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TRACE METAL FRACTIONATION EFFECTS BETWEEN SEA WATER AND AEROSOLS FROM BUBBLE BURSTING

by

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RÉSUMÉ

Des expériences de laboratoire ont été poursuivies en ajoutant des traceurs radioactifs : ^{65}Zn , ^{75}Se , ^{137}Cs et ^{152}Eu à de l'eau de mer naturelle afin de déterminer les différences de composition en éléments, entre l'eau de mer et les aérosols, en fonction des classes de tailles des particules. Un flux d'air provoquait la formation de bulles qui s'élevaient et éclataient à la surface d'un récipient contenant de l'eau de mer après adjonction des traceurs radioactifs, à pH 8. Les aérosols produits étaient collectés par un impactor à cascade qui séparait les particules en classes de tailles aux fins d'analyses. Dans une expérience typique, environ 30 ml d'eau de mer, collectés dans un récipient en polyéthylène quelques heures avant le début de l'expérience, le long de la côte sablonneuse du Golfe du Mexique, étaient traversés par un courant d'air propre, qui engendrait des bulles à une profondeur de 1 à 10 cm. Deux échantillons ou plus ont été récoltés par l'impactor à cascade pendant 12 à 24 heures. Les activités présentes sur les surfaces d'impaction ont été alors mesurées par spectrométrie gamma.

Les enrichissements par rapport au sodium varient en général systématiquement avec les tailles des particules et peuvent être en excès d'un facteur 10, mais ils apparaissent très dépendants des conditions particulières de chaque expérience, comme la distance parcourue par les bulles avant l'éclatement et le temps d'équilibration entre les traceurs ajoutés et les constituants naturels de l'eau de mer. Les effets du fractionnement, souvent importants, apparaissent comme la règle plutôt que comme l'exception. En conséquence, le transfert effectif des polluants de l'eau vers l'air constitue un problème spécifique qui devrait être étudié pour chaque substance intéressante, et ceci dans des conditions variables. Pour le moins, nos résultats indiquent qu'en l'absence de données expérimentales précises, on ne peut pas poser que la composition des aérosols marins, même en première approximation, soit identique à celle de l'eau de mer.

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ABSTRACT

Laboratory experiments were performed using radioactive tracers of ^{65}Zn , ^{75}Se , ^{22}Na , ^{137}Cs and ^{152}Eu added to natural sea water to determine differences in elemental composition between sea water and aerosol droplets as a function of particle size. The experiments were conducted using a flow of air as a stream of bubbles rising and bursting at the surface of a vessel containing sea water with added radioactive tracers at pH 8. The resultant aerosol cloud was drawn through a cascade impactor which separated particle size fractions for analysis. In a typical experiment 30 ml of sea water, collected in polyethylene no more than a few hours before along a sandy Gulf of Mexico beach, and a stream of clean air, giving bubbles with a rise distance through the water of 1 to 10 cm, were used, and two or more sequential samplings, usually 12 to 24 hours in duration, were made by cascade impactor. The impaction surfaces were then counted by gamma ray spectrometer.

Enrichments relative to Na in general vary systematically with particle size and may exceed a factor of 10 but appear to depend on the particular conditions of each experiment, such as the rise distance of the bubbles and the equilibration time between the added tracers and natural constituents in sea water. Fractionation effects, often quite large, appear to be the rule rather than the exception. Consequently, efficient transfer of pollutants from water to air is a distinct possibility and should be documented for each substance of interest under varying conditions. At the very least, our results indicate that in the absence of data it is unwise to assume the composition of the marine aerosol, even as a first approximation, to be the same as sea water.

INTRODUCTION.

The announcement in September 1972 [1] in the U.S.A. of the intent to construct nuclear power plants sited in the ocean a few km from shore prompted our inquiry into the possible hazard of spilled radioactivity rendered airborne by sea spray. It has been demonstrated [2, 3] that traces of phosphate may be enriched several hundred times in droplets from bubble bursting, but similar evidence for nuclear reactor waste products is not reported in the literature. Geochemical evidence now shows anomalously high concentrations of certain trace elements in atmospheric aerosol particles, relative to simple dispersal of soil dust or sea spray [4, 5, 6], and sea surface fractionation effects remain an unexplored possibility to account for this evidence. Therefore, extensions of the present investigation may help understand such effects and their bearing on the composition of natural and pollution aerosols. Moreover, similar work might relate to the possible transfer of pollutants to the atmosphere in certain industrial processes involving aeration by bubbling or spraying. The primary objective of the present study, however, has been to document the gross features of fractionation of certain radioactive tracers added to natural near shore sea water and the effects of varying certain parameters. Since significant fractionation effects have been found, further investigations of chemical mechanisms and of the general natural and pollution aerosol problem may be warranted.

The experiments were performed using natural sea water in a special laboratory apparatus in order to vary separately several parameters which may regulate ion fractionation effects in nature. The age and organic content of the sea water, rise distance of the bubbles, and the observable characteristics of the bubbles as they break are important parameters studied in this investigation.

Because of the present focus on the properties of radioactivity added to sea water, no attempt was made to achieve isotopic exchange with natural constituents of sea water. Fractionation of natural constituents may be quantitatively different and should be studied separately.

EXPERIMENTAL.

Figure 1 represents schematically the aerosol generation chamber in which the experiments were performed. Clean air from a tank is moistened by bubbling through distilled water and led into the test solution through stainless steel or glass capillaries, providing 5-30 bubbles per second of ~ 3 mm and ~ 1 , ~ 0.3 or ~ 0.1 mm diameter, respectively. Air flow drawn during aerosol collection entered the chamber through a Whatman 41 dust collection filter. The test solution of unfiltered sea water was contained in either of two polyethylene containers permitting bubble rise distances of ~ 1 cm and ~ 10 cm.

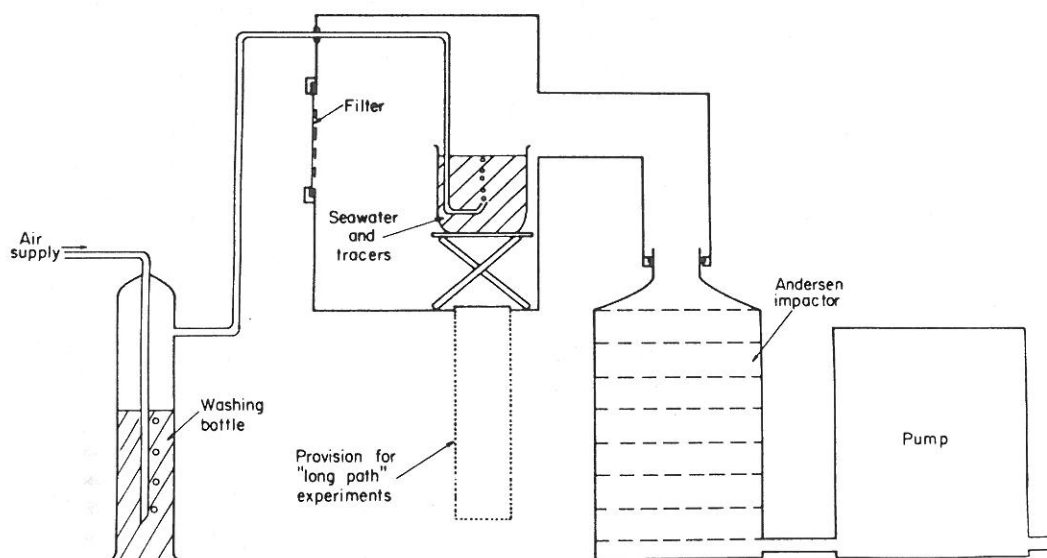


FIG. 1. — Schematic diagram of laboratory apparatus. Distance from point of bubble generation to aerosol collection by Andersen sampler was ~ 35 cm horizontally and ~ 10 cm vertically.

Aerosols were collected generally over a 12-24 hour period using an Andersen sampler, a six-stage cascade impactor operated at 28 liters/minute, with aerodynamic cut-off diameters for the stages varying by approximately a factor of two between $9 \mu\text{m}$ and $0.5 \mu\text{m}$ [7, 8]. Each stage of the impactor was covered with a polyethylene foil which was removed after each experiment for radioactivity counting in a Ge(Li) γ -ray spectrometer. In most experiments an after-filter was also used to collect particles $< 0.5 \mu\text{m}$ diameter.

Carrier-free tracers were added to natural unfiltered sea water as a neutralized mixture of high specific activity commercially obtained HCl solutions, adjusted to $\text{pH} = 8$ by addition of dilute NaOH. In all cases 2.58-year ^{22}Na ($E_{\gamma} = 511$ and 1275 keV) was included as a reference because fractionation of Na^+ relative to H_2O is believed to be insignificant during bubble rise and bursting. Either 245-day ^{65}Zn ($E_{\gamma} = 511$ and 1115 keV) alone or in combination with 121-day ^{75}Se ($E_{\gamma} = 136, 265, 280, \dots$ keV) was used in the major experiments, and 30-year ^{137}Cs ($E_{\gamma} = 662$ keV) or 13-year ^{152}Eu ($E_{\gamma} = 344, 1407, 128, \dots$ keV) in some preliminary runs. In all cases the added metal from the tracer solution was less than the amount already in the sea water. Zn and Se were chosen in the major experiments because of their biological importance, abundance in reactor wastes, contrasting aqueous chemical properties, known atmospheric chemical abundance anomalies, and availability of suitable tracers.

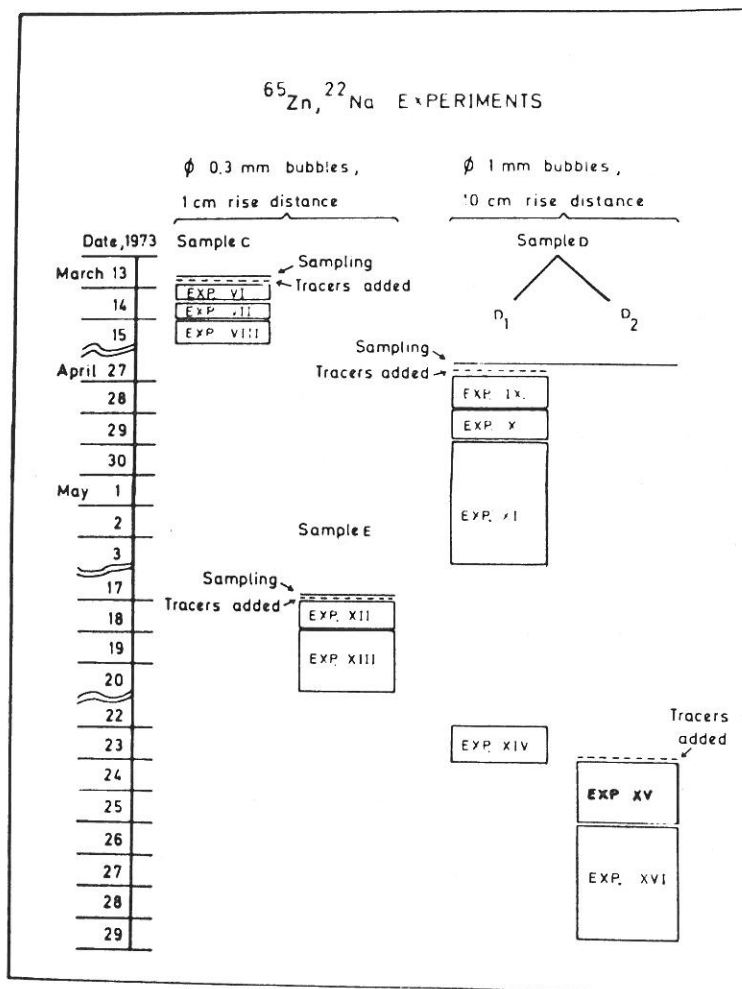


FIG. 2. — Scheme for Zn and Na experiments.

Immediately before and after each experiment, 0.1 ml of the test solution was sampled by a polypropylene pipet, and jet droplets were collected by impaction on a glass slide held over the test solution for comparison with the size fractionated aerosol generated during the experiment. The average of sea water composition before and after each experiment was used as the reference for calculating aerosol fractionation factors, F , from

$$F = \frac{(M / ^{22}\text{Na})_{\text{aerosol}}}{(M / ^{22}\text{Na})_{\text{sea water}}}$$

where M represents counting rates of ^{65}Zn or ^{75}Se in the major experiments and ^{152}Eu or ^{137}Cs in some preliminary experiments.

All sea water samples were collected in polyethylene bottles shortly before a sequence of experiments was undertaken. An unpolluted marsh area in the St. Marks National Wildlife Refuge on the north Florida coast of the Gulf of Mexico was selected for sampling, and careful note was made of tide variations, occurrence of rain, and other

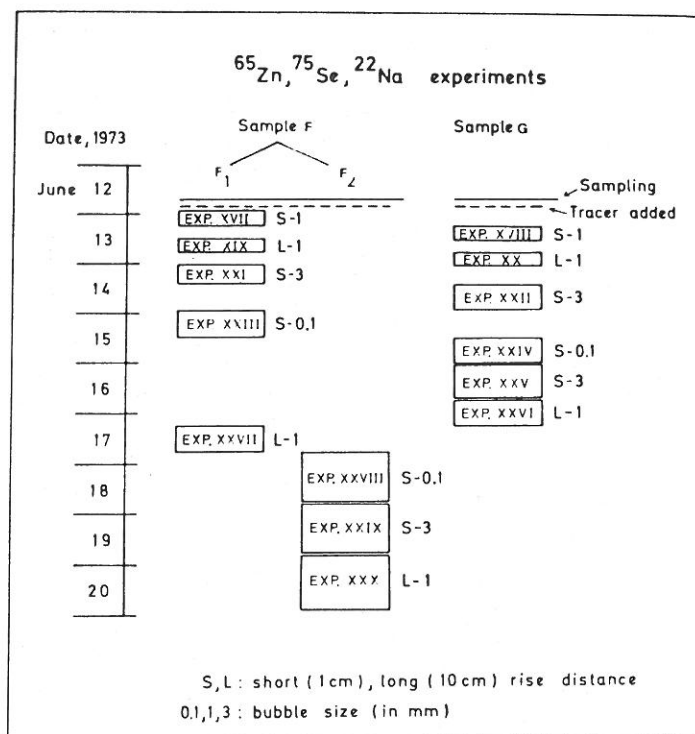


FIG. 3. — Scheme for Zn, Se and Na experiments.

factors at the time of water collection which may have affected organic content of the water or other possibly important properties.

Figures 2 and 3 present two schedules of experiments designed to test the influence of water aging, tracer equilibration time, bubble size and rise distance, and changes brought about by prolonged bubbling on aerosol composition. In any one column the sequence of experiments was performed using the same subsample of sea water. Experiments VI, VII and VIII are examples of runs done in sequence on the same sea water solution to test the effect of prolonged bubbling. Experiments XV and XVI show the effect of aging of sea water before tracer addition, in contrast with experiments XXVIII, XXIX and XXX where tracers were added before aging of sea water. Experiments were done with several combinations of bubble sizes, rise distances and length of bubbling time (indicated by vertical dimensions of the rectangles). Although the results do not show variations which are easy to interpret in terms of differences in initial sea water characteristics, it should be pointed out that samples C and E were taken at high and low tide, respectively, and D after heavy rainfall runoff into the coastal waters.

RESULTS AND DISCUSSION.

In figure 4 some typical trends are shown in the amounts of tracers found on the individual impactor stages. As expected from the literature on marine aerosol composition as it varies with particle size [9], there is a smooth trend of decreasing abundance with particle size, although the quantitative shape of the size distribution curves may depend on slight differences in the geometric arrangements for the different experiments. In

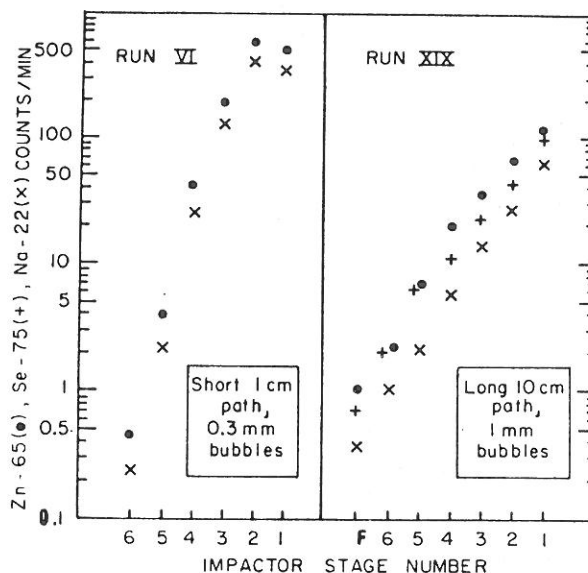


FIG. 4. — Radioactivity collected on the impactor stages as a function of particle size for two representative experiments.

the present investigation, however, emphasis has been placed on element ratios within aerosol size ranges, and the ratios should not depend on such differences.

Figures 5 and 6 show for these same experiments the variation of Zn/Na and Se/Na ratios with particle size, and between jet drop samples taken before and after the runs. The Zn/Na ratio appears to decrease appreciably in the sea water test solution during the experiments and is much less in the jet drops after compared with before the experiments. For Se/Na, where the aerosol has only slight enrichment of Se, the test solution and jet drop composition differences are less marked. In all cases, size distribution trends are smooth within the statistical errors of radioactivity measurement, shown as vertical bars of one standard deviation.

Inspection of figure 5 for a representative run with short bubble rise path shows that Zn is enriched in the aerosol size fractions, collected in experiment VI, by 4-5 times over the sea water, without strong dependence on particle size. The following experiments in the sequence, VII and VIII, which are outlined in figure 2, show Zn to be enriched by only half this amount, suggesting an effect of prolonged bubbling. The similar sequence of short bubble rise path experiments, XII and XIII, shows fractionation factors for Zn/Na not significantly different from unity for all particle sizes in both runs, an unusual result in this investigation. It suggests that the fractionation effects may depend strongly on initial water characteristics which in this case may have differed from the other experiments.

The long bubble rise experiments of the Zn and Na series are illustrated in figure 7. Experiments IX, X and XI show a consistently high Zn/Na ratio not strongly dependent on particle size; there is little if any decrease with prolonged bubbling. After standing three weeks without bubbling the same solution was run again, experiment XIV, and a very much lower Zn enrichment in the aerosol was found. However, experiments XV and XVI show that the same water standing in a polyethylene sampling bottle in the laboratory two months before tracer addition gave a very high Zn enrichment in the aerosol. These results suggest that aging effects which affect fractionation

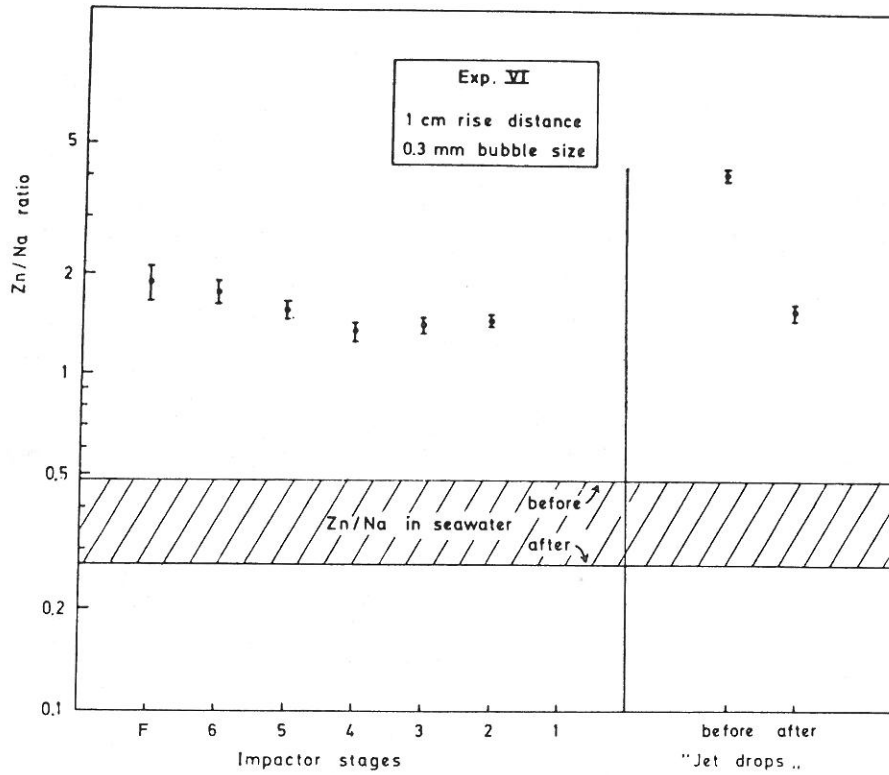


FIG. 5. — Zn/Na ratios for a representative experiment.

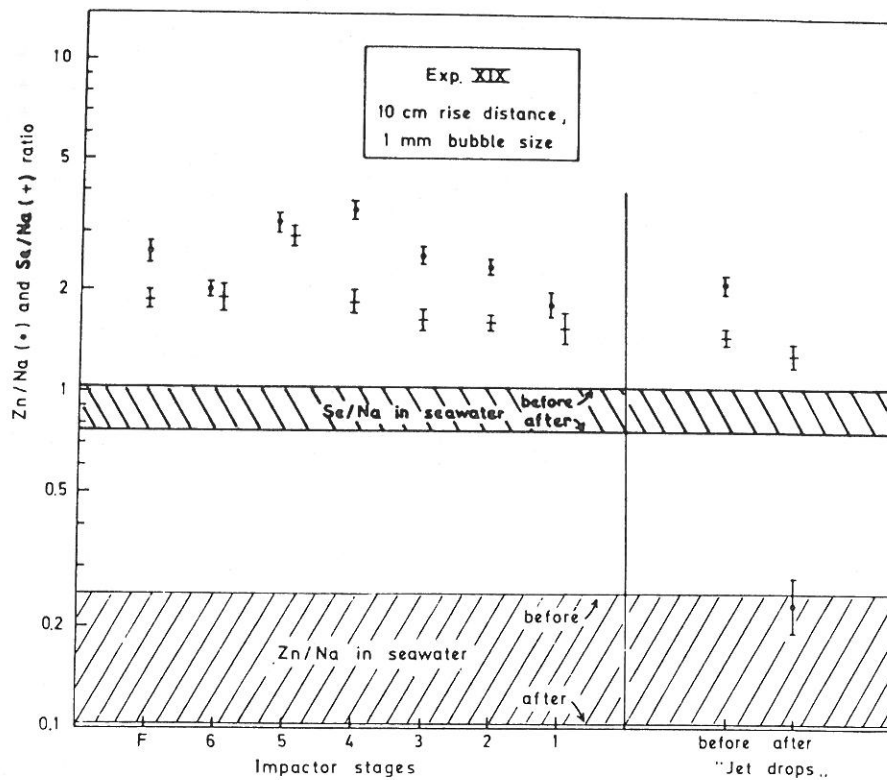


FIG. 6. — Zn/Na and Se/Na ratios for a representative experiment.

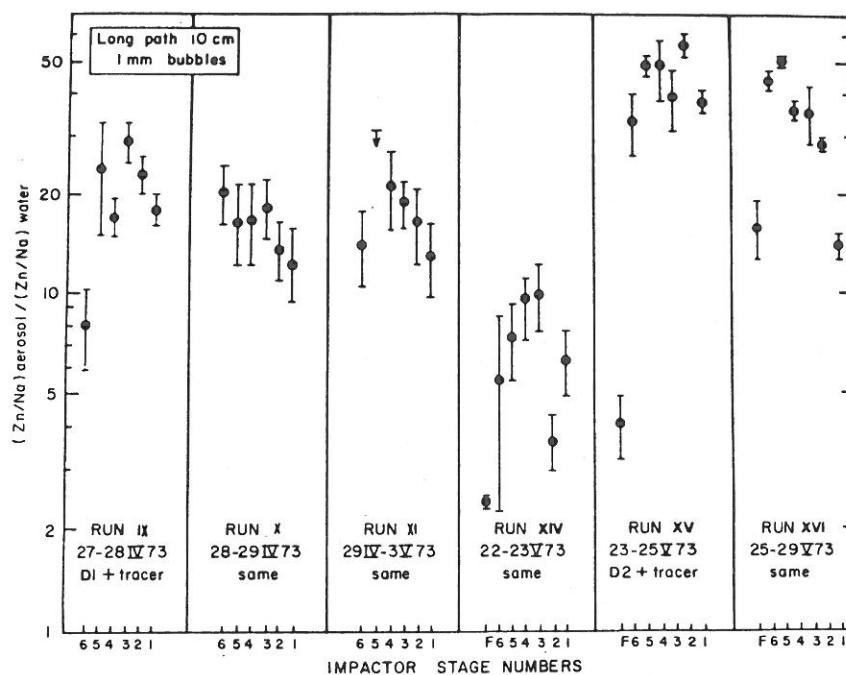


FIG. 7. — Zn/Na fractionation factors F for selected experiments with long bubble rise distances in the Zn and Na series.

of Zn and Na include tracer equilibration time and perhaps to a lesser extent prolonged bubbling action, but apparently not simple storage of water after collection.

For another series of experiments involving Zn, Se and Na tracers and outlined in figure 3, the long bubble rise path results are illustrated in figure 8. Two identical samples of sea water were collected in separate polyethylene bottles designated F and G. Splits of F were made after tracer addition, and one of these, F_2 , was set aside for several days while the other, F_1 , was used for short and long path runs using different bubble sizes.

Interleaved with these in time a similar series of experiments was done with water sample G. Afterwards, runs with water sample F_2 were done.

The long bubble rise path results of runs XIX and XX show strong Zn enrichments in the aerosol, consistent with the results shown in figure 7. However, for the two preceding runs XVII and XVIII done with the same bubble size, but short bubble rise, the Zn/Na fractionation factors F , averaged over all particle sizes, were 2.8 and 2.5 times lower, respectively. This result points strongly to an effect of enhanced enrichment with longer bubble rise path length, implying a mechanism of Zn enrichment by the scavenging action of rising bubbles rather than a mechanism involving only the action of the bursting bubble at the end of its rise. A similar effect for bacteria scavenging has been shown by Blanchard and Syzdek [10]. Since the longer of the two path lengths employed in these experiments is still short compared to average rise distances of small bubbles in actual ocean environments, much larger aerosol enrichments of ^{65}Zn radioactivity, freshly introduced into sea water, may be expected under natural conditions. However, as shown by runs XXVI, XXVII and XXX (figure 8) as well as in figure 7 already discussed, equilibration of the radioactivity with the sea water appears to suppress the fractionation of ^{65}Zn . This conclusion is tentative, of course, and awaits

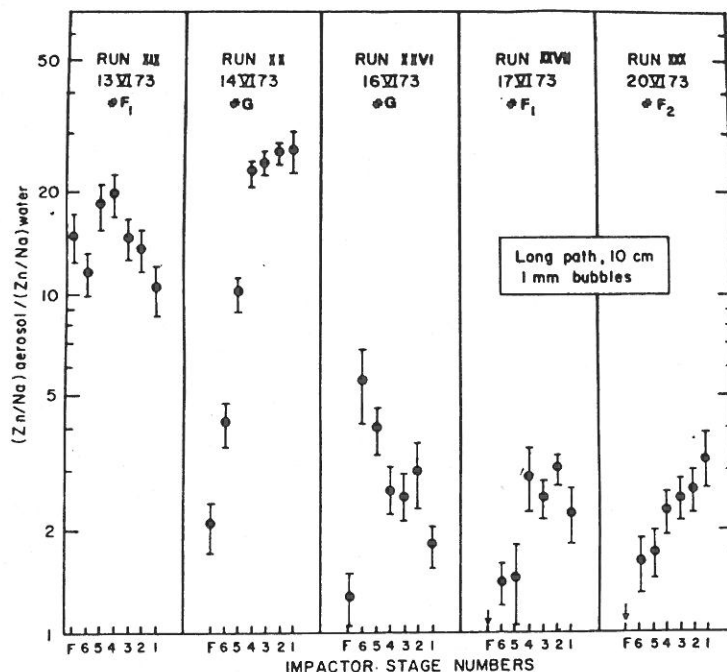


FIG. 8. — Zn/Na fractionation factors F for selected experiments with long bubble rise distances in the Zn, Se and Na series.

evaluation, among other things, of wall effects in the experimental approach which may not be present under natural conditions.

Fractionation effects for Zn and Na appeared to be enhanced to a certain extent by large bubble size. Experiments XXI and XXII showed statistically significant 30 % and 50 %, respectively, greater average Zn/Na fractionation factors F over all aerosol sizes than did experiments XVII and XVIII, in spite of the prolonged bubbling which appears in some cases to suppress Zn/Na fractionation. We see the effect of bubble size in runs XXVIII and XXIX where the average Zn/Na fractionation factors F were 1.0 and 1.9, respectively. Small fractionations for the smallest bubble sizes are also found in both of the runs XXIII and XXIV where values of F average only slightly greater than unity, except for the $< 0.5 \mu\text{m}$ diameter size fractions.

Se and Na fractionation effects are consistently seen in these experiments to be much smaller than for Zn and Na. Table I presents a summary of Se/Na fractionation factors F for the runs of figure 3 as averages over all impactor size ranges, in comparison with the corresponding Zn/Na values. Although most values show an enrichment of Se in the aerosol size fractions, the effect is slight compared to that for Zn. In view of the anionic character of Se in aqueous solution at $\text{pH} = 8$ and the cationic character of Zn under the same conditions, this difference may be a major factor involved in the fractionation mechanism. However, in view of the almost certain involvement also of organic substances in sea water which may complex these elements to varying degrees, we cannot at this time define the reaction mechanisms further.

Preliminary experiments with ^{152}Eu and ^{137}Cs tracers showed enrichment of Eu in the aerosol, relative to Na, to be as great or greater than that for Zn. Results for Cs indicate a slightly lower Cs/Na ratio in the aerosol than in the sea water. We

TABLE I

Sc/Na and Zn/Na aerosol fractionation factors, F'

Experiment	Average F' for all size fractions	
	Sc/Na	Zn/Na
XVII	1.8	5.3
XVIII	2.0	6.6
XIX	2.3	14.7
XX	1.8	16.8
XXI	1.7	7.0
XXII	2.7	9.7
XXIII	1.9	1.7
XXIV	1.6	2.5
XXVI	1.9	2.9
XXVII	1.6	2.0
XXVIII	1.3	1.0
XXIX	2.4	1.9
XXX	1.1	2.1

believe future experiments should be directed to documenting these apparent differences and relating them to differences in chemical properties in aqueous solution.

In conclusion, enrichments in general vary in a non-random manner with particle size and may exceed a factor of 10 for any particle size, but appear to depend on the particular conditions of each experiment, such as the rise distance of the bubbles and the equilibrium time between added tracers and natural constituents in the sea water. Our general finding is that fractionation effects, often quite large, are the rule rather than the exception for these tracers studied in coastal waters. Consequently, efficient transfer of pollutants from water to air is a distinct possibility and should be documented for each substance of interest under varying conditions. At the very least, our results indicate that in the absence of data it is unwise to assume the composition of the marine aerosol, even as a first approximation, to be the same as sea water [11].

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REFERENCES

- [1] WASHINGTON POST, 1972, 24 September.
- [2] MACINTYRE F. (1965). — Ion fractionation in drops from breaking bubbles. Ph. D. Thesis, Massachusetts Institute of Technology, U.S.A.
- [3] MACINTYRE F. and WINCHESTER J.W. (1969). — Phosphate ion enrichment in drops from breaking bubbles. *J. Phys. Chem.*, 73, pp. 2163-69.
- [4] RAHN K.A. (1971). — Sources of trace elements in aerosols — An approach to clean air. Ph. D. Thesis, University of Michigan, Ann Arbor, U.S.A.
- [5] HOFFMAN G.L., DUCE R.A. and HOFFMAN E.J. (1972). — Trace metals in the Hawaiian marine atmosphere. *J. Geophys. Res.*, 77, pp. 5322-29.
- [6] ZOLLER W.H., GLADNEY E.S. and DUCE R.A. (1974). — Atmospheric concentrations and sources of trace metals at the South Pole. *Science*, 183, pp. 198-200.
- [7] ANDERSEN A.A. (1966). — A sampler for respiratory health hazard assessment. *J. Amer. Ind. Hyg. Assoc.*, 27, pp. 160-65.
- [8] FLESCH J.P., NORRIS C.N. and NUGENT A.B., Jr. (1967). — Calibrating particulate air samples with monodispersive aerosols. *J. Amer. Ind. Hyg. Assoc.*, 28, pp. 507-16.
- [9] JUNGE C. (1963). — *Air Chemistry and Radioactivity*, Academic Press, New York.
- [10] BLANCHARD D.C. and SYZDEK L. (1972). — Concentration of bacteria in jet drops from bursting bubbles. *J. Geophys. Res.*, 77, pp. 5087-99.
- [11] A more complete presentation of experimental data on which the conclusions of this paper are based can be found in «Laboratory tracer experiments on fractionation during bubble bursting», a technical report obtainable from J.W. Winchester, Dept. of Oceanography, Florida State University, Tallahassee, FL 32306, U.S.A.



