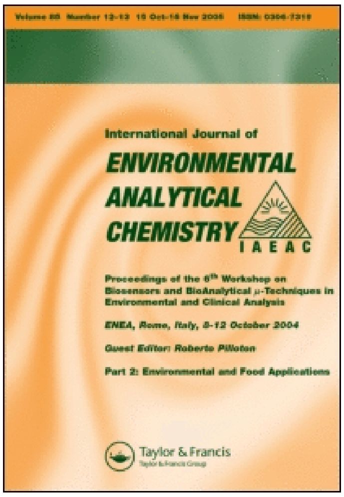

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Application of X-ray Fluorescence Spectrometry to the Study of the Marine Environment

C. J. Toussaint[a]; R. Boniforti[b]
[a] Joint Research Centre, lspra Establishment, Commission of the European Communities, Lspra, Italy [b] Comitato Nationale per l'Energia Nucleare, Laboratorio Contaminazione Marina, Fiascherino-La, Spezia, Italy

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Application of X-ray Fluorescence Spectrometry to the Study of the Marine Environment

C. J. TOUSSAINT

Joint Research Centre, Ispra Establishment, Commission of the European Communities, 21020 Ispra (Italy)

and

R. BONIFORTI

Comitato Nationale per l'Energia Nucleare, Laboratorio Contaminazione Marina 19030-Fiascherino-La Spezia (Italy)

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The possibility of using X-ray techniques for the study of pollution of a marine ecosystem by heavy metals has been investigated.

In this preliminary study data are reported, obtained on the concentrations of Cr, Cu, Fe, Mn, Ni, Pb and Zn of various samples of marine organisms, sediments and sea water which have been collected in the Mediterranean sea together with atmospheric particulates on the coast near La Spezia. Improvements in the analytical procedure are proposed.

KEY WORDS: X-ray fluorescence, heavy metals, marine environment.

INTRODUCTION

Pollution by metals of components of the marine ecosystem has been primarily observed in coastal waters as a consequence of river inflow, industrial and domestic sewage discharge, and direct dumping of wastes.[1] As heavy metals are highly persistent and can be toxic to life in only trace amounts, investigation of their distribution is necessary. For the Mediterranean sea the analytical data are limited[2], even though the UNEP (United Nations Environment Programme) project concerning the pollution of the Mediterranean Sea has recently organized the cooperation of the bordering countries towards a systematic survey of several pollutants of major concern. Because a correlation between element contents in water, sediments, and organisms has been shown to exist for several elements, methods have been developed for analyzing some metal elements in those components. Owing to the possible correlation between transport of metals by aeolian action and their concentration in the marine ecosystem, the analysis of trace elements in atmospheric particulate matter both off-shore and on the coast has also been carried out.

SAMPLING METHODS

Water

Surface water samples (average collecting depth ~1 m) were collected on 15 May 1977 during a cruise aimed at checking techniques for atmospheric correction of satellite (LANDSAT) data correlating atmospheric optical parameters with meteorological conditions, and to provide data for the assessment of algorithms for mapping of chlorophyll, yellow coloring matter, and suspended matter. Meteorological conditions are listed in Table I. The sampling device consisted of a Van Dorn bottle (sampling volume 3.5 l) made from PVC[3], that does not release any element in detectable amount to the water sample. Immediately after collecting, water was transferred to polyethylene bottles previously cleaned with 10% nitric acid and rinsed with distilled water.

TABLE I

Sampling conditions of the water samples

Stations	Position φN	Position λE	Sampling time	Wind D	Wind Strength	Sea D	Sea Strength	Sky	Visibility Km
S0	44 04 30	09 52 00	0840–0915	W	2–3		Smooth	Rain	6
S1	44 03 50	09 51 06	0932–0945	W	2		Smooth	Cloudy	7–8
			1330–1340	SW	2			Partly clouded	10
S2	44 03 26	09 51 44	0951–1003	N	2	SW	3	Cloudy	8–9
S3	44 03 12	09 52 16	1015–1028	N	2	SW	2–3	Cloudy	10
S4	44 02 48	09 52 52	1357–1402	SW	2	SW	2	Clear	8
S5	44 02 27	09 53 30	1048–1056	SE	2	SW	2 long	Cloudy	8–9
S7	44 01 46	09 54 42	1116–1122	SE	2	SW	2 long	Cloudy	10
S8	44 01 24	09 55 17	1420–1426	SW	2	SW	2 long	Clear	8–9
S9	44 01 03	09 55 54	1138–1145	SW	2	SW	2 long	Partly clouded	8–9

ORGANISMS

Immediately after collection, samples of fish and shellfish were frozen at −20°C. The dissection of the fish has been carried out with the organisms only partially thawed thereby obtaining muscle uncontaminated by drip and allowing easier cutting. As to shellfish shells were allowed to open by gentle heating, taking care to avoid contamination of the soft tissues as much as possible.

In both cases dissection was carried out using plastic or quartz knives. The species were chosen according to their taxonomic position and typical environment encountered in the region. Two species are sessile molluscs, one a mobile mollusc, one a benthic elasmobranch fish, and three teleost fishes.

SEDIMENTS

Sediments were collected by a stainless-steel (Mo 2.5%) corer and frozen immediately after collection in order to avoid chemical modifications possibly induced by biological activity.

ATMOSPHERIC PARTICULATE

Air particulates were collected by a low volume total suspended particulate sampler.

A measured volume of air was passed through a membrane filter (Millipore), using a collection time of 2–4 h.

X-ray EQUIPMENT

The X-ray fluorescence spectrometer used in this work is the SRS-1 sequential spectrometer with a PDP-8 digital computer, molybdenum, tungsten and chromium target X-ray tubes, LiF 200 and PET analyzing crystals, scintillation and flow counters.

The X-ray diffraction diagram was obtained by a Philips diffractometer, using Cu Kα ($\lambda = 1.5418$ A) radiation with a graphite monochromator placed behind the sample.

EXPERIMENTAL PROCEDURE AND PRELIMINARY RESULTS

1. Water

Since the limit of detection for analysing water by direct X-ray fluorescence methods is at best about 0.5–1.0 mg/l for most metals and because the expected levels are generally ten to thousand times less, preconcentration is necessary. A sample of 500 ml of sea water is first passed through a Millipore filter (pore width 0.2 μm), where suspended metals are collected. The filter is then analysed directly, without further treatment to determine the particulate fraction.

The filtrate is concentrated by slow controlled evaporation to about 100 ml, and then the sample is heated, adding 5 ml HC1 suprapur to dissolve the formed residue. After this treatment, precipitation of the metals is carried out using the organic chelating reagent diethyldithiocarbonate [4,5] and collecting the precipitate on Millipore filter discs. Standard samples were prepared by precipitating known amounts of metals using the same technique. Commercially available CSI (Columbia Scientific Industries, Austin, Texas, USA) standards, prepared by micropipetting measured volumes of gravimetrically-prepared standard solutions by the multidrop technique onto a Millipore filter have also been used.

Preliminary results for the particulate and dissolved fractions of sea water (Mediterranean) are shown in Table II. From these data one can note that for manganese, nickel and copper the particulate fraction contains higher amounts that the dissolved fraction, while the reverse is true for zinc and lead.

Figure 1 shows the geographical distribution of the sea water sampling sites.

Since preconcentrations of water by evaporation, even under controlled conditions, can result in some losses of volatile metals, for future samples we are studying a preconcentration technique based on a combination of multi-element chelation by 8-hydroxyquinoline with subsequent absorption on active carbon.[6,7] by which is seems possible to obtain enrichment factors of about 10.000, and another technique which uses filter papers containing silica gel to which thiocarbaminate groups have been chemically bound.[8]

ORGANISM

Fish samples were prepared by cutting up the fish and weighing it. Before decomposition, they were oven dried at 105°C until constant weight. Decomposition of the samples was carried out by taking 0.1 g (dry weight) of the fish samples followed by digestion in a Parr (Parr Instrument Co., Moline, Ill. USA) acid digestion bomb at 150°C, with 2.5 ml of concentrated suprapur nitric acid. After dissolution precipitation of heavy metals was carried out by the earlier described procedure. It has been found that only fish-fillets can be used, otherwise one precipitates great quantities of Mg-phosphates together with heavy metals, and the advantages of the thin-film analysis technique are lost. Results of metal analysis for different organisms are given in Table III. One can note that concentrations of various metals show high variability also for the same species, as can be expected from biological variability. Figure 2 shows the geographical location of collecting.

TABLE II
Element concentrations (μg/l) in seawater

Sampling	Site	Cr	Mn	Fe	Ni	Cu	Zn	Pb
S_0	P	3.7	11.8	18.5	57.8	35.3	≦0.1	1.0
	D	3.5	≦0.1	50.0	13.3	8.0	25.0	5.0
S_1	P	4.0	15.0	21.2	93.0	13.8	≦0.1	0.6
	D	5.0	≦0.1	31.3	2.5	≦0.1	1.0	9.0
S_2	P	3.5	6.8	39.3	7.6	≦0.1	0.3	1.0
	D	5.0	≦0.1	45.0	10.3	≦0.1	11.0	32.0
S_3	P	0.9	6.9	20.0	12.0	≦0.1	≦0.1	1.0
	D	6.2	≦0.1	24.0	25.0	≦0.1	5.0	3.0
S_4	P	2.7	5.3	46.7	22.2	27.2	≦0.1	2.7
	D	1.0	0.2	8.0	11.3	≦0.1	10.0	18.0
S_5	P	3.2	9.4	43.6	43.0	9.0	3.7	1.2
	D	6.5	≦0.1	51.1	12.0	≦0.1	10.0	9.0
S_7	P	3.3	7.4	53.6	30.5	19.3	≦0.1	0.6
	D	3.0	≦0.1	14.0	14.5	≦0.1	2.0	3.0
S_8	P	5.1	3.0	49.2	19.6	34.9	≦0.1	2.2
	D	5.0	≦0.1	34.4	22.0	≦0.1	22.0	40.0
S_9	P	3.1	10.9	56.3	49.6	34.9	≦0.1	1.0
	D	2.3	0.2	33.0	10.0	≦0.1	15.0	2.0
F_1	P	≦0.1	17.4	79.2	98.6	≦0.1	≦0.1	1.0
	D	8.0	0.5	10.0	22.5	10.0	25.0	34.0

P = particulate fraction
D = dissolved fraction

SEDIMENTS

Since the uptake of heavy metals from sediments by marine organisms depends on the physico-chemical form, the analysis of total amount of heavy metals in the sediment will not be very meaningful. Therefore, we applied various methods of sediment treatment[9] to study the release of heavy metals from a defined fraction (<0.177 mm) of a sediment, collected near La Maddalena (Mediterranean). The different extraction methods consist of: extraction with EDTA, extraction with hydroxylammonium

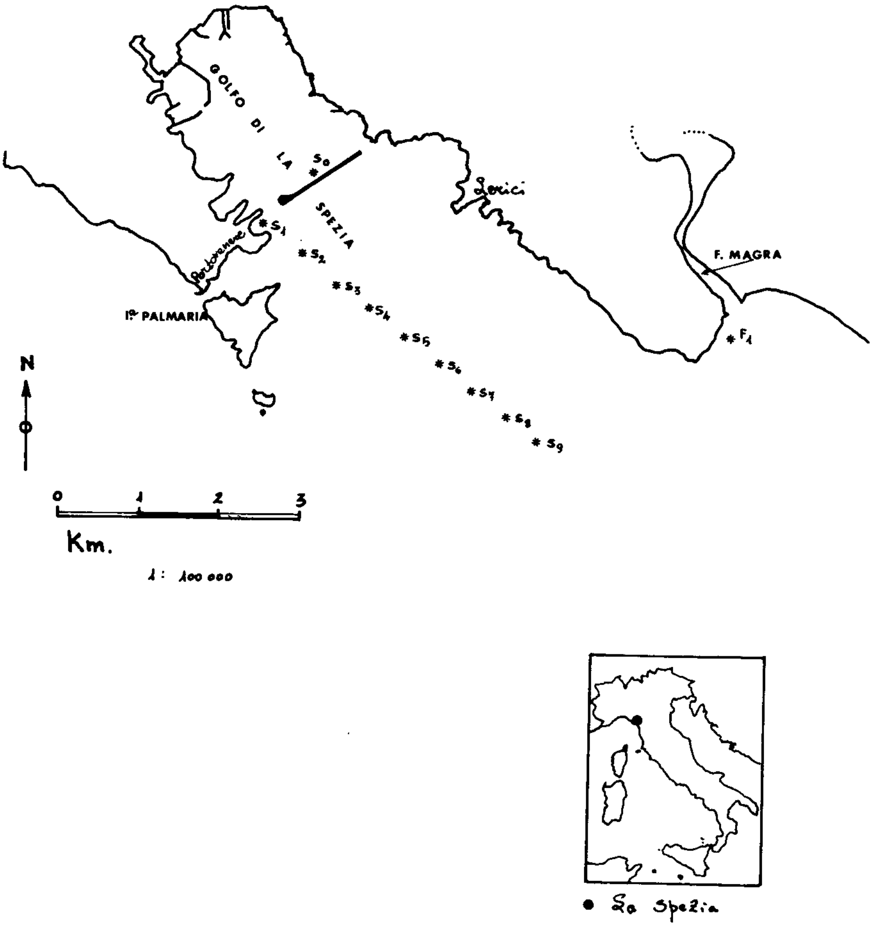

FIGURE 1 Geographical location of collecting of the sea water samples.

chloride, extraction with various mineral acids, and extraction by a digestion bomb.

For the extraction at room temperature, aliquots of 5 g of the sieved fraction were shaken for 12 hours with 100 ml of:

a) 0.05 N ethylenediaminetetraacetic acid (EDTA) disodium salt at pH 5.

b) a mixture of 1 N hydroxylammoniumchloride and 25% acetic acid and

c) 0.5 N HCl.

TABLE III
Element concentrations (μg/kg dry weight) in different marine organisms collected from the La Maddalena Archipelago and the Palmaria Island

Species	Collecting site(*)	Tissue	Sample weight	Cu	Cr	Fe	Zn	Pb	Ni	Mn
Tellinacea	Capo d'Orso	muscle	pooled sample	107×10^3	2.5×10^3	508×10^3	50	50	†	50
Tellina Spec.	Punta Fico	muscle	pooled sample	50	50	715×10^3	2.5×10^3	50	†	8×10^3
	Palau Punta Nera	muscle	pooled sample	50	50	225×10^3	50	50	†	50
	Cala Stagnali	muscle	pooled sample	50	50	506×10^3	50	50	†	50
Pinna nobilis	Rods of Santo Stefano	mantle	unknown	50	50	55×10^3	360×10^3	10×10^3	†	50×10^3
	Rods of Santo Stefano	mantle	unknown	7.5×10^3	1.8×10^3	108×10^3	16×10^3	1.5×10^4	†	1×10^3
	Port Pozzu	mantle	unknown	50	50	120×10^3	125×10^3	95.5×10^3	†	330×10^3
Sepia officinalis	La Maddalena	soft parts	unknown	50	1×10^3	50	0.6×10^3	†	†	†
Maena maena	La Maddalena	muscle	119 g	1.2×10^3	50	4×10^3	50	50	50	50
Maena maena	La Maddalena	muscle	140 g	1.1×10^3	50	4.2×10^3	50	50	0.4×10^3	50
Maena maena	La Maddalena	muscle	104 g	0.5×10^3	1.3×10^3	1×10^3	50	50	50	50
Mullus surmuletus	La Maddalena	muscle	68.5 g	50	50	1.4×10^3	50	50	50	50
Mullus surmuletus	La Maddalena	muscle	84 g	1×10^3	50	2.1×10^3	50	0.5×10^3	18×10^3	50
Mullus surmuletus	La Maddalena	muscle	104 g	2.8×10^3	50	50	0.9×10^3	50	50	50
Torpedo marmorata	La Maddalena	muscle	unknown	50	50	3×10^3	0.4×10^3	†	†	†
Scorpena porcus	La Maddalena	muscle	unknown	†	50	5.7×10^3	0.2×10^3	0.8×10^3	70	†
Mitilus edulis	Palmaria (La Spezia)	soft parts	pooled sample	4.7×10^3	50	149×10^3	50	3×10^3	50	50

(*)With the exception of La Spezia, all collecting sites are located in the N/Sardinia
(†)Not determined

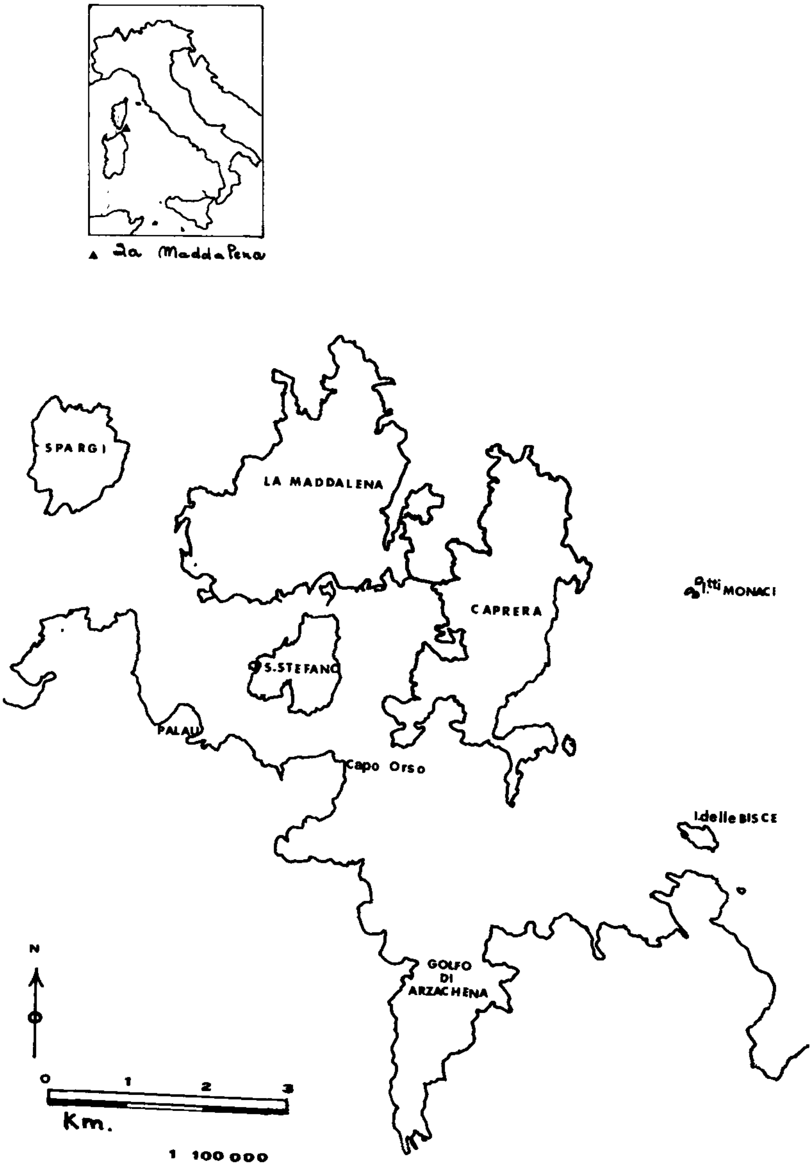

FIGURE 2 Locations of sampling of marine organisms.

TABLE IV
Element concentrations (μg/kg DW) in marine sediments using various extraction methods

Collecting site	Total carbon %	Sulfur %	Extraction method	Cr	Mn	Fe	Ni	Cu	Zn	Pb
La Maddalena (N/Sardinia)	10,0	0.12	EDTA	0.5×10^3	$\leqq 50$	4×10^3	$\leqq 50$	2×10^3	0.5×10^3	6×10^3
			Hydroxyl-ammonium chloride	0.5×10^3	0.8×10^3	17×10^3	$\leqq 50$	0.2×10^3	0.5×10^3	$\leqq 50$
			HCI	0.2×10^3	$\leqq 50$	60×10^3	$\leqq 50$	0.2×10^3	3×10^3	0.9×10^3
			HNO_3	$\leqq 50$	38×10^3	4040×10^3	$\leqq 50$	11×10^3	8×10^3	15×10^3
			Aqua regia	$\leqq 50$	30×10^3	4520×10^3	$\leqq 50$	11×10^3	9×10^3	34×10^3
			$HNO_3 + HC10_4$	19×10^3	58×10^3	5190×10^3	$\leqq 50$	10×10^3	9×10^3	19×10^3
			$HC10_4 + HNO_3 + HF$ (digestion bomb)	40×10^3	90×10^3	4000×10^3	60×10^3	55×10^3	18×10^3	30×10^3

The metals extracted by hot acids are obtained by digestion of 1 g of the sediment fraction with

a) 25 ml of HNO_3 (65 %)

b) 25 ml aqua regia and

c) 25 ml HNO_3 (65 %) + $HClO_4$ (70 %) 1 : 1

In all the 3 cases, boiling is carried out twice till dryness, and the remaining residue is dissolved in diluted HCl.

For the extraction of total metals, the sieved sample is ground to <0.074 mm and one gram of this sample is digested in a digestion bomb with 6 ml HF (40 %) + 4 ml HNO_3 (65 %) + 1 ml $HClO_4$ (70 %). All acids used were suprapur.

The metals in solution obtained by all the extraction procedures are finally precipitated as indicated, filtered through a Millipore filter and examined by X-ray fluorescence analysis.

In Table III results of the different sediment treatments are shown. These results confirm that the extraction procedure has a very great effect on the amounts of metals released from the sediment.

Since the total carbon content of the sediment seems to play an important role in the formation of some metal complexes, we have determined this value together with that of total sulphur.

Finally a structural characterization of the sediment under investigation has been carried out (see Figure 3).

AIR PARTICULATES

After collection on Millipore filter the particulate is directly analysed without further treatment. The samples were collected on the coast near La Spezia. Table V shows data from selected locations. Remarkable are the high nickel and copper values of the location "Campo Sportivo", which is very probably due to the fact it is situated in the neighbourhood of an industrial area.

CONCLUSION

The obtained results are sufficiently encouraging to start a complete and systematic study of a marine ecosystem. In the framework of the Environmental Program the X-ray method will be utilised for the study of the Bay of La Spezia and surrounding zones (Viareggio-Levante).

The experience drawn from this preliminary survey has suggested some improvements in the analytical scheme, concerning the analysis of organisms and sediments.

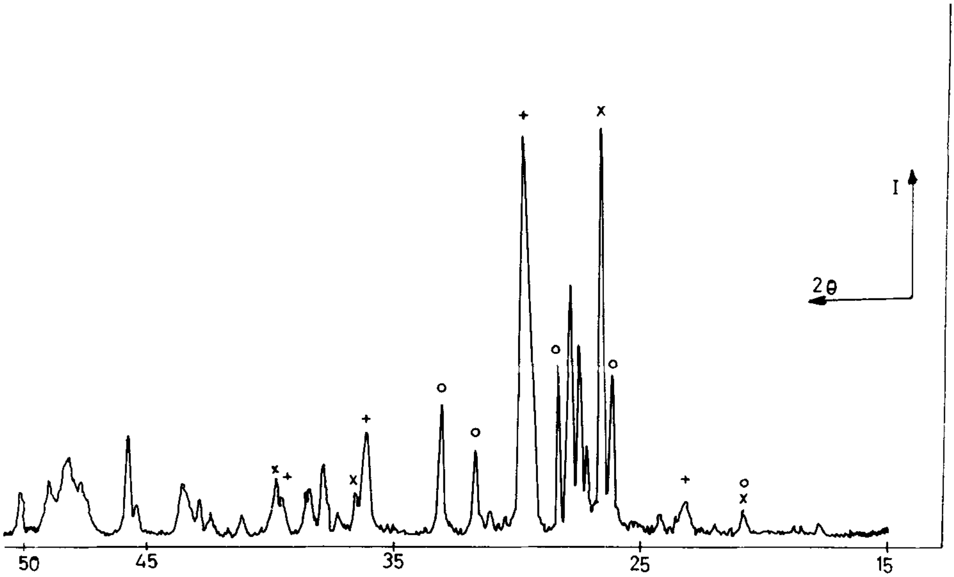

FIGURE 3 X-ray diffraction pattern of the analysed sediment. Scanning speed 1°.2θ min. Full scale 1.10^3 cps. One notes the presence of phases: calcite (+), alpha Quartz (×) and potassium sodium carbonate (0).

TABLE V

Element concentrations ($\mu g/m^3$) in the air of different locations near La Spezia

Collecting site	Data and overall duration of sampling	Pb	Zn	Ni	Fe	Cr	Mn	Cu
Fiascherino	7 Dec. 1976 41 hours	0.05	0.11	0.07	0.07	0.05	0.02	0.21
La Rocchetta	9 Dec. 1976 24 hours	0.07	0.37	0.20	0.20	0.02	0.03	0.23
Campo Sportivo	13 May 1977 44 hours (*)	0.63	0.20	5.24	2.20	0.40	1.08	2.98

(*)The weather was raining 15 out of 44 h of collecting.

As to organisms the future analysis of heavy metals will be accompanied by the analysis of K and/or Ca, thereby allowing to express the results not only in concentration but also as ratio of heavy metals to two of the (relatively) constant major constituents. For the sediments, beside the fraction <0.177 mm also a portion of the non-sieved sample will be treated in the same manner as the sieved fraction.

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