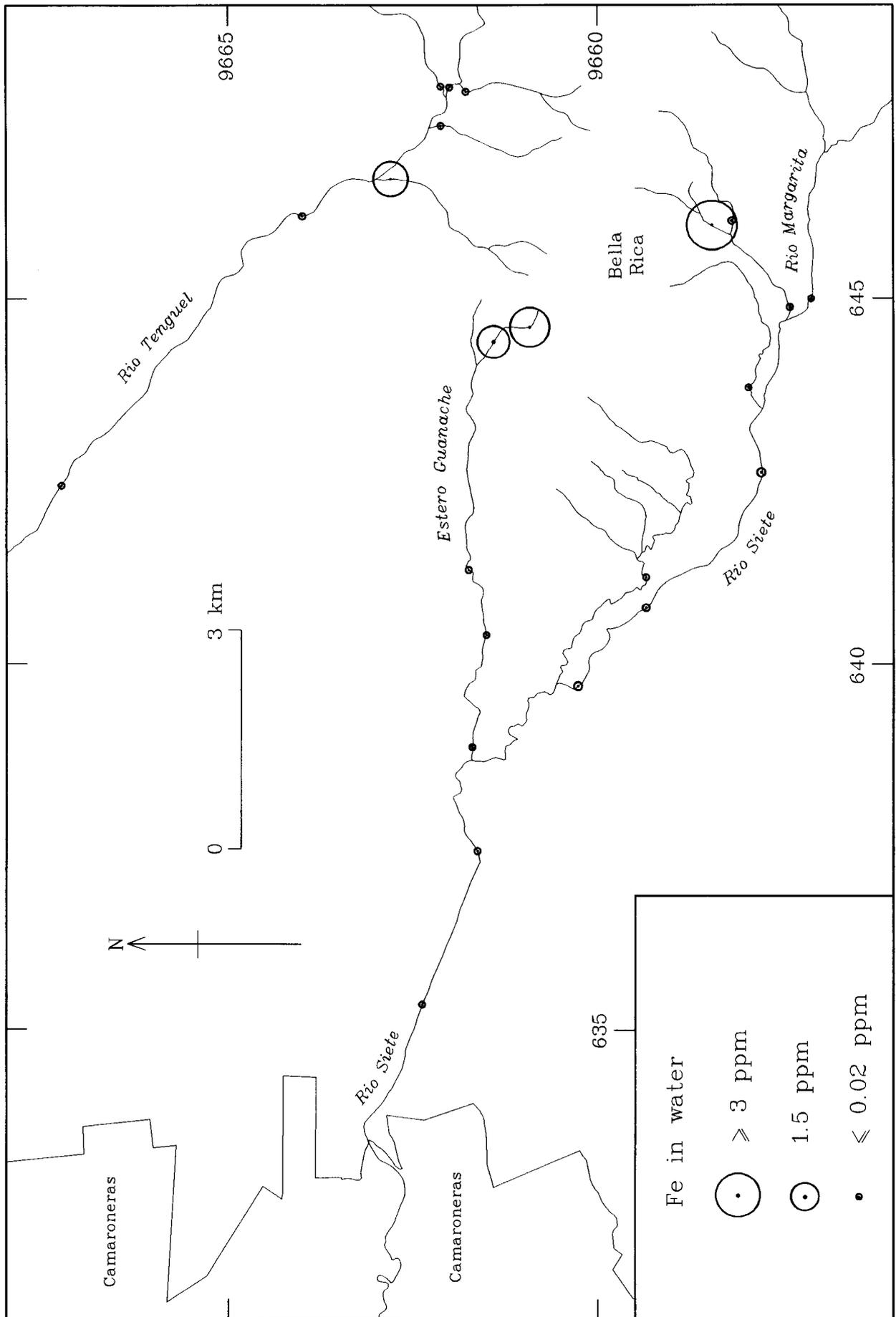


Figure 8: Fe in filtered stream water : Ponce Enríquez district, Ecuador

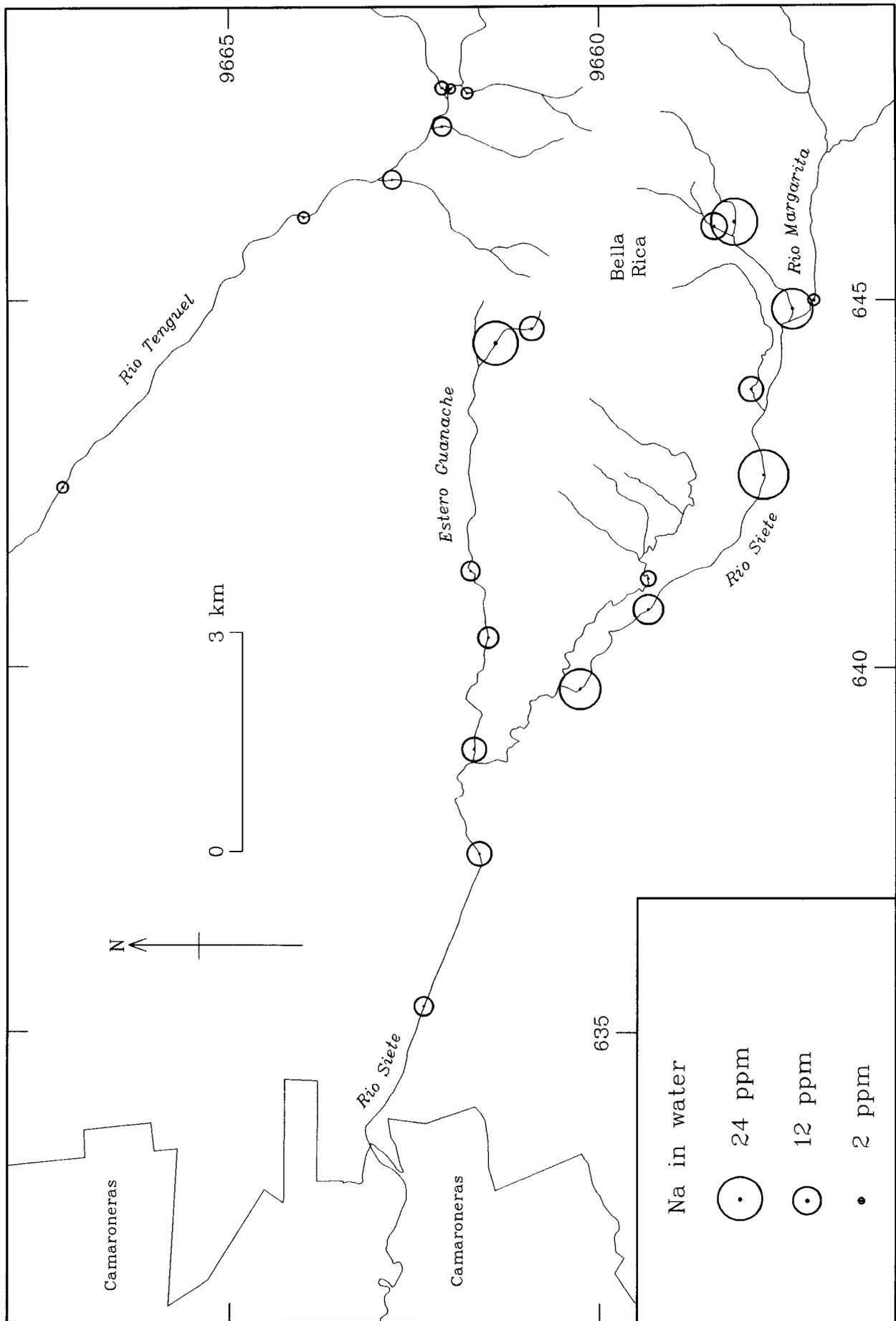


Figure 9: Na in filtered stream water : Ponce Enríquez district, Ecuador

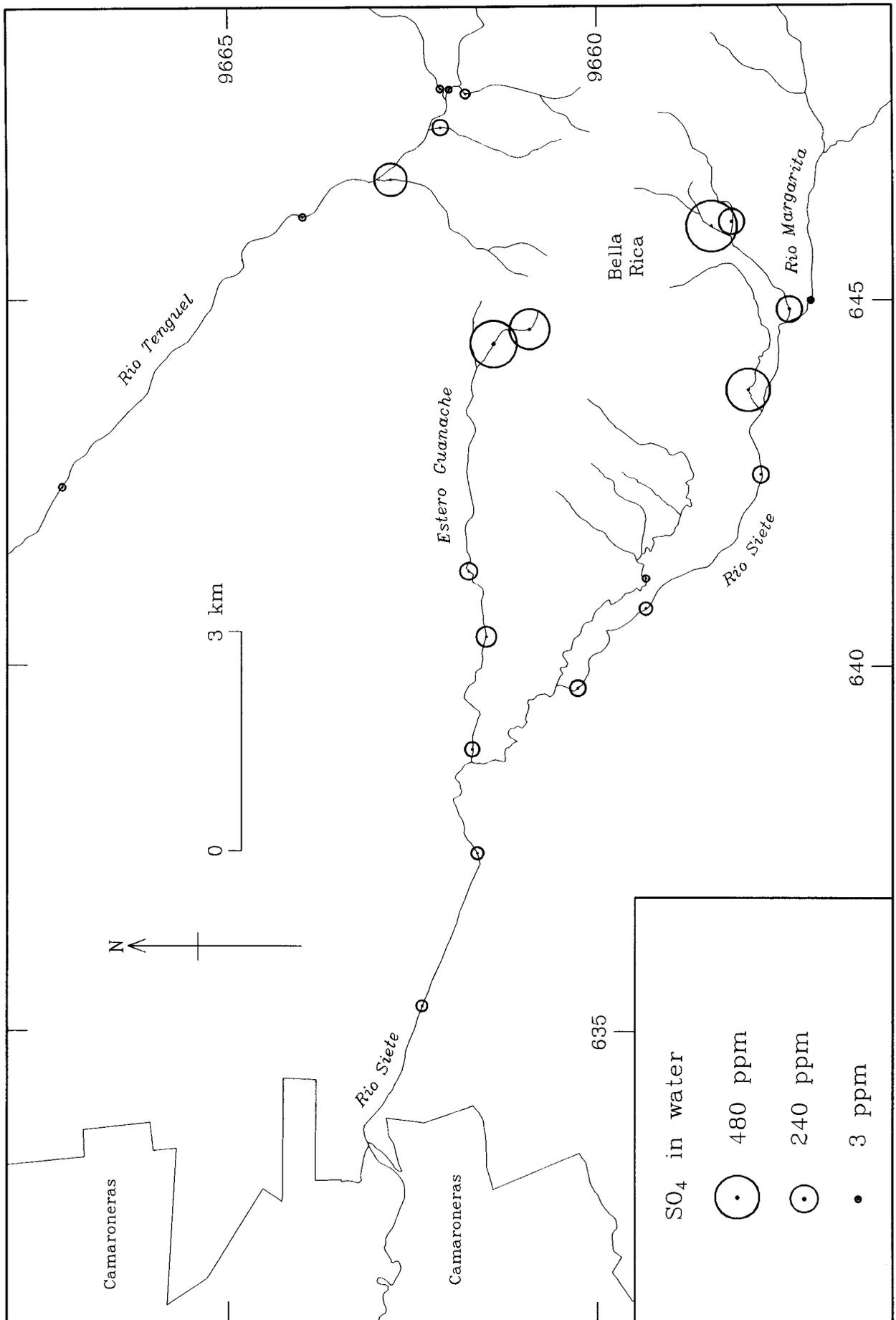


Figure 10: SO₄ in filtered stream water : Ponce Enríquez district, Ecuador

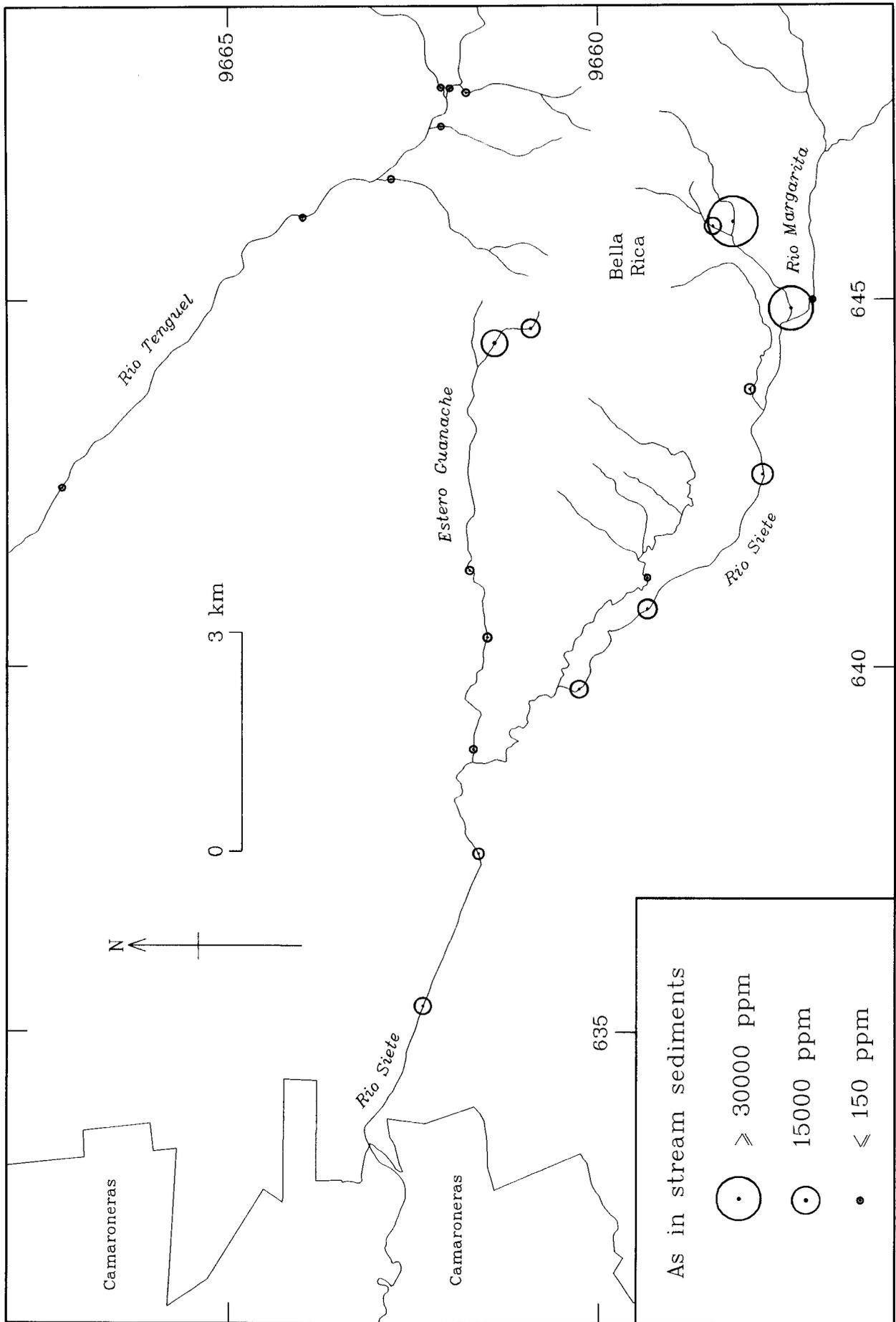


Figure 11: As in -150 μ m fraction of stream sediments : Ponce Enríquez district, Ecuador

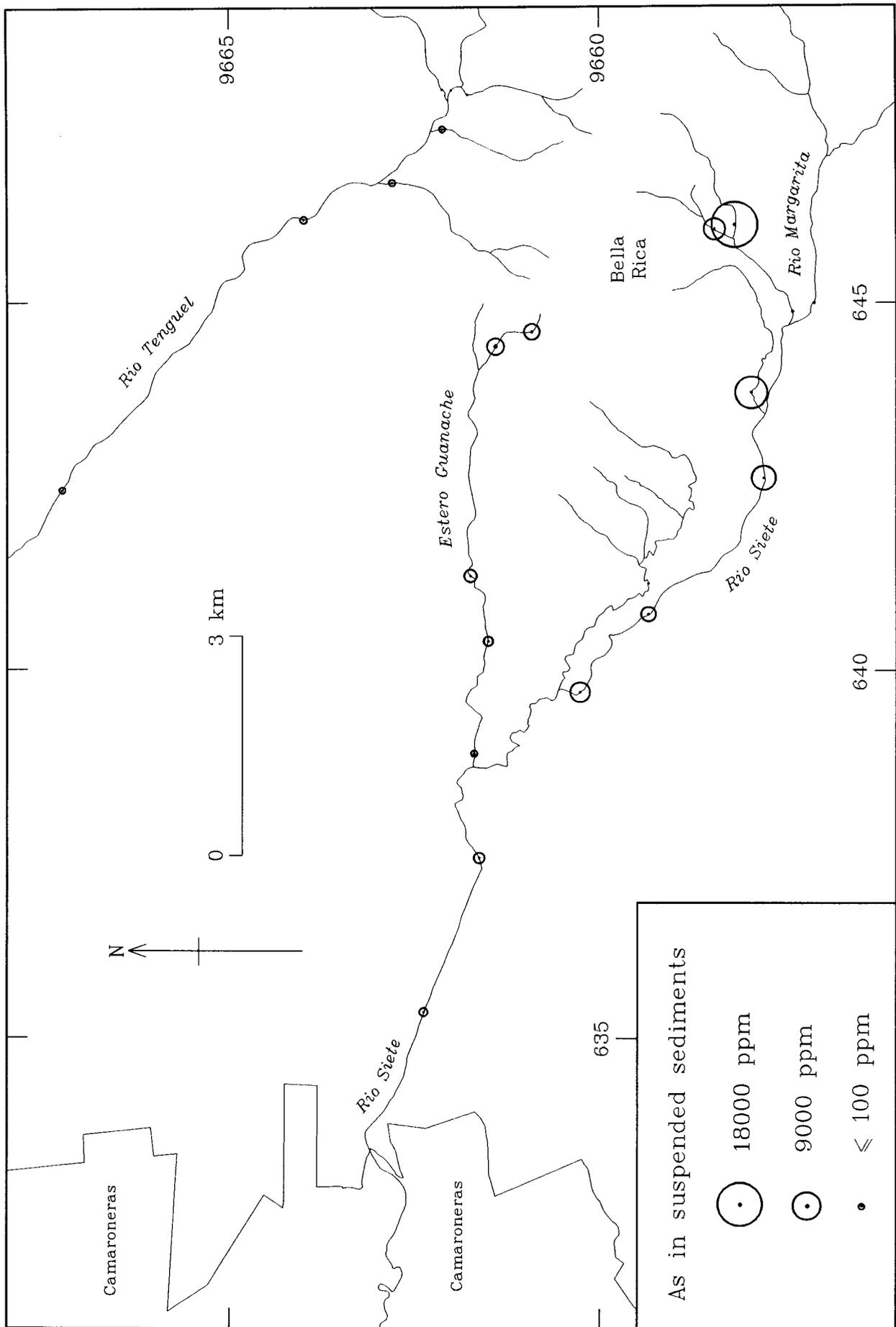


Figure 12: As in suspended sediments : Ponce Enríquez district, Ecuador

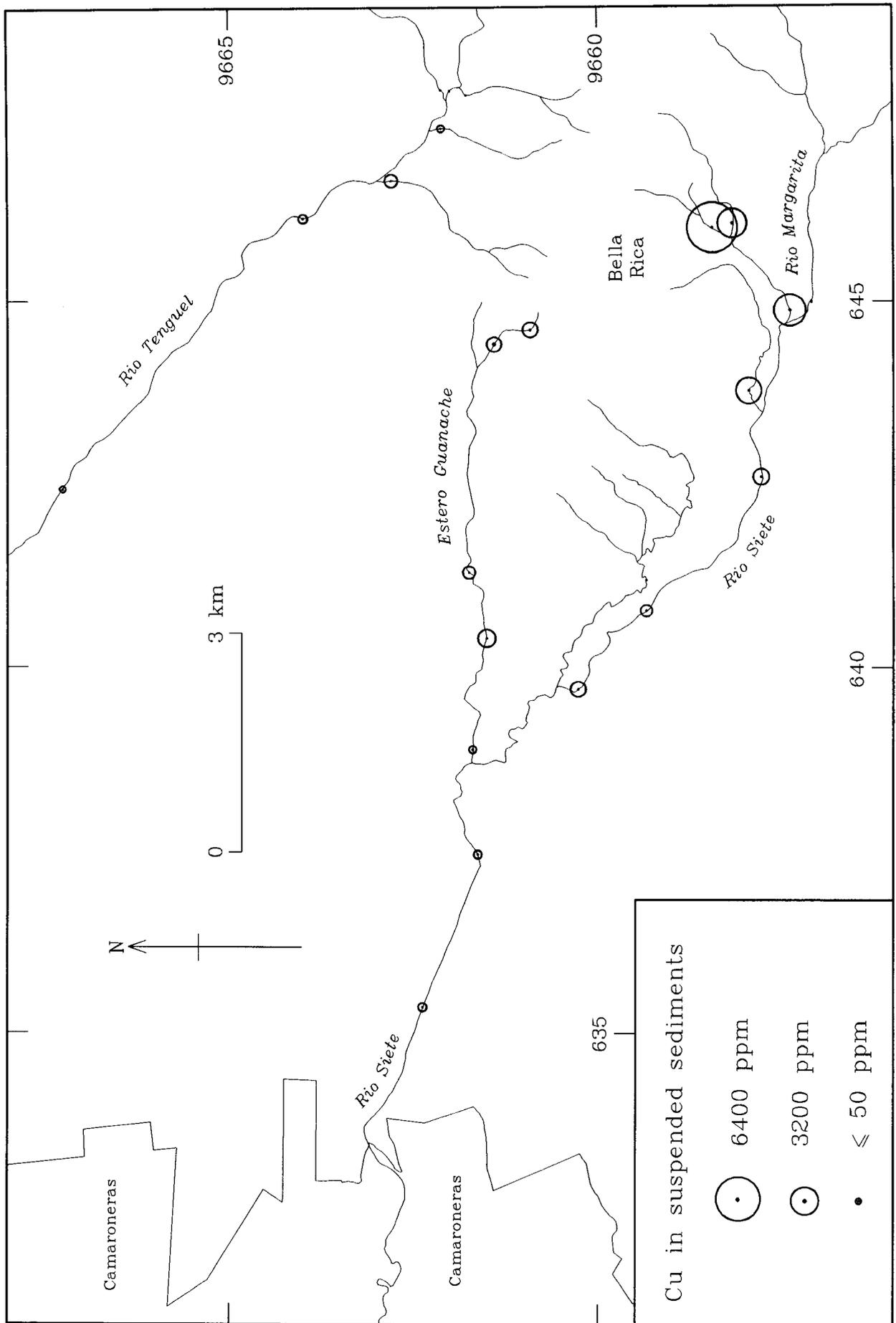


Figure 14: Cu in suspended sediments : Ponce Enríquez district, Ecuador

Appendix 1: Stream Water Chemistry: Ponce Enríquez District, Ecuador

Sample	Al(µg/l)	As(µg/l)	B(mg/l)	Ba(µg/l)	Ca(mg/l)	Cd(µg/l)	Cl(mg/l)	Co(µg/l)	Cu(µg/l)	Fe(mg/l)	K(mg/l)	Li(µg/l)
1	7	1.1	0.01	10	7	2	0.5	6	1	0.002	0.5	0.5
2	3616	7.1	0.06	23	74	9	4.3	233	3299	2.296	5.2	0.5
3	2189	0.1	0.29	26	95	8	5.6	241	1205	1.800	6.9	3.3
5	7	0.1	0.08	17	128	5	8.5	158	1	6.048	2.4	1.4
6	41	320.0	0.16	7	80	2	3.5	18	3906	0.080	1.3	0.5
7	16	300.0	0.17	8	81	2	4.0	15	1632	0.056	1.3	0.5
8	19	240.0	0.20	6	83	2	4.3	18	2848	0.049	1.9	0.5
9	7	17.3	0.08	11	115	2	7.7	52	8	0.018	1.6	0.5
10	7	0.1	0.01	6	9	2	0.5	6	1	0.002	0.3	0.5
11	7	2.5	0.01	9	6	2	0.2	6	1	0.005	0.3	0.5
12	19	0.4	0.01	7	7	2	0.7	6	3	0.062	0.5	0.5
14	28	0.5	0.01	9	7	2	0.2	6	1	0.016	0.3	0.5
15	43	470.0	0.03	8	36	2	2.0	6	2723	0.168	0.8	0.5
17	7	5.8	0.02	11	13	2	3.0	6	1	0.013	0.8	0.5
18	7	250.0	0.02	7	29	2	1.7	6	1636	0.089	0.7	0.5
19	44	36.4	0.04	13	31	2	2.5	28	8	0.040	1.4	0.5
21	7	14.1	0.05	15	37	2	3.7	45	10	0.005	2.2	0.5
28	7	77.3	0.02	12	24	2	3.5	6	17	0.012	1.0	0.5
29	7	22.6	0.04	15	26	2	5.3	12	4	0.009	1.4	0.5
30	7	108.8	0.03	9	26	2	3.8	6	809	0.043	1.0	0.5
31	13	450.0	0.03	10	37	2	2.0	14	7277	0.165	0.9	0.5
32	20	430.0	0.03	8	36	2	1.9	6	7172	0.101	0.9	0.5
33	7	1.5	0.02	6	13	2	0.9	6	1	0.002	0.3	0.5
34	12	0.1	0.03	12	70	2	4.6	6	3	0.016	1.1	0.5
35	5900	0.1	0.04	26	50	2	2.7	163	599	1.971	2.5	3.7

Values below detection limit (LoD, Table 1) set to 0.5 LoD
Duplicate samples indicated in *italics*

Appendix 1: Stream Water Chemistry: Ponce Enríquez District, Ecuador

Sample	Mg(mg/l)	Mn(mg/l)	Na(mg/l)	Ni(µg/l)	NO3(mg/l)	P(mg/l)	Si(mg/l)	SO4(mg/l)	Sr(mg/l)	Y(µg/l)	Zn(µg/l)
1	2	0.001	3	5	0.1	0.03	9.2	3	0.03	0.5	54
2	35	0.001	10	153	22.2	0.03	21.3	374	0.16	11.4	535
3	38	4.245	21	165	19.1	0.03	20.7	449	0.21	12.4	821
5	36	4.252	11	95	22.2	0.03	10.9	487	0.16	1.7	200
6	14	0.146	22	22	36.7	0.03	8.1	212	0.13	0.5	407
7	14	0.106	13	12	40.0	0.03	8.2	191	0.12	0.5	65
8	15	0.151	19	16	35.6	0.03	7.8	215	0.14	0.5	75
9	32	2.818	10	42	16.8	0.03	9.2	412	0.15	0.5	61
10	4	0.001	4	5	0.1	0.03	14.1	12	0.02	0.5	36
11	2	0.001	2	5	0.1	0.03	8.2	3	0.02	0.5	36
12	3	0.020	3	5	0.8	0.03	8.5	10	0.02	0.5	45
14	3	0.001	3	5	0.4	0.03	8.7	9	0.02	0.5	40
15	6	0.048	24	23	6.9	0.03	8.1	114	0.07	0.5	134
17	7	0.004	5	5	0.1	0.03	11.2	8	0.03	0.5	42
18	6	0.084	13	5	5.7	0.03	8.7	75	0.06	0.5	38
19	13	1.154	7	15	5.2	0.03	14.1	127	0.08	0.5	68
21	15	1.553	8	28	6.3	0.03	13.2	155	0.09	0.5	70
28	8	0.321	7	5	4.0	0.03	10.6	58	0.06	0.5	49
29	11	0.649	10	5	3.0	0.10	12.7	94	0.07	0.5	52
30	8	0.357	10	5	4.3	0.03	10.8	70	0.06	0.5	46
31	7	0.065	19	13	5.4	0.03	8.4	109	0.07	0.5	64
32	6	0.058	20	15	4.8	0.03	8.4	104	0.07	0.5	61
33	6	0.001	3	5	0.5	0.03	13.4	40	0.02	0.5	49
34	18	0.048	7	5	178.2	0.03	12.0	108	0.14	0.5	44
35	27	2.875	7	110	3.8	0.03	22.0	294	0.16	29.4	169

Appendix 1: Stream Water Chemistry: Ponce Enriquez District, Ecuador

Sample	pH	Eh	Conductivity	Alkalinity
1	7.6	413	88	32
2	3.8	634	906	0
3	4.6	497	1006	3
5	6.0	350	910	3
6	9.7	218	575	70
7	9.7	224	575	76
8	8.3	279	654	77
9	6.7	362	919	8
10	7.3	397	124	37
11	7.3	394	79	26
12	7.1	396	94	25
14	7.1	394	94	25
15	8.8	275	392	63
17	8.0	369	170	58
18	7.8	335	306	53
19	7.0	443	368	15
21	6.9	424	429	11
28	7.2	360	265	40
29	6.8	262	338	29
30	7.1	337	309	44
31	8.1	342	380	60
32	8.1	224	380	62
33	7.1	404	169	22
34	6.9	471	631	17
35	3.9	598	691	0

Appendix 2: Stream Bottom Sediment Chemistry (mg/kg in <150µm fraction) : Ponce Enríquez District, Ecuador

Sample	As	Cd	Cu	Fe	Hg	Mn	Pb	Zn
1	44	3	65	47750	0.44	708	13	74
2	8366	17	2443	166500	3.00	378	666	555
3	13680	19	4900	189050	13.00	535	467	651
5	7212	18	7045	191500	2.00	571	136	420
6	42435	24	8327	221004	3.00	440	380	879
7	46049	24	9134	225200	3.00	434	400	924
8	25979	22	8185	175500	3.00	613	358	897
9	3020	14	3649	140000	2.00	607	89	300
10	29	4	287	57000	0.15	773	13	62
11	96	4	126	53500	0.25	755	13	77
12	129	7	523	93500	0.69	1000	13	76
13	157	7	601	97000	0.83	857	13	76
14	151	7	655	90000	0.84	1198	13	89
15	10126	19	5424	159500	4.00	652	304	629
17	79	6	162	84250	0.10	1441	13	112
18	8720	17	5000	148000	5.00	800	256	598
19	1354	9	1423	105000	0.85	474	140	201
20	1539	9	1508	103500	1.00	618	118	251
21	1660	9	1761	96000	4.00	646	196	392
28	7258	12	2912	132000	3.00	975	175	347
29	899	8	1134	156250	3.00	1009	117	291
30	3392	9	1428	100000	1.00	532	85	177
31	7780	17	4266	143950	7.00	1022	376	644
32	7096	17	4307	153500	8.00	1056	389	672
33	833	15	3223	199500	0.30	913	13	104
34	84	8	568	118500	0.33	1721	13	104
35	282	8	1651	94500	0.86	272	59	64
36	231	7	1455	91000	0.58	218	35	54

Values below detection limit (LoD) set to 0.5 LoD
Duplicate samples indicated in *italics*

Appendix 3: Stream Suspended Sediment Chemistry (mg/kg) : Ponce Enriquez District, Ecuador

Sample	Easting	Northing	As	Cd	Cu	Fe	Hg	Mn	Pb	Zn	Load (g/l)
1	644000	9657120	nd	nd	nd	nd	nd	nd	nd	nd	nd
2	643610	9660920	4024	13	1360	133830	0.59	301	617	394	1.09
3	643410	9661410	4510	11	1311	107869	1.19	379	911	447	0.88
5	645000	9658460	6375	18	6437	171851	9.61	1093	254	439	6.15
6	645060	9658190	16332	14	3389	129691	1.09	661	202	639	2.56
7	645060	9658190	22626	16	4383	148389	1.38	665	246	672	2.98
8	643880	9657410	18290	14	3800	131734	1.59	746	247	743	3.05
9	642780	9657970	10614	17	2869	146987	3.57	800	1061	398	4.57
10	646890	9662120	nd	nd	nd	nd	nd	nd	nd	nd	nd
11	646880	9662000	nd	nd	nd	nd	nd	nd	nd	nd	nd
12	645130	9664000	427	3	460	40842	0.01	199	94	47	0.18
13	645130	9664000	251	4	436	39906	0.02	190	97	43	0.17
14	641440	9667250	14	2	17	1474	0.02	22	141	23	0.01
15	641620	9657800	7444	13	1494	87519	1.28	857	388	506	0.98
17	640200	9659350	nd	nd	nd	nd	nd	nd	nd	nd	nd
18	639780	9659350	3589	8	839	51823	0.56	597	268	339	0.30
19	640300	9661750	2660	7	976	45524	0.32	529	106	491	0.18
20	640300	9661750	2624	7	945	45540	0.26	515	64	462	0.19
21	639400	9661510	1398	9	1730	75663	0.41	790	89	324	0.60
28	634350	9662380	957	2	387	16144	0.10	196	123	108	0.02
29	637870	9661700	182	2	225	11635	0.07	154	131	67	0.02
30	636440	9661630	1997	1	352	23793	0.13	278	333	172	0.04
31	638700	9660270	5647	11	1363	86326	1.61	921	349	447	1.00
32	638700	9660270	5400	11	1326	81708	1.39	887	341	446	0.83
33	646820	9661780	nd	nd	nd	nd	nd	nd	nd	nd	nd
34	646360	9662120	25	1	199	16534	0.01	274	124	27	0.03
35	645640	9662800	271	6	1024	74765	0.32	211	27	46	0.94
36	645640	9662800	296	7	1121	87647	0.48	229	25	50	0.92

Values below detection limit (LoD) set to 0.5 LoD

Duplicate samples indicated in *italics*

nd = no data

Appendix 4 : Spearman Correlation Matrix for Stream Water Chemistry

	Al (µg/l)	As (µg/l)	B (mg/l)	Ba (µg/l)	Ca (mg/l)	Cd (µg/l)	Cl (mg/l)	Co (µg/l)	Cu (µg/l)	Fe (mg/l)	Hg (µg/l)
Al (µg/l)	****	0.00	0.39	0.24	0.37	0.31	0.07	0.47	0.51	0.64	0.24
As (mg/l)	0.25	****	0.24	-0.44	0.27	-0.20	-0.10	-0.05	0.67	0.39	0.62
B (mg/l)	0.39	0.22	****	0.45	0.92	0.48	0.82	0.86	0.62	0.59	0.26
Ba (µg/l)	0.24	-0.31	0.45	****	0.40	0.54	0.56	0.65	0.07	0.32	-0.12
Ca (mg/l)	0.37	0.11	0.92	0.40	****	0.50	0.82	0.78	0.59	0.67	0.26
Cd (µg/l)	0.31	-0.34	0.48	0.54	0.50	****	0.50	0.61	0.15	0.56	0.13
Cl (mg/l)	0.07	0.01	0.82	0.56	0.82	0.50	****	0.64	0.34	0.41	0.08
Co (µg/l)	0.47	-0.09	0.86	0.65	0.78	0.61	0.64	****	0.42	0.56	0.03
Cu (µg/l)	0.51	0.65	0.62	0.07	0.59	0.15	0.34	0.42	****	0.62	0.62
Fe (mg/l)	0.64	0.12	0.59	0.32	0.67	0.56	0.41	0.56	0.62	****	0.47
Hg (µg/l)	0.24	0.46	0.26	-0.12	0.26	0.13	0.08	0.03	0.62	0.47	****
K (mg/l)	0.43	-0.02	0.90	0.72	0.83	0.57	0.84	0.89	0.51	0.60	0.08
Li (µg/l)	0.33	-0.53	0.43	0.57	0.45	0.55	0.35	0.59	0.02	0.54	0.13
Mg (mg/l)	0.33	-0.12	0.88	0.66	0.89	0.58	0.90	0.83	0.39	0.51	0.03
Mn (mg/l)	0.12	0.06	0.73	0.55	0.67	0.20	0.69	0.64	0.32	0.44	0.20
Na (mg/l)	0.26	0.54	0.78	0.10	0.78	0.31	0.61	0.46	0.79	0.63	0.68
Ni (µg/l)	0.57	-0.01	0.83	0.53	0.81	0.61	0.56	0.91	0.51	0.68	0.20
NO3 (mg/l)	0.40	0.25	0.80	0.23	0.89	0.41	0.72	0.56	0.66	0.61	0.31
P (mg/l)	-0.19	0.10	0.11	0.21	-0.10	-0.08	0.26	0.03	-0.07	-0.19	-0.12
Si (mg/l)	0.12	-0.55	0.12	0.62	0.10	0.40	0.26	0.39	-0.20	-0.04	-0.27
SO4 (mg/l)	0.46	0.07	0.93	0.49	0.96	0.56	0.77	0.88	0.57	0.69	0.21
Sr (mg/l)	0.43	-0.03	0.91	0.64	0.93	0.58	0.84	0.85	0.50	0.62	0.16
Y (µg/l)	0.49	-0.47	0.49	0.66	0.50	0.80	0.41	0.71	0.18	0.65	0.06
Zn (µg/l)	0.58	0.13	0.84	0.49	0.76	0.57	0.58	0.82	0.58	0.63	0.25
pH	-0.14	0.57	-0.32	-0.74	-0.33	-0.55	-0.50	-0.58	0.15	-0.19	0.31
Eh	0.30	-0.69	-0.11	0.47	-0.04	0.34	-0.07	0.27	-0.27	-0.07	-0.37
Conductivity	0.43	0.03	0.92	0.53	0.98	0.54	0.84	0.83	0.56	0.66	0.22
Alkalinity	-0.20	0.70	-0.20	-0.68	-0.26	-0.54	-0.31	-0.56	0.26	-0.17	0.38

Appendix 4 : Spearman Correlation Matrix for Stream Water Chemistry

	K (mg/l)	Li (µg/l)	Mg (mg/l)	Mn (mg/l)	Na (mg/l)	Ni (µg/l)	NO3 (mg/l)	P (mg/l)	Si (mg/l)	SO4 (mg/l)
Al (µg/l)	0.43	0.33	0.33	0.12	0.26	0.57	0.40	-0.19	0.12	0.46
As (mg/l)	-0.05	-0.20	-0.13	-0.02	0.67	0.14	0.40	-0.11	-0.66	0.18
B (mg/l)	0.90	0.43	0.88	0.73	0.78	0.83	0.80	0.11	0.12	0.93
Ba (µg/l)	0.72	0.57	0.66	0.55	0.10	0.53	0.23	0.21	0.62	0.49
Ca (mg/l)	0.83	0.45	0.89	0.67	0.78	0.81	0.89	-0.10	0.10	0.96
Cd (µg/l)	0.57	0.55	0.58	0.20	0.31	0.61	0.41	-0.08	0.40	0.56
Cl (mg/l)	0.84	0.35	0.90	0.69	0.61	0.56	0.72	0.26	0.26	0.77
Co (µg/l)	0.89	0.59	0.83	0.64	0.46	0.91	0.56	0.03	0.39	0.88
Cu (µg/l)	0.51	0.02	0.39	0.32	0.79	0.51	0.66	-0.07	-0.20	0.57
Fe (mg/l)	0.60	0.54	0.51	0.44	0.63	0.68	0.61	-0.19	-0.04	0.69
Hg (µg/l)	0.08	0.13	0.03	0.20	0.68	0.20	0.31	-0.12	-0.27	0.21
K (mg/l)	****	0.55	0.93	0.75	0.58	0.82	0.70	0.13	0.37	0.89
Li (µg/l)	0.55	****	0.54	0.58	0.18	0.59	0.18	-0.08	0.42	0.54
Mg (mg/l)	0.93	0.54	****	0.70	0.54	0.77	0.74	0.03	0.45	0.90
Mn (mg/l)	0.75	0.58	0.70	****	0.52	0.56	0.48	0.16	0.19	0.72
Na (mg/l)	0.58	0.18	0.54	0.52	****	0.58	0.79	0.03	-0.24	0.72
Ni (µg/l)	0.82	0.59	0.77	0.56	0.58	****	0.63	-0.19	0.24	0.90
NO3 (mg/l)	0.70	0.18	0.74	0.48	0.79	0.63	****	-0.13	-0.09	0.82
P (mg/l)	0.13	-0.08	0.03	0.16	0.03	-0.19	-0.13	****	0.13	-0.03
Si (mg/l)	0.37	0.42	0.45	0.19	-0.24	0.24	-0.09	0.13	****	0.23
SO4 (mg/l)	0.89	0.54	0.90	0.72	0.72	0.90	0.82	-0.03	0.23	****
Sr (mg/l)	0.93	0.56	0.95	0.68	0.67	0.84	0.81	0.03	0.33	0.94
Y (µg/l)	0.66	0.86	0.63	0.37	0.19	0.71	0.29	-0.10	0.55	0.61
Zn (µg/l)	0.80	0.50	0.72	0.53	0.64	0.89	0.65	-0.03	0.18	0.83
pH	-0.58	-0.53	-0.62	-0.42	0.14	-0.43	-0.16	-0.19	-0.76	-0.46
Eh	0.17	0.31	0.22	-0.12	-0.47	0.22	-0.11	-0.32	0.73	0.05
Conductivity	0.90	0.52	0.94	0.69	0.73	0.86	0.84	-0.03	0.24	0.97
Alkalinity	-0.45	-0.54	-0.51	-0.30	0.26	-0.46	-0.10	0.03	-0.72	-0.40

Appendix 4 : Spearman Correlation Matrix for Stream Water Chemistry

	Sr (mg/l)	Y (µg/l)	Zn (µg/l)	pH	Eh	Conductivity	Alkalinity
Al (µg/l)	0.43	0.49	0.58	-0.14	0.30	0.43	-0.20
As (mg/l)	0.07	-0.24	0.22	0.70	-0.63	0.15	0.69
B (mg/l)	0.91	0.49	0.84	-0.32	-0.11	0.92	-0.20
Ba (µg/l)	0.64	0.66	0.49	-0.74	0.47	0.53	-0.68
Ca (mg/l)	0.93	0.50	0.76	-0.33	-0.04	0.98	-0.26
Cd (µg/l)	0.58	0.80	0.57	-0.55	0.34	0.54	-0.54
Cl (mg/l)	0.84	0.41	0.58	-0.50	-0.07	0.84	-0.31
Co (µg/l)	0.85	0.71	0.82	-0.58	0.27	0.83	-0.56
Cu (µg/l)	0.50	0.18	0.58	0.15	-0.27	0.56	0.26
Fe (mg/l)	0.62	0.65	0.63	-0.19	-0.07	0.66	-0.17
Hg (µg/l)	0.16	0.06	0.25	0.31	-0.37	0.22	0.38
K (mg/l)	0.93	0.66	0.80	-0.58	0.17	0.90	-0.45
Li (µg/l)	0.56	0.86	0.50	-0.53	0.31	0.52	-0.54
Mg (mg/l)	0.95	0.63	0.72	-0.62	0.22	0.94	-0.51
Mn (mg/l)	0.68	0.37	0.53	-0.42	-0.12	0.69	-0.30
Na (mg/l)	0.67	0.19	0.64	0.14	-0.47	0.73	0.26
Ni (µg/l)	0.84	0.71	0.89	-0.43	0.22	0.86	-0.46
NO3 (mg/l)	0.81	0.29	0.65	-0.16	-0.11	0.84	-0.10
P (mg/l)	0.03	-0.10	-0.03	-0.19	-0.32	-0.03	0.03
Si (mg/l)	0.33	0.55	0.18	-0.76	0.73	0.24	-0.72
SO4 (mg/l)	0.94	0.61	0.83	-0.46	0.05	0.97	-0.40
Sr (mg/l)	****	0.65	0.81	-0.52	0.15	0.97	-0.43
Y (µg/l)	0.65	****	0.62	-0.66	0.48	0.60	-0.66
Zn (µg/l)	0.81	0.62	****	-0.30	0.09	0.78	-0.28
pH	-0.52	-0.66	-0.30	****	-0.62	-0.46	0.94
Eh	0.15	0.48	0.09	-0.62	****	0.08	-0.76
Conductivity	0.97	0.60	0.78	-0.46	0.08	****	-0.38
Alkalinity	-0.43	-0.66	-0.28	0.94	-0.76	-0.38	****