Journal of Environmental Radioactivity 177 (2017) 24–31

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad

Combining lead isotopes and cluster analysis to distinguish the Guarani and Serra Geral Aquifer Systems and contaminated waters in a highly industrialized area in Southern Brazil

Isadora Aumond Kuhn [a, *], Ari Roisenberg [b]

[a] Brazilian Geological Survey, Brazil
[b] Federal University of Rio Grande do Sul, Brazil

ARTICLE INFO

Article history:
Received 22 January 2017
Received in revised form
19 May 2017
Accepted 20 May 2017

Keywords:
Groundwater
Lead isotopes
Cluster analysis
Guarani aquifer system

ABSTRACT

The Rio dos Sinos Watershed area is located at the Middle-West region of the Rio Grande do Sul State, Southern Brazil, along thirty two municipalities and affecting 1.5 million inhabitants and many important industrial centers. Three main aquifers are recognized in the study area: the unconfined-fractured Serra Geral Aquifer System, the porous Guarani Aquifer System, and the Permian Aquitard. This study aims to understand groundwater, surface water and human activity interactions in the Rio dos Sinos Watershed, evaluating the application of stable lead isotopic ratios analyzed for this propose. Thirty six groundwater samples, 8 surface water samples and 5 liquid effluents of tanneries and landfills samples were measured using a Thermal Ionization Mass Spectrometer Thermo-Finnigan and a Neptune Multi-Collector Inductively Coupled Plasma Mass Spectrometer. Groundwater isotopic ratios have a wider range compared to the surface water, with less radiogenic averages $^{208}Pb/^{204}Pb$ = 38.1837 *vs* 38.4050 (standard deviation = 0.2921 *vs* 0.1343) and $^{206}Pb/^{204}Pb$ = 18.2947 *vs* 18.4766 (standard deviation = 0.2215 *vs* 0.1059), respectively. Industrial liquid effluents (tanneries and industrial landfill) have averages $^{208}Pb/^{204}Pb$ = 38.1956 and $^{206}Pb/^{204}Pb$ = 18.3169, distinct from effluent samples of domestic sanitary landfill (averages $^{208}Pb/^{204}Pb$ = 38.2353 and $^{206}Pb/^{204}Pb$ = 18.6607). Hierarchical cluster analysis led to distinguish six groups of groundwater, representing the three aquifers that occur in the area, two clusters suggesting groundwater mixtures and one demonstrating a highly contaminated groundwater. By analyzing the cluster results and wells' stratigraphic profiles it was possible to distinguish the different aquifers in the area. The Serra Geral Aquifer System has $^{206}Pb/^{204}Pb$ ratios between 18.4718 and 18.7089; $^{207}Pb/^{204}Pb$ between 15.6692 and 15.6777; $^{208}Pb/^{204}Pb$ between 38.6826 and 38.7616; $^{207}Pb/^{206}Pb$ between 0.8372 and 0.8623; $^{208}Pb/^{206}Pb$ between 2.0671 and 2.0964 and the Guarani Aquifer System has a wider range ($^{208}Pb/^{204}Pb$ ranged from 37.9393 to 38.1279 and $^{206}Pb/^{204}Pb$ ranged from 18.0892 to 18.3217). Water mixing of these two aquifer systems is reflected by transitional results. The results confirm that the hierarchical cluster analysis of lead isotopes is a useful tool to discriminate different aquifer conditions, reflecting mostly the influence of the natural lead isotopic composition of the aquifers instead of the anthropogenic activities (urban and industrial), except when the groundwater is highly contaminated by human activity.

1. Introduction

About 50% of Brazilian city's water supply is from groundwater resources. In Rio Grande do Sul State, Southern Brazil, groundwater exploration is increasing, mainly due to the intense degradation of surface waters. Besides this, the relationship between groundwater and surface water quality is not well understood.

The Rio dos Sinos Watershed (RSW) is located in Eastern region of the Rio Grande do Sul State and it is composed by 32 municipalities, with about 1.5 million inhabitants. Rio dos Sinos is the most contaminated river of the state and the main contamination sources are related to the poor sewage collection system and the intense industrial activity. Tannery is a traditional activity in the

* Corresponding author.
E-mail addresses: isadora.kuhn@cprm.gov.br (I.A. Kuhn), ari.roisenberg@ufrgs.br (A. Roisenberg).

http://dx.doi.org/10.1016/j.jenvrad.2017.05.013
0265-931X/

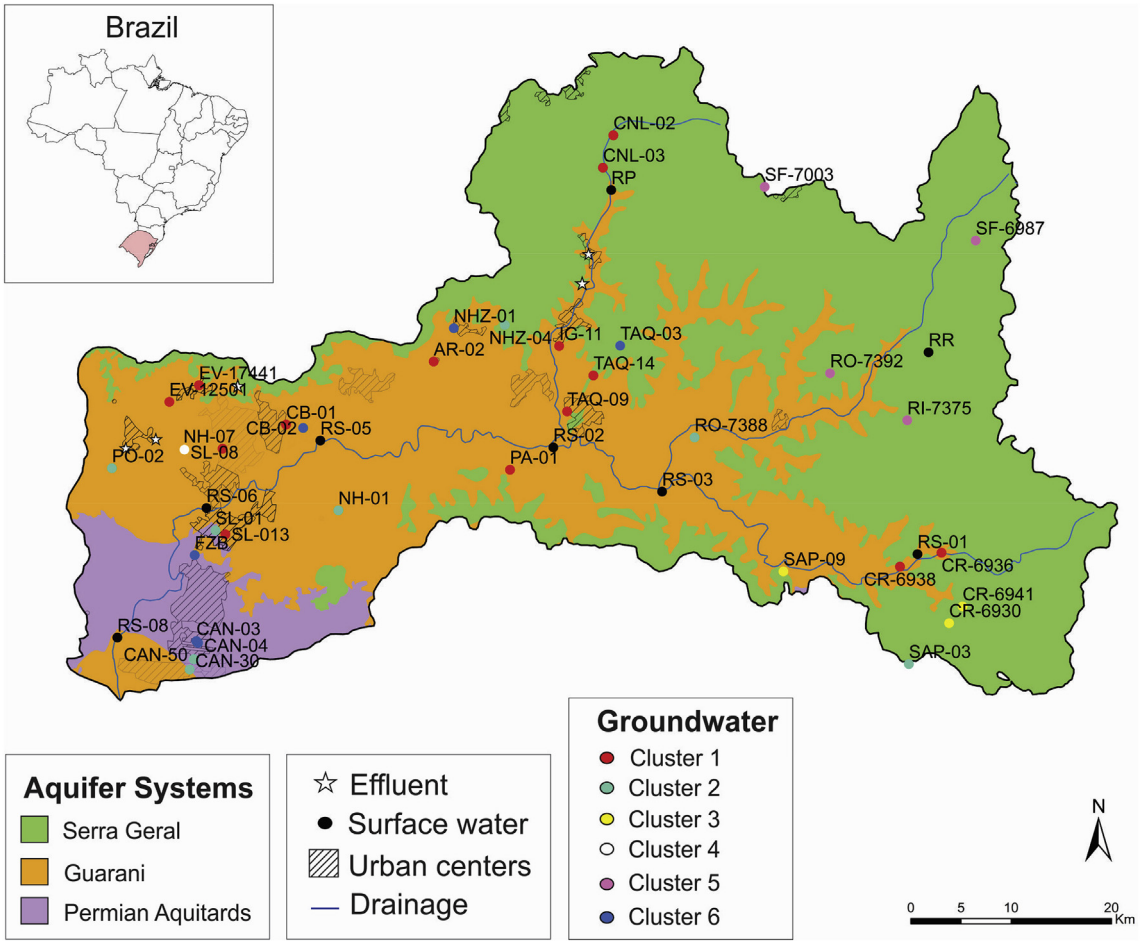

Fig. 1. RSW's hydrogeological map with sampling points and the groundwater clusters resulting from cluster analysis.

region, related with the livestock. It is responsible for the generation of large volumes of solid and liquid residues enriched in metals such as Al, Cr, Pb, Hg and Cd (Rodrigues and Formoso, 2006). The bad waste disposals, inadequate treatment and leakage of liquid effluents are related with the loss of rivers' water quality.

Hence, most academic studies and governmental projects have focused on the surface water of the RSW, while the groundwater is less well known. A recent work of multi-elemental hydrogeochemistry by Abreu and Roisenberg (2017) in groundwater samples of 37 wells distributed along the RSW revealed punctual contamination by Pb, Cu and Sb. The authors performed hierarchical cluster analysis and concluded that in most of the cases chemical characteristics reflects the natural aquifers composition.

Lead isotope analysis is an efficient tool for tracing contamination sources and pathways, being considered the contamination source's fingerprint. Stable lead isotopes methodology has been applied mainly in atmospheric and soil pollution (e.g., Bollhoffer and Rosman, 2000a,b; Chow and Johnstone, 1965). Few studies have applied this methodology for probing groundwater quality and origin. In groundwater studies stable lead isotopes signatures have presented a very large variation, related to multiple lead sources (e.g., Potot et al., 2012; Millot and Négrel, 2015), leading to a hard interpretation set and vague conclusions. Hierarchical cluster analysis of lead isotopic signatures allowed distinguishing groundwater groups that made it possible to determine isotopic characteristics for the aquifer systems presents in the study area.

The objective of this study was to track back the anthropogenic contamination in the RSW using stable lead isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) in groundwater, surface water, industrial and landfill liquid effluent samples. Furthermore, the objective was to evaluate the application of lead isotopic analysis in distinct groundwater systems, surface water and industrial and landfill liquid effluent samples and to evaluate the application of lead isotopic analysis in these environmental compartments.

1.1. Geology of the study area

The RSW is subdivided in three segments: High Sinos Region, where most of the springs are located. It has diffuse urban occupation and soil use is predominantly rural. The Medium Sinos Region has greater population and industrial density, but it is still incipient. The most impacted area of the watershed is the Low Sinos Region, which has the main urban and industrial areas and comprises of the main leather and shoes industries in Brazil. The RSW is located in the southeastern edge of the Paraná Sedimentary Basin. It is an extensive intracratonic basin, developed on Gondwana during Paleozoic and Mesozoic that was recovered by a thick pack of volcanic rocks with approximate total thickness of 7000 m (Milani et al., 2007). The outcrops along the RSW are composed by Permian sedimentary rocks of Rio do Rastro and Piramboia Formations and Mesozoic units of the Botucatu sandstone and volcanic rocks belonging to the Serra Geral Formation.

The Rio do Rastro Formation is composed by fine-grained sandstones and mudstones originated in marine and continental