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Characterizing suspended sediments from the Piracicaba River Basin by means of k_0–INAA

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ABSTRACT

The inorganic chemical characterization of suspended sediments is of utmost relevance for the knowledge of the dynamics and movement of chemical elements in the aquatic and wet ecosystems. Despite the complexity of the effective design for studying this ecological compartment, this work has tested a procedure for analyzing suspended sediments by instrumental neutron activation analysis, k_0 method (k_0–INAA). The chemical elements As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, K, La, Mo, Na, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Yb and Zn were quantified in the suspended sediment compartment by means of k_0–INAA. When compared with World Average for rivers, high mass fractions of Fe (222,900 mg/kg), Ba (4990 mg/kg), Zn (1350 mg/kg), Cr (646 mg/kg), Co (74.5 mg/kg), Br (113 mg/kg) and Mo (31.9 mg/kg) were quantified in suspended sediments from the Piracicaba River, the Piracicamirim Stream and the Marins Stream. Results of the principal component analysis for standardized chemical element mass fractions indicated an intricate correlation among chemical elements evaluated, as a response of the contribution of natural and anthropogenic sources of chemical elements for ecosystems.

1. Introduction

The inorganic chemical characterization of suspended sediments is of utmost relevance for the knowledge of the dynamics and movement of chemical elements in the ecosystems. Studies involving the collection, processing and subsequent chemical analysis of suspended sediments are considered complicated because of the characteristics of this kind of matrix [1]. The main issues are the horizontal and vertical cross sectional variations, the variation of silt/clay ($<63\,\mu m$) fractions and its relation to the chemical transport, the temporal variation and the correlation of sediment flux with a constant/variable discharge. Divergences could also be expected depending on the type of sampler and sampling design used, as well as the sample mass collected in the field. Moreover, heterogeneity and errors because of the analytical techniques employed for chemical determination should be taken into account for environmental geochemists and researchers in general [1].

Despite the inherent complexity for sampling and analyzing suspended sediments, the compilation of the chemical composition of suspended matter in World Rivers [2] is clearly desirable. Likewise, the more intricate the environmental issues related to agricultural and industrial pollution, the higher is the importance of punctual assessment of chemical element pathways. For that reason, generation of knowledge by applying analytical techniques to study suspended matter in small rivers and streams is pretty appropriate for geochemical community, as well as for other environmental associated researchers.

Recently comparability of results is acclaimed for all environmental studies. The use of adequate technique could minimize analytical uncertainties [1,3]. In the case of analysis of sediments in suspension by spectrometric techniques, dissolution of solids is dependent on the sample matrix. For instance, carbonates are easily soluble than igneous and metamorphic matrices. Chemical comparisons based on these results become complicated across geological gradients/boundaries [1].

Neutron activation analysis (NAA) is a nuclear multi-elemental technique, which is well suited for determining chemical composition of suspended sediments, especially when its instrumental mode and the k_0 standardization [4] are used. The main advantages of k_0–NAA, as applied at Centro de Energia Nuclear na Agricultura (CENA), have already been described [5].

Therefore, this work has tested a procedure for analyzing suspended sediments by k_0–INAA within the context of Project Interface SSV "Innovation in the biomonitoring of wet ecosystems from the Piracicaba River Basin: Interface Sediment/Soil–Vegetation–Fauna (SSVF)". The project aims at the assessment of environmental quality of ecological compartments of riparian areas from the Piracicaba region, São Paulo State, Brazil, in which

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suspended sediment could be a very helpful ecological compartment to understand chemical element pathway.

2. Experimental

The municipality of Piracicaba with an area of 1385.38 km^2 is mainly characterized by agricultural activities. Among them, sugarcane and pasture together account for about 1000 km^2 [6]. Diverse industries are also found here, mostly associated with agricultural activities. However, vegetation, mainly riparian forests, occupies a considerable area of about 116 km^2 in spite of this intensive land use. The major rivers are Piracicaba and Tietê, the latter being mainly polluted in the City of São Paulo. As mentioned before, the Project Interface SSVF aimed at the assessment of environmental quality of ecological compartments of riparian areas from the Piracicaba. Several riverine areas were selected from the Piracicamirim Stream (PM; n=4), Marins Stream (M; n=3) and Piracicaba River (n=10), as shown in Fig. 1.

According to Köppen, Piracicaba's climate is classified as Cwa (mild mid-latitude, humid subtropical, mild with dry winter and hot summer). Fig. 2A shows averaged precipitation and temperature during the period between 1917 and 2009, data collected from the climatic station located at the Escola Superior de Agricultura Luiz de Queiroz, Universidade de São Paulo (S22 42′30′; W47 38′00″). Fig. 2B presents mean values of discharge ($m^3 s^{-1}$) for the Station PCB02800 (Artemis) for the Piracicaba River [7,8]. With the mean discharge value of 140 $m^3 s^{-1}$ and the basin area, the Piracicaba River can be considered a river of medium dimension [1].

For suspended sediment sampling, composite water samples of 20 l were collected in rivers from the Piracicaba city and surrounding streams (Fig. 1), stored in plastic gallons and in cold chamber at 8 °C for 6 months until the sediment decantation. After this period, surface water was extracted by suction, leaving the sediments in the bottle bottom. The remaining suspension was transferred to high-density polyethylene bottles for centrifugation and, later, freeze-dried for obtaining the test material. A recent work [2] suggests that even mobile chemical elements, such as Ca and K, are transported in the solid form. Therefore, the procedure used for obtaining the solid material should not yield significant losses of chemical elements in the solution [2] or because of the adsorption of metals onto the container walls.

Analytical portions of approximately 100 mg were directly weighted in polyethylene capsules for neutron irradiation. Compared with other techniques [1], this procedure is quite simple because chemical treatment for dissolution is not involved. Moisture was estimated by oven-drying separate portions (up to 500 mg) at 85 °C until constant mass. Portions of 200 mg of the reference materials International Atomic Energy Agency (IAEA) Soil 7 and National Institute of Standards and Technology Standard Reference Material (NIST SRM) 2710 Trace Elements in Montana Soil were also analyzed for quality control purposes. Together with samples, pieces of Ni–Cr alloy (mass=10 mg) were sandwiched between vials for monitoring thermal neutron flux [9]. The material was irradiated in a thermal neutron flux of approximately 10^{13} $cm^{-2} s^{-1}$ for 4 h in the Research Nuclear Reactor IEA-R1 of the Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear, São Paulo, Brazil. After 2 days of decay time, irradiated material was transported to CENA. This step allows the quantification of radionuclides with half-lives higher than 0.5 day.

Induced radioactivity was measured at 5, 7, 16 and 60 days after irradiation using two Ortec germanium detectors with 45% and 50% of efficiency at the 1332 keV photopeak from ^{60}Co. Monitors were measured at 10 and 15 days after irradiation, in which the thermal neutron flux during the irradiation was $9.4 \times 10^{12} \pm 5.8 \times 10^{11}$ $cm^{-2} s^{-1}$. For this particular irradiation position, f and α were 69 and 0.067, respectively.

The quantification of chemical elements was done by means of the software Quantu dedicated to k_0–INAA, which also permits the estimation of analytical uncertainties and detection limits [10]. For Hg and Se mass fractions, appropriate correction for spectral interferences were applied. Whenever necessary, corrections were also carried out for chemical elements present in the vials (blank). Results of chemical elements were reported on a dry weight basis.

For assessing the quality of the analytical results, E_n number was calculated in a Microsoft Excel worksheet taking into account the difference between obtained and reference values and the respective expanded analytical uncertainties at the 95% confidence level. Multivariate analysis was based on standardized chemical element mass fractions (mean n=0; standard deviation

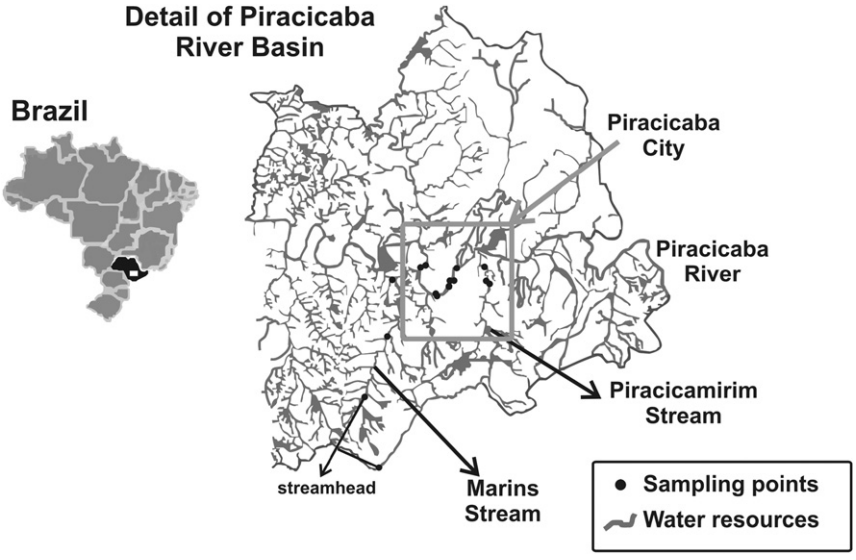

Fig. 1. Hydrological map of the Piracicaba River Basin in the Piracicaba City, São Paulo State, Brazil. Detail of sampling points in the Piracicaba River, Piracicamirim Stream and Marins Stream.