

Reports

Beryllium-7 in Ocean Water

Abstract. *Concentration of the radio nuclide beryllium-7, produced by cosmic rays, was measured in waters collected from both the Atlantic and Pacific oceans. This short-lived nuclide is well suited as a tracer for interactions at the air-sea interface and for the measurement of rapid mixing processes in the surface layer of the ocean.*

A number of natural and artificial radioisotopes present in the oceans are useful tracers for the study of mixing, circulation, and diffusion processes. Because of either their half-lives or the mode of introduction, most of these nuclides cannot be used for a continuing study involving the rapid mixing that occurs above the thermocline. The cosmic ray-produced radioisotope ^7Be , with a half-life of 53 days, could be used to monitor such processes over a time interval of perhaps 200 days. This isotope, a spallation product of oxygen and nitrogen, is continuously produced in the atmosphere at a rate that is dependent on both altitude and latitude (1). According to Lal *et al.* (2), it becomes associated with atmospheric aerosols and is deposited on the earth's surface after an average residence period in the troposphere of about 30 days, and thus should present a relatively steady influx of ^7Be to the ocean surface.

The major limitation associated with the use of this isotope as a tracer of ocean processes is its very low concentration in seawater. From calculations based on a box model, Lal (3) predicted a ^7Be concentration of 180 dpm/1000 liter (dpm, disintegrations per minute) in the mixed layer of the ocean (75 m). Lal *et al.* (4) reported concentrations of 10 to 70 dpm/1000 liter for waters of the Indian Ocean on the basis of measurements of the radio-beryllium collected on jute or sponge impregnated with ferric hydroxide that was towed through the seawater. Differences between the measured and calculated values were ascribed to seasonal variations in the injection rate into the ocean.

Through the combined use of a collector designed for the sampling of large volumes of seawater and ultrasensitive counting techniques, we were able to measure the ^7Be in surface

waters of the northern equatorial Atlantic Ocean between the Bahamas and the Ivory Coast, Africa, and in a vertical profile in the Pacific Ocean at a station some 350 miles (560 km) off the Oregon coast. Our sampling equipment is similar to that used in earlier studies of the natural and artificial radioisotopes in the hydrosphere (5). Basically, it consists of a pump and a filtration assembly that also contains sorption beds. The filtration unit accommodates eight membrane filters (6) (diameter, 305 mm; pore size, 0.3 μ) which are operated in parallel, providing a total filtration area of about 5000 cm^2 . The outlet streams from the filters are directed through an adsorption bed of aluminum oxide (7), measuring 0.6 cm deep by 20 to 30 cm in diameter (depending on the specific filtration unit employed) and containing 200 to 400 g of adsorbent. The seawater was exposed only to plastic throughout the sampling line, pump, and filtration unit in order to avoid both sample contamination and adsorption of trace impurities.

We employed two different methods for sampling. The samples from the 1967 Atlantic cruise of the R.V. *Pillsbury*, University of Miami, were each taken over an extended period of time while the ship was under way. These were collected at a flow rate of about 4 liter/min from a depth of 2 m. Pacific Ocean samples were taken from aboard the R.V. *Yaquina* of Oregon State University, while on station, using a flow rate approximating 30 liter/min. In laboratory studies that simulated the sampling conditions in the Atlantic and Pacific oceans, but with the use of seawater to which ^7Be had been added, it was determined that the aluminum oxide bed retained 84 and 73 percent, respectively, of the nonfilterable ^7Be . There are always some reservations when an efficiency determined in such a manner is applied to a field study; however, we will use these values until such time as they can be evaluated under natural conditions (8).

After 1000 to 5000 liters of seawater had been sampled, the filters were removed, dried, and compressed into a polyvinyl chloride ring, 1.25 by 5 cm in diameter; the aluminum oxide was dried and mixed, and a sample of 180 g was placed in a plastic petri dish, 1.25 by 10 cm in diameter. The radionuclide content of these samples was then determined by counting the material directly for 1000 minutes in an anticoincidence-shielded, multidimensional, gamma-ray spectrometer (9).

The spectrometer used in this study consists of two anticoincidence-shielded sodium iodide crystals, 22.9 cm in diameter and 20.3 cm thick, between which the samples were accurately posi-

Table 1. Concentrations of ^7Be in ocean water. The term surface is used to indicate a depth of 2 m.

Sample location		Collection date	Sample depth (m)	⁷ Be concentrations (dpm/1000 liter)	
North latitude	West longitude			Particulate	Soluble
Atlantic Ocean					
25° 30'	74° 00'	7/24/67	Surface	30 ± 10	310 ± 36
25° 38'	72° 20'	7/25/67	Surface	N.D.*	360 ± 50
25° 10'	65° 55'	7/26/67	Surface	N.D.	290 ± 42
24° 28'	62° 18'	7/27/67	Surface	N.D.	240 ± 18
24° 48'	59° 20'	7/28/67	Surface	20 ± 47	310 ± 72
8° 50'	38° 28'	8/16/67	Surface	20 ± 27	250 ± 107
5° 48'	16° 35'	8/21/67	Surface	70 ± 33	400 ± 48
				Average	309
Pacific Ocean					
44° 40'	130° 49'	6/25/67	20	70 ± 35	220 ± 32
44° 40'	130° 49'	6/26/67	20	10 ± 20	260 ± 26
44° 40'	130° 49'	6/26/67	328	N.D.	30 ± 37
44° 40'	130° 49'	6/26/67	656	N.D.	N.D.
44° 40'	130° 49'	6/26/67	984	N.D.	N.D.
44° 40'	130° 49'	6/26/67	1640	N.D.	N.D.

* N.D., not detected; this implies a ^7Be concentration of less than 10 dpm/1000 liter.

tioned for counting. The noncoincident signals from the two crystals are recorded on the axes of a computer memory, having a total of 4096 channels, operated in a 64 by 64 channel array. Any coincident gamma rays from a decay event that are seen by both detectors are recorded in the energy-energy plane of the array in a position characteristic of the respective gamma-ray energies. Beryllium-7 is determined by the contribution of the 477-keV transition resulting from the de-excitation of its daughter ${}^7\text{Li}$. As in single-crystal gamma-ray spectrometry, each radioisotope has a characteristic gamma spectrum and thus contributes a constant proportion of its photopeak counting rate to the energy regions assigned to other isotopes. These contributions and the counting efficiencies for individual radioisotopes were determined from spectra obtained by counting standard sources of each of the isotopes in the geometries employed for sample analysis. These factors were then employed in a series of simultaneous equations which were solved for the decay rate of each isotope with the aid of a UNIVAC-1108 computer.

The aluminum oxide is not specific for retention of ${}^7\text{Be}$; indeed, ${}^{40}\text{K}$, ${}^{95}\text{Zr}$, ${}^{95}\text{Nb}$, ${}^{103}\text{Ru}$, ${}^{106}\text{Ru}$, ${}^{106}\text{Rh}$, ${}^{144}\text{Ce}$, ${}^{144}\text{Pr}$, ${}^{228}\text{Th}$, ${}^{226}\text{Ra}$, and ${}^{234}\text{Th}$ - ${}^{234}\text{Pa}$ were also retained. The presence of ${}^7\text{Be}$ was verified by half-life measurements that also substantiated the identification and the correction factors employed for the other isotopes. The occurrence of ${}^7\text{Be}$ in the samples was further confirmed by measurement of one of the samples with a high-resolution, lithium-drifted, germanium-diode detector.

The measured concentrations of ${}^7\text{Be}$ in the ocean water samples, together with the standard deviation (1σ) of the measurements are presented in Table 1. Less than 10 percent of the reported error resulted from the corrections for the other isotopes to the ${}^7\text{Be}$ energy interval, the remainder was due to the statistical uncertainties in the background counting rate.

These data show that the major fraction of ${}^7\text{Be}$ is present as a soluble species or, more properly stated, in a form that is not removed by a $0.3\text{-}\mu$ filter. Merrill *et al.* (10) found that an average of one-third of the total concentration of nonradioactive beryllium in seawater obtained from a depth of 1000 m was present in particulates removable by a $0.45\text{-}\mu$ filter. Beryllium-7 in rainfall exists as a soluble form (11); thus the high ratios of soluble to in-

soluble ${}^7\text{Be}$ that we found in surface water suggest either that the radioisotope does not exchange rapidly with the stable isotope in seawater, or that the ratio of soluble to insoluble stable beryllium is greater in surface waters than in deep waters.

Although there is some variation between samples, the surface concentration of ${}^7\text{Be}$ was relatively uniform across the Atlantic Ocean. The average concentration of the soluble fraction was 309 dpm/1000 liter; the particulate concentration, more highly variable than that of the soluble portion, averaged 20 dpm/1000 liter. Thus, the total average activity of ${}^7\text{Be}$ was 329 dpm/1000 liter. An indication of the depth to which the radioberyllium might be expected to occur can be obtained by postulating a simple model that assumes rapid and complete mixing of surface water to a discrete depth. This depth may be expressed as $D = R/C$, where D is the depth in meters, R the steady-state input rate in disintegrations per minute per square meter, and C is the measured concentration in disintegrations per minute per 1000 liters. If we take the value 9000 dpm/m² (11) as the average deposition rate for ${}^7\text{Be}$ activity in these latitudes and 330 dpm/1000 liter for the concentration of ${}^7\text{Be}$ in the surface water, the depth of total mixing is calculated to be about 30 m. The assumption of homogeneity in the surface layer, while valid when considering the long time periods required for total ocean mixing, is certainly oversimplified. Wind stress and the resultant wave action will cause a more rapid mixing at the ocean surface, and vertical turbulence will decrease with depth until it is suppressed at the top of the thermocline. The necessity of a more detailed model may be inferred from the observation that the samples taken in the Pacific Ocean from a depth of 20 m contained less ${}^7\text{Be}$ than the Atlantic surface water at a lower latitude. Since both the tropospheric production rate and stratospheric injection rate indicate a greater input of ${}^7\text{Be}$ at the higher latitude of the Pacific samples, we would expect higher concentrations at the 20-m depth if the mixing time is short compared with the beryllium half-life.

Our concentrations of ${}^7\text{Be}$ are somewhat higher than, but in fair agreement with, the calculated values of Lal (3). They are, however, an order of magnitude higher than his measured concentrations (4), a difference too great to be ascribed to latitudinal or temporal

variations. We feel that much of this discrepancy can be attributed to differences in the two sampling methods used. Kharkar (12) concluded that sponge impregnated with ferric hydroxide was an unsatisfactory collector for quantitative analyses, because of the potential loss of bed matrix and of the difficulty in assessing the quantity of water that actually came into contact with the bed. Other factors could also contribute to the disagreement, among which are differences in depth of the mixed layer and the variable deposition resulting from the degree of precipitation scavenging prior to the sampling period.

Although our data are limited, they do demonstrate the feasibility of measuring ${}^7\text{Be}$ in seawater. Thus, it appears that this short-lived radionuclide will be well suited for use as a tracer of interactions at the air-sea interface and, as such, will permit the calculation of vertical mixing rates to limited depths below the ocean surface. However, before ${}^7\text{Be}$ can be utilized in this fashion, its distribution in the surface waters of the oceans must be better characterized.

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References and Notes

1. D. Lal and B. Peters, in *Progress in Elementary Particle and Cosmic Ray Physics*, J. G. Wilson and S. A. Wouthuysen, Eds. (North-Holland, Amsterdam, 1962), vol. 6, pp. 3-72.
2. D. Lal, T. Rama, R. K. Zutski, *J. Geophys. Res.* **65**, 669 (1960).
3. D. Lal, in *Earth Science and Meteoritics*, J. Geiss and E. D. Goldberg, Eds. (North-Holland, Amsterdam 1963), pp. 115-142.
4. D. Lal, J. R. Arnold, B. L. K. Somayajulu, *Geochim. Cosmochim. Acta* **28**, 1111 (1964).
5. R. W. Perkins and D. E. Robertson, *U.S. At. Energy Comm. Res. Develop. Rep. BNWL-SA-1007* (1966).
6. Available from Millipore Corporation, Bedford, Mass.
7. Alumina, Woelm Neutral, available from Alupharm Chemicals, New Orleans, La.
8. We plan to concentrate the radioberyllium from a large volume of seawater by precipitation scavenging to compare with that removed by the sorption bed.
9. N. A. Wogman, D. E. Robertson, R. W. Perkins, *Nucl. Instrum. Methods* **50**, 1 (1967).
10. J. R. Merrill, E. F. X. Lynden, M. Honda, J. R. Arnold, *Geochim. Cosmochim. Acta* **18**, 108 (1960).
11. T. Rama and R. K. Zutski, *Tellus* **10**, 99 (1958).
12. D. P. Kharkar, *U.S. At. Energy Comm. Document YALE-2912-13*, sect. III-X (1967).
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