

A ^{210}Pb chronological study in sediments from poços de caldas alkaline massif (PCAM), Brazil

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HIGHLIGHTS

- Sedimentation rates.
- Pb-210 chronological method.
- Osamu Utsumi uranium mine.
- Poços de Caldas Alkaline Massif.

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ABSTRACT

The Constant Flux and Constant Sedimentation (CF:CS) of supported/excess ^{210}Pb model was successfully used to study sediment profiles from Antas stream, located in the region of Poços de Caldas city, Minas Gerais State, Brazil. Historical changes in the region were tracked from evaluating the sedimentation rate by the ^{210}Pb method. In that site, Osamu Utsumi mine was the first mining-industrial complex for the production of concentrated uranium in Brazil. Four sediment testimonies were sampled along Antas stream in order to determine sedimentation rates using ^{210}Pb as geochronometer. ^{210}Pb and ^{238}U activity concentrations were determined in sediment samples by alpha spectrometry, allowing to find the excess ^{210}Pb present in the sediments. Additionally, the main oxides, organic matter, particles size and water composition were determined in order to assist the results interpretation from radionuclides data. The results allowed find one (profile PKS-4) or two (profiles PKS-1, PKS-2 and PKS-3) sedimentation rates, probably due to changes in the sediments input regime in the region. The sedimentation rates were in the range between 0.26 and 0.94 g/cm².year, corresponding to the interval of linear sedimentation rate of 0.21 – 0.92 cm/year. The deposition year in the bottom of PKS-4 profile as estimated from the sedimentation rate coincided with the construction year of Bortolan dam (1956). Large touristic interventions carried out at Poços de Caldas city from 1920s coupled to unbridled urbanization, industrialization and demographic growth there in the second half of the twentieth century possibly caused the changes found in the sedimentation rates.

1. Introduction

Mining activities have contributed significantly to the growth and development of various countries. The importance of this sector to the Brazilian economy is significant, especially for iron, niobium, manganese, and aluminum (from bauxite) production (IBRAM, 2008). Besides the economic impact and the job creation, mining activities cause significant impacts to the environment, since their development often implies on the removal of vegetation resources and soil exposure to erosion. They also cause air pollution and changes on the quality of surface and groundwater resources (Mечи and Sanches, 2010).

The water importance for the human subsistence and development has been widely recognized, where Brazil is a relative privileged country in terms of water resources abundance. Some years ago, the increase in the country for manufactured compounds promoted a rapid and disordered industrialization process, also increasing the demand for water (Lacerda, 1994).

The urban and industrial occupation in areas of river basins may imply on greater inputs of pollutants like trace metals that can also cause destabilization and erosion in the environment, promoting the increase of materials in depositional environments and changing all the sediments dynamics. These changes can affect not only living organisms

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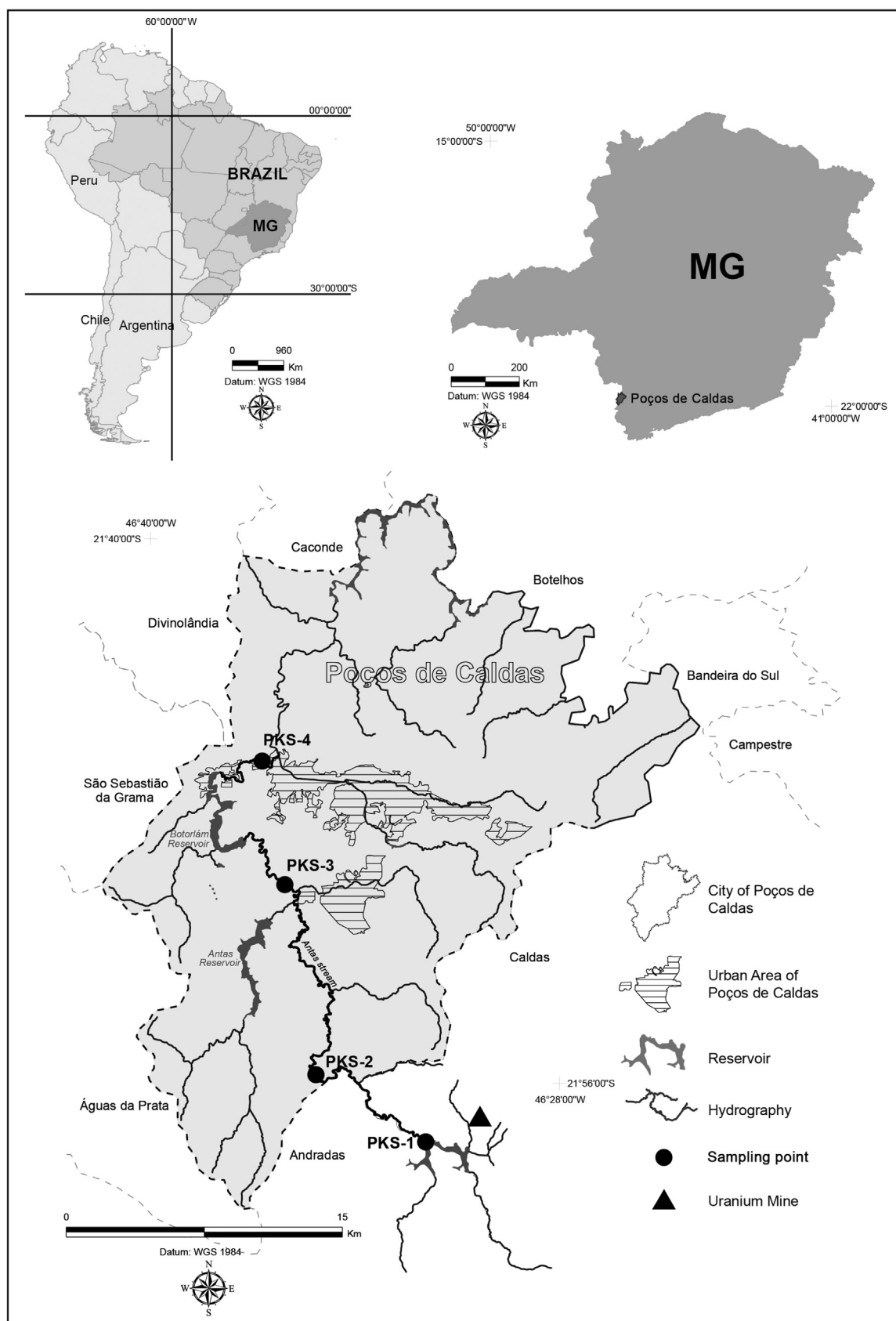


Fig. 1. Location of the study area at Minas Gerais State, Brazil. Adapted from Frayha (2010).

Table 1

The pH, conductivity and ionic concentration (in mg/L) in the bulk composition of the water samples collected at the monitoring points PKS-1, PKS-2, PKS-3 and PKS-4 in Antas stream, Poços de Caldas city, Minas Gerais State, Brazil.

Parameter	PSK – 1	PSK – 2	PSK – 3	PSK – 4
pH	6.1	6.6	4.9	6.6
Conductivity ^a	502	161	110	75
Chloride	1.7	0.3	5.4	4.1
Nitrate	0.3	0.6	1.4	0.7
Sulfate	300	72	30	17
Bicarbonate	10.43	13	7.8	15.6
Calcium	7.0	27.6	13	6.7
Potassium	4.3	4.1	9.2	8.6
Magnesium	11.4	0.8	0.8	0.5
Sodium	1.9	1.7	4.2	3.3

^a In $\mu\text{S}/\text{cm}$.

in such environments, but also human populations using water resources for food and recreation (Rosales-Hoz et al., 2003). Concerning to the mineral exploration impacts, the dispute for water and its resources is often one important point of conflict involving mining and society. According to Rebouças et al. (2006) mining activities involve major changes in the landscape contour, promoting chemical and biological changes in the environment.

The municipality of Poços de Caldas, within this scenario, is configured as a strategic point of environmental contamination, since it is the homebirth of the first mining-industrial complex for the production of concentrated uranium in Brazil, operating from 1982 to 1995. Radioactive wastes generated by acid mine drainage (AMD) occur there, which are chemically treated with calcium hydroxide and flocculants before their release into Antas stream (Mata et al., 2002). Prior studies of the environmental characterization were developed in the region. However, they have only considered the current situation from the analysis of sediments samples from the surface drainage. In this paper, the results obtained for ^{210}Pb allow reconstruct the environmental impact produced during the last 100–150 years, covering the

largest industrial and population growth experienced in the region.

2. Methodological basis for ^{210}Pb dating

^{210}Pb is a radionuclide that presents itself naturally in aquatic sediments, as a result of the ^{238}U decay series. Its half-life is 22.26 years, which makes it especially suitable for studying sediments deposited over the last two centuries (Crikmore et al., 1990). ^{210}Pb is formed by disintegration of the noble gas radon (^{222}Rn , half-life = 3.8 days), which is produced by ^{226}Ra -decay and escapes from rocks and soils of the earth's crust due to its gaseous nature. Once airborne, radon produces several descendants, among them ^{210}Pb that is deposited in the sediments.

The ^{210}Pb deposited in the sediments is known as unsupported (or excess) ^{210}Pb , $^{210}\text{Pb}_{\text{xs}}$, whereas the ^{210}Pb formed by the ^{226}Ra -decay has been named supported (or *in situ* produced) ^{210}Pb , $^{210}\text{Pb}_{\text{s}}$ (Álvarez-Iglesias et al., 2007). The excess ^{210}Pb can be achieved from the difference of the total ^{210}Pb , $^{210}\text{Pb}_{\text{T}}$, and *in situ* produced ^{210}Pb (Bonotto and Lima, 2006). The total ^{210}Pb activity concentration is equal to the ^{210}Po activity concentration as a consequence of the radioactive equilibrium between ^{210}Pb and ^{210}Po in the ^{238}U decay series (Lima, 2000). The *in situ* produced ^{210}Pb may be obtained from the ^{238}U specific activity and applying a correction factor due to escaping ^{222}Rn (Bonotto and Lima, 2006; Sabaris and Bonotto, 2010; Nery and Bonotto, 2011). The analysis of the excess ^{210}Pb in core sediments allows determine the sedimentation rate and deposition time of the sediments in the profile (El-Daoushy, 1988).

The ^{210}Pb quantification in this paper was indirectly performed by ^{210}Po alpha spectrometry deposited upon copper discs, taking into account the existence of radioactive equilibrium between ^{210}Pb and ^{210}Po (Appleby and Oldfield, 1978; Lima, 2000; Bonotto and Lima, 2006). This technique presents a series of advantages: high sensitivity to beta counting; possibility of using the ^{209}Po to control the chemical separation yield; easy ^{210}Po identification, without any error, due to the sensitivity of the alpha spectrometry; simple ^{210}Po extraction from sediments.

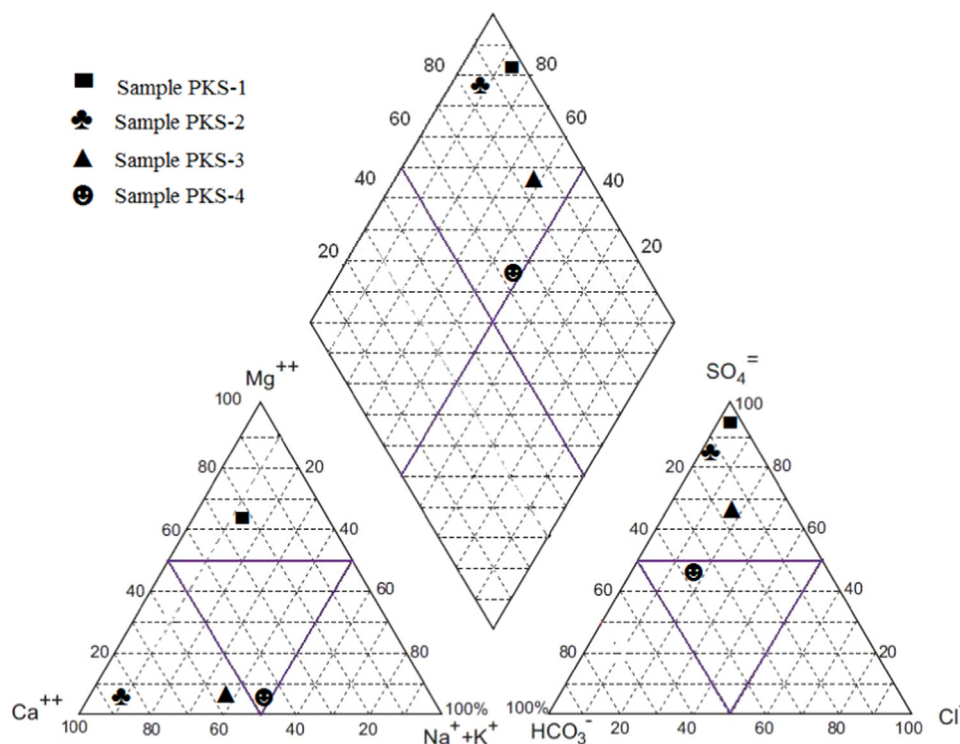


Fig. 2. Results of the chemical analyses of waters from Antas stream in a Piper (1944) diagram.

Table 2

Size distribution of the sediments samples collected at the monitoring points PKS-1, PKS-2, PKS-3 and PKS-4 in Antas stream, Poços de Caldas city, Minas Gerais State, Brazil.

Sampling Point	Depth range (cm)	Grain size (mm)							
		4.000 – 2.000	2.000 – 1.000	1.000 – 0.500	0.500 – 0.250	0.250 – 0.125	0.125 – 0.062	0.062 – 0.031	< 0.031
PKS – 1	0 – 3	5.958	4.435	0.850	1.766	1.434	1.607	1.117	0.362
	3 – 6	5.684	3.350	0.779	1.608	1.129	0.928	0.450	0.073
	6 – 9	8.234	2.380	0.562	1.352	1.210	0.781	1.195	0.026
	9 – 12	9.181	6.919	1.242	2.843	2.541	3.575	0.906	0.517
	12 – 15	4.446	7.102	1.530	2.847	2.733	3.277	0.228	0.003
	15 – 18	3.236	6.006	1.484	3.276	2.308	2.773	1.066	0.361
	18 – 21	3.676	9.261	1.763	3.653	3.168	3.572	0.829	0.174
	21 – 24	4.454	10.452	1.819	3.363	2.296	3.930	0.556	0.012
	24 – 27	2.234	9.658	2.212	4.605	2.945	4.176	1.567	0.512
	27 – 30	2.440	4.517	1.548	3.380	2.418	4.973	0.822	0.136
	30 – 33	2.333	6.245	1.911	3.974	4.091	3.461	0.408	0.002
	33 – 36	3.247	8.193	2.073	5.390	4.933	4.000	1.137	0.240
	0 – 3	4.063	2.965	0.543	1.590	1.913	1.044	0.382	0.064
	3 – 6	1.024	6.060	1.410	3.819	3.208	1.688	0.690	0.104
PKS – 2	6 – 9	0.173	3.652	1.002	2.840	2.421	2.000	0.640	0.005
	9 – 12	0.431	4.508	0.982	2.768	2.333	1.618	0.700	0.001
	12 – 15	0.317	3.915	0.803	2.058	1.619	1.263	0.480	0.001
	15 – 18	0.180	4.219	1.136	3.108	2.361	1.397	0.690	0.025
	18 – 21	0.068	3.447	0.910	2.411	1.970	1.466	0.650	0.003
	21 – 24	0.203	3.998	0.868	2.554	2.398	2.148	0.467	0.001
	24 – 27	0.119	3.772	0.952	2.760	2.593	2.054	0.594	0.016
	27 – 30	0.035	3.447	0.945	3.054	3.502	2.973	0.813	0.014
	30 – 33	1.623	10.653	1.668	4.325	4.255	3.999	0.666	0.001
	0 – 3	0.172	2.820	0.753	0.869	1.652	1.266	0.526	0.134
	3 – 6	0.494	3.743	0.872	2.010	1.768	1.367	0.704	0.242
	6 – 9	1.795	4.159	0.886	2.149	1.996	1.751	0.811	0.249
	9 – 12	0.557	5.124	1.016	2.645	2.574	1.717	0.891	0.362
	12 – 15	0.335	0.709	1.276	3.608	3.824	2.461	1.158	0.292
PKS – 3	15 – 18	2.841	4.917	0.946	2.867	3.280	2.051	0.965	0.427
	18 – 21	0.803	4.966	1.026	2.788	2.803	2.424	1.160	0.158
	21 – 24	2.217	4.436	0.786	2.256	2.571	2.175	1.289	0.310
	24 – 27	0.690	5.052	0.986	2.589	2.561	1.997	1.201	0.191
	27 – 30	0.378	3.639	0.960	3.082	3.451	2.486	1.463	0.322
	30 – 33	0.744	5.942	1.187	3.816	4.243	2.984	1.798	0.388
	33 – 36	0.993	2.335	0.733	2.924	3.826	2.590	1.317	0.554
	36 – 39	0.162	2.675	0.938	3.815	4.571	2.930	1.534	0.500
	39 – 42	1.374	6.271	1.440	4.340	4.052	2.510	1.069	0.552
	42 – 45	0.459	3.568	0.887	3.093	3.540	3.312	1.272	0.213
	0 – 3	0.437	1.681	0.713	2.554	2.492	1.332	0.456	0.174
	3 – 6	0.217	2.433	0.894	2.956	2.663	1.125	0.374	0.130
	6 – 9	1.392	3.182	0.885	2.881	2.592	1.515	0.657	0.182
PKS – 4	9 – 12	0.072	2.805	0.793	1.871	1.845	3.330	1.048	0.268
	12 – 15	0.781	3.519	0.761	1.844	1.990	1.551	0.620	0.377
	15 – 18	0.073	0.894	0.544	2.872	4.182	2.794	1.518	1.361
	18 – 21	0.101	1.138	0.568	4.216	4.039	2.383	1.600	1.184
	21 – 24	0.031	1.399	0.754	3.672	4.615	2.783	1.411	1.385

Udden scale (in mm) and Wentworth classification: GRA = granule (> 2.0 mm), VCS = very coarse sand (2.0 – 1.0 mm), CRS = coarse sand (1.0 – 0.5 mm), MES = medium sand (0.5 – 0.25 mm), FIS = fine sand (0.25 – 0.125 mm), VFS = very fine sand (0.125 – 0.063 mm), CSI = coarse silt (0.063 – 0.031 mm), MSI = medium silt (< 0.031 mm).

3. Experimental

3.1. Study area

The study area is located at the Poços de Caldas Alkaline Massif (PCAM), southeastern of Minas Gerais State, Brazil, on the São Paulo State border (Fig. 1). The research limited itself to Antas stream (Fig. 1), which belongs to the Pardo river hydrographic system. The city of Poços de Caldas in the plateau has a total area of 547 km² and is situated on a site whose average altitude ranges from 943 m to 1575 m (mean = 1300 m). It consists of a single district, bordering with nine municipalities, one at São Paulo State (Águas da Prata).

The Poços de Caldas region is geologically situated at the northeast limit of the Paraná sedimentary basin, bordering with the Precambrian terrains of the *Brasiliano* crystalline complex, on the western edge of *Mantiqueira* Scarp (Ellert, 1959). An intrusive body of Mesozoic-Cenozoic age consisting of alkaline rocks like nepheline (tinguatites,

phonolites, foyaites) predominate in Poços de Caldas region. Several lithological types are of alkaline source, divided into three main groups: volcanic material; effusive and hypabyssal rocks; and plutonic rocks. Geomorphologically, the alkaline massif is inserted in areas of the Atlantic Highlands, with a slightly elliptical shape (major axis of 35 km in the NE-SW direction and lower axis of 30 km in the NW-SE direction). Two large fault systems with predominant directions N60W and N40E are present in the alkaline complex: the first is related to regional tectonics and the last with the former fusion processes (Fraenkel et al., 1985).

The soil covering the region is the result of *in situ* alteration rock. The soil materials and rock blocks are of variable proportion and composed by rocks with varying degrees of fracturing, alluvium, soft soils deposited with organic and clayey materials, *tallus* consisting of transported soil materials and rock fragments of various sizes (Poços de Caldas, 2006).

Table 3

Maximum, minimum, mean, median and standard deviation (SD) of the major oxides in sediments samples collected at the monitoring points PKS-1, PKS-2, PKS-3 and PKS-4 in Antas stream, Poços de Caldas city, Minas Gerais State, Brazil. All values are in %.

Sampling Point		SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	OM
PKS – 1	Mean	39.66	0.80	31.99	6.60	0.49	0.16	0.12	0.15	6.51	0.25	11.87
	Median	39.14	0.79	31.85	6.11	0.19	0.14	0.04	0.11	6.59	0.27	11.77
	SD	3.23	0.10	2.30	1.80	0.57	0.03	0.13	0.12	0.89	0.05	2.14
	Maximum	45.60	1.01	35.13	10.12	1.92	0.22	0.36	0.48	8.37	0.32	17.05
	Minimum	34.93	0.66	27.65	4.68	0.12	0.13	0.02	0.06	5.25	0.17	8.69
PKS – 2	Mean	26.99	2.10	39.46	7.54	0.07	0.21	0.09	0.07	2.22	0.12	19.73
	Median	26.46	2.15	39.94	7.69	0.04	0.21	0.07	0.05	2.13	0.12	19.78
	SD	1.61	0.17	1.64	0.34	0.09	0.01	0.06	0.09	0.37	0.01	0.71
	Maximum	31.39	2.17	40.39	7.97	0.33	0.23	0.28	0.33	3.30	0.13	20.72
	Minimum	25.70	1.60	34.57	7.11	0.04	0.19	0.06	0.04	2.01	0.10	18.60
PKS – 3	Mean	33.74	1.74	34.17	7.56	0.29	0.20	0.04	0.15	3.51	0.12	17.46
	Median	34.10	1.73	34.20	7.52	0.29	0.20	0.02	0.15	3.48	0.11	17.22
	SD	0.96	0.03	0.33	0.16	0.07	0.01	0.03	0.02	0.24	0.01	0.89
	Maximum	34.93	1.81	34.55	7.88	0.39	0.22	0.10	0.19	3.86	0.13	19.00
	Minimum	32.05	1.69	33.51	7.35	0.17	0.19	0.00	0.11	3.12	0.11	16.17
PKS – 4	Mean	28.07	3.31	27.54	16.46	0.13	0.13	0.04	0.04	0.61	0.65	22.72
	Median	27.26	2.50	27.00	16.25	0.07	0.14	0.03	0.04	0.79	0.55	22.86
	SD	2.26	1.23	3.13	2.00	0.10	0.03	0.04	0.02	0.40	0.15	1.16
	Maximum	31.39	4.84	32.17	19.17	0.30	0.16	0.12	0.06	1.03	0.85	24.22
	Minimum	25.44	2.36	24.17	14.02	0.06	0.09	0.01	0.01	0.12	0.53	20.98

3.2. Sampling

The sediments sampling was carried out during the dry season in Antas stream, Poços de Caldas city, Minas Gerais State, Brazil, near its source and downstream monitoring points called PKS-1, PKS-2, PKS-3 and PKS-4 (Fig. 1). These sampling points were geo-referenced with GPS (Global Positioning System) in UTM coordinates system. Four acrylic tubes were used (~ 5 cm diameter and ~ 60 cm long) and previously washed with an acid solution for decontamination. After collection, the tubes with the samples were kept under refrigeration (4 °C).

One liter water samples were also collected in the same sediments collection points, using plastic bottles previously washed in the laboratory. The sites choice was made considering the position of the polluting sources, effluents location and sites accessibility for sampling. In the laboratory, pellet samples were removed from the tubes, the testimonies were cut at 3 cm intervals, packed in sealed plastic bags and refrigerated until analysis.

3.3. Analytical methods

The analysis of the water samples (~1 L) was done at LABIDRO – Isotopes and Hydrochemistry Laboratory (IGCE - Geosciences and Exact Sciences Institute of UNESP – Rio Claro) by a Hach DR2000 spectrophotometer, among other equipments. The samples were analyzed for pH, conductivity, anions (chloride, nitrate, sulfate, bicarbonate) and cations (calcium, magnesium, potassium). Sodium analysis was performed by Atomic Absorption Spectrometry (AAS).

In order to obtain the excess ²¹⁰Pb in the sediments, the samples were analyzed for ²³⁸U and ²¹⁰Po at LABIDRO. For measuring ²¹⁰Po in the sediments, 1 g of sample was attacked with different acids for the ²¹⁰Po extraction. Such ²¹⁰Pb “grandchild” was deposited in a copper disk. Each slice underwent counting in an alpha spectrometer. For the ²³⁸U determination, the slices passed through a series of chemical steps until electrodeposition on stainless steel discs (Lima, 2000). After obtaining the dry disk, the next step was to count the uranium isotopes by alpha spectrometry that is a procedure requiring the use of thin sources containing the extracted material and prepared from the uniform ²³⁸U deposition.

The grain size analysis of the sediments was also carried out at LABIDRO. The samples were thawed, dried and classified through sieving, based on the Udden-Wentworth scale (Lima, 2000). It was used a set of calibrated mesh sieves that allowed to obtain the dry weight in

each grain size range.

The determination of the main oxides levels in the sediments was carried out at LARIN (Ionizing Radiations Laboratory) of UNESPetro (Geosciences Center Applied to Petroleum), IGCE – UNESP – Rio Claro, through S8 TIGER X-rays Fluorescence Spectrometer of high end wavelength dispersion from Bruker Co.

The organic matter (OM) content analysis was held at LABIDRO according to the loss on ignition (LOI) method based on the Heiri et al. (2001) proposition. Dry samples (~ 1 g of total sediment) were used. The sediments were put in small porcelain crucibles. After weighing, the samples were dried at 110 °C for 12 h (overnight) in order to remove any moisture. In the next day, the samples, still hot, were cooled and kept in desiccators with silica gel until reaching the room temperature. After ~30 min, they were weighed for obtaining the dry weight. The second part of the experiments consisted on inserting the sediments into an oven at 550 °C and keeping them there for 5 h (Dean, 1974; Bengtsson and Enell, 1986). Then, the sediments were cooled in a desiccator to reach the room temperature. Finally, the pellet samples were weighed and the difference between this weight and the final weight of the sample (without moisture) corresponded to the organic matter percentage.

4. Results and discussion

4.1. Hydrochemical analyzes

The results of the water samples analysis are shown in Table 1. The parameters analyzed were pH, conductivity, cations (Ca²⁺, K⁺, Mg²⁺, Na⁺) and anions (Cl⁻, NO₃⁻, SO₄²⁻, HCO₃⁻) in order to classify them and verify if they fit the guideline reference values established by the Brazilian laws CONAMA 357/05 (Brasil, 2005) and Rule No. 2.914/11 of Health Ministry (Brasil, 2011). The sulfate concentration at PKS-1 monitoring point was greater than 250 mg/L as established by them. Thus, the waters of Antas stream demonstrate inadequate sanitation for public health close to the uranium mine.

The Piper (1944) diagram (Fig. 2) allows verify the total ions distribution and to identify similarities and differences among the samples. In terms of dissolved anions, the waters are sulfated (PKS-1, PKS-2 and PKS-3) and mixed (PKS-4). In terms of dissolved cations, the waters are magnesian (PKS-1), calcic (PKS-2 and PKS-3) and mixed (PKS-4).

Table 4

Radiochemical analyses of the sediments samples collected at the monitoring points PKS-1, PKS-2, PKS-3 and PKS-4 in Antas stream, Poços de Caldas city, Minas Gerais State, Brazil.

Depth range (cm)	Dry weight (g)	Po-210 activity (dpm/g)	Cumulative dry weight/area (g/cm ²)	Total Pb-210 activity ²¹⁰ Pb _T (dpm/g)	U-238 Specific Activity (dpm/g)	In-situ Pb-210 activity Pb _S (dpm/g)	Excess Pb-210 activity Pb _{XS} (dpm/g)	ln (Pb _{XS}) (dpm/g)
Profile PKS – 1								
0 – 3	62.06	6.38	3.16	6.38	3.99	0.64	5.74	1.75
3 – 6	58.06	9.33	6.12	9.33	1.89	0.30	9.03	2.20
6 – 9	94.92	4.43	10.95	4.43	9.71	1.55	2.88	1.06
9 – 12	96.40	3.01	15.87	3.01	11.15	1.78	1.23	0.20
12 – 15	75.11	3.45	19.69	3.45	6.12	0.98	2.47	0.90
15 – 18	77.07	3.42	23.62	3.42	3.68	0.59	2.83	1.04
18 – 21	71.58	3.85	27.26	3.85	5.13	0.82	3.03	1.11
21 – 24	97.75	3.45	32.24	3.45	5.68	0.91	2.54	0.93
24 – 27	89.63	1.55	36.81	1.55	9.16	1.47	0.08	– 2.47
27 – 30	97.66	2.49	41.79	2.49	4.06	0.65	1.84	0.61
30 – 33	96.25	3.24	46.69	3.24	11.40	1.82	1.42	0.35
33 – 36	91.13	2.95	51.33	2.95	2.45	0.39	2.56	0.94
Profile PKS – 2								
0 – 3	40.01	9.10	2.04	9.10	5.04	0.81	8.29	2.12
3 – 6	50.98	9.24	4.64	9.24	2.35	0.38	8.86	2.18
6 – 9	57.85	13.00	7.58	13.00	0.85	0.14	12.86	2.55
9 – 12	58.03	6.47	10.54	6.47	1.17	0.19	6.28	1.84
12 – 15	52.08	8.30	13.19	8.30	0.78	0.12	8.18	2.10
15 – 18	49.93	9.50	15.74	9.50	1.05	0.17	9.33	2.23
18 – 21	52.61	13.65	18.42	13.65	1.15	0.18	13.47	2.60
21 – 24	50.62	7.76	20.99	7.76	1.26	0.20	7.56	2.02
24 – 27	57.70	9.44	23.93	9.44	0.87	0.14	9.30	2.23
27 – 30	69.82	12.54	27.49	12.54	1.26	0.20	12.34	2.51
30 – 33	75.64	14.40	31.34	14.40	1.18	0.19	14.21	2.65
Profile PKS – 3								
0 – 3	39.91	11.08	2.36	11.08	2.22	0.36	10.72	2.37
3 – 6	45.08	10.07	5.02	10.07	1.51	0.24	9.83	2.29
6 – 9	42.49	12.11	7.53	12.11	1.23	0.20	11.91	2.48
9 – 12	54.50	16.70	10.75	16.70	1.22	0.20	16.50	2.80
12 – 15	60.58	14.53	14.33	14.53	0.96	0.15	14.38	2.67
15 – 18	61.76	18.67	17.98	18.67	0.92	0.15	18.52	2.92
18 – 21	62.62	12.27	21.67	12.27	0.78	0.12	12.15	2.50
21 – 24	54.37	9.93	24.89	9.93	0.93	0.15	9.78	2.28
24 – 27	62.81	12.00	28.60	12.00	1.73	0.28	11.72	2.46
27 – 30	52.57	15.20	31.70	15.20	0.94	0.15	15.05	2.71
30 – 33	63.01	13.71	35.42	13.71	1.13	0.18	13.53	2.60
33 – 36	53.35	14.48	38.57	14.48	1.25	0.20	14.28	2.66
36 – 39	56.71	19.52	41.92	19.52	0.98	0.16	19.36	2.96
39 – 42	55.87	14.59	45.22	14.59	0.61	0.10	14.49	2.67
42 – 45	51.49	12.65	48.26	12.65	1.37	0.22	12.43	2.52
Profile PKS – 4								
0 – 3	39.34	7.64	2.00	7.64	1.59	0.25	7.39	2.00
3 – 6	37.83	7.74	3.93	7.74	3.95	0.63	7.11	1.96
6 – 9	40.39	8.55	5.99	8.55	2.19	0.35	8.20	2.10
9 – 12	37.37	7.06	7.89	7.06	3.33	0.53	6.53	1.88
12 – 15	37.80	5.60	9.82	5.60	2.72	0.44	5.16	1.64
15 – 18	43.97	8.00	12.06	8.00	1.75	0.28	7.72	2.04
18 – 21	48.16	8.84	14.51	8.84	2.35	0.38	8.46	2.14
21 – 24	43.37	8.77	16.72	8.77	2.05	0.33	8.44	2.13

4.2. Size distribution and chemical analysis of the sediments

The particle distribution carried out in the four sampling points is recorded in Table 2. It appears that there is predominance of the granule (GRA) and very coarse sand (VCS) fractions at all collection points. The maximum values of GRA are 51.36% (PKS-1), 31.59% (PKS-2), 15.17% (PKS-3) and 10.18% (PKS-4). The maximum values of VCS are 37.86% (PKS-1), 38.22% (PKS-2), 36.52% (PKS-3) and 29.57% (PKS-4). The fine sand (FIS) and very fine sand (VFS) fractions increase towards the base of the sediments profiles, reaching a maximum value of 30.55% (Table 2).

Table 3 reports the maximum, minimum, mean, median and standard deviation of the major oxides and OM in the sediments. OM was detected in all sampled profiles, with maximum values of 17.05% (PKS-1), 20.72% (PKS-2), 19% (PKS-3) and 24.22% (PKS-4). The Pearson correlation coefficient was evaluated among the oxides analyzed and

OM, indicating the following significant correlations: silica (PKS-2: $r = -0.81$; PKS-3: $r = -0.96$; PKS-4: $r = -0.80$), TiO₂ (PKS-4: $r = 0.73$), Al₂O₃ (PKS-3: $r = 0.79$), Fe₂O₃ (PKS-2: $r = 0.83$), MnO (PKS-4: $r = -0.87$), MgO (PKS-3: $r = 0.77$), CaO (PKS-4: $r = -0.82$), Na₂O (PKS-3: $r = -0.71$; PKS-4: $r = -0.85$), K₂O (PKS-2: $r = -0.67$; PKS-3: $r = -0.96$), and P₂O₅ (PKS-3: $r = 0.92$; PKS-4: $r = 0.73$). Thus, the significant correlations with OM were found at the profiles PKS-2, PKS-3 and PKS-4, whereas inverse relationships were characterized for silica, confirming the trends pointed out by Bonotto and Lima (2006).

The correlations may suggest a similar behavior during transportation of the evaluated components (Thornton, 1983). In general, it was observed that the OM favors the retention up to a certain limit of some oxides in all profiles. Thus, the organic matter in these environments behaves as a complexing factor acting as a regulator of the chemical components in the sediments, thus, taking an important role in fixing or releasing metals into the water column (Aiken et al., 1985).

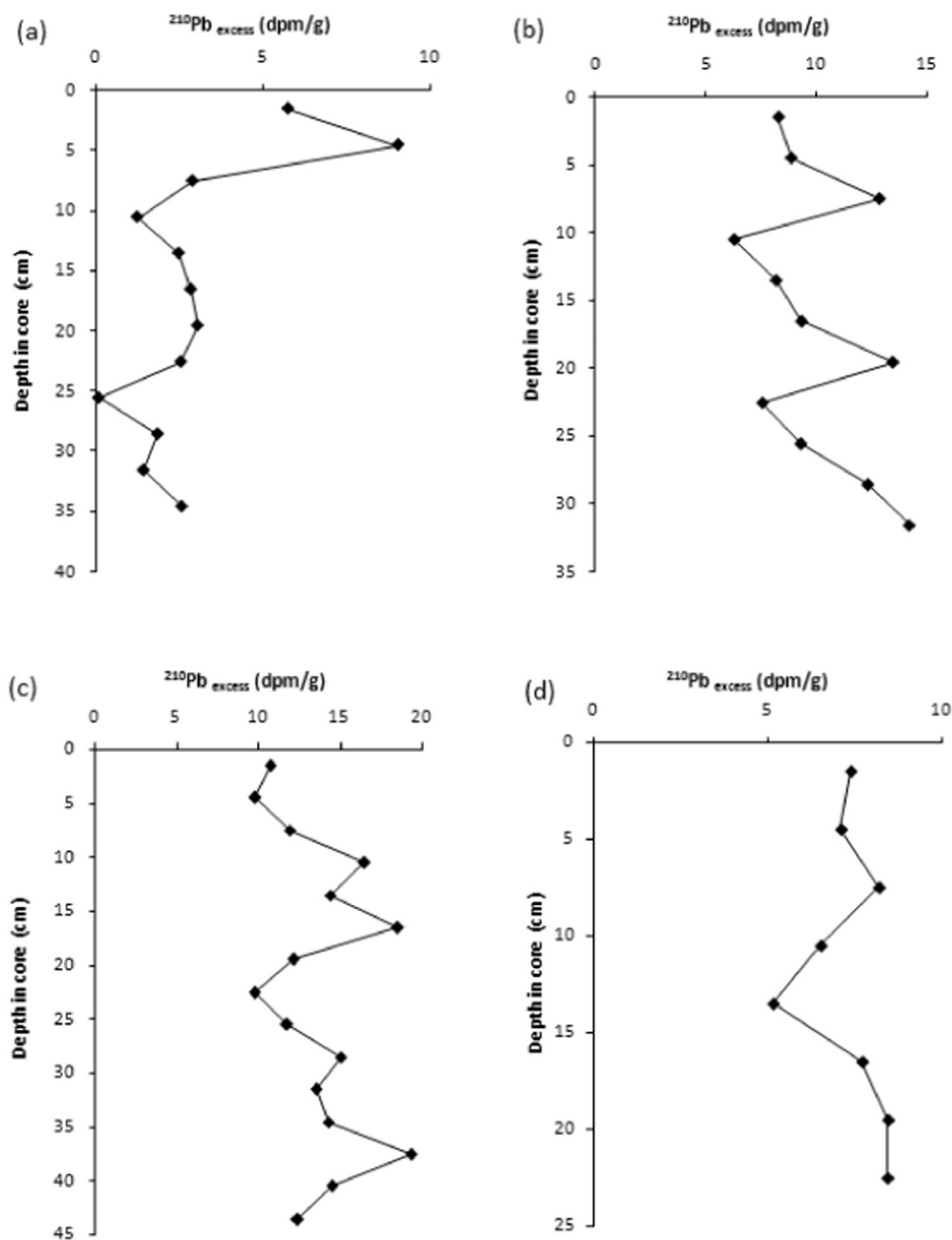


Fig. 3. The excess ^{210}Pb plotted against core depth in sampling points (a) PKS-1, (b) PKS-2, (c) PKS-3 and (d) PKS-4.

The analysis showed that silica (SiO_2) is the main constituent in all testimonies, ranging from mean values of 27–39.7% (Table 3). Significant Pearson correlation coefficient were also found among silica and other analyzed compounds, for instance: TiO_2 (PKS-2: $r = -0.91$), Al_2O_3 (PKS-2: $r = -0.88$; PKS-3: $r = -0.78$), Fe_2O_3 (PKS-1: $r = -0.80$), MnO (PKS-2: $r = 0.89$; PKS-4: $r = 0.95$), MgO (PKS-2: $r = 0.77$; PKS-3: $r = -0.73$), CaO (PKS-2: $r = 0.93$; PKS-4: $r = 0.86$), Na_2O (PKS-2: $r = 0.91$), K_2O (PKS-1: $r = 0.69$; PKS-2: $r = 0.97$; PKS-3: $r = 0.92$), and P_2O_5 (PKS-3: $r = -0.92$).

4.3. Sedimentation rates by the ^{210}Pb method

The results of the total ^{210}Pb activity, supported ^{210}Pb and excess ^{210}Pb of the PKS-1, PKS-2, PKS-3 and PKS-4 profiles are shown in Table 4. The sediment excess profiles of ^{210}Pb activities are shown in Fig. 3. The excess ^{210}Pb activity in PKS-1 core shows a tendency to decrease from the top towards the core bottom. However, some discontinuities can be scanned along the profile, perhaps indicating

changes in the settling rate and/or sudden variation of the granulometric composition of the sediments.

The excess ^{210}Pb in the profiles PKS-2, PKS-3 and PKS-4 (Fig. 3) show no reduction in its activity from the top towards the bottom core. This may reflect the high momentum of the Antas stream, with oscillations on the sedimentation over time, indicating an environment with much variable annual sedimentation rate. Such situation has been pointed out by Ruiz-Fernández et al. (2003, 2007) that considered that the excess ^{210}Pb flow in sedimentary environments is controlled by the climatic characteristics of the region, runoff and origin of the prevailing air mass in the region (oceanic or continental).

The CF:CS (Constant Flux: Constant Sedimentation) model (Crozaz et al., 1964; Krishnaswamy et al., 1971; Koide et al., 1973; Brugam, 1978; Appleby and Oldfield, 1983) takes into account the concentration of excess ^{210}Pb in each slice of the sedimentary column per dry weight. The ^{210}Pb activity, $P(x)$, varies with the dry mass of sediment, m , at a certain depth, according to the equation:

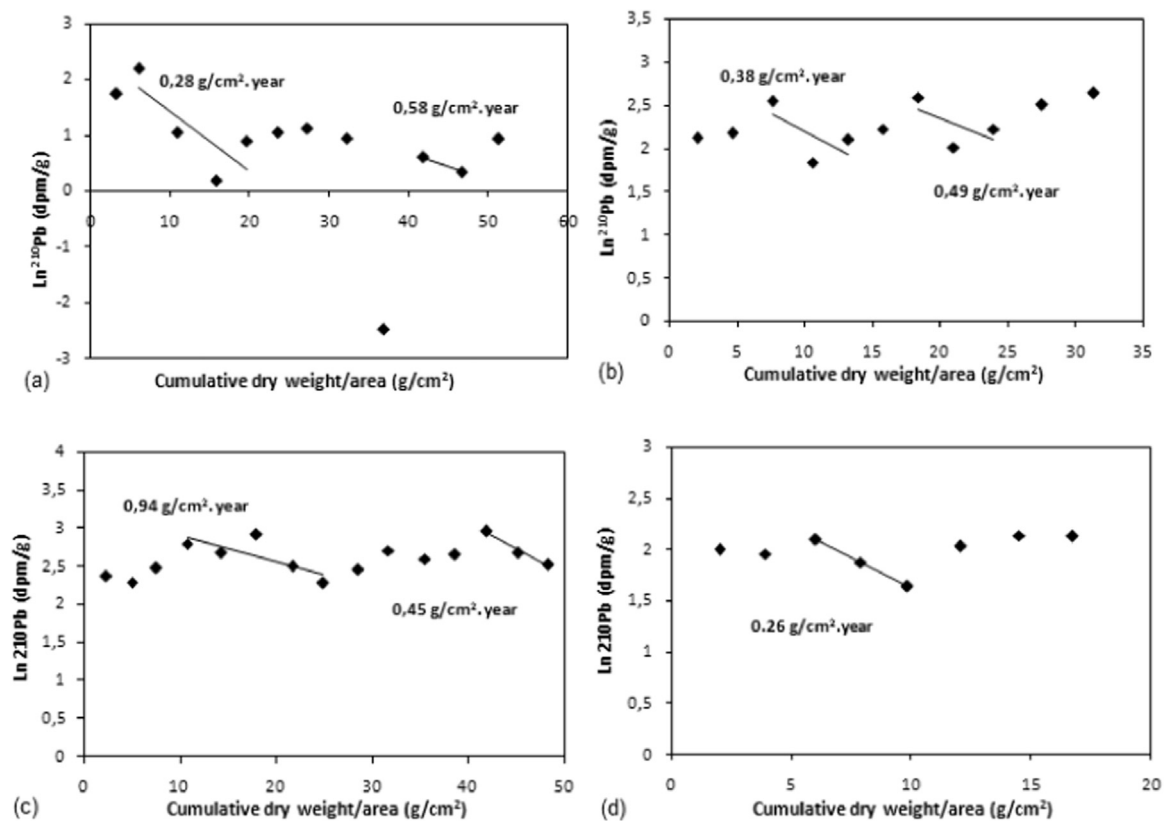


Fig. 4. The logarithm of the excess ^{210}Pb plotted against the cumulative dry weight per area in sampling points (a) PKS-1, (b) PKS-2, (c) PKS-3 and (d) PKS-4.

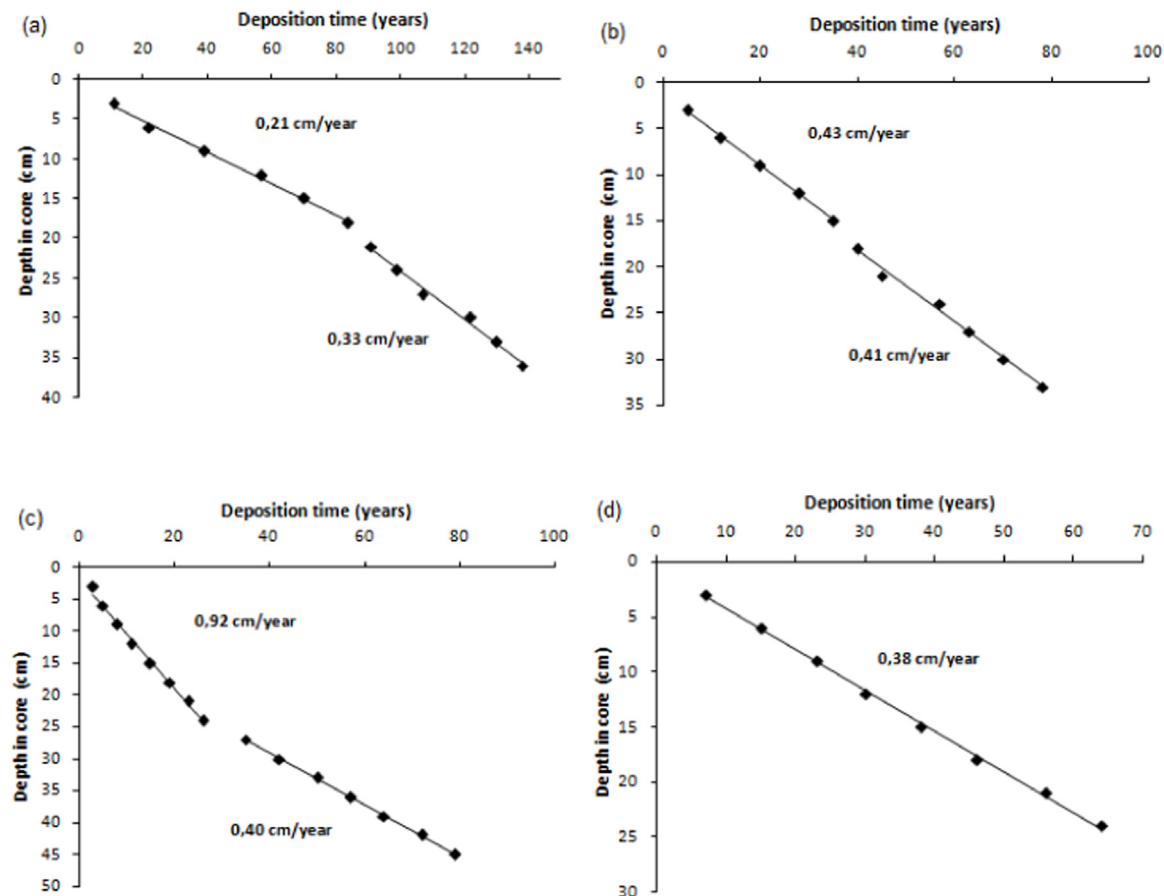


Fig. 5. The deposition time plotted against core depth in sampling points (a) PKS-1, (b) PKS-2, (c) PKS-3 and (d) PKS-4.

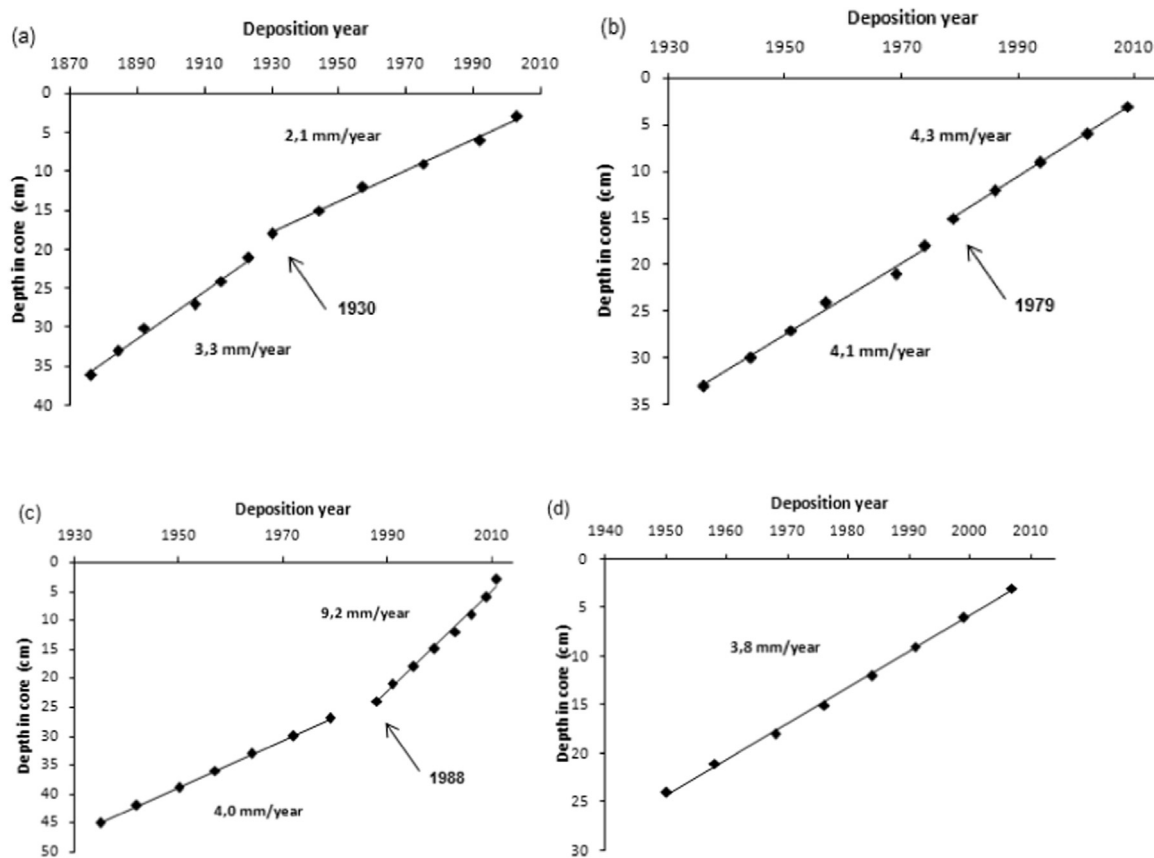


Fig. 6. The deposition year plotted against core depth in sampling points (a) PKS-1, (b) PKS-2, (c) PKS-3 and (d) PKS-4.

$$P(x) = P(0) \times e^{(-\lambda_{210} \cdot m/r)}$$

where: $P(0)$ and $P(x)$ = total inventory of the excess ^{210}Pb at the surface and below the layer x (Bq/cm^2), m is the cumulative dry weight per unit area (g/cm^2), r is the flow sediment or sedimentation rate ($\text{g}/\text{cm}^2 \cdot \text{year}$) and λ_{210} is the decay constant of ^{210}Pb ($0.03114 \text{ year}^{-1}$). The equation can be written as:

$$\ln P(x) - \ln P(0) = (-\lambda_{210}/r)m$$

Fig. 4 shows the $\ln^{210}\text{Pb}_{\text{ex}}$ (dpm/g) plotted against the cumulative dry weight per area in the PKS-1, PKS-2, PKS-3, and PKS-4 profiles. Some straight lines were fitted to the experimental data, allowing find the sedimentation rate on dividing the ^{210}Pb decay constant by the slope modulus.

Two distinct sedimentation rates were obtained in three profiles: 0.28 and $0.58 \text{ g}/\text{cm}^2 \cdot \text{year}$ (PKS-1); 0.38 and $0.49 \text{ g}/\text{cm}^2 \cdot \text{year}$ (PKS-2); 0.45 and $0.94 \text{ g}/\text{cm}^2 \cdot \text{year}$ (PKS-3). One sedimentation rate ($0.26 \text{ g}/\text{cm}^2 \cdot \text{year}$) was found for (PKS-4) (Fig. 4). The variable sedimentation rates in the profiles PKS-1, PKS-2 and PKS-3 show the existence of differentiated events as also demonstrated by Monteiro (2008), Sabaris and Bonotto (2010) and Nery and Bonotto (2011), among other. The sedimentation rates reported in this paper are similar to some determined elsewhere, for instance: Corumbataí River – $2.22 \text{ g}/\text{cm}^2 \cdot \text{year}$ (Lima, 2000); Grande Curuaí lake – $0.42 \text{ g}/\text{cm}^2 \cdot \text{year}$ (Turcq et al., 2004); Amisk lake ($0.02 \text{ g}/\text{cm}^2 \cdot \text{year}$) and Elwater lake ($0.27 \text{ g}/\text{cm}^2 \cdot \text{year}$) in Canada (Turner and Delorme, 1996); Chapala lake, Mexico – $0.44 \text{ g}/\text{cm}^2 \cdot \text{year}$ (Fernex et al., 2001).

The deposition time of the sedimentary layers was estimated by dividing the accumulated mass/area by the sedimentation rate. These values were obtained with reference to the sampling year (2014). They corresponded to: PKS-1 = 138 years; PKS-2 = 78 years; PKS-3 = 79 years; PKS-4 = 64 years. Fig. 5 shows the linear sedimentation rate for each sampled profile: PKS-1 = 0.21 and $0.33 \text{ cm}/\text{year}$; PKS-2 = 0.41

and $0.43 \text{ cm}/\text{year}$; PKS-3 = 0.40 and $0.92 \text{ cm}/\text{year}$; PKS-4 = $0.38 \text{ cm}/\text{year}$. Fig. 5 also shows the deposition time plotted against the core depth.

Fig. 6 shows the deposition age of the sedimentary layers plotted in relation to the core depth. The PKS-1 profile presents a rate of $3.3 \text{ mm}/\text{year}$ from 18 to 36 cm depth (equivalent to year 1930). Above 18 cm depth, the sedimentation rate decreases ($2.1 \text{ mm}/\text{year}$) (Fig. 6a). This change in the sedimentation rate may be related to the large touristic interventions carried out in the Poços de Caldas city from 1920s that contributed to the spa apogee on the 1930 decade (Frayha, 2010).

The PKS-2 profile presents a sedimentation rate of $4.1 \text{ mm}/\text{year}$ from 15 to 33 cm depth (equivalent to 1974). Above 15 cm depth, there is a slight increase in the sedimentation rate ($4.3 \text{ mm}/\text{year}$) (Fig. 6b). The PKS-3 profile (near the urban area of Poços de Caldas city) presents a sedimentation rate of $4.0 \text{ mm}/\text{year}$ from 24 to 45 cm depth (equivalent to 1979), and, above 24 cm depth, there is an increase in the sedimentation rate ($9.2 \text{ mm}/\text{year}$) (Fig. 6c), larger than at other points. According to Poços de Caldas (1992), Ferreira (1996), Megale (2002), Gonçalves (2010) and IBGE (2010), in the second half of the twentieth century, the Poços de Caldas unbridled urbanization, industrialization and demographic growth began. According to Oliveira (2012), the largest population growth is related to the main cycle of expansion and industrial diversification experienced between 1960 and 1990 and concentrated mainly in the peripheries of the city. Finally, the PKS-4 profile (near Bortolan dam) presents an unique sedimentation rate ($3.8 \text{ mm}/\text{year}$) (Fig. 6d), practically coinciding the deposition year at the core bottom (1950) with the construction of Bortolan dam in 1956 (Frayha, 2010).

5. Conclusion

This paper reports the results performed over four sediments

profiles (PKS-1, PKS-2, PKS-3 and PKS-4) collected at Antas stream, Poços de Caldas city, Minas Gerais, State, Brazil. The oxides analysis showed a significant correlation between the Organic Matter (OM) and oxides analyzed in the four profiles, especially silica, which was the major constituent. This indicates that the OM presence can constrain the major oxides concentration in the sediments. The size sediments analysis showed higher levels of the larger fractions (granule and very coarse sand) in the four collection points. The finer fractions take an important role on the metals aggregation. Regarding the ^{210}Pb model for estimating the sedimentation rate, it was possible to find the following values: 0.28 and 0.58 g/cm².year (PKS-1); 0.38 and 0.49 g/cm².year (PKS-2); 0.45 and 0.94 g/cm².year (PKS-3) and 0.26 g/cm².year (PKS-4). They indicate that the rainfall ^{210}Pb deposition in the study area was enough to quantify this radionuclide, allowing to use the CF:CS (Constant Flux: Constant Sedimentation) model to different time scales. The ages of the sedimentary layers seemed to agree with historical events that occurred at Poços de Caldas city, which influenced the studied environments. In addition, the analysis of the physical and chemical parameters in the waters indicated that they exhibit unfavorable conditions for human consumption, according to the Brazilian guidelines for water quality.

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References

- Aiken, G.R., McNight, D., Wershaw, R.L., MacCarthy, 1985. Humic substances in soil, sediment and water. John Wiley & Sons, New York, pp. 691.
- Álvarez-Iglesias, P., Quintana, B., Rubio, B., Pérez-Arlucea, M., 2007. Sedimentation rates and trace metal input history in intertidal sediments from San Simón Bay (Ría de Vigo, NW Spain) derived from ^{210}Pb and ^{137}Cs chronology. *J. Environ. Radioact.* 98, 229–250.
- Appleby, P.G., Oldfield, F., 1978. The calculation of lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *Catena* 5, 1–8.
- Appleby, P.G., Oldfield, F., 1983. The assessment of ^{210}Pb data from sites with varying sediment accumulation rates. *Hydrobiologia* 103, 29–35.
- Bengtsson, L., Enell, M., 1986. Chemical analysis. In: Berglund, B.E. (Ed.), *Handbook of Holocene Paleocology and Paleohydrology*. John Wiley & Sons, Chichester, pp. 423–451.
- Bonotto, D.M., Lima, J.L.N., 2006. ^{210}Pb -derived chronology in sediment cores evidencing the anthropogenic occupation history at Corumbataí River basin, Brazil. *Environ. Geol.* 50 (4), 595–611.
- Brasil, 2005. Resolução Conama No. 357, de 17 de março de 2005 - Dispõe sobre a classificação dos corpos de água e diretrizes ambientais para seu enquadramento bem como estabelecer as condições e padrões de lançamento de efluentes, e dá outras providências. <<http://www.mma.gov.br/conama>>.
- Brasil, 2011. Portaria No. 2914 do Ministério de Saúde, de 12 de dezembro de 2011. <http://bvsms.saude.gov.br/bvs/saudelegis/gm/2011/prt2914_12_12_2011.html>.
- Brugam, R.B., 1978. Pollen indicators of land-use change in Southern Connecticut. *Quatern. Res.* 9, 349–362.
- Crozaz, G., Picciotto, E., de Breuck, W., 1964. Antarctic snow chronology with Pb-210. *J. Geophys. Res.* 69, 2597–2604.
- Crikmore, M.J., Tazioli, P.G., Appleby, P.G., Oldfield, F., 1990. The use of nuclear techniques in sediment transport and sediment problems. UNESCO-International Hydrological Program, Paris, 170 pp.
- Dean, W.E.J.R., 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss ignition: comparison with other methods. *J. Sed. Petrol.* 44, 242–248.
- El-Daoushy, F.A., 1988. A summary on the lead-210 cycle in nature and related applications in Scandinavia. *Environ. Int.* 14, 305–319.
- Ellert, R., 1959. Contribuição à geologia do maciço alcalino de Poços de Caldas. *Geologia FFLC-USP* 18, 5–63.
- Fernex, F., Valle, P.Z., Sanchez, H.R., Michaud, F., Parron, P., Dalmasso, J., Funel, G.B., Arroyo, M.G., 2001. Sedimentation rates in Lake Chapala (Western Mexico): possible active tectonic control. *Chem. Geol.* 177, 213–228.
- Ferreira, J., 1996. Um hectare na história de Poços de Caldas. 11th ed., Gráfica Brasil, Poços de Caldas.
- Fraenkel, M.O., Santos, R.C., Lourenço, F.E.V.L., Muniz, W.S., 1985. Jazida de urânio no planalto de Poços de Caldas, Minas Gerais. In: DNPM (Departamento Nacional de Produção Mineral) (Ed.) *Principais Depósitos Minerais do Brasil*, v. 1, pp. 89–103.
- Frayha, G.Z., 2010. Poços de Caldas polo mesorregional: ambiente, planejamento e qualidade de vida na articulação dos municípios da Média Mogiana e do Sul de Minas Gerais. M.Sc. Dissertation. UNICAMP-Universidade Estadual de Campinas, Campinas (SP), pp. 228.
- Gonçalves, Y.A., 2010. Poços de Caldas: uma leitura econômica. Sul Mineira, Varginha.
- Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility of results. *J. Paleolimnol.* 25, 101–110.
- IBGE (Instituto Brasileiro de Geografia e Estatística), 2010. Densidade demográfica nos censos demográficos de 1872 a 2010, segundo as regiões do Estado de Minas Gerais. <<http://biblioteca.ibge.gov.br/visualizacao/dtbs/minasgerais/pocosdecaldas.pdf>>.
- IBRAM (Instituto Brasileiro de Mineração), 2008. Informações e Análises da Economia Mineral Brasileira. <<http://www.ibram.org.br/sites/>>.
- Koide, M., Bruland, K.W., Goldberg, E.D., 1973. Th-228/Th-232 and Pb-210 geochronologies in marine and lake sediments. *Geochim. Cosmochim. Acta* 37, 1171–1187.
- Krishnaswamy, S., Lal, D., Martin, J., Meybeck, M., 1971. Geochronology of lake sediments. *Earth Planet. Sci. Lett.* 11, 407–414.
- Lacerda, L.D.D., 1994. Biogeoquímica de metais pesados em ecossistemas de manguezal. Ph.D. Thesis. UFF-Universidade Federal Fluminense, Niterói (RJ), pp. 68.
- Lima, J.L.N., 2000. Hidroquímica pluvial e fluvial na Bacia do Rio Corumbataí (SP) e relações com o uso do Pb-210 como geocronômetro. Ph.D. Thesis. UNESP-Universidade Estadual Paulista, Rio Claro (SP), pp. 260.
- Mata, Y.M., González, F., Ballester, A., Blázquez, M.L., Muñoz, J.A., 2002. Inhibition of acid rock drainage from uranium ore waste using a conventional neutralization and precipitation treatment. *Miner. Eng.* 15, 1141–1150.
- Megale, N.B., 2002. Memórias históricas de Poços de Caldas. 2nd ed., Sulminas, Poços de Caldas.
- Mechi, A., Sanches, D.L., 2010. Impactos ambientais da mineração no Estado de São Paulo. *Estud. Av.* 24 (68), 209–220.
- Monteiro, F.F., 2008. Histórico de acumulação de metais-traço em sedimentos estuarinos do Rio Iguaçu e da região da área de Proteção Ambiental de Guapimirim, Baía de Guanabara (RJ). M.Sc. Dissertation. UFF-Universidade Federal Fluminense, Niterói (RJ), pp. 88.
- Nery, J.R.C., Bonotto, D.M., 2011. ^{210}Pb and composition data of near-surface sediments and interstitial waters evidencing anthropogenic inputs in Amazon River mouth, Macapá, Brazil. *J. Environ. Radioact.* 102, 348–362.
- Oliveira, E.M., 2012. Dinâmica locacional das indústrias e a produção do espaço urbano em Poços de Caldas (MG). Oliveira, E.M., 2012. Dinâmica locacional das indústrias e a produção do espaço urbano em Poços de Caldas (MG). M.Sc. Dissertation, UNESP-Universidade Estadual Paulista, Rio Claro, Rio Claro (SP), 177 pp., UNESP-Universidade Estadual Paulista, Rio Claro, Rio Claro (SP), 177 pp.
- Piper, A.M.A., 1944. A graphic procedure in the geochemical interpretation of water-analyses. *Trans. Am. Geophys. Union* 25, 914–928.
- Poços de Caldas, 1992. Plano Diretor. Secretaria de Planejamento e Coordenação, Poços de Caldas.
- Poços de Caldas, 2006. Plano Diretor (Documento de 2002, revisado de acordo com a Lei Federal 10.257/10). Secretaria de Planejamento e Coordenação, Poços de Caldas.
- Rebouças, A.C., Braga, B., Tundisi, J.G., 2006. Águas doces do Brasil: capital ecológico, uso e conservação, 3rd ed. Editora Escrituras, São Paulo, pp. 748.
- Rosales-Hoz, L., Cundy, A.B., Bahena-Manjarrez, J.L., 2003. Heavy metals in sediment cores from a tropical estuary affected by anthropogenic discharges: coatzacoalcos estuary, Mexico. *Estuar. Coast. Shelf Sci.* 58, 117–126.
- Ruiz-Fernández, A.C., Hillaire-Marcel, C., Paez-Osuna, F., Ghaleb, B., Soto-Jiménez, M., 2003. Historical trends of metal pollution recorded in the sediments of the Culiacan River Estuary, Northwestern Mexico. *Appl. Geochem.* 18, 577–588.
- Ruiz-Fernández, A.C., Hillaire-Marcel, C., Paez-Osuna, F., Ghaleb, B., Caballero, M., 2007. ^{210}Pb chronology and trace metal geochemistry at Los Tuxtlas, Mexico, as evidences by a sedimentary record from the Lago Verde crater lake. *Quatern. Res.* 67 (2), 181–192.
- Sabaris, T.P.P., Bonotto, D.M., 2010. Sedimentation rates in Atibaia River basin, São Paulo State, Brazil, using ^{210}Pb as geochronometer. *Appl. Radiat. Isot.* 69, 275–288.
- Thornton, I., 1983. *Applied Environmental Geochemistry*. Academic Press, London, pp. 501.
- Turcq, P.M., Jouanneau, J.M., Turcq, B., Seyler, P., Weber, O., Guyot, J.L., 2004. Carbon sedimentation at Lago Grande de Curuá, a floodplain lake in the low Amazon region: in sight into sedimentation rates. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 214, 27–40.
- Turner, L.J., Delorme, L.D., 1996. Assessment of ^{210}Pb data from Canadian lakes using the CIC and CRS models. *Environ. Geol.* 28, 78–87.