

## Pb AND Sr ISOTOPIC ANALYSES ON WATER SAMPLES BY ID-TIMS: ESTABLISHING THE ANALYTICAL PROCEDURES

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### INTRODUCTION

Questions about the sustainable use of water are world's top subject and the necessity of reducing water pollution and waste generation is of prime importance for human kind future. Groundwater contamination is intrinsically linked with its recharge (Foster & Hirata, 1988). In this way, new analytical tools, capable to evaluate the origin and quality of groundwater recharge, are very useful to achieve this proposal (Lerner, 2001).

Sr and Pb isotopes can be used as environmental indicators for water contamination and possible identification of its source (Charalampides & Monoliadis, 2002; Gosselin, et al., 2004; Ojiambo *et al.*, 2003; Luck & Ben Othman, 2002).

The National Field Manual for the Collection of Water-Quality Data (USGS, 2004) describes protocols and provides guidelines for national surface and groundwater quality assessment. In chapter A5, Wilde et al. (2004) recommend for isotope analysis that the water sample is filtered in a polysulfone filter media, with a 0.45µm pore size membrane.

Some other authors (Ojiambo *et al.*, 2003; Petelet, *et al.*, 1998; Widerland *et al.*, 2002, Takeda, *et al.*, 2000) also recommend acidifying the water samples to pH<2, with suprapur HNO<sub>3</sub>. Many articles are related to isotope concentrations and few to isotope ratios determinations. Most of them are for strontium isotope determinations mainly for rain and surface waters samples. Banks et al. (2005) make many considerations about the effect of filtration on surface water analysis. In this case, samples have high pH and high particulate content. Other Bank's work (Banks *et al.*, 1999) deals with crystalline aquifer, whose water has low particulate contents.

This paper brings a discussion about the effects of filtration, acidification and storage time for Sr and Pb isotopic analyses in water samples from a sedimentary aquifer. Many tests were carried out in order to define the analytical procedures of groundwater isotopic analyses at the Center of Geochronological Research (Centro de Pesquisas Geocronológicas – CPGeo), Geoscience Institute at the University of São Paulo, Brazil.

### STUDY AREA

São Paulo city developed microclimates due to urbanization problems, like air pollution and deforestation. The humid tropical climate is characterized by two distinct seasons: spring/summer, hot and humid, and autumn/winter, cold and dry. Mean precipitation is 1400 mm per year, concentrated in summer months (January, February and March). Mean temperature varies from 17°C at winter and 23°C at summer. These means are higher at more urbanized areas, varying 5°C at different points at the same time. (PMSP, 2004)

The São Paulo Metropolitan Region is situated at the Upper Tietê Hydrographic Basin, which the major river is the Tietê, with some tributary rivers as such Pinheiros, Tamanduateí and Cabuçu (PMSP, 2004).

The samples were all collected in the same well, located at the Geoscience Institute garden, at Cidade Universitária, São Paulo city (46.733°W and 23.559°S). It is approximately 2.5 km away upper stream from the Pinheiros River.

The well, named P2G, is 50 meters depth and extracts water from Tertiary sedimentary rocks from the São Paulo Sedimentary Basin. In general, these sediments are constituted by sandstones, siltstones, claystones and subordinated conglomerates.

The Cidade Universitária district has low occupation density and is rich in vegetation, relatively to others districts in the city. The P2G well was selected due to: (i) its particulate contents are similar to the other wells that have been analyzed in another project dealing with aquifer recharge in the Upper Tietê Basin (Martins *et al.*, unpublished) and (ii) its low vulnerability to the influence from the contaminants present in the rainfall events.

### ANALYTICAL EXPERIMENTS

Water samples were collected in low-density polyethylene (LDPE; Nalgon<sup>®</sup>) sample bottles of 500 ml capacity, which have been previously cleaned, to avoid contamination (Patterson, 1974), by acid washing technique as followed:

1. Bottles were washed with MilliQ deionized water and weak detergent;
2. Ca. 50 ml of an acid mixture of 25% HCl+HNO<sub>3</sub> were added to the bottles and heated on hot plate

at 40°C, for two days (one day in normal and in the next day in up side down position). After that they were left for two days (one day in normal and in the next day in up side down position), resting in an exhaustion hood. Then the bottles were rinsed three times with MilliQ deionized water;

3. Ca. 50 ml of HCl 25% was added to the bottles and they were heated on hot plate (40°C) for two days (one day in normal and in the next day in up side down position). After the bottles rested for two days in an exhaustion hood, the solutions were discarded and the bottles were rinsed three times with MilliQ deionized water;
4. Bottles were filled with suprapure nitric acid 1% and sealed until use;
5. Just before sampling the solutions were discarded, the bottles were rinsed three times with MilliQ deionized water, dried in a class-100 clean bench under laminar flow and sealed.

At field sampling, bottles were rinsed three times with the sample water before collection. To avoid chemical evolution, filtration was done less than 10 hours after collection (Goldstein & Jacobsen, 1987), at a laboratory under class 100 clean hood.

Some samples were filtered in an acid cleaned polysulfone Filter Holder with Receiver (Nalgene®), with capacity of 500 ml, connected to a vacuum line. Cellulose acetate membrane filters (Millipore®), with 0.45 µm pore size and 47 mm diameter. This procedure was also done to determine the solute influence on the water composition and its isotopic ratios.

After filtration the bottle was rinsed with MilliQ deionized water and with the sampled filtered water. Some samples were acidified to pH<2 with ultrapure 50% HNO<sub>3</sub>, to avoid cation precipitation, and some were stored at 4-10°C, to guarantee that no chemical reactions occur.

In order to define the analytical procedure, half of the collected samples were filtered (F) and half were not (NF). Half of the filtered samples were acidified (A) and half were not (NA). The same was done to the unfiltered samples. Then, each sample (F/A, F/NA, NF/A, NF/NA) were divided into two, one for immediately analysis (D) and the other for storage in the refrigerator for approximately one month (1M), before analyzing them. This stage generated eight samples plus their duplicates, totalizing 16 samples.

Additional samples were prepared in order to evaluate the residue chemical dissolution, the ion exchange resin column type and the mass of water used in the experiments.

#### PREPARATION OF WATER SAMPLE

Two ways of chemical dissolution of the residue were tested for Pb analyses:

1. Bulk Dissolution (BD):
  - a) Water sample evaporation at 80°C in a preclean Teflon beaker;

- b) Addition of 3 ml of concentrated HF + 1 ml of concentrated HNO<sub>3</sub> to the residue, and heating at 100°C for 48 hours;
- c) Solution was evaporated;
- d) Addition of 5 ml of 6N HCl to the residue and heating it for 24 hours at 100°C;
- e) Transferring the solution (IC) for a previously weighted Savillex®;
- f) Isotopic dilution (ID) aliquot separation (15% of total solution);
- g) Addition of 10 µl of <sup>208</sup>Pb spike to the ID aliquot;
- h) Solutions (ID and IC) were evaporated;
- i) Addition of 1 ml of 0.7N HBr to the residues;
- j) Pb purification by ionic exchange technique.

#### 2. Partial Dissolution (PD):

- a) Sample evaporation at 80°C in a preclean Teflon beaker;
- b) Addition of 5 ml of 0.7N HBr to the residue and heating for 24 hours at 100°C;
- c) Transferring the solution (IC) for a previously weighted Savillex®;
- d) Isotopic dilution (ID) aliquot separation (15% of total solution);
- e) Addition of 10 µl of <sup>208</sup>Pb spike to the ID aliquot;
- f) Solutions (DI and IC) were evaporated;
- g) Addition of 1 ml of 0.7N HBr to the residues;
- h) Pb purification by ionic exchange technique.

The isotopic dilution (ID) method consists of adding an isotopic tracer (spike) enriched in a specific Sr or Pb isotope with known concentration, into the sample solution. It permits to calculate the unknown concentration of the others isotopes by the mass spectrometer technique.

Two types of ion exchange columns were tested for lead analyses: i) Biorad®, made of polyethylene and filled with Biorad® AG1-X8 (200-400mesh) chloride form resin (ca. 35µl); and ii) Handmade retractil Teflon microcolumn filled with the same resin.

Tests with the amount of water needed for the chemical preparation were also done. Samples with two different weights, approximately 80 mg (Groups E, F, G and H) and 150 mg (Groups A, B, C and D) were analyzed. The capacity of the Savillex® beaker used is 60 or 90 ml, so the more sampled weighted the more stages are necessary to evaporate it.

The chemical attack for strontium isotopic analyses is the same for lead analyses (steps a to f, TA and a to c, PA). After the last step it was separated 1 ml to add 20 µl of <sup>84</sup>Sr spike (DI aliquot) and then added 1 ml of 2M HNO<sub>3</sub> at each aliquot (DI and natural);

The ion exchange columns used for Sr isotopic analyses are handmade retractile Teflon columns, with Sr

spec resin (Eichrom<sup>®</sup> nonionic ester polymer resin, 100-150 mesh). It was the first time this resin was used for Sr analyses at CPGeo and the procedure defined by tests consists of: filling the columns with 80 mg of resin; pre-cleaning the resin with 20 ml of 6M HCl; conversion with 2.2 ml of 0.05M HNO<sub>3</sub>; conditioning with 0.3 ml 2M HNO<sub>3</sub>; deposition of 1 ml of the sample; condition with 0.4 ml of 2M HNO<sub>3</sub>; Ba elution with 1.6 ml of 7M HNO<sub>3</sub>; Sr collection with 3 ml of 0.5M of HNO<sub>3</sub>.

Strontium and lead isotopic ratios were measured in a VG354 multi-collector mass spectrometer.

## RESULTS AND DISCUSSION

Thirty lead isotopic analysis (figs 1 and 2) and 14 strontium isotopic analysis (fig. 3) were done to test the procedures.

Figures 1, 2, and 3 present the results divided into eight groups (A, B, C, D, E, F, G and H), according to the different procedures. Groups A, B, C and D correspond to a same sample split into 16 parts that will be compared among them. Groups E, F, G, and H correspond to samples collected at different dates (they are not the same sample) and were analyzed individually; they cannot be compared between each other. Each group (A, B, C, D) corresponds to the same procedure, with results from samples analyzed in the same day of the collection and samples analyzed 28 days after sampling, plus their duplicates.

Group E used the same chemical procedure of group A, but with less sample quantity. Group F, also with less sample quantity, corresponds to different lead purification techniques. Group G compares results of two different chemical attacks and H compares samples acidified and not acidified that were stored 28 days in refrigerator.

As observed in Figures 1 and 2, lead isotopic ratios do not differ when the chemical procedure is modified, but lead concentration does. The variations on the isotopic ratios are *ca* 5% and *ca* 80% on the lead concentrations. This was also observed by Aily (2001) and Babinski *et al.* (2003) on rain samples.

Group B presented the higher Pb concentrations, probably because they have incorporated lead from the particulate, as these samples were not filtered and were acidified. Group C results show that without acidification the concentration decreases, probably due to either the lead adsorption into the bottles wall or precipitation. As long as the sample is stored in the refrigerator, the probability of lead adsorption or precipitation in samples not acidified increases. The unfiltered samples (groups A and B) presented anomalous behavior, probably for some colloid formation. Samples stored in the refrigerator for 28 days, from groups A, B and C, presented very different concentrations from those obtained on samples analyzed in the day of collection. The best results were from group D, because they are more homogenous and have better reproducibility. Group D samples also reflect the real water composition, because acidification prevents Pb precipitation and/or its adsorption into the bottles wall and the filtering inhibits the lead mixture from the particulate with the lead dissolved in the water sample.

Group E samples (less sample quantity was evaporated) do not present good reproducibility and have higher errors. Group F shows that the Biorad column has more reproducibility than the microcolumn, due to the different velocities. The Pb purification is better when samples are loaded slowly through the resin and have a more effective ion exchange. Group G demonstrates that samples, whose residue underwent to partial dissolution, do not have good reproducibility.

For the Sr analysis, the data presented low variation between the maximum and minimum values of isotopic ratios (0.05%), which are lower than the analytical errors, and larger variation in the Sr concentrations (15%), as described for some authors (Banner, 2004; Gosselin *et al.*, 2004). All Sr isotopic concentrations increased 5-10% after a month stored in the refrigerator. Filtered samples presented lower differences between the original and the duplicate (high reproducibility) Sr concentrations. There is not much difference (<1% for concentrations and <0.015% for isotopic ratios) between filtered/acidified and filtered/not acidified samples.

The different diameter sizes for the two types of ion exchange columns allow different flux velocity and because of that the Pb purification using microcolumn takes less time than the one using Biorad<sup>®</sup> columns, which are larger. However, the results indicate the purification is less effective, and consequently the beam is less stable during mass spectrometer analysis. This instability can be responsible for the larger errors obtained on those samples purified using microcolumns.

## CONCLUSIONS

Pb and Sr isotopic ratios and Sr concentration do not present large variations despite the differences on the procedures applied during sampling and chemical preparation of the water samples. In contrast, Pb concentrations are very depending on these techniques, implying that the analytical procedures have to follow Pb isotopic procedure:

It was determined that all samples to have better reproducibility should be: (i) filtered and mixtures between solute and water composition have to be avoided; (ii) acidified; (iii) submitted to bulk dissolution; and (iv) passed through a Biorad<sup>®</sup> column; because of its better Pb purification.

There was not much difference between the results from the two water samples mass evaporated, if we consider the same chemical procedure used. As the beaker capacity is of 90 mg, a mass of approximately 80mg will take only one stage to evaporate the sample, decreasing the sample exposure to contamination.

The procedures associated to the delay time for analysis (on the same day or after 28 days) do not cause significant differences on the results. This was very important, due to the fact that most project analyzing water samples involve storage in the refrigerator, either because of the distance between lab and field, or the volume of analyses in the lab.

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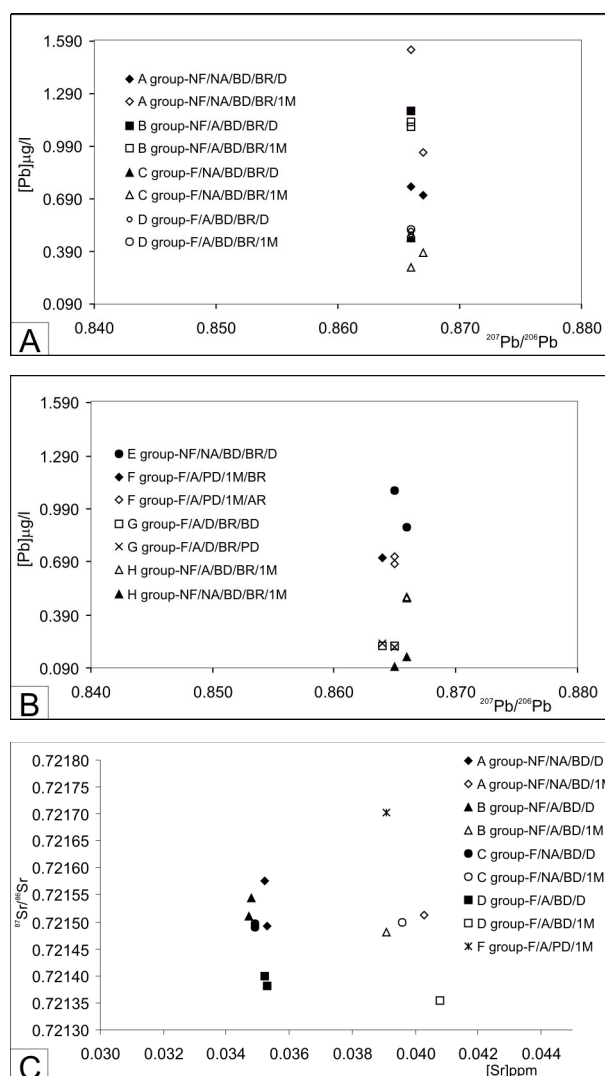


Figure 1. Isotopic ratios and concentrations determined on groundwater samples: A = Pb results on groups A, B, C and D; B = Pb results on groups E, F, G, and H, Sr results on groups A, B, C, D and F. Note: NF=not filtered; F=filtered; A=acidified; NA=not acidified; BD=bulk dissolution; PD=partial dissolution; AR=microcolumn; BR=Biorad column; 1M= stored 28 days in the refrigerator; D=analyzed at the same day of sampling.

## RESUMO

Com o objetivo de estudar os efeitos da filtração, acidificação e tempo de armazenamento de amostras de água de um aquífero sedimentar, em análises isotópicas de chumbo e estrôncio, alguns testes foram realizados no Centro de Pesquisas Geocronológicas da Universidade de São Paulo, Brasil. Trinta análises isotópicas de chumbo e 14 de estrôncio foram realizadas para testar diferentes procedimentos que consistiram em: amostras filtradas e não filtradas; amostras acidificadas e não acidificadas; amostras que sofreram ataque total (HF, HNO<sub>3</sub> e HBr) e ataque parcial (HBr); amostras purificadas em coluna Biorad<sup>®</sup> e amostras que passaram em microcoluna; e quantidades diferentes (80mg e 150mg) de amostra evaporada. As razões isotópicas de Pb e Sr não apresentaram muita diferença em relação aos diferentes procedimentos, assim como as concentrações de Sr. Mas as concentrações de Pb são muito dependentes do tipo de procedimento usado. Dessa forma, o estabelecimento do procedimento analítico foi baseado nos resultados de Pb, que indicaram uma grande reprodutibilidade para as amostras filtradas, acidificadas, que sofreram ataque total e que passaram pela coluna Biorad<sup>®</sup>. Os resultados das amostras armazenadas na geladeira e das analisadas no dia da coleta também são similares. Isso é uma conclusão importante porque a maioria dos estudos hídricos envolve o armazenamento de amostras em geladeira, tanto devido à distância entre campo e laboratório, quanto ao grande volume de amostras a serem analisadas.