Reports

Radionuclides in Mono Lake, California

Abstract. *Several radioisotopes of the naturally occurring uranium and thorium decay series, in addition to fallout plutonium, have unusually high concentrations in the water column of Mono Lake, a natural alkaline, saline lake. Complexing by carbonate ions appears to be responsible for the enhanced solubility of actinide elements with oxidation states of IV to VI. In contrast, fallout strontium-90 has been largely removed from the water, probably as a result of coprecipitation with calcium carbonate. The daughter/parent activity ratios of thorium, radium, and uranium isotopes suggest that thorium is removed from the water column to the sediments on time scales substantially longer than a month and that the desorption of thorium from the sediments to the water column requires less than a few years.*

Information on the behavior of radionuclides in natural waters is necessary for a variety of purposes, including the assessment of procedures for the isolation and storage of nuclear wastes. Simpson *et al.* have reported (*1*) that an unusually high proportion of the plutonium derived from fallout has remained in the water column and has not become associated with the sediments of Mono Lake, an alkaline (pH ~ 10), saline natural lake located about 20 km east of Yosemite National Park. The most likely cause was believed to be the complexing of plutonium by CO_3^{2-}, which is present in Mono Lake at concentrations about three orders of magnitude greater than in seawater. Further experiments discussed here are consistent with the CO_3^{2-} complexing of fallout plutonium (*2*) and of a number of other elements; these results suggest that enhanced mobilities of several heavy elements can result from complexing by ligands common in natural waters.

The activities of isotopes of naturally occurring uranium, thorium, protactinium, radium, lead, and polonium, as well as nuclides derived from the atmospheric testing of nuclear weapons (^{239,240}Pu, ^{238}Pu, ^{137}Cs, ^{90}Sr, and ^{3}H) measured in water samples from Mono Lake during the years 1978 to 1980 are compiled in Table 1 (*3*). In most cases, the activities reported are averages for samples collected from several depths. Except for one unfiltered deepwater plutonium value which was only about one-quarter of the average of the other deepwater plutonium activities, no systematic variations in radionuclide activities were observed with depth, despite the presence of oxygen-free, sulfide-rich water in the bottom half of the lake. Such conditions might be expected to reduce both uranium and plutonium to lower oxidation states so that these elements would be appreciably more reactive with particles and thus would be more likely to be removed from the water column.

The extremely high concentrations of uranium, thorium, and protactinium isotopes in Mono Lake (*4*) as compared with seawater (Table 1) suggest that elements with oxidation states as low as IV (thorium) have considerably enhanced solubility due to CO_3^{2-} complexing; the same is true of elements with higher oxidation states (VI), as, for example, uranium in oxygenated waters. Thus CO_3^{2-} complexing may influence the proportion of fallout plutonium remaining in the water column of Mono Lake, no matter which oxidation state (IV, V, or VI) characterizes plutonium at different depths in the lake (*5*). In contrast, the Mono Lake concentrations of radioactive elements characterized by oxidation states of II, radium, lead, and strontium, were not unusually high (the concentration of ^{226}Ra in the deep ocean is three to seven times higher than the surface-water value in Table 1).

The activities of ^{226}Ra and ^{228}Ra in Mono Lake are about one-third the activities of their parents (^{230}Th and ^{232}Th, respectively); by contrast, in seawater radium is considerably more soluble than thorium. The ^{234}Th/^{238}U activity ratio is approximately unity, an indication that the time scale for the removal of thorium from the water column is much greater than the half-life of ^{234}Th (24 days). The ^{228}Th/^{232}Th activity ratio is about 1.4, in comparison to the ^{234}U/^{238}U ratio of 1.2. The activity of ^{228}Th exceeds that of its parent, ^{228}Ra. Thus the great-granddaughters in both decay chains show enhanced mobility, probably due to α-recoil effects of precursors in the decay chain. Clearly, thorium is transferred from the sediments to the water column on time scales that are comparable to the half-life of ^{228}Th (2 years).

The residence times (τ) of ^{230}Th and ^{231}Pa in the lake with respect to their irreversible removal and burial in the sediments can be estimated from a mass balance for the water column including production, decay, and removal to the sediments, assuming steady state:

$$A_p - A_d - \frac{A_d}{\lambda_d \tau} = 0$$

where λ_d is the decay constant of the daughter nuclide (^{230}Th or ^{231}Pa), A_d is the activity of the daughter nuclide per unit volume of water, and A_p is the activity of the parent nuclide (^{234}U or ^{235}U) per unit volume of water. Both daughters have computed residence times with respect to permanent burial in the sediments of about 700 years. Although Mono Lake has become significantly more saline over the last four decades as a result of the diversion of stream inputs, we did not treat this perturbation explicitly in the residence time calculation, which we view only as illustrative of the order of magnitude of the time scale for the permanent removal of thorium from the water column. The moderate activities of ^{210}Pb and ^{210}Po in Mono Lake are regulated primarily by the concentrations of their parent nuclide, ^{226}Ra.

We conducted a series of experiments in which we used Mono Lake water to establish the chemical form in which uranium, thorium, and plutonium were found in the water column. In the first of these experiments, unfiltered water and sediments from Mono Lake were allowed to equilibrate for a period of days to a week. We observed no significant change in the activities of uranium, thorium, or plutonium during that time. However, after inorganic carbon had been removed from the aqueous phase by acidification and purging of the copious quantities of CO_2 released and the pH had been readjusted to 10, more than 90 percent of the thorium and plutonium moved from the water to the sediment phase and the particle concentration of uranium increased considerably. Although this removal may reflect reduction to less soluble oxidation states during acidification rather than removal as a result of complex destruction, we favor the latter mechanism because more than half the particulate-phase uranium, thorium, and plutonium returned to the water after the Mono Lake water, purged of inorganic carbon, had received additions of Na_2CO_3 sufficient to approximate the

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initial concentration of inorganic carbon of unperturbed Mono Lake water.

In a second set of experiments, we used large dialysis tubes filled with "synthetic" Mono Lake water [Na_2CO_3 + NaCl + HCl (to pH 10)] initially free of radionuclides and immersed in tanks of surface water from the lake. Dialysis membranes with effective molecular weight cutoffs ranging from 3,500 to between 12,000 and 14,000 were permeable to the movement of uranium, thorium, and plutonium from the lake water into the "synthetic" Mono Lake water. The results of these experiments are consistent with the complexing of uranium, thorium, and plutonium in Mono Lake by small molecular weight ligands such as CO_3^{2-} rather than large molecular weight ligands such as humic acids. Numerical values of stability constants (*2*) of Pu(VI) complexes suggest that $PuO_2(CO_3)(OH)^-$ probably would dominate over $PuO_2(CO_3)_2^{2-}$ and $PuO_2(CO_3)(OH)_2^{2-}$ by many orders of magnitude in Mono Lake water and in seawater. Reliable stability constants for plutonium carbonate complexes for oxidation states IV and V [which are not currently available (*2*)] and definitive measurements of the oxidation state of plutonium in Mono Lake water would be required before quantitative treatment could be made of the causes of the substantial difference between the total dissolved plutonium in Mono Lake and in seawater.

The concentrations of fallout nuclides ($^{239,240}Pu$, ^{238}Pu, ^{137}Cs, ^{90}Sr, and ^{3}H) in samples collected from Mono Lake from 1978 to 1980 are quite compatible with what is known about regional fallout isotope delivery rates (*6*), except for ^{90}Sr which is probably largely associated with $CaCO_3$ precipitated along the lake margin. This can be illustrated by a comparison of fallout ^{137}Cs activities for several lakes in the western United States sampled during the period from 1966 to 1969, following the years of maximum fallout concentrations in precipitation (Table 2). Three of the lakes sampled are relatively shallow alkaline, saline closed-basin lakes (Mono, Walker, and Pyramid), and the other two are extremely deep freshwater lakes. The activity per unit volume of fallout ^{137}Cs in a sample of lake water should be proportional to the rate of precipitation (if we may assume relatively uniform activities of fallout nuclides per unit of precipitation over the entire region during the peak fallout years) and inversely proportional to the mean depth of the lake. The integrated fallout ^{137}Cs deposition rates computed from lake water measurements (14 to 111 mCi/km^2) are proportional to the average precipitation amounts and are consistent with fallout precipitation collection data (*6*).

Mono Lake has retained in the water column rather than in its sediments an unusually large proportion of the plutonium delivered as fallout to the lake surface and thus has a considerably higher dissolved activity of $^{239,240}Pu$ (*1*) than is typical of most natural waters (by one to two orders of magnitude). In contrast, the lake water has retained a much smaller proportion of fallout ^{90}Sr than is typical of most natural waters. This can be most readily seen by a comparison of the ratio of ^{137}Cs to ^{90}Sr in Mono Lake (Table 1) with the value of 1.5 typical of fallout. In most shallow freshwater lakes, considerable loss of ^{137}Cs to the sediments occurs while ^{90}Sr is almost entirely retained in the water column (*7*). In saline waters, both ^{137}Cs and ^{90}Sr are usually considered soluble, to the first approximation (*8*). Thus the ratios of fallout ^{137}Cs to ^{90}Sr in natural waters almost always are ≤ 1.5. In Mono Lake the ratio of ^{137}Cs to ^{90}Sr is about 13. The most reasonable explanation is loss from the water column of approximately 90 percent of the fallout ^{90}Sr, perhaps by coprecipitation with $CaCO_3$. Coprecipitation of ^{90}Sr with $CaCO_3$ and calcium phosphate phases has long been a waste-management practice for the control of

Table 1. Radionuclide activities in Mono Lake water (1978 to 1980); T.U., tritium unit.

Nuclide	Number of samples averaged	Activity* (pCi/m^3)	Surface sea-water activity (pCi/m^3)
^{238}U	5	185,000 ± 600	~ 1,100 (*12*)
^{234}U	5	222,000 ± 700	~ 1,300 (*12*)
^{231}Pa	1	115 ± 10	~ 0.1 (*13*)
^{234}Th	1	190,000 ± 16,000	~ 800 (*14*)
^{232}Th	5	700 ± 40	< 0.008 (*15*)
^{230}Th	5	1,410 ± 70	< 0.6 (*13*)
^{228}Th	5	1,020 ± 50	< 0.4 (*16*)
^{228}Ra	1	230 ± 30	~ 20 (*17*)
^{226}Ra	2	500 ± 30	~ 40 (*18*)
^{210}Pb	2	280 ± 15	~ 50 (*18*)
^{210}Po	4	110 ± 25	~ 30 (*19*)
$^{239,240}Pu$	19	14 ± 4	~ 0.8 (*20*)
^{238}Pu	16	0.56 ± 0.25	
^{137}Cs	7	2,000 ± 275	~ 120 (*21*)
^{90}Sr	3	160 ± 25	~ 80 (*22*)
^{3}H	4	230,000 ± 7,000	
^{3}H		70 ± 2 T.U.	~ 15 T.U. (*23*)

*Activities may be expressed as disintegrations per minute if the numerical values in this column are multiplied by 2.22.

Table 2. Fallout nuclides in western U.S. lakes (1966 to 1969); T.U., tritium unit.

Lake*	Nuclide	Activity (pCi/m^3)	Mean depth (m)	Fallout deposition in lake water (mCi/km^2)	Average annual precipitation (cm)	Lake surface area (km^2)	Drainage basin area/lake area
Mono (S)	^{137}Cs	930 ± 200	19		43	200	8
Mono (D)	^{137}Cs	1580 ± 400		30			
Walker (S)	^{137}Cs	640 ± 100	29	19	23	120	80
Pyramid (S)	^{137}Cs	330 ± 50	48	14	35	460	16
Pyramid (D)	^{137}Cs	250 ± 50					
Crater (A)	^{137}Cs	340 ± 40	325	111	171	50	1.3
Crater (A)	^{90}Sr	230 ± 16					
Crater (A)	^{3}H	25 ± 2 T.U.					
Tahoe (S)	^{137}Cs	190 ± 15	305	58	70	500	2.6
Tahoe (S)	^{90}Sr	170 ± 12					
Tahoe (S)	^{3}H	24 ± 2 T.U.					

*Mono Lake is in California, Walker and Pyramid lakes are in Nevada, Crater Lake is in Oregon, and Lake Tahoe lies on the border between California and Nevada. The first three are alkaline, saline lakes, and the last two are freshwater lakes. The letter in parentheses indicates a surface value (S), a deep value (D), or an average of values from several depths (A). We estimate the volume of Mono Lake to have been 20 to 30 percent greater at the time of sample collection (1966) reported here than in 1978 to 1980 (Table 1), based on changes in reported Cl^- concentrations at different times (*11*).

the ground-water migration of this fission product (*9*). In addition, Mono Lake is well known for its elaborate $CaCO_3$ structures (*10*) formed as stream and spring water tributaries deliver dissolved calcium to the lake (*11*) which has extremely high concentrations of CO_3^{2-} ($\sim 0.3M$). The ratio of fallout ^{137}Cs to ^{90}Sr reported here for Mono Lake is the highest for any natural water of which we are aware.

The total quantities of fallout isotopes in Mono Lake are similar to those that would be expected from regional fallout data. The most unusual aspects of the fallout nuclide distributions in Mono Lake are that fallout plutonium has remained in the water column and ^{90}Sr has largely left the water column. The behavior of radioisotopes (including both anthropogenic and natural nuclides) in natural waters can be strongly dependent upon the major-element chemistry of the water, and information of this type must be included explicitly in any projections of the behavior of radioactive material in natural water systems.

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References and Notes

1. H. J. Simpson, R. M. Trier, C. R. Olsen, D. E. Hammond, A. Ege, L. Miller, J. M. Melack, *Science* **207**, 1071 (1980).
2. J. M. Cleveland, in *Chemical Modeling in Aqueous Systems: Speciation, Sorption, Solubility, and Kinetics*, E. A. Jenne, Ed. (Symposium Series 93, American Chemical Society, Washington, D.C., 1979), pp. 321–338.
3. Measurements of ^{238}U, ^{234}U, ^{232}Th, ^{230}Th, and ^{228}Th were made on small samples (< 1 liter) filtered through glass fiber filters, returned to the laboratory, and analyzed by chemical preparation and α-spectrometry procedures frequently used for environmental samples. For ^{234}Th, we used β-counting after chemical preparation with a 2-liter sample of filtered lake water. We concentrated $^{239,240}Pu$, ^{238}Pu, ^{210}Pb, and ^{210}Po from large samples in the field (80 to 240 liters) by precipitation with $Fe(OH)_3$ and analyzed them by α-spectrometry. We measured ^{228}Ra by γ-counting of its daughter, ^{228}Ac, using $CaCO_3$ precipitated from a large field sample (80 liters). We measured ^{226}Ra by scintillation counting of its gaseous daughter product, ^{222}Rn. We measured ^{137}Cs by γ-counting of an exchange resin frequently used for the extraction of fallout ^{137}Cs from environmental samples (ammonium molybdophosphate). We measured ^{90}Sr by β-counting, using chemical preparation procedures developed for the analysis of coral samples. We measured ^{3}H by liquid scintillation counting after enrichment by electrolysis. The ^{231}Pa was coprecipitated with $Fe(OH)_3$ from a 20-liter sample, purified, and measured by α-counting [T. L. Ku, *J. Geophys. Res.* **73**, 2271 (1968)].
4. D. Thurber, *Bull. Volcanol.* **28**, 1 (1965); R. F. Anderson, thesis, Massachusetts Institute of Technology–Woods Hole Oceanographic Institution (1980).
5. G. H. Coleman, *The Radiochemistry of Plutonium* (Publication NAS-NS-3058, National Academy of Sciences–National Research Council, Washington, D.C., 1965); R. E. Connick, in *The Actinide Elements*, G. T. Seaborg and J. J. Katz, Eds. (McGraw-Hill, New York, 1954), pp. 221–300; R. P. Larsen and R. D. Oldham, *Science* **201**, 1008 (1978); D. M. Nelson and M. B. Lovett, *Nature (London)* **276**, 599 (1978); E. A. Bondietti and J. R. Trabalka, *Radiochem. Radioanal. Lett.* **42**, 169 (1980).
6. The total delivery of fallout ^{137}Cs to collection stations at San Francisco and Medford, Ore., through 1970 was 30 to 40 mCi/km^2 (average precipitation rate at both stations, ~ 50 cm/year), assuming a $^{137}Cs/^{90}Sr$ ratio of 1.5 [*Report HASL-308* (Atomic Energy Commission, Washington, D.C., 1976), appendix].
7. M. A. Wahlgren and D. M. Nelson, *Verh. Int. Verein. Theoret. Angew. Limnol.* **19**, 317 (1975).
8. W. S. Broecker, E. R. Bonebakker, G. G. Rocco, *J. Geophys. Res.* **71**, 1999 (1966).
9. K. E. Cowser and T. Tamura, *Health Phys.* **9**, 687 (1963); J. A. Varga and D. G. Jacobs, *Report ORNL TM-3130* (Oak Ridge National Laboratory, Oak Ridge, Tenn., 1970).
10. P. Cloud and K. R. Lajoie, *Science* **210**, 1009 (1980).
11. D. T. Mason, *Limnology of Mono Lake, California* (Publications in Zoology vol. 83, Univ. of California Press, Berkeley, 1967); H. J. Simpson, thesis, Columbia University (1970).
12. T. L. Ku, K. G. Knauss, G. G. Mathieu, *Deep-Sea Res.* **24**, 1005 (1977).
13. W. S. Moore and W. M. Sackett, *J. Geophys. Res.* **69**, 5401 (1964).
14. S. G. Bhat *et al.*, *Earth Planet. Sci. Lett.* **5**, 483 (1969).
15. A. Kaufman, *Geochim. Cosmochim. Acta* **33**, 717 (1969); W. S. Moore, *Earth Planet. Sci. Lett.* **53**, 419 (1981).
16. K. G. Knauss, T. L. Ku, W. S. Moore, *Earth Planet. Sci. Lett.* **39**, 235 (1978).
17. A. Kaufman, R. M. Trier, W. S. Broecker, H. W. Feely, *J. Geophys. Res.* **78**, 8827 (1973).
18. K. W. Bruland, M. Koide, E. D. Goldberg, *ibid.* **79**, 3083 (1974).
19. M. P. Bacon, D. W. Spencer, P. G. Brewer, *Earth Planet. Sci. Lett.* **32**, 277 (1976); Y. Nozaki, J. Thomson, K. K. Turekian, *ibid.*, p. 304; Y. Nozaki and S. Tsunogai, *ibid.*, p. 313; J. Thomson and K. K. Turekian, *ibid.*, p. 297.
20. H. Livingston, D. R. Mann, V. T. Bowen, in *Analytical Methods in Oceanography*, T. Gibb, Jr., Ed. (American Chemical Society, Washington, D.C., 1975), p. 124.
21. The ratio of ^{137}Cs to ^{90}Sr in surface waters of the deep North Atlantic is assumed to be identical to the fallout ratio of 1.5.
22. V. T. Bowen, V. E. Noshkin, H. L. Volchok, T. T. Sugihara, *Science* **164**, 825 (1969).
23. W. Roether, thesis, University of Heidelberg (1967).
24. We thank S. Emerson of the University of Washington and D. Imboden of the Swiss Federal Institutes of Technology for their help during our 1980 field sampling and especially for providing dissolved oxygen and sulfide profiles of the highest quality. Financial support was provided by Department of Energy contract EY2529. This is Contribution No. 3313 from Lamont-Doherty Geological Observatory of Columbia University.
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Elevated Concentrations of Actinides in Mono Lake

Abstract. *Tetravalent thorium, pentavalent protactinium, hexavalent uranium, and plutonium (oxidation state uncertain) are present in much higher concentrations in Mono Lake, a saline, alkaline lake in eastern central California, than in seawater. Low ratios of actinium to protactinium and of americium to plutonium indicate that the concentrations of trivalent actinides are not similarly enhanced. The elevated concentrations of the ordinarily very insoluble actinides are maintained in solution by natural ligands, which inhibit their chemical removal from the water column, rather than by an unusually large rate of supply.*

Many elements are chemically removed from natural waters by adsorption on particle surfaces rather than by precipitation of inorganic salts (*1*). The effective solubility of reactive elements can be regarded as the result of a competition between complexation by dissolved ligands and uptake at adsorption sites on settling particles (*2*). The concentration and mobility of reactive elements in a given body of water will therefore depend on chemical composition. We demonstrate in this report that certain actinide elements that are extremely insoluble under most environmental conditions have greatly elevated concentrations in Mono Lake, a highly alkaline (pH ~ 10) lake in eastern central California with a salt content about twice that of seawater (*3*).

Simpson *et al.* (*4*) found unexpectedly high concentrations of plutonium in Mono Lake. The chemical removal of dissolved plutonium by adsorption to particles or bottom sediments is ordinarily very rapid, and in freshwater lakes nearly all the plutonium delivered by atmospheric fallout is found in the sediments. In Mono Lake, on the other hand, about half the plutonium inventory has remained in the water, and plutonium concentrations are about 100 times greater there than in other lakes and estuaries and in coastal seawater. Simpson *et al.* questioned whether the elevated concentrations result from the complexation of plutonium by the high concentration of CO_3^{2-} or whether an unusually large proportion of the total plutonium is somehow maintained in the relatively more soluble VI (or V) oxidation state rather than in the chemically reactive and less soluble III and IV oxidation states (*5*, *6*). The oxidation state of plutonium in Mono Lake has yet to be measured.

Actinide elements in the same oxidation state tend to have similar chemical properties (*7*). We have measured the concentrations of four natural actinides, actinium, thorium, protactinium, and uranium, and two other actinides derived from nuclear fallout, plutonium and americium, in Mono Lake water. The oxi-

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