TRANSURANIC ACCUMULATION IN PLANKTON FROM THE SPANISH MEDITERRANEAN COASTAL ENVIRONMENT

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Broadly speaking, zooplankton and phytoplankton include mobile and immobile microbial marine species, respectively. From a classical point of view, phytoplankton are photosynthetic organisms and zooplankton are phytoplankton consumers, therefore representing the first and second levels of the marine trophic chain. However, real food-chains may be very complex depending on the species involved (FENCHEL, 1988). In regard to size classification, a widely accepted cut-off between "classical" phytoplankton and adult zooplankton is 200 µm (SIEBURTH, 1972), though some zooplankton species may have smaller sizes (microzooplankton). Furthermore, though most phytoplankton species have dimensions larger than 20 µm, some species may also be smaller (picoplankton). For practical reasons, 20 µm and 200 µm are the adopted plankton cut-off sizes in our work. As transuranic concentrations in the Mediterranean Sea are low, zooplankton was collected by towing through surface waters, for 30-60 minutes, a large 200 µm mesh conical net (diameter: 1 m, length: 5 m) provided with a flow-meter. It should be noted that when the net saturates, some phytoplankton species may also be collected. Phytoplankton was collected by filtering large volumes of water through 20 µm depth cellulose filters (SCHLEICHER and SCHUELL, #520B). Other size fractions filtered were 8µm (Schleicher and Schuell, #AE99) and 0.2 µm (Gelman Sciences, Suporcap-100). The smaller fractions include increasingly larger proportions of suspended detrital particles. Samples reported in this work were collected during the MED'92 research expedition on board the N.O. Urania.

Phytoplankton and suspended particles. Large volume (c. 1000 liter) water samples were sequentially passed through 20 µm, 8 µm and 0.2 µm filters, and analysed for plutonium (Table 1). The phytoplankton fractions (microplankton: > 20 µm) showed activites ranging from 59-364 $\mu Bq \cdot m^{-3}$. The concentrations observed in the medium sized particles (nanoplankton: 8-20 µm), mostly constituted by small phytoplankton species, were low (28-119 $\mu Bq \cdot m^{-3}$) though smallest particles (picoplankton and suspended detritic and inorganic particles: 0.2-8 µm) showed concentrations of the same order as phytoplankton (43-218 $\mu Bq \cdot m^{-3}$). Therefore, about 50% of the particulate plutonium observed in the N.W. Mediterranean Sea appeared to be associated with the phytoplankton fraction (> 20 µm).

	Pu-239,240 ($\mu Bq \cdot m^{-3}$)		
Station	> 20 µm	8-20 µm	0.2-8 µm
Barcelona	168 ± 23	28 ± 24	144 ± 56
Golf de St. Jordi	364 ± 158	119 ± 63	218 ± 84
Garrucha	59 ± 20		43 ± 27 *

* 0.2-20 µm

Table 1. Plutonium concentrations in suspended particles (phytoplankton: > 20 µm) from the NW Mediterranean Sea, August 1992 (uncertainties = ±1σ). * 0.2-20 µm

Zooplankton. Zooplankton biomass was larger in the northern stations (Barcelona and Golf de St. Jordi, mean 18 ± 2 mg dw/m^3) indicating higher productivity related to higher nutrients input. The mean specific biomass in the Palomares area was only 5±2 mg dw/m^3. The wet to dry ratio ranged from 6 to 12. The transuranic concentrations and isotopic ratios in 4 zooplankton samples from the N.W. Mediterranean Sea are shown in Table 2. Concentrations ranged from 3.13-9.45 $\mu Bq(^{239,240}Pu) \cdot m^{-3}$ and 0.54-0.90 $\mu Bq(^{241}Am) \cdot m^{-3}$ corresponding to concentration factors (CF), computed as indicated in IAEA (1985), ranging from $(2.90\text{-}9.5) \cdot 10^3$ for Pu and $(2.9\text{-}14) \cdot 10^3$ for Am.

Location	Pu-239,240		Pu-238	Am-241		Am-241
	$\mu Bq \cdot m^{-3}$	CF $\cdot 10^3$	Pu-239,240	$\mu Bq \cdot m^{-3}$	CF $\cdot 10^3$	Pu-239,240
Barcelona	8,4 ± 0,6	4,7 ± 0,3	0,065 ± 0,014	0,54 ± 0,11	2,9 ± 0,7	0,064 ± 0,013
Golf St. Jordi	9,5 ± 0,4	8,2 ± 0,8	0,099 ± 0,011	0,9 ± 0,3	3,8 ± 1,5	0,095 ± 0,034
Palomares	3,13 ± 0,14	3,9 ± 0,2	0,026 ± 0,007	0,61 ± 0,06	7,9 ± 1,5	0,194 ± 0,021
P. Macenas	2,90 ± 0,12	4,8 ± 0,4	0,024 ± 0,008	0,80 ± 0,08	14 ± 3	0,274 ± 0,030

Table 2. Transuranic concentrations in zooplankton (> 200 µm) from the N.W. Mediterranean Sea, August 1992 (uncertainties = ±1σ).

K_d's, concentration factors and isotopic ratios. The particulate (> 0.2 µm) Pu amounted from 0.8% to 10% of the overall sea water activity, with K_d ranging from $(0.1\text{-}1.2) \cdot 10^5$ $l \cdot Kg^{-1}$. This is only slightly smaller (but within the range) than the phytoplankton CF recommended by IAEA (1985) and that reported in the literature (FISHER *et al.*, 1983). The phytoplankton (> 20 µm) CF for plutonium could not be derived as the sample mass was too low to be determined by standard methods on the filtered material.

The mean CF's for zooplankton were $4.4 \cdot 10^3$ for plutonium and $4.2 \cdot 10^3$ for americium, slightly higher (but within the range) than the values recommended by the IAEA (1985). The plutonium isotopic ratios showed the presence of bomb plutonium in the Palomares area samples (Palomares and P. Macenas), though activites were not higher. The distortion observed in the Golf de St. Jordi sample confirms the presence of plutonium from a nearby nuclear power plant (Vandellós I). The americium to plutonium ratio indicates a varying degree of sediment-originated radionuclides in the samples, going from a predominatly water origin (Barcelona) to a largely sediment origin (P.Macenas).

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ACTIVITIES OF URBINO UNIVERSITY FOR MARINE RADIOACTIVITY RESEARCH IN THE MEDITERRANEAN SEA

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Over the last ten years the General Chemistry Institute of the Urbino University (Italy) has been involved in the determination of artificial radionuclides (Plutonium and Sr-90) (TESTA *et al.*, 1990) and cosmogenic P-32 in environmental samples collected in the Mediterranean Sea area. These studies have been mainly carried out in collaboration with ENEL-CRTN (Milano), ENEA-CRAM (La Spezia) and Parma University.

The first research subject was the determination of Pu-239+240, Pu-238 and Sr-90 in sea sediment cores, surface sediments, algae and mussels. Extraction chromatography with tri-n-octylphosphine oxide (TOPO) and with di(2 ethyl hexyl)phosphoric acid (HDEHP) supported on microporous polyethylene powder (Microthene) was used for plutonium and Sr-90 (Y-90) separation, respectively (TESTA *et al.*, 1993). The determination of plutonium isotopes was obtained by alpha spectrometry after electroplating; Sr-90 was measured by counting a Y-90 oxalate source with a low background beta detector and following the Y-90 decay. The addition of Pu-242 (En α = 4.9 MeV) as the yield tracer and the analysis of the relevant alpha spectrum facilitated obtaining a precise figure for the recovery of any measure. Similarly the Y-90 chemical yield was obtained by a complexometric titration of the recovered yttrium. The accuracy and reproducibility of the method were checked by multiple analyses of IAEA and NBS certified samples.

Over the period 1985-1991 six sediments cores were collected at three different sites: Gaeta Gulf (Naples), Taranto Gulf (Ionian Sea) and Western Mediterranean Sea (Algeria). The relevant results are summarized in Table I.

Table I : Plutonium and Sr-90 in some sediment cores from the Mediterranean Sea.

Site (year)	Depth m	Core length cm	Maximum concentration (h,cm)		(Bq/kg)
			Pu-239+240	Pu-238	Sr-90
Gaeta Gulf A (1985)	50	10	2.2 (4-8)	0.06 (4-8)	27.4 (4-6)
Gaeta Gulf B (1985)	50	10	1.9 (6-8)	0.06 (6-8)	12.1 (0-2)
Gaeta Gulf (1989)	50	20	3.2 (12-16)	0.11 (12-16)	8.0 (8-12)
Taranto Gulf A (1989)	1500	15	1.0 (0-7)	0.03 (0-7)	-
Taranto Gulf B (1989)	2000	20	0.9 (7-11)	0.06 (7-11)	-
Algeria (1991)	2800	20	0.2 (0-2)	N-D	

h= core horizontal section depth

Plutonium and Sr-90 were also measured in some Northern Adriatic Sea samples (algae, mussels and surface sediments).The results were as follows :

1) Algae: plutonium concentration ranged from $<3.5\ 10^{-3}$ to $2.4\ 10^{-2}$ Bq/kg; Sr-90 concentrations varied between 0.5 and 1.7 Bq/kg.

2) Mussels: the mean plutonium concentration was $5.4\ 10^{-2}$ Bq/kg; Sr-90 concentrations were below the detection limit (0.9 Bq/kg).

3) Surface sediments: Pu-239+240 and Pu-238 concentrations (Bq/kg) ranged from $6.0\ 10^{-2}$ to 1.47 and from $<1.3\ 10^{-2}$ to $3.3\ 10^{-2}$, respectively. The Sr-90 concentration varied between <2.4 and 6.5 Bq/kg. The ratio Pu-238/Pu-239+240 and Sr-90/Pu-239+240 were 0.039 (8 samples) and 14.5 (10 samples), respectively.

The second research subject was the establishment of chemical and radioanalytical procedures for the determination of cosmogenic P-32 with the aim to evaluate the phosphorus cycle in the marine ecosystem (LAL *et al.*, 1988). For this purpose P-32, as phosphate ion, was measured in sea water, phytoplankton and zooplankton. Because of the low P-32 concentration, large water volumes had to be analyzed by retaining the phosphate ion on XAD-7 resin supporting $Fe(OH)_3$. After elution with 6 M HCl and Fe^{3+} elimination with methyl isobuthyl ketone (MIBK), phosphorus was purified by two selective precipitations as ammonium phosphomolybdate (AMP) and as $MgNH_4PO_4$. This salt was counted by a low background beta detector following the P-32 decay (T1/2 = 14.3 days). Some preliminary tests were carried out in the La Spezia Gulf (Northern Tyrrhenian Sea) where a small pilot plant with suitable filters and XAD-$Fe(OH)_3$ cartriges was checked. On the basis of the results shown in Table II, the following conclusions can be drawn. The total phosphorus concentration (3.07 mg/m^3) is in good accordance with the values reported in the literature for the Mediterranean Sea (~ 3 mg/m^3). The P-32 specific activity (302 dpm/g P) is higher than that reported by LAL *et al.* (1988) for the open ocean (100-250 dpm/g P), but this difference may be due to a river contribution in the La Spezia Gulf. The specific activity in phytoplankton+zooplankton is higher than in the dissolved inorganic phosphorus (DIP), due probably to the nonhomogeneity of the sampling site.

Table II : P-32 determination in La Spezia Gulf

Sample	Water volume (m^3)	P conc. (mg/m^3)	P-32 conc. (dpm/m^3)	Specific activity (dpm P-32/gP)
Phytoplankton + Zooplankton	100	0.09	0.03	369
Sea Water (DIP)	10	2.98	0.90	302
Total	_	3.07	0.93	-

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