INFLUENCE OF *POSIDONIA OCEANICA* ON THE DISTRIBUTION OF NATURAL AND ANTHROPOGENIC RADIONUCLIDES IN COASTAL SEDIMENTS OF THE NORTHWEST MEDITERRANEAN SEA

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Abstract
Samples were collected adjacent to the Island of Porquerolles in the Northwest Mediterranean Sea to study the distribution of natural and anthropogenic radionuclides in heavily oxygen-depleted sediments associated with the decomposition of organic carbon derived from the sea grass *Posidonia oceanica*. Elevated isotopic concentrations of uranium (^{234}U and ^{238}U up to 200 Bq/kg d.w.) were likely due to the high organic carbon and very low oxygen content of the sediment.
Keywords: Western Mediterranean, Sediments, Radionuclides

Introduction
Coastal sediments are ultimate sinks for particulate matter in the water column and as such, represent important repositories of historical information on contaminant levels in the marine environment. The present study sought to obtain new information on the distribution of natural and anthropogenic radionuclides in coastal sediments and to investigate how their concentrations are regulated by diagenetic processes associated with the decomposition of organic carbon derived from *Posidonia oceanica*. In order to interpret the sedimentary processes and to study contamination over the last century, a dating method derived from the excess of ^{210}Pb was used together with ^{137}Cs horizon produced by global fallout and from the Chernobyl accident [1,2].

Samples and methods
Sediment samples were collected in 2002 near the Island of Porquerolles in the Northwest (NW) Mediterranean Sea by the Scientific Centre of Monaco [3]. Weapons tests conducted by the French navy had formerly disturbed both sea grass cover (*Posidonia oceanica*) and sediments in the study area, resulting in extensive growth of the green alga *Caulerpa taxifolia* [3]. Two sediment cores (100 mm in diameter and 0.8 long) were collected by divers at a region of overlap between two weapons-damaged areas (St. 1 and 2). A third core was collected by divers at a control site 6 km away from the damaged area (St. 3). A more distant reference core (St. 4) was collected offshore near Monaco. The St. 1 core was stored in a refrigerator and exposed to a sensitive photographic film for one week. The cores were freeze-dried and sliced transversely into 10 mm thick sections, and pulverized using an agate mortar and pestle prior to radiochemical analysis. Samples were analysed for anthropogenic (^{137}Cs, ^{238}Pu, ^{239,240}Pu and ^{241}Am) and natural (^{226}Ra, ^{210}Pb, ^{210}Po, ^{234}U, ^{235}U and ^{238}U) radionuclides and for organic carbon (OC). ^{210}Pb(excess) was derived from the measured ^{210}Pb (total) and ^{226}Ra profiles, in order to date the cores by reference to their sediment accumulation rates.

Results and discussion
The sediment cores obtained at St. 1, St. 2 and St. 3 all bore the hallmarks of anoxia: dark-grey colour, strong H_2S smell and the organic remains of *Posidonia oceanica* dispersed throughout. OC is oxidized by O_2 and via the reduction of NO_3^-, SO_4^{2-} and Mn/Fe oxides in sediments. The contribution of reduced species to O_2 consumption is effectively enhanced in coastal areas where anoxic conditions can be established even in surficial sediments due to high inputs of organic matter [4]. The sediments found at Porquerolles were highly anoxic, as evidenced by a lack of Mn peaks in the surface layers, whereas St. 4 showed a high concentration of Mn in the surface layer caused by the formation of MnO_2 (Mn analyses carried out by XRF). Organic carbon plays a critical role in determining the distribution of major elements and radionuclides in coastal sediments via its influence on diagenesis [5,6]. The surface OC content of Porquerolles sediments was much higher than previously reported (3.4 to 5.7 % versus < 1% in the western Gulf of Lions [4]) and could be attributed to the substantially greater density of vegetation cover. Fragments of *Posidonia oceanica* were found throughout the Porquerolles' sediment profiles following weapons tests that killed the sea grass beds and caused the rapid formation of new layer of organically rich sediment [3]. The OC content of the distant reference core taken at St. 4 was much lower (0.6 to 1.1 %) and was comparable with values determined in previous investigations [4]. The ^{210}Pb$_{(ex.)}$ profiles of Porquerolles sediments revealed the impacts of weapon tests, which produced mixed sediment layers and high sediment accumulation rates up to 1.2 cm yr^{-1}, higher than have been reported elsewhere in NW Mediterranean [1,7]. The photographic film placed on the sediment core collected at St. 1 displayed evidence of exposure to radiation emitted from the sediment surface. A few "hot" particles were isolated from the sediment at depths close to 40 cm from the surface, and analysed by SIMS. These analyses confirmed the presence of highly enriched U particles (AMS analyses of "hot" particles are still in progress). The origin of "hot" particles in the sediment is not yet known. Radiometric analyses of bulk sediment samples revealed U isotope concentrations at Stations 1 and 2 (^{234}U and ^{238}U up to 200 Bk/kg d.w.) well in excess of those measured at Stations 3 and 4. The peak U concentrations were observed at depths of around 40 cm, which coincided with a peak in OC concentration. High oxidation state of uranium (VI) dissolved in pore water tends to be reduced to immobile U(IV) and precipitate beneath the redoxcline. When the degradable organic matter in sediment is completely consumed, no further incorporation of U occurs in the sediment, and authigenic U is recycled to the ocean [6]. The high OC load and strong reducing conditions in the sediment at Porquerolles likely explains the high total U content. The average activity ratio of ^{234}U/^{238}U is 1.107 ± 0.018, consistent with the world's ocean value of 1.12 ± 0.01 [8]. The average activity ratio of ^{235}U/^{238}U is 0.038 ± 0.006, which is close to the natural level (0.047), but different from values characterising either an enriched U (0.091), or a depleted U (0.019). ^{239,240}Pu and ^{241}Am levels in surface sediments ranged from 1.0 to 5.7 Bq/kg and from 0.3 to 1.0 Bq/kg d.w., respectively. ^{137}Cs levels were between 0.3 and 6.2 Bq/kg. We may conclude: While high uranium content observed at St. 1 may be due to the high organic carbon and very low oxygen content of the sediment, the origin of uranium enriched particles in the sediment is not yet known, and further investigations are on the way to explain this anomaly.

References
1 - Zuo, Z., Eisma, D., Gieles, R., Beks, J., 1997. Accumulation rates and sediment deposition in the northwestern Mediterranean. *Deep Sea Research* II, 44: 597-609.
2 - Masqué, P., Fabres, J., Canals, M., Sanchez-Cabeza, J. A., Sanchez-Vidal, A., Cacho, I., Calafat, A. M., Bruach, J. M., 2003. Accumulation rates of major constituents of hemipelagic sediments in the deep Alboran Sea: a centennial perspective of sedimentary dynamics. *Marine Geology*, 193: 207-233.
3 - Chisholm, J.R.M., Povinec, P.P., Briet, V., Gastaud, J., Jaubert, J.M., Lee, S-H., Levy-Palomo, I., Marchioretti, M., Minghelli-Roman, A., 2007. A century of warfare shoots holes in anti-*Caulerpa* campaign. *Nature Precedings*, doi:10.1038/npre.2007.1240.1.
4 - Accornero, A., Picon P., De Bovée, F., Charrière, B., Buscail, R., 2003. Organic carbon budget at the sediment-water interface on the Gulf of Lions continental margin. *Continental Shelf Research*, 23: 79-92.
5 - Ogrinc, N; Fontolan, G; Faganeli, J; Covelli, S., 2005. Carbon and nitrogen isotope compositions of organic matter in coastal marine sediments (the Gulf of Trieste, N Adriatic Sea): indicators of sources and preservation. *Marine Chemistry*, 95: 163-181.
6 - Mangini, M., Jung, M., Laukenmann, S., 2001. What do we learn from peaks of uranium and of manganese in deep sea sediments? *Marine Geology*, 177: 63-78.
7 - Sanchez-Cabeza, J.A., Masque, P., Ani-Ragolta, I., Merino, J., Frignani, M., Alvisi, F., Palanques, A., Puig, P., 1999. Sediment accumulation rates in the southern Barcelona continental margin (NW Mediterranean Sea) derived from ^{210}Pb and ^{137}Cs chronology. *Progress in Oceanography*, 44: 313-332.
8 - Lee, S.-H., La Rosa, J., Levy-Palomo, I., Oregioni, B., Pham, M., Povinec, P., Wyse, E., 2003. Recent inputs and budgets of ^{90}Sr, ^{137}Cs, ^{239,240} Pu and ^{241}Am in the northwest Mediterranean Sea. *Deep-Sea Research* II, 50: 2817-2834.