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Enrichment of ^{210}Pb and ^{210}Po in the sea-surface microlayer

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Chemical fractionation at the air–sea interface is frequently suggested[1–5] as a possible mechanism contributing to the enrichment of a number of trace metals in the marine atmosphere[6,7]. The origin of the long-lived radon daughters (^{210}Pb, ^{210}Bi and ^{210}Po) in the atmosphere is of special interest because of their use in the estimation of tropospheric aerosol residence times[8]. It has been proposed[9] that injection of a fractionated marine component by bubbles bursting at the sea surface might be responsible for the occurrence of anomalously high atmospheric ^{210}Po/^{210}Pb ratios in Antarctica[10] and Hawaii[11]. Here we report the first measurements of ^{210}Pb ($t_{1/2} = 22.3$ yr) and ^{210}Po ($t_{1/2} = 138$ d) in the sea-surface microlayer. These measurements were made to determine whether or not a significant flux of these radionuclides from the sea surface to the atmosphere could occur. We also introduce a method for treating chemical data that we believe may be useful in determining the origin of the trace-metal enrichments often observed[1,2] in the microlayer.

The sea-surface microlayer is the uppermost thin skin of the oceanic water column. It is often characterised by anomalously high concentrations of heavy metals and other trace substances thought to be associated with particulate matter and surface-active organic material[1,2]. The thickness of the microlayer is defined by the method used to sample it. We used a plastic screen in a modification of the technique of Garrett which samples the upper 300 ± 50 μm (refs 12, 13). Because this was an initial attempt to detect enrichments of ^{210}Pb and ^{210}Po in the microlayer, we deliberately chose to collect our screen samples in calm sea conditions when visible surface slicks were present. Bulk surface-water samples were collected by immersing polyethylene jugs to a depth of about 20 cm and allowing them to fill. We also analysed a single sample of foam collected along the shore of a coastal pond. This material is believed to represent a more concentrated example of the anomalously enriched layer than samples provided by the screen technique[14,15]. Details of the analytical procedures are given elsewhere[16].

Results are shown in Table 1. In all cases both ^{210}Pb and ^{210}Po showed enrichments in the sea-surface microlayer samples in comparison with bulk surface-water samples. The degree of enrichment seemed to correlate with film pressure (depression of surface tension) estimated by the oil-drop method[13,17], although film pressures were always near the limit of detection. The greatest enrichments occurred in the foam sample from Oyster Pond. Thus a correlation exists between enrichments of the radionuclides and the presence of surface-active material.

To assess the role of the sea surface in supplying metal-rich aerosols, one must determine whether the enrichments in the microlayer are maintained by deposition of atmospheric material or by concentration of the metals from seawater. Only in the latter case can the sea act as a source. The ^{210}Po/^{210}Pb activity ratio may provide an important clue. Table 2 lists representative values of the ^{210}Po/^{210}Pb ratio in atmospheric fallout and in seawater and marine particulate matter from both coastal and open-ocean environments. The atmospheric ratio is much lower than the ratios in bulk surface seawater measured in this study, yet the ^{210}Po/^{210}Pb ratios in the microlayer samples show only small departures from the bulk seawater values. This comparison suggests that the ocean may be an important source of the enrichments found in the microlayer.

A more quantitative treatment of this question can be made by consideration of a simple model in which the surface-microlayer enrichment consists of two components: an atmospheric component and an oceanic component supplied by concentration from seawater and upward transport to the air–water interface. This latter supply process may involve chemical fractionation. It is assumed that processes removing material from the microlayer, either physical injection into the atmosphere or mixing downward in the water column, involve no chemical fractionation. With this assumption we can write for ^{210}Pb:

$$\Delta_{\mathrm{Pb}} = \mathrm{Pb}_{\mathrm{m}} - \mathrm{Pb}_{\mathrm{b}} = \varepsilon_{\mathrm{Pb}}\mathrm{Pb}_{\mathrm{b}} + \mathrm{Pb}_{\mathrm{a}} \qquad (1)$$

where the ^{210}Pb enrichment, Δ_{Pb}, is the difference between the ^{210}Pb concentration in the microlayer, Pb_{m}, and the concentration in bulk surface seawater, Pb_{b}. This concentration difference consists of an enriched oceanic component, $\varepsilon_{\mathrm{Pb}}\mathrm{Pb}_{\mathrm{b}}$, and an atmospheric component, Pb_{a}. A similar equation can be written for ^{210}Po:

$$\Delta_{\mathrm{Po}} = \mathrm{Po}_{\mathrm{m}} - \mathrm{Po}_{\mathrm{b}} = \varepsilon_{\mathrm{Po}}\mathrm{Po}_{\mathrm{b}} + \mathrm{Po}_{\mathrm{a}} \qquad (2)$$

Finally we assume that the atmospheric ^{210}Po/^{210}Pb ratio, R_{a}, is known:

$$R_{\mathrm{a}} = \mathrm{Po}_{\mathrm{a}}/\mathrm{Pb}_{\mathrm{a}} \qquad (3)$$

Equations (1)–(3) contain four unknown quantities, so it is not possible to solve them uniquely. It is possible, however, to derive a relationship between two important quantities. Let α denote the fractionation between ^{210}Pb and ^{210}Po during their transport from bulk seawater to the microlayer. This fractionation is given by

$$\alpha = \varepsilon_{\mathrm{Po}}/\varepsilon_{\mathrm{Pb}} \qquad (4)$$

so if $\alpha > 1$, then ^{210}Po is preferentially (relative to ^{210}Pb) transported to the microlayer. This condition is probably necessary if the sea surface is to act as a source for the anomalously high ^{210}Po/^{210}Pb ratios in Antarctic aerosols[10], because ^{210}Po/^{210}Pb < 1 in most ocean surface water. (Coastal waters in Vineyard Sound (Table 1) and other locations[18,19] are often the exception with ^{210}Po/^{210}Pb > 1. The origin of the unsupported ^{210}Po in these waters is not understood. Over most of the ocean surface,

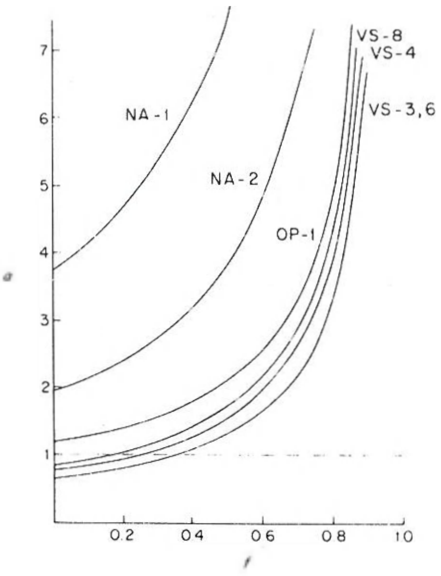

Fig. 1 Results of the model calculations for $R_{\mathrm{a}} = 0.1$. Each screen sample is represented by a curve. In those cases for which more than one bulk surface-water sample was collected on the same date and in the same location, the results from Table 1 were averaged. For $\alpha = 1$ there is no chemical fractionation. For $f = 1$ all of the enrichment of ^{210}Pb in the microlayer is contributed from the atmosphere. The curves are fairly insensitive to variations of R_{a} in the range 0–0.2.

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Table 1 Analytical results*

Sample	Type	Description of sampling conditions	Film pressure† (dyn cm^{-1})	^{210}Pb (d.p.m. per 100 kg)	^{210}Po (d.p.m. per 100 kg)	Activity ratio ^{210}Po/^{210}Pb	Activity ratio ΔPo/ΔPb
Vineyard Sound, Massachusetts (14 July 1977)							
VS-1	Bulk	—	—	3.5 ± 0.1	9.6 ± 0.4	2.8 ± 0.2	—
VS-2	Bulk	—	—	1.8 ± 0.1	6.8 ± 0.3	3.8 ± 0.3	—
VS-3	Screen	Visible surface slicks, deliberately sampled	>1	12.5 ± 0.3	29.6 ± 0.9	2.4 ± 0.1	2.2
VS-4	Screen	Slicks present but avoided	~1	6.6 ± 0.3	18.3 ± 0.6	2.8 ± 0.1	2.6
Vineyard Sound, Massachusetts (5 September 1977)							
VS-5	Bulk	—	—	5.0 ± 0.2	7.0 ± 0.4	1.41 ± 0.09	—
VS-6	Screen	Visible slick, some quantities of foam sampled	>1	41.3 ± 1.6	51.5 ± 1.9	1.25 ± 0.06	1.2
VS-7	Bulk	—	—	3.2 ± 0.1	7.0 ± 0.7	2.2 ± 0.2	—
VS-8	Screen	Patches of slick present but avoided	<1	6.0 ± 0.2	10.0 ± 0.5	1.7 ± 0.1	1.6
Oyster Pond, Falmouth, Massachusetts (29 September 1977)							
OP-1	Foam	—	—	1,360 ± 30	430 ± 50	0.31 ± 0.04	0.32
OP-2	Bulk	—	—	36.8 ± 1.0	9.6 ± 0.7	0.26 ± 0.02	—
North Atlantic Ocean 45°50′N, 64°10′W (16 September 1977)							
NA-1	Screen	Patches of slick present, sample gathered both in and out of slick	~1	16.4 ± 0.3	15.0 ± 0.7	0.91 ± 0.05	2.6
NA-2	Screen	Patches of slick present, sample gathered both in and out of slick	~1	21.3 ± 0.7	21.7 ± 1.2	1.02 ± 0.06	1.7
NA-3	Bulk	—	—	14.7 ± 0.5	10.5 ± 0.6	0.71 ± 0.05	—

* Uncertainties listed are standard errors based on counting statistics.

† These are approximate values. All measurements were near the detection limit, and there was often some variation in film pressure during each sampling period because of slick patchiness.

however, ^{210}Po/^{210}Pb < 1 because of biological uptake and transport of ^{210}Po to deeper water[20].) We now let f denote the fraction of the microlayer ^{210}Pb enrichment that is contributed from the atmosphere, and we can write

$$f = \mathrm{Pb}_a/(\varepsilon_{\mathrm{Pb}}\mathrm{Pb}_b + \mathrm{Pb}_a) \tag{5}$$

With these definitions and with equations (1)–(3), we derive the following equation:

$$\alpha = (\Delta_{\mathrm{Po}}/\Delta_{\mathrm{Pb}} - fR_a)/(1-f)R_b \tag{6}$$

where $R_b = \mathrm{Po}_b/\mathrm{Pb}_b$. Thus for any microlayer/bulk-seawater sample pair we can define a relationship between α and f. Note that this relationship is independent of the degree of dilution of the microlayer sample by bulk seawater.

Figure 1 shows curves based on equation (6) and the data in Table 1. Although our data do not allow a unique solution, the curves in Fig. 1 allow some limitations to be placed on their interpretation. We note that as f approaches a value of 1.0 (no oceanic contribution), α increases very rapidly. In other words, the more dominant the atmospheric contribution to the microlayer enrichment of ^{210}Pb becomes, the more strongly fractionated the oceanic contribution must be to compensate for the low ^{210}Po/^{210}Pb ratio in the atmospheric component. We believe that a reasonable interpretation of the data requires that at least part of the microlayer enrichments be supplied by concentration of ^{210}Pb and ^{210}Po from the bulk seawater.

At the other extreme, by setting $f = 0$ (no contribution from the atmosphere), we obtain the minimum possible value for α. To explain our open-ocean results (samples NA-1 and NA-2), we require $\alpha > 1$ no matter how small a value is assumed for f; that is, concentration of ^{210}Pb and ^{210}Po from the bulk seawater must involve chemical fractionation such that ^{210}Po is preferentially transported to the interface. For the coastal water samples (sample OP-1 and the VS samples), $\alpha = 1$ (little or no fractionation) if no atmospheric contribution is assumed. This reflects the similarity of ^{210}Po/^{210}Pb ratios in microlayer and bulk surface-water samples at the coastal sampling sites. Only for $f \geq 0.4$ must significant fractionation be postulated.

Experiments in which columns of seawater are bubbled with air suggest that trace-metal enrichments in the microlayer may be maintained by transport of particulate matter to the interface[5]. If this were the predominant mechanism for ^{210}Pb and ^{210}Po, and if it acted indiscriminately for all types of particulate matter, then it would be possible to estimate α from the known distribution of ^{210}Pb and ^{210}Po between dissolved and particulate forms in surface seawater by using the expression

$$\alpha = (^{210}\mathrm{Po}/^{210}\mathrm{Pb})_{\text{particulate matter}}/(^{210}\mathrm{Po}/^{210}\mathrm{Pb})_{\text{bulk seawater}} \tag{7}$$

In open-ocean surface water[21,22] this quantity is in the range 2.4–8.8 (median 6.7). Coastal surface waters (ref. 18 and unpublished data) are characterised by values closer to 1.0, probably because of the contribution of resuspended bottom sediment to the particulate matter. This difference may account for the segregation of our open-ocean samples from our coastal samples (Fig. 1), but further testing of this hypothesis is required.

We have shown that the sea-surface microlayer is enriched in ^{210}Pb and ^{210}Po. Our interpretation of the data suggests that a significant fraction of the enrichment is maintained by concentration from the bulk surface seawater. In the open ocean this concentration process results in preferential transport of ^{210}Po to the air–sea interface. In coastal environments there may be a

Table 2 Representative values of the ^{210}Po/^{210}Pb activity ratio in seawater, marine particulate matter and atmospheric fallout

Material	Median	Range	Refs
Surface North Atlantic			21, 22
Seawater	0.52	0.08–1.09	
Particulate matter	4.6	0.9–5.3	
Long Island Sound, US			18
Water (total)	0.89	0.80–1.44	
35 μm Seston	1.3	1.2–2.4	
333 μm Seston	12	1.4 – 62	
Atmospheric fallout New Haven, Connecticut	0.03	~0 – 0.16	18

lesser degree of chemical fractionation. Because coastal waters often have ^{210}Po/^{210}Pb activity ratios > 1, the sea surface is, in either case, a potential source of aerosols with ^{210}Po/^{210}Pb > 1 as suggested by Turekian *et al.*[9]. The natural flux of microlayer material from the sea to the atmosphere, however, is not known.

Note finally that our analytical treatment of the microlayer enrichments was limited because only two elements were used. Further analysis by a multi-element approach is suggested.

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