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Lead-210 and Polonium-210 disequilibria in the northern Gulf of Mexico hypoxic zone

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ABSTRACT

We report water column dissolved and particulate ^{210}Pb and ^{210}Po profiles along with ancillary data from the northern Gulf of Mexico continental shelf collected during the summers of 2011 and 2012. The dissolved ^{210}Po/^{210}Pb ratio in bottom water was >1 at 10 out of 12 stations whereas the ^{210}Po/^{210}Pb activity ratio in surface water was approximately 0.2–1.3. This lower dissolved ^{210}Po/^{210}Pb surface ratio indicates that ^{210}Po is generally more efficiently scavenged than ^{210}Pb in surface layers. The particulate ^{210}Po/^{210}Pb ratio was 1.6–5.1 in surface water and 2.5–10.4 in bottom water indicating that ^{210}Po tends to be more enriched in deep water particulate material as compared to surface material. The ^{210}Po and POC are significantly correlated ($r^2 = 0.93$) with the POC/^{210}Po ratio varying between 205 and 2094 μmol C dpm^{-1}. These general patterns suggest that ^{210}Po is scavenged from the surface waters and regenerated or added to bottom waters relative to ^{210}Pb. The addition of Po to bottom water (either in the dissolved or particulate phase) likely requires a sedimentary source of Po, relative to Pb, to the overlying water column. Dissolved oxygen concentrations and water column stratification vary throughout the region, and we find no correlation between dissolved O_2 concentration and ^{210}Po excess. ^{210}Po enrichment does, however, appear to be coupled to the release of the redox sensitive trace metals Fe and Mn and remineralization of silica in bottom waters to some extent. We suggest that the cycling of these redox sensitive metals, coupled with the degradation of organic matter is the likely driving mechanism for ^{210}Po remobilization that produces the observed water column ^{210}Po distributions.

1. Introduction

^{210}Po ($t_{1/2}$ = 138.376 d) is produced from the decay of ^{210}Pb ($t_{1/2}$ = 22.2 yr) via decay of ^{210}Bi ($t_{1/2}$ = 5.012 d) and is the final radioactive product in the naturally occurring ^{238}U decay chain that decays to stable ^{206}Pb. The primary source of ^{210}Pb in the natural environment is the exhalation of ^{222}Rn ($t_{1/2}$ = 3.8 d) from the continents into the atmosphere. Although ^{210}Po is produced from ^{210}Pb decay within the atmosphere, this activity represents a relatively small fraction (10–20%) of the ^{210}Pb activity because of the short atmospheric residence time of ^{210}Pb-containing aerosols (Kim et al., 2005a; Harada et al., 1989). Within a water body or its underlying sediments, the ^{210}Po production can also occur from the in situ decay of ^{226}Ra to ^{210}Pb and subsequently to ^{210}Po (Kim et al., 2005b).

^{210}Pb and ^{210}Po are both particle reactive but have differing particle affinities and binding mechanisms. ^{210}Pb becomes quickly adsorbed to sedimentary particle surfaces, whereas ^{210}Po can be incorporated via biological activity into the cytoplasm and cell wall of some species of phytoplankton, more like a nutritional element (Fisher et al., 1983). This partitioning of ^{210}Po into biological material is similar to that of sulfur and protein within the cell (Fisher et al., 1983; Stewart and Fisher, 2003a,b). In the water column, the biogeochemical differences between ^{210}Pb and ^{210}Po result in ^{210}Po being more efficiently removed from surface waters in marine and lacustrine environments compared to ^{210}Pb, which is removed via particle scavenging. ^{210}Po's higher affinity for biogenic particles generally results in an upper water column ^{210}Po deficit relative to ^{210}Pb because of biogenic material export (sinking). Thus, studying the deficit of ^{210}Po in the surface ocean can provide valuable insight into particle dynamics and organic carbon export in the open ocean (Stewart et al., 2007; Kim et al., 2005b).

In addition to the above evidence for a biological influence on ^{210}Po geochemistry, more targeted studies have noted the chemical similarities between sulfur and ^{210}Po (Harada et al., 1989; Balisterieri et al., 1995; Swarzenski et al., 1999). Polonium is considered a class B, sulfur-seeking metal, and is associated with proteins and sulfur-containing compounds (Stewart et al., 2007). Higher trophic level organisms such as marine copepods indicate a relatively high assimilation efficiency of ^{210}Po by consumption of zooplankton (Stewart and Fisher, 2003b). The high assimilation efficiency coupled with a slow Po loss rate makes zooplankton an effective conduit for the transfer of ^{210}Po to higher trophic levels and bioaccumulation of the radioisotope in the

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marine food web and may lead to elevated doses to human. This enrichment among higher trophic levels in the marine environment is primarily derived from the direct consumption of foods rather than from the intake of seawater (Kim et al., 2005b). In fact, ^{210}Po has been found to concentrate in the hepatopancreas of several marine invertebrates, and several studies have shown ^{210}Po to be specifically associated with protein in this organ (Fisher et al., 1983). Uptake of this radioisotope by marine organisms has been well documented in coastal environments in varying locations around the world (Carvalho, 2011; Bustamante et al., 2002). In fact, estimates demonstrate that approximately 4 kg of scallop flesh intake would be sufficient to reach the annual permissible intake of 1 mSv of ^{210}Po for humans (Bustamante et al., 2002).

Multiple studies have shown that ^{210}Po can be mobilized from hypoxic sediments in low oxygen lacustrine environments, but to our knowledge no data for ^{210}Po mobilization in the coastal marine environments exists (Benoit and Hemond, 1990; Kim et al., 2005b; Talbot and Andren, 1984). Talbot and Andren (1984) conducted a study on seasonal variations of ^{210}Po in an oligotrophic lake in Wisconsin, USA. The study revealed a depletion of ^{210}Po in the surface waters relative to bottom water suggesting a diagenetic mobilization of Po, consistent with other work in seasonally anoxic lakes or ponds (Benoit and Hemond, 1990; Kim et al., 2005b). Low oxygen conditions have also been shown to remobilize other radionuclide pairs from the ^{238}U decay series, such as ^{226}Ra/^{210}Pb (Balisterieri et al., 1995). These authors showed that diffusion of ^{210}Po from bottom sediments was occurring but they were unable to identify the exact mechanism of ^{210}Po release from the sediments. Sulfate-reducing bacteria have also been found to effective release polonium in culture experiments provided the sulfide levels did not rise above 10 μM (LaRock et al., 1996; Cherrier et al., 1995). Removal of ^{210}Po and ^{210}Pb from sediment could also impact ^{210}Pb-based sediment rate calculations, especially when utilizing the alpha spectrometry method, which assumes ^{210}Po and ^{210}Pb to be in equilibrium. The major objective of this work is to utilize ^{210}Po–^{210}Pb disequilibria to determine whether the northern Gulf of Mexico sediments are a source of ^{210}Po to the overlying hypoxic water column.

2. Study area

The Gulf of Mexico 'Dead Zone' is adjacent to the Mississippi River and spans the continental shelf from Texas to Mississippi with its average size, over the years 2006–2010, being about 17,000 km^2 (www.gulfhypoxia.net). Hypoxia in the Gulf of Mexico is generally defined as a dissolved oxygen concentration of <2 mg L^{-1}. The northern Gulf of Mexico is an important spawning ground for juvenile marine fishes and other organisms representing the United States' most economically viable oyster harvesting area (http://www.epa.gov/gmpo/about/facts.html). The areal extent of the northern Gulf of Mexico Dead Zone, coupled with the potential importance of hypoxia on Po geochemistry make this area an ideal site to study the ^{210}Po and ^{210}Pb dynamics. However, as a nuance to the current study, we note that the waters that blanket the shallow shelf region likely undergo rapid spatial and temporal chemical change, relative to the timescales of biogeochemical processes that occur in marine sediments. This dynamic feature of the northern Gulf of Mexico likely imparts significant non-steady state chemical conditions or signatures within these waters.

3. Methodology

3.1. Sample stations

Water column samples were collected from various stations on the continental shelf from two oceanographic research cruises during August 2011 and July/August 2012 (Fig. 1). Six water column profiles were collected per year for both years, for a total of 12 profiles. The intensity and distribution of the hypoxic zone varies both annually and seasonally, and the sampling cruises were planned to collect samples during the peak hypoxic period (Turner et al., 2002). The number of samples per station was dependent on the depth of the water column. Water samples were collected approximately every 5–7 m in the water column, with a sample taken within a meter of the water–sediment interface.

3.2. Sample collection

Dissolved water column samples were collected via ship rosette system and consisted of 8–10 L of seawater. The water samples were pressure filtered from the Nisken bottles directly into acid-cleaned polycarbonate containers, using a 0.45 μm nuclepore filter to separate any particulate matter. The samples were then acidified with concentrated HCl to pH 1–2 and spiked with known amounts of ^{209}Po and stable Pb^{2+} yield monitors to quantify any subsequent losses of Po and Pb. A Fe^{3+} co-precipitate (30 mg of Fe^{+3}/mL) was also added to each sample and after an equilibration period of 6–8 h, the pH was brought back up to approximately pH 8–8.5, using concentrated NH_4OH. Samples were allowed to precipitate and settle for 8–10 h. The precipitate was transferred to 1 L polypropylene bottles. One liter bottles were stored on board for processing upon arrival to shore. Further radiochemical purifications and measurements were conducted back in the laboratory at Louisiana State University to determine the final ^{210}Po and ^{210}Pb activities. The ^{210}Po analytical methods used to determine ^{210}Po activity in the water column are similar to those described in Nozaki (1986) and Masque et al. (2002).

Particle samples were collected only in 2011 using battery-operated submersible pumps (McLane Research Laboratories, Inc., Falmouth, USA). The pump deployment consisted of a vertical array of three pumps at various depths. Large-volume water samples (~70–150 L) were filtered at a flow rate of 4–6 L min^{-1} through acid washed 150 mm pre-filters (51 μm polycarbonate screen) and then onto acid washed pre-combusted (at 450 °C for 8 h) 1 μm nominal, 150 mm diameter Quartz Microfiber Filter (QMA) (Whatman, Kent, U.K.) to capture suspended particles. After the recovery of pumps, the filters were taken out and three 22 mm diameter subsamples were collected for particulate ^{210}Po/^{210}Pb analysis and particulate organic carbon (POC) analysis. The particles captured on the screens were immediately transferred to 47 mm QMA filters and a subsample from this filter was utilized for ^{210}Po/^{210}Pb and POC analysis. The subsamples for POC analysis were dried onboard at 60 °C.

Iron, manganese, and major nutrient samples were collected during the 2011 cruise directly from the rosette system with an HCl-cleaned plastic syringe and either not filtered (for total dissolvable metal analysis) or filtered through AcroPak 200 capsule filters with 0.8/0.2 μm Supor membrane for the dissolved analyses. Filters were rinsed with sample prior to collection. Iron and manganese samples were acidified to a pH of approximately 2 using trace element clean (11 N) HCl and nutrient samples were not acidified. Dissolved oxygen concentrations were recorded with an O_2 sensor as part of the ships CTD system.

3.3. Analytical methods

3.3.1. ^{210}Po and ^{210}Pb analysis

Polonium was auto-deposited directly onto silver planchets following methods described by Flynn (1968) and Fleer and Bacon (1984). After the initial plating of polonium onto the silver planchets was complete, the plating solutions were immediately cleaned of all residual Polonium remaining using an AGX-I resin column, re-spiked with ^{209}Po yield tracer and stored for 9–10 months, allowing ^{210}Po to be regenerated from the decay of ^{210}Pb. This freshly produced ^{210}Po represented the concentration of ^{210}Pb in the original sample. The silver planchets were then counted on Canberra Alpha Analyst high-resolution silicon-surface barrier (PIPS) alpha detectors to determine ^{210}Po activities. A 1 mL aliquot was extracted from the final plating solution and