

## Hydrochemical characterization of ground waters in Salto and Indaiatuba Municipal Districts-São Paulo State, Brazil

Sibele Ezaki<sup>1</sup>

Raphael Hypolito<sup>2</sup>

Annabel Pérez Aguilar<sup>1</sup>

Francisco Moschini<sup>3</sup>

<sup>1</sup> Geological Institute/Secretariat of Environment of São Paulo State

<sup>2</sup> Geosciences Institute/University of São Paulo

<sup>3</sup> Municipal Prefecture of Salto

Preliminary hydrochemical characterization of groundwaters in Salto and Indaiatuba Municipal Districts, São Paulo State, identified drilling wells with saline waters and with high fluoride and total dissolved solids (TDS) concentrations, which constitute restrictions for the potential use of water. The sources of these anomalies can be related to hydrolysis of feldspars from granitic rocks and to percolation of hydrothermal fluids through faults. Water resources associated to exploration of wells is very important in studied area. Thus, further and more detailed hydrogeochemical studies from the Crystalline, Tubarão and Intemperism mantle Aquifers are required.

**Keywords:** *Ground water, Hydrochemistry, Quality*

### 1 INTRODUCTION

The quality evaluation of drinking water and groundwaters destined to other categories of uses involves the knowledge of hydrogeochemical processes considering soil-rock-water interactions, as well as anthropogenic interferences caused by ancient and present activities.

The purpose of this project was to carry out an hydrogeochemical study of phreatic and deep groundwater in areas that include industrial and residencial zones in the Salto and Indaiatuba Municipal Districts.

Due to the low availability of water in sedimentary and crystalline aquifer systems in studied area and to the common occurrence of saline waters, the population has mainly extracted water by using excavated wells.

A preliminary hydrochemical characterization of aquifer groundwaters of the studied area is presented.

### 2 GEOLOGICAL CONTEXT

In the geological context, the studied area is situated at the eastern border of the Paraná Sedimentary

Basin, where sediments of Itararé Subgroup from the Tubarão Group (Permian-Carboniferous) recover Crystalline Rocks (pre-Cambrian). These sediments were deposited under glacial-marine-fluvial environmental conditions and were consolidated as variable and discontinuous types of rocks represented by intercalations and associations of sandstones, shales, mudstones, diamictites, and rhythmities (DAEE-UNESP 1979; Salvetti 2005).

The Crystalline Rocks are constituted of metamorphic rocks of the Amparo Complex, represented by migmatites, gneisses, schists, and quartzites (Ebert 1968, 1971; Neves 2005), which were intruded by granitoid rocks (Janasi et al. 1990, Artur, 2003, Gallemebeck, 1997).

Sedimentary and crystalline rocks, in their water saturated portions, correspond to the Tubarão and Crystalline Aquifers. The first is characterized by the flow of water through voids in grains, and in the second by water flows that circulate through fractures, faults, and joints. Saprolitic material originated after the alteration of crystalline rocks, which constitutes the intemperism mantle, is considered as being a sub-



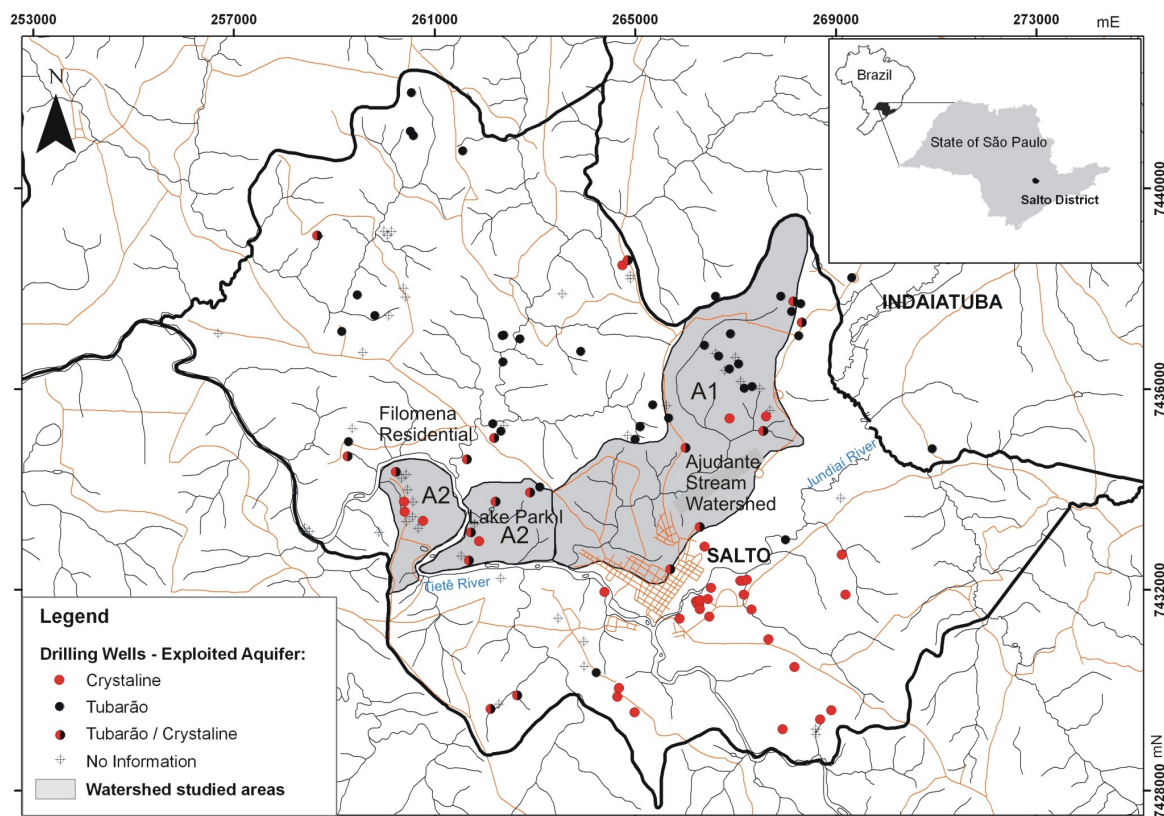


Figure 1

*Distribution of drilling wells in Salto Municipal District, São Paulo State.*

system of the Crystalline Aquifer System due to its specific circulation and water storage characteristics, corresponding to an aquifer of granular porosity.

### 3 METHODS

A compilation of the different types of wells existing in the municipal districts of Salto and Indaiatuba was done by using records that belong to the DAEE (Departamento de Águas e Energia Elétrica) and to particular perforation companies. In the Salto Municipal District, from 150 drilling wells (DW) that were registered, only 131 of them that had localization information were considered in this study. From 401 drilling wells registered in the Indaiatuba Municipal District, only 25 were considered in this study because they were localized in the neighborhood from Salto District in similar geological contexts.

Within the area where are present the 156 compiled drilling wells, 44 reports had fluoride analyzes and 36 TDS analyzes.

Two pilot-areas were selected for water sample geochemical complementary studies. The criteria used for selecting these two areas were that both had industries, that compiled geochemical data from records showed anomalies, and that within a single stream watershed were present wells near the contact of sedimentary and igneous rocks. The first pilot-area corresponds to the Ajudante Stream Watershed (A1) and the second to an area localized in the margins of the Tietê's River (A2) (Figure 1). A1 is occupied by industries and by a landfill that is localized near the spring of the Ajudante Stream, which before discharging in the Tietê River, crosses through an area of dense urban occupation. Wells in A1 are localized in Itararé Subgroup sediments and in granitic rocks. In A2, in one of the margins of the Tietê River was built a residential joint ownership and the other margin is occupied by an industrial district.

Groundwater chemical properties and inter-rela-

tions between superficial and groundwater were studied with more detail in pilot-areas.

In these two pilot-areas shallow and deep groundwater samples were collected from 18 shallow excavated wells (SEW) and from 13 DW. SEW collect water from soils and from intemperism mantle, which represent the Phreatic Aquifer. From the 13 DW, 6 are localized in the Crystalline Aquifer, 4 in the Tubarão Aquifer, and 3 do not have litology information. An average depth of DW e SEW was calculated considering wells present in pilot-areas, corresponding to 140 m (with depths varying from 91 until 300m) 18 m (with depths varying from 10 until 30 m), respectively.

Physical-chemical and chemical parameters of groundwater samples were analyzed. Fluoride and TDS analyzed in water samples from the 13 DW (pilot-area) were considered instead of analyzes data from reports, from which were used 22 TDS and 30 fluoride analyze registers.

The pH, Eh, electrical conductivity (EC) and alka-

linity parameters from these samples were measured during field works. Afterwards all samples were filtered through a 0.45  $\mu\text{m}$  acetate membrane and, in the sequence, were divided in two aliquots, being one preserved at 4°C (for anion analyses) and the other was mixed with HNO<sub>3</sub> until pH of the solution was bellow 2 (for cation analyses).

Hydrochemical analyses were done in laboratories from the Geosciences Institute from the University of São Paulo. Al<sup>3+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Cr<sub>total</sub>, Cu<sup>2+</sup>, Fe<sub>total</sub>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Sr<sup>2+</sup> Zn<sup>2+</sup> were analyzed by atomic spectrophotometry absorption using a GBC 932B Plus; Na<sup>+</sup> e K<sup>+</sup> were determined by light photometry using a Micronal 262, and F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> were analyzed by liquid cromatography using a Dionex-ICS 90.

To calculate average water sample parameters for both pilot-areas, chemical data from more 9 reports of DW were considered (5 localized in the Crystalline Aquifer and 4 in the Tubarão Aquifer). Results are presented in Table 1.

**Table 1**

*Principal characteristics of DW (present in the Crystalline and Tubarão Aquifers) and SEW (present in soil and intemperism mantle, which constitute the Phreatic Aquifer)*

Parameter	Detection Limit	Potability (Portry N° 518/04)	Aquifer		
			Crystalline n=11	Tubarão n =8	Prheatic n=18
Depth (m)	-	-	131,00	156,50	18,18
Eh (mV)	-	-	101,50	121,83	221,84
pH	-	-	7,64	7,51	6,02
EC ( $\mu\text{S}/\text{cm}$ )	-	-	562,83	330,20	162,63
STD (mg/L)	-	-	365,84	214,63	105,71
Na <sup>+</sup> mg/L	0,1	200,0	80,15	64,82	11,72
K <sup>+</sup> mg/L	0,1	-	0,86	0,77	3,01
Ca <sup>2+</sup> mg/L	0,001	-	28,42	42,42	7,98
Mg <sup>2+</sup> mg/L	0,0001	-	8,86	4,44	7,98
Fe <sup>total</sup> mg/L	0,006	0,30	0,14	0,20	0,17
NO <sub>3</sub> <sup>-</sup> mg/L	0,019	10	0,32	0,07	10,02
Cl <sup>-</sup> mg/L	0,008	250	34,01	25,01	10,32
SO <sub>4</sub> <sup>2-</sup> mg/L	0,001	250	136,51	103,19	3,39
Total Alcalinity (mg/L CaCO <sub>3</sub> )			122,82	75,88	44,21
F <sup>-</sup> mg/L	0,001	1,5	1,57	2,08	0,10

Note: N = number of considered wells



For hydrochemical groundwater classification Piper diagrams were used and fluoride and total dissolved solids (TDS) data was statistically interpolated (Kriging method) using Surfer 8.0 program.

#### 4 PRELIMINARY RESULTS AND DISCUSSION

From the total of the 156 registered wells 47 of them explore water from the Crystalline Aquifer, 53 from Tubarão Aquifer, and 28 explore water from two different aquifers, being referred as mixed wells. In these mixed wells the well crosses one of the aquifers for at least 20% of its total depth. Considering mixed wells, 23 explore water from the Tubarão and Crystalline Aquifers.

Hydrochemical DW and SEW waters classification using Piper diagrams is presented in Figure 2.

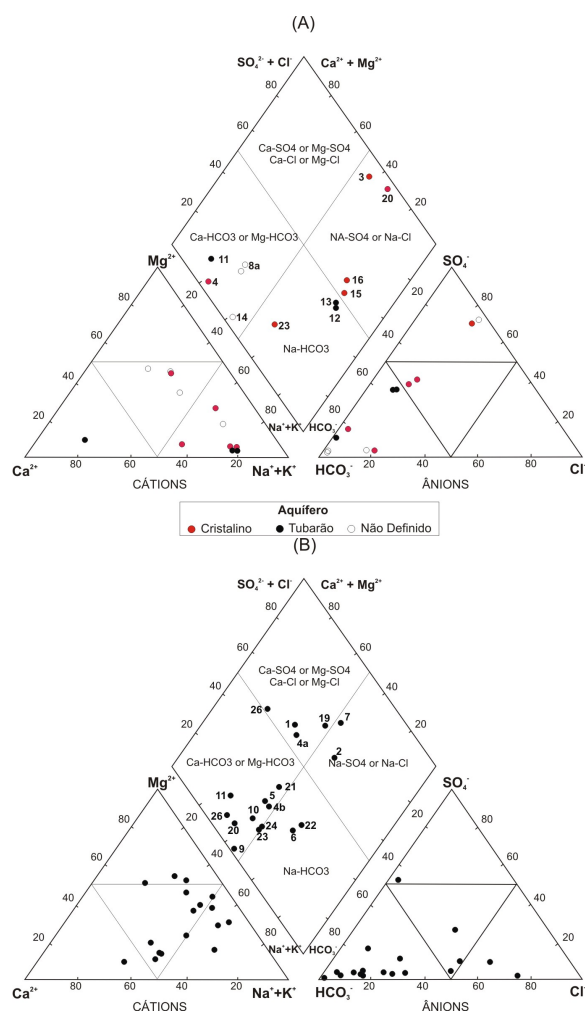
Using Piper's diagrams (Figure 2A), waters from DW are classified predominantly as Ca-HCO<sub>3</sub> or Mg-HCO<sub>3</sub> waters, Na-HCO<sub>3</sub> waters, or as Na-Cl or Na-SO<sub>4</sub> waters. Na-Cl or Na-SO<sub>4</sub> waters are usually associated to crystalline rocks, being the salinity average of the Crystalline Aquifer a little bit higher in relation with those related with the Tubarão Aquifer (Table 1).

Waters from SEW (Figure 2B) are classified, mainly, as Ca-HCO<sub>3</sub> or Mg-HCO<sub>3</sub> waters and, secondarily, as Na-HCO<sub>3</sub>. Chlorate or sulfate waters are also present. Chlorated water was collected in a well nearby Salto's Landfill, being Cl<sup>-</sup> concentration probably due to landfill contamination processes.

When compared to deep aquifer waters, the groundwater obtained through excavated well, show lower pH values that varied from 5.0 to 7.7, with an average value of 6.0. These values indicate influence of rain waters. Its salinity, expressed in terms of electric conductivity, is also smaller, having an average value of 126,3  $\mu\text{S}/\text{cm}$  (values ranging from 15.0 to 435.0  $\mu\text{S}/\text{cm}$ ). These shallower waters also have lower ionic and Ca<sup>2+</sup>, Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> concentrations in comparison with groundwater from deep wells

The waters of the drilling wells show higher pH and electric conductivity values. The pH values vary from 6.0 to 9.89, corresponding average value to 7.6. The conductivity values vary from 109 to 1225

$\mu\text{S}/\text{cm}$ , corresponding average value to 367.5  $\mu\text{S}/\text{cm}$ , being also more mineralized.



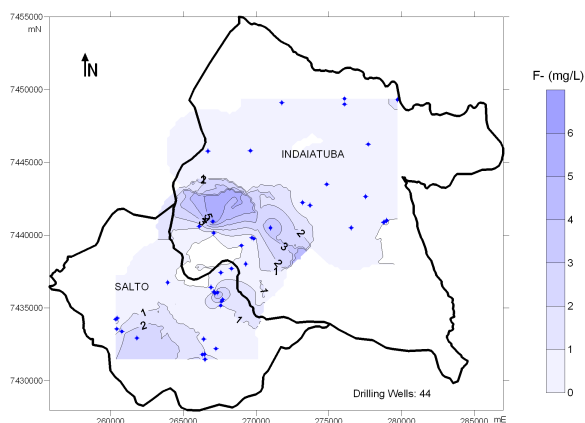
**Figure 2**

*Piper Diagrams showing groundwater hydrochemical classification from pilot-areas wells: DW (A) and SEW (B).*

Analyzing the groundwaters fluoride concentrations, in 27% of the deep drilling wells this concentration is higher than 1,5 mg/L, which corresponds to water potable limit established by the Ministry of Health (Regulation N<sup>o</sup> 518/04) (Figure 3). The use of fluoride-rich waters is mainly industrial but waters also provide residences. The fluoride anomaly occurs in wells whose depths vary between 150 and 300 meters, being correlated to high pH values and Na-HCO<sub>3</sub> or Na-SO<sub>4</sub> groundwaters. Within pilot-areas, wells from three sub-areas show anomalous fluoride concentrations: 1) in the

southwest part of studied area where are localized the Santa Filomena residential joint ownership and the Lake Park Industrial District; 2) in the northern part of Salto Municipal District, close of the limit with Indaiatuba Municipal District, where are localized the Tranquili Gianinni Industrial District, with wells wells used by th Chancellor Laundry and the Ipê industry, and the Municipal Landfill; 3) in Indaiatuba Municipal District in wells that belong to the General Motors-GM industry.

The source of fluoride in water can be related to hydrothermal percolation fluids or to hydrolysis of F-rich biotite and amphiboles present in granitic rocks. The presence of F-rich mafic minerals in granitic rocks from the area was characterized by Gallemebeck (1997).



**Figure 3**

*Fluoride concentration of drilling well groundwaters in Salto and Indaiatuba Districts.*

The average TDS values for water samples corresponding to the 36 DW were: 288mg/L for the Crystalline Aquifer (range of values varying from 71 to 796 mg/L); 207mg/L for the mixed Tubarão/Crystalline Aquifer (range of values varying from 119 to 452 mg/L); 266 mg/L (range of values varying from 132 to 288 mg/L). A map of TDS isovalues is shown in Figure 4.

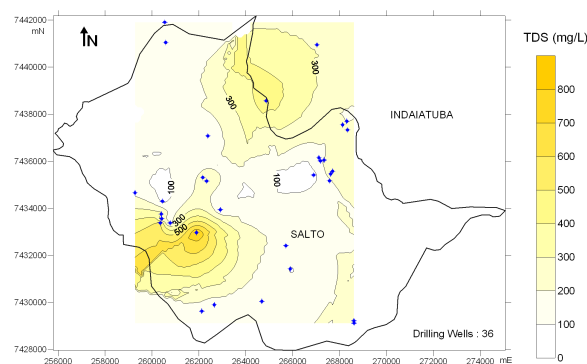
The concentration of TDS in waters reflects its salinity and is conductivity. Thus, high TDS values found in DW are associated to the presence of saline waters in studied area.

The higher TDS concentrations in water samples were found in the Filomena residential joint ownership and the Lake Park Industrial District (A2),

which are localized close to Tietê River that represents the main discharge of studied area. As previously discussed, water samples from wells from this sub-area also show anomalous high fluoride concentrations.

In A2 high TDS values are also associated to high hardness water values, which implied in disablement of DW, especially those used by industries due to salt incrustations in tabulations or because it caused interferences in chemical industrial processes.

In all area, due to taste and hardness aspects of groundwaters that also present characteristics of saline water, within residential joint ownerships, the construction of SEW for water consumption is common, besides the existence of DW.



**Figure 4**

*TDS concentration of drilling well groundwaters in Salto and Indaiatuba Districts.*

Considering DW length, water samples from those having until 100 m lengths and that were localized in fractured Crystalline Aquifer presented Ca-HCO<sub>3</sub> waters, whereas those having between 100 and 200 m length, presented mainly Na-HCO<sub>3</sub> waters having some of them also Na-SO<sub>4</sub> and Na-SO<sub>4</sub>-Cl<sup>-</sup> in water composition. This is suggestive for the existence of water chemical variation associated to depth. As discussed by Gascoyne & Kaminemi (1994), the saline waters in crystalline rocks are typically depleted in Na<sup>+</sup> relative to Cl<sup>-</sup>, which makes them different if compared with saline marine waters and evaporate deposit originated waters. The variation of Ca-Na-HCO<sub>3</sub>-rich waters to Na-Ca-HCO<sub>3</sub>-rich waters with increased depth has can be associated to plagioclase and feldspars hydrolysis by which Na<sup>+</sup> and Ca are released to fluid

coupled with loss of Ca by precipitation and/or ion exchange (for Na<sup>+</sup>) on clay minerals in the fractures.

In pilot-areas obtained Na<sup>+</sup> and Cl<sup>-</sup> chemical analyzes for water samples indicate a predominance of Na<sup>+</sup> (average value corresponding to 80 ml/L, with values ranging from 35 to 153 ml/L) over Cl<sup>-</sup> (average value corresponding to 34 ml/L, with values ranging from 02 to 107 ml/L), being then suggestive that the presence of saline waters is related to interperism of granitic rocks. Also, chemical profile variation with depth is similar to that previously discussed.

The presence of Na-SO<sub>4</sub> and Na-SO<sub>4</sub>-Cl in crystalline water samples may be due to lixiviation of sulfides by hydrothermal fluids from wall-rocks that in oxidized conditions are transformed into sulfates. Although, the influence of brines or sea water residues that migrated from sedimentary rocks must not be disregarded. Further investigations are necessary to establish processes responsible for the presence of saline waters in the area.

## 5 CONCLUDING REMARKS

Preliminary hydrochemical characterization of ground waters in Salto and Indaiatuba Municipal Districts of São Paulo State showed the presence of anomalies related to waters from DW such as salinity and high fluoride and TDS concentrations. These geochemical anomalies constitute restrictions in the use of water.

Further detailed studies involving geochemistry of water, rocks and soils, investigations of natural or anthropogenic mechanisms that control the behavior of pollutants, so as the characterization of geological structures and the use and occupation of land, will supply information for establishing procedures and decisions for an appropriate water resource management, including protection, regulation or restriction of groundwater use, as well as well establishing procedures to supervise water's quality.

## 6 REFERENCES

- Artur, A. C. (2003) *Complexo Granitóide Plurisserial Socorro: geologia, petrologia e recursos minerais*. Tese de Livre-Docência. Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista, Campus de Rio Claro, 139 p., anexos.
- DAEE-UNESP (1979) *Mapeamento faciológico do Subgrupo Tubarão*. Convênio DAEE-UNESP, Escala 1:50.000.
- Ebert, H. (1968) Ocorrências da fácies granulítica no sul de Minas Gerais e em áreas adjacentes, em dependência da estrutura orogênica: hipóteses sobre sua origem. *Anais da Academia Brasileira de Ciências*, 40 (Suplemento):215-229.
- Ebert, H. (1971) Os Paraibides entre São João Del Rei, Minas Gerais e Itapira, São Paulo e a bifurcação entre Paraibides e Araxáides. In: Congresso Brasileiro de Geologia, 25, São Paulo, 1971. *Boletim de Resumos das Comunicações*. SBG, São Paulo, p. 177-178.
- Galembeck, T. M. B. (1997) *O Complexo Múltiplo, centrado e plurisserial Itu – SP*. Tese de Doutorado, Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista, 1v., 2 mapas, 374 p
- Gascoyne, M. & Kaminemi, D.C. (1994) The hydrogeochemistry of fractured plutonic rocks in the Canadian Shield. *Hydrogeology Journal*, v.2, N°2, 43-49.
- Janasi, V. de A.; Vasconcelos, A. C. B. C.; Vlach, S. R. F.; Motidome, M. J. (1990) Granitóides da região entre as cidades de São Paulo e Piedade (SP): facilogia e contexto tectônico. In: Congresso Brasileiro de Geologia, 36, Natal, 1990. *Anais...*, Natal, SBG, v.4, p. 1925-1935.
- Neves, M. A. (2005) *Análise integrada aplicada à exploração de água subterrânea na bacia do rio Jundiá (SP)*. Tese de Doutorado. Instituto de Geociências e Ciências Exatas da Universidade Estadual Paulista, Campus de Rio Claro, 200p.
- Salveti, R. A. P. (2005) *Sistemas Depositionais e Paleogeografia do Subgrupo Itararé (Neopaleozóico da Bacia do Paraná), na Região entre Itu e Indaiatuba, SP*. Mestrado (Dissertação). São Paulo. Instituto de Geociências – USP. 100 p.

## 7 ACKNOWLEDGEMENTS

The authors thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (research grant 06/51699-0) and the Conselho Nacional de Desenvolvimento Científico Tecnológico (research grant 306270/2006-4).

