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Transuranium radionuclide pollution in the waters of the La Maddalena National Marine Park

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Abstract

Following the grounding and subsequent explosion, in October 2003, of a nuclear submarine in the waters of the La Maddalena National Marine Park, fears arose of possible radioactive leakages. However, isotopic analyses on algae showed that the gamma-ray emitting artificial radionuclides that one might expect to leak from a damaged nuclear reactor (such as U-235, I-131, Cs-137) were absent, and that U-238/U-234 activities were in equilibrium with values typical of sea water; this excluded any direct anthropogenic contamination as a result of the accident.

We used alpha autoradiographic techniques to detect possible traces of transuranium radionuclides; 160 samples of algae, granites, sea urchins, gastropods, limpets, cuttlefish and jellyfish were collected from the area, as well as from other Mediterranean coastlines and the Baltic Sea. All samples were autoradiographed, and selected samples further analysed by alpha spectrometry.

There were no alpha track concentrations above background levels in our control Mediterranean specimens. In the samples from the La Maddalena and Baltic areas two different track distributions were observed:

- those homogeneously distributed over the surfaces examined;
- groups (10 to over 500) of radially distributed alpha tracks (forming "star" bursts, or "hot spots") emanating from point sources.

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By comparing radionuclide activities measured by alpha spectroscopy with alpha track densities, we extrapolated Pu activities for all samples. About 74% of algae had Pu activities of less than 1 Bq/kg and 0.25 Bq/kg, 16% had accumulated Pu to levels between 1 and 2 Bq/kg, and a very few specimens had concentrations between 2 and 6 Bq/kg.

Plots showed that alpha tracks and stars concentrate around the northern and eastern margins of the Rada (*Basin*) di Santo Stefano, sites facing the nuclear submarine base on the eastern shore of the island of Santo Stefano. What is the source of these nuclides: last century's atmospheric nuclear testing, Chernobyl or a local source? Their concentrated, extremely localised occurrence seems difficult to explain in terms of left-over worldwide nuclear pollution. A local source seems more plausible.

Keywords: Alpha autoradiography; Transuranium radionuclides; Marine pollution

1. Introduction

The La Maddalena National Marine Park consists of an archipelago of small granitic islands on the northern tip of the island of Sardinia, separated from the French island of Corsica by the Straits of Bonifacio (see location map, Fig. 1).

Towards the end of October 2003 a nuclear powered submarine ran violently aground onto granitic shoals (Secca dei Monaci) in the vicinity of the island of Santo Stefano (only 6 miles from the town of La Maddalena), Santo Stefano being the submarine's home base. There followed a major explosion which severely damaged the submarine.

2. Initial isotopic analyses

Fears that radioactive material might have leaked from the submarine quickly prompted several agencies, both Italian and French, governmental and independent, to examine the situation. Samples of algae and sea water were taken from the area for analysis; the French independent radiation control agency CRIIRAD (CRIIRAD, 2004a, Bull. No. 1) was the first to make available the results of their isotopic analyses using gamma ray spectroscopy. It became clear that gamma-ray emitting artificial radionuclides that one might expect to leak from a damaged nuclear reactor (such as U-235, I-131) were either absent or, as in the case of Cs-137, in the very low concentrations found at other sampling points around the country.

Subsequent radiochemical/alpha spectrometric analyses by the Italian laboratory U-Series showed that U-238 and U-234 activities were in equilibrium, with values in keeping with those of sea water. The CRIIRAD and U-Series analyses therefore confirmed that the submarine accident had not caused any particular radioactive pollution.

Interestingly, the CRIIRAD analyses reported that two out of their six algae analysed revealed the presence of abnormal concentrations of Th-234, with activities

Fig. 1. Location map of the La Maddalena National Marine Park with relation to the islands of Sardinia, Corsica and the Mediterranean Sea.

ranging from 3900 to 4700 Bq/kg, as compared to the normal values of the order of a few dozen Bequerels. This disequilibrium was attributed to the natural selective absorption of thorium by certain algal species, in this case the red and coralline algae (*Jania rubens* and *Corallina elongata*). Indeed, CRIIRAD later (CRIIRAD, 2004b, Bull. No. 2) demonstrated that the excess Th-234 in algal samples isolated from their marine environment decreased at the same rate as the isotope decayed (half life 24 days), as it could not be replaced by further preferential absorption from the surroundings. In this paper, we report several other species of algae which also absorb particular radionuclides in a preferential way.

3. Transuranium radionuclides

At first, in the foregoing investigations, the detection of Pu was not attempted. Am-241, if present, was below gamma-ray spectrometric detection limits. Pu-239 is particularly dangerous in that it is both highly toxic chemically and a radioactive source; if assimilated by the body, it tends to substitute calcium in the structure of bones, and may lead to the formation of tumours. Pu-239 is the main by-product formed by the neutron bombardment of U-238 during the functioning of a nuclear reactor. Pu-239 decays emit primarily alpha rays together with several very weak gamma-ray emissions. Most laboratories are only equipped to study gamma rays using multi-channel germanium spectrometers: these instruments cannot see the alpha rays emitted by plutonium. Even those labs equipped to detect alpha rays using silicon crystal spectrometers cannot use samples "as is"; concentrations are so low that one needs to use lengthy, tedious radio-chemical procedures to concentrate individual transuranium isotopes to levels high enough for the spectrometers to see them. Nevertheless, both CRIIRAD and ourselves were able to send a few samples to other laboratories for classical radiochemical/alpha spectrometric analyses of Pu and Am.

4. Analytical techniques – alpha autoradiographs

Not satisfied by the small number of samples which could be analysed radiochemically/spectrometrically, we overcame the problem using alpha autoradiographic techniques (Fleischer, 1979, 1998; Fleischer et al., 1975; Aumento, 1979; Evans, 2004). The algae were prepared for analysis in two different ways:

(1) 50 g or so are dried in a temperature-controlled oven at 50 °C for 3 days; a weight loss of 60–80% is common. The dry algae are then pulverized, and 2 × 2 cm flat samples prepared by compressing the powders inside 4 × 4 cm plastic analytical weighing "boats"; the sample thickness is not important.
(2) Smaller quantities of wet individual algal species (when possible to separate them) are evenly distributed in the same 4 × cm weighing "boats"; sandwiches are made with other loaded boats, the multiple assemblies then squeezed using "C-Clamps" and placed in the same ventilated oven at 50 °C for 3 days. When dry, the resulting thin, compressed algal sheets can be removed from the boats with ease, and cut into 2 × 2 cm squares.

In both cases, sample thickness is not important, since the autoradiographs will only record the sample's surface alpha activity down to a few microns depth.

The samples so prepared, both in the form of dried compressed sheets and dried homogeneous powders, are placed in direct contact with a film sensitive only to alpha rays of a particular energy (Kodak Pathè LR-115 Type 2; sensitivity range 1.2–4.8 Mev) for known periods of time; each emission of an alpha particle from the sample surface produces a linear damage on the film's coating which, subsequent to chemical development, can be observed with a microscope. The number of tracks observed over a given area after a given contact time gives an indication of the alpha activity of the sample surface, and consequently a relative idea of concentration. However, whereas the technique cannot distinguish directly between different transuranium radionuclides and other alpha emitting isotopes, it has the advantage of speed; several dozen samples can be analysed simultaneously in a matter of a few days.

We visited the Maddalena area on two occasions, 20–22 February and 5–8 May 2004; over 160 samples of algae, granites, sea urchins, gastropods, limpets, cuttlefish and jellyfish were taken. All specimens, several in duplicate, both in the form of solid compressed sheets and as homogenized powders, were autoradiographed, together with blank LR-115 films; for further control purposes, algal samples collected along the Upper Latium and Lower Tuscany Tirrenian coastlines were included, as were samples from other sites within the Mediterranean and Baltic seas.

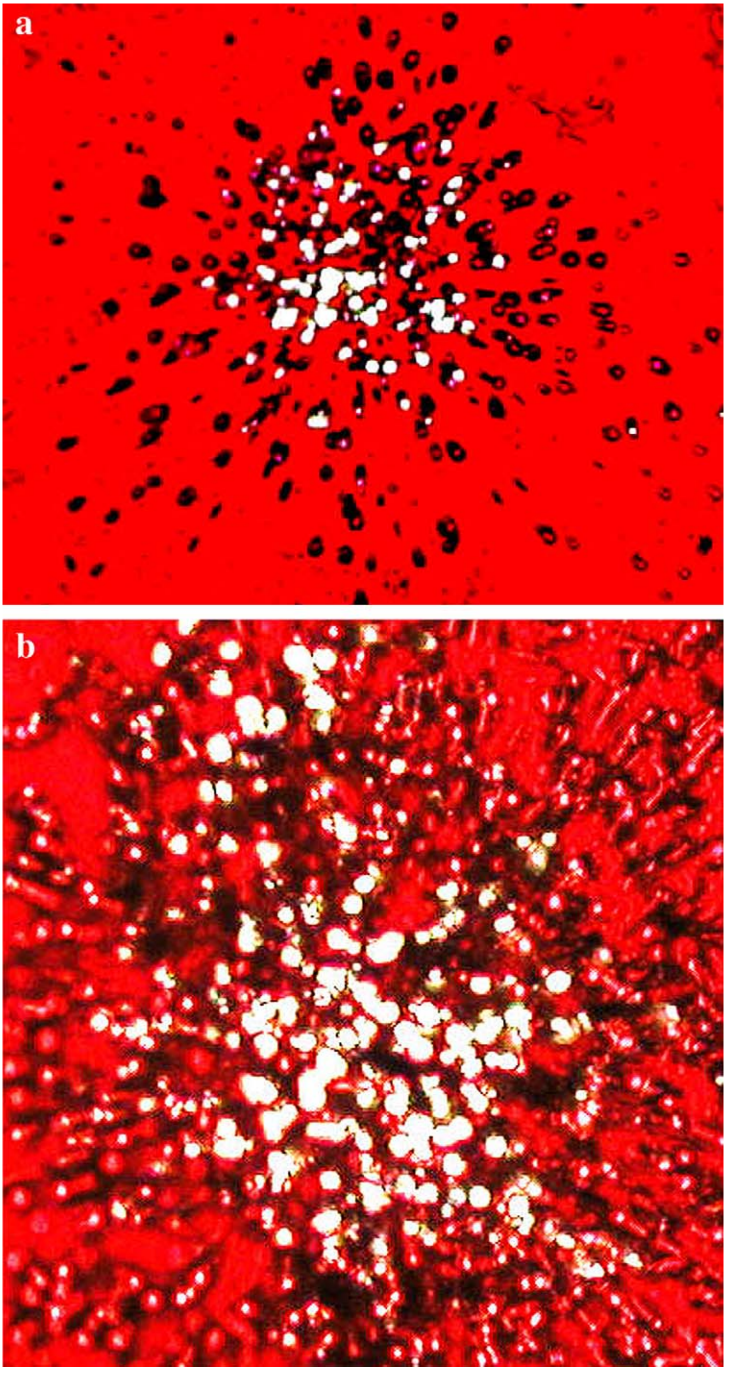
5. Results

There were no alpha particle track concentrations above background values in the 26 Tirrenian specimens (see Table 1). In the remaining 124 samples from La Maddalena, Caprera and Palau coastlines (and the Baltic Sea), two different track distributions were observed:

- All samples, both in the forms of compressed sheets and homogeneous powders, had homogeneously distributed tracks over the surfaces examined, with concentrations ranging from 0 to 50 tracks (average: 8) per cm^2 per each day's exposure; these tracks are produced by single alpha particle emissions emanating from the near surface distribution of nuclides incorporated into the algae directly from solution in sea water during their growth.
- In 33 samples (30 algae, plus one each of jelly fish egg case, sea urchin and limpet; see Table 1) superimposed onto these homogeneous fields were radially distributed tracks emanating from point sources; these track's concentrations could contain from as few as 10 to as many as >500 individual tracks, forming "star bursts" (see Fig. 2a and b), each covering circular areas from 0.2 mm to 0.5 mm diameter. These stars, better known as "hot spots", are produced by the decay of minute, solid radioactive particles incorporated onto or very close to the surfaces of the

Table 1
Sample locations, visual descriptions, classifications (where possible), alpha tracks densities (tracks per field per 30 day exposures), number and sizes of hot spots, and tentative conversion to bulk Pu activities

Tirrenian coast (sedimentary/volcanic terrain)	0.0 Bq/kg
Giglio Island (granitic)	0.06
Bermuda (coralline/volcanic base)	0.20
Hyeres (S. France; sedimentary)	0.07
N. Adriatic (sedimentary)	0.08
Helsinki (granitic)	3.50


a
b

algae. Other such particles embedded deeper within the algal tissues do not show up on the autoradiographs due to the limited range an alpha particle can travel through matter (a few microns).

6. Identification of the alpha tracks

There remains the question of identifying the source of the alpha tracks, i.e., which radionuclides are responsible for their emissions. The parallel distribution of the homeogeneous and hot-spot alpha tracks, showing a continuous progression from one form of occurrence to the other, as well as the similar lengths of the tracks in both types of occurrences, suggest that both sets are the result of the decay of radionuclides with similar energies of emission. The latter could include natural or anthropogenic sources, or a sum of two or more emitters.

Natural alpha-emitting radionuclides include radium, thorium, uranium and polonium. These could be released from radioactive minerals in the country rock, including apatite, zircon, monazite, allanite and uranophane. However, these minerals are very rare in the Maddalena granites, but can occasionally be found in very thin pegmatitic dykes (see http://web.tiscali.it/quasarminerali/). Even though the areas sampled (La Maddalena, mainland Sardinia, the island of Giglio) consist of very homogeneous granites of similar chemistries, high concentrations of alpha tracks were found only around a single area, that of a restricted part of La Maddalena (see Figs. 5 and 6); hot-spot occurrences were similarly restricted to that same area and to Baltic Sea specimens.

Possible artificial alpha emitting radionuclides include the transuranium nuclides of plutonium and americium, indicative of anthropogenic sources (see below). It was therefore essential to carry out specific identifications of the origin of these alpha tracks. This was accomplished through radiochemical concentrations and alpha ray spectroscopy for Pu and Am of selected samples over the range of alpha track concentrations found; furthermore, a homogenized composite sample of 14 La Maddalena algae with previously measured alpha track densities was also analysed by radiochemical/alpha ray spectrometry. Pu-239/240 was positively identified in all samples. Am-241 levels were below the detection limits of ≤ 0.15 Bq/kg dry.

7. Alpha track − plutonium activity conversions

Pu activities measured by radiochemistry/alpha spectrometry correlated well with alpha track densities over the range 0.6–3.5 Bq/kg Pu, suggesting that a major

Fig. 2. (a) Massive alpha particle "hot spot" recorded from the surface of a dark brown alga at Station #5 (see maps of Figs. 5 and 6 for location). The hot spot consists of well over 150 nuclear tracks emitted from a central point which have pierced the 7 μm thick red cellulose nitrate layer of the LR-115 film; some 200 more, inclined away from the centre, have only partially penetrated the layer prior to the particles' loss of kinetic energy. Image size approximately 0.2 mm across. (b) Smaller "hot spot" from a fibrous green alga (*Gladophora* sp?) showing the radial structure more clearly. The specimen came from an adjacent Station, #6.

contributor to the formation of alpha tracks was indeed Pu. If so, one can calculate an approximate conversion factor from tracks to PU:

$$\text{tracks/field/30 days} \div 7.7 = \text{Pu Bq/kg}$$

However, this conversion factor must be used with caution. Due to their low penetration capacity, alpha tracks give an indication of total radionuclide activities on the surface, or just a few microns below the surface of samples. Some estimate of activities within the samples can be obtained by comparing surface track densities of solid samples with track densities measured on pulverized, homogenized and reconstituted samples. In each of these cases we are looking at alpha track densities from small samples, with areas of little more than 1 cm × 1 cm, whereas radiochemical/alpha spectrometric analyses are on bulk samples (weights around 1 k wet).

Fig. 3 shows a histogram of the alpha track data tentatively converted to Pu-239/240 activity per kg wet. We see that in most algae (74%) total activity is less than 1 Bq/kg, a level considered safe in food sources by the EU/EURATOM. Only 16% of algae have accumulated Pu to levels between 1 and 2 Bq/kg, and a few rare specimens have activities between 2 and 6 Bq/kg. The average for La Maddalena algae is less than 0.5 Bq/kg. Not only the red and coralline algae, but different species, including the green and brown ones, have different, variable capabilities of concentrating radionuclides (see Fig. 4).

Algae from our other control sites gave the Pu activities as in Table 1.

8. Alpha track distribution around Maddalena

The inlets formed by the islands of Maddalena, Caprera, Santo Stefano and the Palau coastline are shallow (never more than 50 m deep, often less than 10 m), with

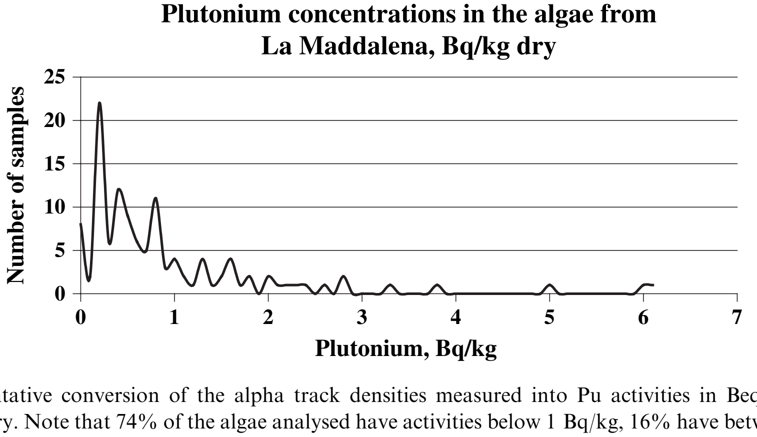


Fig. 3. Tentative conversion of the alpha track densities measured into Pu activities in Bequerels per kilogram dry. Note that 74% of the algae analysed have activities below 1 Bq/kg, 16% have between 1 and 2 Bq/kg, and the remaining single specimens have activities ranging up to 6 Bq/kg. For comparison purposes, Baltic Sea algae are quoted as having an average of 3 Bq/kg.

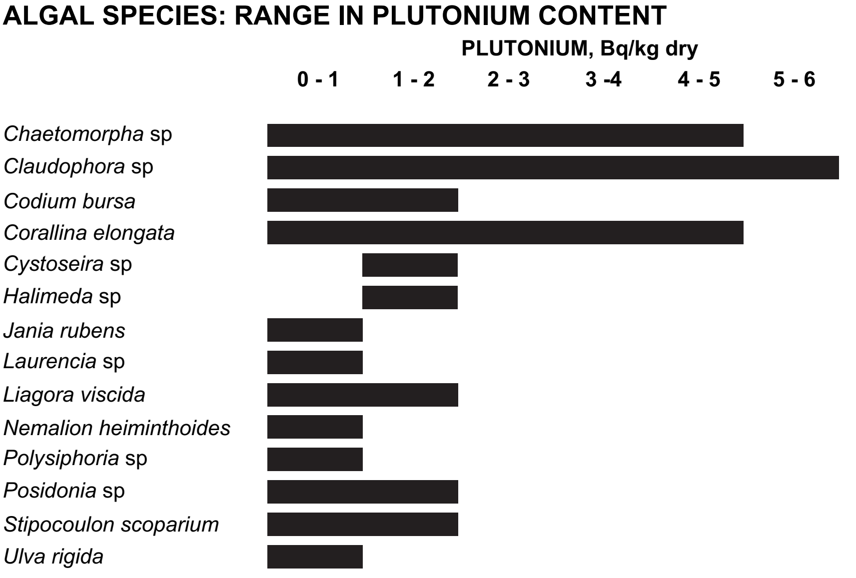


Fig. 4. Range of Pu activities found in different specimens of the algal species collected around the La Maddalena Archipelago.

rocky granitic bottoms extensively covered by *posidonia* grasses. The dynamic energy of the water masses in the inlets and passages is low, with very little, localised sediment transport (Brondi et al., 1976). It is controlled by winds and surface currents. Both of these are predominantly westerlies during the autumn–winter seasons, changing to easterlies in the summer.

The work of Brondi et al. (1976) on the distribution and composition of sediments in the area showed that minerals derived from the weathering of the granites did not travel far from their source rock; this is important because those sediments that had traces of minerals with a possible radioactive content (apatite, zircon, monazite) were shown to lie in areas well removed from sites where high concentrations of alpha tracks and hot spots were detected. This distributional discordance further dissociates alpha track origins from natural sources.

The spatial distributions of both the alpha tracks and hot spots along the Maddalena coastlines are very well defined. Figs. 5 and 6 attempt to give a simplified, visual appreciation of the relative concentrations of tracks and hot spots in the area: actual concentrations, and their variations, of individual tracks and hot spots are to be found in Table 1. The figures show how in the winter/spring seasons both the alpha track and hot spot concentrations are to be found along the coastlines of the Rada di S. Stefano (S. Stefano basin) facing west/south west. We have found them all the way from Nido d'Aquila (west of the town of Maddalena) to Punta Nera, Cala Chiesa, Cala Camiciotto (east of Maddalena), and on to Cala Stagnali, Punta Coda, and Porto Palme on the adjacent island of Caprera. The highest concentrations were found around the northern and eastern margins of the Rada

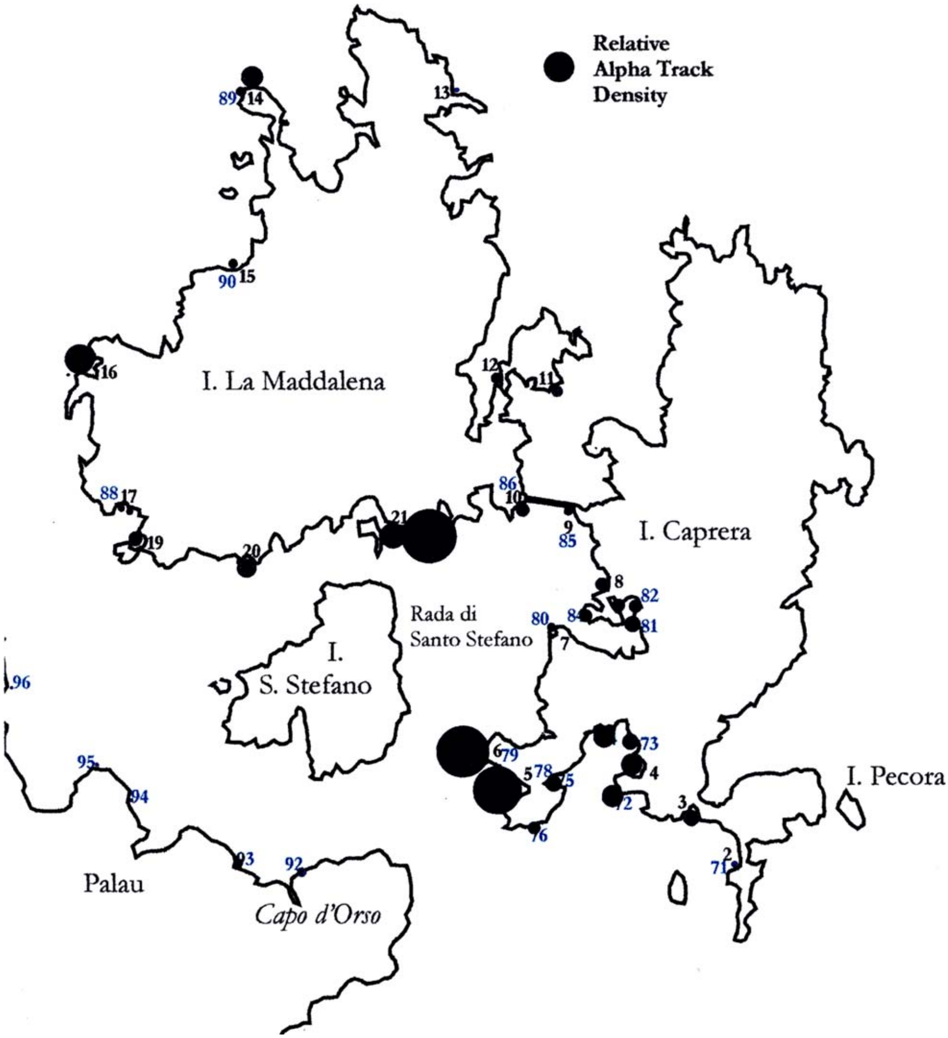


Fig. 5. Station locations around the Maddalena Archipelago, with a visual representation of the relative concentrations of individual alpha tracks found represented as circles of different sizes (actual data given in Table 1).

di Santo Stefano, all sites looking into the wind and prevailing currents towards the nuclear submarine base on the eastern shore of the island of Santo Stefano. In contrast, algae from the whole Palau mainland coastline to the south, and sites on the Tirrenian coast, were practically free of alpha tracks.

The presence of the massive alpha track hot spots, whatever their origin, is more worrisome than homogeneously distributed high values: they are indicative of very localized concentrations of solid radionuclide-rich particles onto very small areas of

Fig. 6. Station locations around the Maddalena Archipelago, with a visual representation of the relative sizes of alpha track "hot spots" represented as stars of different sizes.

algal tissues. These microscopic areas of live tissue will receive, throughout their life span, orders of magnitude higher doses of alpha particles than surrounding tissues; the damage will be localized, but extreme. Radiation doses, always considered by the various radioprotection agencies such as the ICRP (International Commission for Radiation Protection) and the WHO as being homogeneously distributed, are not realistic (LLRC, 2004). In view of the existence of "hot spots", in 2000 the UNESCAR (United Nations Committee of the Effects of Atomic Radiation) confirmed that radiation dose values calculated from models using volumetric means have no significance (UNESCAR, 2000).

9. Conclusions

Where do these radionuclides come from? The atmospheric testing of atomic bombs in the fifties and sixties contaminated the whole world with transuranium particles (Taylor, 2001). In subsequent years these particles were redistributed on the surface of our planet as a result of differences in local conditions such as rainfall, topography, erosion, winds and currents. Some areas have been swept clean of these pollutants; on the contrary, others have received more contaminants from ongoing anthropogenic activities. These include nuclear incidents, minute losses of cooling fluids in nuclear power plants, illegal dumping at sea (even of decommissioned nuclear submarines), poor safety features at nuclear fuel re-processing plants (Doll, 1999), and other accidents.

None of these more recent sources should exist around the Maddalena National Marine Park. Localised events in other seas and distant lands (Sellafield, La Hague) have not affected this area of the Mediterranean, as evidenced by data along the adjacent granitic northern Sardinian coast and the Italian peninsula. And yet, as a result of the October 2003 incident, which focused our attention onto the area, we found radionuclides absorbed recently (given the relatively short life span of algae) in marine life forms living in one particular area of the Park. These concentrated, extremely localised occurrences seem difficult to explain in terms of either left-over worldwide nuclear pollution or from the weathering of granites. Large, solid transuranium rich particles capable of producing these ‘‘hot spots’’ are unlikely to have survived integrally during decades in turbulent wave action waters. A local source seems more plausible. We see from their distribution patterns that they were concentrated by prevailing current/wind actions onto areas quite distinct from those where sedimentary processes deposited trace amounts of possible radioactive minerals derived from the weathering of granites. Their distribution has a definite geographical relationship to the submarine base on the island of Santo Stefano. We suggest that losses of minute quantities of radionuclides from transiting nuclear submarines, and especially from servicing/(and refuelling?) procedures at their base should be investigated further using appropriate techniques.

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