Hydrogeochemical investigation of the influence of ceramic industry wastes on the Fazenda Itaqui basin, Brazil

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Abstract Contamination from ceramic industries has been studied in an area near Santa Gertrudes, Brazil. Current investigations show that lead is the main contaminant in groundwater, soil, and river and lake sediments. Boron is also present in high concentrations, even in surface water, relative to both background concentrations and standards, although it is not a typical contaminant. Other metals are occasionally found in high concentrations. Some experiments and field investigations have been done mainly to study the behaviour of lead. Their results show that lead tends to be fixed by the soil and sediment, whereas boron tends to be present in all environments. Therefore, boron may pose the highest risk for the environment and human health. The studies are on-going.

Key words boron; ceramics; heavy metals; hydrogeochemistry; lead; Santa Gertrudes (Brazil)

INTRODUCTION

Contamination of soil, groundwater and surface water with heavy metals and other inorganic compounds has been studied for some decades in Brazil. However, most studies do not take into account an integrated view, i.e. one that covers the entire range from the source to their dynamics in the hydrogeological cycle.

Understanding of the hydrogeochemical behaviour of contaminants related to industrial waste is important for risk assessment and appropriate waste management. The behaviour of Pb, B and Zn has been studied in the main ceramics industrial complex of Brazil (>50% of national production), situated in Santa Gertrudes.

In addition, the same environmental investigations have been conducted in a reference area ("background"), situated beyond the influence of the industrial activities but having similar pedo-geological and topographic conditions, so that results from the Santa Gertrudes area can be compared to the "background condition".

This research is part of a larger project entitled "Management of industrial waste disposal and associated potentially contaminated areas, in the Santa Gertrudes glazed ceramics industrial complex, state of São Paulo, Brazil".

STUDY AREA

The Fazenda Itaqui drainage basin, situated in the city of Santa Gertrudes (Figs 1 and 2), has received glaze and pigment/colouring industrial effluents and sludge, which

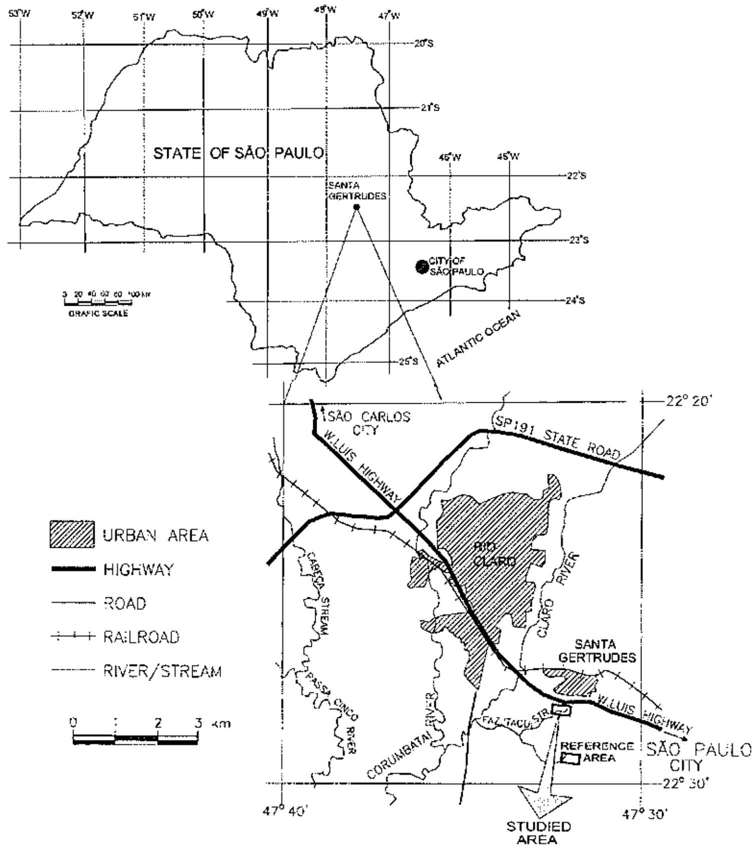

Fig. 1 Location of Santa Gertrudes, the study and the reference areas, in the state of São Paulo, Brazil.

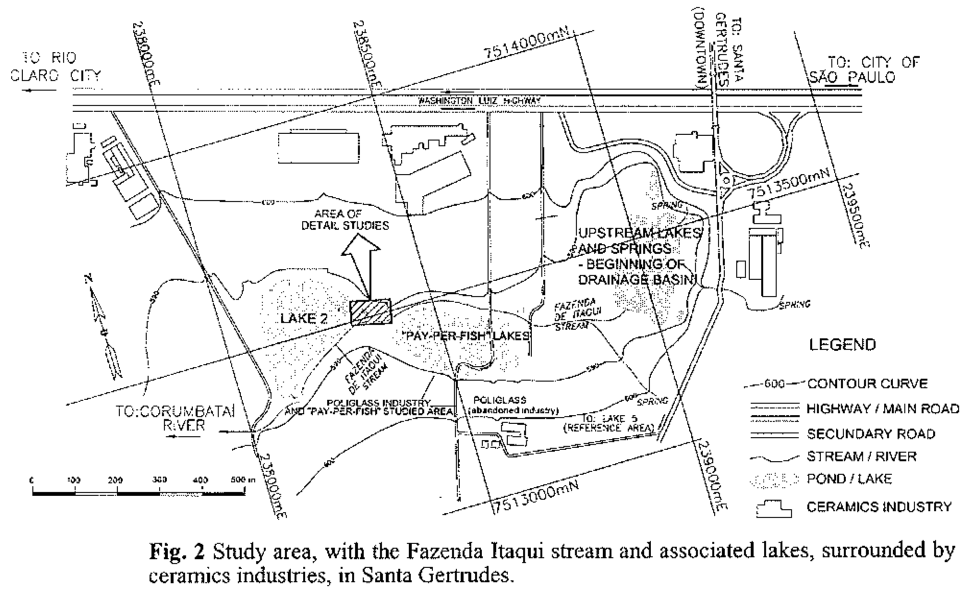

Fig. 2 Study area, with the Fazenda Itaqui stream and associated lakes, surrounded by ceramics industries, in Santa Gertrudes.

were inadequately disposed of by the ceramic industries that surround the basin. The Fazenda Itaqui stream is a tributary of the Corumbataí River, one of the main water resources of the region.

The climate of Santa Gertrudes is Cwa in terms of the Köppen classification, with an annual average precipitation of 1301 mm (DAEE, 1998).

The Permian Corumbataí Formation (Pc), comprising reddish-brown, reddish-purple or ash fractured and non-fractured mudstones, outcrops in the area (Fig. 3). Thus the regional hydrogeology includes irregular layers of aquitards (non-fractured mudstones) and "fractured sedimentary aquifers" (fractured mudstones). Local aquifer characteristics are related to geotectonic events or basic igneous rock intrusions.

Unconsolidated sediments also occur, a mixture of waste disposed by industry on the areas of clay-rich recent alluvium. These are situated in the lower areas of the drainage basin and form a sedimentary unconfined local aquifer, which is the main object of the groundwater investigations here.

The hydrogeological base is a sill of basic igneous rocks of the Serra Geral Formation.

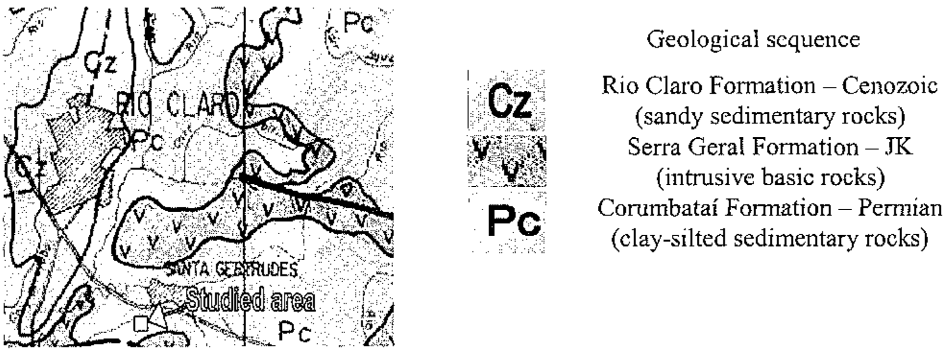

Fig. 3 Geological map of Santa Gertrudes region (DAEE & UNESP, 1982).

METHODS

Samples were taken of solids (soil; stream, lake and pond bottom sediments), liquids (groundwater, surface and rain water) and industrial material (raw, effluent/waste and other industrial materials used in the glazed ceramics assembly line).

Field investigations included description of physical and hydrological conditions: geological and pedological characteristics, local hydrological–hydrogeological regime and physical processes such as erosion and silting-up.

Hydrogeological investigations included bail slug tests in monitoring wells, use of a permeameter in non-deformed samples, and auxiliary investigations (geophysics including GPR, EM and ER investigations; study of aquifer–river–lake hydrological relationships etc.).

Laboratory experiments, including selective sequential extraction (Tessier *et al.*, 1979; Becket, 1989; and others), sohxlet extractors (Hypolito, 1972), and column experiments have been carried out.

PRELIMINARY RESULTS

Lead is used as a melt fastener in glazes used as ceramic ground covers. As a result of the industrial processes, a lead-rich paste-like waste is produced (usually also rich in other metals such as Zn, Ba, Cr, Co, Cu, Ni, Na, Al and Zr, as well as boron). The waste "stabilization" process used by local industries includes increasing pH with chemical products, which causes the precipitation of a paste-like sludge; the floating solution is removed and recycled. In the past, part of this sludge was disposed of and the solution was released in areas surrounding the Fazenda Itaqui stream, causing their contamination.

Average lead concentrations in natural surface soils are 32 (3–189) mg kg^{-1} (Kabata-Pendias & Pendias, 1984); most are between 10 and 67 mg kg^{-1}. According to the Environmental Agency of the state of São Paulo, Brazil (CETESB, 1997), concentrations in soil of over 100 mg kg^{-1} probably reflect contamination effects.

Initial investigations have shown that the lead content in soil in the study area is 150–5500 mg kg^{-1} in affected areas which, in comparison to the reference area (30–60 mg kg^{-1}), indicates contamination. These values vary as a function of the nature of the solid material. Generally, the local typical soils are reddish-purple to brownish-red, very heterogeneous, and have a high clay content (40–70%) and their main mineralogy includes kaolinite, illite, quartz and a variety of oxides, mainly of iron and aluminium.

The bottom sediments of lakes, ponds and streams, collected by piston-core samplers, have greater lead concentrations at shallow depths (229–1570 mg kg^{-1} at depths of 0–0.25 m, and 21–99 mg kg^{-1} below). This indicates that industrial waste disposal and deposition of sediments have caused contamination. These values are much higher than those found in the reference area (20–39 mg kg^{-1}).

In soil samples obtained from the drilling of monitoring wells in affected areas, the greater concentrations (1500–5500 mg kg^{-1}) are related to the saturated zone and shallow depths, with anomalously low concentrations immediately above the water table (<500 mg kg^{-1}).

In surface water, the legal water quality standard for lead in streams such as the Fazenda Itaqui is 30 μg l^{-1} (Brazilian federal law) or 100 μg l^{-1} (state of São Paulo law). According to Moore (1989), lead concentration in surface water is typically <50 μg l^{-1}. There are no Brazilian standards for lead concentration in groundwater, but the federal limit for drinking water is 50 μg l^{-1}.

In water samples from Santa Gertrudes, lead has been detected in very variable concentrations in monitoring wells (30–2000 μg l^{-1} in affected areas, in comparison to 1–10 μg l^{-1} in the reference area) and rain water (20–1500 μg l^{-1}), but in low concentrations in surface water samples from lakes, ponds and the Fazenda Itaqui stream (1–30 μg l^{-1}, generally <10 μg l^{-1}).

The higher concentrations in groundwater samples are related to landfill or disposal areas, which constitute the local unconfined alluvial aquifer surrounding the Fazenda Itaqui stream. The hydrogeological characteristics of these areas were determined during investigations: hydraulic conductivity = 2.3×10^{-7}–9.9×10^{-7} m s^{-1}; water table depths = 0–0.75 m; hydraulic gradients = 0.022–0.01 m m^{-1}. Groundwater has a pH of between 7 and 8.5, a high content of TDS and high alkalinity, and, in some cases, negative Eh. In the reference area, pH is between 5.5 and 6.5, and TDS and alkalinity are lower.

It seems atmospheric particulate material has an important role in lead transportation, as shown by sampling atmospheric particulates and rainwater in pluviometers.

Sequential extraction experiments have been done on samples of bottom sediments and soil and they have shown that most extractable lead is related to oxides and organic matter, and sometimes also to carbonates (particularly in the cases with higher pH and alkalinity in associated groundwater). In the reference area, extractable lead is mainly related to oxides (>50%).

It was observed that the process of impact in the study area is the result of natural processes (erosion, silting-up, climate seasons and variations) and anthropogenic contribution (waste disposal, liquid effluent release, acceleration of natural processes related to land use). Within this scenario, lead tends to be fixed or sorbed by soil and sediments, and with the exception of nearby mainly contaminated areas, the concentration in water samples is low. Comparing extractable solutions from the reference and impacted areas, it also seems that, during those processes, organic matter is more selective in comparison to oxides.

Boron has a concentration of 36–334 mg kg^{-1} in soil samples (higher values in the saturated zone) and 37–478 mg kg^{-1} in bottom sediments (higher values at shallow depths) in impacted areas, higher to reference areas (respectively, 38–45 and 30–49 mg kg^{-1}).

In water samples, the concentration of B in groundwater is 139–504 mg l^{-1} in impacted areas (3.6–4.0 mg l^{-1} in the reference area) and lower in surface water (lakes, ponds, springs and streams). Thus, although boron is present in all environments, its concentration is relatively higher in water samples and in the impacted areas.

Occasionally, zinc, chromium, nickel, copper, barium and zirconium are present at high concentrations, particularly zinc in soil and sediments.

INITIAL CONCLUSIONS

Preliminary investigations have showed that lead is the main contaminant in groundwater, soil and sediments. Boron is present at high concentrations mainly in water samples. Table 1 shows the Pb and B results from the study and reference areas in relation to standards.

Table 1 Pb and B results. Comparison of study area, reference area and standards.

Type of sample	Element	Study area (impacted areas)	Reference area (out of industrial zone)	Standards
Groundwater samples	Pb	30–2000 μg l^{-1}	1–10 μg l^{-1}	50 μg l^{-1} [a]
	B	139–504 mg l^{-1}	3.6–4 mg l^{-1}	–
Surface water samples	Pb	1–30 μg l^{-1}	1–8 μg l^{-1}	30[b]–100[c] μg l^{-1}
	B	<1–125 mg l^{-1}	<1–5 mg l^{-1}	5 mg l^{-1} [d]
Bottom sediment samples	Pb	21–1570 mg kg^{-1}	20–39 mg kg^{-1}	–
	B	37–478 mg kg^{-1}	30–49 mg kg^{-1}	–
Soil samples	Pb	150–5500 mg kg^{-1}	30–60 mg kg^{-1}	–
	B	36–334 mg kg^{-1}	38–45 mg kg^{-1}	–

[a] Brazilian federal drinking water limit.
[b] Limit to rivers of class 2, Brazilian federal law.
[c] Limit to rivers of class 2, state of São Paulo law.
[d] Canadian drinking water limit.

NEXT STEPS

All these studies are in progress. The next stages of the research include: (a) soil/sediment–water interactions and study of the behaviour and mechanisms of mobility and fixation of contaminant metals; (b) the role of boron in the local hydrogeochemical cycle and its environmental consequences; (c) evaluation of metal partitioning between suspended sediment and surface water; (d) monitoring of a tropical storm event and its local environmental consequences; and (e) complementary experiments. These investigations will lead to an integrated hydrogeochemical model of the study area.

The results of this study will be added to a larger project on management of industrial areas; the Santa Gertrudes work is the pilot project. In parallel, technological characterization of the glazed ceramics industrial waste leading to improvement of industrial processes to avoid losses and decrease the quantity of waste, will be made.

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REFERENCES

Beckett, P. H. D. (1989) The use of extractants in studies on trace metals in soils, sewage sludges, and sludge-treated soils. *Adv. Soil Sci.* **10**, 143–176.

CETESB (Environmental Agency of the state of São Paulo) (1997) Quality reference standards and intervention values for soil and groundwater in the state of São Paulo, Brazil (in Portuguese). *Partial Report*, CETESB, São Paulo, Brazil.

DAEE (1982) Geological map of Campinas–Piracicaba region (in Portuguese). Departamento de Águas e Energia Elétrica & UNESP–Universidade Estadual Paulista, Brazil.

Hypolito, R. (1972) Intemperic weathering of diabasic rocks (in Portuguese). PhD Thesis, Institute of Geosciences, University of São Paulo (USP), Brazil.

Kabata-Pendias, A. & Pendias, H. (1984) *Trace Elements in Soils and Plants*. CRC Press Inc., Boca Raton, Florida, USA.

Tessier, A., Campbell, P. G. C. & Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**, 844–851.