Environ Earth Sci (2013) 69:2351–2355
DOI 10.1007/s12665-012-2064-6

ORIGINAL ARTICLE

Trace metal and radionuclide pollution in marine sediments of the Aegean Sea (Izmir Bay and Didim)

S. Aközcan · A. Uğur Görgün

Received: 21 June 2012 / Accepted: 19 October 2012 / Published online: 2 November 2012

Abstract To determine radioactivity and trace metal levels, surface sediments were collected from two important areas (İzmir Bay and Didim) in the Aegean Sea region of Turkey, and were analyzed for concentrations of ^{210}Po, ^{210}Pb and trace metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn). The average ^{210}Po and ^{210}Pb massic activities in sediments varied in the range of 24 ± 5 to 126 ± 6 Bq kg^{-1} dry wt. and 18 ± 3 to 59 ± 4 Bq kg^{-1} dry wt., respectively. Izmir Bay exhibited the highest polonium activities in sediments, likely due to specific sedimentation processes and other sediment characteristics. The trace metal results showed that the Izmir Bay is facing trace metal pollution. The metal concentrations in sediment samples are low compared to those from the other neighboring marine environments.

Keywords Sediment · Trace metal · ^{210}Po · ^{210}Pb · Aegean Sea

Introduction

The importance of monitoring radionuclides and trace metals is related to the impact of these elements on the marine environment. Several natural and artificial radionuclides have been used in environmental studies, especially in marine processes. ^{210}Po and ^{210}Pb are important natural radionuclides used in studies on the marine environment.

^{210}Po ($t_{1/2}$ = 138 days), a high-energy α-particle emitter in the ^{238}U decay chain, is a naturally occuring radionuclide formed by the beta decay of its grandparent of ^{210}Pb ($t_{1/2}$ = 22.3 years) via ^{210}Bi. The main source of ^{210}Po and ^{210}Pb is ^{222}Rn emanation from the continents. In the aquatic environment, ^{210}Po is largely produced from the decay of ^{210}Pb deposited from the atmosphere (Stepnowski and Skwarzec 2000). The naturally occuring radionuclides ^{210}Po and ^{210}Pb are important because of their contributions to the natural radiation dose and technologically enhanced releases from sources of natural radioactivity (Vreček et al. 2004).

Coastal environments are subjected to metal contamination via inputs from main natural sources (rock weathering, soil erosion, dissolution of water-soluble salts), industrial and urban sources (municipal wastewater-treatment plants, manufacturing industries, and agricultural activities etc.) that are transported via river discharge and eolians processes (Güven and Akıncı 2008; Uluturhan et al. 2011).

Major indicators of pollution in aquatic environments are contaminated sediments. Sediments are the primary repository of radionuclides and chemicals entering the marine environment (Saçan et al. 2010). Thus, marine sediments are commonly used as environmental matrices in chemical and radioactive monitoring programs.

This study presents ^{210}Po,^{210}Pb and trace metal levels that were measured in marine sediments from two points in the Aegean Sea coast (Izmir Bay and Didim).

S. Aközcan (✉)
Department of Physics, Campus of Kavakli,
Kirklareli University, Kavakli,
Kirklareli, Turkey
e-mail: sakozcan35@yahoo.com

A. Uğur Görgün
Institute of Nuclear Sciences, Ege University,
Izmir 35100, Turkey

Fig. 1 The map of the study areas

Materials and methods

Sample collection and preparation

Surface marine sediment samples were collected using van-veen grab for trace metals and radionuclides during 2006–2007 from two stations in the coast of Aegean Sea every month. The locations of sampling stations are given in Fig. 1.

^{210}Po and ^{210}Pb measurements

The marine sediment samples were weighed and oven-dried to a constant weight at 80 °C and then thoroughly mixed. The samples were ground and passed through a 2 mm mesh followed by homogenization.

After the addition of a standardized amount of ^{209}Po (4.88 MeV alpha emission, $t_{1/2} = 109$ year) tracer, each sample was dissolved using three portions of concentrated 20 mL HNO_3 and evaporated to near dryness on a hot plate at 55 °C. Then 2 mL H_2O_2 was added, and evaporated to near dryness. The sample residuals were treated with three portions of 20 mL HCl, and evaporated to near dryness. Finally, the samples were dissolved in 200 mL of 0.5 M HCl, and ascorbic acid of 4 mg was added to the plating solution to reduce iron. The temperature of the solution was kept constant at 70 °C while stirring, and a copper disk was introduced into the solution in such a way that only one side of the disk was available for plating. The polonium was spontaneously deposited onto the surface of the disk for 5 h at 70 °C. The copper disk was then removed, washed with distilled water and dried at room temperature (Flynn 1968).

^{210}Po levels were measured via 5.30 MeV alpha particle emission rates using a high-resolution alpha spectrometer equipped with 450 mm^2 Passivated Implanted Planar Silicon (PIPS) detector (Canberra Model 7401 Alpha PIPS dedector). The spectrometer was connected to a conventional personal computer (PC) using a network connection. The different parameter settings and the viewing of spectra were performed using the commercially available software (Genie-2000 Basic Spectroscopy Software). Contamination of detectors with polonium isotopes such as ^{210}Po and ^{209}Po probably occurs by some other process than alpha recoil. This is probably due to the inherent volatility of polonium at low pressure. Polonium activity is transferred from the sample sources to the detectors, a very serious problem with the long-lived Po-210 and even worse when working with Po-209 ($t_{1/2} = 102$ y) as a yield tracer (Sill and Olsen 1970).

After the first deposition of ^{210}Po, the residual 0.5 M HCl was kept for 1 year to allow ^{210}Po in-growth from the ^{210}Pb contained in the sample solution.

The samples were re-plated and the ^{210}Po activities were determined. The second deposition provided information about the ^{210}Pb content of the samples and thus indicated the extent to which the initial ^{210}Po was supported by its grandparent species.

Well known Bateman equations were used to obtain ^{210}Pb activity from measured ^{210}Po activity.

Lower limit of detection (LLD) was calculated using the Currie definition (Currie, 1968). The concentration of ^{210}Po in a small number of samples was below the detection limit, but most of the ^{210}Po levels were within detection limits (0.0003 Bq). Counting period was adjusted to obtain

Table 1 ^{210}Po and ^{210}Pb concentrations in sediment from different regions of the Aegean Sea

Area	^{210}Po (Bq kg^{-1} dry wt.)	^{210}Pb (Bq kg^{-1} dry wt.)	References
Milos Island	60 ± 8–100 ± 10	10 ± 2–20 ± 2	Boisson et al. (2001)
Gökova Bay	–	50 ± 4–113 ± 8	Ugur and Yener (2001)
Izmir Bay	43 ± 6–132 ± 12	27 ± 5–91 ± 9	Saçan et al. (2010)
Milos Island	20 ± 2–166 ± 8	14 ± 3–107 ± 3	Uğur et al. (2003)
Izmir Bay	36 ± 2–109 ± 8	18 ± 3–59 ± 4	This study
Didim	24 ± 5–126 ± 6	24 ± 2–36 ± 4	This study

relative standard error of approximately 5 %. Final activity calculations were attained to include the appropriate corrections for blanks and also for collection date. Recovery was obtained to vary between 70 and 81 % for samples.

Metal analysis

One gram of the sediment sample was dissolved in concentrated nitric acid in a Teflon beaker and small amount of hydrofluoric acid was added. 5 mL of concentrated H_2SO_4 was added on the sample and the beaker placed on the hot plate at 70–80 °C. After, a small amount of the concentrated HNO_3 was added very slowly and continued heating at 120 °C. When the sample solution became liquid, hydrogen peroxide was added and heating continued at the same temperature for 30 min. The hydrogen peroxide was added until the sample became clear. After that, the sample was diluted to 100 mL with 2 % HNO_3 in a volumetric flask (Topçuoğlu et al. 2002). Trace metal levels (Mn, Fe, Cr, Ni, Zn, Cu, Cd and Pb) were determined by a Perkin-Elmer inductively coupled plasma-optical emission spectrometry (ICP-OES).

Results and discussion

The activity concentrations of ^{210}Po and ^{210}Pb were determined within the range of 24 ± 5 to 126 ± 6 Bq kg^{-1} dry wt. with an average value of 67 ± 2 Bq kg^{-1} and 18 ± 3 to 59 ± 4 Bq kg^{-1} dry wt. with an average value of 37 ± 1 Bq kg^{-1}, respectively. These values were comparable with those given in literature for sediments from different region in Aegean Sea as shown in Table 1. The activity of ^{210}Po and ^{210}Pb in marine sediment samples of Didim and Izmir Bay is also shown in Figs. 2 and 3. The activity of ^{210}Po and ^{210}Pb in sediment samples was found to be high in ^{210}Po compared to ^{210}Pb. The highest ^{210}Po concentrations were measured in Didim (126 Bq kg^{-1}) sediments. The possible source for enhanced ^{210}Po, especially in Didim, is the discharge of Büyük Menderes river. The river flows into Didim station after carrying fertilized agricultural soil.

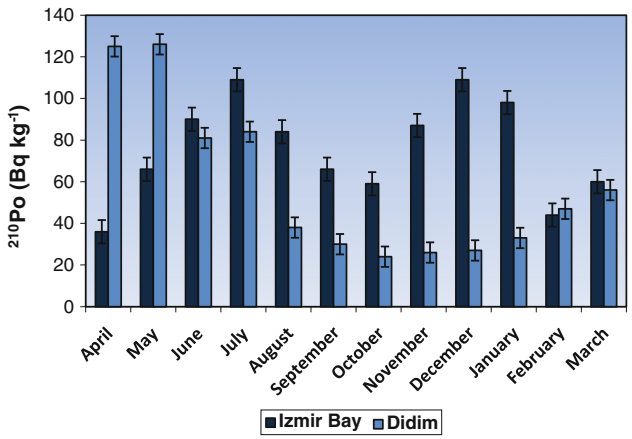

Fig. 2 Activity concentrations of ^{210}Po (Bq kg^{-1} dry wt.) in sediments of the Izmir Bay and Didim

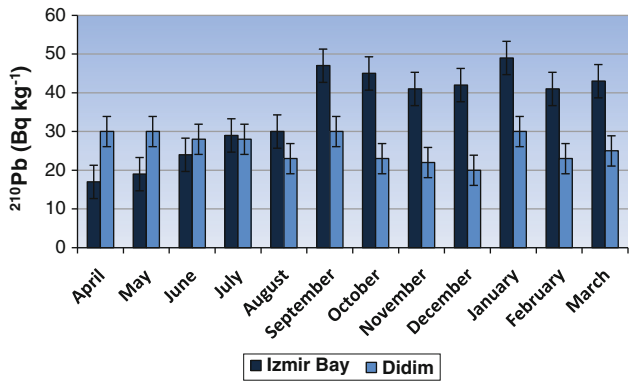

Fig. 3 Activity concentrations of ^{210}Pb (Bq kg^{-1} dry wt.) in sediments of the Izmir Bay and Didim

Likewise, Saçan et al. (2010) studied ^{210}Po and ^{210}Pb concentrations in sediment samples from the Izmir Bay (Aegean Sea), and determined that the highest ^{210}Po activities were observed in winter and summer periods. They pointed out that an increase in ^{210}Po concentrations has been observed in Izmir Bay, probably due to inputs from the Melez stream which is polluted by untreated wastewaters such as industrial, domestic and agricultural sources.

The $^{210}Po/^{210}Pb$ activity ratio is also investigated in the present study. The $^{210}Po/^{210}Pb$ ratio for Didim and Izmir Bay stations is found to be ranged from 0.83 to 4.03, and from 0.88 to 3.21, respectively. Also, the mean $^{210}Po/^{210}Pb$ ratio for Didim and Izmir Bay is determined to be 1.86 and 1.96, respectively. In general, the $^{210}Po/^{210}Pb$ activity ratios are higher than unity in the measured samples. In study, the highest $^{210}Po/^{210}Pb$ activity ratios were obtained in Didim for April.

The range of trace metal concentrations (μg g^{-1} dry wt.) in the Izmir Bay and Didim sediments (respectively) were: Cr 9–65 and 9–22, Cu 9–38 and 3–9, Fe 4709–18470 and 1271–11405, Mn 76–542 and 42–371, Ni 5–33 and 3–18, Pb 0–16 and BDL, Zn 17–85 and 3–30 μg g^{-1}.

Table 2 Minimum and maximum values of metals in sediments during 2006– 2007 from Izmir Bay and Didim (μg g^{-1} dry wt.)

	Mean	Standard deviation	Min.	Median	Max.
Didim					
Cd	BDL	BDL	BDL	BDL	BDL
Cr	17.42	3.92	9.00	17.50	22.00
Cu	5.00	1.81	3.00	5.00	9.00
Fe	4496	3227	1271	4050	11405
Mn	149.80	105.20	42.00	122.00	371.00
Ni	6.75	4.59	3.00	4.50	18.00
Pb	BDL	BDL	BDL	BDL	BDL
Zn	14.00	7.93	3.00	13.00	30.00
Izmir Bay					
Cd	BDL	BDL	BDL	BDL	BDL
Cr	25.92	17.22	9.00	20.00	65.00
Cu	23.50	11.52	9.00	25.50	38.00
Fe	9491	3941	4709	8881	18470
Mn	224.2	174.8	76.00	121.00	542.00
Ni	13.33	8.22	5.00	10.50	33.00
Pb	7.08	6.68	0.00	8.00	16.00
Zn	45.83	26.44	17.00	50.50	85.00

BDL below detection limit

Minimum and maximum concentrations of trace metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) determined in the sediments are presented in Table 2. The highest concentrations of metals were found in the Izmir Bay which is intensely industrialized (mainly iron, paper and pulp factories, antifouling paints, chlorine-alkali plants, chemical industries, textile industries, metal processing, timber processing, cement factories, tanneries, oil, soap and a very busy harbor) compared to Didim.

In the past, various studies were conducted to determine the trace metals in the sediments of Izmir Bay.

Metal concentrations (μg g^{-1} dry wt.) in sediments of Didim and Izmir Bay were compared to other studies in sediments from different regions of the world (Table 3). Comparison of data set revelated that observed trace metal levels in the Didim and Izmir Bay were generally lower than other regions. On the other hand, the levels of metals in this study were higher than Egypt. Different extraction procedures were used in the previous studies and this may have contributed to the differences (Güven and Akıncı 2008).

Conclusions

The following conclusions can be derived:

1. The activity concentrations of ^{210}Po and ^{210}Pb were determined in the surface marine sediments in Izmir Bay and Didim (Aegean Sea).
2. The activity concentrations of ^{210}Po were determined within the range of 24 ± 5 to 126 ± 6 Bq kg^{-1} dry wt.
3. The activity concentrations of ^{210}Pb were determined within the range of 18 ± 3 to 59 ± 4 Bq k^{g-1} dry wt.
4. The highest ^{210}Po concentration was observed at the Didim station.
5. ^{210}Pb activity concentrations in most of the sediment samples were lower than ^{210}Po, and usually $^{210}Po/^{210}Pb$ activity ratios are much higher for natural levels.

Table 3 The metal concentrations in sediments (μg g^{-1} dry wt.) from Izmir Bay and Didim and different regions of the world

Area	Pb	Cr	Cu	Zn	Mn	References
Homa Lagoon (Turkey)	2.43–17	84–129	10–26	46–92	410–729	Uluturhan et al. (2011)
Izmir Bay (Turkey)	3.1–119	19–316	2.2–109	14–412	128–942	Küçüksegin et al. (2011)
Berre (France)	18–82	38–428	11–48	50–151	–	Accornero et al. (2008)
Izmit Bay (Turkey)	55.2–172	38.9–112.4	24.5–102.4	440–1900	–	Pekey (2006)
Venice (Italy)	21–929	–	–	101–8295	–	Bellucci et al. (2002)
Bardawil (Egypt)	0–78	1.4–24	0.78–4.4	3.9–29	2.7–25	Taher (2001)
Saros Gulf (Turkey)	2–80	–	6–44	23–154	114–1740	Sarı and Cağatay (2001)
Aegean Sea (Turkey)	0–16	9–65	3–38	3–85	42–542	This study

6. The overall order of the metal concentrations found in sediments in our study was: Fe > Mn > Zn > Cr > -Cu > Ni > Pb > Cd. Our results show that the distribution of metals in the surface sediment is variable.

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