SEASONAL VARIATIONS OF TOTAL ^{234}Th AND ^{238}U IN SURFACE SEAWATER OF BRANSFIELD STRAIT, OPERANTAR XXIX AND XXX EXPEDITIONS

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Abstract
Seasonal variations of total ^{234}Th and ^{238}U concentrations in surface seawater collected in the Bransfield Strait are discussed. Total ^{234}Th activities in surface seawater samples ranged from 1.3 to 3.7 dpm L^{-1} (station EB 011) during March/11 campaign, while in October/11 total ^{234}Th activity concentrations varied from 0.1 to 2.9 dpm L^{-1}. Highest total ^{234}Th activities were found late in the austral summer season. Activity concentrations of dissolved ^{238}U in surface seawater varied from 2.34 to 2.37 dpm L^{-1}. Taking into account all sampling stations established in March and October/11 the relative variability of total ^{234}Th distribution was 22%.

INTRODUCTION
Understanding the biogeochemical cycling of carbon in the oceans is important in the context of the removal of man-made carbon dioxide from the atmosphere. The Antartic continental margin is considered to be one of the most sensitive areas to climatic change. Although recent investigations show relatively high organic carbon fluxes in some pelagic zones of the Southern Ocean (Pondaven *et al.*, 2000), in many parts of the Antartic oceans, particle fluxes and pelagic organic carbon and calcium carbonate fluxes are smaller than in other oceans. However, in some nearshore Antartic environments such as the Antartic Peninsula, fluxes of biogenic and lithogenic particles are orders of magnitude higher than in Antartic pelagic areas. One of these environments is the Bransfield Strait south of King George Island. Previous studies carried out in the central Bransfield Strait south of King George Island indicate that over 95% of the annual flux at mid-depths occurs during December and January and that 50% of the mid-depth flux consists of biogenic particles (Wefer *et al.*, 1990).

^{234}Th ($t_{1/2}$ = 24.1 d) is continuously produced in seawater by the radioactive decay of ^{238}U. The ^{238}U concentration in seawater is about 3 µg L^{-1} (Spencer *et al.*, 1970). Due to the relatively high chemical-reactive nature of thorium isotopes in the marine environment, it is expected that these isotopes would be removed rapidly from solution by adsorption on to sinking particulate matter. ^{234}Th is considered a useful tracer of oceanic biogeochemical processes occurring over time scales of days to weeks. Due to its high particle reactivity and relatively short half-life, ^{234}Th is commonly used as a proxy to estimate POC export from the upper oceanic water column. This export is usually assessed by quantifying total ^{234}Th deficits with respect to its conservative parent nuclide ^{238}U in seawater.

^{234}Th short half-life makes it sensitive to seasonal changes in the processes of POC production and export. Indeed, this is one of the most significant applications of ^{234}Th/^{238}U disequilibrium within the past 20 years. The approach builds on the observations of ^{234}Th deficiencies in the upper ocean described above and argues that such deficiencies are created by the scavenging of ^{234}Th onto biogenic particles and the sinking of such particles out of the euphotic zone.

This paper presents results of a collaborative research on organic carbon fluxes distribution in the Bransfield Strait in order to evaluate its influence in the CO_2 drawdown. Once the disequilibrium ^{234}Th/ ^{238}U was used to trace particle flux in the upper ocean, seasonal variations of total ^{234}Th and ^{238}U concentrations in surface seawater collected in the Bransfield Strait, Antartic Peninsula is discussed.

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 49 hydrochemical stations were performed at the Bransfield Strait. At each station, 2-liter surface water samples were taken from Niskin bottles within the upper 5 m depth. During the October/11 campaign, a total of 21 hydrochemical stations were occupied and in 3 stations, vertical profiles of total ^{234}Th were collected from Niskin bottles deployed by Rosette within the upper 1000 m on 10 separate casts. Within 1 h of collection, unfiltered 2-liter samples for total ^{234}Th determination were acidified to pH 2 with 6 ml of concentrated HNO_3. After shaking the samples vigorously, ^{229}Th was added as a yield monitor. The sample was shaken again and allowed to equilibrate for 12 h. After equilibration, the pH was adjusted to 8 with concentrated NH_4OH. Extraction of thorium from samples was accomplished by co-precipitation of thorium via MnO_2 precipitate formed by the addition of $KMnO_4$ and $MnCl_2$ solutions (Buesseler *et al.*, 2001). Samples were shaken vigorously after the addition of each reagent and allowed to stand for 12 h followed by filtration onto 47 mm diameter glass fiber filters. Finally, the filtered MnO_2 precipitates were dried overnight and mounted under one layer of Mylar film and two layers of standard aluminum foil in preparation for beta counting. Analyses of total ^{234}Th activities were performed at the Environmental Radiometrics Laboratory of IPEN/CNEN-SP using a gas-flow low background proportional counter from EG&G Berthold, model LB 770, following methods described in Buesseler *et al.*(2001). Initial beta counting for 6-24 h was followed by a final background count in the lab after decay of ^{234}Th for at least six half-lives. Initial count rates were typically 2-4 counts per minute (cpm) for total ^{234}Th and final count rates averaged 0.5 cpm relative to the detector backgrounds of 0.4-0.6 cpm. For total ^{234}Th samples, anion exchange chemistry was performed and recovery of our added ^{229}Th yield monitor was quantified by inductively coupled plasma-mass spectroscopy. Corrections were applied to ^{234}Th activity calculations on the basis of ^{229}Th recoveries. All data are decay corrected to the time of collection and reported with a propagated error that includes uncertainties associated with counting, sample volumes and other calibration errors. Errors were typically ± 0.04 – 0.06 cpm L^{-1} on total ^{234}Th (Oliveira *et al.*, 2011).

RESULTS AND DISCUSSION

It was observed that total ^{234}Th activities in surface seawater samples studied along the Bransfield Strait ranged from 1.3 to 3.7 dpm L^{-1} (station EB 011) during March/11 campaign, while in October/11 total ^{234}Th activity concentrations varied from 0.1 to 2.9 dpm L^{-1}. Highest total ^{234}Th activities were found late in the austral summer season. Activity concentrations of dissolved ^{238}U in surface seawater varied from 2.34 to 2.37 dpm L^{-1}, whereas the minimum value was detected during beginning October/ 11, and is representative of very early summer time. Taking into account all sampling stations established in March and October/11, the relative variability of total ^{234}Th distribution was 22%.

Activity ratios of total $^{234}Th/^{238}U$ varied from 0.57 to 1.52, the highest value observed at station EB11. Activity ratios of total $^{234}Th/\ ^{238}U$ above unit in surface seawater were determined at 11 stations. Non-conservative increases of total ^{234}Th activities related to ^{238}U dissolved (resulting in AR > 1.0) can be representative of several processes, among them: (a) lower resolution of total ^{234}Th measurements; (b) processes of re-suspension and/ or upwelling; (c) other sources of ^{234}Th to the studied system, for example, those related to the ice melting and runoff. Activity ratios of total $^{234}Th/\ ^{238}U$ close to 1.0 indicate lower fluxes of particulate exported, while values around 0.6 in the euphotic zone suggest higher fluxes. In all those 3 vertical profiles, it was observed layers of increased activities bellow the chlorophyll-a maximum values, associated to processes of particle remineralization and resulting in decreased fluxes at these water depths.

In the 3 vertical profiles studied in this research work, the radioactive equilibrium between total ^{234}Th and ^{238}U was observed around 500 m depth at station CHM1, 800 m depth at station CHM3 and 100 m depth at station CHM5.

CONCLUSION

The magnitude of upper ocean particulate organic carbon export was evaluated by quantifying total ^{234}Th deficits with respect to its conservative parent nuclide ^{238}U in seawater. Considering the overall distribution of total ^{234}Th in both cruises carried out in March and October/11, the relative variability of the data was 22%. Non-conservative increases of total ^{234}Th activities related to ^{238}U dissolved were observed in surface seawater at 11 stations and were related to processes associated to ice melting, freshwater runoff and biomass accumulation.

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