

^{210}Po and ^{210}Pb Concentration in Environmental Samples of the Adriatic Sea

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ABSTRACT: This study reports the concentrations of important tracers of the marine environment, ^{210}Po and ^{210}Pb , in different matrices from field samples collected at Central Adriatic Sea (Italy), a non-contaminated marine ecosystem. ^{210}Po concentration appears to decrease with increasing distance from the coast and a significant difference in ^{210}Po concentrations in seawater samples at two different depths is not appreciable. ^{210}Po and ^{210}Pb present the same trend in the different periods of the year. ^{210}Po and ^{210}Pb present high concentration factors and high Kd values: in particular ^{210}Po shows values of $2.4 \cdot 10^4$ in plankton, $3.2 \cdot 10^5$ in the particulate fraction and $1.1 \cdot 10^5$ in sediment; ^{210}Pb shows values of $1.3 \cdot 10^4$ in plankton, $1.8 \cdot 10^4$ in the particulate fraction and $4.9 \cdot 10^4$ in sediment. The $^{210}\text{Po}/^{210}\text{Pb}$ ratio results < 1 in sea water and > 1 in the particulate fraction, sediment and plankton due to a significant fractionation occurring between the two radionuclides during their removal from solution to particle and due to their different biogeochemical cycling pathways in the marine environment. The noticeable accumulation of ^{210}Po in the food chain is not accompanied by an identical accumulation of ^{210}Pb . Due to its biomagnification in the marine food chain, ^{210}Po provides the largest radiation dose to any marine organism under natural conditions. The data reported provide reference values for the Central Adriatic (Mediterranean Sea) coastal environment.

Key words: ^{210}Po , ^{210}Pb , Marine ecosystem, Mediterranean Sea

INTRODUCTION

Naturally occurring ^{210}Po and its grandparent ^{210}Pb are members of the ^{238}U decay series. ^{210}Po is an alpha radioactive emitter which decays ($T_{1/2}$: 138.4 days) to stable lead. A small amount of ^{210}Po in seawater originates from the atmospheric deposition of polonium itself (Cochra, 1992; Nozaki, 1991), but most ^{210}Po in the marine environment is largely produced by the decay, in situ, of ^{210}Pb ($T_{1/2}$: 22.3 years) deposited from the atmosphere. Furthermore, the concentration of ^{210}Po can be locally enhanced by the impact of industrial emissions, in particular the discharges from factories that produce phosphoric acid used in the manufacturing of fertiliser and that generate phosphatic gypsum wastes (Stepnowski and Skwarzec, 2000; Al-Masri *et al.*, 2002; Jia *et al.*, 2003). ^{210}Po is of interest as a potential tracer of particle transfer and vertical flux of particulate matter, and of ocean circulation. In contrast to terrestrial organisms, many marine species incorporate high concentrations of this radionuclide (Carvalho and Fowler, 1993). The alpha decay of ^{210}Po accounts for most of the radioactive dose to marine organisms rather

than anthropogenic radionuclides released into coastal waters. Evaluation of radiological risk to non-human biota has become a subject of scientific research and one of the most important issues in radioecology and radiological protection in recent years (Jia *et al.*, 2003; Desideri *et al.*, 2011). Besides the exposure of the marine animals themselves, the great enriched ^{210}Po concentrations in these can contribute significantly to human radioactivity exposure through seafood consumption (Feroz Khan and Godwin Wesley, 2011). Thus, in addition to the potential of ^{210}Po as a geochemical tracer, its interactions with marine biota are of interest in risk assessment models useful to understand the implications of discharge in the marine environment beyond the natural radiation background (Stewart and Fisher, 2003b).

Many authors have determined ^{210}Po in environmental surveys, but these measures are not accompanied by that of ^{210}Pb , perhaps because of the complexity of the methods, however the importance of measuring ^{210}Pb in addition to ^{210}Po must not be ignored (Cherry *et al.*, 1986; Yamamoto *et al.* 1994).

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Since ^{210}Pb is a continual source of ^{210}Po , knowledge of its content is necessary for an accurate determination of ^{210}Po content at the sampling time. On the other hand, it is necessary to calculate ^{210}Po content at equilibrium, that is, when polonium input (whether technological or natural) has ceased and unsupported ^{210}Po has decayed. Furthermore, the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratio provides information about the time scale of ^{210}Po incorporation.

In this study, ^{210}Po and ^{210}Pb concentrations are determined at coastal site of Central Adriatic Sea (Mediterranean Sea) with the aim to (i) calculate the level background of these radionuclides in a non-contaminated marine environment, (ii) study the fractionation and disequilibrium between ^{210}Po and ^{210}Pb during their scavenging, removal, sinking and assimilation in different matrices (sea water, particulate matter, phytoplankton and zooplankton), (iii) calculate the concentration factors (CFs) for different marine organisms and lastly (iv) evaluate the trend of polonium and lead in the marine food chain. This study will also support a new radioecological reference database for this marine environment.

MATERIALS & METHODS

The samples representing the different components of a marine ecosystem are the following: sea water collected at different distances from the coast (500, 1500, 3000 m) and at different depths (0.5 and 12 m), sediment collected at 3000 m from the coast at 12 m depth, total particulate fraction ($> 0.45 \mu\text{m}$), phyto (50-200 μm) and zooplankton ($> 200 \mu\text{m}$) collected at 1500 m, at surface sea water. The sampling methods are described by the authors in a previous study (Desideri *et al.*, 2011). The samples were collected at a coastal site (Pesaro, Italy) of the Central Adriatic Sea during the monitoring carried out from May 2009 to August 2011 on board a scientific vessel equipped with radar, GPS, and a probe (Idronaut Ocean Seven Mod. 316 CTD) to monitor the physical and chemical parameters, such as temperature, dissolved oxygen, salinity and pH at both surface and along the water column. The transparency of the water column was estimated using a Secchi disc. Chlorophyll *a* (Chl *a*) was determined in 90% acetone homogenates of particulate matter collected on Millipore HA membrane filters using the spectrophotometric method of Strickland and Parsons (1972). After filtration, to separate particulate ($> 0.45 \mu\text{m}$) from the dissolved phase ($< 0.45 \mu\text{m}$), a known activity of ^{209}Po as the yield internal standard was added to water samples (10 L) for polonium determination; for lead determination, a known quantity of Bi^{3+} as the yield internal standard, and Pb^{+2} as carrier were added to 100 L samples. Fe^{3+} was added

to all samples (both 10 L and 100 L) to coprecipitate the radionuclides of interest as hydroxides, in alkaline medium; after digestion for 24 h, the supernatant was siphoned off and the remaining precipitates were centrifuged and dissolved with conc. HCl.

The solutions for polonium determination were diluted until 1M and boiled with a few milligrams of ascorbic acid to reduce Fe^{3+} . In the solution for lead Fe^{3+} was separated by a double extraction with methyl-isobutyl-ketone. As far as the total particulate fraction is concerned, all the filters from the filtration of 100 L of sea water were dissolved and mineralized with conc. HNO_3 and H_2O_2 . The nitric solution was evaporated until dryness, re-dissolved in 1M HCl and filtered. The residue was treated with conc. HF and dissolved in 1M HCl. The solution was subdivided into two fractions for polonium and lead determination. A known activity of ^{209}Po as the yield internal standard to polonium solution and a known quantity of Bi^{3+} as the yield internal standard, and Pb^{+2} as the carrier to lead solution were added. The samples of phyto and zooplankton, from the filtration of 200-500 m^3 of sea water, were filtered through 0.45 mm Whatman filters, dried in an oven until constant weigh at 80°C . The samples were mineralized with HNO_3 and H_2O_2 at $85-90^\circ\text{C}$. The residue was then treated with conc. HF and dissolved in 1M HCl; the solution was subdivided into two fractions for polonium and lead determination. A known activity of ^{209}Po as the yield internal standard to polonium solution and a known quantity of Bi^{3+} as the yield internal standard, and Pb^{+2} as the carrier to lead solution were added. About 300 g of sediment sample was dried in an oven until constant weigh at 110°C . An amount of 2 g of dry sample were treated repeatedly with a mixture of conc. HCl and conc. HNO_3 . The residue was transferred into Teflon beaker and treated with conc. HF and dissolved in 1M HCl. After filtration, the solution was subdivided into two fractions for polonium and lead determination. A known activity of ^{209}Po as the yield internal standard to polonium solution and a known quantity of Bi^{3+} as the yield internal standard, and Pb^{+2} as carrier to lead solution were added.

Polonium was deposited at $85-90^\circ\text{C}$ and pH 1.5-2.0 in continuous for 4 hours in a silver disk placed in a syringe immersed into a 1 M HCl solution. No preliminary separation is required and essentially quantitative recoveries were obtained by using standard ^{209}Po tracer (Jia and Torri, 2007). The silver disk was then measured by μ -spectrometry (^{210}Po alpha particles energy: 5.407 MeV). The measurement was carried out using an alpha spectrometry system (Canberra, USA) with silicon detectors (efficiency, 28%) counting the source for 200,000 s. In this study, ^{210}Pb

was determined through its daughter, ^{210}Bi . This method is based on the chemical separation of ^{210}Bi through its selective extraction by tri-octyl-phosphine oxide in a chromatographic column, its precipitation as Bi_2S_3 , and source counting with a low background μ -detector. The purity of ^{210}Bi source was checked following the ^{210}Bi decay during two weeks (Desideri *et al.*, 2010). The accuracy of the radioanalytical methods used in this study was checked through the analysis of standard samples supplied by the International Atomic Energy Agency (IAEA). The details of the methods used in this study were reported in a previous work (Desideri *et al.*, 2011).

RESULTS & DISCUSSION

The temperature showed a typical seasonal trend with a lowest value on January 2011 (6.4°C) and a highest value on August 2011 (27.3°C). Transparency, dissolved oxygen and chlorophyll *a* were in relation to the eutrophic conditions occurring during the period examined. The lowest and highest values of transparency, dissolved oxygen and chlorophyll *a*, were registered in March 2010 and January 2011, respectively. The salinity trend along the central Adriatic coast is influenced by Po River in-put based on the meteorological conditions (Penna *et al.* 2004); the lowest values of salinity were registered in May 2009 and June 2010. The pH was within the standard range values (Table 1). Table 2 shows the ^{210}Po and ^{210}Pb concentrations at different distances from the coast (500 m, 1500 m, 3000 m) and at different depths (0.5 and 12 m). The uncertainty of the final result is due to the propagation of all random counting uncertainties occurring at any point in the entire measurement process. ^{210}Po concentration did not decline with increasing distance from the coast; a significant difference in ^{210}Po concentrations in seawater samples collected at 3000 m distance, but at two different depths, was not appreciable. Figs 1 and 2 show the comparison between the ^{210}Po and ^{210}Pb mean concentrations in the different matrices collected in 12 monitoring series carried out from May 2009 to August 2010. In seawater, the ^{210}Po and ^{210}Pb concentrations ranged from 0.16 to 0.63 and from 0.19 to 1.20 Bq m^{-3} respectively; mean concentration resulted $0.33 \pm 0.14 \text{ Bq m}^{-3}$ for ^{210}Po and $0.42 \pm 0.26 \text{ Bq m}^{-3}$ for ^{210}Pb . In the total particulate fraction, the ^{210}Po and ^{210}Pb concentrations ranged from 0.16 to 1.96 and from 0.04 to 2.00 Bq m^{-3} respectively; mean concentration resulted $0.64 \pm 0.51 \text{ Bq m}^{-3}$ for ^{210}Po and $0.50 \pm 0.54 \text{ Bq m}^{-3}$ for ^{210}Pb . In phytoplankton, the ^{210}Po and ^{210}Pb concentrations ranged from 30.4 to 233.0 and 19.2 to 210.0 Bq/kg respectively; mean concentration resulted $107.9 \pm 62.5 \text{ Bq/kg}$ for ^{210}Po and $89.8 \pm 62.6 \text{ Bq/kg}$ for ^{210}Pb . In zooplankton, the ^{210}Po and ^{210}Pb concentrations ranged from 71.0 to 227.0 and

9.9 to 182.0 Bq/kg respectively; mean concentration resulted $133.2 \pm 46.9 \text{ Bq/kg}$ for ^{210}Po and $79.6 \pm 59.1 \text{ Bq/kg}$ for ^{210}Pb . The data obtained in this study agree with those reported by other authors (Tables 3 and 4).

In fig. 3, the correlations between the ^{210}Po and ^{210}Pb concentrations in the total particulate fraction, phytoplankton and zooplankton are reported. The two radionuclides showed a good correlation in the particulate phase: R^2 resulted 0.8517 for particulate matter, 0.7075 for phytoplankton and 0.7101 for zooplankton, whereas no correlation between the two radionuclides was found in sea water (data not shown).

^{210}Po and ^{210}Pb presented high concentration factors and high K_d (Tables 5 and 6) in accordance with data reported in literature (Shannon and Cherry, 1970; Stewart and Fisher, 2003a). The lack of ^{210}Po and ^{210}Pb in the dissolved phase is due to the rapid processes of removal of polonium and lead, elements very particle-reactive, from solution to particles. Additionally, the same tables also show the mean ratio of $^{210}\text{Po}/^{210}\text{Pb}$ calculated in the different matrices analysed. In seawater, the ratio $^{210}\text{Po}/^{210}\text{Pb}$ was < 1 (0.78) whereas, in the particulate fraction and in sediment, it resulted > 1 . The $^{210}\text{Po}/^{210}\text{Pb}$ ratio in the plankton fractions also resulted > 1 . This suggests that a significant fractionation occurred between ^{210}Po and ^{210}Pb during their removal from solution to particles as reported by other authors (Bacon *et al.*, 1976; Chung, 1987; Kim, 2001; Sarin *et al.*, 1994). They reported that in atmospheric fall-out the $^{210}\text{Po}/^{210}\text{Pb}$ ratio is 0.1-0.4, and that this ratio increases in seawater and in plankton (Parfenov, 1973). This fact is probably due to the change of chemical form of radionuclides when they enter in the marine environment and to their different biological self-life. But this is mainly due to the more rapid processes of removal of polonium from solution to inorganic and organic particles. Fig. 4 reports the comparison between the ^{210}Po and ^{210}Pb mean concentrations found for phytoplankton and zooplankton in this study, and those found by the same authors in a previous work for mussels, anchovies and epipelagic fish collected in the same area (Meli *et al.*, 2008; Desideri, *et al.*, 2011). The increase in ^{210}Po concentrations was very pronounced in marine organisms feeding on bacteria and phytoplankton at the base of the food chain, such as the small zooplankton organisms, but also in large organisms, such as mussels and anchovies. Organisms occupying upper trophic levels (carnivores, top predators) displayed lower concentrations than planktivorous organisms. Zooplankton is an important intermediate between phytoplankton, which can greatly concentrate metals from seawater, and organisms of higher trophic levels, which are consumed as seafood. Therefore, due

Table 1. Sampling series: date of sampling, temperature, transparency, chlorophyll a, dissolved oxygen, pH and salinity values \pm SD

Series	Date	Temperature		Transparency (m)	Chlorophyll a ($\mu\text{g}\cdot\text{L}^{-1}$)	Dissolved O ₂ ($\text{mg}\cdot\text{L}^{-1}$)	pH	Salinity
		($^{\circ}\text{C}$)	(m)					
1	May 2009	21.33 \pm 0.08	7.1 \pm 0.15	2.24 \pm 0.11	7.52 \pm 0.16	8.34 \pm 0.01	27.25 \pm 0.07	
2	July 2009	24.92 \pm 0.04	8.0 \pm 0.11	1.18 \pm 0.14	6.79 \pm 0.04	8.21 \pm 0.03	33.32 \pm 0.09	
3	October 2009	17.11 \pm 0.07	2.1 \pm 0.12	2.47 \pm 0.13	7.04 \pm 0.07	8.21 \pm 0.04	34.08 \pm 0.08	
4	March 2010	7.76 \pm 0.07	1.0 \pm 0.13	53.85 \pm 0.11	15.13 \pm 0.09	8.30 \pm 0.08	27.42 \pm 0.11	
5	May 2010	15.27 \pm 0.09	6.0 \pm 0.12	2.07 \pm 0.18	7.48 \pm 0.01	8.16 \pm 0.03	35.84 \pm 0.07	
6	June 2010	23.27 \pm 0.07	6.1 \pm 0.18	4.78 \pm 0.16	7.99 \pm 0.14	8.31 \pm 0.05	27.06 \pm 0.14	
7	September 2010	23.21 \pm 0.04	3.1 \pm 0.11	1.84 \pm 0.13	6.02 \pm 0.11	8.11 \pm 0.14	34.46 \pm 0.04	
8	November 2010	16.43 \pm 0.05	4.2 \pm 0.14	2.67 \pm 0.12	6.65 \pm 0.14	8.09 \pm 0.02	35.12 \pm 0.08	
9	January 2011	6.47 \pm 0.08	0.8 \pm 0.15	28.16 \pm 0.13	10.05 \pm 0.08	8.27 \pm 0.06	28.32 \pm 0.03	
10	March 2011	7.97 \pm 0.08	1.8 \pm 0.14	5.01 \pm 0.12	9.85 \pm 0.11	8.21 \pm 0.04	33.59 \pm 0.01	
11	May 2011	18.77 \pm 0.15	3.5 \pm 0.11	3.53 \pm 0.11	7.62 \pm 0.13	8.23 \pm 0.01	33.49 \pm 0.06	
12	August 2011	27.30 \pm 0.08	5.0 \pm 0.16	1.87 \pm 0.26	6.33 \pm 0.18	8.13 \pm 0.04	35.13 \pm 0.14	

Table 2. ^{210}Po , and ^{210}Pb concentration ($\text{Bq}\cdot\text{m}^{-3}$) in seawater samples collected at different distances from the coast and depth (m) during the years 2009 and 2010 (n.d., not determined)

Sample code	Sea water (distance from the coast, sampling depth)	^{210}Po	^{210}Pb	$^{210}\text{Po}/^{210}\text{Pb}$
May 2009				
1A	500 m, 0.5m	0.42 ± 0.08	n.d.	
1B	1500 m, 0.5m	0.16 ± 0.03	0.5 ± 0.15	0.32
1C	3000 m, 0.5m	0.21 ± 0.04	n.d.	
1D	3000 m, 12m	0.24 ± 0.05	n.d.	
July 2009				
2A	500 m, 0.5m	0.50 ± 0.10	n.d.	
2B	1500 m, 0.5m	0.32 ± 0.06	1.1 ± 0.28	0.29
2C	3000 m, 0.5m	0.16 ± 0.03	n.d.	
2D	3000 m, 12m	0.49 ± 0.10	n.d.	
October 2009				
3A	500 m, 0.5m	0.50 ± 0.10	n.d.	
3B	1500 m, 0.5m	0.44 ± 0.09	0.4 ± 0.10	1.10
3C	3000 m, 0.5m	0.49 ± 0.10	n.d.	
3D	3000 m, 12m	0.35 ± 0.07	n.d.	
March 2010				
4A	500 m, 0.5m	0.25 ± 0.05		
4B	1500 m, 0.5m	0.53 ± 0.11	0.2 ± 0.04	0.48
4C	3000 m, 0.5m	0.47 ± 0.09		
4D	3000 m, 12m	0.30 ± 0.06		

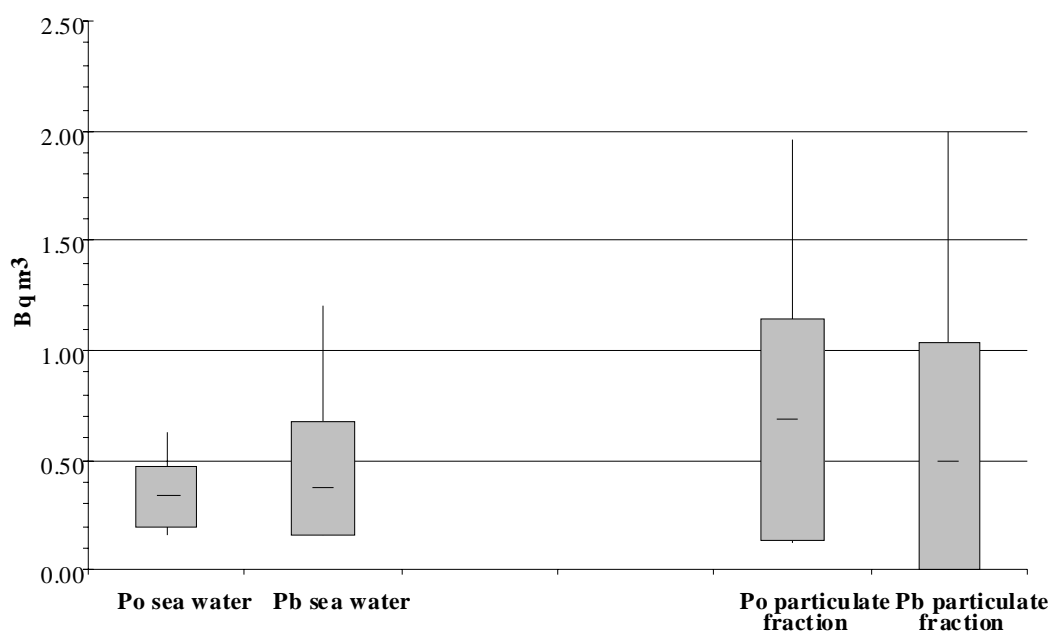


Fig. 1. ^{210}Po and ^{210}Pb concentration ($\text{Bq}\cdot\text{m}^{-3}$) in sea water and particulate samples collected at 1500 m from the coast at 0.5 m depth

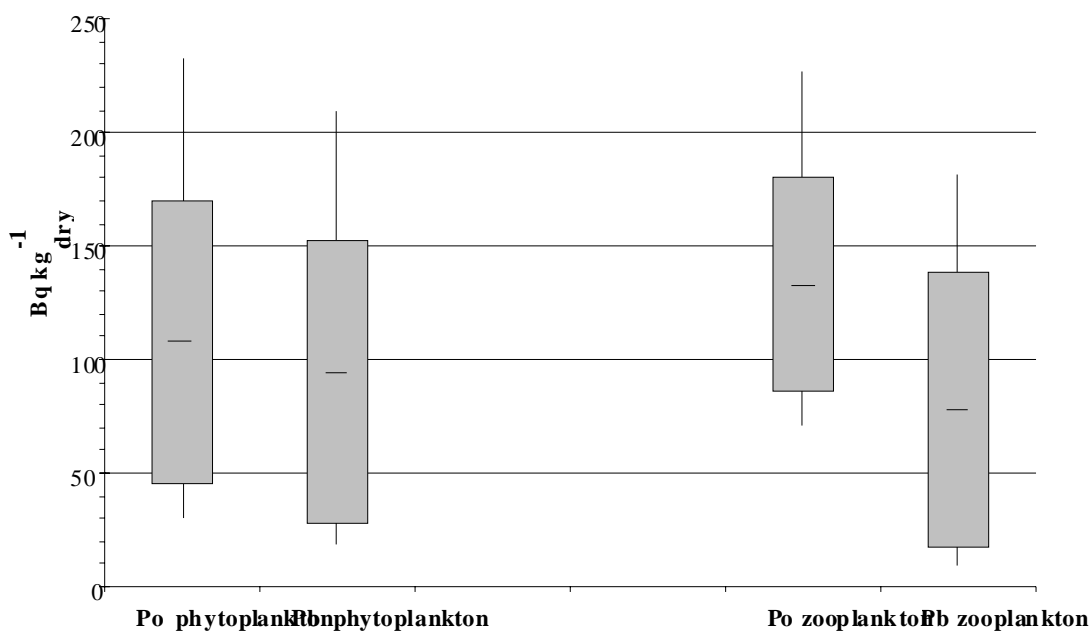


Fig. 2. ^{210}Po and ^{210}Pb concentration ($\text{Bq}\cdot\text{kg}^{-1}_{\text{dry}}$) in phytoplankton and zooplankton samples collected at 1500 m from the coast at surface sea water

Table 3. ^{210}Po and ^{210}Pb mean concentrations ($\text{Bq}\cdot\text{m}^{-3}$) obtained in sea water and total particulate fraction worldwide

Site	$^{210}\text{Po}_{\text{water}}$	$^{210}\text{Pb}_{\text{sol}}$	$\frac{^{210}\text{Po}_{\text{sol}}}{^{210}\text{Pb}_{\text{sol}}}$	$^{210}\text{Po}_{\text{part}}$	$^{210}\text{Pb}_{\text{part}}$	$\frac{^{210}\text{Po}_{\text{part}}}{^{210}\text{Pb}_{\text{part}}}$
Adriatic Sea, Italy (Meli et al., this paper)	0.33±0.14	0.42±0.26	0.78	0.65	0.51	1.27
South China Sea (Yang W. et al., 2006)	0.11-1.73	0.87-2.51	0.13-0.69	0.19-0.75	0.16-0.39	1.19-1.9
North-western Mediterranean Sea (Masquè P. et al, 2002)	0.48-1.92	0.72-1.83		0.11-0.39	0.025-0.064	
Sub equatorial Atlantic ocean (Sarin et al., 1999)	0.60-1.47	1.42	0.27-0.39			
Norwegian Fjords (Swarczewski et al., 1999)				0.41		
Irish Coast (Ryan et al., 1999)	0.19-1.96			0.95-44.3		
Japan, Misaki Coast (Tateda and Yamamoto, 1997)	2.4					
Pacific Ocean, Equator (Nozaki et al., 1997)	0.78-1.8					
Baltic Sea (Skwarzec et al., 1988)	0.5					
East central Indian ocean (Cochra et al., 1983)	0.92-1.32					
Cape of Good Hope (Shannon et al., 1970)	0.73					
Washington Coast (Shell et al., 1977)				0.18-0.85		

Table 4. ^{210}Po and ^{210}Pb mean concentration ($\text{Bq}\cdot\text{kg}^{-1}_{\text{dry}}$) obtained in phytoplankton and zooplankton worldwide

Site	$^{210}\text{Po}_{\text{phyto}}$	$^{210}\text{Pb}_{\text{phyto}}$	$\frac{^{210}\text{Po}_{\text{phyto}}}{^{210}\text{Pb}_{\text{phyto}}}$	$^{210}\text{Po}_{\text{zoo}}$	$^{210}\text{Pb}_{\text{zoo}}$	$\frac{^{210}\text{Po}_{\text{zoo}}}{^{210}\text{Pb}_{\text{zoo}}}$
Adriatic Sea, Italy (Meli et al., this paper)	107.9±62.5	89.9±62.6	1.20	133.2±46.9	79.6±59.1	1.67
Malaysia, South China Sea (Mohamed et al., 2005)	-	-	-	364.7±21	93.7±6.8	4.01
Japan, Coast Misaki (Tateda et Yamamoto, 1997)	126.0	-	-	167.0	-	-
Cape of Good Hope (Shannon et al., 1970)	40.0	-	-	148.0	-	-
Cape of Good Hope (Shannon and Cherry, 1967)	104.0	-	-	174.0	-	-
Cape of Good Hope (Cherry, 1964)	188.0	-	-	249.0	-	-
North-East Atlantic (Carvalho, 2011)						4.4

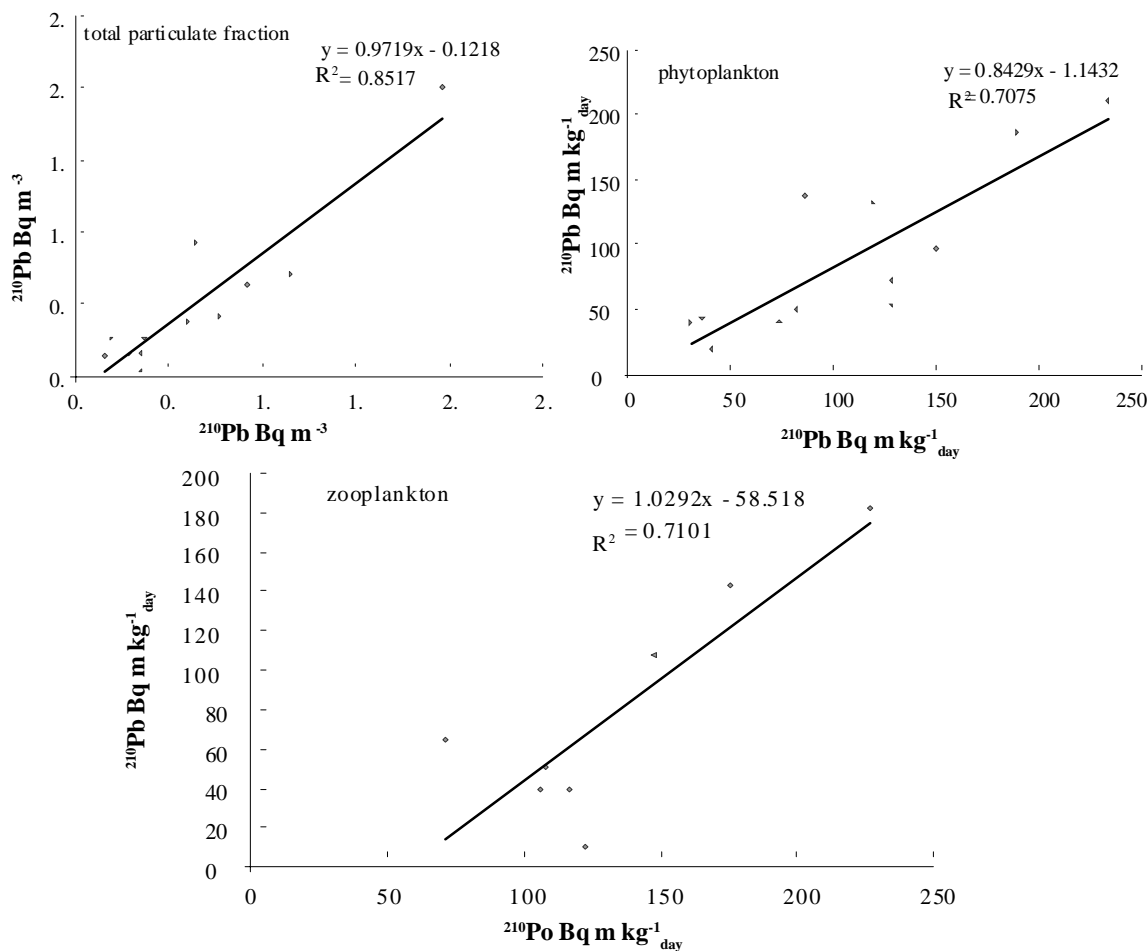


Fig. 3. Relationship between ^{210}Po and ^{210}Pb concentrations in the total particulate fraction, phytoplankton and zooplankton

Table 5. Mean concentrations (\pm SD) of ²¹⁰Po and ²¹⁰Pb, concentration factor (CF) (matrix/sea water) and ²¹⁰Po/²¹⁰Pb in plankton samples

Matrix	²¹⁰ Po (Bqkg ⁻¹ _{wet})	²¹⁰ Po	CF	²¹⁰ Pb (Bqkg ⁻¹ _{wet})	²¹⁰ Pb CF	²¹⁰ Po/ ²¹⁰ Pb
Sea water (Bqkg ⁻¹)	3.3 10 ⁻⁴ ± 1.4 10 ⁻⁴			4.2 10 ⁻⁴ ± 2.6 10 ⁻⁴		0.78
Phytoplankton	7.2 ± 4.2	2.2 10 ⁴		5.99 ± 4.2	1.4 10 ⁺⁴	1.20
Zooplankton	8.9 ± 3.1	2.7 10 ⁴		5.30 ± 3.9	1.3 10 ⁺⁴	1.67

Table 6. ²¹⁰Po and ²¹⁰Pb mean concentrations (\pm SD), Kd (matrix/sea water) and ²¹⁰Po/²¹⁰Pb in total particulate fraction and sediment

Matrix	²¹⁰ Po (Bqkg ⁻¹ _{dry})	²¹⁰ Po	Kd	²¹⁰ Pb (Bqkg ⁻¹ _{dry})	²¹⁰ Pb	Kd	²¹⁰ Po/ ²¹⁰ Pb
Sea water (Bqkg ⁻¹)	3.3 10 ⁻⁴ ± 1.4 10 ⁻⁴			4.2 10 ⁻⁴ ± 1.4 10 ⁻⁴			0.78
Particulate fraction	104 ± 82	3.2 10 ⁵		75.6 ± 81.6	1.8 10 ⁴		1.27
Sediment	41.6 ± 12.5	1.1 10 ⁵		28.3 ± 8.4	4.9 10 ⁴		1.45

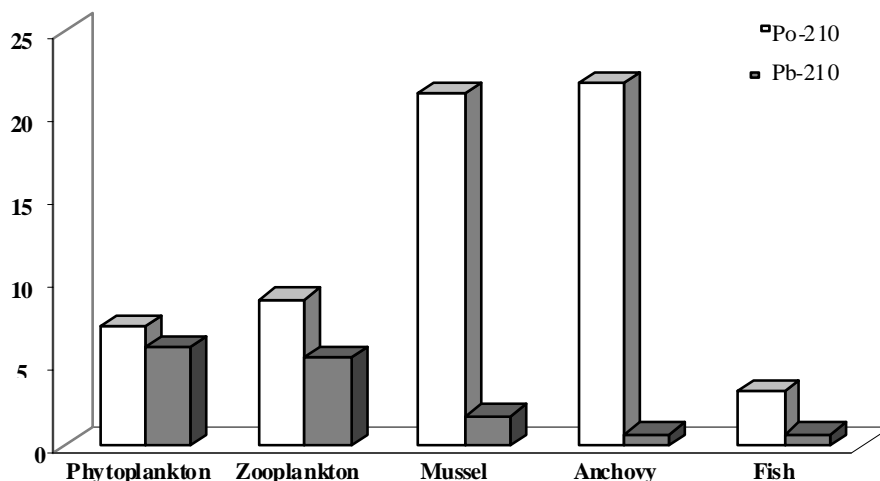


Fig. 4. Mean concentration (Bq·kg⁻¹_{wet}) of ²¹⁰Po and ²¹⁰Pb in phytoplankton, zooplankton, mussel, anchovy and epipelagic fish

in part to its biomagnification in the marine food chain, ²¹⁰Po is responsible for the highest radiation doses to aquatic organisms under natural conditions.

As far as ²¹⁰Pb is concerned, unlike ²¹⁰Po, it showed little assimilation by zooplankton from phytoplankton food and was not accumulated in mussels and fishes. Some authors (Stewart and Fisher, 2003a) have suggested that ²¹⁰Po becomes incorporated into the cytoplasm of phytoplankton that is associated with amino acids and sulphur-containing proteins, whereas ²¹⁰Pb, being a surface-bound particle, reactive as ²³⁴Th, is associated with cell walls and other structural components of phytoplankton that are not assimilated in animal tissue and sink in fecal material. Therefore, ²¹⁰Po can be used as tracer of the diet of marine organisms as proposed by other authors (Yang

et al., 2006); unlike ²¹⁰Po, the use of ²¹⁰Pb as a diet tracer seems very limited.

In fig. 3, the correlations between the ²¹⁰Po and ²¹⁰Pb concentrations in the total particulate fraction, phytoplankton and zooplankton are reported. The two radionuclides showed a good correlation in the particulate phase: R² resulted 0.8517 for particulate matter, 0.7075 for phytoplankton and 0.7101 for zooplankton, whereas no correlation between the two radionuclides was found in sea water (data not shown).

²¹⁰Po and ²¹⁰Pb presented high concentration factors and high Kd (Tables 5 and 6) in accordance with data reported in literature (Shannon and Cherry, 1970; Stewart and Fisher, 2003a). The lack of ²¹⁰Po and ²¹⁰Pb in the dissolved phase is due to the rapid processes of removal of polonium and lead, elements

very particle-reactive, from solution to particles. Additionally, the same tables also show the mean ratio of $^{210}\text{Po}/^{210}\text{Pb}$ calculated in the different matrices analysed. In seawater, the ratio $^{210}\text{Po}/^{210}\text{Pb}$ was < 1 (0.78) whereas, in the particulate fraction and in sediment, it resulted >1 . The $^{210}\text{Po}/^{210}\text{Pb}$ ratio in the plankton fractions also resulted >1 . This suggests that a significant fractionation occurred between ^{210}Po and ^{210}Pb during their removal from solution to particles as reported by other authors (Bacon *et al.*, 1976; Chung, 1987; Kim, 2001; Sarin *et al.*, 1994). They reported that in atmospheric fall-out the $^{210}\text{Po}/^{210}\text{Pb}$ ratio is 0.1-0.4, and that this ratio increases in seawater and in plankton (Parfenov, 1973). This fact is probably due to the change of chemical form of radionuclides when they enter in the marine environment and to their different biological self-life. But this is mainly due to the more rapid processes of removal of polonium from solution to inorganic and organic particles. Fig. 4 reports the comparison between the ^{210}Po and ^{210}Pb mean concentrations found for phytoplankton and zooplankton in this study, and those found by the same authors in a previous work for mussels, anchovies and epipelagic fish collected in the same area (Meli *et al.*, 2008; Desideri, *et al.*, 2011). The increase in ^{210}Po concentrations was very pronounced in marine organisms feeding on bacteria and phytoplankton at the base of the food chain, such as the small zooplankton organisms, but also in large organisms, such as mussels and anchovies. Organisms occupying upper trophic levels (carnivores, top predators) displayed lower concentrations than planktivorous organisms. Zooplankton is an important intermediate between phytoplankton, which can greatly concentrate metals from seawater, and organisms of higher trophic levels, which are consumed as seafood. Therefore, due in part to its biomagnification in the marine food chain, ^{210}Po is responsible for the highest radiation doses to aquatic organisms under natural conditions. As far as ^{210}Pb is concerned, unlike ^{210}Po , it showed little assimilation by zooplankton from phytoplankton food and was not accumulated in mussels and fishes. Some authors (Stewart and Fisher, 2003a) have suggested that ^{210}Po becomes incorporated into the cytoplasm of phytoplankton that is associated with amino acids and sulphur-containing proteins, whereas ^{210}Pb , being a surface-bound particle, reactive as ^{234}Th , is associated with cell walls and other structural components of phytoplankton that are not assimilated in animal tissue and sink in fecal material. Therefore, ^{210}Po can be used as tracer of the diet of marine organisms as proposed by other authors (Yang *et al.*, 2006); unlike ^{210}Po , the use of ^{210}Pb as a diet tracer seems very limited.

CONCLUSION

This paper reported ^{210}Po and ^{210}Pb concentrations in different marine matrices collected

in central Adriatic Sea, from May 2009 to August 2011 with the main goal of determining their background levels in a non-contaminated marine ecosystem. The radionuclides taken into account are, in fact, important tracers of the marine environment. ^{210}Po concentration does not decline with increasing distance from the coast; a significant difference in ^{210}Po concentrations in seawater samples collected at 3000 m distance but at two different depths, is not appreciable. In the inorganic and organic particulate phase, ^{210}Po and ^{210}Pb concentrations present a very good statistical correlation. ^{210}Po and ^{210}Pb presented high concentration factors and high Kd in agreement with what is reported in literature. The lack of ^{210}Po and ^{210}Pb in the dissolved phase was due to the rapid processes of removal of polonium and lead from solution to particles.

As far as the $^{210}\text{Po}/^{210}\text{Pb}$ ratio is concerned, in sea water it was < 1 , instead, in the particulate fraction, sediment and plankton, it was >1 . This suggests that a significant fractionation occurs between ^{210}Po and ^{210}Pb during their removal from solution to particles as reported by other authors. This can mainly be attributed to the more rapid processes of removal of polonium than lead from solution to inorganic and biological particles. Due in part to its biomagnification in the marine food chain, ^{210}Po was responsible for the largest radiation dose to any organism under natural conditions.

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