Reports

Sediment Movement on the Continental Shelf near Washington and Oregon

Abstract. The nuclides zinc-65 and cobalt-60 associated with river-borne particulate matter are incorporated in sediment on the Continental Shelf near the Columbia River. Changes in the relative concentrations of zinc-65 and cobalt-60 and in the ratio of the activity of zinc-65 and cobalt-60 suggest that radioactive sediment moves northward 12 to 30 kilometers per year along the shelf and 2.5 to 10 kilometers per year westward away from the coast.

A large and relatively constant supply of radionuclides has been added to the Columbia River by the Hanford reactors over a period of many years. This makes it possible to study the movement and distribution of water (1) and sediment (2) in the river and in the adjacent northeast Pacific Ocean (3, 4). Sediments on the Continental Shelf near the Columbia River contain Zn65 (4), half-life 245 days, and Co⁶⁰, halflife 5.3 years. The activity of each nuclide is greatest in the sediment near the river mouth and decreases with increasing distance. We believe that this change in activity is due in large part to radioactive decay of the nuclides after they become associated with river-borne particulate matter which is later deposited on the Continental Shelf. The decrease of activity with time permits us to estimate the rate of movement of sediment. We have calculated the results by means of two simple models that provide estimates of the minimum and maximum rates of sediment movement.

With the simplest model it is assumed that the change in radioactivity with increasing distance from the river mouth is due solely to radioactive decay and that there is no mixing with previously deposited sediment. Therefore we can estimate the minimum rate of movement because the model slightly overestimates the time involved.

The second model is based on the variations in the activity ratio $[A(Zn^{65})/A(Co^{60})]$, which is not affected by mixing with nonradioactive sediment because the activity of each nuclide per gram of sediment is diminished by the same relative amount. 18 NOVEMBER 1966 The half-period of the activity ratio, approximately 280 days, is long enough to provide useful information about the movement of the sediment for several years preceding its collection. The elapsed time is less than that given by the simpler model; consequently the calculated rate may be a maximum. By comparing the variation in the activity ratio with changes in the relative abundance of Co^{60} , we can estimate the amount of mixing with nonradioactive sediment necessary to cause the change.

To meet the requirements of the simplest model where only the radioactive decay of Zn⁶⁵ or Co⁶⁰ is considered, certain conditions must be satisfied: (i) the Columbia River must have been the main source of the nuclides: (ii) the radionuclides must have been injected into the river in relatively constant amounts for several years preceding the sample collection; (iii) the nuclides must have been associated with particulate matter in the river before they entered the ocean; and (iv) there must have been no major removal or addition of either nuclide, other than decay, after the particulate matter was incorporated in the sediment.

We believe these conditions were satisfied reasonably well. Although Zn^{65} and Co^{60} occur in atmospheric fallout (5), comparisons of the abundance of these two nuclides relative to fission products (such as Zr^{95} -Nb⁹⁵) in the sediment (4) indicate that from 1962 through mid-1964 (6) fallout was a smaller source of Zn^{65} and Co^{60} than the Columbia River was.

The annual average rate of transport of Zn^{65} (7) as it passes Vancouver,

Washington, has been relatively constant: 1961, 44 curie/day; 1962, 29 curie/day; 1963, 28 curie/day. We have no comparable data for Co^{60} . Both nuclides are associated principally with riverborne particulate matter (Fig. 1A) by the time they enter the ocean.

The Zn⁶⁵ and Co⁶⁰ associated with Columbia River sediment are not easily removed by ion exchange (8). The uptake of Zn⁶⁵ by Columbia River sediment is largely an irreversible process and the Zn⁶⁵ is not easily removed by mixing with salt water (9). Zinc and cobalt behave similarly when associated with many clay minerals (10). Hence we assume that neither Zn⁶⁵ nor Co⁶⁰ is readily removed from the sediment after it enters the ocean.

The decrease in Zn65 activities in the sediment (4, 11) outside the area of rapid shoaling (Fig. 2) suggests that the rate of sediment movement is between 20 and 25 km/yr north and south, parallel to the coastline, and 12 km/yr westward away from the river mouth. A similar calculation for Co⁶⁰ suggests that the rate of sediment movement northward is 12 km/yr and 2.5 km/yr south and west of the river mouth. The relative abundance of both nuclides decreases by a factor of three to ten within the area of rapid shoaling, presumably because of mixing with nonradioactive sediment.

In order to use the activity ratio to determine rates of sediment movement



Fig. 1. (A) Relative amounts of Zn^{e5} and Co^{e0} associated with river-borne particulate matter in 1964. (B) Activity ratios for water and particulate matter from the lower Columbia River during 1964.

we must first demonstrate that the two nuclides are supplied to the river in relatively constant proportions and that the activity ratio of the riverborne particulate matter is relatively constant at the time it reaches the ocean.

From 1960 through 1964, the Hanford reactors (7) released Zn^{65} and Co^{60} to the river in relatively constant proportions. The average activity ratio of reactor effluent was 45; yearly averages ranged from 41 to 59. Within any given year the activity ratio of reactor effluent undergoes large seasonal changes for unknown reasons.

Studies (2, 8, 12) of water and suspended particulate matter from the river indicate that in 1964 the activity ratio of suspended particulate matter was relatively constant $[A(Zn^{65})/A(Co^{60}) \simeq 50]$ and changed little downstream from Hood River, Oregon, approximately 340 km from the reactors (Fig. 1B).

During very high flow of the Columbia River, the water, and presumably its suspended sediment, travels this distance in about 2.5 days; during low flow it requires about 11 days to travel from the reactors to Hood River, Oregon (1).

The activity ratios of particulate matter in the river and in the marine sediment accumulating near the river mouth are similar. The activity ratio does not change drastically after the particulate matter leaves the river and is incorporated in marine sediment on the Continental Shelf (Fig. 1B). Hence, it appears that little Zn^{65} or Co^{60} is removed after the Columbia River sediment enters the ocean. We assume an initial activity ratio of 50 in sediment recently derived from the Columbia River.

The activity ratio of the sediment is greatest near the river mouth and generally decreases with increasing dis-



Fig. 2. Sample locations of sediment containing Zn^{e_5} and Co^{e_0} . The activity ratios are shown as a function of distance from the area of rapid shoaling (shown by the large circle) near the river mouth. Samples from north of the river mouth shown in (A), west in (B), and south in (C). The upper straight line in (A) and (C) indicates the change in the activity ratio corresponding to an apparent velocity of 0.1 cm/sec; the lower line corresponds to 0.05 cm/sec. The straight line in (B) corresponds to 0.025 cm/sec. Activity ratio shown by: solid circle, greater than 20; open circle, 10 to 19; solid triangle, less than 10.

tance from the river (Fig. 2). The largest activity ratios occur in the area where rapid shoaling has occurred since 1877 (13). The decrease away from the river mouth can be explained if we assume that the maximum rate of sediment movement is 30 km/yr parallel to the coast and 10 km/yr away from the coast toward the edge of the Continental Shelf.

Comparison of the activity ratios and the abundance of Co^{60} suggests that within the area of rapid shoaling 1 volume of radioactive sediment mixes with 2 or 3 volumes of nonradioactive sediment in less than 2 months. Similarly, the radioactive sediment farthest from the river has apparently mixed with 15 equal volumes of nonradioactive sediment within approximately 2 years.

The activity ratio is obviously affected by the type of sediment. For example, Co⁶⁰ was not detectable in the sands (mean grain size 90 to 180 μ) within 20 km of the coast. This precludes the use of the activity ratio to determine rates of sediment movement in that area. The presence of Zn65 in these nearshore sediments (4) indicates, however, that they probably receive some Columbia River particulate matter. The sediment containing both Zn65 and Co60 is muddy sand, generally containing more than 30 percent silt- and clay-sized material and more than 0.5 percent organic carbon. There is no evidence of a progressive change in grain size, in sorting, or in organic-carbon concentration that could cause the observed variations in the activity ratio.

The data do not indicate whether the entire sediment mass or only fractions of a certain size are moving along the Continental Shelf. Studies of Columbia River sediment (8) suggest that much of the radioactivity in the sediment is associated with the silt- and clay-sized fractions. Our data suggest that the same situation probably prevails in the marine sediment. It is conceivable, therefore, that variations in the activity ratio result from the movement of only a small part of the sediment.

Unfortunately, we lack other data on sediment movement or near-bottom currents to check our results, but we can compare them with the relatively well-known movements of surface waters in this region (14). During late spring and summer these waters move southwestward at speeds between 5 and

20 cm/sec, averaging 8 cm/sec. During the remainder of the year the surface waters near the coast flow northward at speeds between 10 and 20 cm/sec. Thus the apparent maximum speed of particle movement is approximately 0.02 to 0.01 that of the surface waters (15).

M. GRANT GROSS

Department of Oceanography, University of Washington, Seattle, and U.S. National Museum, Washington, D.C.

JACK L. NELSON Pacific Northwest Laboratories, Battelle Memorial Institute, Richland, Washington

References and Notes

- J. L. Nelson, R. W. Perkins, W. L. Hau-shild, Water Resources Res. 2, 31 (1966).
 R. W. Perkins, J. L. Nelson, W. L. Hau-shild, Limnol. Oceanog. 11, 235 (1966); J. L. Nelson, in Hanford Radiological Sciences Research, and Development Activation Research.
- *Research and Development Annual Report* for 1964, BNWL-36III (Pacific Northwest Laboratory, Richland, Washington, 1965), p.
- 371.
 3. M. G. Gross, C. A. Barnes, G. K. Riel, Science 149, 1088 (1965); C. Osterberg, N. Cutshall, J. Cronin, *ibid.* 150, 1585 (1965).
 4. M. G. Gross, J. Geophys. Res. 71, 2017 (1965).
- (1966)
- (1966).
 5. D. Chakravarti, G. B. Lewis, R. F. Palumbo, A. H. Seymour, *Nature* 203, 571 (1964).
 6. R. W. Perkins, J. M. Nielsen, C. W. Thomas, *Science* 146, 762 (1964).
 7. Environmental Studies and Evaluation Group,
- Evaluation of Radiological Conditions in the Vicinity of Hanford for 1963, Publ. 80991 (Hanford Atomic Products Operation, Rich-
- (Hanford Atomic Products Operation, Inter-land, Washington, 1964).
 8. J. L. Nelson, R. W. Perkins, J. M. Nielsen, W. L. Haushild, "Reactions of radio-nuclides from the Hanford reactors with Columbia River sediments," presented at the Summerium on Disposal of Radioactive nuclides from the Hanford reactors with Columbia River sediments," presented at the Symposium on Disposal of Radioactive

Wastes into Seas, Oceans, and Surface Waters, 16 to 20 May 1966 (International Atomic Energy Agency, Vienna, 1966).
9. V. G. Johnson, thesis, Oregon State Uni-1966.

- versity, 1966. 10. K. G. Tiller and J. F. Hodgson, *Clays Clay* N. G. Hiler and S. F. Hougson, Clays Chay Minerals, Proc. Natl. Conf. Clays Clay Minerals 9, 393 (1962).
 Samples of marine sediment were collected in August 1963 by combining the uppermost for the proceeding of the path and have been at an each law.
- In August 1963 by combining the uppermost 1 cm from two samples taken at each lo-cation by grab-type samplers. The sediment was placed in a plastic jar and dried without desalting. The radioactivity was determined with a Nal(T1) crystal (7.6 by 7.6 cm) connected to a multichannel γ -ray spectrom-eter for 100 minutes. The equipment was provided by the Laboratory of Padiation ovided by the Laboratory of ology, Univ. of Washington. discussion of data-reduction provided by Radiation of Biology, (See 5 for procedures.)
- 12. Samples of river water, collected three times each week and composited on a weekly basis at Pasco, Washington, Hood River, Oregon, and Vancouver, Washington, were immediat Pasco, washingston, were immediately filtered through 300-m_{μ} membrane filters to recover the particulate matter. Filters and water samples were dried, and radio-activity was determined with an anticoin-activity was determined with an anticoin-W. Perkins, Nucl. Instr. trometer [see R. W. Methods 33, 71 (1965)].
- 13. J. B. Lockett, Proceedings of the 8th Conference on Coastal Engineering, Mexico City, 1962 (The Engineering Foundation Council Council on Wave Research, New York, 1963), p. 695.
- 14. T. F. Budinger, L. K. Coachman, Barnes, Columbia River effluent in the North-east Pacific Ocean, 1961, 1962: Selected aspects of physical oceanography (Depart-Selected aspects of physical oceanography (Depart-ment of Oceanography Technical Report 99, February Univ. of Washington, Seattle, 1964).
- We thank W. Haushild and his asso-15. L. Ciates, U.S. Geological Survey, Portland, Oregon; D. E. Engstrom and A. H. Seymour, Laboratory of Radiation Biology, University Laboratory of Radiation Biology, University of Washington; and C. A. Barnes and K. K. Turekian for assistance. Supported by AEC contract AT(45-1)-1725 and ONR contracts Nonr-477(10) and 477(37), project NR 083 012 with the University of Washington, and by AEC contract AT(45-1)-1830 with Pacific Northwest Laboratories. Contribution No. 402 from the Department of Occorporengu, Univ from the Department of Oceanography, University of Washington.

14 September 1966

yield the substance in highly purified form (biologic activity, 10 to 15 MRC units per milligram).

Ultracentrifugation was carried out with the Beckman-Spinco model L2-65 equipped with the SW-65 rotor holding three tubes. The tubes (volume, 4.65 ml) contained buffer in a gradient of 5 to 20 percent sucrose; peptides dissolved in 0.1 ml of buffer were layered atop the sucrose gradients. The centrifuge was operated at 65,000 rev/min at 4°C to yield forces ranging from 118,000g at the top to 420,000g at the bottom of the gradient.

The sedimentation of porcine corticotropin (molecular weight, 4567) and bovine parathyroid hormone (molecular weight, approximately 9000) had been well characterized (1) in this system, and these two homogeneous polypeptides were thus useful reference standards. After centrifugation for 40 hours the contents of each tube were drained from the bottom to give serial fractions of 135 µl each. Albumin (0.5 ml of a 0.1-percent solution) was added to the thyrocalcitonin fractions, which were then stored frozen until tested; thyrocalcitonin was located by injecting fractions into groups of rats used for bioassay (4). Corticotropin and parathyroid hormone were detected as protein by the method of Lowry et al. (see 5).

The distribution of corticotropin (ACTH), bovine parathyroid hormone (BPTH), and the hypocalcemic activity of purified thyrocalcitonin (TCT) is shown in Fig. 1. The active fraction of thyrocalcitonin sedimented at a lower speed than did parathyroid hormone -at a speed only slightly higher than did corticotropin. The same relative sedimentation rates of corticotropin and thyrocalcitonin activity were found in an experiment in which acetate buffer, pH 4.75, was used. If one assumes that S_{20W} for corticotropin is 0.73 (6), S_{20W} for thyrocalcitonin is 0.78 when calculated by the method of Martin and Ames (2). In all, three such experiments have been carried out, one with each of the thyrocalcitonin preparations; in all instances the results were similar.

Thus the biologic activity of thyrocalcitonin showed a sedimentation rate too low to be compatible with previous estimates of molecular weight (3). This discrepancy cannot be attributed to alterations of thyrocalcitonin through purification (preparations at three different stages of purification gave sim-

Thyrocalcitonin: Ultracentrifugation in Gradients of Sucrose

Abstract. Analysis of thyrocalcitonin, by density-gradient ultracentrifugation at high speed, showed that its molecular weight (5000 to 6000) is considerably less than was heretofore recognized.

High-speed ultracentrifugation (1) has been used recently to examine the sedimentation of small polypeptides in gradients of sucrose. This method, a modification of the procedure of Martin and Ames (2), is advantageous when the purity of a peptide is uncertain because biologic or immunologic activity rather than protein concentration can be used to measure sedimentation rates. While testing the method with several polypeptide hormones, we found that the sedimentation constant for thyrocalcitonin was less than earlier analyses had suggested (3). This finding, indicating that unhydrolyzed thyro-

calcitonin is a smaller molecule than has been recognized heretofore, may be important to further studies of the chemical characterization of this biologic substance.

Three preparations of thyrocalcitonin were used: each was derived from material extracted from hog thyroid tissue with a solution of 8M urea in 0.2NHCl. One preparation was a crude extract obtained by the trichloroacetic acid-precipitation method (3), the second was fractionated from the crude extract by gel filtration on Sephadex G-75, the third was further chromatographed on carboxymethylcellulose to