Available online at www.sciencedirect.com

SCIENCE DIRECT®

Science of the Total Environment 357 (2006) 146–159

Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind

www.elsevier.com/locate/scitotenv

Distribution of ^{137}Cs, ^{238}Pu and $^{239+240}Pu$ in sediments of the southeastern Brazilian shelf–SW Atlantic margin

Rubens C.L. Figueira[a,b,*], Moyses G. Tessler[b], Michel M. de Mahiques[b], Ieda I.L. Cunha[c]

[a]*Centro de Tecnologia e Ciências Exatas, Universidade Cruzeiro do Sul, São Paulo, Brazil*
[b]*Instituto Oceanográfico da Universidade de São Paulo, São Paulo, Brazil*
[c]*Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN, São Paulo, Brazil*

Received 19 October 2004; accepted 7 March 2005
Available online 28 July 2005

Abstract

In this work levels of ^{137}Cs, ^{238}Pu and $^{239+240}Pu$ as well as activity ratios of anthrophogenic radionuclides in sediment samples from the southeastern Brazilian shelf are presented. Instrumental gamma spectrometry was used to determine ^{137}Cs and alpha spectrometry to determine ^{238}Pu and $^{239+240}Pu$ after a radiochemical procedure. The levels ranged from 0.30 to 1.79 Bq kg^{-1} for ^{137}Cs, from 15 to 150 mBq kg^{-1} for ^{238}Pu and, from 18 to 117 mBq kg^{-1} for $^{239+240}Pu$. There was a bathymetric differentiation in the radionuclides distribution. ^{137}Cs values were generally higher in the samples collected at water depths of less than 100 m. On the other hand, plutonium isotopes exhibit higher values at greater depths. The mean ratio of $^{239+240}Pu/^{137}Cs$ obtained was 0.112 ± 0.072 which is in agreement with the value reported for the Atlantic from atmospheric fallout of nuclear explosions in the past. The $^{238}Pu/^{230+240}Pu$ ratios varied widely (from 0.339 to 2.088) and showed the influence of the SNAP-9A accident in the ^{238}Pu levels for this area. The main goal of this work was to present unpublished anthropogenic radionuclide levels and activity ratios related to the contamination of the southeastern Brazilian shelf.

Keywords: ^{137}Cs; ^{238}Pu; $^{239+240}Pu$; Southeastern Brazilian continental shelf; Radionuclide levels; Marine sediments; Artificial radioactivity; Radiochemical separation

1. Introduction

Radioactive pollution is as harmful as other forms of pollution. Thus the monitoring of anthropogenic radionuclides in the marine environment is of great importance, since the seas and oceans constitute the major repositories of this kind of element.

* Corresponding author. Instituto Oceanográfico da Universidade de São Paulo, Departamento de Oceanografia Física, Química e Geológica, 05508-900 Praça do Oceanográfico, 191, São Paulo SP, Brazil. Tel.: +55 11 30916627; fax: +55 11 30916610.
E-mail address: figueira@curiango.ipen.br (R.C.L. Figueira).

0048-9697/$ - see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.scitotenv.2005.03.032

Concentrations of anthropogenic radionuclides in the marine realm generally vary from region to region, according to the location and magnitude of the different sources of contamination. Radionuclides have been released into the environment from a multiplicity of sources, both planned and accidental (Calmet and Sjöeblom, 1992; Livingston and Povinec, 2000).

Radionuclides are powerful tracers for a variety of marine processes. Due to the relatively well-defined temporal and spatial characteristics of the introduction of radionuclides into the ocean, the knowledge of their input, transport and fate within the different marine compartments provides many insights into a large number of processes within the water column, and in both biological and sedimentary systems. The distinctly different geochemical behaviour of these radionuclides in the aqueous system makes this set of tracers valuable for investigating water circulation and sedimentary processes (Baskaran et al., 1996; Noureddine and Baggoura, 1997; Livingston and Povinec, 2000).

Among the radionuclides produced artificially and released into the marine environment ^{137}Cs and ^{239}Pu are of great importance. ^{137}Cs has a high fission yield and a half-life of 30 years, while ^{239}Pu has a longer half-life (24,000 years) and is extremely dangerous when released into the environment.

In the marine environment, these radionuclides may be retained by the sediments through fixation in suspended matter and sedimentation, direct precipitation of colloidal forms and the direct fixation by adsorption and deposition of organic matter which had previously incorporated the radionuclides (Ligero et al., 2004).

In the Southern Hemisphere, the main source of radioactive contamination for the South Atlantic is the fallout from past nuclear tests. The radionuclide inventories for this area are approximately 17.5 PBq of ^{137}Cs and 0.5 PBq of $^{239+240}$Pu (Aarkrog, 2003). Another main source of radioactive contamination was the accident with the SNAP-9A satellite, which contained a nuclear power generator onboard that released 0.6 PBq of ^{238}Pu into the atmosphere. Due to this accident, seawater samples from the Southern Hemisphere have shown enhanced ^{238}Pu/$^{239+240}$Pu activity, nearly an order of magnitude greater than that in ocean water from the Northern Hemisphere (Whitehead, 1988; Holm et al., 1991; Aarkrog, 2003). Detectable levels of artificial radionuclides have also been reported in the Antarctic region (Jia et al., 2000; Marzano et al., 2000; Desideri et al., 2003; Pourchet et al., 2003).

A research programme to establish the environmental radioactivity in marine samples from the southeastern Brazilian shelf has been carried out since 1993 to determine the levels of antrophogenic radionuclides. This area shows low levels of artificial radionuclides due to the atmospheric fallout, as previously reported in the literature (Cunha et al., 1993, 1999; Figueira et al., 1998, 2001, 2004; Saito et al., 2001a,b; Godoy et al., 2003). This work presents the levels of ^{137}Cs, ^{238}Pu and $^{239+240}$Pu and the activity ratios of manmade radionuclides in surface sediment samples collected in 1997 on the southeastern Brazilian shelf. The results obtained here are important for our knowledge of artificial radioactivity in the Southeastern Atlantic, an area for which the data on such parameters is scarce. In this sense our results may be taken as reference values for the monitoring of this region.

2. Study area

The study area corresponds to the southeastern Brazilian upper margin (Fig. 1), between the latitudes 28°40′S and 23°00′S, an area of approximately 320,000 km^2. The shelf width ranges from 73 to 231 km with an inclination of between 1:656 and 1:1333, the shelf break being located at between 120 and 180 m depth. As a rule, the inner shelf is covered with quartzose sandy sediments. From the 50-m isobath to the shelf break muddy sediments prevail. A few areas characterized by the occurrence of carbonate gravels are related to the presence of relict sediments (Mahiques et al., 2004). Most of the drainage systems run from the coastal range westwards into the interior, being part of the Parana-La Plata river basin; only small rivers draining granitic, gneissic and migmatitic terrains, run directly into the sea.

The southern sector of the study area presents allochthonous sediments, originating in the younger rocks of the Andean chain and reaching the shelf via

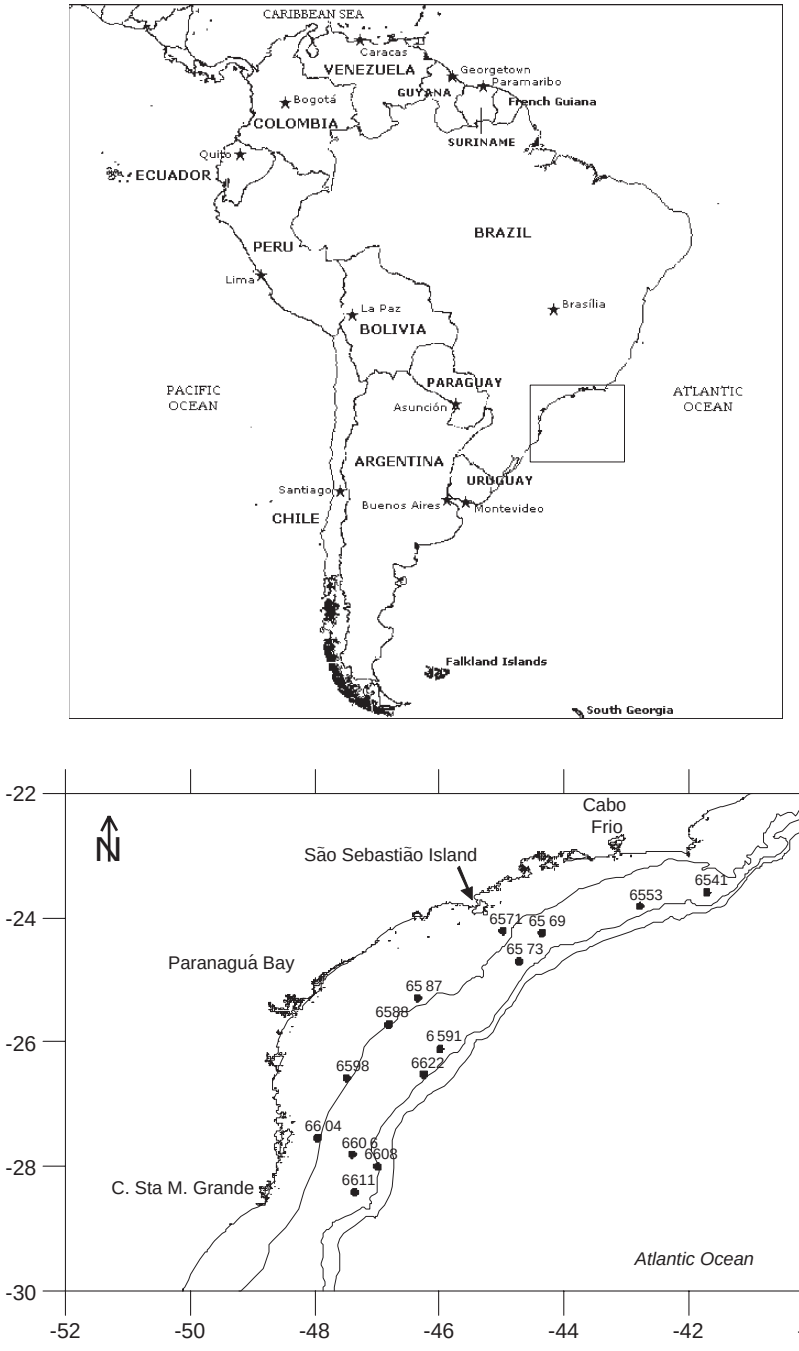

Fig. 1. Study area and sampling stations.

the River La Plata. The sedimentation in the northern sector is determined by the action of the Brazil Current, presenting a mixture of terrigenous and pelagic fractions (Mahiques et al., 2002, 2004). These regions also present differences as regards the clay mineralogy, mainly montmorillonite in the south and

a mixture of kaollinite–illite–montmorillonite in the north (Rocha et al., 1975).

3. Experimental

3.1. Equipment

The following equipment were used to analyze the radionuclides in the marine sediments studied: a hyper pure Ge detector with a resolution of 1.9 keV for the peak of 1332.40 keV of ^{60}Co, model GEM 60190, by EGG&ORTEC, and associated electronic appliances. An alpha spectrometer coupled to a surface barrier detector, model 576A, by EGG&ORTEC, and associated electronic appliances.

3.2. Sediment sampling

Sediment samples were collected by the R.V. "Prof. W. Besnard" in 1997 with a box-corer and a Petersen grab sampler. For the box-core samples only the topmost (2×10 cm) was considered for the analyses. For the samples collected with the Petersen grab sampler, about 8 l of wet sediment sample were taken. The samples were dried, homogenized and transferred to plastic containers. The water content as well as grain size was determined for each sample.

3.3. Determination of ^{137}Cs, ^{238}Pu and $^{239+240}$Pu in sediment samples

3.3.1. Cs analysis

^{137}Cs was assayed by gamma counting by means of its photopeak of 661 keV (Fig. 2). The method consisted of detector calibration, determination of detector counting efficiency, cumulative counts of both background and samples at regular intervals of time counted, photopeak smoothing and linear regression (Figueira et al., 1998). Comparison between the linear regression curves of background and sediment sample permitted the determination of sediment radionuclide activity, discounting background activity for each time registered. Detector calibration was performed by means of several gamma ray emitting nuclides. IAEA reference materials were employed to determine the detector counting efficiency in the radionuclide photopeak region.

In order to verify the precision and accuracy of the analytical method we have analysed the following reference materials: Soil-6 (soil, from IAEA), IAEA-307 (seaweed), IAEA-352 (tuna fish), and IAEA/SD-N-2 (marine sediment). The values obtained are presented in Table 1 and are conclusive in terms of the reliability of the analytical procedures here employed in the determination of the low levels of ^{137}Cs in the environmental samples.

3.3.2. ^{238}Pu and $^{239+240}$Pu analysis

^{238}Pu and $^{239+240}$Pu determinations were carried out by radiochemical separation. The analytical procedures employed in our methodology, with some modifications, followed the methods for analyses of plutonium in soils and sediments described by various authors (Meadows et al., 1975; Holm, 1986; IAEA, 1989; Cunha et al., 1999; Jones et al., 1999; Beks, 2000; Michel et al., 2002; Ugur and Yener, 2002; Vioque et al., 2002). The reliability of our methodology (Fig. 2) was confirmed by analysing reference materials from International Atomic Energy Agency: marine sediments (IAEA-300, IAEA-367, IAEA-368) and soils (Soil-6) as well as by participation in intercomparison analyses organized by the IAEA (IAEA-384 sample).

About 2 to 15 g of the sediment were leached with nitric acid solution and a few drops of hydrogen peroxide, in the presence of ^{242}Pu tracer. Plutonium was coprecipitated with iron hydroxide. The precipitate was dissolved in 8 M nitric acid solution, after the addition of sodium nitrite, during heating. The solution was loaded into the conditioned anion exchange column (Dowex AG1-X8, 100–200 mesh). Americium, iron and uranium were eluted by 8 M nitric acid solution, while thorium was desorbed from the column by passing 10 M hydrochloric acid through it. Plutonium was eluted by using 10 M hydrochloric acid in the presence of 0.6 g of ammonium iodide. Iodine was eliminated by heating the solution and by the addition of concentrated nitric acid. The solution was evaporated to almost total dryness and 0.3 M sodium sulphate solution (1 ml) was added. After the evaporation of the solution, 300 μl of concentrated sulphuric acid were added and plutonium was

electrodeposited (pH = 1.5 to 2.2, constant current of 1.8 A for 75 min) and assayed by alpha spectrometry. Blank analysis was performed simultaneously with the sediment analysis. The results of ^{238}Pu and $^{239+240}$Pu in reference materials are presented in Table 2. The results obtained show that our methodology is appropriated for the detection of low concentrations of plutonium.

4. Results and discussion

4.1. Analysis of the results for sediment samples

The radiochemical procedure for ^{137}Cs and plutonium isotopes in marine sediments from the southeastern Brazilian shelf are presented in Fig. 2. The quantity of sediments employed for the analyses var-

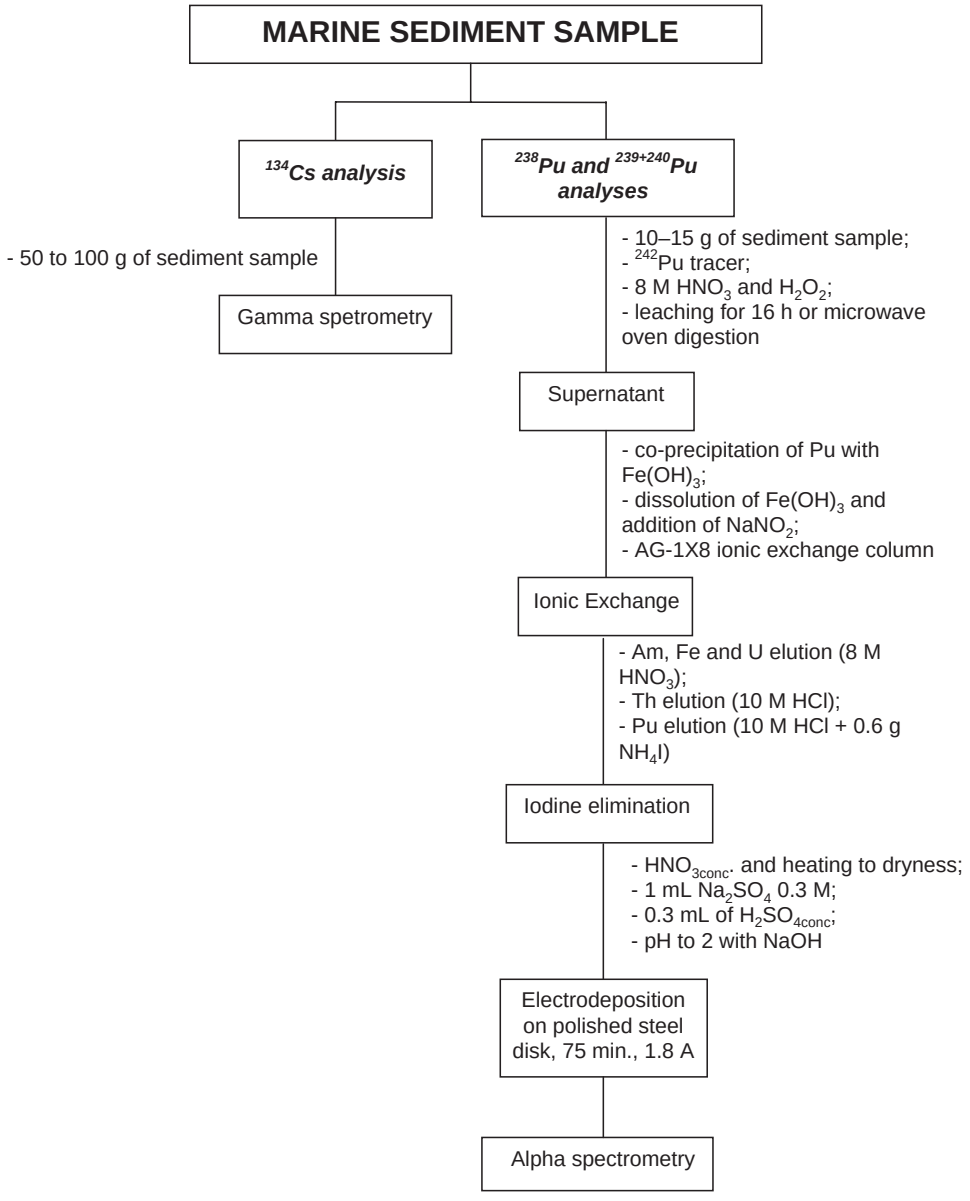

Fig. 2. Methodology for ^{137}Cs, ^{238}Pu and $^{239+240}$Pu analyses of marine sediment samples.

Table 1
Values of ^{137}Cs (Bq kg^{-1}) in reference materials from the International Atomic Energy Agency (IAEA)

Reference material	Certified value[a]	Value obtained	RSD (%)[b]	RE (%)[c]
Soil-6	53.65 (51.43–57.91)	54 ± 1	1.8	0.6
IAEA-307	4.9 (4.5–5.2)	4.7 ± 0.5	10.6	4.1
IAEA-352	2.7 (2.5–2.8)	3.3 ± 0.5	15.1	22.2
IAEA/SD-N-2	0.8 (0.5–1.0)	0.61 ± 0.09	14.7	23.8

[a] Certified value and confidence interval.
[b] Relative standard deviation (RSD).
[c] Relative error (RE).

ied from 50 to 100 g for ^{137}Cs and 10 to 15 g for plutonium isotopes. Table 3 shows the results obtained in the analysis of the sediment samples from the study area. Data show that the levels varied from 0.30 to 1.79 Bq kg^{-1} for ^{137}Cs, from 15 to 150 mBq kg^{-1} for ^{238}Pu and from 18 to 117 mBq kg^{-1} for $^{239+240}Pu$. The radionuclide levels were compared with those of other areas of the North and South Atlantic and the results are presented in Table 4.

The radionuclide levels for the Brazilian coast are similar to those for such areas as Antarctica, the Tyrrenean Sea and the Turkish and Algerian coasts which have not been directly affected by the radioactive contamination due to the effluents from nuclear facilities, deposition of radioactive waste or the Chernobyl accident. Due to this type of contamination, other areas such as the Irish Sea, the English Channel and the Barents Sea present higher artificial radionuclide levels.

A study of the distribution of the radionuclide concentrations in the study area was undertaken (Figs. 3 and 4) and, as stated previously by Mahiques et al. (2004), as regards geochemical and sedimentological parameters, there is a clear difference between the sediments northward and southward from São Sebastião Island. The area off São Sebastião Island marks the boundary between the two main sedimentary zones, which are characterized by differences both in the organic and inorganic fractions of the sediments.

In the sector southward from São Sebastião Island there was a northward increase in ^{137}Cs levels, ranging from 0.50 to 1.79 Bq kg^{-1}. To the north of São Sebastião Island the values were almost constant at levels between 0.30 and 0.62 Bq kg^{-1}. The geographical variations in plutonium distribution also presented the same differentiation between the sectors northward and southward of São Sebastião Island, the lowest values for plutonium being found in the northern sector. These results seem to indicate that these radionuclides are transported by the main hydrodynamic agents of the area, especially by the Subtropical Front that carries water northwards from the Argentinean shelf (Mahiques et al., 2004).

Table 2
Values of ^{238}Pu and $^{239+240}Pu$ (Bq kg^{-1}) in reference materials from the International Atomic Energy Agency (IAEA)

Reference material	Certified value[a]	Value obtained	RSD (%)[b]	RSE (%)[c]
IAEA-300	3.55 (3.44–3.65)	3.6 ± 0.6 (n = 6)	16.7	1.4
IAEA-367	38 (34.4–39.8)	40 ± 1 (n = 6)	2.5	5.2
IAEA-368	31 (29–34)	27 ± 2 (n = 2)	7.4	14.8
IAEA-375	0.299 (0.245–0.339)	0.34 ± 0.04 (n = 1)	11.8	13.7
Soil-6	1.040 (0.962–1.110)	1.2 ± 0.3 (n = 3)	25.0	15.4
IAEA-384	107.0 (105.4–108.9)[d]	95 ± 8 (n = 4)	8.4	11.2
	38.95 (38.10–39.60)[e]	36 ± 2 (n = 4)	5.5	7.6

n is the number of determinations.
[a] Certified value and confidence interval.
[b] Relative standard deviation (RSD).
[c] Relative error (RE).
[d] Values for $^{239+240}$ Pu.
[e] Values for ^{238} Pu.

Table 3
Levels of radionuclides and grain size content in sediments from the southeastern Brazilian shelf

Sample	Lat.	Long.	Depth sampling (m)	^{137}Cs (Bq/kg)	^{238}Pu (mBq/kg)	$^{239+240}$Pu (mBq/kg)	Silt (%)	Clay (%)	Silt+Clay (%)	$^{239+240}$Pu/ ^{137}Cs	^{238}Pu/ ^{137}Cs	^{238}Pu/ $^{239+240}$Pu
6571	−24.212	−44.983	78	0.44 ± 0.11	38 ± 2	112 ± 5	7.99	5.99	13.98	0.255	0.086	0.339
6587	−25.290	−46.353	86	1.79 ± 0.10	28 ± 2	82 ± 4	75.29	13.13	88.42	0.046	0.016	0.341
6598	−26.575	−47.489	97	1.52 ± 0.17	38 ± 1	18 ± 1	56.35	41.32	97.67	0.012	0.025	2.088
6604	−27.536	−47.962	98	1.39 ± 0.07	15 ± 1	44 ± 2	61.62	30.82	92.44	0.032	0.011	0.341
6588	−25.717	−46.816	100	1.44 ± 0.12	27 ± 1	63 ± 3	73.53	25.95	99.48	0.044	0.019	0.429
6541	−23.597	−41.707	143	0.55 ± 0.09	91 ± 4	58 ± 3	47.36	23.68	71.04	0.105	0.165	1.569
6569	−24.248	−44.351	147	0.30 ± 0.09	61 ± 3	44 ± 2	7.94	7.94	15.88	0.147	0.203	1.386
6573	−24.710	−44.724	155	0.62 ± 0.07	79 ± 4	59 ± 3	7.99	2.00	9.99	0.095	0.127	1.339
6606	−27.801	−47.401	176	0.56 ± 0.07	83 ± 4	113 ± 5	0.48	8.00	8.48	0.202	0.148	0.735
6611	−28.406	−47.363	197	0.51 ± 0.11	88 ± 4	69 ± 3	55.62	39.20	94.82	0.135	0.173	1.275
6553	−23.818	−42.780	227	0.50 ± 0.08	<MDC	96 ± 4	10.31	4.12	14.43	0.192	–	–
6591	−26.112	−45.997	410	0.87 ± 0.10	131 ± 6	77 ± 3	72.41	25.34	97.75	0.089	0,151	1.701
6622	−26.516	−46.255	474	1.18 ± 0.08	150 ± 5	117 ± 4	49.46	35.97	85.43	0.099	0.127	1.282
6608	−28.001	−46.995	500	0.83 ± 0.09	<MDC	<MDC	20.02	18.02	38.04	–	–	–
Mean				0.89	69	73				0.112	0.104	1.069
S.D.				0.48	43	30				0.072	0.070	0.608
Median				0.73	70	69				0.099	0.127	1.279
Max				1.79	150	117				0.255	0.203	2.088
Min				0.30	15	18				0.012	0.011	0.339

MDC is the Minimum Detectable Concentration and was 4.2 mBq kg^{-1} for Pu isotope analysis.

There is also a bathymetric differentiation in the radionuclides distribution. ^{137}Cs values are generally higher in the samples collected at water depths of less than 100 m, an exception to this pattern being sample 6571. On the other hand, plutonium isotopes exhibited higher values at greater depths. Fig. 5 shows the levels of radionuclides in terms of depth of sampling.

A comparison of the levels of ^{137}Cs, ^{238}Pu and $^{239+240}$Pu by grain size has been carried out. A significant correlation between ^{137}Cs concentration and clay (<2 μm) and silt (2–63 μm) contents was found, as shown in Fig. 6, thus attesting the role played by grain size in the fixation of ^{137}Cs (Cundy and Croudace, 1995; He and Walling, 1996; Park et al., 2004). Plutonium isotopes did not show a significant correlation with grain size.

An analysis of the behaviour of the plutonium isotopes in their relation to each other revealed a good correlation, taking into account both the shallow (less than 100 m depth) and deep samples, as stated in Fig. 7. Samples 6598 and 6606 are exceptions to this trend.

Table 4
Levels of ^{137}Cs, ^{238}Pu and $^{239+240}$Pu in marine sediments from southeastern Brazilian shelf as compared with those in regions of Antarctica and the Northern Hemisphere

Region	Author	^{137}Cs	^{238}Pu	$^{239+240}$Pu
Southeastern Brazilian shelf	this study	0.30–1.79	0.015–0.150	0.018–0.117
Antarctica (Italian station)	Desideri et al. (2003)	0.14–1.5	<0.0003–0.0125	<0.0003–0.0806
Antarctica (Ross Sea)	Jia et al. (2000)	<0.10–0.96	<0.0003–0.0125	<0.0003–0.0169
English Channel	Boust (1999)	0.12–3.13	0.008–0.448	0.204–1.007
Irish Sea	Jones et al. (1999)	13–4417	1–123	4–780
Spitsberg-Bear (Barents Sea)	Heldal et al. (2002)	0.5–9.3	0.001–0.1	0.01–2.4
Tyrrenean Sea	Desideri et al. (2004)	0.32–19.8	0.0044–0.011	0.04–0.54
Aegean Turkish Coast	Ugur and Yener (2002)	3.2–14.9	0.002–0.09	0.13–0.85
Western Algerian Coast	Noureddine and Baggoura (1997)	6.9–8.5	0.02–0.05	0.3–0.6

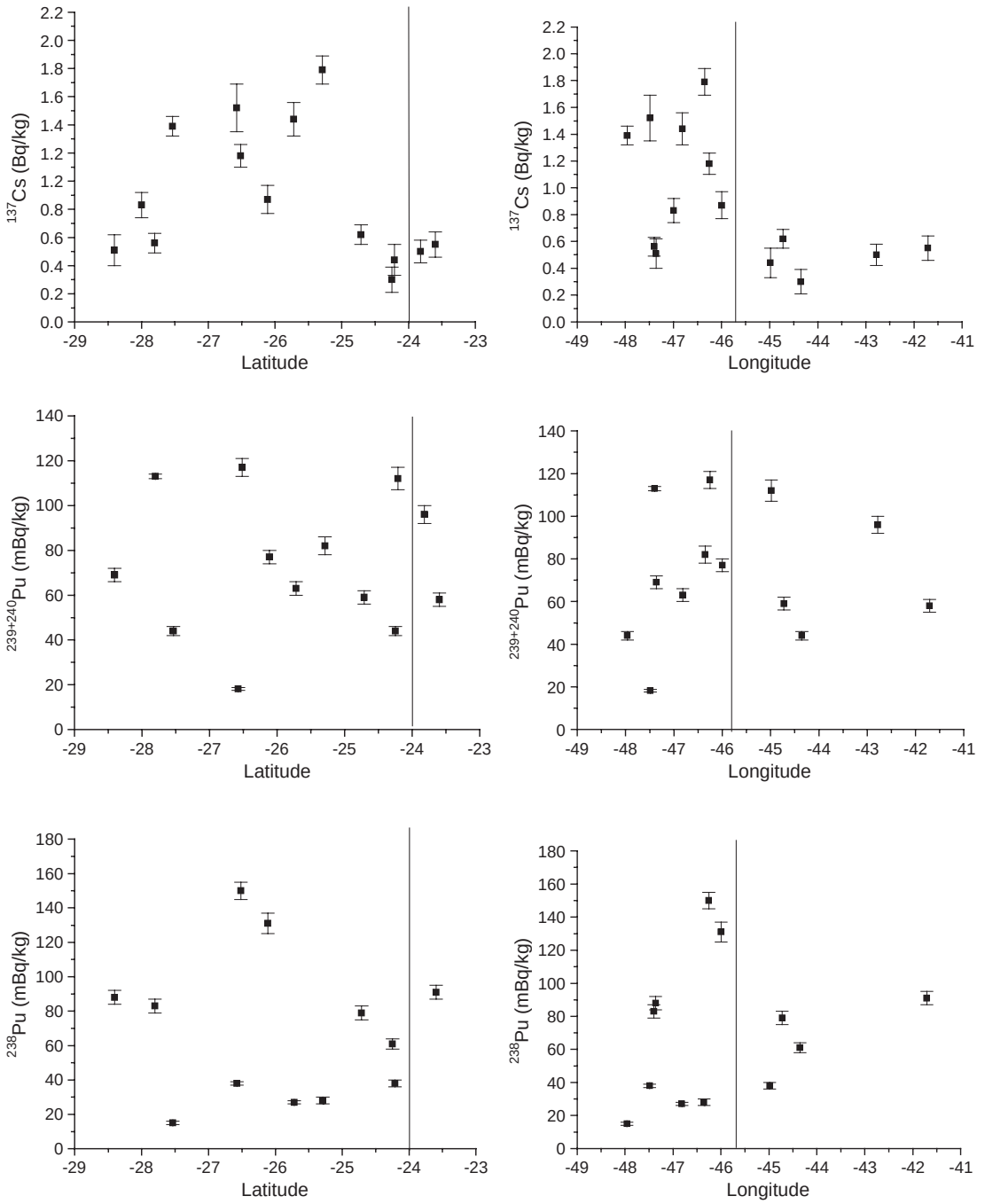

Fig. 3. Latitudinal and longitudinal variations of ^{137}Cs, ^{238}Pu and $^{239+240}Pu$ levels in the study area. The vertical lines in the middle of the graphs represent the position of São Sebastião Island.

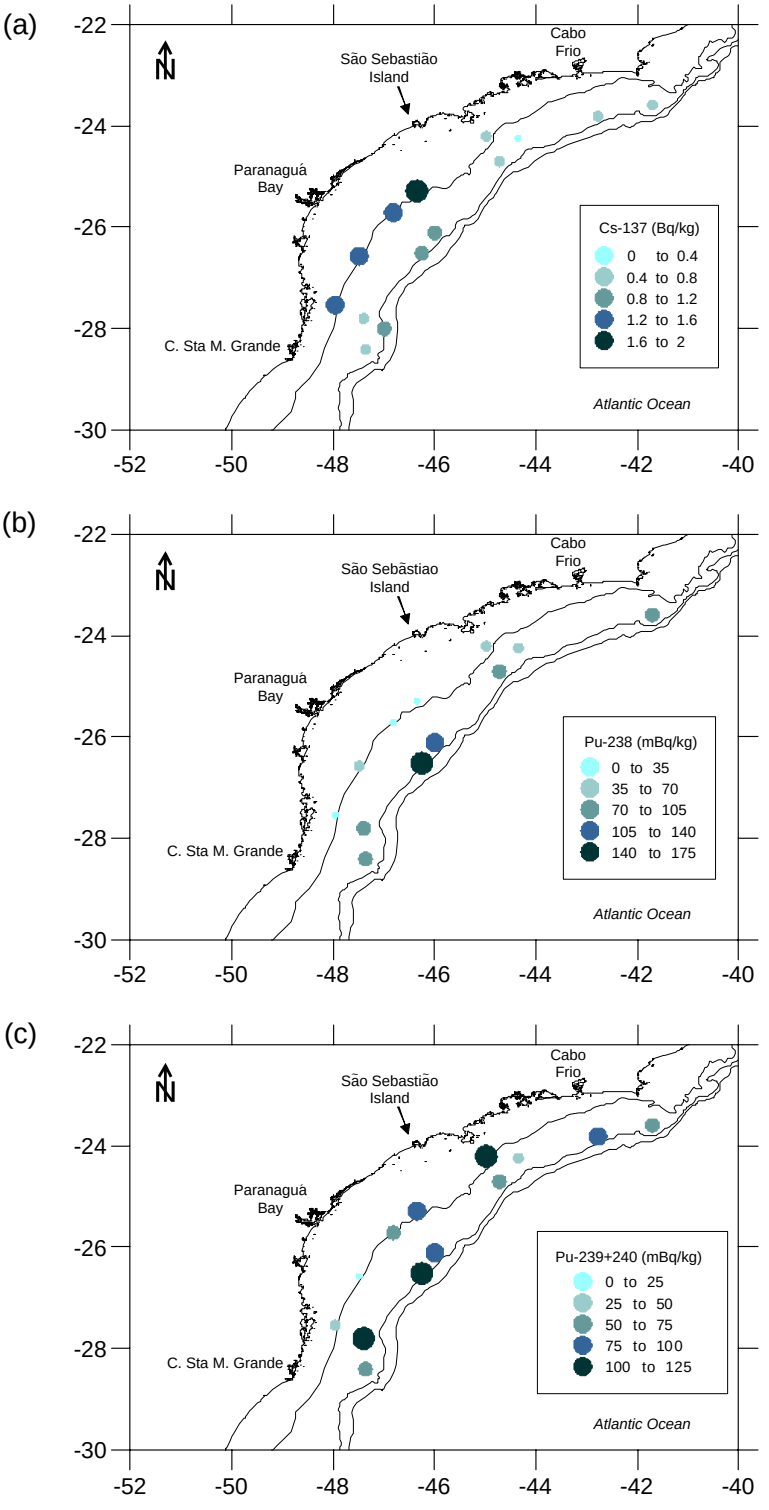

Fig. 4. Distribution of radionuclides in the study area: ^{137}Cs (a), ^{238}Pu (b) and $^{239+240}$Pu (c).

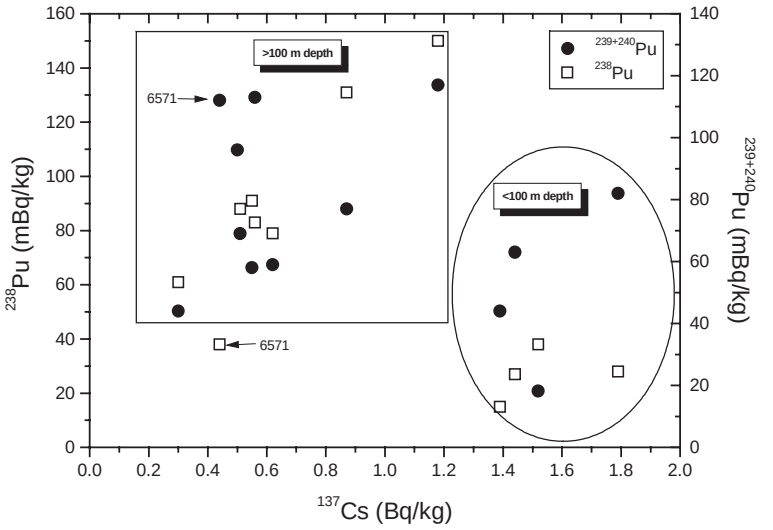

Fig. 5. Levels of radionuclides by sampling depth.

4.2. Analysis of the radionuclide activity ratios

The activity ratios ($^{239+240}Pu/^{137}Cs$, $^{238}Pu/^{137}Cs$ and $^{238}Pu/^{239+240}Pu$) have been used to obtain information as to the sources (such as global fallout, nuclear reprocessing plants and nuclear accidents) of these radionuclides (Baskaran et al., 1996; Jones et al., 1999; Gascó et al., 2002; Michel et al., 2002; Heldal et al., 2002).

Table 3 shows the radionuclide activity ratios in the sediment samples from the southeastern Brazilian shelf. Ratios of $^{239+240}Pu/^{137}Cs$ varied from 0.012 to 0.255, with mean values of 0.112 ± 0.072. This range can be compared with the mean value of 0.17 ± 0.08 reported for the Atlantic slope sediments (Livingston and Bowen, 1979).

A wide spatial variation was obtained in the $^{239+240}Pu/^{137}Cs$ ratios and this is related to the geochemical behaviour of these radionuclides. Bowen et al. (1980) also suggested that fallout of $^{239+240}Pu$ is different from that of ^{137}Cs because this latter has a noble gas as precursor, and it does not lead to significantly higher concentrations of ^{137}Cs. Baxter et al. (1995) have mentioned in their article that plutonium has a spatial inhomogeneity in the oceans with subsequent non-conservative behaviour, thus the inventory of plutonium is not uniformly mixed and activity concentrations vary widely.

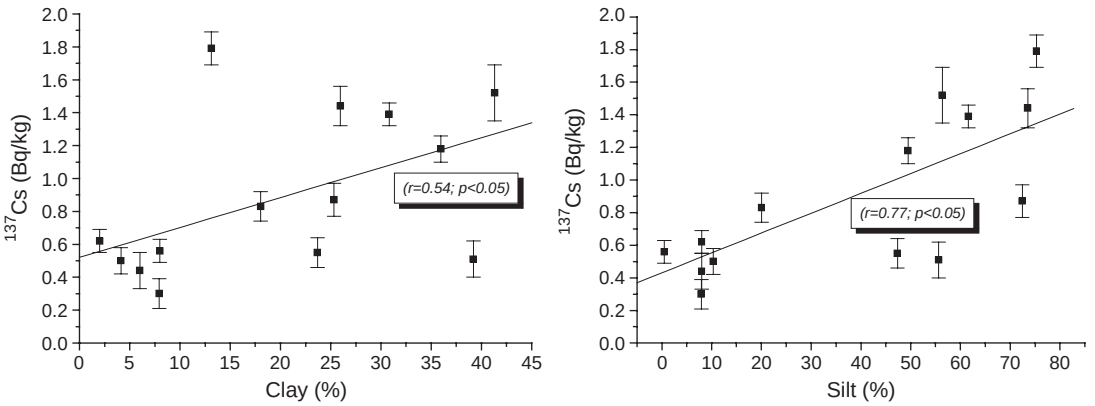

Fig. 6. Levels of ^{137}Cs according to clay and silt content in the sediment samples.

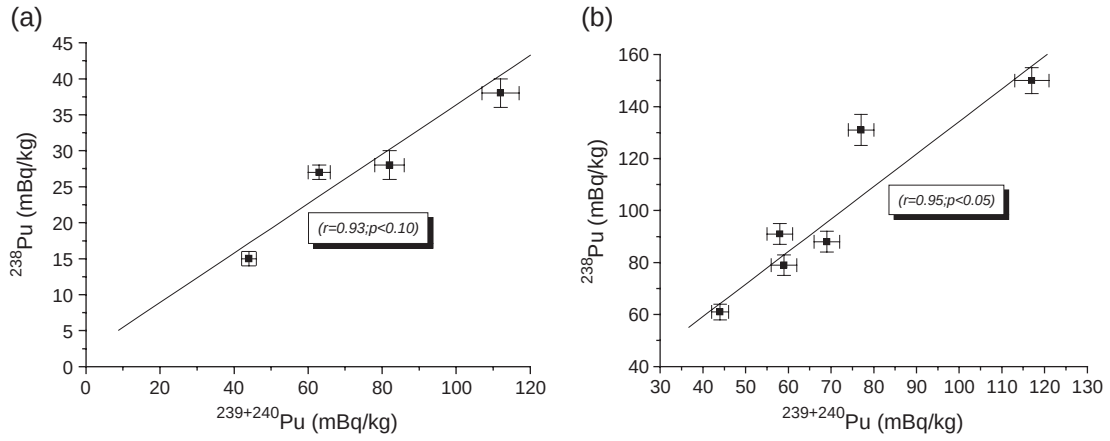

Fig. 7. Correlations of ^{238}Pu and $^{239+240}$Pu in the marine sediments: (a) above the 100 m isobath, (b) below the 100 m isobath.

Hirose et al. (1992) have explained this pattern as due to the difference in the scavenging rates as between the cesium and the plutonium in surface sea water. While most of the cesium remain in the water column, plutonium is readily adsorbed by particulate matter and the ratios may increase in the sediments by the sinking of Pu-enriched particles.

The distribution coefficient (K_d) may help to explain the behaviour of Pu and Cs in the sediments of the study area. An estimate of K_d for both radionuclides was performed by using levels of $^{239+240}$Pu and ^{137}Cs in seawater collected in 1997 in the same region (Figueira et al., 2001). The values of K_d obtained (10 4 for Pu and 10 2 for Cs) agree with data previously published in the literature (10^4–10^5 for Pu and 10^2–10^3 for Cs; IAEA, 1985) showing that plutonium isotopes may be removed due to their great affinity with suspended particulate matter, particularly organic matter, and the slight removal of ^{137}Cs may be due to its lesser affinity with particulate matter (Moon et al., 2003).

Ratios of ^{238}Pu/$^{239+240}$Pu varied from 0.339 to 2.088 Bq kg^{-1}, with a mean value of 1.069 ± 0.608. According to UNSCEAR (1982), the ^{238}Pu/$^{239+240}$Pu ratio in global fallout is 0.0254; this ratio does not differ significantly as between the two hemispheres. However, a satellite (SNAP-9A) containing plutonium reentered the atmosphere of the Southern Hemisphere in 1964, thus, increasing the measured ^{238}Pu levels especially in the Southern Hemisphere beyond those to be expected from nuclear weapon testing. Approximately 22% of the ^{238}Pu reached the Northern Hemisphere, while the remainder settled in the Southern Hemisphere. This event changed the global fallout in the Northern Hemisphere to 0.036 and in the Southern Hemisphere to 0.182 (Linsalata et al., 1980; Sholkovitz, 1983; Aarkrog, 1988; Jia et al., 2000).

The values obtained in this study do not agree with these last estimates, which seem to be very low, since the accident with the SNAP-9A released about 0.51 PBq of ^{238}Pu in the Southern Hemisphere, equivalent to double the amount released by all the nuclear tests put together. So it is difficult to establish a value for the ^{238}Pu/$^{239+240}$Pu ratio because nuclear accidents with satellites may modify the proportion of ^{238}Pu in the sediments relative to that from fallout. There is, further, a lack of experimental data relating to the ^{238}Pu concentration in the Southern Hemisphere. Just as a comparison, the mean ratio of ^{238}Pu/$^{239+240}$Pu in sediment samples from Antarctica ranged from 0.20 to 0.23. These values are 5–10 times higher than those found in the Northern Hemisphere (Desideri et al., 2003) and seven times higher than those for Adriatic Sea sediments, whose value is 0.034 (Jia et al., 1999), these results thus point to a different source for the ^{238}Pu (Marzano et al., 2000; Jia et al., 2000).

5. Conclusions

The determination of ^{137}Cs, ^{238}Pu and ^{239}Pu in marine sediments from the southeastern Brazilian

shelf provides important information about the behaviour of these radionuclides in this area of the South Atlantic. The results lead us to the following conclusions:

(1) The values obtained for the radionuclide levels in the marine sediments were relatively low as compared with those from other areas of the world which have been directly affected by effluents from reprocessing plants, dumped nuclear reactors or influenced by the Chernobyl accident.
(2) A bathymetric differentiation in radionuclide distribution was found. ^{137}Cs values were generally higher in the samples collected at water depths of less than 100 m. On the other hand, plutonium isotopes exhibited higher values at greater depths.
(3) ^{137}Cs showed a good correlation with grain size (clay and silt content) and this is related to the chemistry of this element and its processes of fixation in sediment particles. Plutonium isotopes did not show a significant correlation with grain size. Due to their highly complex chemical behaviour, other parameters, such as those for organic matter, affect the distribution of plutonium isotopes significantly. The organic matter fraction has not been determined in this work, making it impossible to obtain a more detailed study of the geochemistry of plutonium.
(4) The mean ratio of $^{239+240}$Pu/^{137}Cs obtained for the study area (0.112 ± 0.072) agreed with the value reported for atmospheric fallout and showed that the main source of radioactive contamination in Brazil was the nuclear explosions which occurred in the past.
(5) There was a geographical variation in the distribution of Cs and Pu, related to the main hydrodynamic agents that act on the southeastern Brazilian shelf. The values of K_d obtained have helped to understand the difference in the behaviour of these radionuclides as between the shallower and deeper areas.
(6) The experimental values of the ^{238}Pu/$^{239+240}$Pu ratios presented here indicate a change of atmospheric fallout by virtue of the SNAP-9A accident in 1964. However, the values expected for the Southern Hemisphere as stated by UNSCEAR and by Aarkrog (1988) have been underestimated.

Finally, the results presented here are the first report on activity ratios for this area of the Southern Atlantic Ocean. These values obtained are important for the understanding of the behaviour of radionuclides in the marine environment and in the field of isotope geochemistry as well as for the detection of additional contributions of ^{137}Cs, ^{238}Pu and ^{239}Pu from atmospheric fallout in this area. In view of the limited data available for the South Atlantic area, the values of activities and ratios of manmade radionuclides presented here may be taken as reference values for this region.

Acknowledgements

The authors wish to thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for their financial support.

References

Aarkrog A. Worldwide data on fluxes of ^{239,240}Pu and ^{238}Pu to the oceans. Inventory of selected radionuclides in the oceans. Vienna: IAEA; 1988. p. 103–37. IAEA-TECDOC-481.

Aarkrog A. Input of anthropogenic radionuclides into the World Ocean. Deep-Sea Res II 2003;50:2597–606.

Baskaran M, Aslbill S, Santschi P, Brooks J, Champ M, Adkinson D, et al. Pu, ^{137}Cs and excess ^{210}Pb in Russian Arctic sediments. Earth Planet Sci 1996;140:243–57.

Baxter MS, Fowler SW, Povinec PP. Observations on plutonium in the oceans. Appl Radiat Isot 1995;46:1213–23.

Beks JP. Storage and distribution of plutonium, ^{241}Am, ^{137}Cs and ^{210}Pb$_{xs}$ in North Sea sediments. Cont Shelf Res 2000;20:1941–64.

Boust D. Distribution and inventories of some artificial and naturally occurring radionuclides in medium to coarse-grained sediments of the channel. Cont Shelf Res 1999;19:1959–75.

Bowen V, Noshkin VE, Livingston HD, Volchok HL. Fall-out radionuclides in Pacific Ocean: vertical and horizontal distribution largely from GEOSECS stations. Earth Planet Sci Lett 1980;49:411–34.

Calmet D, Sjöeblom K. Inventory of radioactive material entering the marine environment. IAEA Bull 1992;3:25–8.

Cundy AB, Croudace IW. Physical and chemical associations of radionuclides and trace metals in estuarine sediments: an exam-

ple from Poole Harbour, Southern England. J Environ Radioact 1995;29:121–211.

Cunha IIL, Munita CS, Paiva RP, Teixeira AT. Levels of ^{137}Cs in seawater and fish from the Brazilian coast. Sci Total Environ 1993;139/140:431–5.

Cunha IIL, Figueira RCL, Saito RT. Application of radiochemical methods and dispersion models in the study of environmental pollution in Brazil. J Radioanal Nucl Chem 1999;239(3): 477–82.

Desideri D, Giuliani S, Testa C, Triulzi C. ^{90}Sr, ^{137}Cs, ^{238}Pu, $^{239+240}$Pu and ^{241}Am levels in terrestrial and marine ecosystems around the Italian base in Antarctica. J Radioanal Nucl Chem 2003;258(2):221–5.

Desideri D, Giuliani S, Meli MA, Testa C, Triulzi C, Vaghi M. Presence of ^{137}Cs, Pu isotopes and ^{241}Am in Ligurian and Tyrrenean Seas sediments. J Radioanal Nucl Chem 2004; 260(1):9–12.

Figueira RCL, Silva LRN, Figueiredo AMG, Cunha IIL. Instrumental analysis by gamma spectrometry of low level Cs-137 in marine samples. Goiânia, ten years later. Vienna: IAEA; 1998. p. 327–9.

Figueira RCL, Saraiva ESBG, Cunha IIL. Simultaneous analysis of ^{137}Cs, ^{90}Sr, ^{238}Pu and $^{239+240}$Pu in Brazilian seawater. J Radioanal Nucl Chem 2001;248(3):801–4.

Figueira RCL, Tessler MG, Mahiques MM, Zanini KA, Saito RT, Cunha IIL. ^{210}Pb and ^{137}Cs levels in marine sediments from southeastern coast of Brazil, South Atlantic Area. Proceedings of 11th International Congress of the International Radiation Protection Agency, May 23–28, 2004, Madri, Spain; 2004.

Gascó C, Antón MP, Delfanti R, González AM, Meral J, Papucci C. Variation of the activity concentrations and fluxes of natural (^{210}Po, ^{210}Pb) and anthropogenic (^{239,240}Pu, ^{137}Cs) radionuclides in the Strait of Gibraltar (Spain). J Environ Radioact 2002;62:241–62.

Godoy JM, Carvalho ZL, Fernandes FC, Danelon OM, Ferreira AC, Roldão LA. ^{137}Cs in marine samples from the Brazilian southeastern coastal region. J Environ Radioact 2003;70:193–8.

He Q, Walling DE. Interpreting particle size effects in the adsorption of ^{137}Cs and unsupported ^{210}Pb by mineral soils and sediments. J Environ Radioact 1996;30(2):117–37.

Heldal HE, Varskog P, Føyn L. Distribution of selected anthropogenic radionuclides (^{137}Cs, ^{238}Pu, ^{239,240}Pu and ^{241}Am) in marine sediments with emphasis on the Spitsbergen-Bear Island Area. Sci Total Environ 2002;293:233–45.

Hirose K, Aoyama M, Sugimura Y. Plutonium and cesium isotopes in rivers waters in Japan. J Radioanal Nucl Chem, Articles 1992; 156(1):183–200.

IAEA — International Atomic Energy Agency. Sediment K_ds and concentration factors for radionuclide in the marine environment. Technical reports series no. 247. Vienna: IAEA; 1985. 71 pp.

IAEA — International Atomic Energy Agency. Measurement of radionuclides in food and in the environment. Technical reports series no. 295. Vienna: IAEA; 1989. 125 pp.

Jia JG, Testa C, Desideri D, Guerra F, Meli MA, Roselli C, Bell M. Soil concentration, vertical distribution and inventory of plutonium, ^{241}Am, ^{90}Sr and ^{137}Cs in Marche region of Central Italy. Health Phys 1999;77:52–61.

Jia JG, Triulzi C, Marzanno FN, Belli M, Vaghi M. The fate of plutonium, ^{241}Am, ^{90}Sr, ^{137}Cs in the Antarctic ecosystem. Antarct Sci 2000;12(2):141–8.

Jones DG, Roberts PD, Strutt MH, Higgo JJ, Davis JR. Distribution of ^{137}Cs and inventories of ^{238}Pu, $^{239+240}$Pu, ^{241}Am and ^{137}Cs in Irish Sea intertidal sediments. J Environ Radioact 1999;44:159–89.

Holm E. Review of alpha-particle spectrometric measurements of actinides. Int J Appl Radiat lsot 1986;35:285–90.

Holm E, Roos P, Persson RB, Bojanovski R, Aarkrog A, Nielsen SP, Livingston HD. Radiocesium and plutonium in Atlantic surface waters from 73°N to 72°S. In: Kershaw PJ, Woodhead DS, editors. Radionuclides in the study of marine processes. London: Elsevier Applied Science; 1991. p. 3–11. (apud) Aarkrog A. Input of anthropogenic radionuclides into the World Ocean. Deep-Sea Res II 2003;50:2597–606.

Ligero RA, Ramos-Lerate I, Barrera M, Casas-Ruiz M. Relationships between sea-bed radionuclide activities and some sedimentological variables. J Environ Radioact 2004;77:7–19.

Linsalata P, Wrenn ME, Cohen N, Singh NP. ^{239,240}Pu and ^{238}Pu in sediments of Hudson river estuary. Environ Sci Technol 1980; 14:1519–23.

Livingston HD, Bowen VT. Pu and ^{137}Cs in coastal sediments. Earth Planet Sci 1979;43:29–45.

Livingston HD, Povinec PP. Anthropogenic marine radioactivity. Ocean Coast Manag 2000;43:689–712.

Mahiques MM, Silveira ICA, Sousa SHM, Rodrigues M. Post-LGM sedimentation on the outer shelf/upper slope of the northernmost part of São Paulo Bight, south-eastern Brazil. Mar Geol 2002; 181:387–400.

Mahiques MM, Tessler MG, Ciotti MM, Silveira ICA, Sousa SHM, Figueira RCL, et al. Hydrodynamically driven patterns of recent sedimentation in the shelf and upper slope off Southeast Brazil. Cont Shelf Res 2004;24:1685–97.

Marzano FN, Fiori F, Jia G, Chiantore M. Anthropogenic radionuclides bioaccumulation in Antarctic marine fauna and its ecological relevance. Polar Biol 2000;23:753–8.

Meadows JWT, Schweiger JS, Mendoza B, Stone R. Procedure for plutonium analysis of large (100 g) soil and sediment samples. Reference methods for marine studies II Technical reports series no. 169. Vienna: IAEA; 1975. p. 89–96.

Michel H, Barci-Funel G, Dalmasso J, Ardisson G, Appleby PG, Haworth E, El-Daoushy F. Plutonium and americium inventories in atmospheric fallout and sediment cores from Blelham Tarn, Cumbria (UK). J Environ Radioact 2002;59: 127–37.

Moon DS, Hong G, Kim Y, Baskaran M, Chung CS, Kim SH, et al. Accumulation of anthropogenic and natural radionuclides in bottom sediments of the Northwest Pacific Ocean. Deep-Sea Res II 2003;50:2649–73.

Noureddine A, Baggoura B. Plutonium isotopes, ^{137}Cs, ^{90}Sr and natural radioactivity in marine sediments from Ghazaouet (Algeria). J Environ Radioact 1997;34(2):127–38.

Park G, Lin XJ, Kang HD, Lee HL, Kim Y, Doh SH, et al. Properties of ^{137}Cs in marine sediments off Yangnam, Korea. J Environ Radioact 2004;77:285–99.

Pourchet M, Magand O, Frezzoti M, Ekaykin A, Winther JG. Radionuclides deposition over Antarctica. J Environ Radioact 2003;68:137–58.

Rocha J, Milliman JD, Santana CI, Vicalvi MA. Continental margin sedimentation off Brazil. Part 5: Southern Brazil. Contrib Sedimentol 1975;4:117–50.

Saito RT, Figueira RCL, Tessler MG, Cunha IIL. ^{210}Pb and ^{137}Cs geochronologies in the Cananéia-Iguepe estuary (São Paulo, Brazil). J Radioanal Nucl Chem 2001a;249(1):257–61.

Saito RT, Figueira RCL, Tessler MG, Cunha IIL. Geochronology of sediments in the Cananéia-Iguape estuary and in southern continental shelf of São Paulo State, Brazil. J Radioanal Nucl Chem 2001b;250(1):109–15.

Sholkovitz ER. The geochemistry of plutonium in fresh and marine water environments. Earth-Sci Rev 1983;19:95–161.

Ugur A, Yener G. Plutonium isotopes, ^{241}Am, ^{137}Cs activity concentrations in marine sediments of Gökova Bay, Aegean Turkish Coast. J Radioanal Nucl Chem 2002;252(1):47–51.

UNSCEAR — United Nations Scientific Committee on the Effects of Atomic Radiation. Ionizing radiation: sources and biological effects, United Nations. Aarkrog A. Worldwide data on fluxes of ^{239,240}Pu and ^{238}Pu to the oceans. Inventory of selected radionuclides in the oceans. Vienna: IAEA; 1988. p. 103–37. IAEA-TECDOC-481.

Vioque I, Manjón G, Garcia-Tenorio R, El-Daoushy F. Determination of alpha-emitting Pu isotopes in environmental samples. Analyst 2002;127:530–5.

Whitehead NE. Inventory of ^{137}Cs and ^{90}Sr in the world's oceans. Inventory of selected radionuclides in the oceans. Vienna: IAEA; 1988. p. 51–69. IAEA-TECDOC-481.