

Unusual $^{210}\text{Po}/^{210}\text{Pb}$ ratios in the surface water of the Gulf of Lions

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Abstract – Concentrations of ^{210}Po and ^{210}Pb have been measured in sea water collected in the Grand Rhône Canyon. Concentrations of ^{210}Pb are at similar levels to those found in other Mediterranean sea water samples, and are at the levels which would be expected in comparison with global sea water data. The same applies to the ^{210}Po concentrations in samples from below 100 m depth. Surface samples from above 100 m have ^{210}Po at levels rather higher than expected, and their $^{210}\text{Po}/^{210}\text{Pb}$ ratios are about 1 or more as compared with the usual open ocean ratio of about 0.5. These data can be interpreted as indicating another source of supply of ^{210}Po to the surface layer in addition to the normal atmospheric input. We suggest that an episodic advective particulate input, probably originating in the output of the Rhône river and perhaps involving resuspension of fine particulates from the bottom sediments as a result of storm conditions, is the most likely candidate for this additional source. © Elsevier, Paris

scavenging / Mediterranean Sea / radionuclide budget / residence time

Résumé – **Rapports $^{210}\text{Po}/^{210}\text{Pb}$ inhabituels dans l'eau superficielle du golfe du Lion.** Les activités en ^{210}Po et ^{210}Pb total ont été mesurées dans la colonne d'eau du canyon du Grand Rhône, sur la marge continentale du Golfe du Lion. Les activités en ^{210}Pb sont similaires à celles précédemment estimées pour les eaux méditerranéennes et présentent des valeurs attendues par comparaison avec les autres océans. Il en est de même pour les activités en ^{210}Po au-dessous de 100 m de profondeur. En revanche, entre 0 et 100 m, le ^{210}Po atteint des valeurs beaucoup plus élevées que celles généralement observées, et le rapport $^{210}\text{Po}/^{210}\text{Pb}$ est égal ou supérieur à 1, très différent de celui de l'océan d'environ 0,5. Ces données impliquent l'existence d'une source supplémentaire de ^{210}Po , autre que les retombées atmosphériques. Nous suggérons que cette source résulte d'un apport advectif et épisodique de particules, probablement originaire du Rhône et peut-être de la resuspension de sédiment sur le plateau ou le haut de pente à la suite d'une tempête. © Elsevier, Paris

enlèvement / mer Méditerranée / bilan de radioélément / temps de résidence

1. INTRODUCTION

Natural radionuclides of the uranium decay series have been widely used in the study of chemical scavenging processes and particle transport in marine environments. Among them, ^{210}Po ($T_{1/2} = 138.4$ days) and ^{210}Pb ($T_{1/2} = 22.3$ years), members of the ^{238}U decay chain, present

many advantages. They are both particle-reactive, their half-lives are adapted to the study of biogeochemical processes on time scales of a few years, and their rates of supply to the oceans can generally be determined (atmospheric input and in situ decay of ^{226}Ra for ^{210}Pb , and mainly in situ decay of ^{210}Pb for ^{210}Po). Furthermore, study of radioactive disequilibria in the pairs ^{210}Po - ^{210}Pb

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and ^{210}Pb - ^{226}Ra (the daughter being more reactive with particles than the parent for both pairs) in the oceanic water column allows the rates of scavenging processes to be determined.

From January 1988 to January 1989, the second experiment of the ECOMARGE programme (Monaco et al., 1990) took place in the eastern part of the Gulf of Lions margin, in the Northwestern Mediterranean Sea. This programme was mainly focused on the study of biogeochemical cycles of basic elements and the fluxes of particles from the continental margin to the deep sea. In order to obtain information about particulate matter, sediment traps were moored on the continental slope, and sea water samples were collected at various stations in the study area. In this paper, we present results on the total ^{210}Po and ^{210}Pb concentrations collected in the water column of the Grand-Rhône Canyon area. Results on the sediment trap experiment are reported in another paper [33].

2. HYDROGRAPHIC FEATURES

Numerous papers described the major hydrodynamic features of the Gulf of Lions margin [22, 23]. Three water masses have been recognised: the surface water of Atlantic origin (≈ 0 –200 m depth); the Levantine Intermediate water (≈ 200 –800 m) and the Western Mediterranean Deep Water (below ≈ 800 m). Within the surface layer, the euphotic layer and the maximum depth of the thermocline are both above 100 m; below 100 m a cold subsurface layer (Winter Intermediate Water) has been observed seasonally at the shelf-break depth (150–200 m; [12, 10]).

3. MATERIAL AND METHODS

Seven stations were sampled on the continental slope from 300 to 1350 m water depth (figure 1, table I). Six were located in the Grand Rhône Canyon and the last one on the open slope (BTS 32). Vertical profiles were collected during two different cruises in January 1988 (stations BTS 5, 6, 8 and 32) and May 1988 (stations BTS 110, 111 and 112). While the January samples were taken under normal hydrographic conditions, May sampling occurred at the end of a three day strong gale induced by northwesterly winds. This event and its effects on the slope water column have been extensively described by

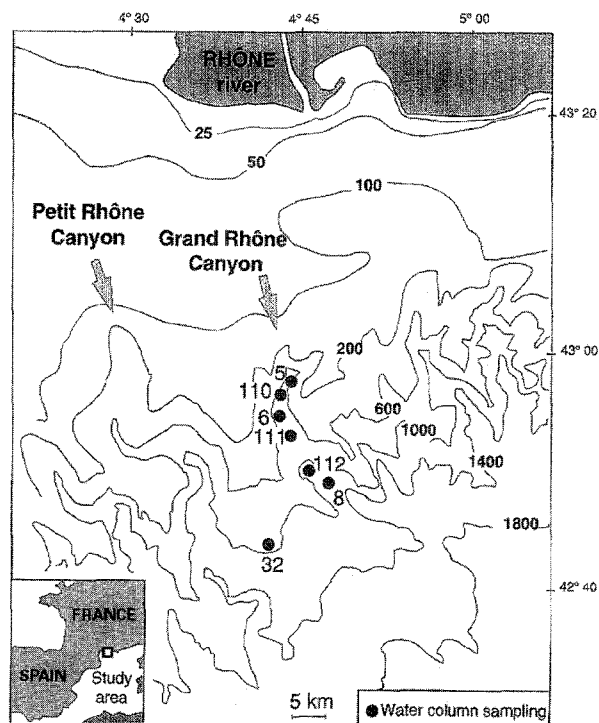


Figure 1. Location of the water column stations on the Grand Rhône canyon area (Gulf of Lions continental margin, Northwestern Mediterranean Sea).

Figure 1. Situation des stations de prélèvement dans la colonne d'eau du canyon du Grand Rhône (marge continentale du Golfe du Lion, Mer Méditerranée).

Durrieu de Madron [12]. As the sampling was conducted at the same time as a sediment trap experiment in the Grand Rhône Canyon (ECORHONE experiment, [33]), the sea water samples were generally collected at the same nominal depths as sediment traps, namely 80, 200, 600 and 900 m.

Two litre subsamples of sea water were taken from samples collected with 30 L Niskin PVC bottles, stored in a pre-cleaned polyethylene cubitainer and acidified to pH 2. Total (dissolved and particulate) ^{210}Po and ^{210}Pb were analysed according to the method described by Shannon and Orren [41] and Heussner et al. [16]. 1.5 L of water sample were mixed with APDC (*AmmoniumPirrolidinedithioCarbonate*, 13 mL, 4 %) and MIBK (*Methyl-IsoButylKetone*, 75 mL) in a separating funnel. After 30 min, the solvent was recovered in a beaker and then reduced by evaporation on a hot plate, at a temperature close to 110 °C. The solution was leached successively

Table I. Station locations from the ECORHONE experiment on the continental slope of the Gulf of Lions continental margin (Northwestern Mediterranean Sea).**Tableau I.** Situation des stations de prélèvements dans la colonne d'eau sur la pente continentale du Golfe du Lion (Mer Méditerranée, expérience ECORHONE).

Station	Latitude	Longitude	Water depth (m)	Location	Sampling date
BTS 5	42° 57' 66" N	4° 48' 45" E	319	Grand Rhône Canyon	22 January 1988
BTS 6	42° 53' 77" N	4° 47' 41" E	754	Grand Rhône Canyon	22 January 1988
BTS 8	42° 49' 00" N	4° 53' 20" E	1353	Grand Rhône Canyon	24 January 1988
BTS 32	42° 50' 70" N	4° 48' 90" E	1036	Open slope	26 January 1988
BTS 110	42° 55' 10" N	4° 47' 12" E	735	Grand Rhône Canyon	22 May 1988
BTS 111	42° 52' 66" N	4° 48' 22" E	853	Grand Rhône Canyon	22 May 1988
BTS 112	42° 50' 10" N	4° 49' 80" E	1100	Grand Rhône Canyon	22 May 1988

with 3 mL of pure HNO_3 , $\text{HNO}_3\text{-HClO}_4$ and HCl. Between each acid, the solution was taken to dryness. The leachate was dissolved in 200–250 mL of 0.3 N HCl and heated to 90 °C; 100 mg of ascorbic acid was then added to reduce the Fe(III) sometimes present in the solution. A 5 cm diameter silver plate was then hung in the beaker using a yarn; the temperature of the solution was allowed to fall to 60 °C and ^{210}Po deposition was continued at this temperature for 15 h. The silver plate was placed between ZnS(Ag) phosphors and both sides were counted on a total alpha-counter. Samples solutions were stored in the beakers for at least six months before replating and recounting to determine ^{210}Po ingrowth from ^{210}Pb . ^{210}Po and ^{210}Pb activities were corrected for decay and ingrowth from the time of collection and plating recoveries. The efficiency of extraction process was found by Shannon and Orren [41] to be 92 % for ^{210}Po and 85 % for ^{210}Pb . We have used these values for all samples, although we note that Heussner et al. [16] found them conservative. Radakovitch [32] checked the overall recovery of a ^{209}Po spike and found value of 91 %, very close to that of Shannon and Orren [41]. A further source of error is in the digestion and deposition process. We followed the careful procedure described in detail by Heussner et al. [16] and we used the efficiency of 99 ± 1 % which they cite. The errors we report in *table II* are statistical counting errors into which the 1 ± 1 % losses in the two deposition processes have been propagated.

4. RESULTS AND DISCUSSION

The results are listed in *table II* and shown as depth profiles in *figure 2*. In *table III*, they are summarized after separation into "surface water" (0–100 m) and "deep

water" categories. The choice of 0–100 m for the "surface water" includes the euphotic zone and the thermocline and avoids the seasonal subsurface complications; furthermore, it allows easy comparison with most previously published data. For comparison, *table III* includes previously reported data for the two nuclides in Mediterranean sea water. Since these data are so sparse, we also include a summary of global surface water data for the latitude band 15° to 55° N from Cherry and Heyraud [5], the deep water average for the North Atlantic from the same paper, and the deep water data of Bacon [1] for two stations in the North Atlantic, fairly close to the entrance to the Mediterranean Sea.

4.1. ^{210}Pb distribution

Our *table II* data are seen to be unexceptional insofar as ^{210}Pb levels are concerned. The fact that the median ^{210}Pb concentrations are lower in the Mediterranean surface water than in the global average for the 15° to 55° N latitude band is noted but is to be expected: the main source of ^{210}Pb in surface water is the atmospheric fall-out of ^{210}Pb , which is almost certainly lower in the Mediterranean than in North Atlantic and North Pacific Oceans that provide the bulk of the data from which the global average was calculated [14, 46]. Depth profiles of ^{210}Pb for the four January stations (BTS 5, 6, 8 and 32) show relatively little variation with depth except perhaps a tendency for a sub-surface minimum. Those for the three May stations show wider variations which may reflect the preceding strong gale conditions but which do not show a definite pattern.

Comparison of ^{210}Pb with its in situ progenitor ^{226}Ra is of interest, but is difficult because of the very limited data available for ^{226}Ra in the Mediterranean. In water sam-

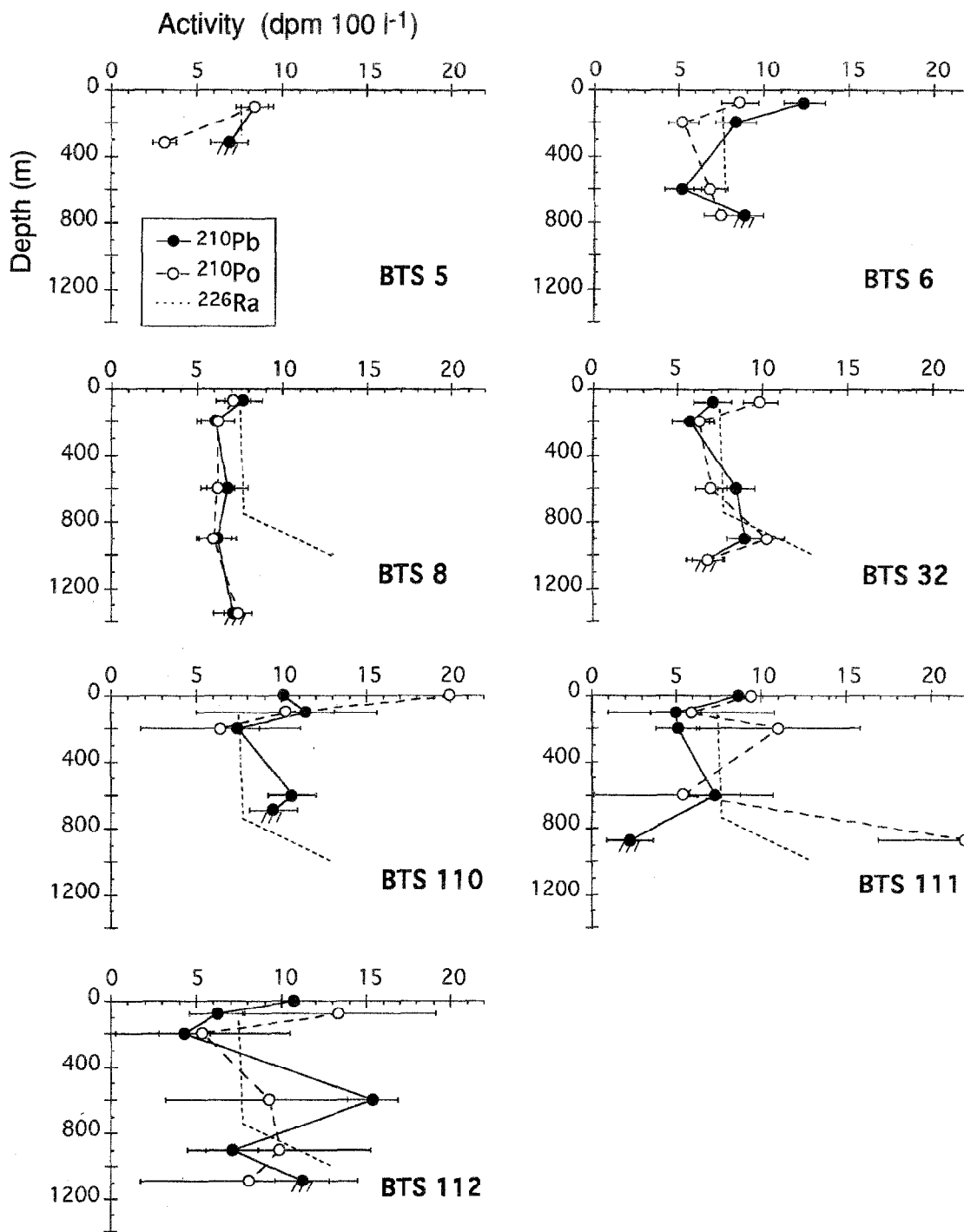


Figure 2. Profiles of total ²¹⁰Po, ²¹⁰Pb and ²²⁶Ra concentrations on the Grand Rhône canyon area (Northwestern Mediterranean Sea). The ²²⁶Ra profile was estimated from data reported by Bojanowski [4] and Schmidt and Reys [40] (see text for details).

Figure 2. Profils des concentrations totales en ²¹⁰Po, ²¹⁰Pb et ²²⁶Ra dans le canyon du Grand-Rhône (Mer Méditerranée). Le profil de ²²⁶Ra est estimé à partir des données de Bojanowski [4] et Schmidt and Reys [40] (cf. discussion pour les détails).

Table II. Total ²¹⁰Po and ²¹⁰Pb concentrations in water stations from the ECORHONE experiment on the Grand Rhône Canyon area. ND: not determined. The large errors on the ²¹⁰Po values for the May samples reflect the fact that these samples were only available for analysis several months after collection.

Tableau II. Activités en ²¹⁰Po et ²¹⁰Pb total sur les stations de prélèvement dans la colonne d'eau de l'expérience ECORHONE, dans le canyon du Grand-Rhône. ND: non déterminé. Les fortes erreurs observées sur les activités de ²¹⁰Po au mois de mai sont dues au fait que ces échantillons n'ont été disponibles pour l'analyse que plusieurs mois après la collecte.

Depth (m)	²¹⁰ Pb dpm/100 L	²¹⁰ Po dpm/100 L	²¹⁰ Po/ ²¹⁰ Pb
BTS 5, 322 m, Grand Rhône Canyon, 1/22/88			
100	8.4 ± 1.1	8.4 ± 0.8	1.00 ± 0.17
318	6.9 ± 1.1	3.1 ± 0.7	0.45 ± 0.12
BTS 6, 761 m, Grand Rhône Canyon, 1/22/88			
80	12.4 ± 1.2	8.6 ± 1.1	0.69 ± 0.11
200	8.4 ± 1.2	5.3 ± 0.9	0.62 ± 0.14
600	5.3 ± 1.1	6.9 ± 1.0	1.32 ± 0.32
757	8.9 ± 1.1	7.5 ± 1.0	0.84 ± 0.15
BTS 8, 1354 m, Grand Rhône Canyon, 1/24/88			
74	7.7 ± 1.1	7.1 ± 1.0	0.93 ± 0.18
200	6.1 ± 1.1	6.2 ± 1.0	1.03 ± 0.24
600	6.8 ± 1.2	6.2 ± 1.0	0.90 ± 0.21
900	6.2 ± 1.1	6.0 ± 1.0	0.96 ± 0.23
1352	7.1 ± 1.1	7.4 ± 0.8	1.04 ± 0.19
BTS 32, 1036 m, Open slope, 1/26/88			
78	7.1 ± 1.1	9.9 ± 1.0	1.39 ± 0.25
200	5.8 ± 1.1	6.3 ± 0.9	1.09 ± 0.25
600	8.5 ± 1.1	7.0 ± 0.9	0.83 ± 0.15
900	9.0 ± 1.1	10.3 ± 1.0	1.15 ± 0.18
1026	6.7 ± 1.1	6.8 ± 0.9	1.02 ± 0.21
BTS 110, 700 m, Grand Rhône Canyon, 5/22/88			
0	10.1 ± 1.6	20.0 ± 5.5	1.98 ± 0.63
100	11.5 ± 1.6	10.3 ± 5.3	0.90 ± 0.47
200	7.4 ± 1.3	6.4 ± 4.7	0.86 ± 0.65
600	10.6 ± 1.4	ND	ND
690	9.51 ± 1.4	ND	ND
BTS 111, 880 m, Grand Rhône Canyon, 5/22/88			
0	8.7 ± 1.4	9.4 ± 5.0	1.08 ± 0.6
100	5.0 ± 1.5	5.9 ± 4.9	1.18 ± 1.05
200	5.1 ± 1.3	11.0 ± 4.8	2.17 ± 1.11
600	7.3 ± 1.5	5.4 ± 5.3	0.74 ± 0.75
870	2.3 ± 1.4	22.1 ± 5.1	9.65 ± 6.29
BTS 112, 1100 m, Grand Rhône Canyon, 5/22/88			
0	10.7 ± 1.8	ND	ND
76	6.2 ± 1.6	13.4 ± 5.7	2.17 ± 1.08
200	4.3 ± 1.5	5.4 ± 5.1	1.25 ± 1.26
600	15.4 ± 1.5	9.3 ± 6.1	0.60 ± 0.40
900	7.1 ± 1.5	9.9 ± 5.4	1.39 ± 0.81
1090	11.2 ± 1.6	8.1 ± 6.4	0.72 ± 0.58

ples from seven stations from the Rhône river mouth to the basin, Bojanowski [4] reported ²²⁶Ra activities from 4.9 to 10 dpm/100 L from 0 to 250 m depth, and between 8.3 and 14 dpm/100 L below 250 m. These values are in agreement with those found by Schmidt and Reys [40] at three deep water stations in the abyssal plain: 13 dpm/100 L at 1000 m depth. Since little is known about ²²⁶Ra profiles over continental slopes, we assume that ²²⁶Ra increases linearly with depth as it does in the major part of the open ocean [6, 19, 35]. We then estimate a ²²⁶Ra profile from 7.5 dpm/100 L at 125 m depth (mean of the surface water activities, [4]) to 13 dpm/100 L at 1000 m depth. This profile is superimposed on figure 2. According to it, our ²¹⁰Pb levels are in excess of ²²⁶Ra above 100 m at all stations, and in deficit below 100 m, except at 600 m depth at two of the May stations. Such a "crossover" feature reflects the well-known decrease in importance of the atmospheric input of ²¹⁰Pb with depth.

Assuming that advection and diffusion terms are negligible, the steady-state balance equation for ²¹⁰Pb in the surface layer of the water column is usually written ([42] and many of the references in table IV) in a form equivalent to:

$$F_{Pb} + \lambda_{Pb} I_{Ra} = \lambda_{Pb} I_{Pb} + \mu_{Pb} I_{Pb} \quad (1)$$

where F_{Pb} is the atmospheric input of ²¹⁰Pb into the surface layer (dpm cm⁻² y⁻¹), λ_{Pb} is the radioactive decay constant of ²¹⁰Pb, I are the inventories (dpm cm⁻²) of ²²⁶Ra and ²¹⁰Pb in the water column down to 100 m depth and μ_{Pb} is the removal rate of ²¹⁰Pb from the surface layer by all processes other than radioactive decay. We can rewrite this equation thus:

$$\tau_{Pb} = (\mu_{Pb})^{-1} = R / [(F_{Pb}/I_{Ra}) + \lambda_{Pb}(1-R)] \quad (2)$$

where τ_{Pb} is called the surface layer residence time of ²¹⁰Pb and where the ²¹⁰Pb/²²⁶Ra ratio I_{Pb}/I_{Ra} is designated by R . The ²¹⁰Pb residence time can be calculated directly from the equation since all the other parameters are known or can be estimated. We use $\lambda_{Pb} = 0.03114$ y⁻¹, $I_{Ra} = 0.75$ dpm cm⁻² estimated from the data of Bojanowski [4] and $F_{Pb} = 0.58$ dpm cm⁻² y⁻¹ (mean of two values measured on adjacent areas, in Monaco [15] and in the Camargue [17]). Inventories of ²¹⁰Pb in the surface waters (0–100 m) are calculated from values given in table II.

The median ²¹⁰Pb concentration of 8.5 dpm (100 l)⁻¹ in our surface samples (cf. table III) implies I_{Pb} at 0.85 dpm

Table III. Data from *table II* summarised and compared with other data from the Mediterranean, the North Atlantic and a global summary from the 15°–55° N latitudinal band.**Tableau III.** Résumé des données du *tableau II* et comparaison avec d'autres données concernant la Méditerranée et l'Atlantique nord ainsi qu'un résumé global pour la bande latitudinale 15–55° N.

	²¹⁰ Pb (dpm/100 L)			²¹⁰ Po (dpm/100 L)			²¹⁰ Po/ ²¹⁰ Pb		
	Range	Median	n	Range	Median	n	Range	Median	n
Surface water (≤100 m)									
<i>Table II</i>	5.0-12.4	8.5	10	5.9-20.0	9.4	9	0.69-2.18	1.08	9
Heyraud & Cherry, 1983	5.8-16.9	11.3	10	4.0-9.8	5.8	10	0.28-1.08	0.43	10
Bojanowski, 1982	3.6-6.3	•	•	4.0-19.2	•	•	•	•	•
Cherry & Heyraud, 1988 (15–55° N)	5.8-26.8	14.7	66	4.0-15.2	8.9	44	0.21-1.10	0.57	44
Radakovitch, 1994	8.4-13.1	10.1	9	1.3-4.5	4.1	10	0.23-0.55	0.39	9
Deep water (≥ 200 m)									
<i>Table II</i>	3.1-15.4	7.2	22	3.1-22.1	6.9	20	0.45-9.65	0.99	20
Bojanowski, 1982	3.3-13.1	•	•	5.1-22.1	•	•	•	•	•
Bacon, 1977, stations 32 and 34	5.1-12.9	7.7	29	5.3-12.7	7.9	29	0.77-1.38	0.96	29
Cherry & Heyraud, 1988	•	8.3	•	•	•	•	•	•	•
North Atlantic average)									

cm⁻² in a 100 m deep box, which gives a mean ²¹⁰Pb residence time of 1.5 y. This residence time is determined primarily by I_{Pb} and F_{Pb}: variations of 50 % in I_{Ra} will change it by no more than 2 %. We note that the range of ²¹⁰Pb concentrations in our surface water samples is narrow, and implies a range in τ_{Pb} of 1.2 to 2.3 for the seven different stations. This range lies within previously reported values for τ_{Pb} in the same surface box thickness, viz. 0.4 to 5 years [2, 27, 28, 34, 42, 43]. Removal rates of ²¹⁰Pb on the Rhône continental slope are thus similar to those generally observed in the open ocean, and do not show much spatial or temporal variation.

4.2. ²¹⁰Po distribution

Our ²¹⁰Po and ²¹⁰Po/²¹⁰Pb data are also unexceptional insofar as the deep water samples are concerned. The ²¹⁰Po medians and depth profiles show a decrease in ²¹⁰Po below 100 m (except for BTS 111), but no other features which are both striking and consistent. The ²¹⁰Po data for the May stations are in fact subject to such large errors that any trends which do exist will in fact probably not be evident in the profiles. In the surface water samples, our data for ²¹⁰Po and ²¹⁰Po/²¹⁰Pb are more interesting. The ²¹⁰Po levels in the surface samples have a median concentration higher than the other Mediterranean surface water data, at a value which is similar to the 15°–55° N global compilation (despite the higher ²¹⁰Pb level in the latter data). The ²¹⁰Po/²¹⁰Pb ratios indicate very clearly that our surface water samples have a higher

²¹⁰Po/²¹⁰Pb ratio than the other data in *table III*. It is this difference which is the most interesting feature of our samples, and it requires detailed discussion.

In *table IV* we provide a more thorough summary of published data for the ²¹⁰Po/²¹⁰Pb ratio in surface sea water. The first ten references provide data from open ocean sea water. The next two also provide data from the open ocean, but are samples associated specifically with upwelling effects. The remaining eight are data from coastal or estuarine or shelf regions. The results are clear: all the open ocean data, except the two specifically associated with upwelling effects, have a median ²¹⁰Po/²¹⁰Pb at 0.7 or less, and are statistically distinguishable from our surface water samples with their median of nearly 1.1. The two "upwelling" medians are both at about unity, and are not distinguishable from our data. The "non-open ocean" medians vary: four are 0.7 or less, and the other four 1.1 or more. The former are distinguishable from our data, and the latter are not. From the table as a whole, it is clear that values of about 0.7 or less for the ²¹⁰Po/²¹⁰Pb ratio in surface sea water are the norm, and that values of about unity or more are recognized in the references concerned as requiring explanation. The same applies to our data, and we shall use a surface layer box-model to illustrate the problem.

The balance equation for ²¹⁰Po is analogous to that for ²¹⁰Pb :

$$F_{Po} + \lambda_{Po} I_{Pb} = \lambda_{Po} I_{Po} + \mu_{Po} I_{Po} \quad (3)$$

Table IV. $^{210}\text{Po}/^{210}\text{Pb}$ ratios in surface sea water (0–100 m). Only references which give four or more data points for total (i.e. dissolved plus particulate) ^{210}Po and ^{210}Pb are included. n = number of data. The first ten references are open ocean data; the next two are open ocean data associated to upwelling effects; the last eight are from coastal or estuarine or shelf regions. P is the probability that the data are from the same population as the surface seawater samples from Table II (Mann-Whitney U-test, two-tailed). NS implies $P > 0.05$, i.e. the two populations are not statistically distinguishable.

Tableau IV. Rapports $^{210}\text{Po}/^{210}\text{Pb}$ dans les eaux de surface de l'océan (0–100 m). Seules les références comprenant plus de quatre données d'activité en ^{210}Po et ^{210}Pb total (dissous plus particulaire) sont indiquées. n = nombre de données. Les dix premières références correspondent à des données d'océan ouvert, les deux suivantes à des zones d'océan ouvert associées à des upwellings, les huit dernières à des zones côtières, estuarine ou de plateau continental. P est la probabilité que les données appartiennent à la même population que nos valeurs pour les eaux de surface résumées dans le tableau 2 (test U de Mann-Whitney, bilatéral). NS implique que $P > 0,05$, et que les deux populations ne sont pas statistiquement différentes.

Reference	n	Range	Median	P
Shannon et al., 1970	24	0.1-2.0	0.5	< 0.01
Nozaki and Tsunogai, 1976	19	0.3-0.7	0.5	< 0.0001
Nozaki et al., 1976	53	0.2-1.8	0.6	< 0.0001
Bacon, 1977	18	0.1-1.4	0.5	< 0.001
Cochran et al., 1983	23	0.0-1.3	0.6	< 0.001
Chung & Finkel, 1987 and 1988	7	0.5-1.1	0.7	< 0.01
Nozaki et al., 1990	15	0.4-0.9	0.6	< 0.001
Nozaki et al., 1991	33	0.2-1.4	0.4	< 0.0001
Sarin et al., 1994	11	0.2-0.6	0.4	< 0.01
Ritchie & Shimmield, 1991	4	0.2-0.5	0.4	< 0.01
Thomson & Turekian, 1976	8	0.4-1.1	0.9	NS
Kadko, 1993	5	0.9-1.2	1.0	NS
Schell, 1977	25	0.2-4.9	1.7	NS
Santschi et al., 1979	8	0.4-1.8	0.7	< 0.02
Li et al., 1981, winter samples	8	1.1-2.6	1.3	NS
Li et al., spring samples	33	0.3-1.6	0.6	< 0.001
Heyraud & Cherry, 1983	10	0.3-1.1	0.4	< 0.001
Bacon et al., 1988	11	0.3-1.5	1.1	NS
Zuo & Eisma, 1993	33	0.3-4.0	1.8	NS
Radakovitch, 1994	9	0.2-0.6	0.4	< 0.001

where F_{Po} is the atmospheric input of ^{210}Po into the surface layer, λ_{Po} is the radioactive decay constant of ^{210}Po and I_{Po} is the inventory of ^{210}Po in the water column down to 100 m depth (dpm cm^{-2}). The atmospheric input term F_{Po} is small (about $0.04 \text{ dpm cm}^{-2} \text{ y}^{-1}$ in this part of the Mediterranean Sea; [15]). The mean I_{Pb} at 0.85 dpm cm^{-2} in a 100 m deep box gives $F_{\text{Po}}/I_{\text{Pb}} \approx 0.05 \text{ y}^{-1}$. With the ^{210}Po decay constant at 1.83 y^{-1} and with $R = 0.5$, the second term in the denominator of equation (2) dominates the first; however, as R increases, this dominance

disappears, and the denominator becomes negative when R is larger than about 1.026. "Normal" values of R between 0.4 and 0.7 give τ_{Po} between 0.35 and 1.20 y. Values generally found in the literature are around 0.6 y (cf table IV). R at 0.9 gives τ_{Po} at 3.9 y, rising asymptotically to 20 y when R is larger than about 1.03. Our value of $R = 1.08$ gives negative values of the residence time that imply negative removal rates, which are meaningless in a steady-state situation. They imply that the balance equation is defective, and the defect lies in the estimation of the atmospheric input term F_{Po} or in the assumption that it is the only input term for ^{210}Po (other than radioactive ingrowth from ^{210}Pb). Other significant inputs are clearly possible, particularly in regions close to the continents. In the balance equation, the F_{Po} term must be replaced by a term $F_{\text{Po}} + S_{\text{Po}}$, where S_{Po} represents some other input source. In the references in table IV with high $^{210}\text{Po}/^{210}\text{Pb}$ medians, several possible alternative sources are mentioned. Resuspension of bottom sediments into the surface water column and regeneration of ^{210}Po from particulates, either in situ or as a result of upwelling, are the most common.

For our data, we start by estimating the size of the term which is required. Using equation (3) with F_{Po} replaced by $F_{\text{Po}} + S_{\text{Po}}$, and inserting the I_{Po} and I_{Pb} values implied by the median concentrations in our samples (cf table III), gives:

$$S_{\text{Po}} = 0.125 + 0.94 (\tau_{\text{Po}})^{-1} \quad (4)$$

Inserting the "normal" range for τ_{Po} of 0.35 to 1.20 years in equation (4) gives S_{Po} between 2.8 and $0.9 \text{ dpm cm}^{-2} \text{ y}^{-1}$. What could provide an input of this size? Upwelling is an obvious suggestion, but whereas upwelling has been observed near the coast in the Gulf of Lions, it has never been reported in the surface water in the canyons indenting the slope. More specifically, temperature and salinity data collected on May cruise [12] did not reveal any upwelling event. Another possibility is that invoked by Bacon et al. [2] and Sarin et al. [38] to explain an excess of ^{210}Po in the dissolved phase at the base of the euphotic zone, viz. regeneration of ^{210}Po at this depth from settling particles. We do not possess the data needed to consider such a possibility in detail, but we note that, in any event, it could not explain the ^{210}Po excess at 0 m depth at station BTS 110 and 111. A third possibility would be an atypical atmospheric input pulse from a dust storm or a volcanic eruption (both of which can supply material with a $^{210}\text{Po}/^{210}\text{Pb}$ ratio much higher than the normal atmospheric fall-out; [20, 25]), but we

are not aware of any reports of major events of this type during or just before the collection period. However, we have noted with interest the recent report of Tateda et al. [44] indicating that the atmospheric flux of ^{210}Po measured at Monaco in 1995 was sometimes up to 50 % of the ^{210}Pb flux, as opposed to the normal value of less than 10 %. This suggests that atypical input pulses rich in ^{210}Po can indeed occur in the Mediterranean. According to these authors, such high ^{210}Po flux could be attributed to terrigenous biogenic debris input from land by strong wind (such as those occurring during the gale). A fourth and perhaps the most likely source of ^{210}Po input is an advective input from the surface shelf water to the north and north-west of the collection area, originating probably in an output from the Rhône river. Data are not available to test this possibility adequately, but it does at least seem plausible. In the sediment trap experiment already referred to, about 45 and 56 % of the annual mass flux and the ^{210}Po flux respectively arrived in the 80 m trap during the month before the sampling of our May stations: this peak resulted from a conjunction of two phenomena, viz., the annual flood of the Rhône river, a phytoplanktonic bloom and strong northwesterly wind [13]. The latter likely induced a seaward dispersion of continental and shelf material up to the vicinity of the Grand-Rhône canyon. The ^{210}Po peak flux in the trap translates into an annual flux of about $5 \text{ dpm cm}^{-2} \text{ y}^{-1}$, which could largely explain the ^{210}Po excess observed in the surface layer. Furthermore, the Rhône river flood reached a maximum from 19 to 22 May, and this input may have been delivered quickly to the Grand Rhône canyon area, under the influence of the strong northwesterly gale which induced a seaward drift of the surface waters and significant mixing of the surface layer [12]. Furthermore, satellite imagery has revealed that the thermal plume of the Rhône can be observed as far as the shelf-break under the influence of northwesterly wind [11]. Unfortunately, direct evidence of a Rhône plume over the canyon area cannot be obtained from the hydrographic data available. Indeed, the river plume on the continental shelf is limited to the very surficial waters (<2 m; [26]), and during the ECORHONE experiment, CTD measurements were only made below 10 m depth.

An additional plausible source term could also result from resuspension of fine particulate matter from sediments induced by the storm conditions and their subsequent transport to the surface layer. We have no quantitative evidence to support this suggestion. How-

ever, we note that the particles collected at the end of April by the 80 m deep sediment trap have a high $^{210}\text{Po}/^{210}\text{Pb}$ ratio of about 7 [33], and that resuspension of such particles is able to affect the inventory of ^{210}Po in the water column.

Although these remarks refer to the May samples, they are probably also valid for the January samples. These latter were collected just after the start of the trap experiment, and the initial mass flux data show some signs of another (preceding) input pulse. Furthermore, a gale induced by northwesterly winds also occurred from the 21 to 23 January, and may have affected the water column in a similar way to the May event.

We hypothesise, therefore, that the high $^{210}\text{Po}/^{210}\text{Pb}$ ratios in our surface water data reflect an episodic input of ^{210}Po into the surface layer: this input must be of such nature that it results in a longer-than-normal ^{210}Po residence time of 1.3 y or more. Fine particles probably originating in the output from the Rhône river and/or resuspended material are indicated. However, we cannot determine precisely if such ^{210}Po input occurred only in the particulate phase or also in the dissolved phase, after regeneration of ^{210}Po from the particles. To test this hypothesis adequately and to determine the relative importance of the two sources would require a series of analyses, for both dissolved and particulate ^{210}Po and ^{210}Pb , in the Rhône and in surface sea water samples collected sequentially before, during and after particulate input pulses. The balance equation would of course have to be modified to take the non-steady state situation into account.

We note finally, that the additional input S_{Po} we have suggested for ^{210}Po implies a similar additional input term S_{Pb} for ^{210}Pb . Inserting an S_{Pb} of about $0.4 \text{ dpm cm}^{-2} \text{ y}^{-1}$ lowers our estimate of the ^{210}Pb residence time from 1.5 to 0.9 years: the new estimate remains within the literature range previously cited.

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