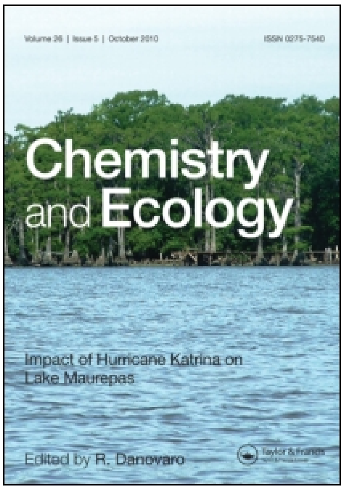

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HEAVY METALS AND RADIOCHEMICAL ANALYSES IN THE SEDIMENTS OF THE RAPALLO HARBOUR

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To assess the natural and anthropogenic radiocontamination, sediment samples were collected in the Tigullio Gulf (Ligurian Sea). The results presented here indicate a significant Cs-137 contamination (about 20 $Bqkg^{-1}$ dry weight) while concentrations of "primordial" natural radioisotopes were similar to those detected in other coastal areas. Gross sedimentation rates, determined through measurements of Be-7 concentrations, were at about 4–5 cm in the last 6 months. Natural and artificial radioactivity concentrations have been compared with data obtained in other Mediterranean areas. Heavy metals (Cu, Cr, Mn, Ni, Zn, Pb, Cd, Hg) concentrations were also determined inside the bay. Most elements displayed quite constant concentrations through the sediment core, except for copper which had showed highest concentrations in the top 16 cm of the sediment.

Keywords: Heavy metals; artificial radioisotopes; natural radioisotopes; sediment; Be-7; Cs-137

1. INTRODUCTION

Coastal environments are often very sensitive areas frequently affected by major pollution events. The sedimentary compartment often represents the final point of pollution accumulation so that monitoring

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of anthropogenic contaminants in shallow soft bottom areas is a steady point in marine science research. In the past decade, several coastal Mediterranean ecosystems have been investigated widely by our research group, and the results have highlighted the major role of confined environments, such as river estuaries, on radionuclides and heavy metals accumulation (Nonnis Marzano and Triulzi, 1994; Bondavalli *et al.*, 1996; Nonnis Marzano *et al.*, 1996).

Chemical and radiochemical determinations have been carried out in the Rapallo Harbour with the aim of an environmental contamination assessment of this Ligurian system. The present investigations were carried out in the frame of the "Esperienze di camere bentiche nel Golfo del Tigullio" project (Benthic chambers experiments in the Tigullio Gulf) (Della Croce, 1998; Fig. 1) in cooperation with the Istituto di Scienze Ambientali Marine of the University of Genoa.

The concentrations of artificial Cs-137 and natural Be-7, K-40, Pb-210, Ra-226 and Th-232 are reported and discussed. In particular, Be-7 concentrations and vertical distributions in the sediments core have been determined to estimate the sedimentation rates inside the Rapallo Harbour. However, in relation to the quite short half life of this radioisotope (53 days) and its seasonal atmospheric deposition, only the surface sediment strata were considered (Queirazza and Guzzi, 1989).

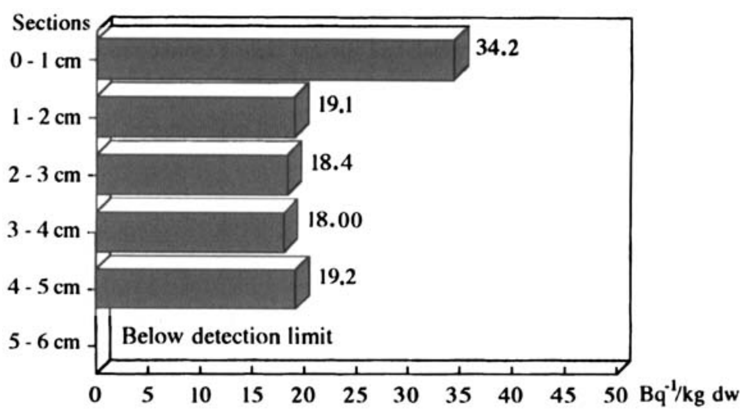

FIGURE 1 Vertical distribution of Be-7 in the Rapallo Harbour sediment core.

Concentrations of both natural and anthropogenic radioactivity have been compared with data obtained in other Mediterranean coastal and offshore areas during previous years (Triulzi *et al.*, 1995; Nonnis Marzano and Triulzi, 1998).

In addition, concentrations of several heavy metals (such as Cu, Cr, Mn, Ni, Zn, Pb, Cd and Hg) have been determined to complete the present environmental monitoring. The chemical data seemed particularly interesting especially for copper although little information was obtained for what the sedimentation rates were confirmed.

2. MATERIALS AND METHODS

Two sediment cores (diameter 6 cm) were collected down to 30 cm depth in the Rapallo Harbour just the day before the positioning of the benthic chamber (October, 1996). The sediment cores have been vertically sectioned into 1 cm layers in the top 10 centimeters and in 2 cm layers in the part underneath the top ten centimetres following the technique described by Ciceri and Martinotti (1988). Corresponding sections of the two cores have been pooled together to obtain enough analytical material for each single stratum.

Each sediment layer has been dried, finely ground and placed in a suitable container after density evaluation through determination of the weight/volume ratio (Ciceri and Martinotti, 1988). Radioanalytical determinations were then carried out by means of a low energy – high purity germanium detector for direct gamma spectrometry (Nonnis Marzano and Triulzi, 1994).

Chemical analyses on heavy metals content were performed by means of spectroscopic techniques (AAS and ICP – AES) after acid solubilization of the sediment samples (Ciceri *et al.*, 1992).

Concentrations of radioactive isotopes are reported as $Bq kg^{-1}$ dry weight. Radioactive concentrations were decay corrected at sampling time, while stable elements are expressed as ppm.

All techniques have been fully described in previous publication with special regard to the chemical and radioanalytical procedures (Ciceri *et al.*, 1992; Nonnis Marzano and Triulzi, 1994).

3. RESULTS AND DISCUSSION

Cs-137 was the only artificial gamma – emitting radionuclide detected in the investigated area. This radionuclide was originated partly by the atmospheric nuclear testing of the '50s–'70s period and more consistently by the Chernobyl accident (April 26, 1986) (Nonnis Marzano and Triulzi, 1994; Nonnis Marzano *et al.*, 1996). In spite of the long time elapsed since the ground deposition of the Chernobyl fallout, the long half life of Cs-137 ($T_{1/2}$ = 30.2 years) has made this caesium isotope still measurable in each single core section (Tab. I). Although the radiocaesium data were lower than values of natural radioactivity, its concentrations were much higher than those detected in other areas of the Ligurian Sea by Papucci *et al.* (1996).

The reported values appear anomalous if we consider that Cs-137 concentrations detected in sediment samples of the Sacca di Goro (a lagoon of the Po River Delta) were lower than 16 $Bq kg^{-1}$ dw in 1996 (Fiori and Nonnis Marzano, 1997). In the past, several authors have often referred to the lagoon ecosystem as a major radiocaesium reservoir (Bondavalli *et al.*, 1996; Desideri *et al.*, 1996; Fiori and Nonnis Marzano, 1997). The slow water circulation inside this shallow harbour (5 metres depth) coupled with consistent freshwater inputs by the "Torrente Boate", and the deposition of fine matter, are likely to be the main responsibility for such a strong accumulation. Chemical and hydrobiological parameters such as ammonium and oxygen contents, water turbidity and fine matter settling, determined during the benthic chambers experiment and seem to confirm this hypothesis (Ceradini and Ciceri, 1997).

On the contrary, natural radioactivity data were similar to the ones detected in other marine areas with terrigenous sediments (Triulzi *et al.*, 1995; Fiori *et al.*, 1997). However, as far as natural radionuclides are concerned, a special emphasis was given to concentrations of Be-7. The distribution of this short-living radionuclide ($T_{1/2}$ = 53 days) in the different core sections, as a function of depth, has allowed a good estimation of the sedimentation rates, which has been estimated at around 4–5 cm over the last 6 months.

It has to be remarked that this calculation refers only to the first few core centimeters, because of the particular radiochemical characteristics of Be-7 (Queirazza and Guzzi, 1989), and the frequent

TABLE I Concentrations of artificial and natural radionuclides in the sediments of the Rapallo Harbour (Genoa)

Strata cm	*Weight* g	*Dry density* gml^{-1}	*Th*-232 $Bqkg^{-1}dw$	*Ra*-226 $Bqkg^{-1}dw$	*Cs*-137 $Bqkg^{-1}dw$	*K*-40 $Bqkg^{-1}dw$	*Pb*-210 $Bqkg^{-1}dw$	*Be*-7 $Bqkg^{-1}dw$
0–1	55.0	1.0	30.5 ± 1.0	24.3 ± 1.0	19.6 ± 1.1	416.6 ± 22.9	215.3 ± 12.2	34.2 ± 3.0
1–2	74.0	1.3	26.9 ± 0.9	23.1 ± 0.9	18.6 ± 1.0	347.9 ± 18.9	176.7 ± 9.9	19.1 ± 2.3
2–3	72.0	1.3	30.4 ± 1.1	23.3 ± 1.1	19.3 ± 1.2	389.5 ± 23.5	178.5 ± 11.9	18.4 ± 3.8
3–4	80.0	1.4	36.8 ± 1.7	27.2 ± 1.6	23.9 ± 1.9	502.0 ± 39.8	289.4 ± 23.9	18.0 ± 4.0
4–5	60.0	1.1	24.6 ± 1.1	20.7 ± 1.1	17.6 ± 1.2	339.9 ± 21.7	179.0 ± 12.7	19.2 ± 4.5
5–6	80.5	1.4	29.7 ± 1.1	18.0 ± 0.8	17.4 ± 1.1	383.3 ± 22.0	149.0 ± 9.9	
6–7	91.3	1.6	29.5 ± 1.0	18.8 ± 0.8	14.1 ± 0.9	397.9 ± 22.5	126.2 ± 8.2	
7–8	92.6	1.6	32.6 ± 1.3	19.3 ± 1.1	11.6 ± 0.9	437.7 ± 27.5	112.1 ± 10.4	
8–9	86.7	1.5	32.1 ± 1.4	16.4 ± 1.0	10.7 ± 1.0	407.8 ± 26.1	110.1 ± 10.8	
9–10	86.7	1.5	33.9 ± 1.3	17.9 ± 0.9	8.7 ± 0.7	443.0 ± 25.9	98.5 ± 8.6	
10–12	165.7	1.5	38.4 ± 1.7	23.8 ± 1.4	10.7 ± 0.9	511.2 ± 40.0	154.5 ± 13.9	
12–14	158.3	1.4	38.5 ± 1.6	23.4 ± 1.2	9.8 ± 0.9	530.5 ± 33.0	174.7 ± 15.8	
14–16	159.6	1.4	41.3 ± 2.0	23.2 ± 1.5	10.6 ± 1.0	508.1 ± 41.0	131.8 ± 14.1	
16–18	156.5	1.4	39.0 ± 1.5	20.8 ± 1.1	8.4 ± 0.7	483.5 ± 36.7	123.1 ± 9.9	
18–20	177.4	1.6	37.6 ± 1.1	19.9 ± 0.8	8.5 ± 0.5	478.9 ± 25.5	108.5 ± 6.6	
20–22	166.2	1.5	37.9 ± 1.9	20.6 ± 1.4	9.2 ± 0.9	502.0 ± 40.7	137.4 ± 15.0	
22–24	173.4	1.5	41.4 ± 1.7	22.5 ± 1.1	9.6 ± 0.9	488.1 ± 31.1	85.8 ± 10.2	
24–26	105.9	0.9	41.9 ± 1.5	22.1 ± 1.1	9.4 ± 0.9	495.3 ± 29.0	143.1 ± 12.1	
26–28	80.0	0.7	39.3 ± 1.5	20.1 ± 1.1	8.9 ± 0.8	483.0 ± 29.7	93.4 ± 9.6	
28–30	101.7	0.9	44.3 ± 2.0	23.5 ± 1.4	9.7 ± 1.0	526.7 ± 41.5	131.0 ± 13.2	
30–32	41.1	0.4	37.7 ± 1.5	17.0 ± 1.1	11.3 ± 1.1	437.9 ± 28.1	77.7 ± 8.5	

dredging of the harbour. In fact, since most of Be-7 is introduced in the lower atmospheric strata during April and May it is worth considering that the first 4–5 core centimetres refer to the past 5–6 months (Fig. 1).

A comparison with artificial and natural radionuclides detected between 1991 and 1996 in surface sediments from other Mediterranean coastal and offshore areas is presented in Table II. As it can be noticed, Cs-137 concentrations in the Rapallo Harbour were similar to the ones detected in the coastal Adriatic Sea. The Adriatic Sea was one of the Mediterranean areas noted in the Chernobyl accident but the Ligurian Sea was less influenced. For this reason, the data from the Rapallo Harbour is much higher than what was expected.

Vertical distribution of concentrations of heavy metals found were quite homogeneous for most elements (such as Cr, Mn, Ni, Zn, Pb, Cd and Hg). By contrast, the vertical distribution of copper displayed much higher concentrations in the top 16 cm (Tab. III). In spite of the major turbation of the harbour brought by annual dredging, these copper concentrations could actually indicate the presence of a relatively recent input. In fact, such input has probably happened in a period of time just after the last dredging.

Although such differences occur, the heavy metals concentrations were in good agreement with the ones reported by CISE Divisione Ambiente (1991) for another Ligurian Gulf, the La Spezia Gulf.

TABLE II Comparison between Cs-137, Th-232 and U-238 ranges of concentrations ($Bq kg^{-1} dw$) detected in different Mediterranean areas (1991–96)

Study area	*Cs*-137	*Th*-232	*U*-238
This work (Rapallo Harbour, 1996)	19.6	30.5	24.3
Offshore Ligurian Sea (Vado Ligure canyon, 1996)	< 0.14–8.56	63.38	34.1
Coastal Adriatic Sea (Po River Delta, 1990)	2.94–18.1	ND	ND
Offshore River Delta, 1990) (Venice - Ancona, 1990)	1.70–2.50	ND	ND
Coastal South. Thyrrenian (Eolian Islands, 1995)	0.30–0.40	3.90–21.3	1.70–18.5
Offshore Islands, 1995) (Eolian. Islands, 1996)	< 0.7–6.10	40.5–138	15.2–69.4

ND: Not determined.

TABLE III Heavy metals concentrations (ppm) in different sediment core sections collected in the Rapallo Harbour (Genoa) in 1996 (Concentrations are $\mu g\,g^{-1}$)

Strata cm	*Cu*	*Cr*	*Mn*	*Ni*	*Zn*	*Pb*	*Cd*	*Hg*
0–1	124	27	238	25	153	72	1.0	0.21
1–2	121	27	231	24	149	70	1.1	0.19
2–3	122	27	232	25	150	75	1.1	0.17
3–4	121	27	233	25	157	71	1.0	0.18
4–5	119	26	228	24	146	78	1.1	0.28
5–6	109	24	227	23	137	72	1.0	0.28
6–7	105	26	237	26	151	78	1.0	0.31
7–8	102	25	228	25	140	70	1.0	0.26
8–9	95	25	219	26	139	77	1.2	0.23
9–10	97	24	219	25	138	70	1.0	0.26
10–12	101	27	224	27	152	89	1.2	0.23
12–14	140	27	212	25	153	74	1.2	0.22
14–16	102	29	207	27	168	85	1.4	0.24
16–18	95	29	245	28	153	82	1.7	0.21
18–20	82	26	229	25	126	70	1.1	0.25
20–22	79	24	246	24	130	66	1.0	0.33
22–24	70	24	227	24	114	62	0.9	0.25
24–26	64	23	233	23	123	55	1.1	0.22
26–28	81	26	233	26	130	64	1.0	0.33
28–30	62	23	205	25	116	62	1.1	0.23
30–32	84	29	229	29	143	90	1.2	0.38
32–34	69	24	238	26	122	58	1.1	0.29

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