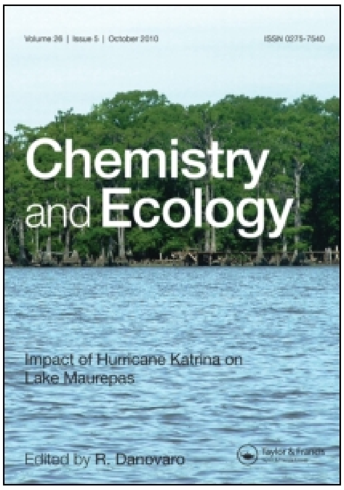

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Chemistry, mineralogy and radioactivity in *posidonia oceanica* meadows from North-Western Sicily

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CHEMISTRY, MINERALOGY AND RADIOACTIVITY IN *POSIDONIA OCEANICA* MEADOWS FROM NORTH-WESTERN SICILY

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(In final form 18 February 2004)

This paper presents measurements of major, minor, metal trace elements and radionuclides in sediments and in *Posidonia oceanica* samples from north-western Sicily (Italy). The mineralogical and chemical composition of sediments were determined by X-ray diffraction and X-ray fluorescence techniques, respectively. A flame atomic absorption spectrophotometry was used to measure concentrations of Cu, Zn, Cd and Pb in *P. oceanica* samples and in sediments. Specific activities of selected radionuclides have been determined by high-resolution gamma spectrometry. Standard statistical analysis was used to assess correlations between different elements and different sample types.

Keywords: *Posidonia oceanica*; Sea sediment; Heavy metals; Radionuclides

1 INTRODUCTION

Posidonia oceanica seagrasses form dense infralittoral communities called meadow ecosystems (Pergent *et al.*, 1999), which are widely distributed throughout the Mediterranean Sea. They give the most important contribution to coastal primary production, and they are the habitat of many species. Because of its bathymetric range (0–40 m), this ecosystem is directly exposed to several anthropogenic impacts, like traffic, industrial and urban pollutions (Shepherd *et al.*, 1989; Pergent *et al.*, 1999; Sanchiz *et al.*, 2000). In particular, heavy metals, natural and anthropogenic radionuclides have been shown to contaminate the *P. oceanica* meadows due to both terrigenous and atmospheric contributions (Calmet *et al.*, 1988; 1991; Maserti *et al.*, 1988; Molero *et al.*, 1999; Pergent-Martini and Pergent, 2000; Sanchez-Cabeza and Molero, 2000). It has also been outlined (Ward, 1989) that

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high levels of heavy metals could affect similar ecosystems (Prange and Dennison, 2000). The status of the pollution in the Mediterranean Sea is inhomogeneous and no impact study has isolated one particular marine organism as a direct biomonitor of the contamination processes. *P. oceanica* has already been proposed as a bioindicator to record environmental alterations (Pergent *et al.*, 1995; 1999; Pergent-Martini, 1998; Pergent-Martini and Pergent, 2000). Geological characteristics of the meadow sites should be considered carefully to distinguish between pollution and natural contributions to chemical element concentrations. Correlations between trace metals concentrations in plant fractions and sediments also play a role (Maserti *et al.*, 1988; Warnau *et al.*, 1996; Nicolaidou and Nott, 1998; Schlacher-Hoenlinger and Schlacher, 1998; Sanchiz *et al.*, 2000). Extrapolation of concentration values from one site to another may be confounded by several factors such as the physiological status of the organisms, environmental variability, and the geochemical characteristics of the habitat.

As part of a more general scientific project (MIR Project, funded by the Italian *Ministero per l'Istruzione, l'Università e la Ricerca*), aimed to integrate different methodologies for the environmental protection, a preliminary survey of metal and radionuclide contaminations in *P. oceanica* and sediments in four sites of the north-western coast of Sicily has been carried out (see Fig. 1). Sites have been chosen to be very similar for geochemical and lithological features but different for proximal pollution conditions. Four heavy metals (Cu, Cd, Pb and Zn), four natural radionuclides (^{40}K, ^{210}Pb, ^{228}Ac and ^{214}Bi) and one artificial radionuclide (^{137}Cs) were selected for study. Data were compared with the major, minor and trace elements measured in sediments collected in the same sites.

The correlation between the values of heavy metal concentrations in *P. oceanica* and sediments could provide some hints to finding remedial actions with respect to the pollution of anthropogenic origin. Moreover, a rough assessment of the state of the marine environment near the north-western coast of Sicily can be obtained from the survey.

FIGURE 1 Map of the geographical area of the investigated sites and the locations of sampling.

2 MATERIALS AND METHODS

2.1 Sampling

Thirty-four samples of sediment were collected in four geographical sites (see Fig. 1), namely Carini, Egadi Islands, Marsala and Trapani, from sedimentary basins inside the *Posidonia* meadows. For each site, three locations near the coast inside the *P. oceanica* meadows (transects) and three bathymetric depths (stations) were considered. Samples from different transects at the same depths were analyzed as a whole. The bathymetric range was between 3 and 10 m.

P. oceanica samples were collected at the same sites and depths (3, 6 and 10 m) as the sediments. Twenty plants were sampled at each station. Sampling of sediments and *P. oceanica*, and plant fractioning (rhizomes, scales, and leaves) were carried out by other colleagues within the same MIR Project, and details can be found elsewhere (Calvo *et al.*, 2002). No root samples were collected.

Epibiota and sediments were removed from *P. oceanica* samples by gentle scraping with a glass slide and rapid rinsing with distilled water, to minimize the loss of elements (Ledent *et al.*, 1995; Campanella *et al.*, 2001).

2.2 Mineralogical Measurements

All sediments were treated after being dried and sieved through a 2-mm meshed sieve. The samples were milled to obtain particles of a size smaller than 4 μm. The powder was directly measured for mineralogical features by X-ray diffraction (XRD).

The samples were mixed with H_3BO_4, and a thin chip was obtained to determine the elemental composition by X-ray fluorescence (XRF). The samples were characterized by X-ray diffractometry using the X' Pert Pro, Philips Analytical. Major and minor chemical elements, were measured by XRF (PW 1400, Philips Analytical).

2.3 Metal Measurements

The sediment samples, after sieving on 2-mm meshes, were dried at 105 °C for 48 h and then milled to obtain a size of approximately 100 μm using a Fritsch Pulverisette 2. Milled samples were then digested using the Open-Cavity Microwave Star 2 (CEM Corporation) (see Cook *et al.*, 1997, for a review of different techniques). Five milliliters of HCl 37% were added to a 500 mg aliquot of the sample, and kept at 75 °C for 5 min. Afterwards, 7.5 ml of 65% HNO_3 were added and heated up to 95 °C; after 15 min, the temperature was raised to 110 °C for 10 min. Fifteen milliliters of H_2O_2 were then added, and the temperature was kept at 110 °C for a further 10 min. After cooling, the solution was filtered, and distilled water was added to make the volume up to 25 ml.

The same drying and milling procedures were used for *P. oceanica* samples. The milled sample was then divided into two parts: the first for flame atomic absorption spectrophotometry (FAAS) analysis and the second for the gamma spectrometry analysis. Both aliquots were stored in hermetically sealed polyethylene containers until analysis time.

For FAAS analysis, a quantity of 500 mg was digested in the above-mentioned open-cavity microwave using the following procedure. Five milliliters of 65% HNO_3 and 5 ml of distilled and deionized water were first added to the 500 mg sample aliquot and heated for 3 min at 50 °C; the temperature was then raised to 70 °C and maintained for 10 min. Five milliliters of 70% $HClO_4$ were then added and temperature was raised to 98 °C for

7 min. The mixture was then kept at 106 °C for 5 min, at 120 °C for 4 min, at 140 °C for 2 min and at 180 °C for 2 min. Digested samples, filtered through 0.2 μm pores, were cooled and diluted to 25 ml with distilled and deionized water. All the glassware was cleaned by soaking in a 10% HNO_3 solution for 24 h, then rinsed three times with deionized water to prevent any contamination. All the chemical reagents were of Merck suprapure grade.

Zn, Cu, Cd, and Pb concentrations were measured using a Varian AA20 Plus FAAS. The spectrophotometer was equipped with a deuterium background corrector and an ACT 80 atom concentrator tube, which was positioned in the air/acetylene flame to make the sensitivity two to three times greater than that of a standard FAAS. The detection limits of Zn, Cu, Cd, and Pb are 0.6, 0.6, 0.25, 0.9 $\mu g\ g^{-1}$, respectively.

The National Research Council of Canada PACS-2 marine sediment was used as a certified reference material for sediment measurements. The Community Bureau of Reference (European Union) RM 60 (*Lagarosiphon major*) was used as a certified reference material for *P. oceanica* measurements.

2.4 Radioactivity Measurements

Gamma activity counts of ^{40}K, ^{228}Ac, ^{214}Bi and ^{137}Cs were carried out by high-resolution gamma spectrometry using three different HPGe detectors. The HPGe detector used to analyze rhizomes and sediments had an operability range of 150–10,000 keV, a relative efficiency of 32% and a resolution of 1.8 keV at 1.33 MeV. A second detector, with an operability range of 5–400 keV and an active area of 20 cm^2, was used to detect 46.5 keV gamma rays emitted by ^{210}Pb in rhizome samples.

The first detector was calibrated against a standard soil (SRM4353 from the National Bureau of Standards) containing all the radionuclides of interest except ^{210}Pb. The second detector was calibrated for ^{210}Pb against a standard source provided by the Italian Laboratory for the Metrology of Ionizing Radiations. A third low-background germanium detector was used for scale analysis. This was an Ortec GMX-50220, with an operability range of 3–10,000 keV, a relative efficiency of 51%, 1.99 keV at 1.33 MeV and 658 eV at 5.9 keV resolutions. The same sources as those above were used for calibration.

Data were corrected to take into account different sample densities (which, for sediments, ranged between 0.4 and 1.6 $g\ cm^{-3}$; Cutshall *et al.*, 1983; Rizzo and Puccio, 1992).

The small amount of *Posidonia* available for activity determinations, about 8–15 g dry weight for each sample, required a counting time of 3.5×10^5 s to yield (and only in a few cases) values of specific activity above the detection limit (Currie, 1968).

About 150–200 g for each sample of sediment was used for radioactivity determination; the counting time was 2.5×10^5 s.

3 RESULTS AND DISCUSSION

The geochemical features of the sediments for major mineralogical composition, obtained by XRF, are listed in Table I. These refer to hydrated samples. The mineralogical data obtained by XRD are listed in Table II. The values shown in the two tables are the mean values and ranges (in parenthesis) of percent concentration for three samples at the same depth.

The XRF and XRD data of the sediments show a fairly homogeneous percentage of CaO, indicating a common carbonate lithology; statistical differences have been tested using the standard *F*-test, showing a *P*-value of 0.2765 for a 95% confidence level (see, for instance,

TABLE I XRF major elements data for sediments as a mass percentage in the hydrated samples: mean values over three samples from different transects in the same site (see main text), collected at the same depth (ranges in parentheses).

	SiO_2	TiO_2	Al_2O_3	P_2O_5	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O
Egadi										
Station 1	8 (2–14)	0.05 (0.04–0.05)	0.65 (0.60–0.70)	0.06 (0.03–0.07)	0.2 (0.2–0.3)	7 (4–13)	0.09 (0.08–0.09)	43 (38–46)	0.2 (0.1–02)	0.08 (0.08–0.10)
Station 2	3 (1–7)	0.04 (0.03–0.04)	0.44 (0.36–0.49)	0.05 (0.03–0.07)	0.2 (0.1–0.2)	6 (4–11)	0.09 (0.08–0.09)	46 (41–49)	0.3 (0.1–0.5)	0.02 (0.01–0.05)
Station 3	5 (1–11)	0.04 (0.04–0.04)	0.46 (0.40–0.53)	0.06 (0.04–0.07)	0.3 (0.2–0.4)	5 (3–8)	0.09 (0.08–0.09)	46 (44–49)	0.2 (0.1–0.3)	0.03 (0.01–0.06)
Trapani										
Station 1	6 (5–7)	0.06 (0.04–0.08)	1.00 (0.57–1.36)	0.07 (0.05–0.08)	0.8 (0.7–0.9)	3 (2–3)	0.10 (0.09–0.10)	47 (46–48)	0.4 (0.2–0.6)	0.07 (0.04–0.10)
Station 2	5 (1–11)	0.06 (0.04–0.08)	0.80 (0.51–1.14)	0.05 (0.03–0.07)	0.9 (0.5–1.4)	3 (2–4)	0.10 (0.09–0.10)	48 (47–48)	0.3 (0.2–0.4)	0.05 (0.01–0.10)
Station 3	4 (1–7)	0.06 (0.04–0.07)	0.90 (0.53–1.05)	0.06 (0.05–0.07)	0.7 (0.4–1.1)	3 (2–5)	0.10 (0.09–0.10)	48 (47–48)	0.4 (0.2–0.7)	0.06 (0.01–0.09)
Marsala										
Station 1	8 (2–16)	0.06 (0.05–0.07)	0.80 (0.73–0.86)	0.07 (0.06–0.07)	1.2 (2.0–0.8)	3 (2–3)	0.11 (0.10–0.12)	46 (44–48)	0.8 (0.3–1.8)	0.08 (0.03–0.10)
Station 2	10 (2–23)	0.06 (0.04–0.07)	0.81 (0.50–1.11)	0.09 (0.08–0.11)	1.7 (1.1–2.1)	3 (2–4)	0.10 (0.10–0.11)	45 (40–48)	0.4 (0.3–0.5)	0.08 (0.01–0.16)
Station 3	10 (2–22)	0.07 (0.05–0.10)	1.01 (0.6–1.52)	0.11 (0.09–0.12)	1.5 (0.9–1.9)	3 (2–4)	0.10 (0.09–0.11)	44 (40–48)	0.6 (0.4–0.8)	0.10 (0.04–0.19)
Carini										
Station 1	10 (4–21)	0.02 (0.02–0.02)	0.31 (0.32–0.30)	0.08 (0.07–0.08)	0.3 (0.2–0.3)	4 (3–4)	0.09 (0.09–0.09)	42 (39–44)	2.6 (1.9–3.4)	0.04 (0.04–0.04)
Station 2	3 (2–4)	0.02 (0.01–0.02)	0.35 (0.41–0.29)	0.07 (0.06–0.07)	0.4 (0.3–0.4)	4 (3–4)	0.09 (0.09–0.09)	44 (43–45)	3.9 (3.6–4.3)	0.05 (0.03–0.06)
Station 3	2 (1–3)	0.02 (0.02–0.02)	0.42 (0.37–0.50)	0.06 (0.06–0.07)	0.3 (0.2–0.5)	4 (3–4)	0.10 (0.09–0.10)	49 (48–50)	0.6 (0.4–0.7)	0.02 (0.01–0.04)

TABLE II XRD mineralogical features of sediments are shown as mass percentage: mean values over three samples from different transects in the same site (see main text), collected at the same depth (ranges in parentheses).

	Quartz SiO_2	*Calcite* $CaCO_3$	*Magnesian calcite* $Ca(1-x)Mg(x)CO_3$	*Aragonite* $CaCO_3$	*Dolomite* $CaMg(CO_3)_2$	*Feldspar* $(K,Na)Si_3O_8$
Egadi						
Station 1	8 (1–15)	21 (17–22)	23 (2–42)	16 (1–27)	32 (2–72)	0
Station 2	3 (1–7)	22 (14–35)	37 (5–63)	17 (4–27)	21 (2–55)	0
Station 3	5 (0–16)	22 (6–38)	35 (14–63)	22 (9–31)	16 (9–39)	0
Trapani						
Station 1	5 (4–6)	34 (17–50)	38 (29–48)	23 (13–29)	0	0
Station 2	4 (0–12)	23 (19–24)	48 (25–67)	25 (14–39)	0	0
Station 3	3 (0–6)	26 (10–47)	48 (28–71)	23 (19–30)	0	0
Marsala						
Station 1	6 (1–15)	23 (13–34)	45 (31–57)	25 (18–29)	0	1 (0–1)
Station 2	7 (1–22)	26 (9–36)	45 (28–68)	22 (13–27)	0	0
Station 3	7 (1–20)	20 (11–25)	49 (30–62)	23 (20–06)	0	1 (0–3)
Carini						
Station 1	13 (4–21)	28 (18–38)	29 (28–32)	18 (14–21)	12 (9–15)	0
Station 2	3 (2–4)	19 (27–11)	56 (47–66)	20 (18–21)	2 (1–3)	0
Station 3	2 (1–3)	8 (0–14)	53 (35–62)	34 (24–45)	2 (1–4)	1 (0–2)

Miller and Miller, 2000). Nevertheless, the dolomitic lithologies induce an increment of MgO (see the Egadi site data), according to the role of the magnesian calcite. Fisher's Least Significant Difference (LSD) test shows, in this case, that the MgO values for Egadi are statistically different from MgO values for other sites, at the 95% confidence level.

The trace metal concentrations in sediments, *P. oceanica* rhizomes, scales and leaves are shown in Tables III, IV, V and VI, respectively. Unfortunately, no root samples were available for analysis. Values are expressed as the means of three pooled samples at the same depth for the same site. The confidence limits, as arising from the 95% confidence limits for the calibration parameters (main source of measurement uncertainty) are also shown

TABLE III Trace-metal concentrations ($\mu g\ g^{-1}$ dry weight) in sediments and 95% confidence (mainly arising from the calibration procedure; see the main text for details).

	Cu (13.3 ± 2.7)[*]	*Pb (8–20)*[†]	*Zn (10–40)*[†]
Egadi			
Station 1	3.9 ± 0.4	8 ± 1	38 ± 6
Station 2	4.3 ± 0.4	6 ± 1	43 ± 7
Station 3	4.6 ± 0.5	8 ± 1	25 ± 3
Trapani			
Station 1	4.1 ± 0.4	6.0 ± 0.9	18 ± 3
Station 2	9.0 ± 0.8	5.3 ± 0.9	20 ± 2
Station 3	3.8 ± 0.3	10 ± 2	23 ± 4
Marsala			
Station 1	2.7 ± 0.3	6.9 ± 0.9	24 ± 4
Station 2	2.7 ± 0.3	10 ± 1	32 ± 3
Station 3	2.6 ± 0.3	8 ± 1	22 ± 3
Carini			
Station 1	2.0 ± 0.2	6.9 ± 0.9	12 ± 2
Station 2	2.2 ± 0.2	8.2 ± 0.9	13 ± 2
Station 3	2.4 ± 0.2	10 ± 1	20 ± 4

Note: Samples from different transects collected at the same depth have been analysed as a whole.

[*] Pergent *et al.* (1999).

[†] Sanchiz *et al.* (2000).

TABLE IV Trace-metal concentrations (μg g^{-1} dry weight) in *Posidonia oceanica* rhizomes (values are means over three samples from different transects and collected at the same depth).

	*Cd (1–2)**	*Cu (5.4–15.3)*†	*Pb (2.5–8.0)**	*Zn (40–80)**
Egadi				
Station 1	0.60 ± 0.07	12.6 ± 0.6	2.4 ± 0.2	82 ± 9
Station 2	0.67 ± 0.08	11.8 ± 0.7	2.5 ± 0.3	100 ± 10
Station 3	0.57 ± 0.08	7.5 ± 0.4	4.5 ± 0.4	110 ± 20
Trapani				
Station 1	1.8 ± 0.2	13.0 ± 0.8	4.6 ± 0.5	80 ± 10
Station 2	1.3 ± 0.2	11 ± 1	4.2 ± 0.5	150 ± 20
Station 3	1.2 ± 0.2	6.1 ± 0.5	3.9 ± 0.4	110 ± 10
Marsala				
Station 1	1.7 ± 0.3	9.9 ± 0.8	4.3 ± 0.5	290 ± 40
Station 2	1.5 ± 0.2	7.3 ± 0.8	3.9 ± 0.4	170 ± 30
Station 3	1.8 ± 0.2	7.5 ± 0.9	4.6 ± 0.4	310 ± 40
Carini				
Station 1	2.0 ± 0.3	9.7 ± 0.4	6.4 ± 0.5	110 ± 20
Station 2	2.3 ± 0.4	9.2 ± 0.2	11 ± 1	90 ± 20
Station 3	1.8 ± 0.2	11.3 ± 0.4	8.1 ± 0.7	90 ± 20

*Sanchiz *et al.* (2000).
†Baroli *et al.* (2001).

(Miller and Miller, 2000). Data for sediments are under the detection limit of our equipment for cadmium (0.25 μg g^{-1}). A literature reference value (Pergent *et al.*, 1999) for Cu and reference ranges for Pb and Zn (Sanchiz *et al.*, 2000) are also shown.

Many factors, such as differential metal uptake, chemical and physical water conditions, seawater nutrients and ligands, and interactions between metals can contribute to metal concentrations in *P. oceanica*, as already noted for aluminum (Malea, 1993).

Our results show that the distribution of Cd in *P. oceanica* is similar in rhizomes and scales, while the highest level was obtained in leaves in every site (between group homogeneity and differences tested by *F*-test and LSD test). The *F*-test coupled with the LSD test has also shown that Cu is present in similar concentrations in rhizomes and leaves,

TABLE V Trace-metal concentrations (μg g^{-1} dry weight) in *Posidonia oceanica* scales (values are means over three samples from different transects and collected at the same depth).

	*Cd (0.6–2.0)**	*Cu (6.0–17.0)**	*Pb (5.2–11.2)**	*Zn (22.9–60.4)*†
Egadi				
Station 1	1.4 ± 0.2	6.6 ± 0.8	9.1 ± 0.9	100 ± 10
Station 2	1.7 ± 0.3	5.7 ± 0.5	8.3 ± 0.9	230 ± 40
Station 3	1.7 ± 0.3	5 ± 1	7.7 ± 0.9	230 ± 30
Trapani				
Station 1	1.2 ± 0.1	7 ± 1	9.5 ± 0.8	250 ± 40
Station 2	0.8 ± 0.1	6.1 ± 0.9	7.9 ± 0.7	240 ± 40
Station 3	1.2 ± 0.2	4.7 ± 0.7	10 ± 1	280 ± 30
Marsala				
Station 1	1.6 ± 0.2	4.2 ± 0.8	7.8 ± 0.8	500 ± 100
Station 2	1.5 ± 0.2	3.7 ± 0.7	8.2 ± 0.9	290 ± 40
Station 3	2.2 ± 0.4	4 ± 1	7.5 ± 0.9	350 ± 40
Carini				
Station 1	1.5 ± 0.2	6.5 ± 0.8	10.8 ± 0.8	80 ± 10
Station 2	1.5 ± 0.2	7 ± 1	9.0 ± 0.9	80 ± 20
Station 3	1.8 ± 0.3	7 ± 1	12 ± 1	90 ± 10

*Baroli *et al.* (2001).
†Pergent *et al.* (1999).

TABLE VI Trace-metal concentrations (μg g^{-1} dry weight) in *Posidonia oceanica* rhizomes (values are means over three samples from different transects and collected at the same depth).

	*Cd (1.0–8.6)**	*Cu (5.7–20.2)*†	*Pb (0.7–10)**	*Zn (105–180)**
Egadi				
Station 1	2.8 ± 0.5	13 ± 1	14 ± 1	220 ± 30
Station 2	2.7 ± 0.5	9 ± 1	14 ± 2	190 ± 40
Station 3	3.1 ± 0.5	7 ± 1	8.8 ± 0.7	210 ± 30
Trapani				
Station 1	2.3 ± 0.4	11 ± 2	11 ± 1	170 ± 30
Station 2	2.4 ± 0.4	8 ± 1	7.4 ± 0.6	180 ± 20
Station 3	3.1 ± 0.6	8 ± 1	13 ± 1	280 ± 30
Marsala				
Station 1	2.7 ± 0.4	5 ± 1	9 ± 1	700 ± 100
Station 2	3.1 ± 0.5	6.2 ± 0.6	7.5 ± 0.7	310 ± 50
Station 3	1.9 ± 0.3	2.5 ± 0.6	8.7 ± 0.8	290 ± 30
Carini				
Station 1	4.0 ± 0.6	10 ± 1	9.8 ± 0.8	180 ± 20
Station 2	3.7 ± 0.6	10 ± 2	10 ± 1	180 ± 30
Station 3	3.3 ± 0.6	12 ± 2	12 ± 1	180 ± 30

Note: Samples from different transects collected at the same depth have been analysed as a whole.
*Sanchiz *et al.*, 2000.
†Campanella *et al.*, 2001.

and is present in smaller amounts in scales. The levels of Pb were always higher in scales than in rhizomes, their differences being statistically significant and proved by *F*-test (*P*-value 0.0001). The mean concentration of Pb in leaves shows values close to those measured in scales (*P*-value from the *F*-test 0.0733). Zinc is present in high concentrations in all tissues of *P. oceanica* and less concentrated in rhizomes than in scales and leaves (LSD test). Levels of Zn found in the leaves from Station 1 of the Marsala site (700 ± 100 μg g^{-1} dry weight) were found to be a few times higher than in leaves from other stations. These values are comparable with those found by Sanchiz *et al.* (2000) in El Portús (Spain).

Statistical analysis, with a mean comparison and LSD test for concentrations of trace metals in the same portion of the plant from different sites, has shown that the most significant differences are the highest values for Pb in Carini site and the highest values for Zn in Marsala site. This applies to both rhizomes and scales. Comparison of values within the same site has shown that values in different stations (*i.e.* different depths) are fairly homogeneous, the Zn concentration from Station 1 in Marsala site being the only noticeable difference.

Some authors have found a positive correlation between levels of some metals in sediment and in *P. oceanica* (see Maserti *et al.*, 1988, for mercury). This correlation was not found for other elements, such as aluminum (Malea, 1993). Table VII shows the correlation matrix for trace metals in sediments and tissues. No element shows a significant correlation between its concentration in sediments and its concentration in tissues, in agreement with Sanchiz *et al.* (2000). Cu concentrations in different portions of the plant show a positive and significant correlation. The same applies for Zn. Cu and Zn are always negatively correlated. Cu and Pb in scales are positively correlated.

The mean levels of metals of our survey are generally low and in agreement with literature data (Warnau *et al.*, 1995; Sanchiz *et al.*, 2000; Baroli *et al.*, 2001; Campanella *et al.*, 2001) in uncontaminated areas of the Mediterranean Sea.

Tables VIII–X show the radionuclide specific activities measured in sediments and in *P. oceanica* rhizomes and scales. Data are shown if the value is larger than the critical limit (Currie, 1968). The lowest detection limits (LDL), calculated according to Currie (1968), for sediments (for a 200 g sample and a measurement time of 2.5 × 10^5 s), have

TABLE VII Correlation matrix for trace metal concentrations in sediments and in *Posidonia oceanica* tissues.

	Cd (rh)	*Cd (sc)*	*Cd (lv)*	*Cu (sd)*	*Cu (rh)*	*Cu (sc)*	*Cu (lv)*	*Pb (sd)*	*Pb (rh)*	*Pb (sc)*	*Pb (lv)*	*Zn (sd)*	*Zn (rh)*	*Zn (sc)*	*Zn (lv)*
Cd (rh)	1	0.059	0.226	−0.429	−0.086	0.253	−0.003	0.154	**0.741**	0.328	−0.369	**−0.788**	0.228	−0.055	0.082
Cd (sc)		1	−0.090	**−0.656**	−0.294	−0.304	−0.363	0.293	0.146	−0.058	0.056	0.125	0.409	0.102	0.151
Cd (lv)			1	−0.394	−0.184	0.297	0.486	0.393	0.553	0.551	0.130	−0.322	−0.514	**−0.597**	−0.215
Cu (sd)				1	0.261	0.051	−0.015	−0.552	−0.399	−0.358	−0.194	0.141	−0.139	0.099	−0.239
Cu (rh)					1	**0.717**	**0.654**	−0.524	−0.088	0.290	0.385	0.171	−0.369	−0.322	−0.235
Cu (sc)						1	**0.876**	−0.161	0.475	**0.666**	0.426	−0.323	**−0.695**	**−0.771**	**−0.607**
Cu (lv)							1	0.080	0.288	**0.774**	0.573	−0.066	**−0.825**	**−0.812**	−0.524
Pb (sd)								1	0.333	0.434	0.162	−0.049	−0.093	−0.171	0.036
Pb (rh)									1	0.455	−0.133	**−0.721**	−0.189	−0.461	−0.217
Pb (sc)										1	0.443	−0.344	−0.555	**−0.653**	−0.381
Pb (lv)											1	0.436	−0.526	−0.404	−0.228
Zn (sd)												1	−0.023	0.167	0.110
Zn (rh)													1	**0.788**	**0.732**
Zn (sc)														1	**0.804**
Zn (lv)															1

Note: sd: sediments; rh: rhizomes; sc: scales; lv: leaves. Significant values, at the level of significance 0.05 (two-tailed test), are shown in bold.

TABLE VIII Specific activities (Bq kg^{-1} dry weight) in sediments.

	^{40}K	^{214}Bi	^{228}Ac
Egadi	33 ± 3	12 ± 1	1.7 ± 0.2
Trapani	29 ± 2	7.9 ± 0.6	3.3 ± 0.4
Marsala	41 ± 3	8.7 ± 0.7	3.6 ± 0.4
Carini	34 ± 3	7.7 ± 0.6	2.5 ± 0.3

Note: See main text for details on the lowest detection limits (LDL). Uncertainty measurements (±σ) are also shown.

TABLE IX Specific activities (Bq kg^{-1} dry weight) in *Posidonia oceanica* rhizomes.

	^{40}K	^{214}Bi
Egadi		
Station 1	110 ± 10	3.1 ± 0.4
Station 2	140 ± 10	3.4 ± 0.4
Station 3	100 ± 10	5.0 ± 0.6
Trapani		
Station 1	210 ± 20	2.4 ± 0.3
Station 2	140 ± 10	3.5 ± 0.4
Station 3	120 ± 10	2.1 ± 0.3
Marsala		
Station 1	150 ± 20	2.1 ± 0.3
Station 2	240 ± 20	1.5 ± 0.2
Station 3	110 ± 10	4.5 ± 0.5
Carini		
Station 1	350 ± 30	<LDL
Station 2	300 ± 30	<LDL
Station 3	<LDL	6.1 ± 0.7

Note: Samples from different transects collected at the same depth have been analysed as a whole. Uncertainty measurements (±σ) are also shown.

TABLE X Specific activities (Bq kg^{-1} dry weight) in *Posidonia oceanica* scales.

	^{40}K	^{210}Pb
Egadi		
Station 1	55 ± 4	43 ± 6
Station 2	65 ± 5	57 ± 9
Station 3	56 ± 4	55 ± 8
Trapani		
Station 1	74 ± 6	60 ± 10
Station 2	56 ± 4	50 ± 8
Station 3	54 ± 4	49 ± 7
Marsala		
Station 1	42 ± 3	36 ± 5
Station 2	39 ± 3	41 ± 6
Station 3	34 ± 3	47 ± 7
Carini		
Station 1	47 ± 4	90 ± 10
Station 2	24 ± 2	110 ± 20
Station 3	<LDL	140 ± 20

Note: Samples from different transects collected at the same depth have been analysed as a whole. Uncertainty measurements (±σ) are also shown.

been estimated to vary in the ranges 0.3–0.5, 1.3–6.0, 0.5–1, 0.5–1.2 and 7–10 Bq kg^{-1} for ^{137}Cs, ^{40}K, ^{214}Bi, ^{228}Ac and ^{210}Pb, respectively. Ranges of variation for LDL in tissues (for a 5–15 g dry weight sample and a measurement time of 3.5×10^5 s) have been estimated as 1.8–3.1 (1–1.5), 30–50 (13–23), 7–11 (2.7–4.2), 5.5–10 (2.5–5) and 14–25 (7–13) Bq kg^{-1} for ^{137}Cs, ^{40}K, ^{214}Bi, ^{228}Ac and ^{210}Pb in scales (rhizomes), respectively. The small amount of available sample has not allowed us to lower these detection limits.

The availability of large quantities of *P. oceanica* (about 10 kg wet weight per sample) and longer measurement times enabled Molero *et al.* (1999) and Sanchez-Cabeza and Molero (2000) to detect specific activities of different isotopes well below our lowest detection limits. As far as ^{40}K is concerned, they obtained a range of 186–532 Bq kg^{-1} dry weight, although no details were reported on the tissues analysed. It should be noted that an activity of 100 Bq of ^{40}K is present in about 3.2 g of total potassium. The ^{228}Ac specific activity values have been found to be below the LDL in most cases for *P. oceanica* samples.

4 CONCLUSIONS

The chemical and mineralogical composition of sediments, trace-metal concentrations and radionuclide specific activities in sediments and *P. oceanica* samples from meadows in north-western coast of Sicily (Italy) have been determined. X-ray fluorescence and diffractometry, atomic absorption spectrophotometry and high-resolution gamma spectrometry have been used. Standard statistical techniques have allowed detailed comparisons among values from different sites and/or different types of samples.

This work has confirmed that *P. oceanica* is a good biomonitor of heavy-metal pollution. No correlation of trace-metal concentrations in sediments and plant has been detected. Nevertheless, a correlation between Cd concentration in plant and seawater has been reported, and a similar behavior assumed for Pb, in the literature (Sanchiz *et al.*, 2000). Therefore, metal concentrations in *P. oceanica* might indirectly be a measure of bioavailable metal concentrations in the environment rather than total concentrations.

The plant/sediment ratio of concentrations is particularly large for Zn. This also applies to Cd, since it was always under the detection limits in sediments. This indicates that bio-enhancement takes place in *Posidonia*.

The potassium concentrations (proportional to ^{40}K activity determined by gamma spectrometry), with values in rhizomes higher than in scales, is in general agreement with the known important role of this element in plant growth.

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