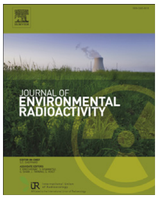
Journal of Environmental Radioactivity 164 (2016) 395–399

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

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



Uranium and plutonium in anoxic marine sediments of the Santiago River mouth (Eastern Pacific, Mexico)

María Guadalupe Almazán-Torres [a], Eduardo Ordóñez-Regil [a, *],
Ana Carolina Ruiz-Fernández [b]

[a] Departamento de Química, Instituto Nacional de Investigaciones Nucleares, Carr. México-Toluca S/N, La Marquesa, Ocoyoacac, Estado de México, C.P. 52750, Mexico
[b] Instituto de Ciencias del mar y limnología, UNAM, Calz. Joel Montes Camarena S/N, Mazatlan, Sinaloa, C.P. 82040, Mexico

ARTICLE INFO

Article history:
Received 4 February 2016
Received in revised form
18 July 2016
Accepted 4 August 2016
Available online 15 September 2016

Keywords:
Sediments
U-isotopic ratio
U and Pu in seawater
Santiago River

ABSTRACT

The uranium (U) and plutonium (Pu) content with depth in a sediment core collected in the continental shelf off the mouth of the Santiago River in the Mexican Pacific was studied to evaluate the contamination effects of the effluent of the Santiago-Lerma River as it moves into the sea. The large mass of terrestrial detritus delivered by the river influences the physicochemical and geochemical processes in the seafloor. Abnormal concentrations of U and Pu in sediments were examined as indicative of the effects of anoxic conditions. One of the indicators of pollution of seawater is the bacterial activity of the shallow seabed layer; and among the prevailing bacteria, the magnetotactic ones induce the formation of euhedral and framboidal shapes (pyrite). These pyrite entities are by-products of anoxic environments loaded with decomposing detrital material and are very abundant in the surface layers of the sediment core analyzed. The pyrite formation is the result of a biochemical reaction between iron and organic sulphur reduced by bacteria, and the pyrite entities precipitate to the seafloor. In the same upper zone of the profile, ^{238}U is readily immobilized, while ^{234}U is oxidized and dissolved in seawater by the effect of hot atom chemistry. This may cause the activity ratio (AR) ^{234}U/^{238}U disequilibrium (near 0.41). Furthermore, in the shallow layer of the sediment core, an abnormally high concentration of $^{239+240}$Pu was detected. In this upper layer, the activity concentrations found were 3.19 Bq kg^{-1} for ^{238}U, 1.32 kg^{-1} for ^{234}U and 2.78 Bq kg^{-1} for $^{239+240}$Pu. In the lower fractions of the sediment core, normal values of AR ^{234}U/^{238}U (≈ 1) were found, with traces of $^{239+240}$Pu.

1. Introduction

The ubiquitous presence of uranium (U) worldwide is a proven fact. It may be found anywhere from the highlands to the oceanic trenches, including all kinds of rocks in the continental crust and in the inner earth mantle [Plank and Langmuir, 1998]. Radionuclides in seawaters mainly result from riverine inputs and atmospheric deposition of aerosols and gases, and then the radionuclides are dispersed and transported by advection and precipitated by geochemical processes [Strok et al., 2010]. Uranium in seawater is normally found in an AR ^{234}U/^{238}U of about 1.15. The deviation from equilibrium of the U isotopes in water has been explained in basis of the recoil energy of the ^{234}Th atoms formed after ^{238}U radioactive decay. Indeed, the displaced ^{234}Th from the normal site of the crystal lattice by alpha recoil near of sediment grain surface decays to ^{234}U in the aqueous phase, which renders the ^{234}U more easily leached by water (Eq. (1)) [Awudu and Darko, 2011; Ordóñez-Regil, 1986]. Moreover, the seawater rich in organic matter reacts strongly with thorium which is readily solubilized into the ocean. The corollary is that the ^{238}U is found in excess in seafloor sediments and depleted in ^{234}U [Veeh, 1967].

$$^{238}\mathrm{U} \xrightarrow[4.5\,E9\,y]{\alpha} {}^{234}\mathrm{Th} \xrightarrow[24.1\,d]{\beta} {}^{234}\mathrm{Pa} \xrightarrow[1.18\,m]{\beta} {}^{234}\mathrm{U} \xrightarrow[2.4\,E5\,y]{\alpha} {}^{230}\mathrm{Th} \tag{1}$$

Among the 24 sediment cores extracted during the oceanographic mission Tehua V in August 2007, a core collected in the continental shelf off the mouth of the Santiago River was unique

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* Corresponding author.
E-mail addresses: guadalupe.almazan@inin.gob.mx (M.G. Almazán-Torres), eduardo.ordonez@inin.gob.mx (E. Ordóñez-Regil), caro@ola.icmyl.unam.mx (A.C. Ruiz-Fernández).

http://dx.doi.org/10.1016/j.jenvrad.2016.08.007
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because the pollution caused by the flow of the Rio Santiago was very noticeable. Most rivers are polluted by anthropogenic discharge from heavy industrial facilities, enriching the concentration of trace elements [Rosales-Hoz et al., 2003]. It has been documented that the Santiago River is the most polluted river in Mexico, due to the discharges of urban and industrial wastes from all the cities that are located along its pathway [Ruiz-Fernandez et al., 2009]. The discharge of the contaminated river waters into the seawater could affect the biological and physicochemical conditions on the seabed [De la Lanza-Espino, 2001]. The sediments in these areas are unusually rich in organic matter and the oxygen content is low, the sediments become reducing with the noticeable production of hydrogen sulfide. In these conditions, anaerobic bacteria that form aggregates of pyrite, known as framboids [Merinero-Palomares and Martínez Frías, 2010; Devouard et al., 1998], would displace the faunal composition related to the upwelling along the Mexican Pacific Coast.

The sediment core considered here was especially interesting because of its marked anthropogenic influence, similar to the effects noted by Ivanovich (1993) and Rosales-Hoz et al., (2003). The study of U isotopic ratios is especially useful for determining the movement of tides and microflora that conform to the plankton [Roth and Poty, 1985]. However, it has been established that the sediments are not only the product of the accumulation of native minerals that form the mineral layer, but they also are enriched with materials of carried from inland waters such as the sand or organic matter [Jagam and Simpson, 1993].

In oxidic conditions, U in seawater is mainly found in oxidation state U(VI). Organic-enriched sediments can become anoxic depending on the temperature and the concentration of organic matter; and at anoxic conditions the U(VI) is reduced partially to U(IV) [Butler et al., 2000]. Due to the diversity of the origin of the components of the sediments, the concentrations of U in the different sediment strata are expected to result from a mixture of old and new materials [Srivastava et al., 2011]. Another trace element affected by the redox conditions of ocean water is plutonium (Pu), an artificial transuranic element that appeared worldwide during the second half of the 20th century. Its concentration increased sequentially after the fallout from early detonations of nuclear weapons in the atmosphere, followed by the proliferation of nuclear power plants, reprocessing plants and nuclear device accidents [Anton et al., 1994; Zal U'yun et al., 2010]. Some studies in marine waters and sediments have shown that the distribution of $^{239+240}$Pu is carried out heterogeneously along the continental shelf to abyssal plains [Carpenter, 1981]. But the fate of Pu is mainly controlled by the precipitation onto particulates suspended in seawater [Hirose and Aoyama, 2002.]. Such is the case of Mexican coasts on both the Pacific and Atlantic, where varying concentrations of Pu isotopes have been found [Scott et al., 1983].

This paper presents the results of U isotopic analysis in a marine sediment core exposed to contaminated riverine input. It was expected that an abnormal AR of U would result from the effects of fluvial pollution on the redox conditions. As the U concentration is obtained by the technique of partial dissolution of sediment samples, there would be a consequent error in the calculation of the AR ^{234}U/^{238}U, which is reason why the radiochemical separation of both radionuclides is mandatory [Sam et al., 2000]. For this, the labile part of the sediments (organic and carbonate) were separated and the U and Pu from the mineral fractions were determined. In our laboratory conditions, $^{239+240}$Pu was found in all fractions [Ordóñez-Regil et al., 2013; Ruiz-Fernandez et al., 2009].

2. Experimental

2.1. Materials and methods

2.1.1. Collection of marine sediments

The sediment core was collected from the continental shelf (48-m depth) offshore of the mouth of Santiago River (Nayarit coast) during the oceanographic mission Tehua V in August 2007. The sampling location was near the center of the estuarine plume 10 km NW from the mouth of the Santiago River and 5 km E from the coast (Fig. 1). The sediment core was extracted by using a Reyneck box sampler. A transparent PVC tube (10 cm I.D.) was inserted into the box corer to collect the sediment core, which was extruded and subsampled at 1 cm intervals.

2.1.2. Physicochemical characterization

The specific surface area of sediment samples was determined by the N_2 Brunauer-Emmett-Teller (BET) method using a Micromeritics Gemini 2360 surface area analyzer. For this, 0.5 g dry and degassed samples were analyzed, applying a multipoint N_2 adsorption-desorption method at room temperature and yielding a multipoint isotherm.

Thermal analysis was carried out in an SDT Q600 of Thermo Analyzer, which was used in order to have simultaneous thermogravimetry (TGA) and differential scanning calorimetry (DSC). To enhance the performances of this analysis, the SDT instrument was coupled to a mass spectrometry (MS) at the endpoint of SDT furnace. A weighed small amount of dried sediment sample was directly placed in a platinum crucible. The analysis was carried out under N_2 flow at the heating rate of 10 °C min^{-1} in the range from room temperature to 900 °C.

Mineral phases in the sediment samples were determined via X-ray diffraction patterns obtained by means of a diffractometer D-5000 Siemens using a copper anode ($\lambda = 1.543$ Å). The Kα radiation was selected with a diffracted beam monochromator. Diffraction patterns were obtained in the range of 4–70°.

Morphology analysis was carried out with a scanning electron microscope JEOL 5900LV at 25 kV. The samples were mounted on an aluminum holder with carbon conductive tape and covered with a thin gold layer approximately 150 Å thick, using a Denton Vacuum Desk II platter. In all cases, the images were obtained using a backscattered electron detector. The elemental chemical composition of samples was determined through Energy Dispersive Spectroscopy (EDS) on an EDAX-4 spectrometer.

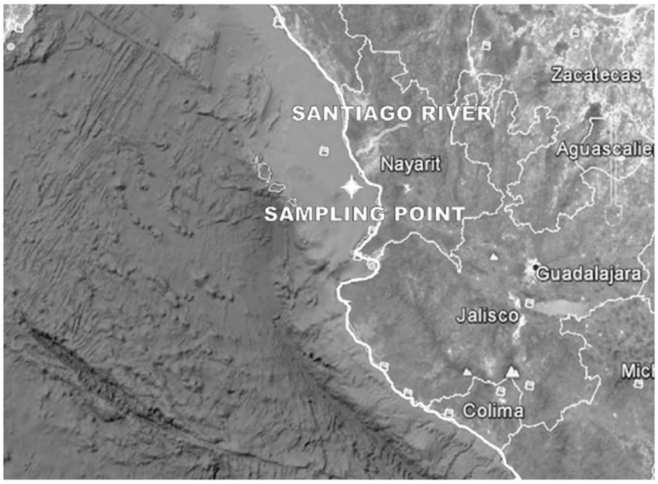

Fig. 1. Sampling point near the Santiago River mouth.