The fate of plutonium, ^{241}Am, ^{90}Sr and ^{137}Cs in the Antarctic ecosystem

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Abstract: A radioecological survey around Terra Nova Bay showed that $^{239+240}$Pu, ^{238}Pu, ^{241}Am, ^{90}Sr and ^{137}Cs activities were detectable in nearly all the samples. The $^{239+240}$Pu and ^{241}Am concentrations in seawater were slightly lower than those in the northern Pacific Ocean. The activity level of $^{239+240}$Pu, ^{241}Am and ^{137}Cs in Antarctic sediments (Ross Sea) was *c.* 5–20 times lower than in northern Adriatic sediments (Mediterranean Sea), but the ^{238}Pu activities were relatively high. The ^{90}Sr concentrations in all the sediment samples from both the Ross and Adriatic seas tended to be low which might be due to an easier exchange of ^{90}Sr in seawater. On the other hand, high concentrations were detected in Antarctic mosses, lichens and algae and their activity levels are comparable to those in central Italy. The radionuclide ratio analyses show that the major part of $^{239+240}$Pu, ^{241}Am, ^{90}Sr and ^{137}Cs is the result of nuclear weapon tests. A higher ^{241}Am/$^{239+240}$Pu ratio might be due to the fallout of earlier atmospheric nuclear tests. The ^{238}Pu/$^{239+240}$Pu ratio in the Antarctic matrices is about seven times higher than in the Northern Hemisphere and this could suggest that the major part of ^{238}Pu originated from the SNAP-9A satellite accident.

Introduction

Antarctica has long been believed to be one of the cleanest areas in the world because of the low level of human activity (Wolff 1990). Research on environmental radioactivity in the Antarctic ecosystems is of great interest for estimating global environmental pollution caused by nuclear weapon tests and nuclear accidents. In particular, radioecological studies can be helpful for understanding the long range water and atmospheric transport of anthropogenic substances and for exploring the mineral resources. For these purposes, the environmental radioactivity investigations started in 1987 in the framework of the Italian National Program for Antarctic Research. The major part of previous radioecological studies has concentrated on ^{137}Cs and natural ^{40}K, ^{232}Th and ^{238}U concentrations in different environmental components of the Antarctic ecosystems (Triulzi *et al.* 1989, 1991, 1995, Nonnis Marzano & Triulzi 1994a, 1997). The aim of this study is to provide further information on the concentration level, distribution and association of highly toxic and long-lived artificial radionuclides, (^{238}Pu, $^{239+240}$Pu, ^{241}Am, ^{90}Sr and ^{137}Cs), in some abiotic (seawater, sea sediment and lake sediment) and biotic (fish, algae, lichen and moss) samples. Such data should be important as a base-line for the estimation of the future impact of such radioactive pollution on this remote area from any nuclear weapon test or accidental release.

Materials and methods

Apparatus

Plutonium and americium were determined by alpha spectrometry (Silena, Italy) with a counting efficiency of 31%, a background of $< 6\cdot10^{-6}\,\text{s}^{-1}$ over the energy regions of interest and a resolution (FWHM) of 15–25 keV (^{242}Pu). The ^{90}Y sources for ^{90}Sr determination were measured by a flow-gas low background ($6.2\cdot10^{-3}\,\text{s}^{-1}$) beta counter (Canberra-2404, USA) with a counting efficiency of 23%. Gamma spectrometry used a multichannel analyser and a high purity germanium detector with an absolute counting efficiency of 0.95–2.1% at different geometry and a resolution of 1.8 keV for the 661.6 keV line of ^{137m}Ba in equilibrium with its parent ^{137}Cs.

Site

The sampling area is located in the Ross Sea region of Antarctica surrounding the Italian Terra Nova Base. The geographic data of the sampling sites are given in Table I.

Sampling and pretreatment

A number of sample types were collected during the various scientific expeditions to different coastal and offshore sites from 1989–96. Superficial lacustrine and marine sediments

Table I. Sampling sites.

Sample	Sample code	Sampling date	Latitude (S)	Longitude (E)
Sea water	SW1 (UF)	15 Jan 1996	74°41'	164°25'
	SW2 (MnO$_2$)	23 Jan 1996	74°41'	164°10'
	SW3 (MnO$_2$)	3 Feb 1996	*	*
Lacustrine sediment	LS8	15 Jan 1991	74°20'	165°07'
	LS17	15 Jan 1991	74°43'	164°01'
	LS12	15 Jan 1992	74°59'	162°33'
	LS15A	1994–95	74°20'	165°07'
	LS15A	1995–96	74°20'	165°07'
Marine sediment	MS38	7 Jan 1991	74°58'	164°49'
	MS22	29 Dec 1990	74°00'	169°12'
	MS77	2 Feb 1995	75°50'	177°44'W
	MS104	10 Feb 1995	71°30'	174°00'
	MSC	25 Jan 1995	74°43'	164°09'
Terrestrial soil	TS8-1	1991–92	74°20'	165°07'
	TS8-2	1991–92	74°20'	165°07'
Moss	M1	15 Jan 1989	74°20'	165°07'
	M2	15 Jan 1989	74°20'	165°07'
	M3	15 Jan 1989	74°20'	165°07'
	M15	15 Jan 1989	74°20'	165°07'
	M14	15 Jan 1991	74°04'	165°19'
Lichen	L1	15 Jan 1989	74°47'	163°38'
Marine algae	A12	15 Jan 1991	74°59'	162°33'
	A17	15 Jan 1991	74°43'	164°01'
	A15	15 Jan 1996	74°20'	165°07'
Fish flesh	FF	15 Jan 1989	74°43'	164°09'
Fish bone	FB	15 Jan 1990	74°41'	164°08'

*collected during navigation.

were collected by grab, while soils were sampled by hand using plastic and metal tools as appropriate. Most of the sediment and soil samples are sandy with a low content of organics and clay. Detailed soil descriptions for Terra Nova Bay can be found elsewhere (Campbell & Claridge 1987, Bettoli *et al.* 1991). Soil was carefully removed from the lichen and moss collections. The lichen species *Usnea antarctica*, *Candelaria* sp., *Lepraria* sp. and *Umbilicaria* sp. were treated as a single biological type. Mosses and algae were not identified. Fish samples were *Pagothenia bernacchii* and *Adamussium colbecki*. All samples were oven-dried at 105°C to constant weight and ground before analysis. All results refer to dry weight.

The superficial seawater samples collected in some inshore and offshore sites for ^{137}Cs, plutonium and [241]Am determination were pretreated as follows:

To concentrate ^{137}Cs in the laboratory the unfiltered (UF) seawater sample was treated by the ammonium phosphomolybdate [AMP: $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot H_2O$] technique. 100 l unfiltered seawater were acidified with HCl to pH 1 and 60 mg Cs carrier and 10 Bq of [134]Cs spike were added to evaluate the radiochemical separation yield. After a 15–20 min stirring to reach an isotopic

equilibrium, 60 g AMP powder was introduced into the solution. After a 3 h slow stirring and a 48 h settling the clarified supernate was carefully siphoned off. The AMP fraction was then centrifuged and the solid residue was oven-dried at 105°C and stored in a standard Plexiglas container for gamma spectrometry counting.

To concentrate Pu and Am, the unfiltered seawater sample was treated by co-precipitation with iron (II) hydroxide. In this technique, 150 l of unfiltered seawater were acidified with 250 ml 6 M HCl to pH 2 and standard [242]Pu and [243]Am tracers together with 10 ml of Fe^{3+} carrier (50 mg Fe^{3+} ml^{-1}) were added. After 30 min stirring to reach an isotopic equilibrium, 100 ml of 2 M sodium hydrogen sulphite were added. After another 30 min stirring, a second 100 ml of the sulphite solution was added. Then the solution was adjusted to pH 10 with concentrated ammonia solution. The solution was well mixed and the precipitate was allowed to settle overnight. The main fraction of the supernate was carefully siphoned off and the hydroxide slurry was centrifuged. After centrifugation, the remaining supernate was discarded and the precipitate was dissolved with 150 ml 7.5 M HNO_3. The valence adjustment and further separation were carried out with the corresponding radioanalytical procedure given below.

A different technique was used during the 1995 expedition to simultaneously concentrate ^{137}Cs, plutonium and [241]Am from large volumes (3 m^3) of seawater filtered with Millipore filter paper (HAWP14250, 0.45 μm). This sampling device pumped the filtered seawater through a NCFC [ammonium hexacyanocobalt (II) ferrate (II)] and MnO_2 beds at a flow rate of 5 l min^{-1}. The resin beds were sent to the laboratory for ^{137}Cs determination in NCFC by means of direct gamma spectrometry, and for plutonium and [241]Am separation from MnO_2 by the radioanalytical procedure described below.

In order to assess the differences in activity levels for the relevant radionuclides in sediments from both northern and southern hemispheres, six superficial sediment samples collected in northern Adriatic Sea were also analysed. The sampling was performed at the border of the Italian and Croatian international waters in 1990–96. Detailed information about the sampling sites and sediment characters are in Nonnis Marzano & Triulzi (1994b).

Radioanalytical methods

[137]Cs determination. All the moss, lichen, soil and sediment samples were counted for ^{137}Cs activity by gamma spectrometry before any radiochemical separation.

Plutonium determination. After ^{137}Cs determination, 30–120 g samples were taken and ashed in a muffle furnace at 600°C; then 20 mg Sr^{2+}, 10 mg Y^{3+}, 2 mg Te^{4+} as the carriers and known

activities of ^{242}Pu and ^{243}Am (10–30 mBq) were added and two leachings were carried out with 7.5 M HNO$_3$ + 0.2 M HF. The leaching solutions were centrifuged and combined. Plutonium was reduced to Pu (III) with NH$_2$OH·HCl and then oxidized to Pu (IV) with NaNO$_2$. After mineralization and filtration through a Millipore filter paper (0.1 µm), the leaching solution was passed through a column consisting of Microthene (microporous polyethylene) supporting TNOA (tri-n-octyl-amine) for Pu (IV) retention. The effluent was collected for ^{90}Sr and ^{241}Am analyses. Then the column was washed with 10 M HCl and 7.5 M HNO$_3$ and plutonium was eluted by a 0.025 M H$_2$C$_2$O$_4$ + 0.15 M HNO$_3$ solution, electrodeposited on a stainless steel disk at pH 1.5–2.0 and counted by alpha spectrometry.

^{90}Sr determination. ^{90}Sr, ^{90}Y and ^{241}Am were co-precipitated as the oxalates at pH 3 by adding oxalic acid and concentrated ammonia to the HNO$_3$ effluent. After filtration the precipitate was ashed at 800°C. 1 mg of Bi^{3+} carrier was added to the residue which was then dissolved by concentrated HCl and 30% H$_2$O$_2$. The solution in 2 M HCl was passed through a Microthene-TNOA column to eliminate bismuth, polonium and the remaining iron. The effluent was adjusted to pH 0.5–1.0 and passed through a KL-HDEHP [di(2-ethylhexyl) phosphoric acid] resin column to retain yttrium. The column was first washed with 1 M HNO$_3$, then washed with 1 M HCl and finally eluted with 6 M HNO$_3$. The effluent and the first washing solution were collected for ^{241}Am determination. The yttrium in the elution solution was precipitated as the oxalate which was then filtered and counted by a low background beta counter. The chemical yield of yttrium was obtained by complexometric titration with EDTA and Zn^{2+} solutions. For the calculation of the ^{90}Sr concentration, see Jia (1994).

^{241}Am determination. The americium portion was adjusted to pH 2 with concentrated ammonia and passed through a KL-HDEHP resin column. After washing with 0.1 M HNO$_3$, ^{241}Am was eluted with 0.07 M diethylenetriamminopentacetic acid + 1 M L-(+)-lactic acid solution (pH 3), purified by extraction with 0.05 M 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone + 0.025 M tri-octyl-phosphine oxide in cyclohexane, electrodeposited from a 0.025 M H$_2$C$_2$O$_4$ + 0.1 M HNO$_3$ solution at pH 1.5–2.0 on a stainless steel disk and counted by alpha spectrometry (Jia *et al.* 1998).

Analytical quality control and detection limits. The procedure was checked by analysing three certified samples supplied by IAEA (IAEA/soil-6, IAEA-367 sediment, IAEA-368 sediment) and the results were in good agreement with the recommended values (Jia *et al.* 1998). In the routine analyses the detection limits of the procedure for 120 g sample and 2–10 day counting were 0.3 mBq kg^{-1} for $^{239+240}$Pu and ^{238}Pu, 0.4 mBq kg^{-1} for ^{241}Am and 0.10 Bq kg^{-1} for ^{90}Sr and that for ^{137}Cs (500 g sample) was 0.12 Bq kg^{-1}.

Results and discussion

The measured $^{239+240}$Pu, ^{238}Pu, ^{241}Am, ^{90}Sr and ^{137}Cs concentrations in seawater, mosses, lichens, algae, fish, soils and lacustrine and marine sediments are summarized in Table II. Errors cited in the table consist only of the 1 σ error due to the counting statistics. Antarctica and the surrounding ocean have long been considered as unpolluted areas, but the five radionuclides are detectable in most of the matrices at low levels. The concentrations of these radionuclides from different samples are quite varied perhaps due to the very different types of samples. Such radionuclides have probably been trapped with different efficiencies by the different matrices. Higher concentrations are detected in some biological specimens which could be considered as bioindicators.

Plutonium, ^{241}Am and ^{137}Cs concentrations in seawater

As shown in Table II, the $^{239+240}$Pu and ^{238}Pu concentrations in an unfiltered seawater sample (SW1) are about 4–6 times higher than the reported values ($^{239+240}$Pu: 2.0 mBq m^{-3}; ^{238}Pu: 0.3 mBq m^{-3}) in the same region and are lower than those in the northern Pacific Ocean ($^{239+240}$Pu: 4–30 mBq m^{-3}) (Hashimoto *et al.* 1989). Unfortunately, in the cited reference the authors did not clarify whether their seawaters was filtered or not, so an explanation of the differences is not possible. The ^{137}Cs concentration is comparable to the previously reported value (0.07–0.4 Bq m^{-3}) for Terra Nova Bay (Nonnis Marzano & Triulzi 1994a). However, no relevant ^{241}Am results were found for comparison. In contrast, the $^{239+240}$Pu, ^{238}Pu, ^{241}Am and ^{137}Cs concentrations in the filtered seawater samples (SW2 and SW3) are about 5–10 times lower than in SW1. This difference could be attributed to filtration. It could be inferred that most of these radionuclides are combined with or adsorbed onto the solid matrices and only about 10% of them are in the soluble form. This is in good agreement with the observations by Kempe & Nies (1987) who reported that soluble isotopes, like ^{137}Cs, sink to the sea floor in contact with faster sinking particles. The Southern Ocean is certainly very rich in particles during the summer (Holdgate 1970).

Plutonium, ^{241}Am, ^{90}Sr and ^{137}Cs activity level in sediments and soils

The mean $^{239+240}$Pu, ^{238}Pu, ^{241}Am, ^{90}Sr and ^{137}Cs concentrations in lacustrine sediments are 0.0441 ± 0.0424, 0.0072 ± 0.0072, 0.0183 ± 0.0169, 0.44 ± 0.22 and 1.67 ± 1.67 Bq kg^{-1} respectively and the corresponding values in marine sediments are 0.0207 ± 0.0341, 0.0038 ± 0.0052, 0.0122 ± 0.0180, 0.13 ± 0.05 and 0.39 ± 0.40 Bq kg^{-1}. It appears that the concentrations in lacustrine sediments are a little higher than in marine sediments. The ^{137}Cs values agree very well with the previous studies in the region (Triulzi *et al.* 1989, 1991, 1995, Bettoli *et al.* 1991, Nonnis Marzano & Triulzi 1994a). For comparison, Table III shows the concentrations in the sediment samples

Table II. $^{239+240}$Pu, ^{238}Pu, ^{241}Am, ^{90}Sr and ^{137}Cs concentrations (Bq kg^{-1}) in environmental matrices collected from Antarctica in 1989–96 (data for seawater in mBq m^{-3})

Sample code	Pu yield %	$^{239+240}$Pu	^{238}Pu	^{238}Pu/ $^{239+240}$Pu	Am yield %	^{241}Am	^{241}Am/ $^{239+240}$Pu	Y yield %	^{90}Sr	^{90}Sr/ $^{239+240}$Pu	^{137}Cs	^{137}Cs/ $^{239+240}$Pu
SW1	36.2	8.1 ± 1.0	1.7 ± 0.6	0.21	96.1	2.5 ± 0.5	0.43	-	n a	-	390 ± 250	48
SW2	60.1	0.64 ± 0.07	0.12 ± 0.03	0.19	37.2	0.29 ± 0.07	0.45	-	n a	-	90 ± 20	141
SW3	90.0	0.71 ± 0.09	0.13 ± 0.04	0.18	79.2	0.53 ± 0.12	0.75	-	n a	-	64 ± 30	90
LS8	75.3	0.0969 ± 0.0068	0.0171 ± 0.0029	0.18	68.8	0.0298 ± 0.0030	0.308	60.9	0.56 ± 0.09	5.8	2.87 ± 0.36	29.6
LS17	87.1	0.0051 ± 0.0010	0.0018 ± 0.0007	0.35	75.7	0.0036 ± 0.0008	0.70	100	0.31 ± 0.04	61	0.27 ± 0.19	53
LS12	80.5	0.0057 ± 0.0009	0.0019 ± 0.0006	0.33	45.6	0.0023 ± 0.0009	0.40	100	0.41 ± 0.04	72	0.14 ± 0.09	24
LS15A	81.7	0.0327 ± 0.0029	0.0081 ± 0.0015	0.25	70.5	0.0144 ± 0.0020	0.440	100	0.18 ± 0.05	5.5	1.16 ± 0.07	35.5
LS15A	82.5	0.0801 ± 0.0065	0.0199 ± 0.0028	0.25	61.1	0.0412 ± 0.0047	0.514	98.4	0.76 ± 0.09	9.5	3.93 ± 0.35	49.1
MS38	91.4	0.0169 ± 0.0022	0.0044 ± 0.0012	0.26	74.5	0.0074 ± 0.0014	0.44	48.4	0.16 ± 0.05	9.5	0.36 ± 0.04	21
MS22	76.9	0.0056 ± 0.0017	0.0014 ± 0.0008	0.25	83.5	0.0066 ± 0.0014	1.2	67.2	0.21 ± 0.08	38	0.96 ± 0.08	171
MS77	90.2	<0.0003	<0.0003	-	74.2	0.0024 ± 0.0013	>1	63.8	<0.10	-	<0.10	-
MS104	90.7	<0.0003	<0.0003	-	66.4	0.0008 ± 0.0005	>1	55.5	<0.10	-	<0.17	-
MSC	85.0	0.0806 ± 0.0051	0.0125 ± 0.0021	0.16	69.0	0.0440 ± 0.0028	0.546	90.0	<0.18	-	0.40 ± 0.04	5.0
TS8-1	84.8	0.0190 ± 0.0020	0.0030 ± 0.0009	0.16	72.8	0.0103 ± 0.0016	0.542	83.4	0.20 ± 0.04	10.5	1.40 ± 0.08	73.7
TS8-2	90.7	0.0010 ± 0.0004	0.0003 ± 0.0003	0.30	78.8	0.0010 ± 0.0005	1.0	100	0.08 ± 0.04	80	<0.12	-
M1	92.6	0.908 ± 0.096	0.140 ± 0.049	0.15	81.6	0.614 ± 0.084	0.676	99.4	16.2 ± 1.9	17.8	41.4 ± 2.5	45.6
M2	77.6	0.788 ± 0.096	0.206 ± 0.051	0.26	68.6	0.216 ± 0.049	0.274	98.9	14.5 ± 2.2	18.4	29.2 ± 9.4	37.0
M3	61.0	0.435 ± 0.061	0.122 ± 0.034	0.28	40.8	0.210 ± 0.042	0.483	54.3	24.4 ± 3.2	56.1	49.9 ± 3.7	115
M15	82.8	0.637 ± 0.028	0.104 ± 0.012	0.16	55.8	0.276 ± 0.012	0.433	31.4	18.8 ± 1.3	29.5	20.7 ± 2.0	32.5
M14	96.5	0.328 ± 0.007	0.0452 ± 0.0025	0.14	64.4	0.178 ± 0.013	0.543	77.8	9.21 ± 0.49	28.1	11.3 ± 1.7	34.4
L1	54.6	4.64 ± 0.38	0.747 ± 0.092	0.16	30.9	1.94 ± 0.14	0.418	-	n a	-	162 ± 4	34.9
A12	93.2	0.658 ± 0.026	0.150 ± 0.013	0.23	59.0	0.305 ± 0.023	0.464	90.6	3.30 ± 0.34	5.0	37.2 ± 2.6	56.5
A17	42.2	0.201 ± 0.009	0.0365 ± 0.0045	0.18	30.4	0.040 ± 0.014	0.20	-	n a	-	10.4 ± 0.41	51.7
A15	83.5	0.417 ± 0.019	0.118 ± 0.010	0.28	69.6	0.149 ± 0.013	0.357	96.6	9.31 ± 0.90	22.3	17.6 ± 2.2	42.2
FF	92.2	0.0455 ± 0.0054	0.0132 ± 0.0027	0.29	44.3	0.0087 ± 0.0026	0.191	97.5	0.11 ± 0.08	2.4	0.97 ± 0.30	21.3
FB	20.4	0.0010 ± 0.0005	<0.0003	-	74.7	0.0006 ± 0.0004	0.60	99.8	0.08 ± 0.03	80	0.30 ± 0.15	300

n a = not analysed.

Table III. $^{239+240}$Pu, ^{238}Pu, ^{241}Am, ^{90}Sr and ^{137}Cs concentrations (Bq kg^{-1}) in the sediment samples collected in the northern Adriatic Sea in 1990–96

Sample code	Pu Yield %	$^{239+240}$Pu	^{238}Pu	^{238}Pu/ $^{239+240}$Pu	Am Yield %	^{241}Am	^{241}Am/ $^{239+240}$Pu	Y Yield %	^{90}Sr	^{90}Sr/ $^{239+240}$Pu	^{137}Cs	^{137}Cs/ $^{239+240}$Pu
MS 303A	81.5	0.334 ± 0.026	0.014 ± 0.004	0.042	64.6	0.132 ± 0.015	0.395	78.0	< 0.32	-	1.55 ± 0.16	4.6
MS 107A	76.0	0.528 ± 0.029	0.022+0.004	0.042	62.4	0.170 ± 0.018	0.322	95.7	0.51 ± 0.16	1.0	2.94 ± 0.29	5.6
MS 209A	84.8	0.387 ± 0.022	0.012 ± 0.003	0.031	60.9	0.148 ± 0.017	0.382	92.3	< 0.32	-	2.31 ± 0.25	6.0
MS 103A	77.8	0.683 ± 0.025	0.018 ± 0.004	0.026	47.8	0.188 ± 0.016	0.275	87.1	< 0.16	-	3.66 ± 0.31	5.4
MS COR	86.8	0.132 ± 0.013	0.005 ± 0.001	0.038	69.7	0.036 ± 0.008	0.273	81.8	0.33 ± 0.06	2.5	17.5 ± 2.1	132
MS GOR	84.0	0.277 ± 0.015	0.010 ± 0.003	0.036	35.9	0.075 ± 0.008	0.271	90.1	0.22 ± 0.08	0.8	12.7 ± 0.9	46
MS ADA	89.0	0.190 ± 0.011	0.004 ± 0.002	0.021	47.9	0.038 ± 0.005	0.200	98.2	0.18 ± 0.06	0.9	17.2 ± 0.8	90
Mean ± σ	82.8 ± 4.7	0.362 ± 0.192	0.012 ± 0.006	0.034 ± 0.008	55.6 ± 12.0	0.090 ± 0.066	0.302 ± 0.069	89.0 ± 7.3	0.24 ± 0.13	1.3 ± 0.8	8.3 ± 7.2	41 ± 51

collected in the Adriatic Sea. The $^{239+240}$Pu, ^{241}Am and ^{137}Cs activity level in Antarctic sediments is 5–20 times lower than in the Adriatic sediments. As expected, the ^{238}Pu concentrations in Antarctic sediments are relatively higher and similar to those from the Adriatic.

The ^{90}Sr concentrations in Antarctic sediments are also similar to the Adriatic. However, it is noticed that the ^{90}Sr concentrations in all the sediments of both sites tend to be very low, i.e. either lower than the detection limit or just above. The radionuclide activity level in sediment mainly depends on the behaviour of the radionuclides and the physico-chemical form of deposition matrices. It is reported that when ^{90}Sr is leached from condensed fallout particles, the amount of exchangeable strontium increases with the time elapsed from the deposition and it reaches an almost constant value (about 40–75%) after three years (Belli & Tikhomirov 1996). Its binding to soil components is less strong than that of plutonium and ^{137}Cs (Taylor 1968, Killey 1982, Coughtrey & Thorne 1983, Desmet 1997). Radiostrontium is characterized by an almost totally reversible sorption in which the main process is ion exchange. This property of easy exchange leads to a low ^{90}Sr activity in sediments. It is reported that the ^{90}Sr activity on the surface soil in the north temperate zone (latitude: 43°43'30", longitude: 12°53'00") is about 20 times higher than $^{239+240}$Pu (Jia et al. 1999). Therefore, from the ^{90}Sr concentrations in the sediments in Table III, it can be inferred that more than 90% of ^{90}Sr in the fallout has been leached out by seawater during sedimentation (Coughtrey & Thorne 1983). The determination of ^{90}Sr in seawater is thus more important than that in sediment.

Only two terrestrial soil samples were analysed. The concentrations of the radionuclides were comparable to those in sediments possibly because of leaching by meltwater.

Plutonium, ^{241}Am, ^{90}Sr and ^{137}Cs activity level in mosses, lichens and algae

The mean $^{239+240}$Pu, ^{238}Pu, ^{241}Am, ^{90}Sr and ^{137}Cs concentrations in mosses are 0.619 ± 0.241, 0.123 ± 0.058, 0.299 ± 0.180, 16.6 ± 5.6 and 30.5 ± 15.5 Bq kg^{-1} respectively. High ^{137}Cs concentrations (8.9–39.0 Bq kg^{-1}) in mosses from this region were also found by other researchers (Battiston et al. 1991, Triulzi et al. 1995). If compared with the activity in samples collected in central Italy, these values are 3–10 times higher than those in the terrestrial mosses ($^{239+240}$Pu: 0.188 Bq kg^{-1}; ^{238}Pu: 0.0117 Bq kg^{-1}; ^{241}Am: 0.0518 Bq kg^{-1}) and nearly the same level as those in tree trunk mosses with the exception of lower ^{137}Cs concentration ($^{239+240}$Pu: 1.39 Bq kg^{-1}; ^{238}Pu: 0.088 Bq kg^{-1}; ^{241}Am: 0.653 Bq kg^{-1}; ^{90}Sr: 16.7 Bq kg^{-1}; ^{137}Cs: 272 Bq kg^{-1}). Only one bulked lichen sample was analysed and its $^{239+240}$Pu, ^{238}Pu and ^{241}Am concentrations are 4–8 times higher and its ^{137}Cs concentration at the same level if compared with the values for tree trunk lichens collected in central Italy ($^{239+240}$Pu: 1.13 Bq kg^{-1}; ^{238}Pu: 0.097 Bq kg^{-1}; ^{241}Am: 0.436 Bq kg^{-1}, ^{137}Cs: 291 Bq kg^{-1}). The results show that both mosses and lichens are highly efficient accumulators of these

radionuclides, which are taken up from meltwaters, substrate solutions, deposited aerosols, water vapour and rain or snow. The high radionuclide concentrations in mosses and lichens could be due to their large surface area per unit dry weight, their propensity for collecting nutrients from the atmosphere, their slow growth rate and long life. Therefore, both mosses and lichens can be recommended as very good biological indicators of radionuclide pollution caused by nuclear weapon tests and nuclear facility accidents.

The mean $^{239+240}$Pu, ^{238}Pu, ^{241}Am, ^{90}Sr and ^{137}Cs concentrations in marine algae are 0.425 ± 0.229, 0.102 ± 0.058, 0.165 ± 0.133, 6.30 ± 4.25 and 21.7 ± 13.9 Bq kg^{-1} respectively and they are nearly the same levels as those in mosses. If compared with the activity level in algae collected in Adriatic Sea ($^{239+240}$Pu: 0.034 Bq kg^{-1}; ^{238}Pu: 0.002 Bq kg^{-1}; ^{241}Am: 0.016 Bq kg^{-1}; ^{90}Sr: 0.10 Bq kg^{-1}; ^{137}Cs: 3.71 Bq kg^{-1}), the values in Antarctica are 6–10 times higher for $^{239+240}$Pu, ^{241}Am and ^{137}Cs and about 50 times higher for ^{238}Pu and ^{90}Sr. This fact could be due to the lower growth rate of algae in Antarctica, and in particular, to a very peculiar morphology of these species with high surface/volume ratio that increases the capturing area (Bargagli et al. 1993).

Plutonium, ^{241}Am, ^{90}Sr and ^{137}Cs concentrations in fishes

As shown in Table II, the $^{239+240}$Pu and ^{137}Cs concentrations in fish flesh seem comparable to those obtained by Roos et al. (1993) ($^{239+240}$Pu: 0.001–0.012 Bq kg^{-1}; ^{137}Cs: 0.1–4.1 Bq kg^{-1}) in the same region, but no ^{238}Pu, ^{241}Am and ^{90}Sr results are available for comparison. The corresponding values for these radionuclides in fish bone are lower than in fish flesh.

Radionuclide ratios and correlation analyses

The radionuclide activity ratios in these matrices can be utilized to identify the different sources of release. Correlations between concentrations of the analysed radionuclides were tested by Pearson's statistical analysis method.

If the ^{238}Pu concentrations in soils, sediments, mosses, lichens and algae are plotted against the $^{239+240}$Pu concentrations (Fig. 1), the correlation equation is found to be [^{238}Pu] = 0.185[$^{239+240}$Pu]$^{0.930}$, (r = 0.993, n = 19, P < 0.05), showing a statistically significant correlation. For comparison, the correlation of ^{238}Pu to $^{239+240}$Pu concentration in Adriatic Sea sediments {[^{238}Pu] = 0.0337[$^{239+240}$Pu]$^{1.022}$, (r = 0.915, n = 7, P < 0.05)} is also given in Fig. 1. The mean concentration ratio of ^{238}Pu /$^{239+240}$Pu in these Antarctic samples is 0.23 ± 0.06 which agrees well with Hashimoto et al. (1989). This value is about seven times higher than that (0.034) in Adriatic Sea sediments and in soils of central Italy (Jia et al. 1999) and indicates the different ^{238}Pu origin. The ^{238}Pu situation in Antarctica is complex. It was reported that the ratio of bomb test fallout ^{238}Pu/$^{239+240}$Pu in the Antarctic was slightly lower than in the Northern Hemisphere (Roos et al. 1994). Therefore, the major part (90%) of the ^{238}Pu in Antarctica could be a result
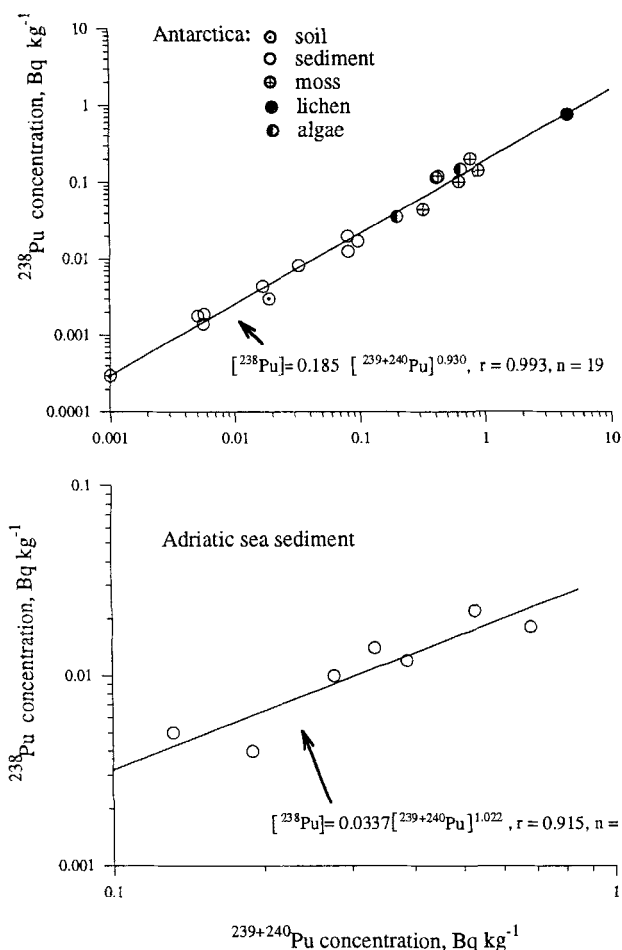
Fig. 1. Correlation between ^{238}Pu and $^{239+240}$Pu concentrations in soils, sediments, mosses, lichens and algae collected from Antarctica and Adriatic Sea.

Fig. 2. Correlation between ^{241}Am and $^{239+240}$Pu concentrations in soils, sediments, mosses, lichens and algae collected from Antarctica and Adriatic Sea.

of ^{238}Pu release from accidental re-entry burn-up of SNAP-9A satellite in the atmosphere of the Southern Hemisphere in 1964. The evidence shows how a failed nuclear-powered device in space provides a potential risk of world-wide radioactive contamination.

A significant correlation between ^{241}Am and $^{239+240}$Pu concentrations in the Antarctic samples was also found (Fig. 2). The equation is $[^{241}$Am$] = 0.382[^{239+240}$Pu$]^{0.904}$, ($r = 0.985, n = 19, P < 0.05$). The high correlation coefficient can be explained by the fact that these nuclides only originate from nuclear explosion tests. The mean ^{241}Am/$^{239+240}$Pu ratio is 0.52 ± 0.24, which is about 73% higher than that (0.30 ± 0.07) in the Adriatic Sea sediments in Fig. 2 $\{[^{241}$Am$] = 0.361[^{239+240}$Pu$]^{1.174}$, ($r = 0.953$, $n = 7$, $P < 0.05$)$\}$ and 49% higher than that (0.35 ± 0.05) in the soils of central Italy. It is interesting to point out that in one soil and one marine sediment the ^{241}Am concentrations are higher than $^{239+240}$Pu and in the other two marine sediments the $^{239+240}$Pu activities are not even detectable but the ^{241}Am activities are. ^{241}Am is not produced directly by nuclear explosions, but is the decay product of the
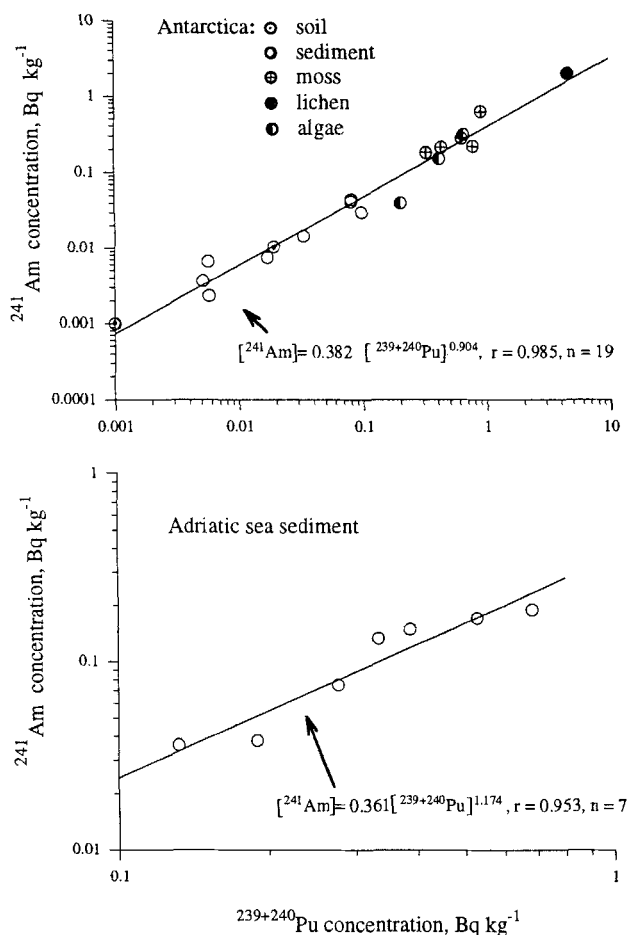
fallout beta emitter ^{241}Pu ($T_{\frac{1}{2}}$: 14.4 y). It is reported that the global fallout ratio of ^{241}Pu/$^{239+240}$Pu in 1962 ranged from 12–16. According to this ratio, it is calculated that the ^{241}Am/$^{239+240}$Pu ratio up to 1997 can be increased to a range of 0.32–0.42 due to the ^{241}Pu decay. This estimated ^{241}Am/$^{239+240}$Pu ratio has been confirmed by a number of radioecological studies in the Northern Hemisphere (Jia *et al.* 1997, 1999), but it seems not to be the case in Antarctica according to our observation. It is reported that high yield US nuclear weapon tests in 1953 (primarily Mike Ivy and Bravo Castle) were characterized by a very high ^{241}Pu/$^{239+240}$Pu ratio (~27) (Koide *et al.* 1981, 1982). The calculations showed that fallout plutonium during 1952–56 constituted about 30% of the total inventory on the Ross Ice Shelf (Koide *et al.* 1979, Roos *et al.* 1994). If the ^{241}Pu/$^{239+240}$Pu ratio is 27, then the ^{241}Am/$^{239+240}$Pu ratio up to 1997 should be 0.75. The higher ^{241}Am concentrations and the observed ^{241}Am/$^{239+240}$Pu ratio difference between Antarctic and Adriatic samples could therefore be the result of earlier fallout deposition. Of course, the ^{241}Am/$^{239+240}$Pu ratio differences could also be caused by the fallout composition, also further complicated by other factors, such
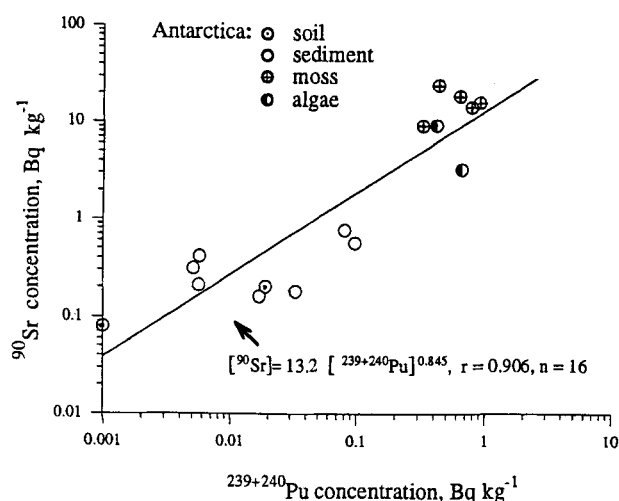
Fig. 3. Correlation between ^{90}Sr and $^{239+240}$Pu concentrations in soils, sediments, mosses and algae collected from Antarctica.
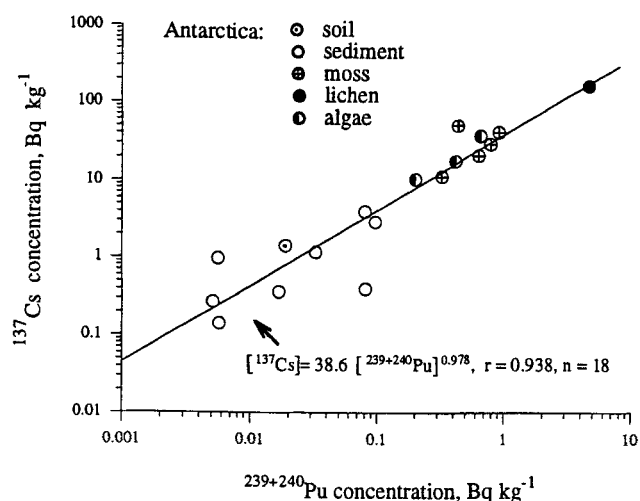

Fig. 4. Correlation between ^{137}Cs and $^{239+240}$Pu concentrations in soils, sediments, mosses, lichens and algae collected from Antarctica.

as the different exchangeability and mobility of americium and plutonium.

The correlation between ^{90}Sr and $^{239+240}$Pu concentrations in Antarctic samples is shown in Fig. 3 and can be expressed as $[^{90}$Sr$] = 13.2[^{239+240}$Pu$]^{0.845}$, ($r = 0.906$, $n = 16$, $P < 0.05$). The mean ^{90}Sr/$^{239+240}$Pu ratio is 29 ± 25 with a range of 5–80. The wide variation of the ratios is perhaps due to the low ^{90}Sr concentrations in lacustrine and marine sediments and to the easy exchange of ^{90}Sr in these matrices. In contrast, the reported ^{90}Sr/$^{239+240}$Pu ratios in soils in the Northern Hemisphere were relatively constant (Jia et al.1999) and they ranged from 5.4 to 17.8 with a mean value of 9.5 ± 3.0. Some of the ^{90}Sr/ $^{239+240}$Pu ratios in the Antarctic samples coincide well with the reported values, but most of them, especially in mosses, show higher values. The reason for such a difference is not yet known. Sr is one of the major nutrient elements for biological species. Due to its relatively high mobility, running meltwater may thus transport and deposit the ^{90}Sr-rich fallout on more organic- or clay-rich ground where mosses are situated. No significant correlation was found between ^{90}Sr and $^{239+240}$Pu concentrations in Adriatic Sea sediments $\{[^{90}$Sr$]=0.514[^{239+} {}^{240}$Pu$]^{0.419}$, ($r = 0.538$, $n = 4$, $P > 0.05$)$\}$.

Figure 4 shows the correlation between ^{137}Cs and $^{239+240}$Pu concentrations in the Antarctic samples with a correlation equation $[^{137}$Cs$] = 38.6[^{239+240}$Pu$]^{0.978}$, ($r = 0.938$, $n = 18$, $P < 0.05$). The mean ^{137}Cs/$^{239+240}$Pu ratio is 51 ± 38 with a range of 5–171. These values are comparable with those obtained for Adriatic Sea sediments in Table III (mean: 41 ± 51, range: 5–132) and for central Italian soils (mean: 78 ± 34, range: 35–155) (Jia et al. 1999). The fluctuation of the ^{137}Cs/$^{239+240}$Pu ratios could be attributed mainly to the localized transport processes immediately following the deposition of ^{137}Cs. However, the correlation between ^{137}Cs and $^{239+240}$Pu concentrations in Adriatic samples $\{[^{137}$Cs$] = 1.19[^{239+240}$Pu$]^{-1.33}$, ($r = -0.741$, $n = 7$, $P > 0.05$)$\}$ is not statistically significant.

After carefully examining the samples in Table III, it was found that the first four sediments with low ratios were collected in June 1990 and the last three with high ratios in July 1996. Therefore, the ^{137}Cs concentrations in the first four samples perhaps were less influenced by the fallout from Chernobyl nuclear accident.

As shown in Table II, the mean yields of plutonium, americium and yttrium in soils, sediments, mosses, lichen and algae are $81.0 \pm 13.5\%$, $63.9 \pm 15.3\%$ and $79.8 \pm 21.8\%$ respectively. These data indicate that the sequential separation and determination procedure for plutonium, ^{241}Am and ^{90}Sr in these matrices worked very satisfactorily.

Acknowledgements

References

Bargagli, R., Battisti, E., Focardi, S. & Formichi, P. 1993. Preliminary data on environmental distribution of Hg in Northern Victoria Land, Antarctica. *Antarctic Science*, **5**, 3–8.

Battiston, G.A., Degetto, S., Gerbasi, R. & Sbrignadello, G. 1991. Radionuclide content in various samples collected near the Italian bases in Antarctica. *Annali di Chimica*, **81**, 469–475.

Bettoli, M.G., Cantelli, L., Tositti, L., Tubertini, O. & Valcher, S. 1991. Distribution of ^{137}Cs in lake sediments and surrounding soils at Terra Nova Bay, Antarctica. *Annali di Chimica*, **81**, 541–548.

BELLI, M. & TIKHOMIROV, F. 1996. *Behaviour of radionuclides in natural and semi-natural environments.* Luxembourg: EUR 16531 EN, 87–93.

CAMPBELL, I.B. & CLARIDGE, G.G.C. 1987. *Antarctica: soils, weathering processes and environment.* Amsterdam: Elsevier Science Publishers, 368 pp.

COUGHTREY, P.J. & THORNE, M.C. 1983. *Radionuclide distribution and transport in terrestrial and aquatic ecosystems: a critical review of data.* Rotterdam: A.A. Balkema, 212–222.

DESMET, G., BLUST, R.J., COMANS, R.N.J., FERNANDEZ, J.A., HILTON, J. & BETTENCOURT, A.D. 1997. *Studies in environmental science 68. Freshwater and estuarine radioecology. Proceedings of an international seminar, Lisbon, Portugal, 21–25 March 1994.* Amsterdam: Elsevier, 87–95.

HASHIMOTO, T., MORIMOTO, T., IKEUCHI, Y., YOSHIMIZU, K., TORII, T. & KOMURA, K.A. 1989. Survey of artificial radionuclides in the Antarctic. *Radioisotopes,* **35**, 209–218.

HOLDGATE, M.W. 1970. Antarctic marine ecosystems. *In* HOLDGATE, M.W., *ed. Antarctic ecology,* vol. 1. London: Academic Press, 70–75.

JIA GUOGANG. 1994. A rapid and accurate method for determination of ^{90}Sr in environmental soils. *Journal of Radioanalytical and Nuclear Chemistry,* **185**, 255–264.

JIA GUOGANG, DESIDERI, D., GUERRA, F., MELLI, M.A. & TESTA, C. 1997. Concentration and vertical distribution of plutonium and americium in Italian mosses and lichens. *Journal of Radioanalytical and Nuclear Chemistry,* **222**, 3–9.

JIA GUOGANG, TESTA, C., DESIDERI, D., GUERRA, F. & ROSELLI, C. 1998. Sequential separation and determination of plutonium, ^{241}Am and ^{90}Sr in soils and sediments. *Journal of Radioanalytical and Nuclear Chemistry,* **230**, 21–27.

JIA GUOGANG, TESTA, C., DESIDERI, D., GUERRA, F., MELI, M.A., ROSELLI, C. & BELLI, M. 1999. Soil concentration, vertical distribution and inventory of plutonium, ^{241}Am, ^{90}Sr and ^{137}Cs in Marche region of Central Italy. *Health Physics,* **77**, 52–61.

KEMPE, S. & NIES, H. 1987. Chernobyl nuclide record from a North Sea sediment trap. *Nature,* **329**, 828–831.

KILLEY, R. 1982. Long-term ^{90}Sr behaviour in a sand aquifer. Proceedings series of environmental migration of long-lived radionuclides. Vienna: IAEA, IAEA-SM-257/86P, 86 pp.

KOIDE, M., MICHEL, R. & GOLDBERG, E.D. 1979. Depositional history of artificial radionuclides in the Ross Ice Shelf, Antarctica. *Earth and Planetary Science Letters,* **44**, 205–223.

KOIDE, M. & GOLDBERG, E.D. 1981. ^{241}Pu/$^{239+240}$Pu ratios in polar glaciers: Antarctica. *Earth and Planetary Science Letters,* **54**, 239–247.

KOIDE, M., MICHEL, R., GOLDBERG, E.D. & HERRON, M.M. 1982. Characterization of radioactive fallout from pre- and post-moratorium tests to polar ice caps. *Nature,* **296**, 544–547.

NONNIS MARZANO, F. & TRIULZI, C. 1994a. Radioecological research on the marine environment facing the Italian Base in Antarctica (1989–91). *International Journal of Environmental Analytical Chemistry,* **55**, 243–252.

NONNIS MARZANO, F. & TRIULZI, C. 1994b. Radioecological survey of Northern and Middle Adriatic Sea before and after Chernobyl event (1979–1990). *Marine Pollution Bulletin,* **28**, 244–253.

NONNIS MARZANO, F. & TRIULZI, C. 1997. Antarctic marine radioactivity survey at Terra Nova Bay, Ross Sea. *Radioprotection Collogues,* **32**, 35–40.

ROOS, P., HOLM, E., PERSSON, R.B.R., AARKROG, A. & NIELSEN, S.P. 1993. Environmental radioactivity in the Antarctic Peninsula area. *Proceedings of International Conference on Environmental Radioactivity in the Arctic and Antarctic, 23–27 August, Kirkenes (Norway),* 183–194.

ROOS, P., HOLM, E., PERSSON, R.B.R., AARKROG, A. & NIELSEN, S.P. 1994. Deposition of ^{210}Pb, ^{137}Cs, $^{239+240}$Pu, ^{238}Pu and ^{241}Am in the Antarctic Peninsula area. *Journal of Environmental Radioactivity,* **24**, 235–251.

TAYLOR, A. 1968. Strontium retention in acid soils of the North Carolina coastal plain. *Soil Science,* **106**, 440–447.

TRIULZI, C., MANGIA, A., CASOLI, A., ALBERTAZZI, S. & NONNIS MARZANO, F. 1989. Artificial and natural radionuclides, alkaline and earth-alkaline elements in some environmental abiotic samples of Antarctica. *Annali di Chimica,* **79**, 723–733.

TRIULZI, C., NONNIS MARZANO, F., MORI, A., CASOLI, A. & VAGHI, M. 1991. Presence of radionuclides in biotic and abiotic matrixes collected in the environment around the Italian base in Antarctica. *Annali di Chimica,* **81**, 549–561.

TRIULZI, C., NONNIS MARZANO, F., CASOLI, A., MORI, A. & VAGHI, M. 1995. Radioactive and stable isotopes in abiotic and biotic components of Antarctic ecosystems surrounding the Italian Base. *International Journal of Environmental Analytical Chemistry,* **61**, 225–230.

WOLFF, E.W. 1990. Signals of atmospheric pollution in polar snow and ice. *Antarctic Science,* **2**, 189–205.