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The Dongri Buzurg manganese mine north of Nagpur, India, where restoration involves the re-establishment of forest on overburden dumps, with teak (L) and other commercial species *(Photo M.J. Heath)*

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Dispersion halos associated with mineralization and mining pollution in the Ribeira River Valley, Paraná and São Paulo, Brazil

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Abstract

The Ribeira River Valley, between the states of São Paulo and Paraná, contains the largest part of the remaining rain forest in Southern Brazil. Mining of gold, lead, copper, limestone, phosphates and fluorite has been a major economic activity in the area. Mining methods and environmental control are poor, resulting in deforestation, land degradation and chemical pollution of soils, sediments, water and aquatic life. The newer and larger mines are subject to some environmental control, but large areas, near non-operating and abandoned mines, contain low-grade ore and tailing piles. The Ribeira River and its tributaries, which drain mining areas, are polluted by heavy metals. From the Rocha Mine to the ocean (250 km), concentrations of lead, copper, zinc and mercury are higher than permissible standards for water supply and aquatic life maintenance. High concentrations have been detected in fish. Detailed studies in the areas of influence of the Rocha, Perau, Barrinha and Canoas mines have demonstrated high concentrations and an extensive dispersion pattern. High lead concentrations, reaching 10,000 ppm, were detected in sediments up to 1.5 km downstream of the Perau Mine. Concentrations greater than 500 ppm are maintained 9 km downstream. Environmental control measures (tailing ponds, wetlands) are proposed to lower heavy metal contents in sediments and waters, as well as better law enforcement. *Key words: mining, environmental geochemistry, heavy metals, Brazil.*

Introduction

This article summarizes knowledge of the geochemical dispersion of base metals, associated with mineralization and mining, in the environment of the Ribeira River basin, in the zone of influence of the Rocha, Perau, Canoas, Panelas and Barrinha base metal mines, where pollution is affecting aquatic life in the basin and in the Iguape-Cananéia-Paranaguá Estuarine-Lagoon Complex (*Figure 1*).

The main base metal deposits of the Ribeira Valley Metallogenic Province have been classified as Perau and Panelas types (Macedo, 1986). Perau type deposits (sediment-hosted stratiform sedimentary-exhalative massive sulphides, mainly galena, pyrite, sphalerite, barite, chalcopyrite), comprise: Perau (3.1 Mt of ore with 4.04% Pb, 1.13% Zn, 57 g/t Ag, mined 1975–1986), Araçazeiro (3 Mt, 4% Pb+Zn, 25 g/t Ag, not yet mined) and Canoas (1.4Mt, 3.5% Zn, 3.1% Pb, 63 g/t Ag, mined 1985–1995. The Panelas type deposits (limestone-hosted hydrothermal veins, with galena, pyrrhotite, pyrite, arsenopyrite, sphalerite and silver) are smaller and in larger number than those of the Perau type. The principal ones are Panelas (86,000 t with Pb, mined until 1986. The smelter operated until 1996, with ore from the

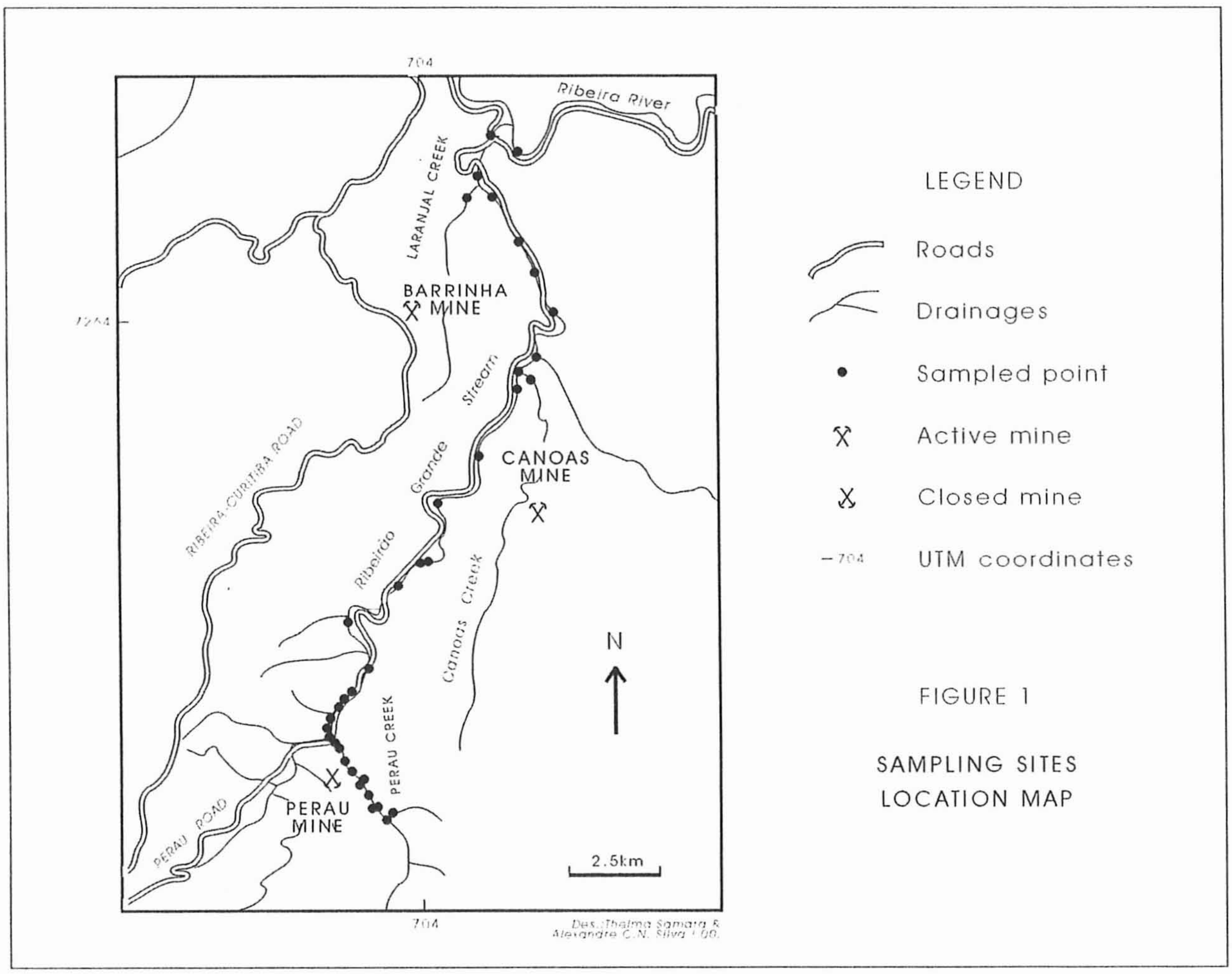

Figure 1 Locality map and sample-site localities

other mines), Rocha (217,000 t, 5–7% Pb, 100–130 g/t Ag, mined until 1988), Furnas (104,000 t, 6.6% Pb, 3 kg/t Ag, mined 1919–1993), Barrinha (80,000 t with 8% Pb and 75,000 t with 3% Pb, mined 1975–1995).

The Ribeira River Valley, between the states of São Paulo and Paraná, contains the largest part of the remaining rain forest in Southern Brazil. The mining of lead, copper, limestone, phosphates and fluorite has traditionally been a major economic activity in the area. Gold mining in the eighteenth and nineteenth centuries was the main factor for the settling of Europeans in the area. Base metal mining began in the 1919 and went on until the 1990s, when the production in the remaining mines was discontinued because of low prices, opening of markets for imports and environmental restrictions. Most mines were small and operated with inadequate mining technology, inadequate environmental control (beginning only in the 1980s), and with no reclamation of degraded land. Vegetation destruction, uncontrolled excavations, and chemical pollution by acid drainage and heavy metals from mine openings and tailing piles, was a rule, and has continued, with little modification, up to the present. The closing of mines aggravated the problem, because bankrupt mines were not forced to reclaim land and the absence of any warranty, like performance bonds, preventing the environmental control agencies from undertaking any rehabilitation themselves.

Dispersion halos associated with mineralization and mining in the Ribeira Valley

Rocks

Damasceno (1967) found a narrow halo (some meters wide) of lead enrichment in carbonatic rocks around Panelas type veins in the Paqueiro prospect. Macedo (1986) detected a 200 m mineralization halo in metasediments and metavolcanics around the Perau sedex deposit, and found it possible to use Cu, Pb, Zn, B, Mg, K, Fn, Mn and Ca contents in rocks as prospecting tools in the area.

Soils

Soil geochemistry has been used for mineral exploration in the area since the 1950s, with good results in Panelas and Perau type deposits. A synthesis is presented by Macedo and Batolla (1981), who give the results of an orientation survey in the Perau mine. Geometric means and possible anomaly thresholds (GMxGD^2) are 30 and 120 ppm for copper; 16 and 100 for lead; 30 and 145 for zinc. Halos are from tens to hundreds of meters wide. In surveys around the principal zones of mineralization, copper was detected as more mobile, with lead and zinc defining with more precision the localization of the ore.

Water and water life

Eysink (1991) and Eysink et al. (1988, 1990) describe studies of heavy metal dispersion in water and aquatic organisms in the Ribeira basin and the Iguape-Cananéia-Paranaguá Estuarine-Lagoon Complex where it discharges. Heavy metal concentrations larger than the limits established by Brazilian and international norms for public supply were found downstream of the main mines and in the complex, in values up to 57.5 times the limit of 30 μg/l for lead and 4.4 times that for zinc, of 180 μg/l.

The anomalous concentrations in sediments and water are reflected in anomalous accumulations of metals in the muscles of fish from the river and from the estuarine-lagoon complex. Eysink et al. (1990) found concentrations larger than the maximum limit for human consumption: Hg—up to 1.5 times the limit in fish from the complex; Cu—81 times in complex and 84 in river fish; Pb—up to 800 times the limit in river fish; and Zn—27 times for the complex and 28 for the river.

Ferreira (1994) studied the dispersion of Cu, Pb and Zn in streams near the Rocha mine, finding values larger than the limit for aquatic life. Large amounts of mine spoil will become available for pollution when submerged by the waters of a new reservoir. This water will have a low pH, induced by decomposition of organic matter at depths of one hundred meters where there will be little water movement. This will greatly increase its potential to dissolve metals.

The Water Resources and Environment Department of the State of Paraná also detected values of 450 and 1000 μg/l in water downstream of the Barrinha and Panelas mines.

A laboratory was established as part of an agreement between the Japan International Cooperation Agency and the Brazilian National Department of Mineral Production, and a survey of water pollution of the Ribeira basin was made, described in JICA/MMAJ (1992,1993). Reported values are up to 15 times the limits established in the São Paulo State laws, for Pb, Zn and Cd. In the case of Barrinha mine, even with values up to 36,000 ppm Pb in sediments, low values were found in water, due the high pH (8.2), which is unfavorable to the solution of heavy metals. This is probably the case for all mines, where unprotected spoil and low-concentration ore piles give rise to high concentrations in stream sediments, without these values being reflected in waters. If there is a change in pH, as is the case when the Ribeira sediments enter the estuarine-lagoon complex or when the piles are submersed by deep reservoir waters, then euxinic conditions and a reducing environment prevail and metals are released into the water.

Corsi (1999) detected values of zinc up to 15 times the limit for public supply downstream of the mines.

Stream sediments

Morgental et al. (1975, 1978) present results of orientation and regional stream sediment surveys made by the Geological Survey of Brazil, which give a good frame of reference to distinguish background dispersion of heavy metals from that caused by mineralization or pollution. The anomalous halo in stream sediments caused by mineralization could be detected, in the -80 mesh fraction of sediments, hundreds of meters downstream of undisturbed occurrences.

The values of geometric average and probable anomaly threshold (MGxDG^2), considered to be the maximum limit of natural dispersion in unmineralized streams, varied in ranges of 6 to 26 ppm and 27 to 100 ppm for Cu, depending on the geology of the drainage basin, in ranges of 11 to 24 and 27 to 240 for Pb, and of 14 to 90 and 85 to 380 for Zn, analyzed by atomic absorption and nitric acid attack of samples.

The maximum acceptable limits presented by Bowden (Eysink, 1988) are 25 for Cu, 40 for Pb and 90 for Zn. They are considered as thresholds for the detection of contamination. These values seem very restrictive, in some cases lower than values found in unmineralized and unpolluted streams of the study area. All geochemical studies made in the area revealed dispersion trains of trace elements, with concentrations several times higher than the maximum admissible limits.

Lopes (1987) detected 122 ppm for Cu, 3596 for Pb and 1598 for Zn, in a stream draining old mining works at the Furnas mine.

Eysink (1988, 1990) detected values up to 2.4 times higher than the Bowden limits for Cu, 1.5 times for Hg, 100 times for Pb and 45.5 for Zn in sediments collected downstream of the principal mines.

Ferreira (1994) found up to 565 ppm Cu, 26,500 Pb and 565 Zn downstream of the Rocha mine.

This author has studied the dispersion halo in active stream sediments of the Perau, Barrinha and Canoas mines in the Perau and Ribeirão Grande streams (Macedo, 1991, 1992, 1993) using atomic absorption analysis of Cu, Pb, Zn, Fe and Mn, with attack by hot HNO_3. Concentrations higher than 20,000 ppm Pb were detected in the -80 +150 mesh fraction up to 1.5 km downstream of the Perau mine; the concentrations decrease to 100 ppm at 17 km from the mine, increase to 292 ppm downstream of the Canoas creek, which drains the Canoas mine, and to 5,000 ppm when the Ribeirão Grande stream receives sediments from the Laranjal creek, where there are concentrations up to 36,000 Pb, derived from the Barrinha mine, decreasing later to 4,000 ppm until the Ribeirão Grande discharges into the Ribeira river, 28 km from the Perau mine. Copper and zinc concentrations show the same pattern (*Figure 2*). The values for Cu, Pb and Zn are much higher than those in unmineralized areas and even higher than anomalies associated with mineralization in areas not yet mined, indicating probable pollution by the mines. The variation of these metals is independent of that of Fe and Mn, indicating that the concentrations are unrelated to lithologic factors.

Corsi (1999) studied the concentrations of Cu, Pb, Zn, Fe, Mn, Cd, As and Sb by atomic absorption analysis, with sequential extraction for Cu, Pb and Zn, in active stream sediment samples taken during the

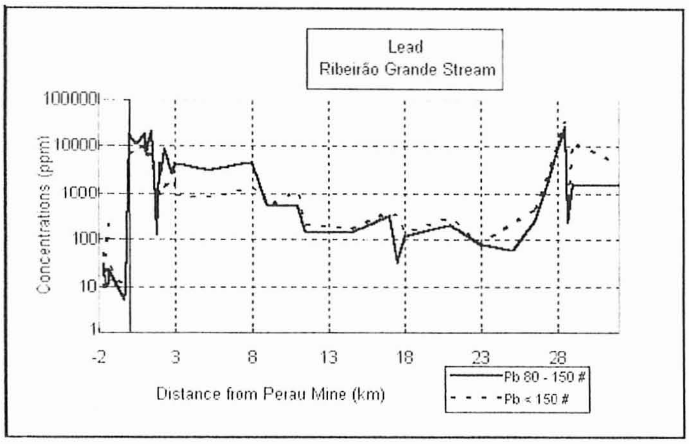

Figure 2 Lead concentrations in sediments - Perau and Grande streams (Macedo, 1993)

dry and wet seasons. For the dry season samples, there is a maximum Pb concentration of 1985 ppm, in the Ribeirão Grande stream near the mouth of Perau creek, decreasing down to the Ribeira River confluence. For wet season samples the maximum was 550 ppm near the mouth of Perau creek, decreasing towards the mouth of Laranjal creek, where it increases to 242 ppm, an increase not repeated in the dry season samples. In the creeks near the now abandoned mines, high concentrations were detected for lead, with maxima of 1084 ppm near Perau, 242 near Canoas and 4040 near Barrinha. Similar patterns were found for the other elements, except Fe and Mn, with lower concentrations for Cu, Zn, As and Sb.

According to the results of the sequential analysis, Corsi (1999) considered the transport of Pb in the Ribeirão Grande stream sediments to be mainly associated with Mn and Fe oxides and hydroxides (based on the release of 28.92% of the total Pb in sediments by hydroxylamine hydrochloride and acetic acid), followed by organic matter and sulphides (24.48% leached by nitric acid plus hydrogen peroxide), carbonates (22.36% removed by sodium acetate), with a smaller proportion in the residual phase (17.47% dissolved by fluorhydric, perchloric and nitric acids) and, in the exchangeable phase, associated to clay minerals (6.74% leached by ammonium acetate).

This is not in accordance with the spatial variation of Fe and Mn, shown in Macedo (1993), which is not controlled by mineralization or mining activities. The concentration-distance graphs of Fe and Mn did not show correlation with the location of mines, and the graphs of Pb controlled by Fe or Mn show the same pattern of the raw data, indicating probably that a small proportion of Pb was transported co-precipitated with Fe or Mn oxides.

This difference between the results of the two surveys can be explained by the time of the sampling. Macedo (1992, 1993) sampled sediments recently contaminated by operating (Barrinha, Canoas) or recently closed (Perau) mines; when Corsi (1999) did her sampling, the first mines were closed for three and Perau for twelve years. A large proportion of the sulphide and carbonate phases, which probably contained most of the heavy metals at the time of the first sampling, would be leached; the remaining metal contents would be fixed by Fe and Mn oxides, organic matter and clay minerals.

The largest fractions of lead are in forms of low bioavailability.

Conclusions

Gold, lead, copper, limestone, phosphates and fluorite mines have contributed to the economy of the Ribeira valley from colonial times to this day. The mining methods, in almost all cases, were inadequate.

Cu, Pb and Zn mineralisations cause natural increases in the concentrations of these elements in all sample media studied (rocks, soils, stream sediments, water) near the deposits, which allowed successful use of dispersion halos and trains in geochemical exploration.

Trace elements were released into the environment when the deposits were mined, with the use of inadequate technology for extraction, smelting and environmental control. All environmental geochemistry studies made in the area have detected contamination by metals in soils, waters and stream sediments, in levels high enough to affect human and animal life.

Comparing the two surveys made in the Ribeirão Grande, which receives water from streams draining the Perau, Canoas and Barrinha mines (Macedo 1993 and Corsi 1999) the pattern of the dispersion train is similar, with higher concentrations detected in the first study. Several causes can be responsible for the difference:

- the sampling for the first study was done in 1990;
- that of the second in 1997 and in 1998;
- at the time of the first study, the Canoas and Barrinha mines were in operation but the Perau Mine had been closed for three years;
- at the time of the second one the first mines had been closed for three and Perau for twelve years;
- differences in the analytical methods between the two studies have probably affected the observed concentrations;
- the absence of details for the second study prevent the evaluation of the difference.

The main environmental problem in the area is the large amount of low-grade ore and spoil piles still present at all mine sites. The piles are without protection, save inadequate and ill-maintained retaining dams at Panelas and Canoas. They are responsible for a continuous flow of pollution into the drainage.

The proposed building of large water reservoirs presents an additional problem, due to the possibility of acidification of the water by the decomposition of organic matter in anaerobic conditions. The lower pH would release, into the water, large amounts of heavy metals now trapped in sediments, causing much bigger downstream pollution problems.

New studies are needed to measure the exact levels of pollution and magnitude of the reservoirs of polluting substances, and legal measures taken to force those responsible for the pollution to control it. A new study is planned by the author to compare samples taken in the 1990s and in this year's dry season in the Ribeirão Grande basin. The samples will be analysed at the same time and with the same method, to study the rate at which pollution levels decrease with time.

Brazilian law demands reclamation of all land degraded by mining, and environmental control of mining operations. This is not feasible when the mines were closed abruptly, and some companies become bankrupt, in the absence of pecuniary warranties for reclamation. The control of heavy metal pollution in the area is made more difficult by the lack of effective enforcement of the environmental law on the right margin of Ribeira River in the State of Paraná, where almost all the mines are located.

Considering the possible adverse effects of pollution on people living on the area, environmental health studies should include the collection of samples from residents in the area, drinking water and agricultural soil, especially near the concentration and smelter plants.

Measures to control pollution from mine water and spoil piles are needed. Tailing ponds, dams and artificial wetlands could be effective in the control of acid drainage and base metal contamination.

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'Missionary' interns from Wheaton College, Illinois

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The Geology and Environmental Science Department at Wheaton College has directed many of its majors in missionary internships over the last seven years. Several of these students spent six months in a non-industrialized nation as participants in the college's HNGR (Human Needs and Global Resources) Program. These interns served with missions organizations, lived with local people, received intensive language training and conducted research on an original environmental project. Student interest in the program continues to grow rapidly, due to the servanthood desire of our majors to apply their education in practice. Their internship experiences typically have strong influence in shaping post-graduate decisions.

The descriptions of interns below include their name, country of service, research topic, type of mission sponsor and some of their positions following graduation from the Geology and Environmental Science Department.

Water Resource Assistant in Ethiopia

Bret Swigle worked with a Lutheran development agency in Ethiopia during 1992. He was primarily an assistant in water-well drilling and in water-resource assessment, and spent significant time correlating the regional landforms and geology with the potential for high-capacity ground water supply. He also observed many of the degradations in Ethiopia that came from civil war and drastic land-use policies.

Erosion assessment in the Philippines

Rachel Reese (in 1993) and **Joanne Scigliano** (in 1997) served with a Baptist mission in the Philippines. In each case, their project concern was with the difficulty in sustaining productive agriculture on very steep, deforested slopes. Many of the World's non-industrialized regions with hilly or mountainous topography and precarious slopes for growing crops. Unfortunately, these undesirable sites are often all that is available to the poor. Fertile agricultural land is either scarce or belongs to the rich in the valley areas. Rachel and Joanne studied various crop and tillage combinations that would produce better yields with less labor and erosion. Erosion is a widespread problem in the Philippines, where rainfall is plentiful and comes in torrential storms.

Tanzanian water supply

Michael Lowe went to Tanzania in 1993 to serve with World Vision's national ministry. Mike split time between office work and his project of regional hydrogeology. The area of Mike's service is south of Lake Victoria, in the Shinyanga District. Seventy years ago this region was densely forested and contained great biodiversity, including many large mammals. Human migration and land-use practices stripped away native vegetation to the extent that thousands of square kilometers are now arid land. Insects, reptiles and a few species of birds are remnants of the previously rich ecosystem. Rainfall patterns have been greatly modified. Flowing streams have become mostly dry valleys. The local people are suffering from the lack of any consistent water supply and the related poor quality of agriculture. Mike developed various alternative solutions for the problem of potable water supply. He first studied the ground water conditions and then suggested measures to protect wells from contamination.