

## TRANSFER OF AMERICIUM FROM SEA WATER TO ATMOSPHERE BY BUBBLE BURSTING

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**Abstract**—Laboratory experiments were performed to determine whether seaspray particles, generated by bubble bursting, could be richer in americium than bulk water. The experiments were conducted adding  $^{241}\text{Am}$  and  $^{22}\text{Na}$  to natural seashore water, blowing bubbles through the water by means of an hydrophobic porous membrane and drawing the resultant aerosol through a cascade impactor for subsequent analysis. The data obtained show that the americium to sodium ratio in aerosol particles is enhanced by several orders of magnitude compared with that in bulk water. The enrichment is the highest for the largest particles and slightly decreases for decreasing particle size. For submicron particles, analytical uncertainty causes doubt as to whether or not any enrichment is present. The results are compared to those obtained *in situ* for plutonium, americium and other trace metals.

### INTRODUCTION

A number of recent works suggest that seaspray particles generated from breaking waves could be richer in americium and plutonium than bulk water. Fraizier *et al.* (1977) observed that terrestrial lichens taken from the Cap de La Hague area contained much more plutonium as they were closer to the shoreline. They related this observation to the possibility that sea salt particles highly enriched in plutonium could be transferred from sea water to adjacent land areas. Linsley (1978) as well as Pattenden *et al.* (1980) suggested that the same hypothetical process could explain the concentrations of plutonium and americium measured in the atmospheric particles near Windscale, Cambay and Eakins (1980), from data collected on transuranics in soil, vegetation and sediment samples, arrived at identical conclusions.

The purpose of this study is to determine from experiments in the laboratory whether seaspray particles can be richer in americium than bulk water. The experiments were carried out by labeling seashore water samples with  $^{241}\text{Am}$  and  $^{22}\text{Na}$ , bubbling air through these samples and collecting the aerosols from the bubble-bursting process. The americium to sodium ratios measured in bulk water and in different size fractions of the spray particles were compared, in order to assess the enrichment of particles relative to seawater.

### EXPERIMENTAL METHODS

#### Aerosol generation chamber

In previous works, the natural bubble-bursting process was reproduced by blowing air through capillary tubes (Van Grieken *et al.*, 1974), or fritted-glass plates (Wilkniss and Bressan, 1971). It has been shown in a recent work (Guichard and Lamaue, 1979) that a better simulation could be

achieved by blowing air at a small rate through an hydrophobic porous membrane.

Figure 1 represents schematically the aerosol generation chamber, described by Guichard and Lamaue, and used in the present work. A flow of air, pre-filtered through a layer of charcoal and an absolute filter, is forced through a teflon membrane of 25 cm dia. and 10  $\mu\text{m}$  pore size which supports a layer of sea water 2 cm deep. This air flow ( $0.3 \text{ l min}^{-1}$ ) produces streams of bubbles that rise and burst at the surface of the water layer. The resultant aerosol cloud is diluted by an additional flow of dry air ( $28 \text{ l min}^{-1}$ ) and drawn through a seven-stage Andersen impactor which separates particle size fractions. It should be observed on the figure that the additional flow of dry air is injected through small holes

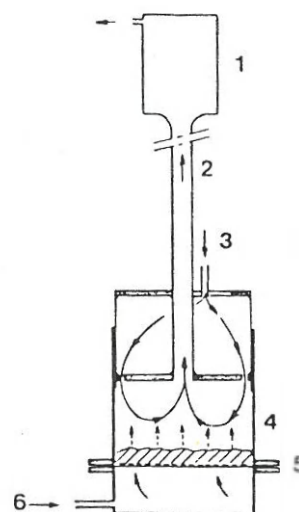


Fig. 1. Aerosol generation chamber for producing aerosols by bubble bursting at the surface of water: (1) Andersen impactor; (2) aerosol drying section; (3) dry air for dilution; (4) layer of sea water; (5) porous hydrophobic membrane and (6) bubbling air.

placed at the periphery of the top plate limiting the chamber. This dry air leaches the surface of the water layer, dilutes the aerosol and escapes by a central tubing leading to the cascade impactor. The transit time of the aerosol between the generation chamber and the cascade impactor is supposed sufficiently long to allow the aerosol droplets to dry completely.

#### Procedure

Several hours before an experiment, a surface water sample was collected with a polyethylene container in coastal waters of the Cap de La Hague area, and stored at low temperature. A few minutes before the beginning of the run, the sample was filtered through a teflon membrane of 10  $\mu\text{m}$  pore size (to eliminate the coarsest debris), and was labeled with 100  $\mu\text{Ci l}^{-1}$  of  $^{22}\text{Na}$  and 4–6  $\mu\text{Ci l}^{-1}$  of  $^{241}\text{Am}$ , in the +3 oxidation state. The molar concentration of americium in the labeled sea water was between  $5.1 \times 10^{-9} \text{ M}$  and  $7.7 \times 10^{-9} \text{ M}$ .

The doubly labeled water was introduced into the chamber previously described. Then the air for bubbling and dilution was admitted into the device. Aerosols were collected generally over a 4 h period, using the Andersen impactor. Each stage of the impactor was covered with a glass-fiber disk which was removed after each experiment for radioactivity counting. In the experiments an after-filter was also used to collect particles less than 0.4  $\mu\text{m}$  dia.

Sample counting was done using a NaI crystal well detector. The samples were prepared to have the same geometry, even though the detector response is relatively insensitive to this parameter. Each sample was counted for 40 min in two energy ranges, one between 46 and 76 keV, and the other between 480 and 660 keV. The actual count rate of each radionuclide was calculated in the usual way from the net count rates in the two channels. The correction factors that were required were determined by measuring sources of  $^{22}\text{Na}$  and  $^{241}\text{Am}$  of the same geometry as the unknown samples.

Immediately before and after each experiment 0.5 ml of the sea water was sampled. The average of sea water composition before and after each experiment was used as the reference for calculating aerosol enrichment factor,  $E$ , from:

$$E = \frac{(^{241}\text{Am}/^{22}\text{Na}) \text{ aerosols}}{(^{241}\text{Am}/^{22}\text{Na}) \text{ sea water}} - 1.$$

#### RESULTS

Two series of experiments were carried out during August and October 1980. Table 1 gives some characteristics of the sea water used. The relatively high

concentration of particulate matter which remains in suspension after the large debris have been eliminated (size > 10  $\mu\text{m}$ ) can be explained by the fact that the samples were taken near the shore. The total concentration of americium in the sea water decreases between the beginning and the end of the experiment as a result of radionuclide deposition on the walls of the chamber. The ratio of particulate americium to the total amount of americium in the sea water increases with time and reaches values of between 0.75 and 0.90. Since the mass concentration of the suspended particulate matter and the fraction of particulate americium are known, the distribution coefficient ( $K_d$ ), defined as the ratio of americium activity  $\text{g}^{-1}$  of matter in suspension to americium activity  $\text{ml}^{-1}$  of filtered sea water, can be calculated.  $K_d$ 's of several  $10^4 \text{ ml g}^{-1}$  are obtained at the beginning of the experiment and several  $10^5 \text{ ml g}^{-1}$  at the end.

The conditions for producing and bursting the bubbles were almost identical in the 5 experiments. The bubbles appear only at a few points on the porous membrane (3 or 4). These preferential bubble points correspond to the membrane pores which resist the passage of air the least. When the bubbles have reached around 2 mm in diameter, they break away from the membrane and from the grid which covers it. Once arrived at the surface of the water, bubbles persist for seconds and can be seen to flow toward one another and thus form clusters of 3–10 bubbles. In each cluster, the largest bubble absorbs the smaller ones by coalescence and bursts when it reaches 1 to 2 cm in dia.

Table 2 gives the amounts of sodium collected on the various stages of the Andersen impactor during the experiment. These amounts have been calculated from the sodium-22 activity measured in the corresponding samples; errors in measuring the sodium amounts result from errors in measuring the sodium-22 activity. The error is around 10% for the amount collected on the first stage, increases to 30% for the fourth stage and is in excess of 50% for the fifth stage. No value has been given from the sixth stage on, because of the extreme inaccuracy of the measurement due to the very small amounts of sodium collected on the last stages. It can

Table 2. M

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Table 1. Characteristics of the samples of sea water used in the 5 experiments of bubbling in natural sea water (bubbling time, 4 h)

Experiment No.	(1)	(2)	(3)	(4)	(5)
Date	8.4.80	8.5.80	8.6.80	10.23.80	10.24.80
Particulate matter in suspension ( $\text{mg l}^{-1}$ )	11.4	11.4	11.4	12.3	14.0
Total americium in the sea water (arbitrary units)	* 0.69	* 0.64	* 0.55	* 0.39	* 0.61
Ratio of particulate to total americium	† 0.38	† 0.18	† 0.54	† 0.31	† 0.28
Americium distribution coefficient	* $5.4 \times 10^4$	* $1.9 \times 10^4$	* $1.0 \times 10^5$	* $3.7 \times 10^4$	* $2.8 \times 10^4$
	† $7.9 \times 10^5$	† $3.7 \times 10^5$	† $2.8 \times 10^5$	† $2.3 \times 10^5$	† $3.5 \times 10^5$

\* At the beginning of the experiment.

† At the end of the experiment.

Table 2. Mass distribution of sodium vs particle size in the aerosol obtained from bubble bursting at the surface of a layer of natural sea water (bubbling time, 4 h)

Stage	Particle size ( $\mu\text{m}$ )	Experiment No.					Average
		(1)	(2)	(3)	(4)	(5)	
Amount of sodium ( $\mu\text{g}$ )							
1	> 5.8	$4.8 \pm 0.5$	$3.3 \pm 0.3$	$4.7 \pm 0.3$	$5.2 \pm 0.3$	$4.1 \pm 0.3$	4.4
2	4.7-5.8	$3.4 \pm 0.5$	$4.5 \pm 0.3$	$5.1 \pm 0.3$	$4.9 \pm 0.3$	$2.8 \pm 0.3$	4.1
3	3.3-4.7	$2.9 \pm 0.5$	$2.8 \pm 0.2$	$3.1 \pm 0.2$	$2.5 \pm 0.2$	$2.7 \pm 0.3$	2.8
4	2.1-3.3	$1.5 \pm 0.4$	$0.8 \pm 0.2$	$0.8 \pm 0.2$	$1.0 \pm 0.2$	$0.7 \pm 0.3$	1
5	1.1-2.1	$0.4 \pm 0.4$	$0.2 \pm 0.2$	$0.3 \pm 0.2$	$0.6 \pm 0.3$	$0.4 \pm 0.3$	0.4
6	0.7-1.1	—	—	—	—	—	—
7	0.4-0.7	—	—	—	—	—	—
Filter	0-0.4	—	—	—	—	—	—
Total		13.0	11.6	14.0	14.2	10.7	12.7

be seen that the greatest amounts of sodium generally correspond to the largest particles and that the amounts regularly decrease with the size of the particles. The shape of the size distribution and the amounts themselves are very similar from one experiment to another.

The results for the americium enrichment factors of the particles are presented in Table 3. Only the enrichment factors for the first stages (1-5) can be evaluated with acceptable accuracy, since the relative error for the enrichment factor is almost equal to that for the sodium amount. All the samples collected show the highest enrichment factor (between 650 and 2000) for the largest particles, with slightly decreasing factors for decreasing particle size. For submicron particles, analytical uncertainty causes doubt as to whether or not any enrichment is present. It can be seen that the results of the five experiments are very similar, except for experiment (4) giving lower factors, without the reason for this difference being known.

#### DISCUSSION

The mass distribution of sodium vs particle size obtained in the present work is approximatively similar to that found by Duce and Woodcock (1971) in spray particles collected at ground level on the windward coast of Hawaii. In the two cases, data show a high concentration of sodium for the largest particles and a regularly decreasing concentration for decreasing

particle sizes. But, the proportion of sodium in the form of submicron particles is smaller in the experimental aerosol than in the natural one. This could be due to a difference between the size spectra of bursting bubbles in artificial and natural conditions.

The americium enrichment values obtained here show that the concentration of americium in the giant particles produced from the surface of the sea water samples is enhanced by several orders of magnitude compared with that in bulk water. The americium enrichment factor for submicron particles was not measured, given the low amount of sodium present on the last stages on the impactor. The existence of relatively high americium enrichment factors (400-2000) for particles larger than  $2 \mu\text{m}$  is in good agreement with the observations made *in situ* by Pattenden *et al.* (1980) as well as Cambray and Eakins (1980). These authors found an excess of plutonium and americium (relative to global fall-out) in aerosol samples collected in West Cumbria and an even greater excess of these radionuclides in deposited material collected at the same locations. They concluded that the excess amounts came from seaspray and could be associated with very large particles. Moreover, they felt that their results could be explained by assuming an enrichment factor near 1000, which is in good agreement with the values obtained here.

It should be noted that such large enrichment factors are not specific of americium. Barker and Zeitlin (1972) found that size-separated aerosol samples collected in Hawaii, were enriched for transition

Table 3. Americium enrichment factor for particles obtained by bubble bursting at the surface of a 2 cm deep layer of natural sea water

Stage	Particle size ( $\mu\text{m}$ )	Experiment No.				
		(1)	(2)	(3)	(4)	(5)
1	> 5.8	$1900 \pm 200$	$1310 \pm 100$	$1350 \pm 81$	$687 \pm 38$	$1200 \pm 88$
2	4.7-5.8	$1260 \pm 190$	$961 \pm 55$	$1010 \pm 56$	$489 \pm 30$	$886 \pm 93$
3	3.3-4.7	$842 \pm 140$	$853 \pm 73$	$964 \pm 84$	$496 \pm 55$	$622 \pm 68$
4	2.1-3.3	$387 \pm 110$	$859 \pm 250$	$1100 \pm 330$	$365 \pm 97$	$644 \pm 240$
5	1.1-2.1	-	-	$1130 \pm 900$	$267 \pm 130$	$555 \pm 410$
6	0.7-1.1	-	-	-	-	-
7	0.4-0.7	-	-	-	-	-
Filter	0-0.4	-	-	-	-	-

metals such as iron, copper and zinc. These enrichments relative to bulk sea water exceeded 3 and 4 orders of magnitude for giant aerosols and for smaller aerosols approaching Aitken size. As these metals are, like americium, highly associated with particulate matter in surface waters, the aerosol enrichment could be due to accumulation of particulate trace metals in the surface microlayer, followed by resuspension into aerosol (Wallace and Duce, 1978; Hunter, 1980).

### CONCLUSIONS

Preliminary experiments have been performed showing it was possible to simulate the process of bubble bursting at the surface of a layer of sea water, and to obtain enrichment factors similar to those expected from observations made *in situ*. Such simulations could be extended to other radionuclides which are of interest, either per se, or as tracers of stable elements present in natural seawater. The flexibility of these experiments would permit to study the effect of varying parameters and to precise the mechanisms of aerosol enrichment.

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