TEMPORAL VARIATION OF LONG-LIVED Ra ISOTOPES IN BRANSFIELD STRAIT SURFACE WATER – OPERANTAR XXIX AND XXX

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Abstract
Radium isotopes have been used in coastal and marine environments for the study of horizontal and vertical mixing processes, water-sediment interactions and the tracing of inputs. The horizontal distributions of these radionuclides during the Austral summer were studied in Operantar XXIX and Operantar XXX expeditions. In March/11, $^{228}Ra/^{226}Ra$ activity ratios up to 4.0 were determined, the highest value being observed at station EB13, closest to the cost in Admiralty Bay. During October/11 ^{226}Ra activities ranged from 18 to 138 mBq 100 L^{-1}, while ^{228}Ra activities varied from < LLD to 140 mBq 100L^{-1} .

INTRODUCTION

The fate of contaminants and natural compounds in coastal waters is determined by a set of biological, geochemical and physical interactions. Although scientists have a basic understanding of the major sources, sinks and transformations for many substances, to assess offshore fluxes of dissolved materials we need to know coastal water residence times (Oliveira *et al.*, 2006). The Bransfield Strait in the Antartic Peninsula is a basin strongly influenced by processes occurring on its continental shelves. The modified shelf waters feed the polar surface layer or ventilate the subsurface layers of the interior basin and products of biogeochemical interactions within the shelf environment are transferred into surface and subsurface layers of the Southern Ocean.

The knowledge of the four natural Ra isotopes in aqueous systems can be used to constrain important environmental processes occurring at the land-sea margin. The high variability of the $^{226}Ra/\ ^{228}Ra$ activity ratio in waters clearly demonstrates the suitability of Ra isotopes relationships to determine fluxes and mixing rates of continental waters into ocean and exchange between groundwater and surface water. Two main geochemical characteristics control the production and input of Ra isotopes in nearshore waters: the existence of particle-reactive Th isotopes in sediments as direct radiogenic parents, and the vastly different environmental behavior of Ra in fresh water and salt water media. Because of the 5.7 year half-life of ^{228}Ra, this isotope has been used effectively to estimate oceanic horizontal eddy diffusivities and coastal water residence times over timescales of less than 30 years. By using both ^{228}Ra and ^{224}Ra ($t_{1/2}$ = 3.7 days), timescales of less than 10 years can be investigated (Moore & Oliveira, 2008).

The cycling of Ra in the oceans can be considered as the most interesting phase of radium geochemistry. The fact that in the oceans ^{226}Ra and ^{228}Ra exist in excess of their respective parents, ^{230}Th and ^{232}Th (more than tenfold in excess for ^{226}Ra), led some authors to hypothesize that the excess radium was being supplied by diffusion from deep sea sediments. Numerous investigations have been conducted worldwide in order to fuller understand ^{226}Ra distributions in the major oceans, with considerable attention devoted to the variability of ^{226}Ra concentrations with regard to depth and latitude, correlation with barium, silica concentrations, salinity, etc. (IAEA, 1990; Moore, 2000). ^{226}Ra concentrations in surface seawater (0 – 500 m) appear to be in a narrow range, and nearly uniform in the Pacific (0.7 – 3.7 mBq L^{-1}) and Atlantic Oceans (0.7 – 3.0 mBq L^{-1}). The Indian Ocean has levels of ^{226}Ra which cover a narrower range (1.1 – 2.2 mBq L^{-1}), however. At the increasing depths, a trend of increasing concentrations is observed uniformly in all of the oceans, which, according to most investigators, results from the injection of ^{226}Ra from ^{230}Th bearing sediments in the ocean floor (IAEA, 1990).In the studies of ^{226}Ra distribution and its geochemistry in the oceans, especially in the Southern Oceans were silicate and carbonate behave differently, silicate is often proposed

as an effective carrier for Ra. Similar to Ba, both Ra and Si seems to be non-conservative in Antartic waters, with significant input from the bottom sediments and particulate dissolution during subsurface mixing (Chung & Applequist, 1980).

The overall goal of this study was to apply an isotopic tracer technique to investigate the rate of exchange between the Antartic Peninsula islands and the Brasnfield Strait interior. This technique was based on the measure of the surface water column ratio of two naturally occurring radium isotopes, $^{228}Ra/\ ^{226}Ra$. Because ^{228}Ra is derived solely through input from shelf sediments, it is an unambiguous marker of water that has been in contact with shelves. Its relative distribution in shelf and basin water is therefore useful for assessing the degree of shelf-basin interaction. The temporal variation of $^{228}Ra/^{226}Ra$ activity ratios was also discussed. Measurements and results reported here are from summer expeditions carried out along the Bransfield Strait in March and October/2011.

MATERIAL AND METHODS

The field work was carried out in the Bransfield Strait, situated west of the Antartic Peninsula. The bottom topography of the Bransfield Strait consists of a central basin deeper than 1000 m that is bounded to the northwest by the steep continental margin of the South Shetland Islands, to the southeast by the Antartic Peninsula and to the southwest, referred to as the Gerlache Strait, by shallow shelves and islands. The shelf slope waters around the South Shetland Islands consist of the water strong influenced by local processes of heating and freshwater runoff referred to as the Shelf Slope Water, and the intrusion water from the Antartic Circumpolar Current deep water which enters Bransfield Strait from the deep through between Brabant and Smith Islands and remains near the South Shetland Islands. At the shelf slope, a western boundary current, the Bransfield Current, was revealed from the relative geostrophic circulation estimates based on hydrographic data. This current determines the water export from the Bransfield Strait through the shelf slope of the South Shetland Islands and transport of nutrients, metals and biota (Zhou *et al.,* 2006).

For the purposes of this study, seawater samples were collected between 8th March - 1st April 2011 (Operantar XXIX) and 13th October – 14th November 2011 (Operantar XXX) onboard the RV Ary Rongel, from Brazilian Navy. The sampling cruises covered an area located between latitudes 63°S - 60°S and longitudes 54°W - 59°W. In March/11, a total of ten horizontal profiles were performed at the Bransfield Strait (covering a network of 49 hydrochemical stations). At each profile, large volume ocean surface samples were collected passively through 50 g of MnO_2-acrylic fiber from the continually-flushed ship's clean water line 5 m below the sea surface. During the campaign carried out in October/11, large volume surface seawater were pumped (196 L) from 21 hydrochemical stations and stored in plastic drums. The sample volume was recorded and percolated at ~1 L min^{-1} through a column of manganese coated acrylic fiber (Mn fiber) to quantitatively remove Ra. After the collection, samples were promptly taken to the "Laboratório the Radiometria Ambiental" and the Mn fibers were leached in a mixture of 5% NH_2OH+HCl and 6 M HCl to extract Ra isotopes. The radiochemical procedure adopted for ^{226}Ra and ^{228}Ra determination is described in detail by Oliveira *et al*., (2001). For these analyses, carriers of Ba^{2+} (20 mg) and Pb^{2+} (20 mg) were added to the samples as yield tracers, in the presence of 1 M citric acid solution. The radiochemical separation was accomplished by addition of 3 M H_2SO_4, with heating. The $Ba(Ra)SO_4$ precipitate was then filtered and the chemical yield determined gravimetrically. Considering that 20 mg of Ba^{2+} carrier was added to the water samples at the beginning of the radiochemical procedure, a final total recovery of $Ba(Ra)SO_4$ precipitate would be 34.8 mg. The chemical recovery of $Ba(Ra)SO_4$ precipitate for these set of samples was (90 ± 5) %. The measurement of ^{226}Ra activity concentrations were carried out by counting the gross-alpha activity of a $Ba(Ra)SO_4$ precipitate using a low-background gas-flow proportional counter model Berthold LB770, after 21 days. The ^{228}Ra activity concentration was determined by gross-beta counting of the same precipitate. Lower limits of detection (LLD) for this method were 2.2 mBq L^{-1} for ^{226}Ra, for 100 minutes counting time, and 3.7 mBq L^{-1} for ^{228}Ra, for 400 minutes counting time, at the 95% confidence level. The overall uncertainties of these measurements were below 10%.

RESULTS AND DISCUSSION

In March/11, $^{228}Ra/^{226}Ra$ activity ratios up to 4.0 were determined, the highest value being observed at station EB13, closest to the cost in Admiralty Bay. During October/11 ^{226}Ra activities ranged from 18 to 138 mBq 100 L^{-1}, while ^{228}Ra activities varied from < LLD to 140 mBq 100L^{-1}. Elevated ^{228}Ra activities were found in surface waters in the vicinity of Bransfield Island and Trinity Peninsula. Contact of the water masses with the shallow lithogenic sediments present in that area likely explains these high ^{228}Ra activities. When combined with physical observations and nutrient distributions (Bastos, 2011), these results suggests that the water mass advected onto the Bransfield Strait originates from the Weddell Sea. This northward advection might represent a supply of trace elements, mainly iron, for the observed phytoplankton bloom.

Regression analyses indicate that the physical properties of the water masses have a subtle control on the radium isotopic characteristics of the surface waters. Higher proportions of siliciclastic source lithologies are positively correlated with $^{228}Ra/^{226}Ra$ activity ratios during summer (+0.3 at the 95% significance level). Surface water ^{226}Ra activity is also controlled to a considerable degree by the presence of dissolved ^{238}U. In summer, the aforementioned relantionship is clearly illustrated by a positive correlation between ^{226}Ra and ^{238}U content (+0.4 at the 95% confidence level).

The change in activity concentration with time as a function of distance offshore was studied for both ^{226}Ra and ^{228}Ra. For ^{226}Ra, a non-conservative increase of the activity concentration with the respective increasing distance from coast was observed. For ^{228}Ra, a linear gradient was observed and implies that mixing controls its distribution in the studied area.

CONCLUSION

This study assessed the quantitative distribution patterns of ^{226}Ra and ^{228}Ra in surface waters of the Bransfield Strait. Higher ^{228}Ra activities and $^{228}Ra/^{226}Ra$ activity ratios in surface waters pattern suggests the presence of a water mass that recently interacted with sediments and therefore has been advected onto the Bransfield Strait.

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