

## Project Report

# Plutonium Isotopes Concentration in Seawater along the Algerian Coast

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The International Atomic Energy Agency has organised in the framework of the regional project RAF/7/004, in collaboration with “Commissariat à l’Energie Atomique” (COMENA) and “Institut des Sciences de la Mer et de l’Aménagement du Littoral” (ISMAL), during August 2001, a scientific campaign along the Algerian coast, on board of the research vessel M.S. Benyahia of ISMAL is. Three stations, at the centre, east and west, were selected to collect five seawater samples for each water column reaching a maximum depth of 2000 m, using a stainless-steel water sampler of a volume of 250 litres. After recording the marine environment parameters (temperature and conductivity), seawater samples were conditioned and preconcentrated to precipitate plutonium isotopes using  $\text{MnCl}_2$  in the form of  $\text{MnO}_2$  in order to proceed to plutonium extraction by radiochemical separation and prepare the source by coprecipitation using neodymium fluoride ( $\text{NdF}_3$ ) by vacuum filtration and an evaluation of the activity by alpha spectrometry. Concentration results in units of  $\mu\text{Bq/l}$  of plutonium isotopes were obtained in the range of  $6.7 \pm 1.00$  to  $25.5 \pm 3.70$  for  $^{239+240}\text{Pu}$  and  $0.21 \pm 0.04$  to  $0.77 \pm 0.15$  for  $^{238}\text{Pu}$ . Distribution of Pu through the plot of its profile was studied and the concentration was estimated. The obtained results were compared to  $^{137}\text{Cs}$  and those found by other authors in the same Mediterranean area.

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## 1. INTRODUCTION

The Mediterranean sea is a semienclosed sea located between Europe, Asia, and Africa, subject to properties and seawater exchanges, coming particularly from the Atlantic Ocean.

This sea is characterized by an important evaporation and a weak rate of dilution. It becomes thus vulnerable; and therefore studying the radioecological marine phenomena is required. This medium is thus exposed to the introduction of natural radioactivity since the creation of the earth, and artificial radioactivity since the advent of nuclear industry. An increase of this radioactivity in the different marine medium compartments has occurred according to physico-chemical properties of the receiving medium and including the radioelements of interest.

The evaluation of the concentration of some artificial radioelements of interest becomes necessary to study their behavior in the marine medium (seawater, sediments, marine organisms, etc.). For this purpose, and within the framework of a radiological monitoring project of the marine medium along the Algerian coast, several sampling campaigns were carried out from 1997 to 2004.

The results presented in this work are those obtained in the oceanographic campaign carried out in August 2001

in the framework of the regional project RAF/7/004 organized by the IAEA, in collaboration with CEA and ISMAL, on board of the research vessel M.S. Benyahia of ISMAL, along the Algerian coast, at the centre, east, and west. Samples of water columns (surface/depth, maximum depth of 2000 m) were collected, treated, and preconcentrated on board, maximal 2000 m), to be subject to a fine radiochemical separation analysis at the laboratory in order to extract Pu isotopes, with the aim of determining Pu profiles against depth (m).

## 2. MATERIALS AND METHODS

### 2.1. Sampling and preconcentration

Three stations (Figure 1) were considered for the measurement campaign, Algiers (N  $36^\circ 54.059$ , E  $003^\circ 20.452$ ) at the centre, Jijel at the east, and Ténés (N  $36^\circ 44.707$ , E  $01^\circ 38.421$ ) at the west. Seawater samples were collected at several layers, from surface seawater to a maximum depth of 2000 m, using a stainless-steel bottle of a volume of 250 liters (Figure 2) in each station. After recording different parameters (temperature in  $^\circ\text{C}$  and conductivity in mS) for each layer, the seawater sample was filtered and transferred through a pump towards a polyethylene tank of a volume

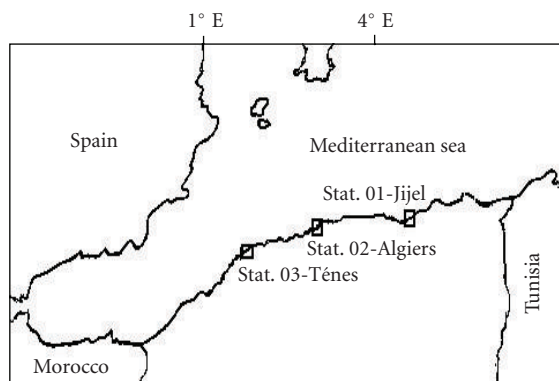


FIGURE 1: Locations of sampling station.



FIGURE 2: Seawater sampler (IAEA).

of 200 liters to be treated and to preconcentrate radioelements of interest, namely,  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ , and, in the case of this work, plutonium isotopes. In addition to the radioactive spikes ( $^{134}\text{Cs}$ ,  $^{85}\text{Sr}$ , and  $^{242}\text{Pu}$ ) and the stable carriers introduced in each sample, an appropriate amount of  $\text{MnCl}_2$  was added in order to precipitate plutonium isotopes in the form of  $\text{MnO}_2$ . After this step of preconcentration, samples were reduced from a volume of 150 liters to a volume of around ten liters, for an analysis by fine radiochemical separation at the laboratory in order to extract, in our case, the isotopes of plutonium and to determine the concentration in  $\mu\text{Bq/l}$ .

## 2.2. Radiochemical analysis

Presence in seawater of some alpha-emitting radioelements particularly plutonium isotopes is known to be at the state of traces. Their concentration, according to the degree of contamination of the medium, can fluctuate between a few  $\mu\text{BqL}^{-1}$  until some  $\text{mBqL}^{-1}$ . Consequently and in order to be able to extract by radiochemical separation the radioelement of interest and to quantify by alpha spectrometry the specific activity, significant quantities reaching hundreds of liters (up to 500 l) must be taken and treated on board with the aim of preconcentration of the required radioelements.

Samples of seawater collected on board of the research vessel M.S. Benyahia of ISMAL were acidified to a pH (1-2), the radioactive tracers corresponding to the radioelements of interest (isotopes of Pu,  $^{137}\text{Cs}$ , and  $^{90}\text{Sr}$ ) were added in order to determine at the end of the analyses the chemical yield. With the aim of preconcentration of plutonium isotopes,  $\text{KMnO}_4$  was added in order to oxidize the organic matter as well as plutonium at the state VI.

The solution is maintained in a basic medium (pH  $\sim 9$ ) by  $\text{MnCl}_2$ , after addition of  $\text{NaOH}$ . Plutonium precipitates in the form of  $\text{MnO}_2$  are stored in a plastic container reaching a volume of around ten liters for its analysis at the laboratory.

The precipitate was then dissolved by adding a quantity of  $\text{HCl}$  2 M and  $\text{N}_2\text{HOH}\cdot\text{HCl}$  while carrying out an agitation so that the solution becomes clear. While heating the last solution,  $\text{Fe(III)}$  as  $\text{FeCl}_3$  dissolved in 0.1 M  $\text{HCl}$  and  $\text{NH}_2\text{OH}\cdot\text{HCl}$  were added in order to reduce Pu to the state of oxidation III.  $\text{Fe(II)}$  and  $\text{Pu(III)}$  were oxidized with the state  $\text{Fe(III)}$  and  $\text{Pu(IV)}$ , respectively, by adding  $\text{NaNO}_2$ ,  $\text{Pu(IV)}$  was precipitated by the ammonium hydroxide to a pH between 8-9. The solution was left overnight for decantation until a minimal pH between 6-7 was reached. The solution was centrifuged; the supernatant recovered and then passed through a paper filter. The latter was washed with concentrated  $\text{HCl}$ ; the filtrate was recovered in the tube of centrifugation with the precipitate. The whole was transferred to a 250 cc glass beaker; evaporated nearly to dryness. The residue was then dissolved with concentrated nitric acid and centrifuged. The supernatant was recovered in a glass beaker after filtration. The obtained solution was transferred in a glass beaker, and iron was tested with ammonium cyanide ( $\text{NH}_4\text{SCN}$ -5 M). Some drops of basic reducing agent (hydrazinium Hydroxide— $\text{N}_2\text{H}_5\text{OH}$ —5M) were added to initiate a reduction-oxidation reaction of ferric-iron ( $\text{Fe(III)}$ ) which is reduced to ferrous-iron ( $\text{Fe(II)}$ ), this will involve a reduction of plutonium to state III. The solution is cooled and 5 grams of sodium nitrite ( $\text{NaNO}_2$ ) are added to convert plutonium to the state of oxidation IV, that is, ( $\text{Pu(III)}$  to  $\text{Pu(IV)}$ ).

An anion exchange column (resin AG1X8 100 to 200 meshes) is conditioned with 100 mL of  $\text{HNO}_3$ -2 M and 50 mL of  $\text{HNO}_3$ -8 M. The solution passed through the column,  $\text{Pu(IV)}$  is retained by the resin. Plutonium is then eluted by pouring through the resin 100 mL of  $\text{HCl}$  9 M +  $1.45\text{NH}_4\text{I}$

Once the elution is carried out, plutonium is trapped in the form of complexes while using  $\text{NdF}_3$  and deposited by vacuum filtration on membrane filters of  $0.1\ \mu\text{m}$  porosity. The evaluation of the spectrum is made by alpha spectrometry [1, 2]. The whole procedure is described in Figure 3.

## 2.3. Evaluation by alpha spectrometry

For the determination of plutonium concentration,  $^{242}\text{Pu}$  was used as radioactive tracer for the determination of the chemical yield of the analysis. The energy position of the radioactive tracer in a spectrum of energy and its interaction with other radioelements of close energy can appear after extraction of the plutonium isotopes, and can be the object of

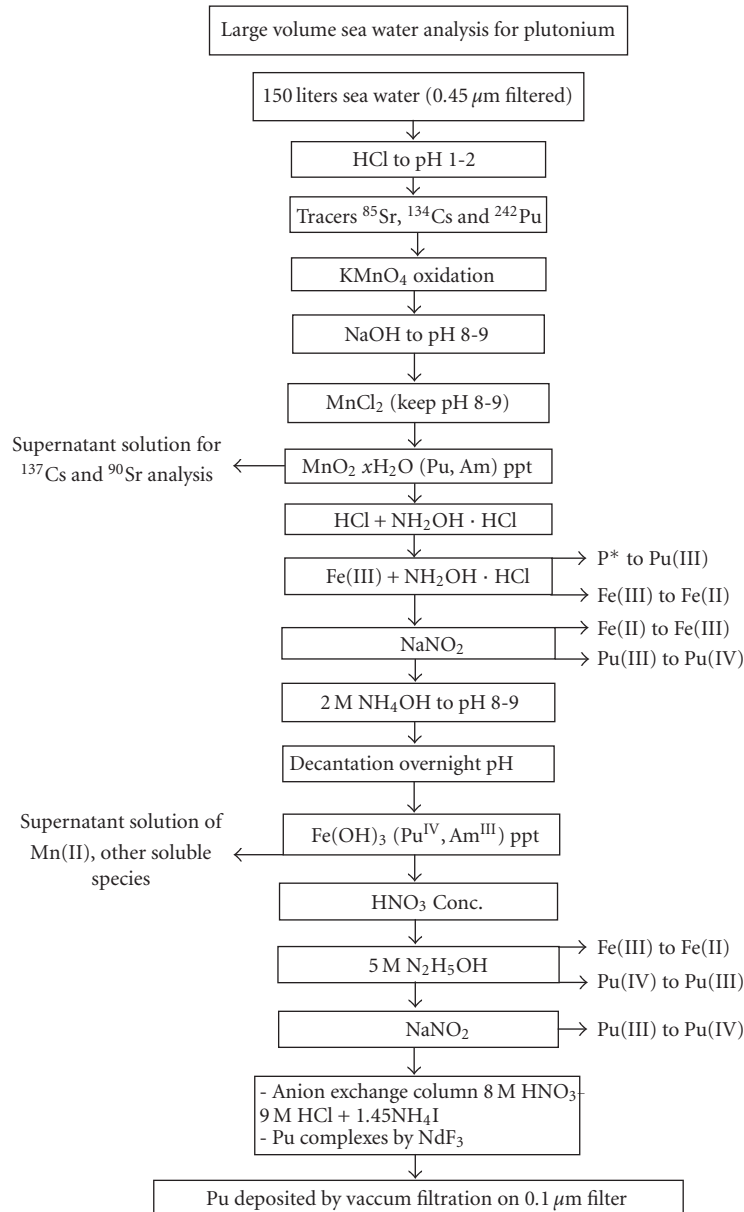


FIGURE 3: Scheme of the whole radiochemical procedure of the Pu in seawater.

TABLE 1: Parameters of T (°C) and C (mS) in stations 02 (Algiers) and 03 (Ténes)-campaign of June 2001.

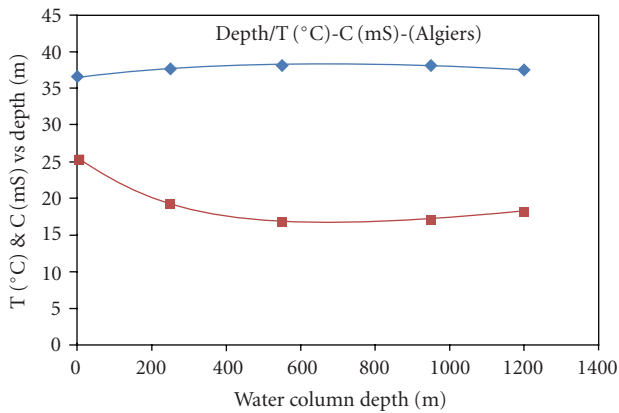
| Station 02-Algiers depth (m) | T (°C) | C (mS) | Station 03-Ténes depth (m) | T (°C) | C (mS) |
|------------------------------|--------|--------|----------------------------|--------|--------|
| 0                            | 25.3   | 38.4   | 0                          | 28.3   | 32.4   |
| 250                          | 19.2   | 39.6   | 250                        | 17.7   | 35.2   |
| 550                          | 17.1   | 40.9   | 600                        | 18.6   | 34.9   |
| 950                          | 17.1   | 41     | 1000                       | 18.7   | 35.7   |
| 1200                         | 18.2   | 40.1   | 2000                       | 18.6   | 35.1   |

tailing phenomena contribution. Once the source is prepared and the counting is carried out using a surface barrier detector, the evaluation by alpha spectrometry can be made reliably if there is no alpha-particle attenuation related to the thickness of the source. In the case of this work, the source

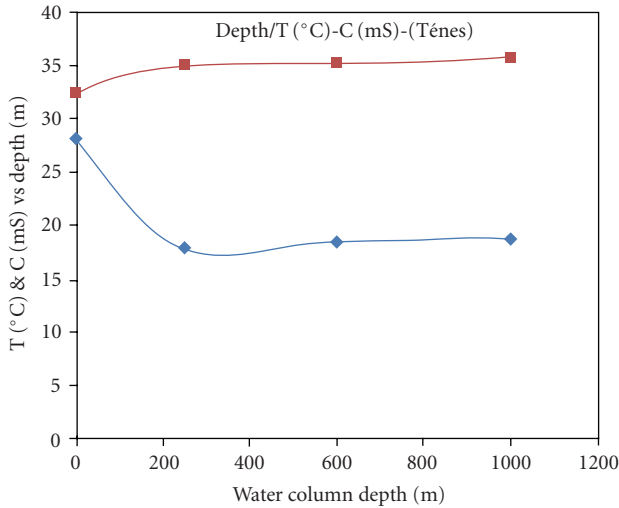
prepared was counted with a PIPS detector. Surfaces of the peaks of interest were delimited while taking into account the background noise and the contribution of the neighbouring peaks to determine the chemical output as well as the specific activity.

TABLE 2: Concentration of  $^{239+240}\text{Pu}$  and  $^{238}\text{Pu}$  along the water column in the stations of Ténés and Algiers.

| Stat. 03 Ténés   | $^{239+240}\text{Pu}$ ( $\mu\text{Bq/l}$ ) | $^{238}\text{Pu}$ ( $\mu\text{Bq/l}$ ) | $^{238}\text{Pu}/^{239+240}\text{Pu}$ | $^{239+240}\text{Pu}/^{137}\text{Cs} \times 10^{-3}$ |
|------------------|--|--|---------------------------------------|--|
| 0 m              | $8.20 \pm 1.00$                            | —                                      | —                                     | $3.00 \pm 0.30$                                      |
| 250 m            | $18.50 \pm 2.70$                           | $0.61 \pm 0.10$                        | $0.03 \pm 0.07$                       | $6.30 \pm 0.60$                                      |
| 600 m            | $16.00 \pm 2.40$                           | $0.57 \pm 0.11$                        | $0.04 \pm 0.08$                       | $6.30 \pm 0.60$                                      |
| 1000 m           | $25.50 \pm 3.70$                           | —                                      | —                                     | $8.20 \pm 0.80$                                      |
| 2000 m           | $22.00 \pm 3.10$                           | $0.47 \pm 0.09$                        | $0.02 \pm 0.05$                       | $12.00 \pm 1.10$                                     |
| Stat. 02 Algiers | $^{239+240}\text{Pu}$ ( $\mu\text{Bq/l}$ ) | $^{238}\text{Pu}$ ( $\mu\text{Bq/l}$ ) | $^{238}\text{Pu}/^{239+240}\text{Pu}$ | $^{239+240}\text{Pu}/^{137}\text{Cs} \times 10^{-3}$ |
| 0 m              | $6.70 \pm 1.00$                            | —                                      | —                                     | $3.00 \pm 0.20$                                      |
| 950 m            | $13.20 \pm 1.10$                           | $0.21 \pm 0.04$                        | $0.02 \pm 0.04$                       | $6.00 \pm 0.60$                                      |
| 1200 m           | $21.70 \pm 1.20$                           | $0.77 \pm 0.20$                        | $0.04 \pm 0.07$                       | $9.30 \pm 0.90$                                      |



(a)



(b)

FIGURE 4: (a) Profile of T ( $^{\circ}\text{C}$ ) and C (mS) versus depth (m): station 02-Algiers-2001. (b) Profile of T ( $^{\circ}\text{C}$ ) and C (mS) versus depth (m): station 03-Ténés-2001.

### 3. RESULTS AND DISCUSSION

The means of collecting seawater column samples as well as locality of the considered stations in this work are shown in Figures 1 and 2. Temperature ( $^{\circ}\text{C}$ ) and conductivity (mS)

parameters recorded along the water column using a Conductivity Temperature and Depth (CTD) probe are given in Table 1 and they are plotted and shown in Figures 4(a) and 4(b). The concentrations of plutonium isotopes, particularly  $^{239+240}\text{Pu}$  and  $^{238}\text{Pu}$ , with the ratios  $^{238}\text{Pu}/^{239+240}\text{Pu}$  and  $^{239+240}\text{Pu}/^{137}\text{Cs}$ , are given in Table 2. However, their profiles against depth (m) are shown in Figures 5(a), 5(b), and 5(c)

In the Ténés station, the concentration of  $^{239+240}\text{Pu}$  and that of  $^{238}\text{Pu}$  varies from  $8.2 \mu\text{Bq/l}$  to  $25.5 \mu\text{Bq/l}$ , and from  $0.47 \mu\text{Bq/l}$  to  $0.61 \mu\text{Bq/l}$ ; the average values are  $18.0 \mu\text{Bq/l}$  and  $0.55 \mu\text{Bq/l}$ , respectively. In the Algiers station, the values vary from  $6.70 \mu\text{Bq/l}$  to  $21.70 \mu\text{Bq/l}$  for  $^{239+240}\text{Pu}$  and from  $0.21 \mu\text{Bq/l}$  to  $0.77 \mu\text{Bq/l}$  for  $^{238}\text{Pu}$ . The results obtained within the framework of this work were compared with other works carried out in the same area in the north of the Mediterranean sea, where concentrations of  $^{239+240}\text{Pu}$  vary between 14 and  $26 \mu\text{Bq/l}$ , in the west, the variation is between 8 and  $33 \mu\text{Bq/l}$  [3–5].

The surface  $^{239+240}\text{Pu}$  concentrations found in this study seem to be in good agreement with values reported by Leon Vintro (their average value is  $7.8 \pm 1.4 \mu\text{Bq/l}$ ). Data reported by other authors indicate that surface Pu concentrations have been exponentially decreasing since 1976 from  $33 \mu\text{Bq/l}$  to  $17 \mu\text{Bq/l}$  [6] down to  $7.5 \pm 1.0 \mu\text{Bq/l}$  (mentioned in this paper). The  $^{239+240}\text{Pu}$  subsurface concentration peak shown in Figures 5(a), 5(b), and 5(c) at about 250-meter water depth can be explained by Pu transport from surface to deeper water layers through its association with suspended matter. However, the second peak at about 1000 m is not only associated with suspended matter but also with water masses movement at deep layers from the other parts of the Mediterranean sea and the north of the Atlantic ocean. The profile of  $^{239+240}\text{Pu}$  and  $^{137}\text{Cs}$  along the water column as shown in Figures 4(a) and 4(b) are similar, but  $^{137}\text{Cs}$  is most affected by water movement. If we estimate the ratios of  $^{239+240}\text{Pu}$  to  $^{137}\text{Cs}$  as presented in Table 2, we will confirm again that Pu isotopes is more effectively removed from surface layers than  $^{137}\text{Cs}$  due to adsorption to suspended particles.

### 4. CONCLUSION

This study enabled us for the first time to obtain results of concentration of  $^{239+240}\text{Pu}$  in a water column in the centre

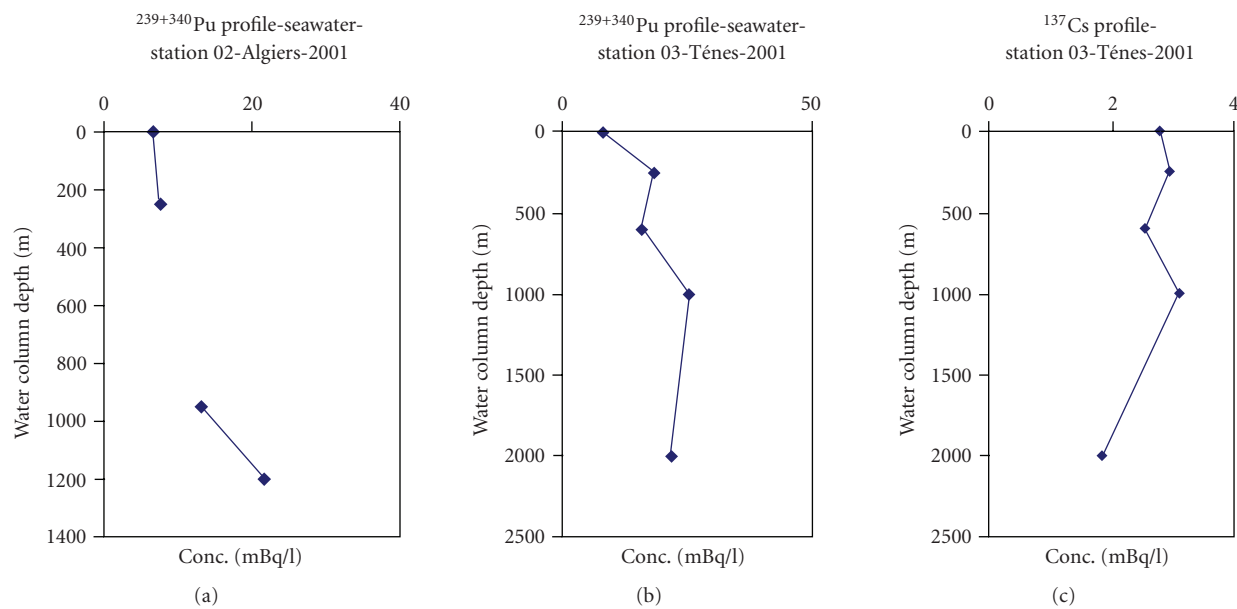


FIGURE 5: (a) Profiles of  $^{239+240}\text{Pu}$  in the water column of station 02-Algiers-2001; (b)  $^{239+240}\text{Pu}$  in the water column of station 03-Tenes-2001, and (c)  $^{137}\text{Cs}$  in the water column of station 03-Tenes-2001.

and the west of the Mediterranean sea, along the Algerian coast. The values seem to be in good agreement compared with those found in other works, but reflect a displacement of the  $^{239+240}\text{Pu}$  along the water column profiles which seem to be similar to those given by other works in the same area, along with the  $^{137}\text{Cs}$ . Concentrations of  $^{239+240}\text{Pu}$  increase along the water column at the station of Tenes and a peak is observed at 1000 meters depth.

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