3 trabalhos

NEW APPROACHES TO CHARACTERISING GROUNDWATER FLOW

10th - 14th September 2001

FINAL PROGRAMME

International Association of Hydrogeologists

in cooperation with

ATH Association of Tracer Hydrology

NEW APPROACHES TO CHARACTERISING GROUNDWATER FLOW

10th - 14th September 2001

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Tuesday September 11- Morning

INVITED SPEAKERS Session 2

Lecture room S0320: *Chairman: P. Dillon*

09.00-09.30 *P.L. Younger:* The Hydrogeology and Hydrochemistry of abandoned deep mines: Progress an pitfalls

09.30-10.00 *M. Veselic:* On the use of trcacer techniques in the unsaturated zone

10.00-10.30 *H. Hötzl:* Determination of transport parameters in aquifers through tracers

10.30 Coffee Break

SESSION 4
Detection and Survey Methods

Session 4.1

Lecture room S0314, *Chairman: T.R.Rüde*

09.00-09.20 *R.I. Acworth & G.R. Dasey:* Electrical imaging of the saline intrusion pattern beneath a tidal creek in a sand aquifer

09.20-09.40 *W.G. Coldewey & P. Göbel*: Effects of stormwater infiltration on the water balance of a city

09.40-10.00 *S.Evers, S.W.Fletcher, R.Ward & R.C.Harris:* A strategy for the protection of groundwater from nitrate leaching using spatial and geostatistical analyses

10.00-10.20 *S. Grams:* Kriging hydrochemical data - problems and solutions

10.20-10.40 Coffee Break

10.40-11.00 *D. Hannich, H. Hötzl, G.-P. Merkler:* Application of geophysical techniques to monitor natural attenuation at contaminated sites

11.00-11.20: *A. L. Bonacin Silva & R. Hypolito:* Hydrogeochemical investigations by the use of a technical-scientific approach in the Fazenda de Itaqui drainage basin situated in the influence area of glazed ceramics industries of Santa Gertrudes, Brazil – initial results

11.20-11.40: *S. Greenhalgh, J. Zhe & B. Zhou*: A trial of cross-hole electric imaging for monitoring aquifer artificial recharge

SESSION 3
Protection of Groundwater

Session 3.2

Lecture room S1128: *Chairman: E.P. Löhnert*

09.00-09.20 *J. M. Sharp, Hansen, J. Krothe:* Effects of urbanization on the hydrogeological System: The physical effects of utility trenches

09.20-09.40 *P. Grathwohl & D. Halm:* Groundwater Risk Assessment at Contaminated Sites (GRACOS)

09.40-10.00 *K.W.F. Howard:* Polluted groundwater - deadly lessons from Walkerton, Ontario, Canada

10.00-10.20 *P.E. Ihalainen:* Hydrogeology around a small quarry in the light of ground-water protection

10.20-10.40 Coffee Break

10.40-11.00 *M. Karnuth, D. Schenk, T. Hofmann:* Elution of contaminants from recycled demolition waste materials

Working Group Hydrogeology and Environmental Geology (LMU, Munich)

International Association of Hydrogeologists

in co-operation with

ATH Association of Tracer Hydrology

XXXI. Congress 2001
New Approaches to Characterising Groundwater Flow

Munich, Germany

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IAH'2001 - Technical Program: **S4**

HYDROGEOCHEMISTRY INVESTIGATIONS, USING TECHNICAL-SCIENTIFIC APPROACH, IN FAZENDA DE ITAQUI DRAINAGE BASIN, SITUATED IN THE INFLUENCE AREA OF GLAZED CERAMICS INDUSTRIES OF SANTA GERTRUDES, BRAZIL – INITIAL RESULTS[1]

André Luiz Bonacin Silva[2]
Raphael Hypolito[3]

In Brazil, although heavy metals and other inorganic compounds contamination or pollution studies in soil, groundwater and surface water have been carried out since some decades, generally, they don't take into account an integrated and detailed view, from the source and form of waste disposal, the behavior and mechanisms of mobility and fixation of these compounds in soil or sediments, until their dynamics in the hydrogeological cycle.

The comprehension of the hydrogeochemical behavior of these potentially contaminants related to industrial waste and sludge disposal in tropical soils and adjacent water resouces, studying water – soil / sediments / rocks - contaminant relationship, will add an important contribution to the knowledge of the anthropic intervention consequences related to hydrological and geochemical cycles.

In this paper, environmental diagnosis and initial monitoring and experimental results are presented, as well as geophysics and hydrogeological field investigations. The studied area, Fazenda de Itaqui drainage basin (in the city of Santa Gertrudes, Brazil), had received rich-lead glaze and pigment / coloring industrial effluents and sludge, which were inadequately disposed in this basin, which is surrounded by the industries. Occasionally, local contamination or pollution problems also include other metals or elements, such as zinc, boron, chromium, nickel, copper and zirconium.

A technical-scientific detailed research project has been developed by USP - University of São Paulo since the end of 1998, including solid (soil, bottom stream and lake / pond sediments), liquid (groundwater, surface and rain water) and industrial material (raw, effluent / waste and other industrial materials used in the glazed ceramics assembly line) sampling and examination. Laboratory experiments, including selective sequential extraction, sohxlet extractors and column experiments has been carried out.

The main objective of this research project has been the evaluation of the availability and behavior of potentially toxic substances (Pb, Zn, B and others) to local environment, as result of glazed ceramics industrial waste disposal.

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[1] supported by FAPESP, under grants 98/06842-1, 97/12827-2 and 98/06845-0

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Hydrogeochemistry investigations, using technical-scientific approach, in Fazenda de Itaqui drainage basin, situated in the influence area of glazed ceramics industries of Santa Gertrudes, Brazil – initial results

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ABSTRACT: The investigated area, situated in Fazenda de Itaqui drainage basin, Santa Gertrudes, Brazil, had received rich-lead glaze and pigment / coloring industrial effluents and sludge, which were inadequately disposed in this basin. A technical-scientific research project has been developed, including the sampling and examination of soil, sediments, groundwater, surface water, rainwater and industrial materials, as well as hydrogeological and geophysical investigations. These studies have been carried out as much in the impacted area as in a reference area ("background"), situated out of influence of the industrial activities. Initial analysis in impacted areas have showed that lead is a contaminant in soil and sediments (150-14,700 mg.kg^{-1}). In water samples, it has been detected in very heterogeneous concentrations in monitoring wells (30-2,000 □g.L^{-1}) and rainwater (20-1,500 □g.L^{-1}), but in low concentrations in superficial water samples of lakes, ponds and streams (generally < 10 □g.L^{-1}). Some experiments have been done to study the behavior of mainly lead and their results show that lead tends to be fixed by the soil and sediments. On the other hand, boron tends to be present in high concentration in all environments, mainly in water samples (up to 504 mg.L^{-1} in groundwater and 125 mg.L^{-1} in superficial water). Other metals, such as zinc, chromium, nickel, copper and zirconium, are occasionally present as contaminants, mainly in soil and sediments. These studies are in progress and will be detailed during next research stages.

1 INTRODUCTION

In Brazil, although heavy metals and other inorganic compounds contamination studies in soil, groundwater and surface water have been carried out for some decades, generally, they don't take into account an integrated and detailed view, from the source and form of waste disposal, the behavior and mechanisms of mobility and fixation of these compounds in soil or sediments, until their dynamics in the hydrogeological cycle.

The comprehension of the hydrogeochemical behavior of these potentially contaminant compounds, related to industrial waste disposal and release in tropical soils and adjacent water resources, studying soil / sediments - water - contaminant relationship, will add an important contribution to the knowledge of some anthropic intervention consequences related to hydrological and geochemical cycles. It is also important for the risk assessment and the required waste management.

As an example of this sort of study, one of the main objectives of this research is the evaluation of the availability and behavior of potentially toxic substances (mainly with Pb, B and Zn) to local environment, as result of glazed ceramics industrial waste disposal and effluent release.

The studied area is inside the main ceramics industrial complex of Brazil (>50% of national production), situated in Santa Gertrudes.

This research is part of a larger project, entitled "Management of industrial waste disposal and associated potentially contaminated areas, in Santa Gertrudes glazed ceramics industrial complex, state of São Paulo, Brazil" (Silva et al., in press), which is also in progress.

2 STUDIED AREA

Fazenda Itaqui drainage basin, situated in the city of Santa Gertrudes (Fig. 1), had received glaze and pigment/coloring industrial effluents and sludge, which were inadequately disposed or thrown on this basin surrounded by those industries (Fig. 2, at the end of this paper). Fazenda Itaqui stream is an affluent of Corumbataí river, one of the main water resources of the region.

The same environmental investigations have been done in a reference area ("background", Fig. 1), situated out of influence of the industrial activities, about 5 km far from the investigated area and with similar pedo-geological and topographic conditions, to make possible a comparison of the results.

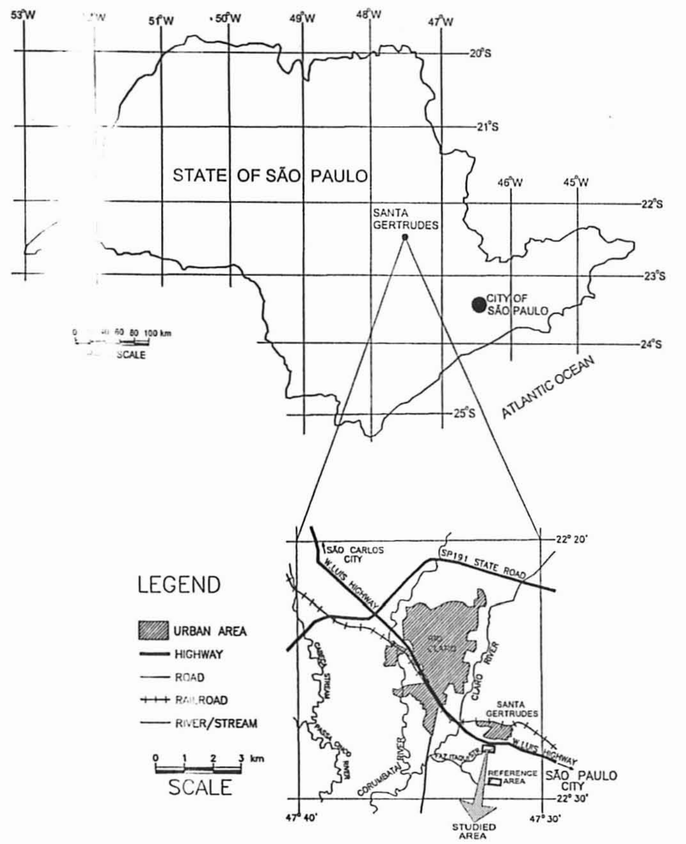


Figure [illegible]. Localization of Santa Gertrudes, the studied and the refe[illegible] areas, in the state of São Paulo, Brazil.

Cli[illegible]te of Santa Gertrudes is Cwa in terms of Köpp[illegible] clas[illegible]cation, with annual average precipitation [illegible] 1,301 mm (DAEE, 1998).

Pe[illegible]an Corumbataí Formation (Pc) crops out in the a[illegible], constituting reddish-brown, reddish-purple or a[illegible] [illegible]actured and non-fractured mudstones. Becau[illegible] [illegible] this specific situation, regional hydrogeology [illegible]udes non-regular layers of aquitards (non-frac[illegible]d mudstones) and "fractured sedimentary aquifers" (fractured mudstones). These ones present local [illegible] [illegible]aracteristics and are related to geotecto[illegible] eve[illegible] or basic intrusions.

Be[illegible], t[illegible]e are unconsolidated sediments, a mix [illegible] waste [illegible]sposed by industries on rich-clay recent [illegible]vial t[illegible]rains. They are situated in the lower are[illegible] [illegible] t[illegible] [illegible]ainage basin, and constitute a sedime[illegible] [illegible] u[illegible]fined local aquifer, main object of gro[illegible]water investigations (area of detail studies, Fig. [illegible]).

[illegible]ical base is a *sill* of basic igneous rock[illegible] [illegible]ral Formation.

3 [illegible] OF INVESTIGATIONS

A t[illegible] [illegible]ntific detailed research project has be[illegible], including solid (soil; stream, lake and [illegible] [illegible]m sediments), liquid (groundwater, surfa[illegible] water) and industrial material (raw, ef[illegible] [illegible] other industrial materials used in the glazed ceramics assembly line) sampling and examination (examples in Photographs 1-4).

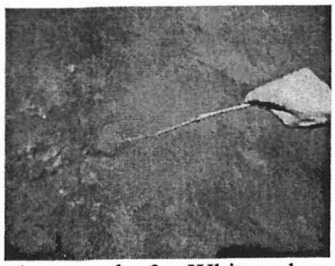
Contamination have been situated in terms of historic reconstitution of industrial waste disposal in Fazenda Itaqui drainage basin, and recent expansion of the production of Santa Gertrudes ceramics industrial complex (Silva et al., in press).

Field investigations were done to describe physical and hydrological conditions: geology-pedology characteristics, hydrological-hydrogeological local cycle and physical processes such as erosion and sanding up.

Hydrogeological investigations included bail-down and slug tests in monitoring wells (Fig. 3), use of permeameter in non-deformed samples (lab experiments), and auxiliary investigations: geophysics including GPR, EM and ER investigations; study of aquifer-river-lake hydrological relationship etc.

Photograph 1. Ashed-white glaze waste disposal and industrial effluent throw in an abandoned industrial area, upstream Fazenda de Itaqui streams, pounds and lakes.

Photograph 2. White glaze waste disposed on sediments of a stream.



Photograph 3. White glaze waste disposed on sediments of the margin of a lake.

Photograph 4. Glazed-ceramics industrial waste (mainly shiver), as result of industrial processes losses.

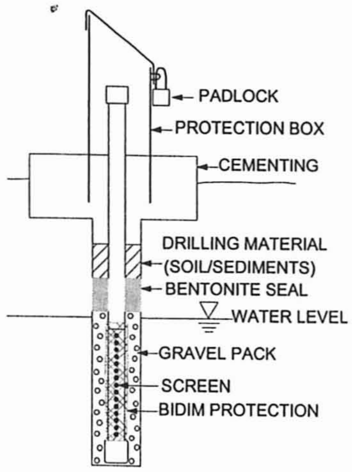


Figure 3. Configuration of small monitoring wells installed in Santa Gertrudes.

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

All these investigations have been correlated to reach the integrated hydrogeochemical model of the investigated area.

4 INITIAL RESULTS

Lead is used as melt fastener in glazes used as ceramics ground cover. As result of industrial processes losses, a lead-rich pasty waste is produced (in general, also other metals-rich, such as Zn, Cr, Ni, Cu, Al, Ba and Zr, as well as boron). This waste also includes pigment and coloring industrial materials, used as part of art-design in ceramics ground cover.

The process of the waste "stabilization" used by local industries includes the increasing of pH with chemical products, which causes the precipitation of a pasty solid sludge. The floating solution is removed and recycled.

In the past, part of this sludge was disposed and the floating solution was released in the surrounding areas of Fazenda Itaqui stream, causing their contamination.

Lead average concentration in natural superficial soils is 32 (3-189) $mg.kg^{-1}$ (Kabata-Pendias & Pendias, 1984), most of them between 10 and 67 $mg.kg^{-1}$. According to the Environmental Agency of the state of São Paulo, Brazil – CETESB (CETESB, 1997), concentrations in soil over 100 $mg.kg^{-1}$ probably reflect pollution /contamination effects.

The main factors which influence the availability and behavior of lead in soil are: pH; soil texture; mechanisms of sorption; clay and clay minerals, oxides and organic matter content and nature (Kabata-Pendias & Pendias, op. cit.; Alloway, 1995).

Initial investigations have showed that the lead content in soil in the studied area is 150-14,700 $mg.kg^{-1}$ in impacted areas, which, in comparison to "background" area (30-60 $mg.kg^{-1}$) and bibliography, indicates contamination.

Those values vary as a function of the nature of solid material. Generally, local typical soils are reddish-purple to brownish-red, very heterogeneous, colorful, have high content of clays (40–70%) and their main mineralogy includes kaolinite, illite, quartz and a variety of oxides, mainly iron and aluminum ones.

In bottom sediments profiles of lakes, ponds and streams, collected by piston-core samplers, the shorter the depth the higher the concentrations: 229-1570 $mg.kg^{-1}$ in shorter depths (0 – 0.25m) and 21-99 $mg.kg^{-1}$ in deeper ones. This behavior indicates that industrial waste disposal or release (anthropic intervention), in addition to transport and deposition of sediments (physical processes), has caused contamination in bottom sediments. Besides, the higher concentrations are much higher than those found in bottom sediments of the reference area: 20-39 $mg.kg^{-1}$.

In soil log samples obtained from the drilling of monitoring wells in the impacted areas, the higher concentrations are related to saturated zone and in shorter depths (500-14,700 $mg.kg^{-1}$), with anomalous lower concentrations right above water table (< 500 $mg.kg^{-1}$), in this case, probably coincident with capillary fringe.

In water samples, it has been detected in very heterogeneous concentrations of lead in monitoring wells (30-2,000 $\mu g.L^{-1}$ in impacted areas, in comparison to 1-10 $\mu g.L^{-1}$ in the reference area) and rainwater (20-1,500 $\mu g.L^{-1}$), but in low concentrations in surface water samples of lakes, ponds and Fazenda Itaqui stream (generally < 10 $\mu g.L^{-1}$, as much in impacted areas, as in the reference one).

In surface water, lead has a legal water quality standard related to Fazenda Itaqui stream class of 30 $\mu g.L^{-1}$ (federal Brazilian law) or 100 $\mu g.L^{-1}$ (state of São Paulo law). According to Moore (1989), lead concentration in surface water is typically <50$\mu g.L^{-1}$. There are no Brazilian standards for lead concentration in groundwater, but federal limit for drinking water is 50$\mu g.L^{-1}$.

In relation to rainwater, it seems that particle material has an important role in lead concentration found in monitoring pluviometers (20-1,500 $\mu g.L^{-1}$). In this case, it also has been detected higher concentrations of fluoride and boron in rainwater samples, which can be associated to the pollution caused by the industrial oven gaseous wastes during the process of ceramics burning.

The higher concentrations in groundwater are related to landfill or disposal areas, which constitute local recent alluvial unconfined aquifer surrounding Fazenda Itaqui stream. In these areas, hydrogeological basement is composed by mudstones of Permian Corumbataí Formation and main hydrogeological characteristics are: water table depths = 0-0.75m; hydraulic gradients = 0.022-0.01m/m; hydraulic conductivity = (2.3 – 9.9) x 10^{-7} $m.s^{-1}$.

In the reference area, pH of groundwater samples is between 5.5 and 6.5 and TDS content is low, generally < 50mg.L^{-1}. In the impacted areas, groundwater has pH between 7 and 8.5 (up to 9.5 in association with industrial actual effluents), high content of TDS (generally > 500mg.L^{-1}) and alkalinity, and, in some cases, negative Eh.

The increase of pH, TDS and alkalinity is associated to water percolation and lixiviation in places where industrial wastes were disposed. On the other hand, the negative values of Eh appear in flood areas (with low hydraulic gradients) and / or locals where the content of organic matter is relatively higher.

Besides, the correlation between different kinds of analysis permitted to indicate: higher values of pH in groundwater, higher content of clay and CEC (cation exchange capacity) in soil and sediments and low groundwater flow contributed to fix lead in solid materials (soil, sediments). It is a dynamic process, which includes physical and chemical processes, accelerated by anthropic interventions.

Sequential extraction experiments (Hypolito, in prep.) have been done in samples of bottom sediments and soil. The results, although preliminary, have showed that main part of extractable lead in impacted areas is related to oxides (15-45%) and organic matter (18-65%). Sometimes lead is also related to carbonates (5-32%), particularly in the cases with higher pH and alkalinity, and associated to saturated zone. In the reference area, extractable lead is mainly related to oxides (generally > 50%).

It must be observed that the process of impact in the studied area is the result of natural processes (erosion, sanding up, climate seasons and variations) and anthropic contribution (waste disposal, liquid effluent throw, acceleration of natural processes related to land use). Inside this situation, lead tends to be fixed by soil and sediments, and with the exception of nearby mainly contaminated areas, the concentration in water samples is low. Comparing extractable solutions in 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 saturated zone) and 37-478 mg.kg^{-1} in bottom sediments (higher values in shorter 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 mg.L^{-1} in reference area) and lower in surface water (lakes, ponds, springs and streams): until 125 mg.L^{-1}. 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 in high concentration, mainly zinc in soil and sediments.

Higher concentrations of zinc in impacted areas are present in soil (133-2,930 mg.kg^{-1}) and bottom sediments (148-4,195 mg.kg^{-1}), much higher than those found in the reference area, respectively, 72-113 and 43-88 mg.kg^{-1}.

5 CONCLUSIONS AND NEXT STEPS

Preliminary investigations have showed that lead is the main contaminant in groundwater, soil and sediments. Boron is present in high concentration mainly in water samples. Table 1 shows the Pb, B and Zn results comparison among study area, reference area and standards / bibliography.

From the correlation among all analysis results; the understanding of anthropic, physical and chemical processes; actual industrial materials analysis results and past registries of the ceramics industries activities, the contamination or pollution by Pb, B, Zn, Cr, Ni, Ba and Zr, when present in the studied area, can be associated to waste disposal or throw of effluents of ceramics industries.

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

The results of this study will be added to a larger project of management of industrial areas (Silva et al., in press), whose pilot project is Santa Gertrudes. Remediation and / or mitigative emergency actions are also in progress.

Besides, about the glazed ceramics industrial waste, it will be done its technological characterization in parallel to the improvement of industrial processes to avoid losses and decrease the quantity of waste.

6 ACKNOWLEDGEMENTS

This project has been supported by FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo), under grants 97/12827-2 and 98/06842-1.

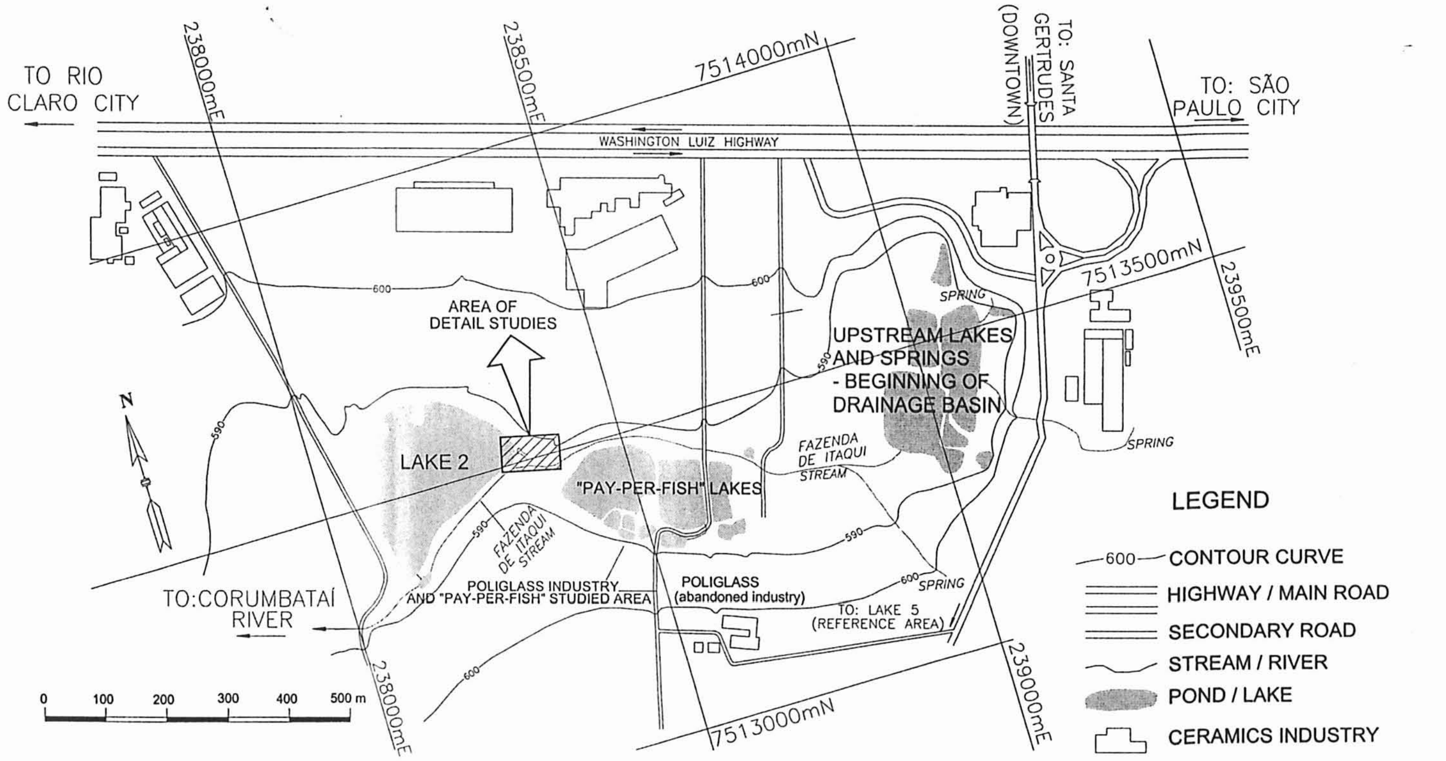


Figure 2 Studied area, with Fazenda Itaqui stream and associated lakes, surrounded by ceramics industries, Santa Gertrudes, Brazil.

Table 1. Pb, B and Zn analysis - initial results - comparison among studied area, reference area and standards.

Type of sample	Element	Studied area (impacted areas)	Reference area (out of industrial zone)	Standards
Ground-	Pb	30-2,000 μg.L^{-1}	1-10 μg.L^{-1}	50 μg.L^{-1} (1)
water	B	139 - 504 mg.L^{-1}	3.6 – 4 mg.L^{-1}	5,0 mg.L^{-1} (2)
samples	Zn	132 – 504 μg.L^{-1}	3 – 10 μg.L^{-1}	5,0 mg.L^{-1} (1)
Surface	Pb	1-30 μg.L^{-1}	1-8 μg.L^{-1}	30 (3) – 100 (4) μg.L^{-1}
water	B	< 1 - 125 mg.L^{-1}	< 1 - 5 mg.L^{-1}	0,75 (3) mg.L^{-1}
samples	Zn	6 – 45 μg.L^{-1}	3 – 8 μg.L^{-1}	0,18 (3) – 5,0 (4) mg.L^{-1}
Bottom	Pb	21 – 1,570 mg.kg^{-1}	20 - 39 mg.kg^{-1}	-
sediment	B	37 – 478 mg.kg^{-1}	30 – 49 mg.kg^{-1}	-
samples	Zn	148 - 4,195 mg.kg^{-1}	43 - 88 mg.kg^{-1}	-
Soil	Pb	150 – 14,700 mg.kg^{-1}	30 – 60 mg.kg^{-1}	-
samples	B	36 – 334 mg.kg^{-1}	38 – 45 mg.kg^{-1}	-
	Zn	133 - 2,930 mg.kg^{-1}	72 - 113 mg.kg^{-1}	-

(1) Brazilian federal drinking water limit, 1990; (2) Guidelines for Canadian Drinking Water Quality, 1987; (3) limit to rivers of class 2, Brazilian federal law, 1986; (4) limit to rivers of class 2, state of São Paulo law, Brazil, 1976. All analysis were done in Activation Laboratories, Ancaster, Canada, and Quimlab, São José dos Campos, state of São Paulo, Brazil.

The authors are also thankful to: geologist Fernando C. Breviglieri, who reviewed English text; CETESB – Environmental Agency of São Paulo state, Piracicaba office; and CEDASA - ceramics industry, which gave support to field investigations.

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