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ISOTOPIC STUDIES OF GROUNDWATER-SEAWATER INTERACTIONS IN THE UBATUBA COASTAL AREA, BRAZIL

Pavel P. Povinec[1*], Joselene de Oliveira[2] , and Elisabete de Santis Braga[3]

[1]Faculty of Mathematics, Physics and Informatics of the Comenius University,
Mlynska Dolina F-1, SK84248 Bratislava, Slovakia
povinec@fmph.uniba.sk

[2]Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Avenida Professor Lineu Prestes 2242
05508-000 São Paulo, SP
jolivei@ipen.br

[3]Instituto Oceanográfico da Universidade de São Paulo
Praça do Oceanográfico, 191 Cidade Universitária
05508-900 São Paulo, SP
edsbraga@usp.br

ABSTRACT

Stable isotopes and nutrients data collected during 2002 and 2003 campaigns offshore Ubatuba are presented and discussed. The isotopic composition (δD, $\delta^{18}O$) of submarine waters is characterised by significant variability and heavy isotope enrichment, indicating that a contribution of groundwater in submarine waters may vary up to 20%, depending on the location and the tide level. The nutrient data showed scaterred distributions with offshore distance and salinity, what implies that in the complex coast with many small bays and islands the mixing patterns have been very complex. The sources of nutrients observed in the visited bays are both due to transport of pollutants by local currents and due to contributions of submarine groundwater. Submarine groundwater discharge in Ubatuba area is fed by coastal contaminated groundwater and re-circulated seawater (with small admixtures of groundwater), which claims for potential environmental concern with implications on the management of freshwater resources in the region.

1. INTRODUCTION

Groundwater-seawater interactions (GSI) have been frequently studied because of their importance for the protection of coastal zones against contamination from land-based sources, as well as for the management of fresh water resources in coastal areas [1]. Several isotope techniques for GSI studies have been developed using stable (^{2}H, ^{18}O, $^{87/86}Sr$, etc.) and radioactive (^{3}H, ^{14}C, Ra isotopes, ^{222}Rn, etc.) isotopes [1,2]. The groundwater-seawater interactions are manifested by at least three major processes: (i) density contrast between seawater and fresh water, (ii) wave and tidal pumping of water into the sediments, and (iii) biological pumping caused by burrowing organisms (bioirrigation). Consequently, the

* Formerly at International Atomic Energy Agency (IAEA), Marine Environment Laboratory (MEL), Monaco, where part of this work was carried out.

magnitude of submarine groundwater discharge (SGD) must be controlled to some extent by physical and biological processes at the sediment-water interface, in addition to hydraulic head-driven discharge from continental aquifers [3]. These processes control the chemical composition of discharging water and the environmental effects of SGD.

Coordinated Research Project (CRP) on "Nuclear and Isotopic Techniques for the Characterisation of Submarine Groundwater Discharge (SGD) in Coastal Zones" was jointly organized by the IAEA's Marine Environment Laboratory (Monaco) and the Isotope Hydrology Section (Vienna), with the aim to develop new isotope techniques for studying SGD. The CRP was carried out in cooperation with UNESCO's Intergovernmental Oceanographic Commission (IOC), the International Hydrological Programme (IHP), and several laboratories. Several expeditions were carried out in the framework of the CRP, including two missions to the Ubatuba coast (São Paulo region, Brazil). In the present paper we summarize stable isotope and nutrient results obtained from these expeditions.

2. METHODS

2.1. Seawater and groundwater samples

Groundwater and seawater samples were collected in a series of small embayments of Ubatuba, in the continental shelf (23°26'S-23°46'S and 45°02'W-45°11'W). Seawater samples in the water column were collected from 1 to about 40 m depth. The sampling campaigns (5-15 August 2002 and 14-26 November 2003) were carried using R/Vs Velliger II and Albacora. Seawater samples were also collected in several transects offshore Ubatuba in 2002, and in a transect on the way to the Victoria Island in 2003. Some of the obtained results were already described, e.g. for radium isotopes [4], ^{222}Rn [5,6] and radioactive and stable isotopes [7].

Groundwater samples were collected from land wells and springs situated at the Fortaleza, Flamengo and Picinquaba Bays and Victoria Island. River water samples were collected at the Fazenda beach (Picinguaba Bay). Water samples were also collected from 7 monitoring borehole wells drilled at the Flamengo Bay using a peristaltic pump, where also seepage chambers [8] and piezometers [9] were located for measuring groundwater seepage rates from the sediment. These samples were collected during low as well as high tides. Water samples for isotope analysis were collected in 1 L polyethylene bottles using a submersible pump. The samples were filtered through 0.45 μm glass microfiber filters (Millipore). Water samples for laboratory salinity measurements were collected in 100 mL glass bottles, and samples for nutrients were collected by 250 mL plastic vials that were pre-washed with 0.5 M hydrochloric acid and sample-rinsed three times. Samples were kept frozen until analysis.

2.2. Measurement of oceanographic parameters

Temperature, conductivity/salinity were measured in the field using portable meters allowing temperature compensation and calibration with appropriate standards. Salinity at visited sites was measured *in situ* using a CTD (MCTD-DBP, Falmouth Scientific Inc, the precision

±0.001). Temporal variations of salinity in monitoring borehole wells were measured by a small "fish" DST-CTD sensor (Star-Oddi, Iceland, the precision of salinity measurements was ± 0.01). Conductivity/salinity measurements in the laboratory were done using portable meters.

2.3. Analysis of stable isotopes

Isotopic analyses were carried out on groundwater and seawater samples and their mixtures. $\delta^{18}O$ measurements were done by the CO_2-H_2O equilibration procedure. δD analyses were carried out using the H_2O-Zn reduction method. The isotopic analyses are reported against the international standard VSMOW (Vienna Standard Mean Ocean Water) using conventional delta (δ) notation in ‰. The precision of measurements (1σ) was ±0.1‰ for $\delta^{18}O$ and ±1‰ for δD. Stable isotopes of hydrogen and oxygen were analysed in the IAEA's Isotope Hydrology Laboratory in Vienna, and in the Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand.

2.4. Analysis of nutrients

Water samples of 25 mL kept in an ice box were used for nutrient analysis using ion chromatography. The total relative uncertainties were below 1 % (at 1 sigma level). Reference samples were analysed simultaneously. The analyses were done in the Institute of Oceanography of the University of São Paulo.

3. RESULTS AND DISCUSSION

3.1. Isotopes in groundwater, river water and seawater

Groundwater springs and wells have hydrogen isotope compositions (δD) in the range of –18.3 to –11.2 ‰, while the oxygen compositions ($\delta^{18}O$) are between –3.9 and –3.17 ‰. The isotope composition of river water sampled at Fazenda Beach varied from –15.6 to –9.3 ‰ for δD, and between –3.61 and –2.91‰ for $\delta^{18}O$, showing typical fresh water values which are close to the values for groundwater wells and springs. Seawater samples except one result had positive values, from 1.3 to 6.6 ‰ for δD, and from -0.02 to 0.32 ‰ for $\delta^{18}O$. The isotope composition of seawater samples is characterised by significant variability and enrichment of heavy isotopes. Isotopic composition of water collected in the borehole wells varied for δD from –14.7 to 3.9 ‰ and from -3.20 to 0.49 ‰ for $\delta^{18}O$. δD values in piezometer pore water samples, provided by Cable & Martin [8], varied from –7.5 to 2.5 ‰ and $\delta^{18}O$ from -1.80 to 0.19 ‰. The water samples collected in the seepage chambers, provided by Bokuniewicz *et al.,* [7], showed isotopic composition between seawater and groundwater. δD results were between 0.0 and 1.7 ‰, and $\delta^{18}O$ values were between -0.22 and 0.15 ‰, documenting that re-circulated seawater with an admixture of groundwater has been playing dominant role in the seepage.

The Local Meteoric Water Line (LMWL) calculated for the São Paulo inland region does not fit with the data Ubatuba set, confirming the influence of the sea on the isotopic composition of rains. The groundwaters lie above the LMWL, and they are depleted in $\delta^{18}O$ with respect to the VSMOW. In contrast, the seawater samples are highly enriched in $\delta^{18}O$. Therefore in majority of cases there has not been significant mixing of groundwater with seawater at the visited sites off Ubatuba. The water samples from monitoring borehole wells and seepage chambers are situated between the both main groups of samples, representing a mixture of groundwater and seawater. The variability in δD and $\delta^{18}O$ enrichment may be caused by seasonal variations, with significant seawater contribution to the collected samples. The original composition of the groundwater component entering the sea floor may be therefore different.

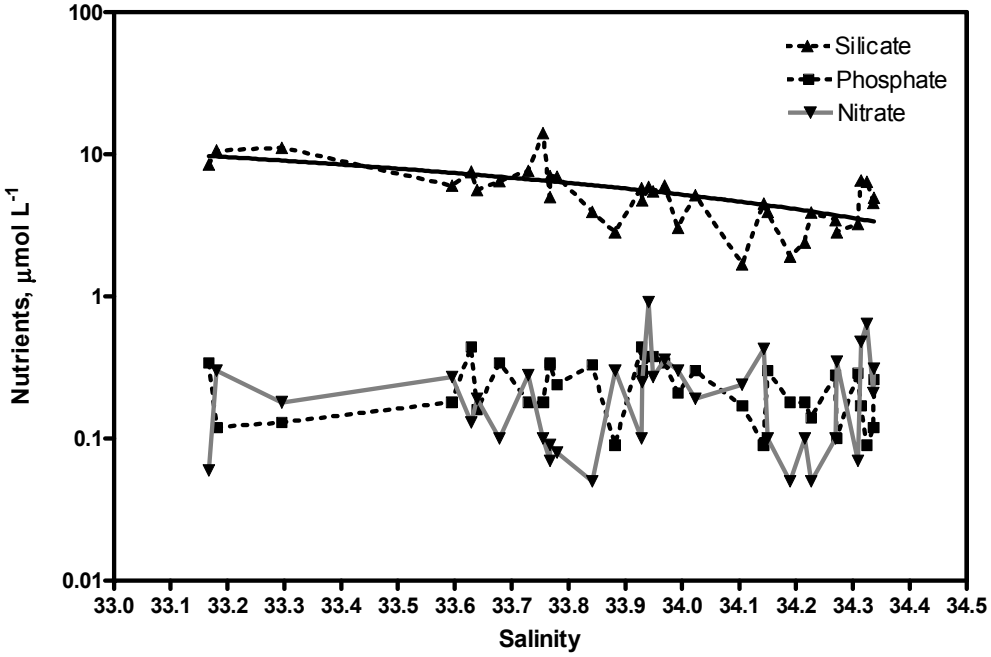

Figure 1. Nutrients vs. salinity sampled in 2003.

The groundwater end-member could be represented by springs observed at the Oceanographic Base, on the road, and at the Corsario, which showed similar isotopic compositions (δD values between -18 and -13 ‰, $\delta^{18}O$ between -3.7 and -3.5 ‰. This would indicate that the contribution of groundwater in submarine waters may vary between a few % and 20 %, depending on the location and the tide level. A significant part of the submarine waters may represent mixtures of re-circulated groundwater and seawater.

3.2. Nutrients

Nutrient data are summarised in Fig. 1 for the 2003 mission as a function of salinity. The results show wide range of values, highest been for silicates (from 1.7 to 14 µmol L^{-1}), phosphates (from 0.1 to 0.4 µmol L^{-1}) and nitrates (from 0.05 to 0.91 µmol L^{-1}). The nutrient data shows scattered distributions - that would indicate that in the complex coast with many small bays and islands the mixing patterns can be very complex. Therefore the sources of

nutrients observed in the visited bays may be mostly due to transport of pollutants by local currents than due to contributions from SGD. This has also been confirmed by short residence time of 1-2 weeks for waters within 25 km of shore [4].

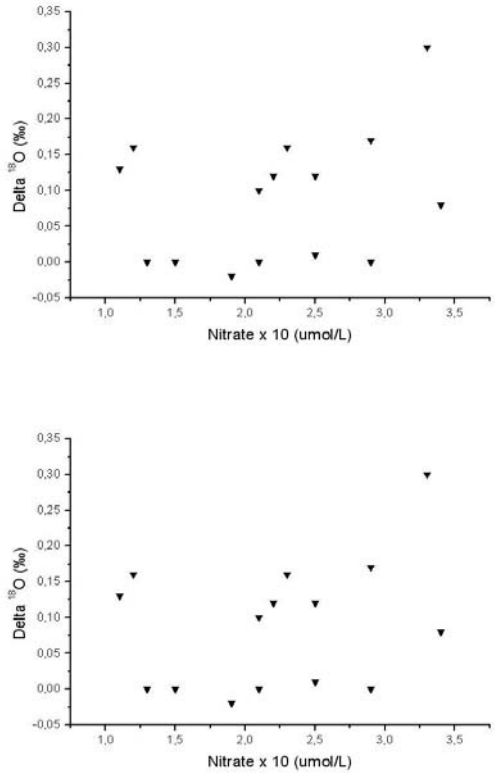

Figure 2. $\delta^{18}O$ vs. NO_3 and SiO_2 plots (2002 data).

A comparison of nutrient data for transects vs. the distance offshore shows that there is not a smooth decrease of levels with distance. It has also been noticed in some places that the sea was much more polluted far from the coast than close to the shoreline. Observed nitrate and phosphate concentrations are typical for the oligomesotrophic region found at the Ubatuba marine ecosystem [10]. Absence of higher nitrate levels indicates negligible infiltration of groundwater contaminated by domestic sewage. The composition of the groundwater end-member could also be investigated by the $\delta^{18}O$ vs. NO_3 (and $Si0_2$) dependence. Fig. 2 shows the results for the samples collected inland (springs and wells), which display a positive relation between $\delta^{18}O$ and NO_3 (as well as $Si0_2$), however, the data are too scattered. The high $\delta^{18}O$ and nitrate/silicate values are probably representative of circulating processes in the coastal area.

4. CONCLUSIONS

On the basis of the isotopic and nutrient results we may conclude that SGD in the Ubatuba area is fed by coastal contaminated groundwater and re-circulated seawater, which claims for potential environmental concern with implications on the management of freshwater resources in the region.

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