ANALYTICAL PROCEDURES FOR DETERMINING Pb AND Sr ISOTOPIC COMPOSITIONS IN WATER SAMPLES BY ID-TIMS

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Few articles deal with lead and strontium isotopic analysis of water samples. The aim of this study was to define the chemical procedures for Pb and Sr isotopic analyses of groundwater samples from an urban sedimentary aquifer. Thirty lead and fourteen strontium isotopic analyses were performed to test different analytical procedures. Pb and Sr isotopic ratios as well as Sr concentration did not vary using different chemical procedures. However, the Pb concentrations were very dependent on the different procedures. Therefore, the choice of the best analytical procedure was based on the Pb results, which indicated a higher reproducibility from samples that had been filtered and acidified before the evaporation, had their residues totally dissolved, and were purified by ion chromatography using the Biorad® column. Our results showed no changes in Pb ratios with the storage time.

Keywords: Pb-Sr isotopes; groundwater; TIMS.

INTRODUCTION

The sustainable use of water is a highly important subject worldwide and the necessity of reducing water pollution and waste generation is of prime importance for the future of human kind. Despite the fact that surface reservoirs are the main sources of water provided by the public utility company in the Metropolitan Region of São Paulo, groundwater sources play an important role as alternative supply sources for private users, corresponding to 12% of the volume produced by the public company.[1] Groundwater contamination is intrinsically linked with its recharge.[2] An understanding of the recharge processes is an important part of the assessment and management of water resources, providing for sustainable development of resource exploitation.[3,4] Therefore, new analytical tools, capable of evaluating the origin and quality of groundwater recharge, are very useful to achieve this aim.[5] Sr and Pb isotopes can be used as environmental indicators of water contamination and for possible identification of its source,[6-9] as they provide different isotopic signatures.

The use of isotopic techniques has been applied to identify recharge sources and routes in groundwater studies for the last decade,[3] but the majority of these deal with strontium, oxygen and hydrogen isotopes,[10-21] whereas Pb is not often examined.[22-26] Stable isotopes (O and H) are considered as water isotopes, tracing the source and pathway of water molecules, while radiogenic isotopes (Sr and Pb) are solute isotopes, and trace the source and pathway of dissolved ions in the hydrologic cycle.[17,25] Some authors use isotopes to investigate atmospheric emissions,[26,27] sediments[28,29] and rain/snow,[9,30-33] and others analyze superficial or sub-superficial waters[34] with higher Sr and Pb concentrations.[34-36]

This paper is focused on urban groundwater that has pH values ranging from 5 to 7 and contains some suspended material. There are currently no articles in the literature about Pb isotope determination by ID-TIMS (isotope dilution and thermal ionization mass spectro-meter) in groundwater from an urban sedimentary aquifer. Thus a new analytical procedure was developed in order to analyze this type of water samples at the Center of Geochronological Research (Centro de Pesquisas Geocronológicas – CPGeo), Geoscience Institute at the University of São Paulo. This paper also discusses the effects of filtration, acidification and storage time for Sr and Pb isotopic analyses in water samples from a sedimentary aquifer. Many experiments were carried out in order to define the best analytical procedure.

The advantage of using radiogenic isotopes is that they do not fractionate in the environment because the isotopic composition remains constant as Sr or Pb are removed from the aqueous environment through precipitation or cationic exchange.[16] Neither weathering nor biological processes fractionate radiogenic isotopes.[37] Therefore, Sr and Pb isotopes can provide information about the solute sources, indicating whether they are anthropogenic or natural.[7]

The groundwater isotopic composition is controlled by the chemical composition of the aquifer rocks as well as their ages,[25] the rain, and leakage from pipes. The high precision of isotopic analysis permits the identification of small differences in the isotopic ratios and concentrations, which then characterizes different groundwater sources.

The isotopic dilution (ID) technique consists of adding an isotopic tracer (spike) enriched in a specific Sr or Pb isotope with known concentration into the sample solution. This allows one to calculate the unknown concentration of the other isotopes by mass spectrometry. A mass spectrometer is designed to separate charged atoms and molecules on the basis of their masses, which are assessed by their motions in magnetic fields.[38] Some advantages of using ID-TIMS analysis are: very low concentrations of many elements can be measured with great accuracy; there is no need to use great amounts of sample; accuracy is based on standard measurements.[38] TIMS is a mass spectrometer (MS) that ionizes the analyte molecules by thermal activity. The resulting ions are accelerated by an electric field and collimated into a beam that enters a magnetic field, which deflects the ions proportional to the masses of the isotopes. The separated ion

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beams are collected in the ion collectors where they are neutralized by electrons that pass through a resistor. The voltage difference in the resistor is amplified and measured, providing resulting signals consisting of a series of peaks and valleys that form the spectrum of the element.[38] It is very important to purify the element to be analyzed using ion exchange separation techniques to avoid isobaric interferences in the mass spectra.[39,40]

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a technique capable of determining concentration and isotope ratios faster than ID-TIMS, and represents an alternative method for studies that do not require high precision results.

STUDY AREA

São Paulo city developed microclimates due to urbanization problems such as 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). The mean precipitation is 1400 mm per year, with the largest proportion occurring in the summer months (January, February and March). The mean temperature varies from 17 ºC in the winter to 23 ºC in the summer. These means are higher in regions with a higher population density and can vary 5 ºC at different points in the city at the same time.[41]

The Metropolitan Region of São Paulo is located within the Upper Tietê Watershed (UTW). The Tietê river is the main watercourse of the UTW, which also comprises some important tributaries such as the Pinheiros, Tamanduateí, and Cabuçu rivers.[41]

The samples were all collected in the same well, located at the Geoscience Institute, at the Campus of the University of São Paulo (USP), with coordinates 46.733ºW and 23.559ºS. It is approximately 2.5 km away from the Pinheiros River.

The well, named P2G, is 50 m deep and extracts water from Tertiary sedimentary rocks present in the São Paulo Sedimentary Basin. In general, these sediments are composed of sandstone, siltstone, argillite and conglomerates. The water has mean values of 5.8 (pH), 358.4 mV (Eh), 33.85 µS cm^{-1} (Electric conductivity) and 24.3 ºC (temperature). The average ionic composition of the water for major ions is (mg L^{-1}): 13.44 (HCO_3^-), 0.47 (SO_4^{2-}), 3.52 (Cl$^-$), 1.64 (Ca^{2+}), 2.71 (Na$^+$), 0.74 (Mg^{2+}), 2.98 (K$^+$), indicating a Na-Ca-K-HCO_3-Cl water type. The mean compositions for other ions are (mg L^{-1}): 0.61 (NO_3^-), 0.07 (F$^-$), 0.33 (Fe), 0.31 (Al) and 0.12 (Ba). The dissolved silica concentration has a mean composition of 16.4 mg L^{-1}. Differences in the electroneutrality of the six samples analyzed were lower than 5%.

The Campus of the University of São Paulo has a low population density and is rich in vegetation compared to others districts in the city. The P2G well was selected due to: its particulate contents are similar to other wells that have been analyzed in another project dealing with aquifer recharge in the UTW[42] and its low vulnerability to the influence of contaminants brought by rainfall events or leakages.

ANALYTICAL EXPERIMENTS

The National Field Manual for the Collection of Water-Quality Data[43] describes protocols and provides guidelines for national surface and groundwater quality assessment. For isotope analysis, it is recommended that the water sample be filtered into polysulfone filter media with a 0.45 µm pore size membrane.[44]

Other authors[8,30,45,46] have also recommend acidifying the water samples with suprapur HNO_3 to pH<2. Bank *et al.*[35] also examines the effect of filtration on surface water analysis. In this case, samples have a high pH and high particulate content. Another work by Bank[36] about the effects of filtration deals with a crystalline aquifer whose water

has low particulate contents, and no isotope analyses were done.

Water samples were collected in low-density polyethylene (LDPE; Nalgon®) bottles of 500 mL capacity, which were previously cleaned[47] as follows: bottles were washed with deionized water using MilliQ equipment from Millipore® (herein named H_2O MQ) and weak detergent; ca. 50 mL of an acid mixture of 25% HCl+HNO_3 was added to the bottles and heated on a hot plate at 40 ºC for 2 days (one day in an upright and the next day in an upside down position). After that, they were left for two days (one day in an upright and in the day after in an upside down position) resting in an exhaustion hood. The bottles were then rinsed three times with H_2O MQ; ca. 50 mL of 25% HCl was added to the bottles and they were heated on a hot plate (40 ºC) for 2 days (one day in an upright position and the day after in an upside down position). After the bottles had sat for 2 days in an exhaust hood, the solutions were discarded and the bottles were rinsed three times with H_2O MQ; bottles were filled with 1% suprapure nitric acid and sealed until use; just before sampling, the solutions were discarded and the bottles were rinsed three times with H_2O MQ, dried in a class-100 clean bench under laminar flow and sealed.

During field sampling, bottles were rinsed three times with sample water before collection. Filtration was done less than 10 h after collection[48] at the laboratory using the class-100 laminar flow hood.

Some samples were filtered using an acid cleaned polysulfone filter holder with receiver (Nalgene®), with capacity of 500 mL, connected to a vacuum line. The filters were cellulose acetate membrane (Millipore®) with a 0.45 µm pore size and 47 mm diameter. This procedure was also done to determine the influence of suspended material on the chemical composition of the water and its isotopic ratios.

After emptying the bottle for water sample filtration and before transferring the filtered water back to the same bottle, it was rinsed twice with H_2O MQ and once with the filtered water sample. After filtration, some samples were acidified to pH<2 with ultrapure 50% HNO_3 to avoid cation precipitation, and some bottles were stored at 4-10 ºC to guarantee that no chemical reactions occurred.

In order to define the analytical procedure, half of the collected samples were filtered (F) and half were not (NF). In addition, half of the filtered samples were acidified (A) and half were not (NA). The same procedure was performed on unfiltered samples. Then, each sample (F/A, F/NA, NF/A, NF/NA) was divided into two, one for immediate analysis (D) and the other for storage in the refrigerator (4 ºC) for approximately one month (1 M). This stage generated eight samples (Table 1 and Figure 1) plus their duplicates, 16 samples in total.

Additional samples (Table 1 and Figure 2) were prepared in order to evaluate the residue chemical dissolution procedure, the ion exchange resin column type and the mass of water used in the experiments.
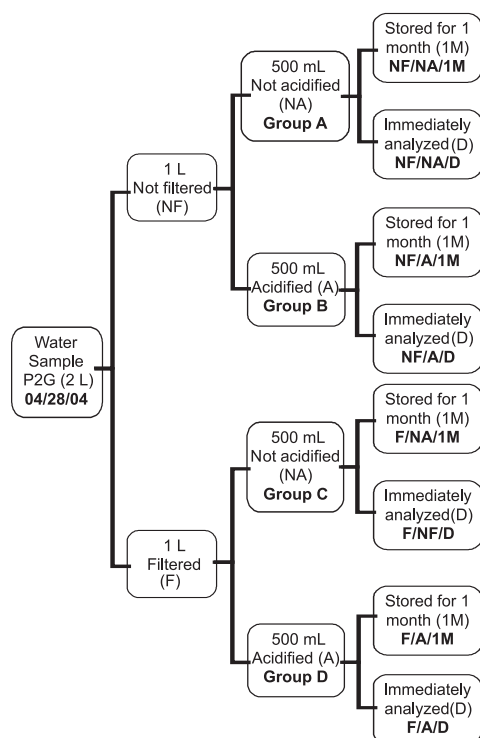
PREPARATION OF THE WATER SAMPLE

Two chemical dissolution techniques of the residue were tested for Pb analyses. The first of these is called Bulk Dissolution (BD), and consists of: water sample evaporation at 80 ºC in a precleaned Teflon PFA beaker from Savillex® (herein named savillex); addition of 3 mL of concentrated HF + 1 mL of concentrated HNO_3 to the residue, and heating at 100 ºC for 48 h; evaporation of the solution; addition of 5 mL of 6N HCl to the residue and subsequent heating for 24 h at 100 ºC; transferring of the isotopic composition (IC) solution to a previously weighted savillex; aliquot separation (15% of total IC solution) for the isotopic dilution (ID); addition of ca. 10 µL of ^{208}Pb spike (the exact mass was determined by weighing the sample before and after adding the spike) to the ID aliquot; evaporation of solutions (ID and

Table 1. Pb and Sr isotopic analyses results from groundwater samples (well P2G)

Group	Sampling date	Procedure*	sample mass (g)	$^{206}Pb/^{204}Pb$	SD	$^{207}Pb/^{204}Pb$	SD	$^{208}Pb/^{204}Pb$	SD	$^{207}Pb/^{206}Pb$	SD	$^{208}Pb/^{206}Pb$	SD	Pb (µg L^{-1})	Sr (mg L^{-1})	$^{87}Sr/^{86}Sr$	SD
A	04/28/04	NF/NA/D/BD/BR-1	144.00	17.996	0.014	15.592	0.014	37.856	0.015	0.866	0.002	2.103	0.002	0.762	0.0352	0.721576	0.000046
	04/28/04	NF/NA/D/BD/BR-2	143.42	18.004	0.011	15.603	0.011	37.900	0.011	0.867	0.002	2.105	0.002	0.715	0.0353	0.721493	0.000029
	04/28/04	NF/NA/1M/BD/BR-1	108.75	17.999	0.013	15.593	0.015	37.875	0.015	0.866	0.003	2.104	0.002	1.546	0.0403	0.721513	0.000048
	04/28/04	NF/NA/1M/BD/BR-2	139.26	17.988	0.011	15.588	0.011	37.843	0.011	0.867	0.002	2.104	0.002	0.954			
B	04/28/04	NF/A/D/BD/BR-1	141.92	18.005	0.009	15.592	0.009	37.866	0.010	0.866	0.001	2.103	0.002	1.197	0.0347	0.721511	0.000025
	04/28/04	NF/A/D/BD/BR-2	150.95	18.000	0.008	15.585	0.009	37.848	0.009	0.866	0.003	2.103	0.002	1.195	0.0348	0.721544	0.000019
	04/28/04	NF/A/1M/BD/BR-1	128.05	18.005	0.007	15.599	0.008	37.893	0.007	0.866	0.001	2.104	0.002	1.103	0.0391	0.721482	0.000023
	04/28/04	NF/A/1M/BD/BR-2	135.86	18.006	0.005	15.595	0.004	37.875	0.005	0.866	0.002	2.103	0.001	1.134			
C	04/28/04	F/NA/D/BD/BR-1	141.15	18.016	0.018	15.610	0.017	37.927	0.017	0.866	0.004	2.105	0.003	0.471	0.0349	0.721490	0.000024
	04/28/04	F/NA/D/BD/BR-2	143.48	17.985	0.022	15.573	0.025	37.804	0.027	0.866	0.006	2.102	0.006	0.467	0.0349	0.721497	0.000016
	04/28/04	F/NA/1M/BD/BR-1	120.52	17.998	0.026	15.591	0.027	37.871	0.029	0.866	0.003	2.104	0.005	0.297	0.0396	0.721499	0.000027
	04/28/04	F/NA/1M/BD/BR-2	136.86	17.957	0.016	15.561	0.015	37.766	0.015	0.867	0.002	2.103	0.002	0.386			
D	04/28/04	F/A/D/BD/BR-1	142.00	18.003	0.010	15.582	0.010	37.835	0.010	0.866	0.002	2.102	0.002	0.512	0.0352	0.721399	0.000022
	04/28/04	F/A/D/BD/BR-2	145.14	17.996	0.012	15.584	0.013	37.851	0.012	0.866	0.002	2.103	0.002	0.491	0.0353	0.721382	0.000013
	04/28/04	F/A/1M/BD/BR-1	105.29	18.002	0.014	15.593	0.009	37.863	0.011	0.866	0.003	2.104	0.001	0.467	0.0408	0.721354	0.000029
	04/28/04	F/A/1M/BD/BR-2	137.11	18.006	0.016	15.592	0.015	37.872	0.016	0.866	0.002	2.103	0.002	0.516			
E	09/08/04	NF/NA/D/BD-1	80.44	18.046	0.021	15.626	0.020	38.030	0.023	0.866	0.002	2.107	0.006	0.886			
	09/08/04	NF/NA/D/BD-2	81.35	18.028	0.011	15.593	0.010	37.910	0.011	0.865	0.003	2.103	0.001	1.095			
F	08/02/04	F/A/1M/PD/BR-1	78.99	18.044	0.008	15.596	0.009	37.950	0.009	0.864	0.001	2.103	0.002	0.716	0.0391	0.721702	0.000018
	08/02/04	F/A/1M/PD/BR-2	81.48	18.053	0.007	15.601	0.007	37.964	0.008	0.864	0.001	2.103	0.001	0.715	-	0.721675	0.000037
	08/02/04	F/A/1M/PD/AR-1	86.76	18.032	0.009	15.593	0.009	37.949	0.009	0.865	0.002	2.104	0.002	0.717			
	F/A/1M/PD/AR-2	08/02/04	55.40	18.046	0.020	15.612	0.021	37.983	0.023	0.865	0.003	2.105	0.007	0.681			
G	10/13/04	F/A/D/BD-1	52.04	18.086	0.042	15.625	0.040	38.026	0.045	0.864	0.006	2.102	0.007	0.216			
	10/13/04	F/A/D/BD-2	56.84	18.026	0.045	15.589	0.042	37.903	0.048	0.865	0.009	2.103	0.007	0.218			
	10/13/04	F/A/D/PD-1	53.21	18.097	0.037	15.644	0.036	38.073	0.038	0.864	0.004	2.104	0.004	0.229			
	10/13/04	F/A/D/PD-2	52.09	18.062	0.039	15.616	0.039	37.990	0.039	0.865	0.011	2.103	0.011	0.207			
H	10/13/04	NF/NA/1M-1	83.35	18.033	0.028	15.608	0.027	37.960	0.031	0.865	0.006	2.105	0.006	0.095			
	10/13/04	NF/NA/1M-2	50.87	18.043	0.038	15.619	0.036	38.012	0.037	0.866	0.006	2.106	0.010	0.151			
	10/13/04	NF/A/1M-1	83.15	18.040	0.016	15.618	0.010	37.993	0.011	0.866	0.008	2.106	0.018	0.493			
	10/13/04	NF/A/1M-2	54.11	18.025	0.010	15.602	0.009	37.925	0.010	0.866	0.005	2.104	0.011	0.487			

SD (standard deviation) are % 1σ (Pb) and 2σ (Sr); *abbreviations: NF=not filtered; F=filtered; A=acidified; NA=non-acidified; BD=bulk dissolution; PD=partial dissolution; AR=micro column; BR=Biorad column; 1M= stored 28 days in the refrigerator; D=analyzed on the day of sampling; -1=original; -2=duplicate.

Figure 1. Diagram showing the different steps used for the water sample preparation (groups A, B, C and D) in order to define the best analytical procedure. All samples were dried, and the residue was acid digested. The solutions were purified by an ion exchange technique using a Biorad column. All samples were collected in the same day
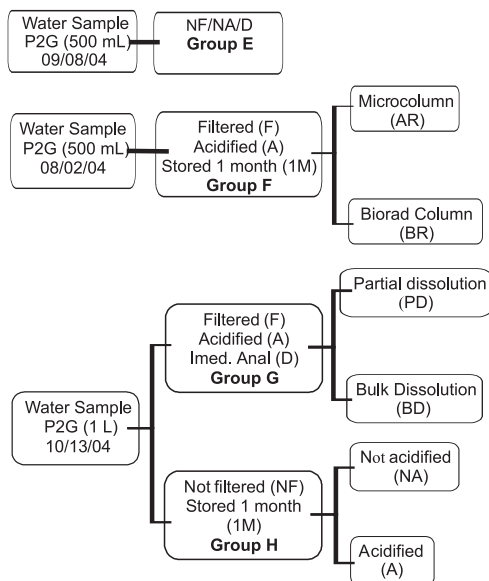
Figure 2. Diagram showing the different chemical experiments used for water sample preparation (groups E, F, G and H) in order to define the best analytical procedures. The samples from these groups were collected during 3 different months

IC); addition of 1 mL of 0.7N HBr to the residues; and purification of Pb by the ionic exchange technique.

The second dissolution technique is a Partial Dissolution (PD), which does not include $HF+HNO_3$ dissolution: evaporation of the sample at 80 ºC in a precleaned savillex; addition of 5 mL of 0.7N

HBr to the residue and heating for 24 h at 100 ºC; transferring of the solution (IC) to a previously weighted savillex; aliquot separation (15% of total IC solution) for isotopic dilution; addition of ca. 10 µL of [208]Pb spike to the ID aliquot; evaporation of solutions (DI and IC); addition of 1 mL of 0.7N HBr to the residues; and purification of Pb by the ionic exchange technique.

The BD procedure dissolves all materials, including silicates, oxides, organic matter and carbonates. In constrast, the PD procedure where only HBr is used to digest the residue, the silicates were not dissolved.

Two types of ion exchange columns (Figure 3) were tested for Pb analyses: Biorad®, made of polyethylene and filled with a Biorad AG1-X8 (200-400 mesh) chloride form resin (ca. 35 µL); and a hand-made retractil Teflon® microcolumn filled with the same resin.
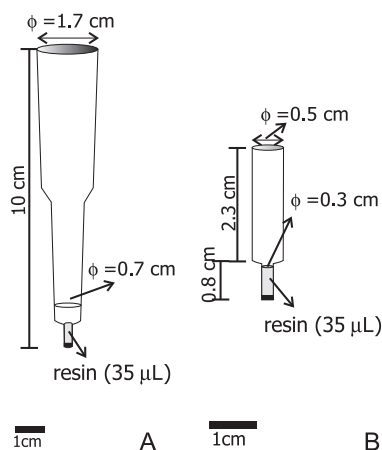

Figure 3. Two types of ion exchange columns were tested for Pb analysis: A) biorad, made of polyethylene and filled with a Biorad AG1-X8 (200-400 mesh) chloride form of resin (ca. 35 µL); and B) a handmade retractil Teflon microcolumn filled with the same resin (ca. 35 µL)

Tests to assess the amount of water needed for the chemical preparation were also performed. Samples with two different weights, approximately 80 g (Groups E, F, G and H) and 150 g (Groups A, B, C and D), were analyzed. The capacity of the savillex used was 60 or 90 mL, so the more sample needed, the more stages were necessary to evaporate it.

The chemical digestion of the residue for strontium isotopic analyses was the same as the Pb analyses (steps **a** to **f**, BD and **a** to **c**, PD). After the last step, 1 mL of solution was separated to add 20 µL of [84]Sr spike (ID aliquot). After evaporation, 1 mL of 2 M HNO_3 was added to each aliquot (ID and IC).

The ion exchange columns used for Sr isotopic (Figure 4) analyses were handmade retractile Teflon columns with Sr spec resin (Eichrom non-ionic ester polymer resin, 100-150 mesh). Because there was no established routine for Sr analyses using this resin, at CPGeo, some experiments were performed in order to define the amount of resin necessary to obtain a good Sr purification and the best yield. The procedure was modified from the work of Deniel and Pin[49] on silicate samples and redefined (by tests) for water samples. It 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 0.05 M HNO_3; conditioning with 0.3 mL 2 M HNO_3; deposition of 1 mL of the sample; conditioning with 0.4 mL of 2M HNO_3; Ba elution with 1.6 mL of 7M HNO_3; Sr collection with 3 mL of 0.5 M HNO_3. An unstable and/or low beam was obtained in the mass-spectrometer if less than 80 mg of resin were used.

The Pb spike used here had a [208]Pb/[206]Pb ratio of 20,000 and
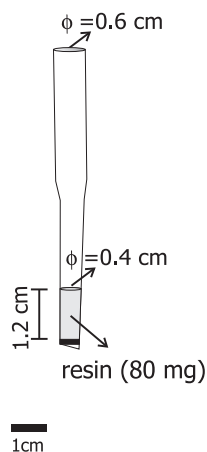
Figure 4. *The ion exchange columns used for Sr isotopic analyses were handmade retractile Teflon columns filled with Sr Spec resin (Eichrom non-ionic ester polymer resin, 100-150 mesh). For optimal Sr purification and the best yield, 80 mg of resin are necessary*

^{208}Pb concentrations of 0.5441 ppm. The ^{84}Sr spike concentration was 0.727937 ppm and its isotopic ratios were: ^{86}Sr/^{84}Sr= 0.044260, ^{87}Sr/^{84}Sr = 0.018679 and ^{88}Sr/^{84}Sr = 0.148794.

After Sr and Pb purification through the ion exchange columns, 5 and 1 μL of H$_3$PO$_4$ (0.1N), respectively, were added to the solutions and then evaporated. For Pb analyses, 2 μL of the sample was loaded onto a degassed Re filament after mixing it with silicagel of saturated concentration. The Sr samples were loaded onto a degassed tantalum filament and then analyzed.

Lead isotopic ratios were measured in a VG354 multi-collector mass spectrometer. For Pb analyses, the Faraday multi-collector in the static mode was used instead of the Daly Detector because it had the best analytical reproducibility. Because the Pb concentrations in the samples were very low (0.10 – 1.5 ppb), more than 50 mL of water was necessary to obtain good precision. Corrections for mass fractionation and the bias factor were based on the NBS 981 standard. The mean annual values (100 determinations), with 1 sigma standard deviation, obtained for the standard after the correction were: ^{207}Pb/^{206}Pb = 0.91464 ± 0.00010; ^{208}Pb/^{206}Pb = 2.1680 ± 0.0010. All ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{207}Pb/^{206}Pb ratios were corrected for an isotopic fractionation of 0.11% a.m.u^{-1} (atomic mass unit), whereas the ^{208}Pb/^{204}Pb was corrected for an isotopic fractionation of 0.07% a.m.u^{-1} and ^{208}Pb/^{206}Pb for 0.0035% u.m.a^{-1}. Total Pb analytical blanks were 40 pg, representing less than 0.5% of the total Pb in the water samples.

Strontium isotopic ratios were measured in a VG354 mono-collector mass spectrometer. To compensate for its lower precision, 100 ratios were measured for each sample. Corrections for mass fractionation were based on ^{86}Sr/^{88}Sr = 0.1194. The mean annual value of the NBS 987 standard, with 2 sigma standard deviation, was: ^{87}Sr/^{86}Sr = 0.71024±0.00007. Total Sr analytical blanks were 2.4 ng.

RESULTS AND DISCUSSION

Thirty lead isotopic analyses (Table 1, Figures 5A and 5B) and fourteen strontium isotopic analyses (Table 1 and Figure 5C) were carried out to test the different analytical procedures.

Figures 5A, B, and C 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 (Figure 1) correspond to the same sample which was split into 16 parts for comparison of results. Groups E, F, G, and H (Figure 2) correspond to samples collected at different dates
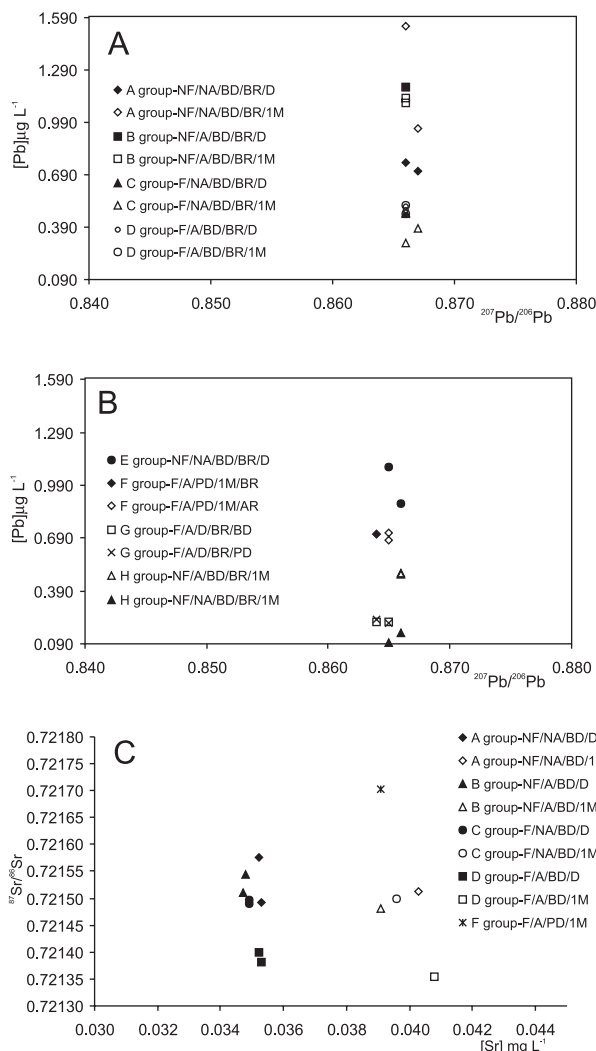
Figure 5. *Isotopic ratios and concentrations determined in groundwater samples: A = Pb results from groups A, B, C and D; B = Pb results from groups E, F, G, and H, Sr results from groups A, B, C, D and F. Note: NF=not filtered; F=filtered; A=acidified; NA=non-acidified; BD=bulk dissolution; PD=partial dissolution; AR=microcolumn; BR=Biorad column; 1M= stored 28 days in the refrigerator; D=analyzed on the same day of sampling*

(they are not the same sample) and analyzed individually; consequently, comparisons between these groups (E, F, G and H) should not be made. Each group (A, B, C, D) corresponds to the same procedure, with results from samples analyzed on the same day of and 28 days after sampling, plus their duplicates.

Group E was analyzed using the same chemical procedure as group A, but with less sample quantity (*ca*. 80 g for group E and *ca*. 140 g for group A). Group F, also using less sample quantity (50-80 g), corresponds to different Pb purification procedures. Group G compares the results of two different chemical dissolutions of the residue, and group H compares acidified and non-acidified samples that were stored for 28 days in the refrigerator.

As observed in Figures 5A and 5B, Pb isotopic ratios do not differ when the chemical procedure is modified, but the Pb concentration does. The variations in isotopic ratios are *ca* 5% and *ca* 80% on the Pb concentrations. The same behavior was previously observed in rain samples.[32,33]

Group B presented higher Pb concentrations, probably because its samples had incorporated Pb from the suspended matter as they were acidified, but not filtered. The results for Group C show that

without acidification, the concentration decreases, probably due to either Pb adsorption into the walls of the bottles or precipitation. As long as the sample is stored in the refrigerator, the probability of lead adsorption or precipitation in non-acidified samples increases (Table 1). The unfiltered samples (groups A and B) presented an anomalous behavior, probably due to some colloid formation. Samples stored in the refrigerator for 28 days, from groups A, B and C, presented very different concentrations from those obtained from samples analyzed on the day of collection. The best results were from group D, because their results (isotopic ratios and concentrations) were more homogenous and had better reproducibility. Group D samples also reflected the water composition, because acidification prevents Pb precipitation and/or its adsorption into the walls of bottles, and filtering inhibits mixing of Pb from the suspended material with the Pb dissolved in the water sample, in the case of acidified samples.

Group E samples (less sample quantity was evaporated) did not present good reproducibility and had higher standard deviations. Group F shows that the Biorad column results has better reproducibility than the microcolumn, due to different flux velocities and interactions of the sample-resin. Pb purification was optimal when samples were loaded onto the resin slowly, resulting in a more effective ion exchange. Group G demonstrates that samples whose residues underwent partial dissolution did not have good reproducibility, probably because the silicate phase was not dissolved.

Sr isotopic ratios presented small variations between the maximum and minimum values of (0.05%), which are lower than the analytical standard deviations. Larger variations were observed for the Sr concentrations (15%), as already described in the literature.[7,25] All Sr concentrations increased 5-10% after storage in the refrigerator for a month. Filtered samples presented smaller differences between original and duplicate (high reproducibility) Sr concentrations. There was not much difference (<1% for concentrations and <0.015% for isotopic ratios) between filtered/acidified and filtered/non-acidified samples.

The different diameter size of the two types of ion exchange columns allows for different flux velocities. The Pb purification process takes less time using the microcolumn than the Biorad columns, which are larger. However, the results indicate that the purification process using the microcolumn is less effective and, consequently, the beam is less stable during mass spectrometer analysis. This instability could be responsible for the larger standard deviations obtained for those samples purified in microcolumns.

CONCLUSIONS

Pb and Sr isotopic ratios and Sr concentrations do not present large variations despite the differences in the procedures applied during sampling and chemical preparation of the water samples. In contrast, Pb concentrations vary depending on these techniques, implying that the chosen analytical procedures have to be based on Pb results.

Our results show that in order to obtain better reproducibility, the samples have to be: filtered, avoiding mixtures between suspended matter and water compositions; acidified; the residue has to be submitted to bulk dissolution; and loaded onto a Biorad column because of its efficient Pb purification. This procedure is validated by the high correlation factor (0.99) obtained between samples analyzed by ID-TIMS and ICP-MS for Sr concentrations.[50]

There was no significant difference between the results for the two mass evaporated water samples, if we consider the same chemical procedure used. As the savillex capacity is 90 mL, a volume of approximately 80 mL will take only one stage to evaporate, limiting the exposure of the sample to contamination.

Examination of a delay time before analysis (on the same day or after 28 days) did not show significant differences in the results if the samples were filtered and acidified. This is very important due to the fact that most projects analyzing water samples involve storage in the refrigerator, either because of the distance between the lab and field or the great volume of analyses to be done in the lab.

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