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Woods Hole Oceanographic Institution

APPLICATIONS OF PB-210/RA-226 AND PO-210/PB-210 DISEQUILIBRIA IN THE STUDY OF MARINE GEOCHEMICAL PROCESSES

By

Michael P. Bacon

February 1976

TECHNICAL REPORT

Prepared for the National Science Foundation under Grant GA-41061 and for the U.S.A.E.C. under Contract AT(11-1)3566.

MASTER

WOODS HOLE, MASSACHUSETTS 02543

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DOCTORAL DISSERTATION

Prepared under National Science Foundation Grant GA-41061 and U.S.A.E.C. Contract AT(11-1) and the Massachusetts Institute of Technology/Woods Hole Oceanographic Institution Joint Program in Oceanography.

Approved for Distribution Derek W Spencer
Derek W. Spencer, Chairman
Department of Chemistry

Robert W Morse
Robert W. Morse
Dean of Graduate Studies

MASTER

EB

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APPLICATIONS OF
PB-210/RA-226 AND PO-210/PB-210 DISEQUILIBRIA
IN THE STUDY OF
MARINE GEOCHEMICAL PROCESSES

by

MICHAEL PUTNAM BACON

B.S., Michigan State University
(1968)

SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
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and the
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November, 1975

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Joint Program in Oceanography, Massachusetts Institute
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BIOGRAPHICAL NOTE

The author

graduated from Reading Memorial High School in 1964 and received a B.S. in Chemistry from Michigan State University in 1968. From 1968 to 1970 he served as a Peace Corps Volunteer in the Palau District of the U. S. Trust Territory of the Pacific Islands. In 1971 he entered the Massachusetts Institute of Technology/Woods Hole Oceanographic Institution Joint Program in Oceanography. The author is a member of Phi Beta Kappa, Sigma Xi and the American Geophysical Union. He is married and has no children.

Publications

M.P.Bacon and J.M.Edmond (1972) Ba and Sr profiles from GEOSECS III in the S. W. Pacific (abstract). Trans. Am. Geophys. Un., 53, 402.

M.P.Bacon and J.M.Edmond (1972) Barium at GEOSECS III in the southwest Pacific. Earth Planet. Sci. Lett., 16, 66-74.

M.Bender, T.Snead, L.H.Chan, M.P.Bacon and J.M.Edmond (1972) Barium intercalibration at GEOSECS I and III. Earth Planet. Sci. Lett., 16, 81-83.

P.G.Brewer, G.T.F.Wong, M.P.Bacon and D.W.Spencer (1975) An oceanic calcium problem? Earth Planet. Sci. Lett., 26, 81-87.

C.R.Denham, M.P.Bacon and R.F.Anderson (1975) Status of the Blake polarity event (abstract).Trans. Am. Geophys. Un., 56, 978.

J.K.B.Bishop, J.M.Edmond, D.Ketten, M.Bacon and W.Silker (1975) The chemistry of particulate matter collected by large volume in-situ filtration of the surface 400 m at 2°N, 9°W in the Atlantic Ocean (abstract). Trans. Am. Geophys. Un., 56, 1001.

M.P.Bacon, P.G.Brewer and D.W.Spencer (1975) Deep-sea scavenging of Pb-210 and Po-210 (abstract).Trans. Am. Geophys. Un., 56, 1001.

ABSTRACT

APPLICATIONS OF PB-210/RA-226 AND PO-210/PB-210 DISEQUILIBRIA IN THE STUDY OF MARINE GEOCHEMICAL PROCESSES

by

Michael Putnam Bacon

Submitted to the Department of Earth and Planetary Sciences on November 25, 1975, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

The distribution of Pb-210 and Po-210 in dissolved (<0.4 micron) and particulate (>0.4 micron) phases has been measured at ten stations in the tropical and eastern North Atlantic and at two stations in the Pacific. Both radionuclides occur principally in the dissolved phase. Unsupported Pb-210 activities, maintained by flux from the atmosphere, are present in the surface mixed layer and penetrate into the thermocline to depths of about 500 m. Dissolved Po-210 is ordinarily present in the mixed layer at less than equilibrium concentrations, suggesting rapid biological removal of this nuclide. Particulate matter is enriched in Po-210, with Po-210/Pb-210 activity ratios greater than 1.0, similar to those reported for phytoplankton. Box-model calculations yield a 2-y residence time for Pb-210 and a 0.6-y residence time for Po-210 in the mixed layer. These residence times are considerably longer than the time calculated for turnover of particles in the mixed layer (about 0.1 y). At depths of 100-300 m, Po-210 maxima occur and unsupported Po-210 is frequently present. Calculations indicate that at least 50% of the Po-210 removed from the mixed layer is re-cycled within the thermocline. Similar calculations for Pb-210 suggest much lower re-cycling efficiencies.

Comparison of the Pb-210 distribution with the reported distribution of Ra-226 at nearby GEOSECS stations has confirmed the widespread existence of a Pb-210/Ra-226 disequilibrium in the deep sea. Vertical profiles of particulate Pb-210 were used to test the hypothesis that Pb-210 is removed from deep water by *in situ* scavenging. With the exception of one profile taken near the Mid-Atlantic Ridge, significant vertical gradients in particulate Pb-210 concentration were not observed, and it is necessary to invoke exceptionally high particle sinking velocities (>10 m/d) to account for the inferred Pb-210 flux. It is proposed that an additional sink for Pb-210 in the deep sea must be sought. Estimates of the dissolved Pb-210/Ra-226 activity ratio at depths greater than 1,000 m range from 0.2 to 0.8 and reveal a systematic increase, in both vertical and horizontal directions, with increasing distance from the sea floor. This observation implies rapid scavenging of Pb-210 at the sediment-water interface and is consistent with a horizontal eddy diffusivity of 3-6 x 10^7 cm^2/s. The more reactive element Po, on the other hand, shows evidence of rapid in situ scavenging. In filtered sea water, Po-210 is deficient, on the average, by ca. 10% relative to Pb-210; a corresponding enrichment is found in the particulate phase. Total inventories of Pb-210 and Po-210 over the entire water column, however, show no significant departure from secular equilibrium, and reliable estimates of particle sinking rates cannot be made.

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CHAPTER I

INTRODUCTION

The distribution of a substance in the ocean is influenced by the mechanisms of its introduction and removal, by water motions and by the extent of its incorporation and transport in particulate phases. Measurements of both natural and artificial radionuclides offer some unique insights into these processes. This thesis describes the use of the natural radiotracers Pb-210 (t 1/2 = 22.2 y) and Po-210 (t 1/2 = 138.4 d), which are members of the natural uranium decay series (Figure I.1), in evaluating aspects of the supply, transport and removal of these elements in the ocean. The choice of these particular radionuclides was based on earlier reports in the literature which indicated that their half-lives are long enough for measurable radioactive disequilibria to be maintained by processes operating in the oceans, but short enough that their activities in sea water can be measured with reasonable ease. A second advantage, which these tracers have in common with several other members of the natural decay series, is that they are supplied to the oceans principally by <u>in situ</u> decay of their parent nuclides (an exception being Pb-210 in the mixed layer, most of which is formed in the atmosphere), and their rates of supply can thus be accurately determined.

Only two modes of supply of Pb-210 to the oceans need to be considered: deposition from the atmosphere and production by radioactive decay of Ra-226 <u>in situ</u>. Supply of Pb-210 by rivers is probably

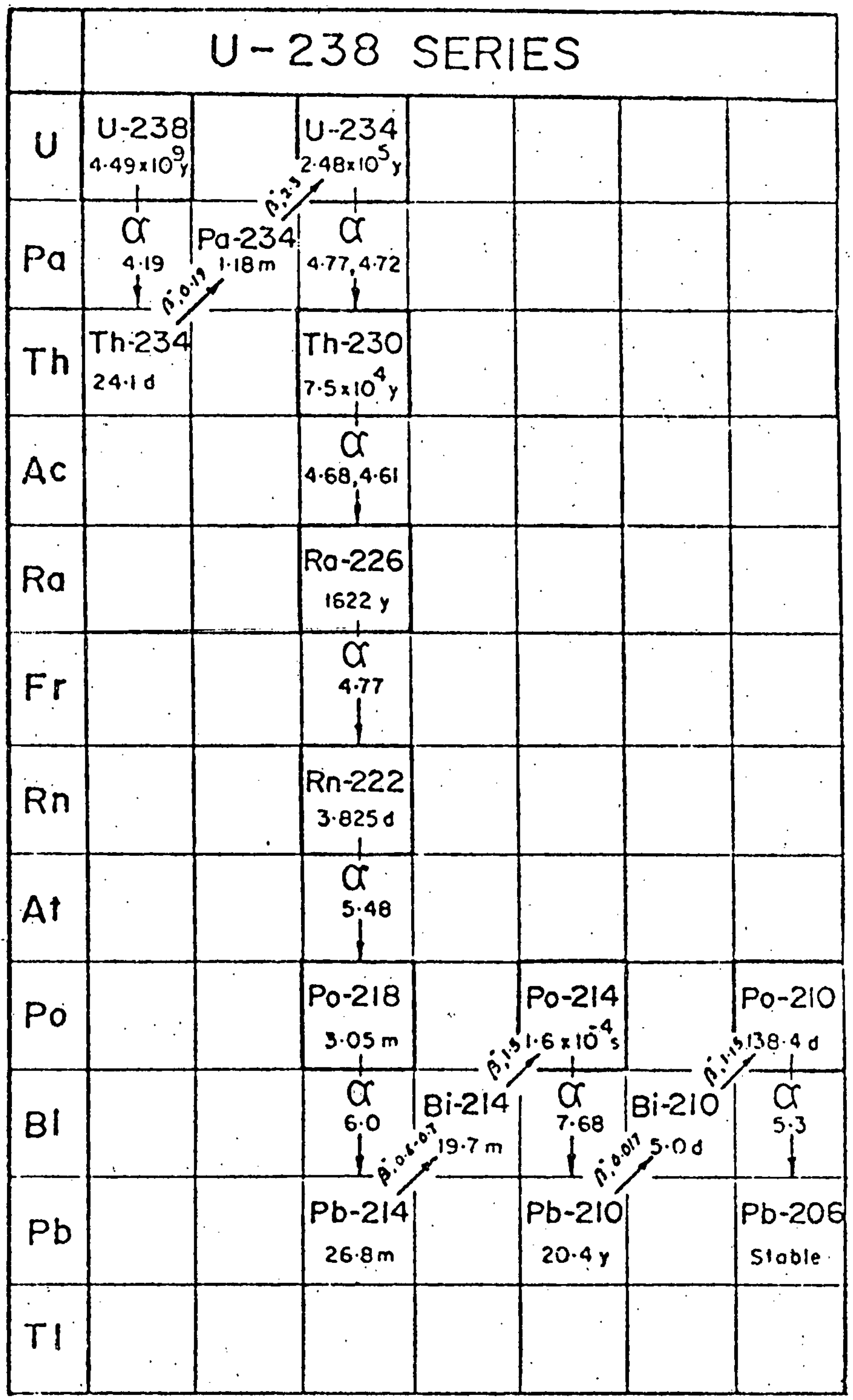

U-238 SERIES
U
Pa
Th
Ac
Ra
Fr
Rn
At
Po
Bi
Pb
Tl
U-238
4·49x10^{9}y
α
4·19
Th-234
24·1 d
β,0·19
Pa-234
1·18 m
β,2·3
U-234
2·48x10^{5}y
α
4·77, 4·72
Th-230
7·5x10^{4}y
α
4·68, 4·61
Ra-226
1622 y
α
4·77
Rn-222
3·825 d
α
5·48
Po-218
3·05 m
α
6·0
Pb-214
26·8 m
β,0·6-0·7
Bi-214
19·7 m
β,1·5
Po-214
1·6 x 10^{-4}s
α
7·68
Pb-210
20·4 y
β,0·017
Bi-210
5·0 d
β,1·15
Po-210
138·4 d
α
5·3
Pb-206
Stable

Figure I.1

unimportant, because Pb-210 is rapidly removed from river water (Goldberg, 1963) and appears to be trapped efficiently in estuaries (L. K. Benninger, personal communication). The presence of Pb-210 in the atmosphere results from decay of Rn-222, a noble gas which escapes from continental surfaces (Israel, 1951), the marine contribution being insignificant (Wilkening and Clements, 1975). There was some early speculation in the literature that significant quantities of Pb-210 may have been formed during periods of nuclear weapons testing (Jaworowski, 1966; Peirson et al., 1966). More recently, however, measurements of Pb-210 in soil and sediment samples from the Pacific Proving Grounds (Beasley, 1969) and in stratospheric air samples collected in the Northern Hemisphere during early 1963 (Feely and Seitz, 1970) have failed to show Pb-210 concentrations above those considered to be natural background levels.

Following production from radon decay, principally in the troposphere, Pb-210 atoms become rapidly attached to aerosol particles (Burton and Stewart, 1960; Junge, 1963), which, according to the most recent estimates, have a residence time of less than one week (Poet et al., 1972; Moore et al., 1973; Martell and Moore, 1974). It is generally presumed that Pb-210 is delivered to the earth's surface mostly by rain (Blifford et al., 1952), but Lambert and Nezami (1965) have indicated that 50% of the total delivery may be in the form of dry fallout.

There are no measurements of Pb-210 deposition rates over the oceans. Burton and Stewart (1960) calculated a flux of 0.37 dpm/cm^2-y on the basis of Pb-210 concentrations measured in rain over the United Kingdom. Israel's (1951) estimate of the global radon emanation rate gives a mean rate of Pb-210 delivery of about 0.4 dpm/cm^2-y. Lambert and Nezami (1965) speculated that Pb-210 delivery rates should depend strongly on latitude, and they produced a curve similar to that for artificial fallout, with maximum rates of delivery occurring at mid-latitudes in both hemispheres. Corresponding latitudinal variations in the Pb-210 concentration of surface sea water were reported by Tsunogai and Nozaki (1971), but these variations were later shown to be better correlated with the distribution of arid land areas, which are the strongest sources of atmospheric radon (Nozaki and Tsunogai, 1973). Longitudinal variations were small, and it was concluded that atmospheric Pb-210 is rapidly transported over the oceans. Turekian et al. (1974), however, argued that Pb-210 concentrations in surface sea water do not bear a direct relation to the rate of supply from the atmosphere but depend also on the rates of biological production in the surface water.

It is not possible to assume a precise value for the rate of Pb-210 deposition over the oceans, but it is probably safe to consider limits of 0.2 and 1.0 dpm/cm^2-y for most of the Northern Hemisphere except at very high latitudes. This range should be compared with the rate of in situ production of Pb-210 from decay of Ra-226, which is about 1.5 dpm/cm^2-y for a 4,000-m water column in the North Atlantic. An evaluation of the atmospheric Pb-210 flux for a particular region of the North Atlantic will be made in Chapter IV, and the significance of this flux to the deep-water Pb-210 budget will be considered in Chapter V.

Because of the short residence time of tropospheric aerosols, the rate of Po-210 production in the atmosphere is relatively small. From Po-210/Pb-210 activity ratios in air and rainwater (Burton and Stewart, 1960; Lambert and Nezami, 1965; Poet *et al*., 1972), it can be seen that the Po-210 flux from the atmosphere should be approximately 10% of the Pb-210 flux. It can be shown from the results of other investigators, and it will be further demonstrated in Chapter IV, that the delivery of Po-210 from the atmosphere can be neglected in considering material balances of this nuclide in the oceans. Moreover, Turekian *et al*. (1974) postulated that Po-rich particles may be released from the sea surface, thus partially balancing the downward flux of Po-210 produced in the atmosphere. Support for this hypothesis was given by Lambert *et al*. (1974), who measured Po-210/Pb-210 activity ratios that occasionally exceeded 1.0 in air samples collected in Antarctica. High ratios were observed most frequently when the ice shelf was the narrowest, *i.e.*, when their sampling station was closest to the presumed marine source.

The fate of Pb-210 that enters the sea surface was first examined by Rama *et al*. (1961), who measured Pb-210 concentrations in surface sea water from the northwest Pacific. They took the annual flux of Pb-210 to the sea surface to be 0.5 dpm/cm^2 and pointed out that this was much larger than the rate of Pb-210 production from decay of Ra-226 in the mixed layer, taken to be 100 m in thickness. A simple box-model calculation led to a 2-y residence time for Pb-210 in the mixed layer. Similar estimates have been given by subsequent authors (Shannon et al., 1970; Nozaki and Tsunogai, 1973). The longer residence times calculated by Turekian et al. (1974) are probably incorrect (Kharkar et al., 1975).

Shannon et al. (1970) measured Pb-210 and Po-210 in sea water and plankton collected off southwest Africa. Activity ratios Po-210/Pb-210 in surface sea water averaged 0.5, indicating rapid removal of Po-210. Both phytoplankton and, to a larger extent, zooplankton were enriched in Po-210 relative to Pb-210. Average concentration factors (g sea water equivalent to 1 g wet plankton) for Pb-210 and Po-210 in phytoplankton were 890 and 5400, respectively. For zooplankton the concentration factors were 870 for Pb-210 and 20,000 for Po-210. A similar food-chain magnification of Po-210 concentrations in marine organisms has also been noted, with some exceptions, by Beasley et al. (unpublished manuscript). The greater enrichment of Po-210 in plankton can be used to explain the more rapid turnover rate of this nuclide in surface sea water (Shannon et al., 1970; Turekian et al., 1974).

Rama et al. (1961) assumed that Pb-210 removed from the surface ocean is re-dissolved upon entering the deep sea. This supply of Pb-210 would be relatively small compared to the in situ production by decay of Ra-226 in the deep water, and they concluded that Pb-210 was essentially in secular equilibrium with Ra-226 in these waters. More recently, however, Craig et al. (1973) discovered a pronounced deficiency of Pb-210 in the deep sea, averaging 50% of the equilibrium value. This condition of radioactive disequilibrium was present in profiles from both the Atlantic and Pacific and was concluded to be a worldwide phenomenon. It was suggested that Pb-210 in the deep ocean is continually removed as a result of *in situ* scavenging by sinking particles, a concept that had earlier been discussed by Goldberg (1954) and Krauskopf (1956). Application of a vertical advection-diffusion model, with allowance for radioactive growth and decay, yielded a 54-y residence time for Pb-210 in the deep Pacific. A similar value (about 40 y) resulted from a box-model calculation for the Atlantic. Subsequent investigators have confirmed the existence of a Pb-210/Ra-226 disequilibrium in the deep ocean (Tsunogai *et al*., 1974; Applequist, 1975).

Despite the importance that has been attached to the role of particulate matter in transporting Pb-210, Po-210 and certain other radionuclides to the sediments, very few radio-chemical analyses of this material have been reported. As a consequence there exist in the literature contradictory interpretations of residence times calculated on the basis of daughter/parent activity ratios measured in unfiltered sea water samples. Bhat *et al*. (1969) discovered a Th-234/U-238 disequilibrium in surface sea water and used their data to calculate a Th-234 sinking velocity. Matsumoto (1975) pointed out that this interpretation was incorrect, because they had assumed all of the Th-234 to be in particulate form. Craig *et al*. (1973) assumed that only a small fraction of the total Pb-210 in sea water is contained in particulate phases and that their 54-y residence time for Pb-210 in the deep water applied to the transfer of Pb-210 from solution to the sinking particles. It was implied that the particles must sink very rapidly. Tsunogai *et al*. (1974), on the other hand, obtained similar data but interpreted them in terms of a slow settling velocity of 32 m/y. These two interpretations are clearly not compatible, because they imply very different distributions of Pb-210 between dissolved and particulate phases.

Recent measurements by Applequist (1975) showed that indeed only 5-10% of the Pb-210 in the deep sea is contained in particles greater than 0.4-micron diameter, as assumed by Craig *et al*. (1973). The model of Craig *et al*. (1973) predicts that particulate Pb-210 activities should increase with depth in the water column. Applequist (1975) showed that such a distribution does occur at two stations in the Pacific but did not determine the particle sinking velocities required to satisfy the model. Data on dissolved and particulate Pb-210 distributions obtained during this investigation from several stations in the Atlantic are used in Chapter V to further test the *in situ* scavenging hypothesis.

Aside from the analyses of surface sea water reviewed above, the behavior of Po-210 has remained largely unexplored. During this investigation Po-210 concentrations in filtered sea water and particulate matter were determined in several vertical profiles. These results, which are discussed in Chapters IV and V, have led to significant conclusions concerning the rates at which some heavy elements may be re-cycled in the thermocline and scavenged within the deep sea.

CHAPTER II

EXPERIMENTAL METHODS

A. Shipboard procedures

Samples collected for this investigation were taken with 270-l stainless-steel Gerard barrels or pairs of 30-l PVC Niskin bottles spaced 5-10 meters apart on the wire. Suspended matter was sampled by pumping (Eastern Industries Model MD-50 magnetic drive pump) 40 to 100 liters of sea water through 142-mm diameter, 0.4-micron pore-size Nuclepore filters. For samples collected with the Gerard barrels, filtration was performed by pumping directly from the sampler. In most cases when 30-l Niskin bottles were used on Meteor-32, it was necessary first to transfer the samples to plastic drums before filtering. Filtration was ordinarily completed within one to three hours following collection. Total volumes of water filtered were measured with Hersey-Sparling water meters installed downstream from the filter holders. Except for unavoidable, brief exposure to bronze parts of the flow meters, the water samples contacted only fittings made of various plastic materials.

Twenty-liter aliquots of filtered water were drawn into plastic vessels containing enough concentrated HCl to bring the pH within the range 1.5-2.0. The samples were then spiked with known amounts of Po-208 (several dpm) and stable Pb (several milligrams) tracers and stored for later treatment. Excess water was removed from the filters by applying mild suction, and the filters were folded and sealed in plastic bags.

B. Analytical methods

1. General

All activity measurements were made by alpha-spectrometry of the Po isotopes (Po-208, 5.11 MeV; Po-210, 5.30 MeV). Samples were processed with Pb and Po tracers present, and chemical yields were always monitored. Following an initial separation and counting of Po, samples were stored for several months during which Po-210 was re-generated by decay of Pb-210. Determination of this newly produced Po-210 gave a measure of the Pb-210 present in the sample, which allowed the initial Po-210 measurement to be corrected for radioactive growth or decay between the time of sampling and the time of Po-210 separation from its parent. An effort was made to minimize this delay in order to preserve Po-210-Pb-210 activity differences, which decrease by a factor of two for every Po-210 half-life (138 days).

2. Extraction procedure

The procedure for extracting Pb and Po isotopes from sea water was based on a method developed by Boyle and Edmond (1975). Cobalt nitrate solution was added as carrier to each acidified sample (pH 1.5-2.0) in an amount sufficient to make the cobalt concentration 0.5 mg/l. A solution of ammonium pyrrolidine dithiocarbamate (APDC) was then added (50 mg APDC per liter of sample) to form a mixture of the insoluble metal chelates. The resulting chelates precipitate as large particles due to their high concentration and are readily collected by filtering the suspension through 0.45-micron Millipore filters after a

20-30 minute reaction time. Yields nearly always exceeded 90% for both Pb and Po. There was some tendency for the particles to cling to the surface of the reaction vessel, but the losses were small enough that no attempt was made to recover particles lost in this way. It was found convenient to carry out the precipitations in disposable plastic Cubi-tainers (Hedwin Corp.), which are also satisfactory for short-term sample storage. Experience on Meteor-32 demonstrated that this procedure is easily carried out at sea, the total processing time being about 1-1/2 hours for a batch of six samples.

3. Sample dissolution

Each Millipore filter containing the sea water extract was placed in a 50-ml Teflon beaker and digested on an electric hotplate with a 3:2 mixture of concentrated HNO_3 and 70% $HClO_4$. Total digestion/evaporation times were 8-12 hours, and both the filter and organic ligand were readily oxidized. The resulting residue was dissolved in 2N HCl and held for subsequent Po separation.

For treatment of the Nuclepore filters, containing the particulate matter, conventional dry ashing methods were avoided because of the almost certain loss of volatile Pb and Po at high temperature (Gorsuch, 1959; Figgins, 1961). The polycarbonate membrane is resistant to direct attack by acids, making wet combustion difficult, but it was found that the filters could be broken into less resistant particles by soaking for a few hours at room temperature in concentrated NH_3 solution. After gentle evaporation of the ammonia, a clean oxidation could usually be achieved by acid digestion. Treatment in a low-temperature asher using an RF-generated oxygen plasma was attempted but was found to offer little advantage. Tracers were added at the start of the acid digestion and allowed to equilibrate with the sample for a few hours at low heat before the higher temperatures required for destruction of the filter were applied. Siliceous residues were removed by addition of a few drops of HF. Occasional sample losses were experienced due to spattering in the final stages of acid digestion, but tracer equilibration should have occurred by that time. Otherwise tracer recoveries were nearly quantitative.

4. Plating procedure

Separation of Po and source preparation for alpha-spectrometry were performed simultaneously by spontaneous deposition on silver discs under conditions specified by Flynn (1968), with the exception that plating times were increased to four hours to assure quantitative deposition. A plot of efficiency versus time is given in Figure II.1. Plating efficiency was determined in two ways: 1) by adding a known quantity of Po-208 tracer and determining the activity deposited and 2) by replacing the silver disc with a clean one and re-plating for the same length of time, the plating efficiency being given by

$$\text{Efficiency} = (1 - \text{CPM}_2/\text{CPM}_1) \times 100\%,$$

where CPM_1 and CPM_2 are the count rates yielded, on the same counter, during the first and second plating periods, respectively. The former method utilized prepared solutions, while the latter employed real sample material. Total deposition is seen to require three hours, and

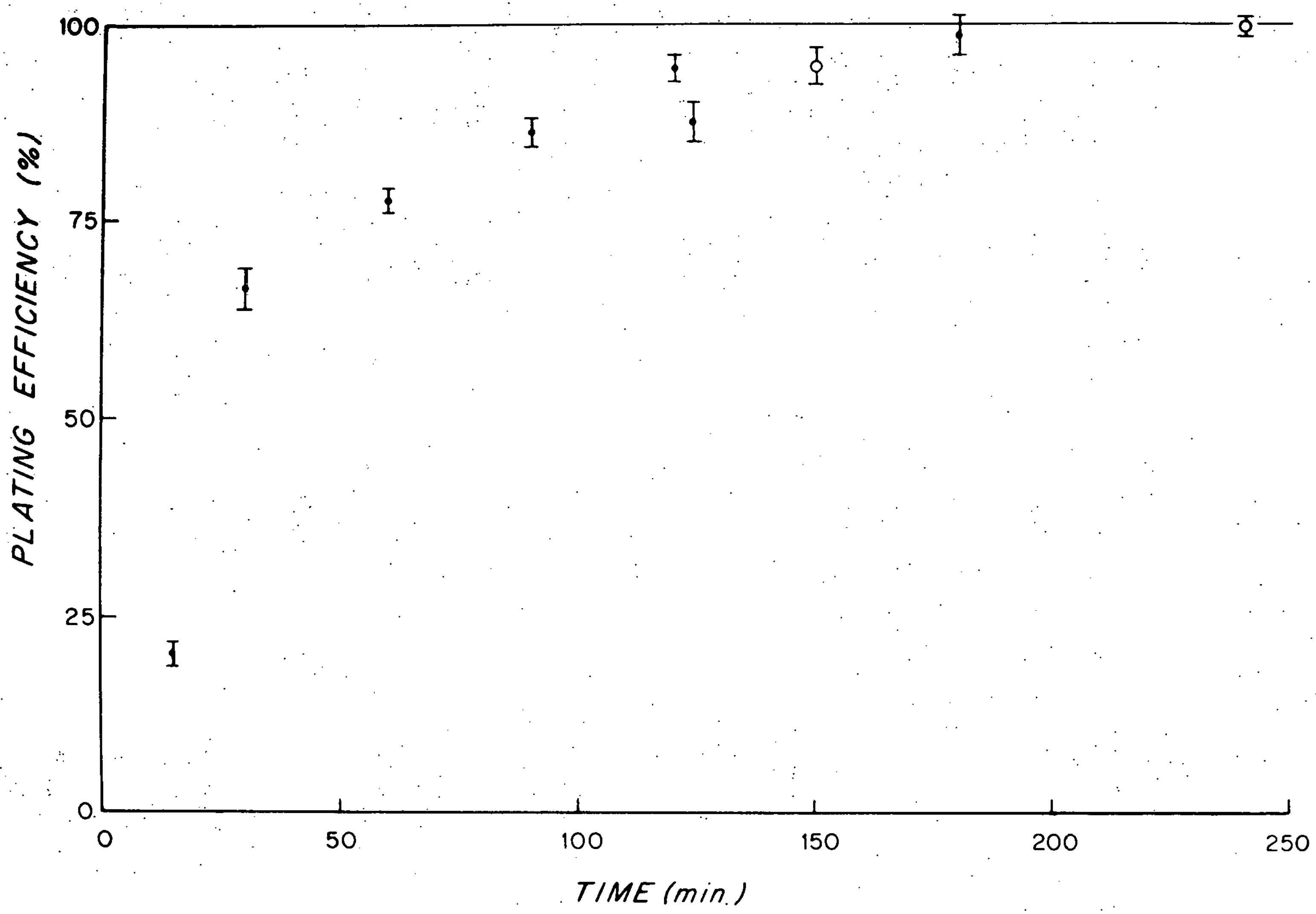


Figure II.1. Polonium plating efficiency as a function of time.

periods of four hours, which were routinely used, were shown by repeated tests to yield better than 99% efficiency.

It is important that neither Bi-210 nor, especially, Pb-210 be co-deposited with Po. Recoveries of Pb and Bi added to plating solutions were measured by atomic absorption after plating for four hours, and no loss of either element was detected. A further test for the presence of unwanted Pb-210 was made by re-counting several of the Po sample mounts after a period of about one year. First and second counts are compared in Table II.1. The activity expected at the time of the second count is calculated as the result of simple decay. The excess found is an approximate measure of the Pb-210 present in the source (actually about 15% lower, because supported Po-210 is not fully grown). Calculated amounts of Pb-210 are in all cases less than 2% of the amounts originally present in the sample solution at the time of plating. Therefore, significant errors should not result if counting is performed within six months of plating. In practice such a delay was seldom exceeded.

After the initial plating, sample solutions were re-acidified and stored in polyethylene bottles for at least six months. A second portion of Po-208 tracer was added, and the samples were again plated and counted.

5. Counting procedure

All counting was by alpha-spectrometry of the Po isotopes with silicon surface-barrier diode detectors (Ortec; Princeton Gamma-Tech). Each detector was mounted inside a stainless-steel vacuum chamber

TABLE II.1

Test for the presence of Pb-210 in Po sample mounts

Sample	Δt (days)	Po-210 (dpm)			
		Count 1	Count 2 (observed)	Count 2 (expected)	Excess
C-163	390	1.00 ± .05	.17 ± .02	.14 ± .01	+.03
C-164	408	.91 ± .05	.13 ± .01	.12 ± .01	+.01
C-165	408	.89 ± .05	.10 ± .01	.12 ± .01	-.02
C-167	404	.63 ± .04	.07 ± .01	.08 ± .01	-.01
C-168	404	.49 ± .03	.07 ± .01	.06 ± .01	+.01
C-169	404	.56 ± .03	.09 ± .01	.07 ± .01	+.02

Errors are calculated on the basis of counting statistics only.

(A. Gordon, designer) containing a Plexiglas sliding-tray sample holder. A vacuum sufficient to prevent loss of resolution by alpha-particle scattering was maintained by continuously pumping with a Welch Duo-Seal rotary oil vacuum pump. The detectors had a sensitive area of 300 mm^2 and a depletion thickness of 100 micron, which is sufficient to stop all alpha-particles of energy less than 10 MeV. Bias was applied to the detectors by Ortec Model 428 voltage supplies, and signals were amplified with Ortec pre-amplifiers (Models 121 and 124) and main amplifiers of various manufacture (Ortec Model 451, Canberra Model 1416-B, Tennelec Model TC202BLR). Following amplification the signals originating in each detector were conducted through a multiplexer-router to a 1024-channel pulse-height analyzer, and amplifier gain was adjusted so that each channel corresponded to an energy band of 15-20 keV. Linearity was established by plotting energy versus channel number for various radioisotope standards. This work was begun with two detectors and a Nuclear Data Model 2200 analyzer. During the course of the study, the system was gradually expanded to include eight detectors, and the analyzer was replaced with a Northern Scientific Model NS-710.

A typical spectrum is shown in Figure II.2. No spectral interferences were ever detected, and none would be expected, because the plating procedure is highly selective (Flynn, 1968), and potential interferences are present at much lower concentrations in sea water. Energy resolution, expressed as full peak width at half-maximum, was about 50-60 keV. Separation of the two Po peaks was ordinarily good

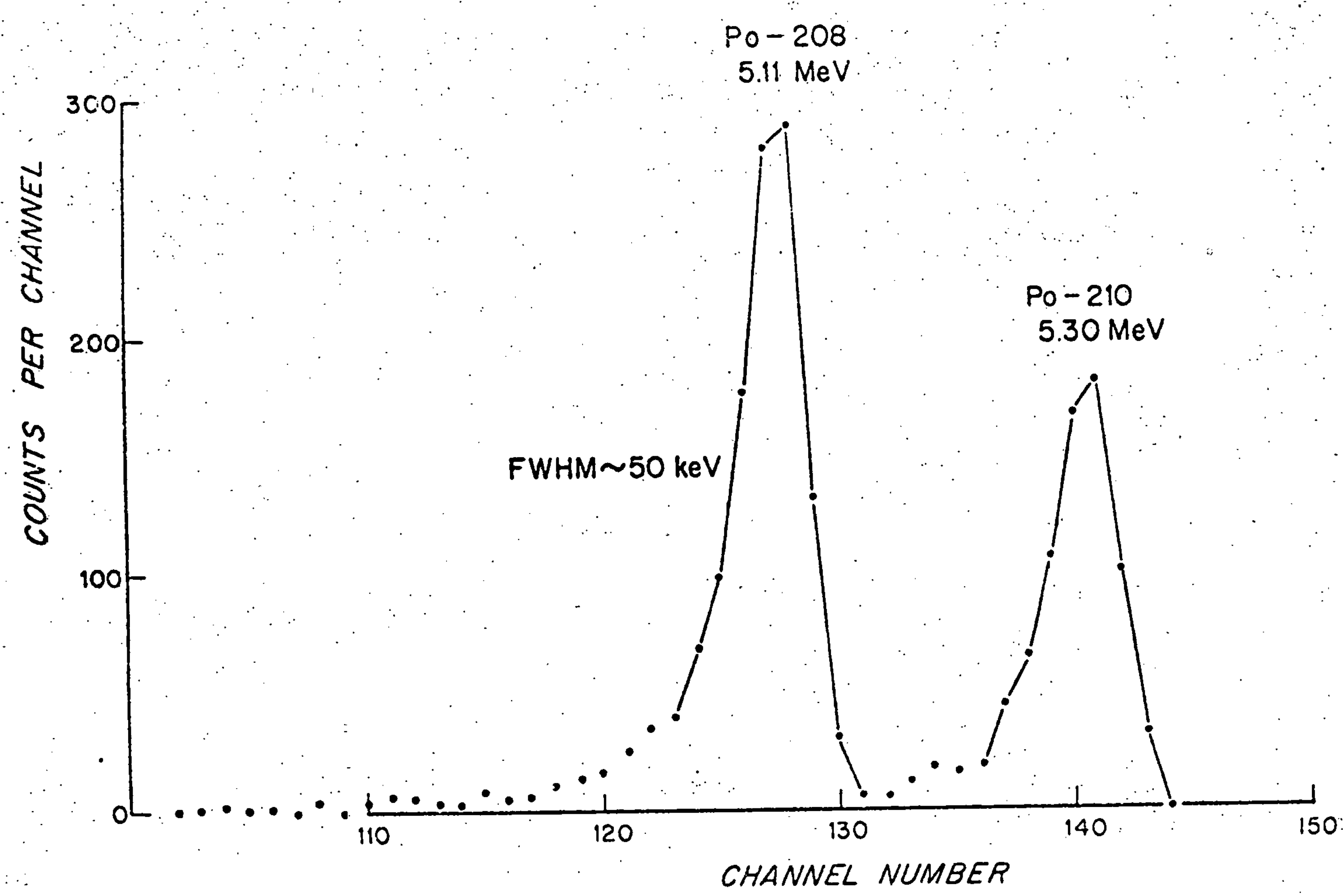


Figure II.2. Typical polonium alpha-spectrum.

but not perfect, and a small correction for tailing of the Po-210 peak into the region of the Po-208 peak was necessary.

Counting times ranged from two to four days per sample.

6. Lead recovery measurement

The amount of added stable Pb tracer remaining in the sample solution after the second plating was measured on a Perkin-Elmer Model 403 atomic absorption spectrophotometer with an air-acetylene flame under standard conditions specified by the manufacturer. The sample matrix was approximated by mixing, in proper proportions, all reagents added to samples, and this matrix was used in preparing a set of standard solutions for determining the linear portion of the absorbance-versus-concentration curve. Sample solutions were then diluted with de-ionized water to a standard volume that would bring the Pb concentration into the working range. An aliquot of the original Pb spike solution was diluted in the same matrix and to the same volume and used as a working standard. Readings were made in the absorbance mode, and the standard spike solution was run before and after each sample in order to compensate for instrument drift. The sample matrix solution, with no added Pb, was run as a blank for zeroing the instrument. Lead recovery was obtained directly from the sample/spike absorbance ratio.

C. Corrections and sources of error

1. Sample size

Water samples were ordinarily weighed at the end of each cruise, but in some cases sample size was determined at sea by volume. Weights were accurate to within 0.5% and volumes to within 3%.

In the case of the particulate samples, total volumes filtered were measured with Hersey-Sparling water meters. During Meteor-32 a good deal of information was obtained on the performance of these meters by taking readings before and after each 20-l water sample was drawn. Volumes measured in this manner were then compared with sample weights measured later. It was found that all six meters in use recorded systematically low volumes by amounts ranging from 3-14%, probably because of the low flow rates of only 1-2 liters per minute. Reproducibility for individual meters, however, was relatively good, averaging about 3%. Appropriate corrections have been applied to the analytical results for systematic errors in meter readings.

2. Counting statistics

For individual counts the statistical counting error for the Po-208/Po-210 ratio was estimated as $(1/N_{208} + 1/N_{210})^{1/2}$, where N_{208} and N_{210} designate the number of counts under each Po peak. For water samples this error was generally in the range 3-5% and for particulate samples 6-8%.

3. Detector background

All of the detectors used in this study were purchased new and had initial backgrounds of less than 0.0005 cpm for both Po-208 and Po-210. The two detectors used at the beginning showed a rise in Po-208 background to about 0.002 cpm due to volatilization of Po under vacuum and its collection by the detector (Sill and Olson, 1970).

Backgrounds for Po-210 showed smaller rates of increase. Periodic checks showed no significant rise above these levels over a period of two years, nor did the newer detectors show any increase over periods of six months or longer. Because a number of the earlier samples were counted immediately after plating, it is suggested that freshly deposited Po may be more volatile than Po in samples that have aged for a few days. For all detectors, in any case, background corrections seldom exceeded 1% of the total sample activity.

4. Spectral resolution

Because the two Po peaks could not be completely resolved instrumentally, it was necessary to estimate the degree of overlap by visual examination of the spectra. This correction was made by assuming identical peak shapes and by assuming that the tail on the Po-210 peak does not contribute significantly to the tail on the Po-208 peak. While it is not believed that significant systematic errors arise from peak overlap, random errors associated with the correction can easily amount to a few percent and are at least as important as the simple counting error in limiting analytical precision. A more desirable tracer for such analyses would be Po-209 (4.88 MeV), which would increase the sample-tracer energy difference by more than a factor of two and allow complete resolution of the two peaks. Unfortunately no source of Po-209 could be located for this study.

5. Blank corrections

A summary of blank determinations is given in Table II.2. Within counting errors, Pb-210 and Po-210 blanks are nearly equal, as one would expect. Some of the blanks, therefore, were counted only once and are reported as Po-210.

A significant source of contamination is present as an isotopic impurity in the "stable" Pb added as yield monitor, and the value of 0.02 dpm/mg Pb measured for the specific activity of Pb-210 in reagent-grade lead nitrate is in good agreement with measurements reported by Weller _et al_. (1965) for commercial lead. An uncontaminated Pb spike was obtained from M. Applequist (Scripps Institution of Oceanography) and was used for all but the Meteor-32 water samples. Aliquots of this spike, each containing about 30 mg Pb, were analyzed and found to contain no detectable activity. Even smaller amounts than this (3-7 mg) were used for spiking samples.

Results given in the first part of Table II.2 indicate levels of contamination arising from laboratory procedures only; those in the second part of the table were used to evaluate the probability of shipboard contamination. Samples C-174 through C-177 consisted of de-ionized water from the Meteor shipboard laboratory. Comparison of C-174 and C-175 with C-176 and C-177 indicates that contamination of the water samples during filtration is unlikely. A blank correction of 0.08 dpm has been applied to all water analyses for which the contaminated spike was used. Otherwise the correction is 0.03 dpm.

TABLE II.2A

Laboratory Blank Determinations

Sample	Pb-210 (dpm)	Po-210 (dpm)	Remarks
1	---	.10 ± .02	Procedural blanks for water samples. "Contaminated" Pb spike present (2.3 mg).
2	---	.05 ± .01	
3	---	None detected	Nucleopore filter blanks. No Pb spike added.
4	---	.02 ± .02	
5	---	.02 ± .01	
6	---	.01 ± .01	
7	---	.065 ± .008	Nuclepore filter blanks. "Contaminated" Pb spike present (2.3 mg).
8	---	.066 ± .008	
9	---	.051 ± .006	
10	---	.049 ± .006	

Errors are calculated on the basis of counting statistics only.

Measured specific activity of "contaminated" Pb spike:

.020 ± .001 dpm Po-210/mg Pb

TABLE II.2B

Shipboard Blank Determinations

Water Sample	Pb-210 (dpm)	Po-210 (dpm)	Remarks
C-174	.08 ± .01	.08 ± .02	Filtered, de-ionized water
C-175	.08 ± .01	.10 ± .02	
C-176	.08 ± .01	.07 ± .02	Unfiltered, de-ionized water
C-177	.05 ± .01	.11 ± .02	
Filter			
P-137	.12 ± .02	.12 ± .01	Corresponds to C-174
P-138	.023 ± .006	.013 ± .005	Corresponds to C-175
P-66	.024 ± .005	.021 ± .005	Subjected to routine handling
P-67	.013 ± .004	.018 ± .006	
P-68	.013 ± .004	.006 ± .002	
P-69	.010 ± .003	.004 ± .002	

Errors are calculated on the basis of counting statistics only.

Samples P-66 through P-70 show that no significant contamination of the filters occurred during routine handling, which consisted of loading and unloading the filter holders and transferring the filters to plastic bags for storage. The only indication of serious contamination is given by P-137, for which the measured value of 0.1 dpm is as much as 50% of the total activity measured in some of the least active samples. The source of this contamination is unknown, and there are, unfortunately, too few data to judge the likelihood of such an occurrence. It should be noted that the Po-210/Pb-210 ratio here is still close to unity. Because most of the particulate samples that were analyzed show a ratio greater than 2, a possible criterion for diagnosing cases of gross contamination would be activity ratios closer to 1. In correcting the analytical data, this last result has been ignored, and a blank correction of 0.015 dpm has been applied to all of the particulate analyses.

In addition to the blank determinations presented in Table II.2, occasional samples and blanks were processed without the addition of tracers in order to check the possibility of cross-contamination during laboratory processing. The amounts of Po-208 and stable Pb recovered in these cases were undetectable.

6. Errors in Pb recovery measurement

Atomic absorption readings were always made in triplicate, and errors in determining Pb recovery should not exceed 2%.

7. Calibration

All of the analytical results reported here were calculated with reference to two Po-210 standard solutions obtained from the

USAEC Health and Safety Laboratory (Po-210-003-I; Po-210-003-V). The certificates that accompanied these standards reported activities to three significant figures, but there was no explicit statement of confidence limits. Polonium-208 tracer solution, which derived from a commercial source, was obtained from Yale University. Calibration of this tracer was performed periodically by mixing with the HASL standard and determining the extent of isotope dilution by alpha-spectrometry. Isotopic purity was verified by alpha-spectrometry.

All dilutions of standard and spike solutions were made with 2N HNO_3 containing 200 mg Bi/l as carrier to prevent possible loss of Po by adsorption on the container walls (S. E. Poet, personal communication). Storage bottles were made of polyethylene. In two years no changes were observed in the activity of Po solutions other than those attributable to radioactive decay.

It is estimated that isotope ratio measurements for calibration were made with an accuracy of 3%. Comparison of two batches of the HASL Po-210 standard revealed a systematic difference of about 2%. Systematic errors in the analyses reported here are therefore believed to be less than 5%.

8. Errors arising from sample handling

Because this study depends on achieving resolution of total activities into dissolved and particulate components, an effort was made to determine whether transfer from one phase to the other might occur as a result of sample handling. The first indication that such effects may be significant came when an attempt was made during Meteor-32 to collect a set of replicate samples for establishing analytical precision. For this purpose a 270-l sample taken with a stainless-steel Gerard barrel tripped at 887 m on Station 23 was used. Because of time limitations on station, filtration was not begun until a few hours after retrieval and extended over an additional 10-15 hours. Approximately equal amounts of sea water were filtered through each of four Nuclepore filters, and six 20-l aliquots of filtered water were collected. The remainder of the filtered water was retained in plastic drums and later re-filtered. Two water samples and two filter samples were obtained from this second filtration.

Each of the water samples and filters was analyzed individually, and the results are given in Table II.3, where samples are listed in the order in which they were filtered. Although there is no record of the absolute time elapsed between successive filtrations, concentrations of particulate Pb-210 and Po-210 show increases correlated with time. Corresponding decreases in the amounts measured in the filtered water are just barely detectable, and there appears to be no systematic change in either of the totals obtained by summing dissolved and particulate analyses. Although the increases in individual particulate activities with time are substantial, it is important to note that the particulate Po-210/Pb-210 ratios remain virtually constant.

An effort was made to reproduce these results and obtain an estimate of the rate of solution-to-particle transfer in a similar experiment

TABLE II.3

Analytical Results for Replicate Samples, Meteor-32

	Pb-210 (dpm/100 kg)			Po-210 (dpm/100 kg)			Po-210/Pb-210		
Sample	Diss.	Part.	Tot.	Diss.	Part.	Tot.	Diss.	Part.	Tot.
* 1	7.4	.41	7.8	7.4	1.1	8.5	1.0	2.6	1.1
	6.6	"	7.0	8.1	"	9.2	1.2	"	1.3
* 2	8.4	.33	8.7	8.5	.9	9.4	1.0	2.7	1.1
	7.6	"	7.9	7.0	"	7.9	.9	"	1.0
3	6.2	.58	6.8	7.5	1.4	8.9	1.2	2.4	1.3
4	6.3	.75	7.0	6.8	1.9	8.7	1.1	2.6	1.2
Mean	---	---	7.5	---	---	8.8			
Coeff. Var'n.	---	---	9.8%	---	---	6.1%			
Second filtration									
5	6.8	.08	6.9	5.8	.8	6.6			
6	5.9	.07	6.0	5.7	.4	6.1			

Mean counting errors: Diss. Pb-210, 4.0%
Diss. Po-210, 6.3%
Part. Pb-210, 7.7%
Part. Po-210, 12.9%

*Duplicate aliquots of filtered water taken.

performed by J. Bishop during R/V Atlantis II Cruise 85. Six 30-l Niskin bottles, spaced five meters apart on the wire, were tripped at 175-200 m and immediately brought aboard. One bottle was sampled upon retrieval, and the others were sampled at 2, 4, 8, 16 and 32 hours. A 10-l sample of unfiltered water was drawn first, and the remaining contents were then filtered through 47-mm, 0.4-micron Nuclepore filters. Only the unfiltered water was saved for analysis.

Analytical results are presented in Table II.4. The possibility of a depth effect cannot be altogether ruled out, but the results are qualitatively in agreement with the earlier findings from Meteor-32. Particulate activities increase with time, while totals and Po-210/Pb-210 ratios show little change. Figure II.3 is a plot of particulate activity versus time. The data are rather badly scattered, partly because of the small volumes (12-17 l) filtered, and are not really adequate to define a particular functionality. A crude approximation of solution-to-particle transfer rates is attempted by making a linear least-squares fit. The estimated rates are 0.019±0.008 (dpm/100 kg)/hr for Pb-210 and 0.013±0.007 (dpm/100 kg)/hr for Po-210. These rates correspond to increases over the initial particulate activity of 5±2% and 4±2% per hour for Pb-210 and Po-210 respectively. Activities in the dissolved phase would be reduced by about 0.2±0.1% per hour.

Reasons for this apparent transfer are not understood. Because the observed rates of change are much higher than those inferred for *in situ* conditions, and because little fractionation of Pb-210 and Po-210

TABLE II.4

Results of Delayed Sampling Experiment, AII 85

	Pb-210 dpm/100 kg		Po-210 dpm/100 kg		Tot.	Tot.
Time (hr)	Tot.	Part.	Tot.	Part.	Po-210/Pb-210	Po-210/Pb-210
0	8.0 ± .6	.52 ± .07	10.2 ± .7	.37 ± .05	1.3	.7
2	8.6 ± .6	.22 ± .03	8.2 ± .6	.19 ± .03	1.0	.9
4	8.3 ± .6	.38 ± .05	8.4 ± .6	.27 ± .04	1.0	.7
8	7.1 ± .6	.86 ± .08	9.8 ± .7	.69 ± .06	1.4	.8
16	8.5 ± .6	.60 ± .07	9.2 ± .7	.39 ± .05	1.1	.7
32	8.9 ± .7	1.02 ± .10	7.9 ± .6	.72 ± .11	.9	.7
Mean	8.2		9.0			
Coeff. Var'n.	7.3%		10.0%			
Mean counting error	5.2%		5.3%			

Errors are calculated as in Section II.D.1 and Appendix II.B

Date:	21 October 1974
Position:	39.0°N 69.3°W
Sampling Depth:	175-200 m

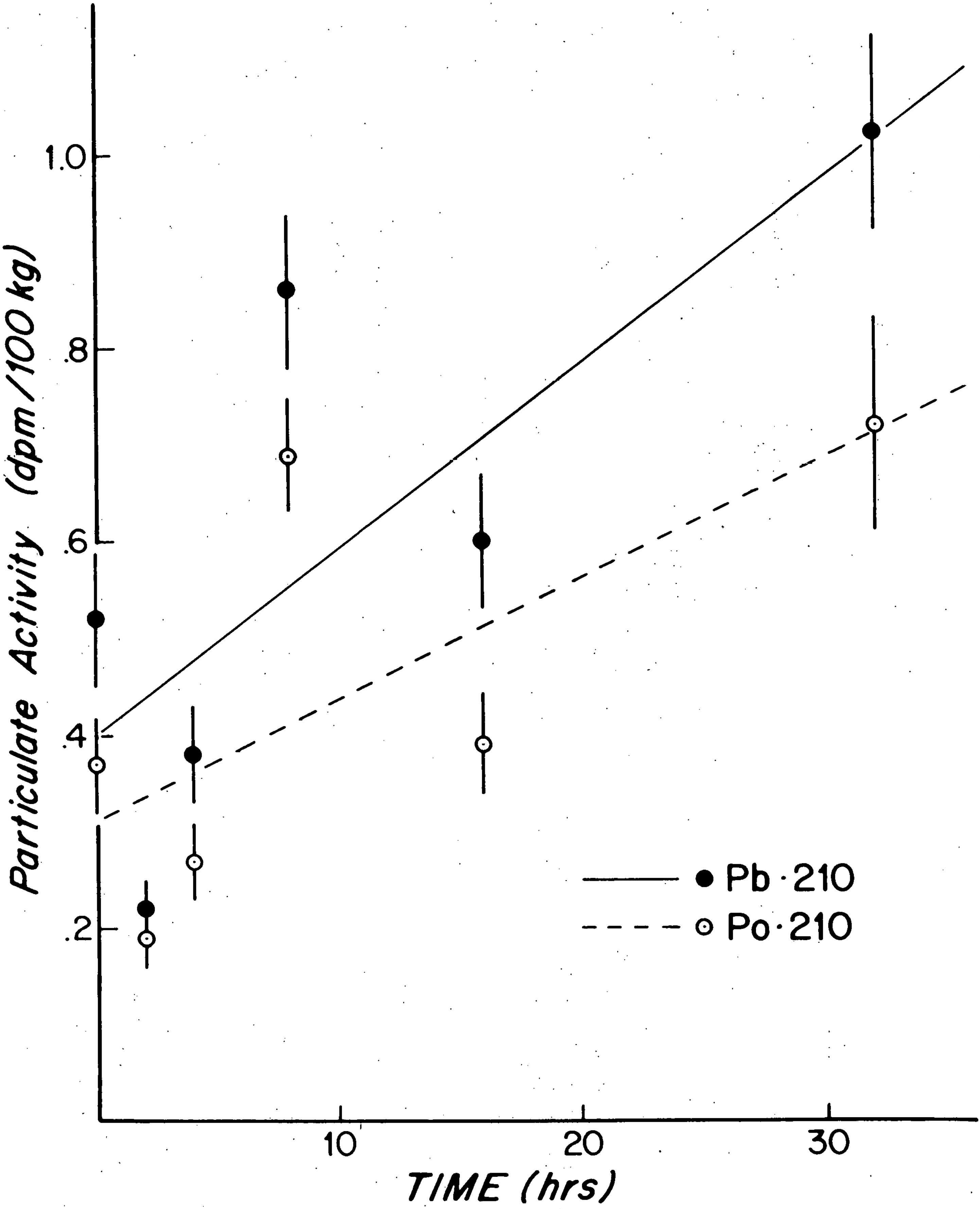


Figure II.3. Changes with time of the particulate Pb-210 and Po-210 concentrations in sea water samples.

was observed, the transfer would seem to be induced by disturbance of the sample. It is possible that increases in temperature or turbulence might significantly accelerate aggregation of particles smaller than 0.4 micron or their collection by larger particles (Stumm and Morgan, 1970). The fact that particulate Pb-210 and Po-210 were recovered from water that had previously been filtered suggests that particle formation (Sheldon _et al_., 1967), possibly resulting from stimulation of bacterial growth, may be a factor. These samples were kept in fairly opaque containers between filtrations, so phytoplankton growth is not likely to have been important. It should also be noted that particles collected during the second filtration were greatly enriched in Po-210 relative to Pb-210. This behavior was unlike that of the samples that were only filtered once, in which no relative enrichment of Po-210 was observed with time. It is likely that more than one process is responsible for the observed changes in the samples.

Whatever the causes might be, the immediate concern for the present study is the magnitude of the effect. For all of the samples used in this investigation, filtration was completed in less than three hours following collection. Solution-to-particle transfer during this delay should not exceed 20% of the initial particulate activity or 1% of the dissolved activity. Because total activities show no apparent change with time, it is concluded that no losses to other surfaces occur and that total activities are unaffected by ordinary delays in sampling.

Additional experiments have been performed to measure the adsorption of Po by Nuclepore and Millipore membranes. Filters immersed for two hours in filtered sea water spiked with Po-208 retained negligible amounts of tracer. In a second experiment Woods Hole surface sea water was filtered through pairs of filters, in separate holders, arranged in series. Very low flow rates were experienced with this arrangement, and volumes could not be recorded due to stalling of the water meter. It took four hours to filter less than 10 liters through the Nuclepore pair. Approximately 30-40 liters were filtered through each pair of Millipore filters in about 1 hour. Table II.5 compares activities measured on the first and second filters. Amounts retained by the second filter were small (comparable to the analytical blank) but detectable, and may have resulted from adsorption. It is more likely, however, that the effect results from retention of particles smaller than the nominal pore size of the filters (Cranston and Buckley, 1972). It is concluded that adsorption of Po-210 by membrane filters does not produce a significant bias in the discrimination between dissolved and particulate phases. On the basis of tracer experiments, Applequist (1975) reached a similar conclusion in the case of Pb-210. Because of uncertainty in the magnitude of the effects described in this section, no corrections for them have been applied to the analytical data.

D. Quality of the data

1. Precision

Due to the presence of other sources of error, the most important

TABLE II.5

Po-210 Collected on Filters Arranged in Series

Sample	Po-210 (dpm) First	Po-210 (dpm) Second	Second/First (%)	Filtration Time
.45μ Millipore (A)	1.2 ± .1	.02 ± .01	2 ± 1	1 hr.
.45μ Millipore (B)	1.4 ± .1	.01 ± .01	1 ± 1	1 hr.
.4μ Nuclepore	.29 ± .03	.03 ± .01	10 ± 3	4 hrs.

being lack of complete spectral resolution, the precision of the analyses reported here is not as good as estimates based on simple counting statistics alone would indicate. This may be seen by examining the total activity measurements obtained on replicate samples given in Tables II.3 and II.4. In evaluating precision from these sets of analyses, it must be assumed that the total activity is independent of the time delay. It is estimated that a cumulative 5% error arises from causes other than random fluctuations in the count rate. Precision of individual analyses was estimated by the approximate formula $((.05)^2 + (C.E.)^2)^{1/2}$ x 100%, where C.F. is the statistical counting error of the Po-208/Po-210 ratio as evaluated in section II.C.2. Additional calculations, detailed in Appendix II.B are required to estimate precision of the Po-210 analyses.

2. Intercalibration

Two Pb-210 intercalibration studies have been performed in conjunction with M. Applequist and Y. Chung of Scripps Institution of Oceanography. The S.I.O. measurements employed beta-counting of the Pb-210 daughter Bi-210 and were based on a Pb-210 standard obtained from a private source. Lead recoveries were determined gravimetrically.

In the first set of comparative measurements (Table II.6), sample mounts prepared and counted at S.I.O. were sent to W.H.O.I., where they were re-dissolved, spiked with Po-208 tracer, plated and alpha-counted. The Pb-210 activity was calculated on the assumption that Po-210 had been completely removed during sample purification at S.I.O. With the possible exception of the 1183-m sample, the agreement is fair. The

TABLE II.6

Results of Particulate Pb-210 Intercalibration GEOSECS Pacific Station 201. Particulate Pb-210 given in dpm/100 kg

Depth	S.I.O.	W.H.O.I.	$\frac{\text{S.I.O.-W.H.O.I.}}{\text{W.H.O.I.}} \times 100\%$
12	.18 ± .08	.16 ± .01	+12.5
389	.31 ± .13	.37 ± .02	-16.2
786	.29 ± .02	.32 ± .02	- 9.4
1183	.38 ± .02	.51 ± .03	-25.5
1706	.61 ± .07	.53 ± .03	+15.1

TABLE II.7

Results of Dissolved Pb-210 Intercalibration GEOSECS Pacific Station 320. Dissolved Pb-210 given in dpm/100 kg

Depth (m)	S.I.O.		W.H.O.I.	$\frac{\text{S.I.O.-W.H.O.I.}}{\text{W.H.O.I.}} \times 100\%$
0	Not measured		7.7 ± .6	--
77	8.5 ± 1.5	Preliminary Counting Only	9.3 ± .6	- 8.6
128	8.2 ± .8		9.8 ± .7	-16.3
204	9.6 ± 1.4		9.3 ± .7	+ 3.2
254	9.4 ± 1.4		9.6 ± .7	- 2.1
505	10.0 ± 1.5		8.5 ± .6	+17.6
704	8.2 ± .8		8.8 ± .6	- 6.8
802	8.9 ± 2.2		9.6 ± .7	- 7.3
1002	10.8 ± .5	Final Data	11.1 ± .7	- 2.7
1504	13.6 ± .6		10.9 ± .7	(+24.8)?
2054	17.0 ± .7		17.8 ± 1.2	- 4.5
2304	17.7 ± .7		20.3 ± 1.2	-12.8
2605	17.0 ± .7		19.4 ± 1.1	-12.4
3004	16.2 ± .7		18.6 ± 1.1	-12.9
3502	16.4 ± .6		19.1 ± 1.4	-14.1
3805	15.9 ± .6		(21 ± 3)*	--
4107	16.7 ± .6		17.8 ± 1.0	- 6.2

---

*Large error due to sample leakage

mean percent difference for all five samples indicates S.I.O. to be lower than W.H.O.I. by 5±8%.

During the pacific GEOSECS expedition, a set of replicate water samples was collected at Station 320. Analyses by M. Applequist and Y. Chung of S.I.O. are compared in Table II.7 with those of the duplicate set performed at W.H.O.I. The first seven S.I.O. results are based on preliminary counting only. The 3805-m W.H.O.I. result is highly uncertain, because the sample container had leaked, and only a few liters were available for analysis. The W.H.O.I. result at 1504 m appears to be spuriously low. When all of the other results are compared, the S.I.O. results are again seen to be lower than the W.H.O.I. values by an average amount of 6±2%. When only the final S.I.O. counts are considered, the discrepancy is 11±2%.

It is not believed that systematic errors arising from the procedures used in either laboratory should produce a discrepancy larger than a few percent. The most likely cause of the disagreement is in the different standards used for calibration by the two groups, and it is intended that a direct cross-check of standards will be performed.

Appendix II.A Details of the Analytical Procedure for Pb-210 and Po-210

1. Sample handling -- shipboard
    - a. Acidify Cubi-tainer (5 or 6 gallon) with 40 ml concentrated, reagent-grade HCl.
    - b. Filter as large a volume of sea water as possible (20-l minimum). Begin filtration as soon as other sampling is completed. For this study 0.4-micron Nuclepore filters were used. For future work it is recommended that 0.45-micron Millipore filters be used, because they are more easily oxidized.
    - c. Draw about 20 l filtered sea water into pre-acidified Cubi-tainers.
    - d. Spike water samples with Po-208 and activity-free lead tracers. A few milligrams of stable lead is sufficient to overwhelm any natural or contaminant background levels. The amount of Po-208 tracer added should be approximately four times the expected sample activity.
    - e. Apply mild suction to remove excess water from the filters. Fold the filters to contain the particulate matter and store in plastic bags.
    - f. Check Cubi-tainers for leakage and then store. If rough handling is anticipated, sturdier containers are advisable.
    - g. Weigh samples at the earliest opportunity. If co-precipitations are to be performed at sea, determine sample size volumetrically.

2. Pre-concentration (after Boyle and Edmond, 1975)
   a. Prepare reagents:
      (1) Cobalt nitrate in deionized water to make 50 mg Co/l.
      (2) APDC in deionized water, 5 g/l.
   b. Add 10 ml cobalt nitrate for each liter of sea water and mix.
   c. Add 10 ml APDC for each liter of sea water and mix.
   d. Wait 15-20 minutes and filter suspension through 142-mm, 0.4-micron Millipore filter (vacuum filtration).
   e. Allow filter to be sucked dry, fold in half, and store in plastic bag. Ignore small amounts of precipitate that may adhere to walls of the container.
3. Sample dissolution
   a. Digest Millipore filters in Teflon beakers with 3:2 mixture of HNO_3 (concentrated) and $HClO_4$ (70%). Use as little of the acid mixture as possible, adding in 10-ml increments as required.
   b. Soak Nuclepore filters in concentrated NH_4OH at room temperature for several hours until filter is broken into small particles. Gently evaporate to remove NH_3 and proceed with acid digestion as above.
   c. For particulate matter samples, add tracers at start of acid digestion, and use a few drops of HF to destroy siliceous material.
   d. When oxidation is complete, evaporate to perchloric acid fumes.

e. Cool and dissolve residue in 2N HCl.

4. Plating procedure (after Flynn, 1968)

   a. Prepare reagents in deionized water:

      (1) Bismuth carrier (10 mg Bi/ml) -- 2.32 g $Bi(NO_3)_3 \cdot 5H_2O$ in 5 ml concentrated HNO_3 and diluted to 100 ml.

      (2) 20% w/v hydroxylamine hydrochloride

      (3) 25% w/v sodium citrate.

   b. Transfer samples to 250-ml beakers and dilute to 50 ml with 2N HCl.

   c. Add 5 ml hydroxylamine hydrochloride, 2 ml sodium citrate and 1 ml bismuth carrier.

   d. Adjust pH to 2.0 with concentrated NH_4OH.

   e. Stir on magnetic hotplate-stirrer and heat to 85-90°C.

   f. Load clean silver disc in Plexiglas holder, immerse in the sample solution, and remove trapped air bubbles.

   g. Plate at 85-90°C for four hours.

   h. Rinse Plexiglas holder with 2N HCl into beaker, remove disc, rinse disc with deionized water and methanol, and store disc in plastic box for counting.

   i. Transfer contents of beaker to polyethylene bottle, rinsing with 2N HCl.

   j. After six months' storage or longer, transfer sample to 250-ml beaker, re-adjust pH, re-plate, and count. Hold solution for lead recovery.

5. Lead recovery measurement

   a. Transfer sample solution to volumetric flask and dilute to appropriate volume for flame atomic absorption analysis.

   b. Dilute original lead spike solution to the same volume and with the same reagents added as for samples. Use this solution as a working standard.

   c. Operate Perkin-Elmer 403 under standard conditions given in manufacturer's handbook and alternate absorbance readings of sample and spike solutions. All sample readings should be made in triplicate.

   c. Calculate recovery directly from sample/spike absorbance ratio.

Appendix II.B Radioactive Growth and Decay Calculations

The computations required to convert raw counting data into absolute sample activities at the time of collection are described below. Each of the necessary steps is listed and explained. In practice the calculations were performed automatically on a Wang Model 520 programmable calculator. The following assumptions are made in performing the calculations:

1.) There is no change in the Pb-210 activity of a water sample between the time of collection and the time of co-precipitation. This time never exceeded 2 months.

2.) At the time of co-precipitation, Ra-226 remains in solution and is not recovered. Thereafter Pb-210 is unsupported and decays according to its half-life.

3.) Lead-210 in particulate matter is entirely unsupported. (Because the decay correction for Pb-210 rarely exceeds 3%, assumptions 1-3 need only hold approximately.)

4.) The production of Pb-210 from atmospheric Rn-222 equilibrating with the stored sample solutions is negligible. This assumption can be verified by simple calculation.

5.) The short-lived Pb-210 daughter, Bi-210, is at all times in secular equilibrium with Pb-210 in the sample. For Po-210 growth periods of six months or longer, this assumption need only hold approximately.

6.) Procedural losses of Pb and/or Po occur only at the time of co-precipitation for water samples or only at the time of sample dissolution for particulate matter samples. This assumption is important only if there occur large differences in recovery rates for Pb and Po and if there is a delay between sample dissolution or co-precipitation and the first plating step. In practice the recoveries were nearly the same for both elements.

7.) Polonium is completely removed from the sample solution during the first plating step. This assumption was verified experimentally (Section II.B.4).

Calculations for water samples

The quantities Pb(n) and Po (n) refer to activities. Decay constants for Pb-210 (λ_{Pb}) and Po-210 (λ_{Po}) are taken to be 0.0000855 d^{-1} and 0.0050083 d^{-1}, respectively, corresponding to half-lives of 22.2 y and 138.4 d.

1.) From the second count determine the Po-210 activity generated in the sample at the time of the second plating, designated Pb(1). This is done by correcting the Po-208 and Po-210 count rates for background and then correcting each for simple decay back to the time of the second plating step. The corrected ratio cpm Po-210/cpm Po-208 is then multiplied by the amount of Po-208 spike (dpm) added at the time of plating.

2.) Calculate the Pb-210 activity in the sample at the time of the first plating step:

$$Pb(2) = (\lambda_{Po} - \lambda_{Pb})Pb(1)/\lambda_{Po}[\exp(-\lambda_{Pb}t_2)-\exp(-\lambda_{Po}t_2)]$$
$$= 0.9829\ Pb(1)/[\exp(-0.0000855\ t_2)-\exp(-0.0050083\ t_2)],$$

where t_2 is the time, in days, between the first and second plating steps.

3.) Calculate the Pb-210 activity in the sample immediately following co-precipitation:

$$Pb(3) = Pb(2)/\exp(-\lambda_{Pb}t_1)$$
$$= Pb(2)/\exp(-0.0000855\ t_1),$$

where t_1 is the time, in days, between co-precipitation and the first plating step.

4.) Correct for losses during co-precipitation:

$$Pb(4) = Pb(3)/R_{Pb},$$

where R_{Pb} is the fractional recovery of the added stable lead.

5.) Subtract the reagent blank:

$$Pb(5) = Pb(4) - B,$$

where B is the blank in dpm. This gives the desired result for Pb-210 activity in the sample at the time of collection.

6.) From the first count determine the Po-210 activity in the sample at the time of the first plating step, Po(1). Raw count rates should be corrected for background and then for decay back to the time of plating. Use measured counter efficiencies to calculate Po(1) and to determine the chemical recovery of added Po-208, R_{Po}.

This treatment differs from that in step 1. It is necessary to determine R_{Po} explicitly, because it may differ from R_{Pb}.

7.) Calculate the Po-210 activity in the sample immediately following co-precipitation:

$$Po(2) = \{Po(1) - [\lambda_{Po}/(\lambda_{Po}-\lambda_{Pb})]Pb(3)[\exp(-\lambda_{Pb}t_1)-\exp(-\lambda_{Po}t_1)]\}/\exp(-\lambda_{Po}t_1)$$
$$= \{Po(1) - 1.0174\ Pb(3)[\exp(-0.0000855\ t_1)-\exp(-0.0050083\ t_1)]\}/\exp(-0.0050083\ t_1).$$

8.) Correct for losses during co-precipitation:

$$Po(3) = Po(2)/R_{Po}.$$

9.) Substract the reagent blank:

$$Po(4) = Po(3) - B.$$

10.) Correct for growth or decay to the time of sampling. This step is identical in form to step 7:

$$Po(5) = \{Po(4)-1.0174\ Pb(5)[\exp(-0.0000855\ t_0)-\exp(-0.0050083\ t_0)]\}/\exp(-0.0050083\ t_0),$$

where t_0 is the time between collection and co-precipitation. This gives the desired result for Po-210 activity in the sample at the time of collection.

Calculations for particulate matter samples

The calculations are identical to those for water samples, with the following exceptions.

1.) Substitute "time of sample dissolution" for "time of co-precipitation".

2.) Following step 5, correct for simple decay of Pb-210 between the time of sampling and the time of sample dissolution:

$$\mathrm{Pb}(6) = \mathrm{Pb}(5)/\exp(-\lambda_{\mathrm{Pb}} t_0)$$
$$= \mathrm{Pb}(5)/\exp(-0.0000855\ t_o).$$

3.) In step 10, substitute Pb(6) for Pb(5).

Calculation of statistical counting errors

Counting errors for individual counts are calculated as in Section II.C.2. The counting error for Pb-210 analyses is equal to this value as determined for the second count. To determine the counting error for Po-210 analyses, propagate individual errors for each count through steps 6-10.

CHAPTER III

THE DISTRIBUTION OF PB-210 AND PO-210 IN DISSOLVED AND PARTICULATE PHASES IN SEA WATER

A. Presentation of the data

This chapter is intended to be a descriptive presentation of the analytical results; specific aspects of the data are discussed more fully in chapters to follow. All of the Atlantic data given here were obtained from samples collected by the writer during Cruise 32 of F/S Meteor in November and December of 1973. Samples from two GEOSECS stations in the Pacific have also been analyzed. Station locations are shown on the index maps (Figures III.1 and III.2) along with some additional stations that will be referred to at various points in the text.

Analytical results are listed in Table III.3 for the Atlantic and Table III.4 for the Pacific, and vertical profiles are plotted in Figures III.5 - III.16. All of these tables and figures will be found together at the end of this chapter. Most of the samples used in this investigation were filtered at the time of collection through 0.4-micron Nuclepore filters, and for these samples both dissolved and particulate activities are reported. Definition of "dissolved" and "particulate" activity is made solely on the basis of retention or non-retention by the filters used. For samples that were not filtered, the results are listed as total activity, and these samples are marked

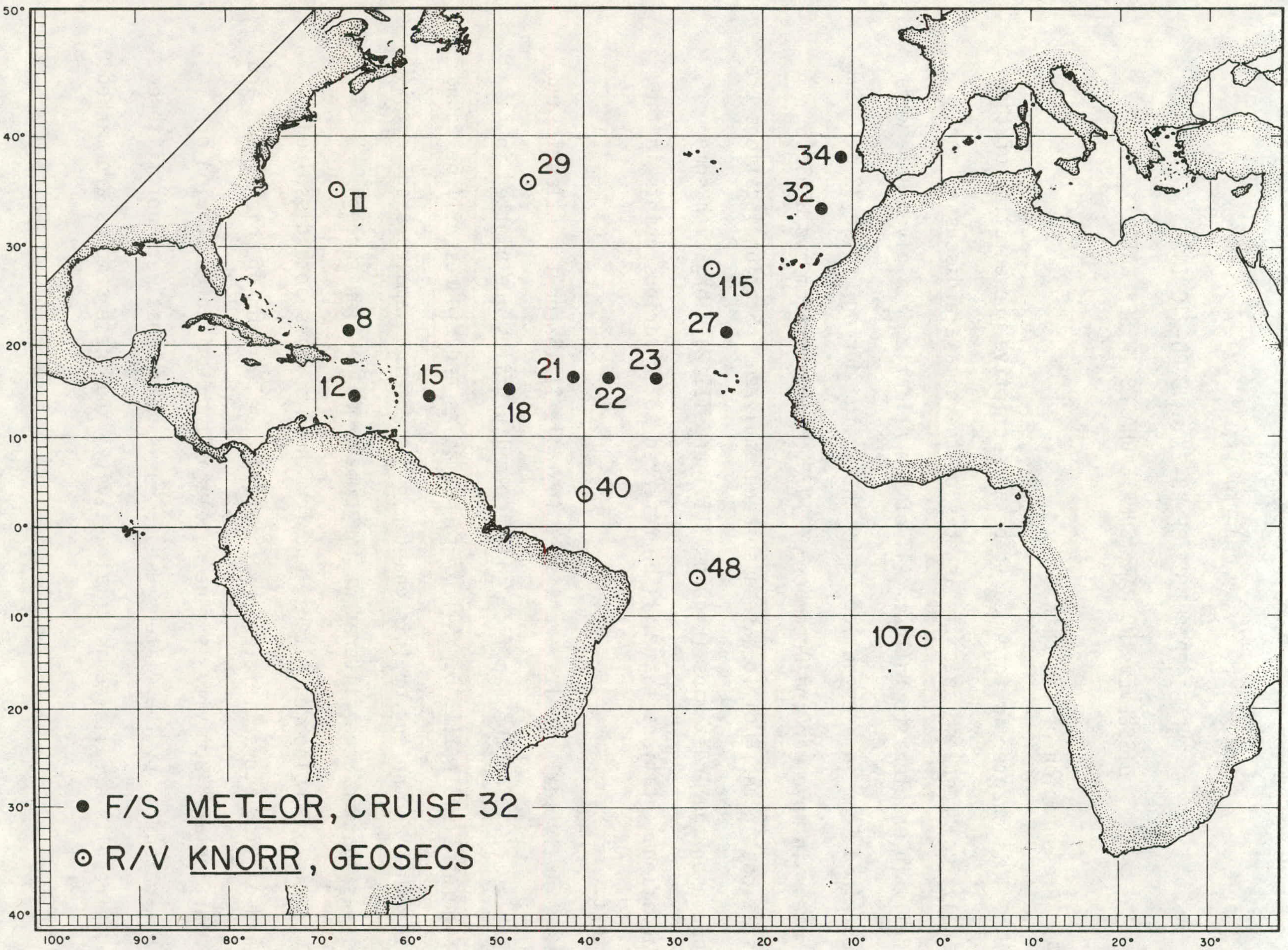


Figure III.1. Locations of Atlantic stations referred to in this thesis.

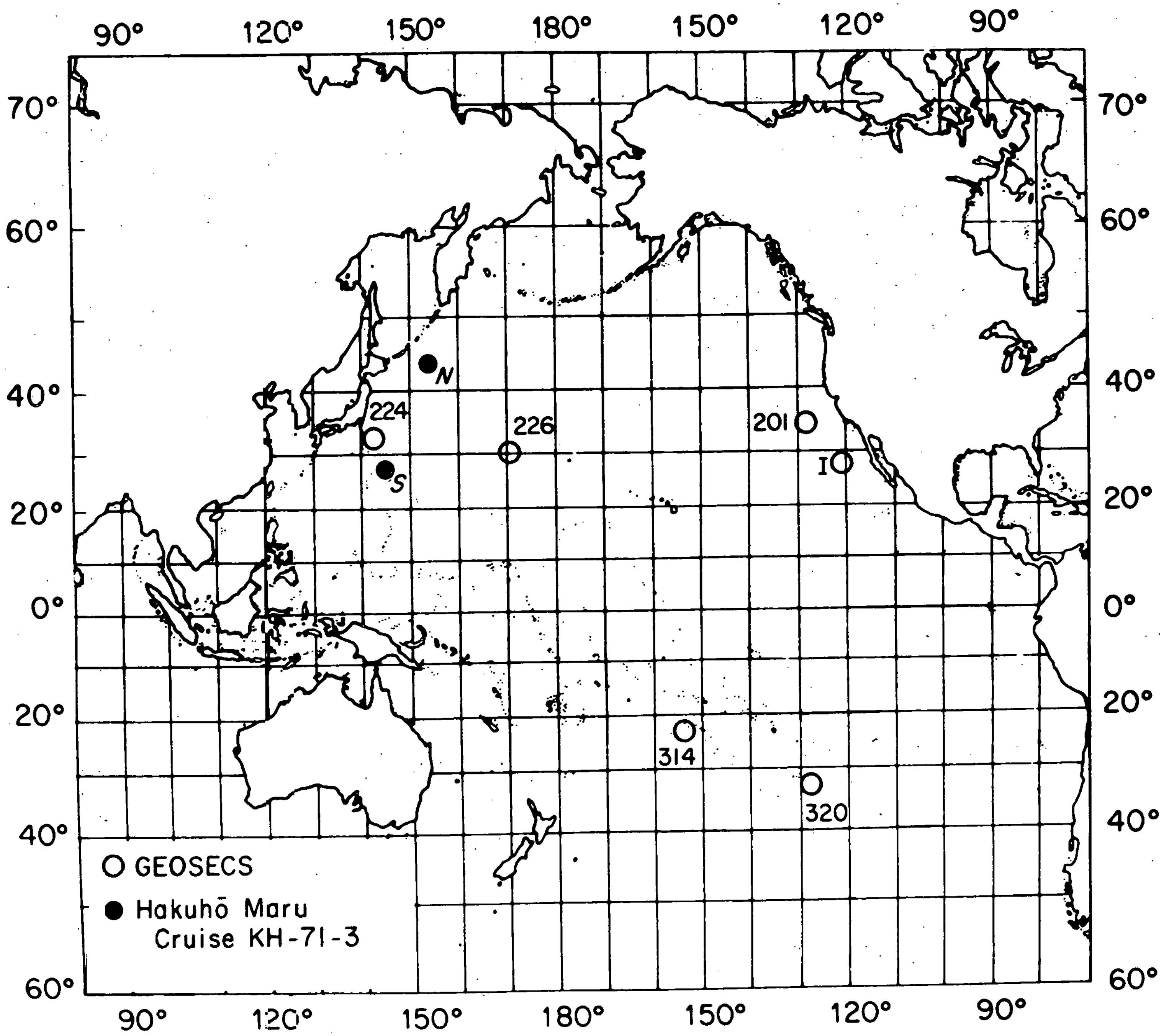


Figure III.2. Locations of Pacific stations referred to in this thesis.

by the notation "NF" in the tables. Results from unfiltered samples have been included in the vertical profiles of dissolved activity, and for this purpose a correction, usually small, was derived by interpolation of the particulate profiles. Data points corrected in this way are indicated by use of a different symbol in the figures. All of the analytical results have been corrected for radioactive growth or decay to the date of collection, and they are given in units of disintegrations per minute per 100 kg sea water (dpm/100 kg). Polonium-210 results are plotted in most of the figures as activity differences relative to the parent Pb-210. Positive values indicate the presence of "excess" Po-210 not supported by radioactive decay of the parent.

It may be seen in the vertical profiles that several of the particulate analyses are spuriously high, and in some of these cases the dissolved activities appear somewhat too low. This effect is most pronounced for the 1813-m sample from Meteor Station 15 (Me-32-15). Many of these apparently bad samples from the Meteor cruise were collected with the same Gerard barrel (#18), and each of the samples taken with this particular sampler has been marked by an asterisk in the tables and by parentheses in the figures.

The effect just described is seen to an extreme degree in the case of the GEOSECS 226 samples (Table III.4), for which the measured particulate activities frequently exceed the dissolved activities. This behavior is unlike that found for any of the other stations, and these results are considered to be grossly in error. It was noted that many of the filters received from this station were heavily loaded with particles of rust, which were evidently produced by corrosion of various pieces of hardware inadvertently dropped into the Gerard barrels during the cruise. These rust particles probably introduced minimal contamination, but newly formed iron hydroxides do act as efficient scavengers for Pb and Po in sea water (Craig *et al*., 1973; J. Thomson and K. K. Turekian, unpublished report). Some of the lowest activities measured in the filtered water correspond to the highest activities found on the filters (note especially the 533-m sample and samples at 2999 m and below). It is, of course, impossible under these circumstances to determine the original distribution of activity between dissolved and particulate phases. Consequently, for this station, dissolved and particulate analyses have been combined and reported as total activities. The results are still rather badly scattered, and large errors could have arisen from uneven distribution of the rust particles within the water samples. Systematic losses to surfaces of corroded objects within the barrels could also have occurred. Because the other GEOSECS profile (Station 320) measured for this study did not include particulate samples, the extent to which this problem may be common to all of the GEOSECS samples is not known. Applequist (1975) has presented two GEOSECS profiles (Stations 201 and 314) in which a fairly consistent distribution of Pb-210 between dissolved and particulate phases can be seen. Of the other GEOSECS samples that he examined, only occasional filters showed evidence of serious interference by rust particles.

Nonetheless, in the absence of particulate analyses from Station 320, all of the GEOSECS results reported here must be regarded with some suspicion.

B. Estimation of Ra-226 distribution

An important source of Pb-210 in the oceans is the radioactive decay of the parent Ra-226, and the Ra-226 distribution must be known if the Pb-210 results are to be interpreted. Radium analyses of the Meteor samples are being made at the University of Heidelberg, but the results are not yet available for inclusion in this report. Consequently, Ra-226 distributions at the Meteor stations have been estimated from distributions at nearby GEOSECS stations measured at the Lamont-Doherty Geological Observatory (Broecker _et al_., unpublished data).

For the purpose of extrapolating the measured Ra-226 profiles to points of sampling for the present study, the similarity of Ra-226 and Si distributions (Ku _et al_., 1970; Edmond, 1970) has been used. Figure III.3 is a plot of Ra-226 versus Si for the four available profiles that lie closest to the Meteor track. For each of the stations a linear relationship between Ra-226 and Si is defined, and all of the correlations for the individual stations are significant at a confidence level greater than 99%. Linear regression coefficients and y-intercepts along with their 95% confidence limits are summarized in Table III.1. The regression lines for Stations 29 and 40 are seen to be nearly identical as are the two lines for Stations 107 and 115. However, these two pairs of stations, which are located on opposite sides of the

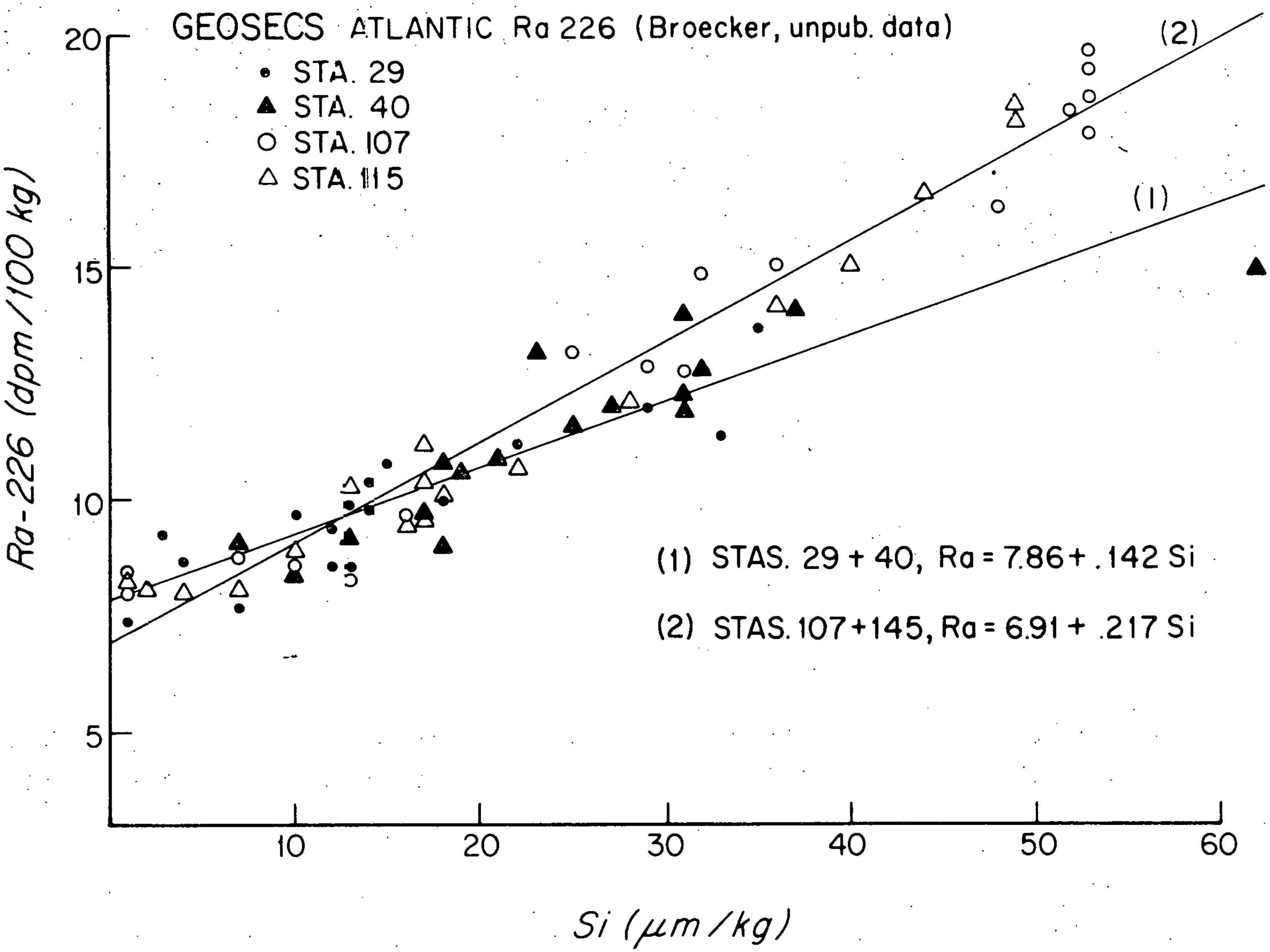


Figure III.3. Ra-226 versus Si for four Atlantic GEOSECS stations. (W. S. Broecker et al., unpublished data) The straight lines are least-squares fits for stations west (1) and east (2) of the Mid-Atlantic Ridge.

TABLE III.1

Ra-Si Relationships at Four Atlantic GEOSECS Stations.
Confidence limits are given at the 95% level.
Si (x) is in units of μm/kg, and
Ra-226 (y) is in units of dpm/100kg.

Station	Slope	y-intercept
29	.144 ± .040	7.76 ± .72
40	.136 ± .043	8.07 ± .55
107	.217 ± .023	6.99 ± .87
115	.216 ± .023	6.88 ± .64

Mid-Atlantic Ridge, show a difference between them in the Ra-Si relationship that is significant at the 95% confidence level. Therefore, in estimating the Ra-226 distribution from the measured Si distribution at the Meteor stations, two different relationships, obtained by combining the data from each pair of GEOSECS stations, have been used. For stations west of the Mid-Atlantic Ridge (Me-32-8, 12, 15, 18), the equation used is Ra = 7.86 + .142 Si, where Ra is in dpm/100 kg, and Si is in um/kg. For stations east of the ridge (Me-32-21, 22, 23, 27, 32, 34), the relationship is Ra = 6.91 + .217 Si. The standard error for predicting Ra from Si, based on the variance about the regression, is in the range 0.8-1.0 dpm/100 kg (5-10% of the predicted value). The Ra-226 activity estimated for deep water of the Venezuelan Basin (Me-32-12) is 11.8 dpm/100 kg and compares very well with the value of 12.2 dpm/100 kg measured by Szabo et al. (1967). In addition, values estimated for Me-32-8 are in excellent agreement with their results for stations north of the Greater Antilles.

C. Distribution of Pb-210

Ordinarily more than 90% of the Pb-210 in sea water occurs in the dissolved (<0.4 micron) phase. Activities near the surface are almost always in excess of Ra-226 activities, commonly by a factor of 1.5-2.5, a result that is in agreement with earlier work (Rama et al., 1961; Goldberg, 1963; Craig et al., 1973, Applequist, 1975). This Pb-210 excess is maintained by delivery to the sea surface of unsupported Pb-210 produced in the atmosphere by Rn-222 decay (Rama et al., 1961).

In some cases the largest Pb-210 excess is found at the immediate surface (Me-32-15, 18, 21, 22), but it is just as common for sub-surface maxima to occur in the 100-200 m depth range (Me-32-8, 12, 23, 27, 32; GEOSECS 320).

Below the surface or near-surface maxima, Pb-210 concentrations show a fairly smooth decrease through the thermocline, and the effect of the atmospheric source appears to fall off rapidly. At depths of approximately 500 m, Pb-210 and Ra-226 profiles cross, and below these depths Pb-210 is invariably depleted all the way to the bottom. It is interesting to note that, for all of the Me-32 profiles between 14° and 22°N (Stations 8-27), the point of crossing occurs at nearly the same potential density surface (σ_θ=27.0 ±0.1). This surface occurs slightly above the O_2-minimum in this region.

At mid-depths there is a tendency for Pb-210 profiles to parallel those of Ra-226, and the two profiles often show a common maximum at about 1,000 m (Me-32-18, 21, 22, 23). This similarity is to be expected if the principal source of Pb-210 is the decay of Ra-226 and if Pb-210 removal processes are not confined to a particular level in the deep water column. Curious exceptions to this general behavior are noted in three of the profiles (Me-32-18, 22, 23) at a depth of about 2,000 m, where Pb-210 maxima (in each case defined by only a single point) coincide with Ra-226 minima.

Close to the bottom, Pb-210 and Ra-226 profiles always show some tendency to diverge, with Pb-210 concentrations decreasing toward the bottom and Ra-226 concentrations remaining constant or increasing slightly. A broad Pb-210 maximum frequently results. This effect is least pronounced, but still detectable, at Me-32-12 in the Caribbean (Venezuelan Basin), where other properties show the water column to be well-mixed vertically below sill depth (1960 m). The observation that Pb-210 and Ra-226 profiles diverge toward the bottom has been made previously (Craig et al., 1973); its confirmation here is regarded as highly significant, because it implies that Pb-210 removal processes do not operate uniformly with depth in this region. These implications are further discussed in Chapter V.

Particulate Pb-210 concentrations are ordinarily in the range 0.2-0.5 dpm/100 kg and show little systematic variation with depth. Uncommonly high surface values were measured at Me-32-12 (1.7 dpm/100 kg) and Me-32-21 (1.1 dpm/100 kg), and deep water values at Me-32-12 in the Caribbean appear to be somewhat higher (0.7-0.8 dpm/100 kg) than those typical of the other Atlantic stations.

An exceptional profile occurs at Me-32-18, where a well-defined particulate Pb-210 maximum occurs at about 3200 m. This station was located approximately 250 km west of the Mid-Atlantic Ridge crest, and it is suggested in Chapter V that the anomalous distribution observed here may be related to processes unique to this location. A very similar particulate Pb-210 profile was obtained by Somayajulu and Craig (1973) at GEOSECS 48, a station similarly situated with respect to the ridge axis (see index map, Figure III.1).

Unusually high particulate Pb-210 concentrations are also found close to the bottom at Me-32-15 and are possibly an indication of high rates of scavenging within the near-bottom nepheloid layer. Relatively low values in the dissolved Pb-210 profile may also be seen near the bottom. The existence of a nepheloid layer at this station could not be confirmed by observation, but the distributions of light scattering and total suspended load in the 11°N section given by Betzer et al. (1974a) show that a nepheloid layer should be present in this region.

D. Distribution of Po-210

With the exception of Me-32-8, dissolved Po-210 shows a deficiency at the surface, the extreme case being Me-32-15, where dissolved Po-210 was virtually undetectable at the surface. This Po-210/Pb-210 disequilibrium has been noted previously, and it has been ascribed to the preferential removal of Po-210 by plankton (Shannon et al., 1970; Turekian et al., 1974).

Below the mixed layer, Po-210 concentrations increase rapidly and usually pass through maxima at depths of 100-300 m. Within these maxima Po-210 often occurs in excess of Pb-210, an effect which has not been reported in previous literature. The existence of unsupported Po-210 implies the operation of processes that rapidly supply Po-210 to this layer of the water column. This evidence for re-cycling of Po-210 within the thermocline will be discussed in Chapter IV.

Within the deep water Po-210 concentrations show considerable scatter, and it is not possible to recognize any features that are

TABLE III.2

Summary of Po-210/Pb-210 Activity Ratios Below 1,000 m For All Me-32 Stations. Confidence limits for the mean were calculated at the 95% level.

Depth(m)	Median	Mean
Dissolved		
> 1,000 (all)	.87	.88 ± .05
1,000 - 2,000	.91	.95 ± .08
2,000 - 3,000	.80	.82 ± .14
3,000 - 4,000	.81	.81 ± .17
> 4,000	.89	.90 ± .07
Total		
> 1,000 (all)	.98	1.06 ± .06
1,000 - 2,000	1.00	1.07 ± .08
2,000 - 3,000	.98	1.02 ± .18
3,000 - 4,000	.92	1.03 ± .18
> 4,000	.99	1.11 ± .19

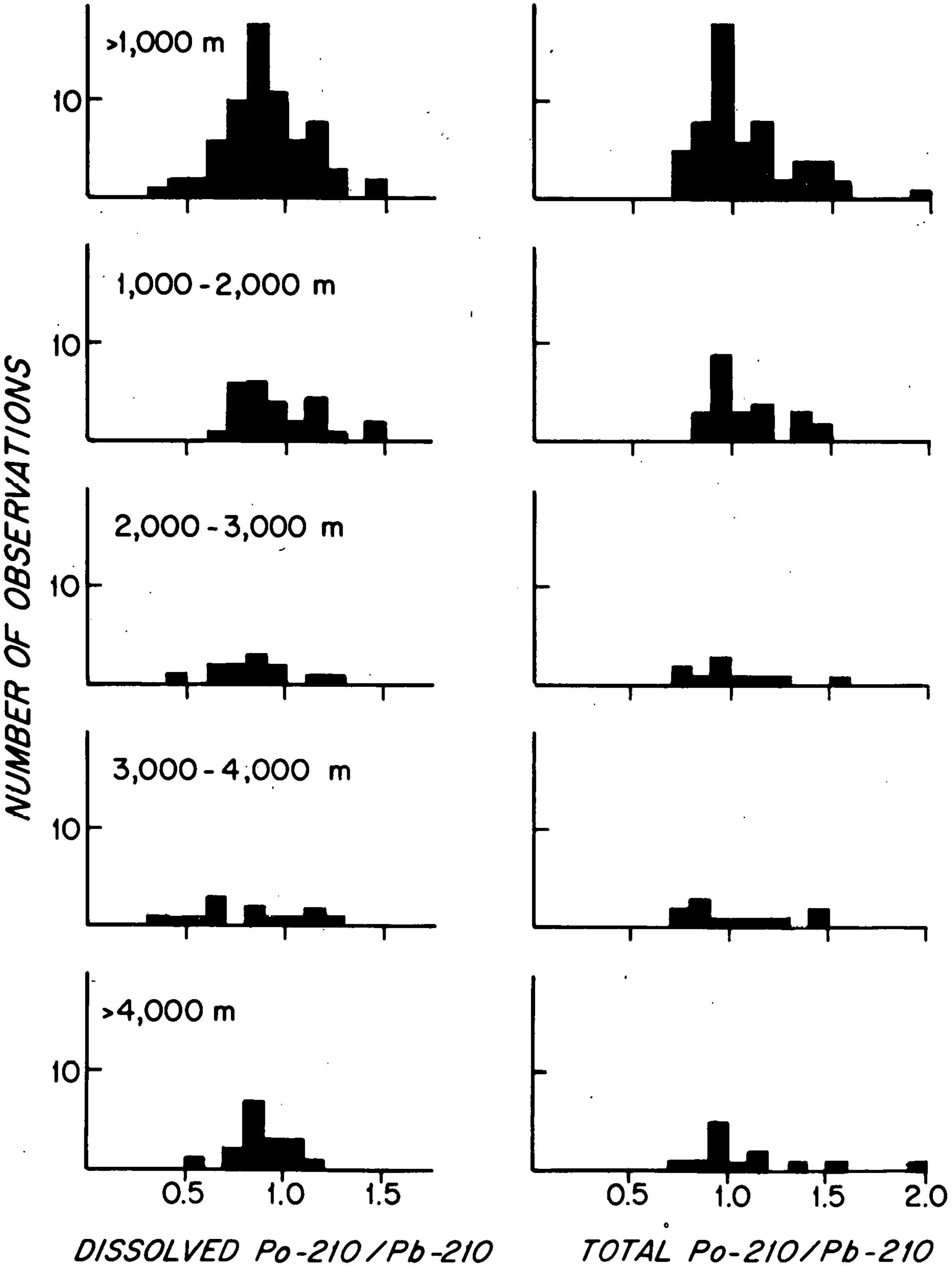


Figure III.4. Frequency distributions of Po-210/Pb-210 activity ratios at depths below 1,000 m for all Me-32 stations.

reproduced from one profile to the next. Histograms of Po-210/Pb-210 activity ratios below 1,000 m are shown in Figure III.4 and statistics are summarized in Table III.2. On the average, dissolved Po-210 activities are less than those of Pb-210 by about 12%, a difference that is significant at the 95% confidence level. There do not appear to be significant variations in the activity ratio with depth, but a weak suggestion of a minimum exists in the means for 1,000-m intervals.

In the particulate phase Po-210 nearly always exists in excess of Pb-210, an observation that is consistent with the notion that Po-210 deficiencies in the dissolved phase are maintained by interaction with particulate matter. At the surface, particulate Po-210/Pb-210 activity ratios range from 1.0-5.2, similar to the range observed for phytoplankton (Shannon et al., 1970). Particulate Po-210 excesses are maintained throughout the deep water and on the average are just sufficient to balance dissolved Po-210 deficiencies. Total Po-210/Pb-210 activity ratios are not significantly different from 1.0 (Table III.2; Figure III.4).

TABLE III.3. Analytical results for the Atlantic. Samples marked "NF" in far right-hand column were not filtered; those marked by asterisk were from questionable sampler (see text). Hydrographic data are preliminary results from Meteor 32 furnished by W. Roether.

Meteor-32, Station 8, 21.5°N 66.5°W, 7-8 November 1973, 5440 m.

Depth	Pot. Temp.	Sal.	Si	Pb-210			Po-210			
				Diss.	Part.	Tot.	Diss.	Part.	Tot.	
(m)	(°C)	(°/oo)	(µm/kg)	(dpm/100 kg)						
7	--	36.420	1.3	11.2	.31	--	11	1.6	--	
95	--	36.626	.8	16	.22	--	14	1.1	--	
296	17.508	36.451	1.6	12.7	.31	--	16	.6	--	
613	12.008	35.548	8.6	8.5	.87	--	8	1.8	--	*
798	7.704	34.966	18.9	7.5	.43	--	7.2	.8	--	
1497	4.110	35.003	12.4	3.1	.56	--	3	2.3	--	
2592	2.776	34.961	23.9	4.6	.34	--	3.9	1.0	--	

All samples were collected in 270-l stainless-steel Gerard barrels.
Mean estimated analytical precision (coefficient of variation)

a) Dissolved Pb-210, 7%
b) Particulate Pb-210, 10%
c) Dissolved Po-210, 19%
d) Particulate Po-210, 18%

Meteor-32, Station 12, 14.5°N 66.0°W, 11-12 November 1973, 4880 m.

Depth	Pot. Temp.	Sal.	Si	Pb-210			Po-210			
				Diss.	Part.	Tot.	Diss.	Part.	Tot.	
(m)	(°C)	(°/oo)	(μm/kg)	(dpm/100 kg)						
8	28.042	34.213	3.0	13.8	1.7	--	3	1.6	--	
48	28.001	34.271	2.9	12.8	2.1	--	5	1.0	--	
118	25.129	36.613	1.2	17	.48	--	16	1.1	--	
298	15.909	36.136	4.1	10.9	.77	--	14	1.0	--	
593	7.763	34.856	19.3	7.5	.81	--	5	1.5	--	*
791	5.753	34.837	24.7	6.4	.51	--	6	.8	--	
1188	4.337	34.963	26.2	5.0	.53	--	5.0	1.3	--	
1486	4.050	34.972	27.1	4.1	.76	--	6	1.2	--	
1784	3.959	34.977	27.6	4.5	.71	--	3.3	1.5	--	
2183	3.885	34.977	27.9	4.9	.81	--	2.0	2.2	--	
2489	3.858	34.983	27.9	4.4	.74	--	3	1.6	--	
3187	3.858	34.985	27.9	4.7	.78	--	1.8	1.5	--	
3983	3.846	34.976	28.0	4.4	.85	--	5	1.8	--	
4779	3.853	34.982	28.2	3.8	.74	--	4	.5	--	
4849	3.843	34.981	28.6	4.0	.68	--	4	2.1	--	

All samples were collected in 270-l stainless-steel Gerard barrels.
Mean estimated analytical precision (coefficient of variation)
- a) Dissolved Pb-210, 7%
- b) Particulate Pb-210, 8%
- c) Dissolved Po-210, 28%
- d) Particulate Po-210, 19%

Meteor-32, Station 15, 14.7°N 57.5°W, 17-18 November 1973, 5370 m.

Depth	Pot. Temp.	Sal.	Si	Pb-210			Po-210			
				Diss.	Part.	Tot.	Diss.	Part.	Tot.	
(m)	(°C)	(°/oo)	(um/kg)	(dpm/100 kg)						
7	27.250	34.774	3.2	21	.33	--	.2	1.6	--	
78	27.318	36.435	1.0	--	--	21	--	--	16	NF
149	23.429	36.989	.8	15	.46	--	17	1.2	--	
200	--	36.69	2.1	--	--	15	--	--	25	NF
401	12.386	35.582	8.2	9.5	.48	--	10	.9	--	
601	7.988	34.935	18.4	--	--	8.4	--	--	7.5	NF
799	6.254	34.787	23.8	7.8	.34	--	6.0	1.0	--	
1191	5.087	34.970	18.9	--	--	7.5	--	--	6.5	NF
1813	3.625	34.984	14.9	2.6	1.4	--	3.1	4.9	--	*
2615	2.784	34.956	22.3	4.0	.41	--	4.8	2.0	--	
3215	2.340	34.932	25.8	--	--	4.8	--	--	7.0	NF
3813	1.986	34.902	31.3	3.9	.24	--	4.6	1.2	--	
4409	1.824	34.893	36.0	--	--	4.3	--	--	3.6	NF
4806	1.673	34.879	46.8	3.7	.21	--	2.9	1.4	--	
5200	1.436	34.840	61.4	2.2	1.07	--	2.6	3.7	--	
5344	1.385	34.837	63.6	2.9	.51	--	2.6	2.6	--	

All samples were collected in 270-l stainless-steel Gerard barrels.
Mean estimated analytical precision (coefficient of variation)

a) Dissolved and total Pb-210, 8%
b) Particulate Pb-210, 10%
c) Dissolved and total Po-210, 14%
d) Particulate Po-210, 11%

Meteor-32, Station 18, 15.7°N 48.5°W, 21-22 November 1973, 3820 m.

Depth	Pot. Temp.	Sal.	Si	Pb-210			Po-210			
				Diss.	Part.	Tot.	Diss.	Part.	Tot.	
(m)	(°C)	(°/₀₀)	(um/kg)	(dpm/100 kg)						
6	--	36.432	1.0	21	.54	--	5	1.4	--	
59	25.806	36.900	.6	15.8	.61	--	7	1.9	--	
84	23.857	37.154	.4	14.3	.85	--	11	2.6	--	*
112	22.694	37.201	.5	14.3	.28	--	17	.7	--	
142	--	37.070	.8	12.0	1.08	--	16	1.3	--	
211	17.671	36.472	2.9	11.8	.41	--	13	.6	--	
295	16.671	35.867	6.3	11.3	.42	--	11	.7	--	
392	11.680	35.405	10.9	9.1	.32	--	9.5	.8	--	
619	8.277	34.972	17.8	7.2	.96	--	6.6	2.0	--	*
713	6.787	34.827	22.3	7.9	.36	--	7.0	.8	--	
804	6.188	34.775	24.3	8.1	.37	--	6.5	1.0	--	
980	5.435	34.840	24.4	7.9	.46	--	6.7	1.5	--	
1144	5.045	34.958	22.1	7.5	.27	--	9.6	.6	--	
1369	4.341	34.994	19.1	7.2	.37	--	8.1	.8	--	
1970	3.426	34.982	20.8	8.1	.42	--	6.8	.9	--	
2464	2.806	34.964	28.8	7.0	.67	--	6.8	2.1	--	
2717	2.570	34.946	32.8	6.8	1.02	--	4.9	2.9	--	
3208	2.390	34.931	37.5	7.8	1.6	--	4.9	3.1	--	

Station 18 (cont.)

Depth (m)	Pot. Temp. (°C)	Sal. (°/₀₀)	Si (µm/kg)	Pb-210 Diss. (dpm/100 kg)	Pb-210 Part. (dpm/100 kg)	Pb-210 Tot. (dpm/100 kg)	Po-210 Diss. (dpm/100 kg)	Po-210 Part. (dpm/100 kg)	Po-210 Tot. (dpm/100 kg)
3504	2.232	34.919	40.5	7.2	.92	--	3.5	3.5	--
3788	2.136	34.918	42.4	6.6	.95	--	3.4	2.9	--

Samples at 1369 m and above were collected in 270-l stainless-steel Gerard barrels; samples at 1970 m and below were collected in pairs of 30-l PVC Niskin bottles.

Mean estimated analytical precision (coefficient of variation)

a) Dissolved Pb-210, 7%
b) Particulate Pb-210, 9%
c) Dissolved Po-210, 13%
d) Particulate Po-210, 15%

Meteor-32, Station 21, 16.3°N 41.1°W, 24-25 November 1973, 4690 m.

Depth	Pot. Temp.	Sal.	Si	Pb-210			Po-210			
				Diss.	Part.	Tot.	Diss.	Part.	Tot.	
(m)	(°C)	(°/oo)	(μm/kg)	(dpm/100 kg)						
7	25.909	36.977	.5	18	1.11	--	8	1.3	--	
47	26.011	37.259	.5	17	.55	--	7	1.9	--	
97	23.605	37.287	.5	17	.27	--	17	1.5	--	
147	21.063	37.112	.7	13.3	1.25	--	19	1.6	--	
194	18.640	36.702	1.5	--	--	15.5	--	--	19	NF
247	16.844	36.361	2.5	12.0	.26	--	13	1.1	--	
396	12.790	35.654	7.9	7.0	.33	--	10	1.0	--	
489	11.058	35.388	11.4	--	--	9.7	--	--	9	NF
595	8.857	35.099	16.6	6.4	1.03	--	5.6	2.1	--	
791	6.563	34.880	22.9	7.4	.28	--	6.5	.9	--	
980	5.725	34.914	23.3	8.4	.45	--	6.4	1.0	--	
1176	5.108	34.971	21.8	Lost	.46	--	Lost	1.2	--	
1468	4.280	35.003	19.4	7.6	.45	--	7.1	1.5	--	*
1966	3.306	34.972	21.7	7.5	.40	--	8.9	1.5	--	
2462	--	34.950	22.1	8.0	.36	--	7.2	.8	--	

All samples were collected in 270-l stainless-steel Gerard barrels.
Mean estimated analytical precision (coefficient of variation)
a) Dissolved and total Pb-210, 7%
b) Particulate Pb-210, 9%
c) Dissolved and total Po-210, 11%
d) Particulate Po-210, 14%

Meteor-32, Station 22, 16.5°N 37.0°W, 26-27 November 1973, 5450 m.

Depth	Pot. Temp.	Sal.	Si	Pb-210			Po-210		
				Diss.	Part.	Tot.	Diss.	Part.	Tot.
(m)	(°C)	(°/oo)	(μm/kg)	(dpm/100 kg)					
7	25.742	37.046	.4	17	--	--	2	--	--
77	24.060	37.288	.3	15	--	--	8	--	--
156	19.920	36.996	.8	16	--	--	15	--	--
236	14.588	35.910	6.0	9.5	--	--	12	--	--
295	13.130	35.661	8.2	10.2	--	--	10	--	--
345	11.986	35.485	9.9	10.6	--	--	9	--	--
394	11.132	35.360	11.6	8.4	--	--	11	--	--
492	9.567	35.164	15.4	8.6	--	--	9	--	--
684	7.290	34.909	21.4	9.3	--	--	9	--	--
881	6.104	34.856	24.4	10.0	--	--	6.2	--	--
1176	5.186	34.975	22.2	8.8	--	--	5.4	--	--
1569	4.053	34.996	20.6	7.3	--	--	8	--	--
1963	3.376	34.976	22.2	9.0	--	--	8	--	--
2356	2.932	34.954	27.8	8.2	--	--	6.6	--	--
2749	2.631	34.942	32.7	9.5	--	--	7	--	--
3282	2.339	34.924	38.2	11.7	--	--	7	--	--
3777	2.130	34.904	42.1	11.1	--	--	9	--	--
4272	2.007	34.895	45.1	10.7	--	--	10	--	--

Station 22 (cont.)

Depth (m)	Pot. Temp. (°C)	Sal. (°/oo)	Si (μm/kg)	Pb-210 Diss. (dpm/100 kg)	Pb-210 Part. (dpm/100 kg)	Pb-210 Tot. (dpm/100 kg)	Po-210 Diss. (dpm/100 kg)	Po-210 Part. (dpm/100 kg)	Po-210 Tot. (dpm/100 kg)
4768	1.877	34.883	48.6	9.4	--	--	8.4	--	--
5215	1.834	34.882	49.2	8.9	--	--	8.1	--	--
5414	1.835	34.889	--	8.7	--	--	7.4	--	--

All samples were collected in 30-l PVC Niskin bottles.
Mean estimated analytical precision (coefficient of variation)
a) Dissolved Pb-210, 7%
b) Dissolved Po-210, 15%

Meteor-32, Station 23, 16.5°N 31.9°W, 28 November 1973, 4940 m.

Depth	Pot. Temp.	Sal.	Si	Pb-210			Po-210			
				Diss.	Part.	Tot.	Diss.	Part.	Tot.	
(m)	(°C)	(°/oo)	(um/kg)	(dpm/100 kg)						
7	25.352	36.713	.3	9.9	.22	--	4.3	1.0	--	
96	21.299	36.903	2.6	8.3	.15	--	9.7	.8	--	
145	17.845	36.517	4.2	--	--	11.9	--	--	14	NF
195	15.921	36.178	8.5	9.6	.24	--	14	.9	--	
294	12.713	35.616	8.5	--	--	9.7	--	--	11	NF
392	10.968	35.358	12.0	8.3	.29	--	9.4	1.1	--	
510	8.889	35.071	16.6	7.2	.28	--	8.4	.9	--	
610	7.740	34.949	19.8	--	--	8.8	--	--	8.2	NF
710	7.454	34.915	20.6	8.5	.28	--	7.9	1.0	--	
1008	5.633	34.913	24.3	--	--	9.4	--	--	8.7	NF
1206	5.202	34.989	22.0	9.0	.18	--	8.5	1.7	--	
1403	4.556	35.006	21.0	--	--	9.3	--	--	8.7	NF
1600	3.991	35.001	21.7	7.8	.28	--	7.2	1.6	--	
1964	3.432	34.978	22.8	9.4	.27	--	7.5	.8	--	
2456	2.906	34.956	28.0	8.1	.19	--	9.1	1.6	--	
2948	2.557	34.938	34.2	11.4	.15	--	7.1	1.6	--	
3515	2.271	34.918	40.4	11.8	.18	--	11	1.6	--	
4014	2.032	34.898	46.4	13	.24	--	11	1.3	--	

Station 23 (cont.)

Depth (m)	Pot. Temp. (°C)	Sal. (°/₀₀)	Si (μm/kg)	Pb-210 Diss.	Pb-210 Part.	Pb-210 Tot.	Po-210 Diss.	Po-210 Part.	Po-210 Tot.
				(cpm/100 kg)					
4513	1.947	34.896	49.1	11.2	.20	--	10	1.9	--
4873	1.870	34.878	49.7	9.8	.31	--	10	2.0	--

Samples at 1600 m and above were collected in 270-l stainless-steel Gerard barrels; samples at 1964 m and below were collected in pairs of 30-l PVC Niskin bottles.

Mean estimated analytical precision (coefficient of variation)
  a) Dissolved and total Pb-210, 7%
  b) Particulate Pb-210, 10%
  c) Dissolved and total Po-210, 10%
  d) Particulate Po-210, 12%

Meteor-32, Station 27, 21.7°N 24.0°W, 2 December 1973, 4950 m.

Depth (m)	Pot. Temp. (°C)	Sal. (°/oo)	Si (μm/kg)	Pb-210			Po-210		
				Diss.	Part.	Tot.	Diss.	Part.	Tot.
				(dpm/100 kg)					
8	23.208	36.630	.1	7.0	.16	--	4	.7	--
96	19.344	36.420	2.3	6.6	.51	--	10	.2	--
195	16.978	36.473	1.9	13.4	.38	--	13	.5	--
294	14.837	36.046	4.1	11.2	.56	--	13	1.1	--
393	13.304	35.797	5.6	10.6	.52	--	9	.4	--
492	11.812	35.572	8.2	8.3	.52	--	11	.4	--
591	10.271	35.386	11.9	8.2	.35	--	9	.7	--
789	7.771	35.096	18.4	8.0	.40	--	11	.7	--
985	6.310	35.004	21.1	7.7	.35	--	6	1.1	--
1181	5.773	35.066	19.9	7.3	.44	--	8	1.2	--
2216	3.276	35.004	28.2	Lost	.42	--	Lost	1.1	--
3014	2.422	34.934	37.0	10.2	.33	--	11	1.4	--
4002	2.025	34.898	44.8	14.1	.31	--	12	1.9	--
4894	1.978	34.898	46.6	12.4	.30	--	11	1.6	--

Samples at 1181 m and above were collected in 270-l stainless-steel Gerard barrels; samples at 3014 m and below were collected in pairs of 30-l PVC Niskin bottles.

Mean estimated analytical precision (coefficient of variation)

a) Dissolved Pb-210, 7%
b) Particulate Pb-210, 9%
c) Dissolved Po-210, 14%
d) Particulate Po-210, 26%

Meteor-32, Station 32, 33.8°N 13.4°W, 11 December 1973, 4440 m.

Depth	Pot. Temp.	Sal.	Si	Pb-210			Po-210			
				Diss.	Part.	Tot.	Diss.	Part.	Tot.	
(m)	(°C)	(°/oo)	(μm/kg)	(dpm/100 kg)						
7	19.005	36.628		16	.29	--	7.2	1.3	--	
97	18.954	36.619		--	--	20	--	--	7.8	NF
196	14.823	36.041		--	--	15	--	--	14	NF
295	13.874	35.935		12.3	.55	--	11.6	.60	--	
393	12.918	35.800		--	--	12.6	--	--	12.7	NF
491	12.186	35.677		10.4	.53	--	10.6	1.1	--	
590	11.317	35.579		--	--	11.9	--	--	9.7	NF
687	10.758	35.556		8.8	.43	--	7.9	.82	--	
787	10.403	35.654		7.9	.30	--	7.2	.85	--	
886	9.887	35.677		6.9	.25	--	6.8	.58	--	
1034	9.445	35.768		6.2	.86	--	5.4	.8	--	
1182	--	35.829		6.2	.24	--	6.2	.46	--	
1280	8.821	35.818		7.0	.20	--	5.7	.70	--	
"	"	"		--	--	6.7	--	--	6.4	NF
1379	8.183	35.751		7.0	.16	--	5.8	.64	--	
1477	7.426	35.636		5.9	.54	--	4.7	.8	--	*
"	"	"		--	--	6.8	--	--	6.7	NF*
2195	3.701	35.072		7.6	.14	--	6.1	1.0	--	

Station 32 (cont.)

Depth (m)	Pot. Temp. (°C)	Sal. (°/oo)	Si (μm/kg)	Pb-210 Diss.	Pb-210 Part.	Pb-210 Tot.	Po-210 Diss.	Po-210 Part.	Po-210 Tot.
				(dpm/100 kg)					
3021	2.522	34.940		10.0	.23	--	6.9	1.0	--
3519	2.236	34.910		11.2	.21	--	9.2	1.3	--
4018	2.112	34.900		11.2	.16	--	9.1	1.1	--
4368	2.071	34.897		10.6	.32	--	7.5	1.0	--

Samples at 1477 m and above were collected in 270-l stainless-steel Gerard barrels; samples at 2195 m and below were collected in pairs of 30-l PVC Niskin bottles.

Mean estimated analytical precision (coefficient of variation)
a) Dissolved and total Pb-210, 7%
b) Particulate Pb-210, 1[illegible]%
c) Dissolved and total Po-210, 8%
d) Particulate Po-210, 13%

Meteor-32, Station 34, 38.5°N 11.5°W, 13 December 1973, 4930 m.

Depth (m)	Pot. Temp. (°C)	Sal. (°/₀₀)	Si (µm/kg)	Pb-210 Diss.	Pb-210 Part.	Pb-210 Tot.	Po-210 Diss.	Po-210 Part.	Po-210 Tot.	
				(dpm/100 kg)						
288	12.529	35.767		10.2	.89	--	10	1.5	--	*
359	11.989	35.699		9.2	.59	--	8.7	.7	--	
521	11.300	35.646		8.0	.39	--	8.2	.7	--	
682	12.004	36.075		6.7	.62	--	9.3	.8	--	
842	11.473	36.111		7.7	.46	--	8.0	.8	--	
1004	11.400	36.252		4.7	.96	--	6.8	1.0	--	
1165	10.902	36.247		5.3	.62	--	4.2	1.1	--	
1326	9.954	36.115		4.7	.43	--	4.6	1.0	--	
1407	8.978	35.933		4.3	1.3	--	3.9	1.6	--	
1569	6.952	35.555		5.3	.48	--	4.1	1.5	--	

All samples were collected in 270-l stainless-steel Gerard barrels.
Mean estimated analytical precision (coefficient of variation)

a) Dissolved Pb-210, 8%
b) Particulate Pb-210, 10%
c) Dissolved Po-210, 11%
d) Particulate Po-210, 22%

TABLE III.4. Analytical results for the Pacific. Dissolved and particulate analyses for GEOSECS 226 are considered to be in error (see text). Hydrographic data are preliminary results taken from the GEOSECS leg reports.

GEOSECS, Station 226, 30.6°N 170.6°E, 9-11 November 1973, 5590 m.

Depth	Pot. Temp.	Sal.	Si	Pb-210			Po-210		
				Diss.	Part.	Tot.	Diss.	Part.	Tot.
(m)	(°C)	(°/₀₀)	(μm/kg)	(dpm/100 kg)					
10	24.7	35.03		--	.23	--	--	2.7	--
40	24.7	35.03		--	.19	--	--	1.1	--
80	23.7	34.85		18.7	.09	18.8	13.4	1.3	14.7
150	16.2	34.73		19.8	.27	20.1	21.5	.5	22.0
250	14.4	34.58		14.2	.46	14.7	22.3	.4	22.7
350	13.2	34.43		14.0	.37	14.4	14.0	.5	14.5
452	10.46	34.292		12.3	.46	12.8	14.9	1.6	16.5
533	8.56	34.147		3.8	18.0	21.8	3.5	13.4	16.9
645	6.41	34.042		12.1	1.7	13.8	7.4	4.6	12.0
904	3.90	34.211		14.8	2.5	17.3	15.9	13.1	29.0
1192	--	34.403		15.4	4.0	19.4	17.8	5.5	23.0
1480	3.38	34.500		16.7	3.4	20.1	15.7	9.2	24.9
1542	--	34.495		13.3	4.2	17.5	3.4	21.0	24.4
2499	1.46	34.642		23.6	1.0	24.6	8.6	12.1	20.7
2999	1.28	34.665		1.5	28.3	29.8	2.0	30.0	32.0
3495	1.20	34.673		14.3	13.5	27.8	6.3	12.1	18.4
3980	--	34.686		9.6	12.5	22.1	6.2	15.5	21.7
4901	1.03	34.678		5.6	15.8	21.4	4.4	26.6	31.0
5434	.97	34.688		7.5	14.6	22.1	1.4	10.4	11.8

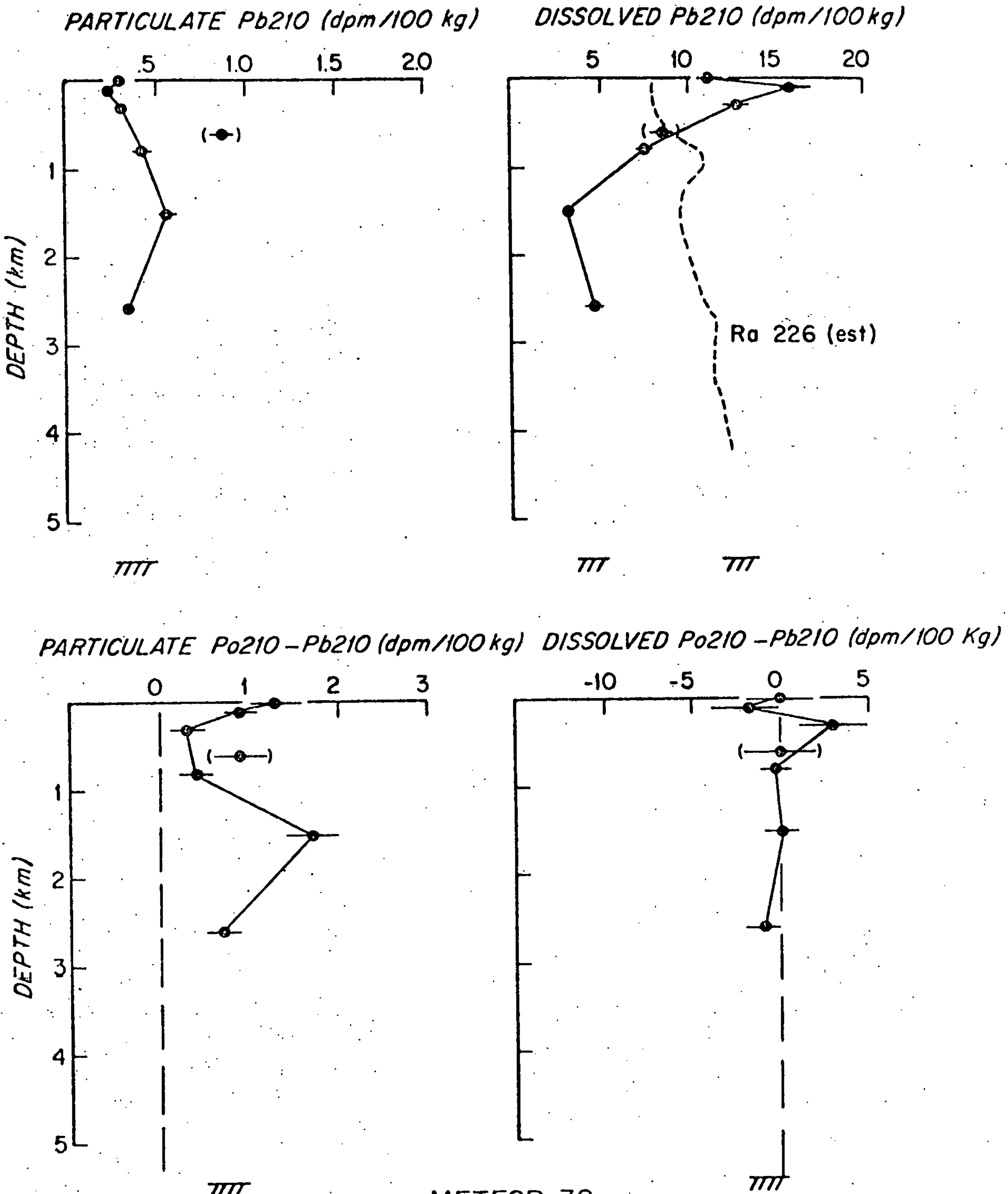
Samples at 350 m and above were collected by surface pump; samples at 452 m and below were collected in 270-l stainless-steel Gerard barrels.

GEOSECS, Station 320, 33.3°S 128.4°W, 24-26 April 1974, 4170 m.

Depth	Pot. Temp.	Sal.	Si	Pb-210 Diss.	Pb-210 Part.	Pb-210 Tot.	Po-210 Diss.	Po-210 Part.	Po-210 Tot.
(m)	(°C)	(°/oo)	(μm/kg)	(dpm/100 kg)					
0	19.7	34.64		7.7 ± .6			4.0 ± .6		
77	15.74	34.656		9.3 ± .6			5.5 ± .7		
128	13.81	34.693		9.8 ± .7			10.4 ± .7		
204	12.14	34.647		9.3 ± .7			10.9 ± .8		
254	10.96	34.616		9.6 ± .7			9.9 ± .7		
505	6.84	34.388		8.5 ± .6			7.5 ± .6		
704	5.82	34.324		8.8 ± .6			10.2 ± .8		
802	5.35	34.308		9.6 ± .7			9.7 ± .9		
1002	4.32	34.328		11.1 ± .7			9.5 ± .8		
1504	2.51	34.550		10.9 ± .7			10.7 ± .8		
2054	1.888	34.645		17.8 ± 1.2			16.4 ± 1.7		
2304	1.707	34.660		20.3 ± 1.2			19.1 ± 1.4		
2605	1.54	34.668		19.4 ± 1.1			15.8 ± 1.4		
3004	1.414	34.678		18.6 ± 1.1			18.6 ± 1.4		
3502	1.30	34.686		19.1 ± 1.4			16.5 ± 2.3		
3805	1.26	34.688		20.9 ± 3.2			15.3 ± 5.6		
4107	1.16	34.691		17.8 ± 1.0			14.6 ± 1.2		

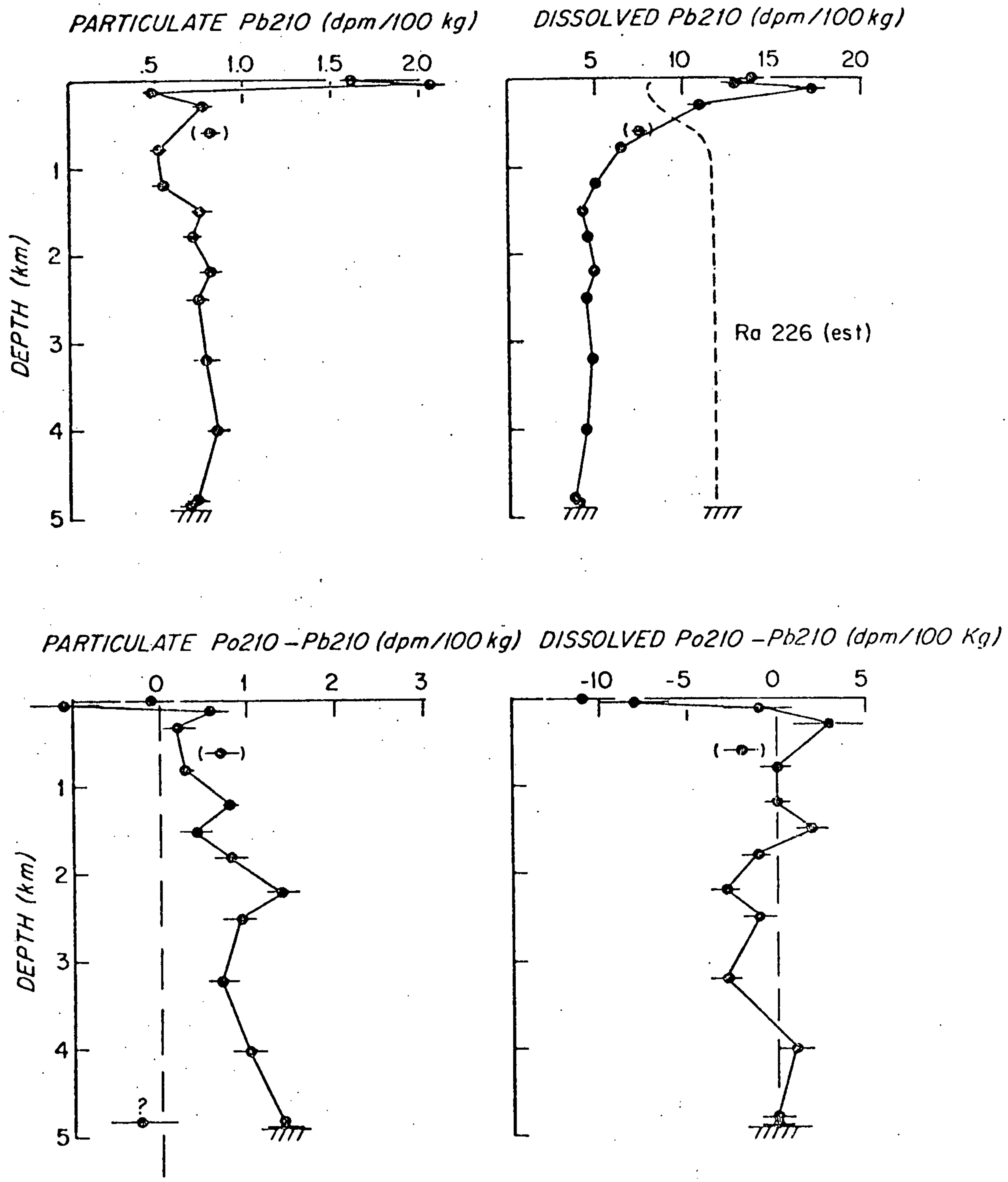
All samples were collected in stainless-steel Gerard barrels.

Figures III.5 - III.14. Vertical profiles of Pb-210 and excess Po-210 for Me-32 stations. Corrected results for unfiltered samples are plotted as open circles; results from questionable sampler are marked by parentheses (see text). Radium profiles are estimated as described in the text.



METEOR 32
STATION 8

Figure III.5



METEOR 32
STATION 12

Figure III.6

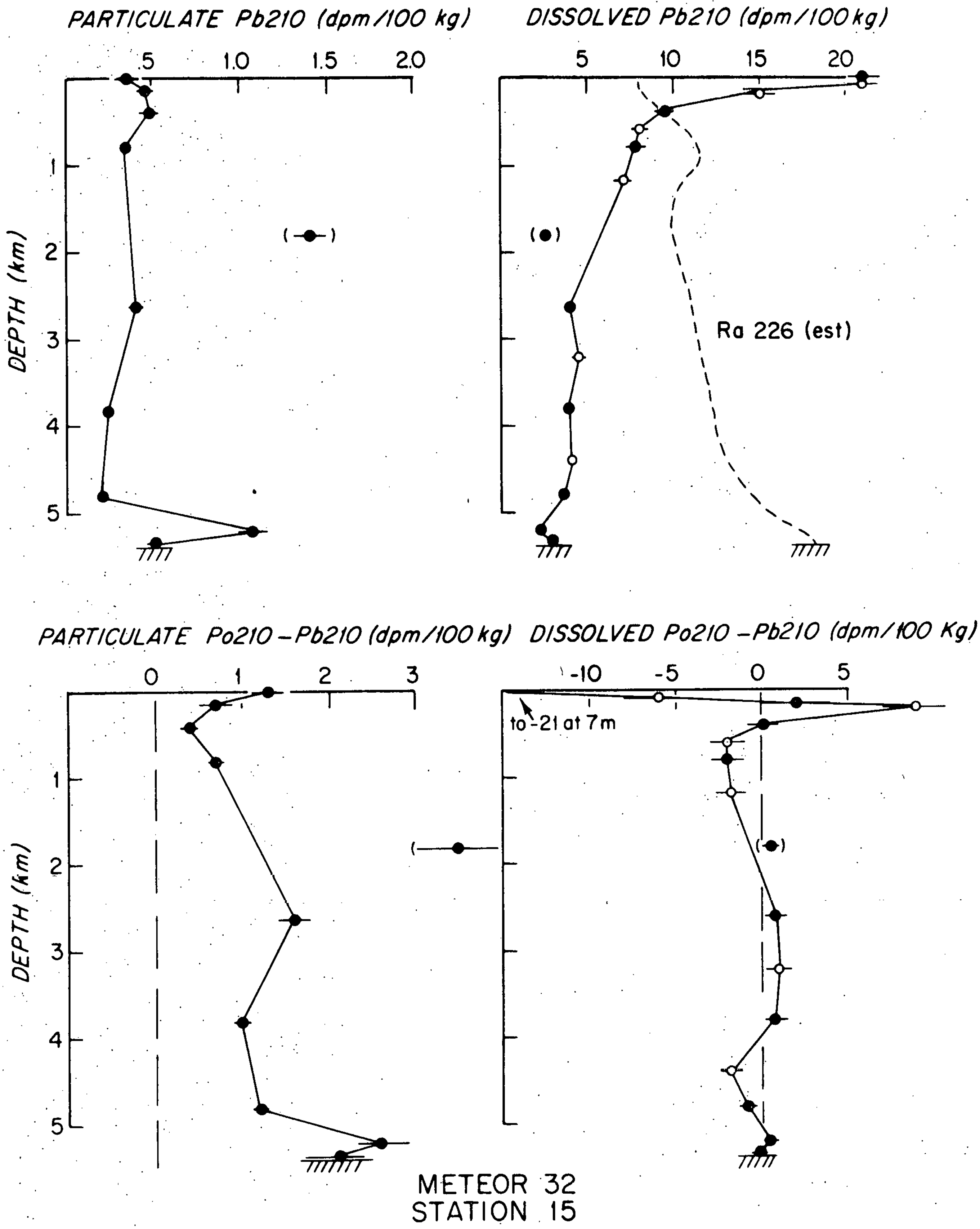
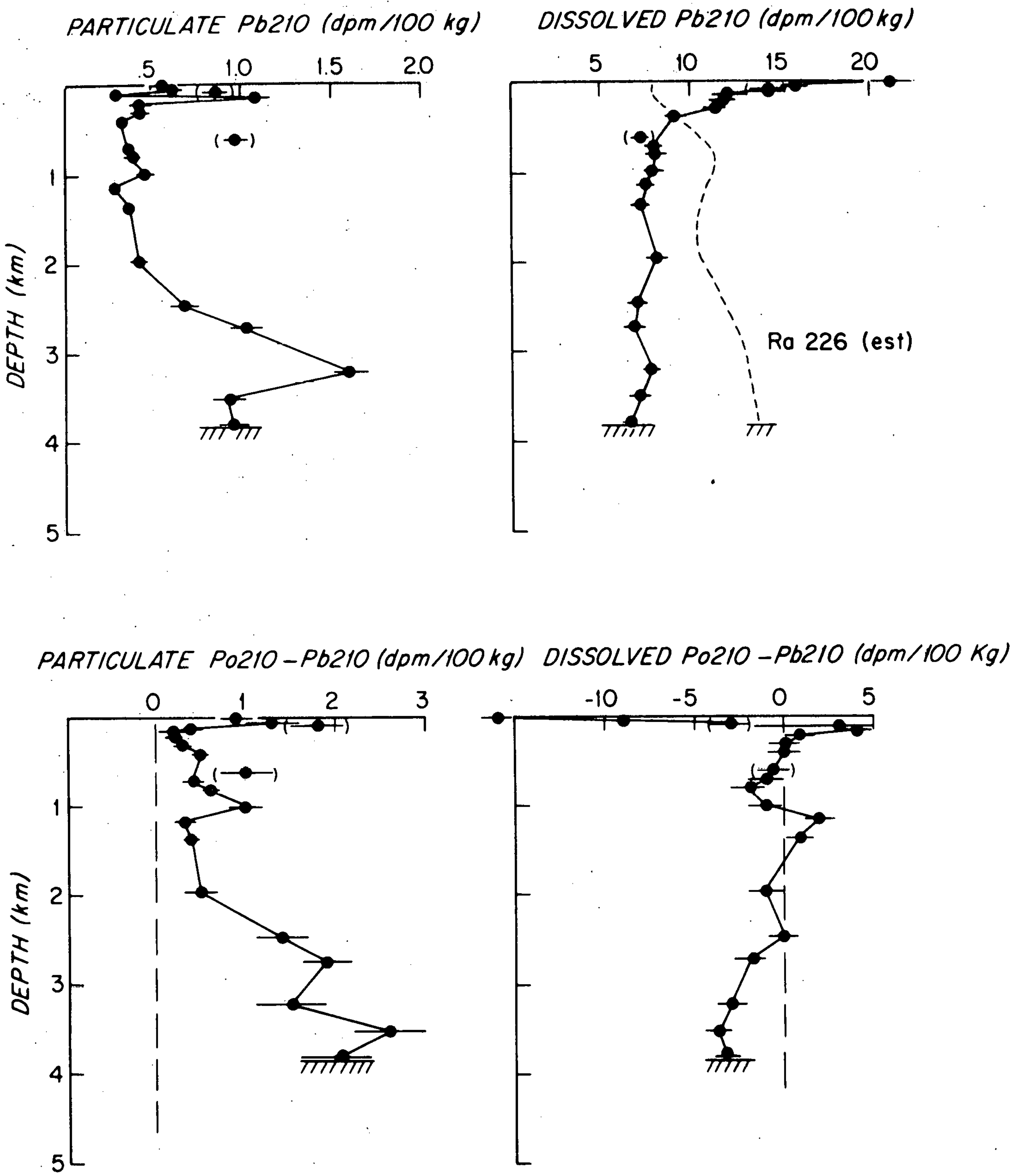

PARTICULATE Pb210 (dpm/100 kg)
.5
1.0
1.5
2.0
DISSOLVED Pb210 (dpm/100 kg)
5
10
15
20
Ra 226 (est)
DEPTH (km)
1
2
3
4
5
PARTICULATE Po210 – Pb210 (dpm/100 kg)
0
1
2
3
DISSOLVED Po210 – Pb210 (dpm/100 Kg)
-10
-5
0
5
to -21 at 7 m
DEPTH (km)
1
2
3
4
5
METEOR 32
STATION 15

Figure III.7


PARTICULATE Pb210 (dpm/100 kg)

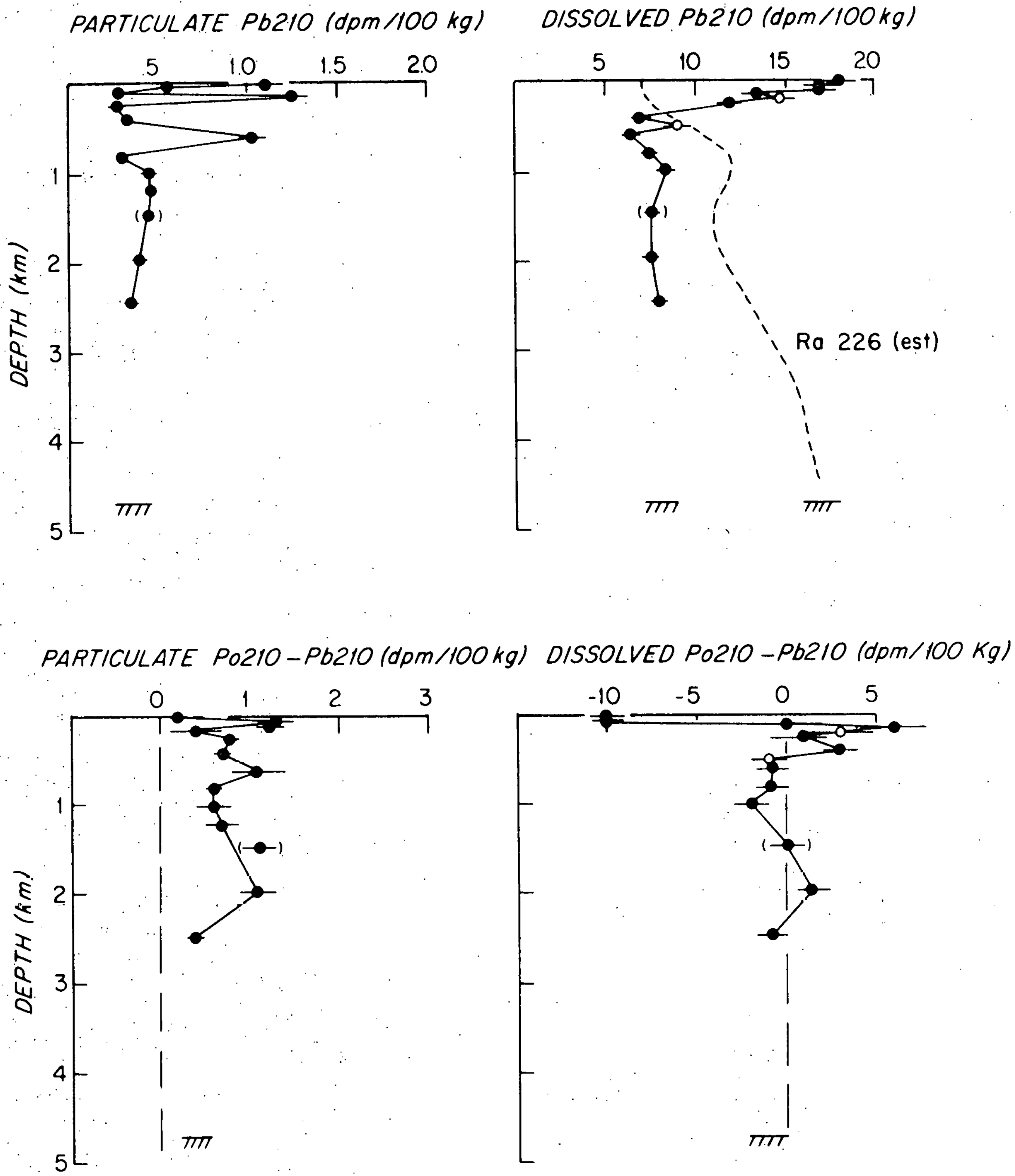
DISSOLVED Pb210 (dpm/100 kg)

PARTICULATE Po210 – Pb210 (dpm/100 kg)

DISSOLVED Po210 – Pb210 (dpm/100 Kg)

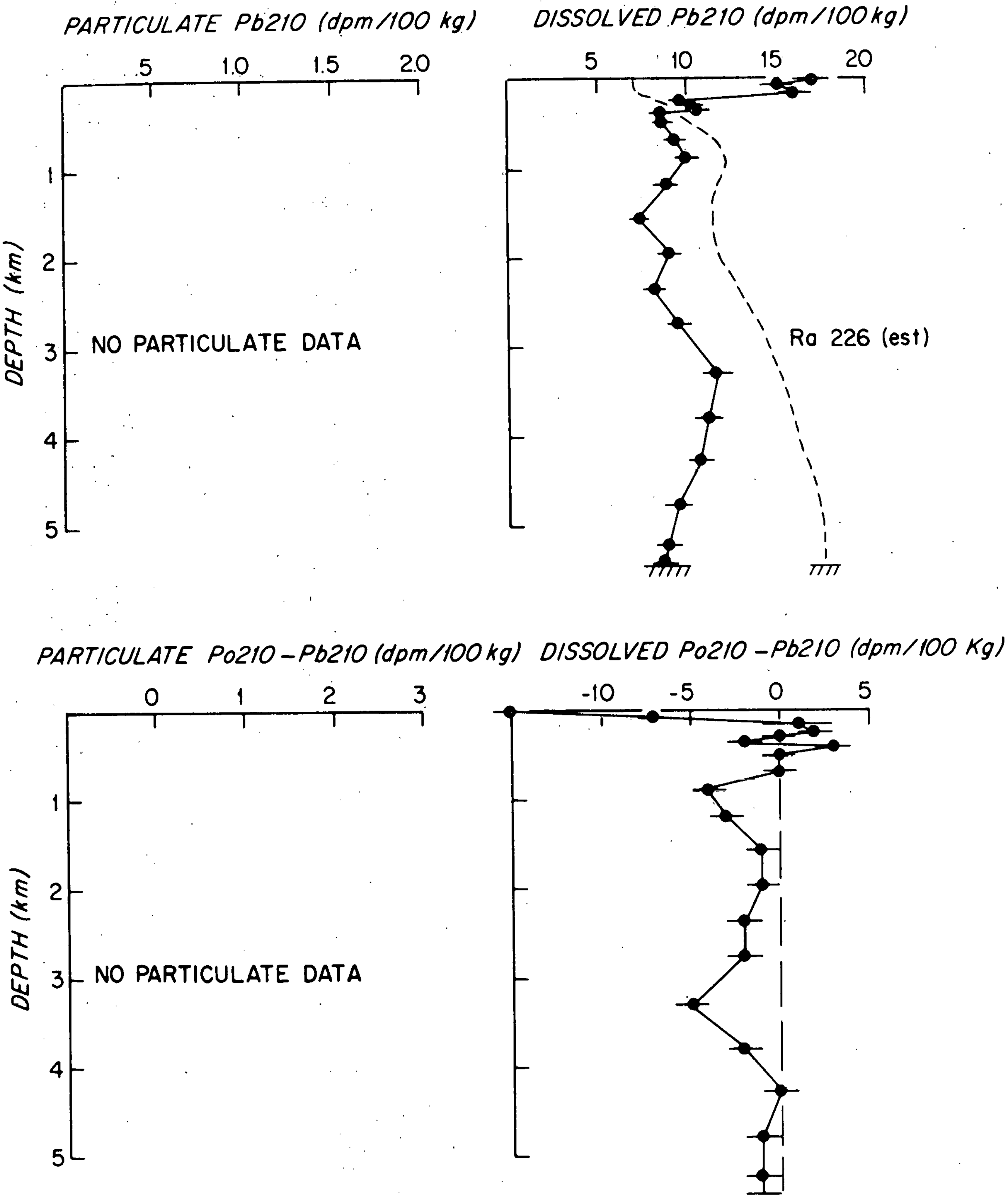
METEOR 32
STATION 18

Figure III.8



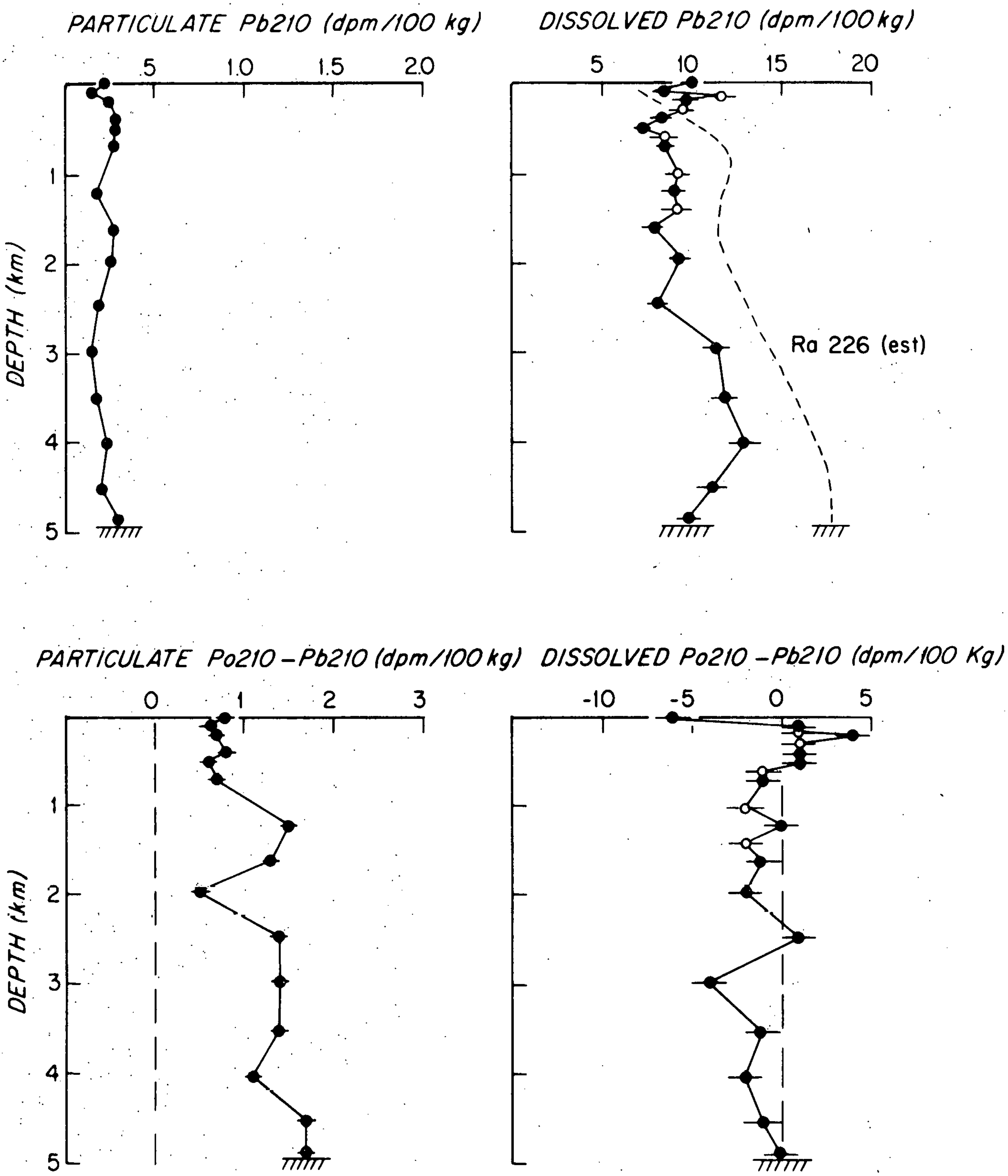
METEOR 32
STATION 21

Figure III.9



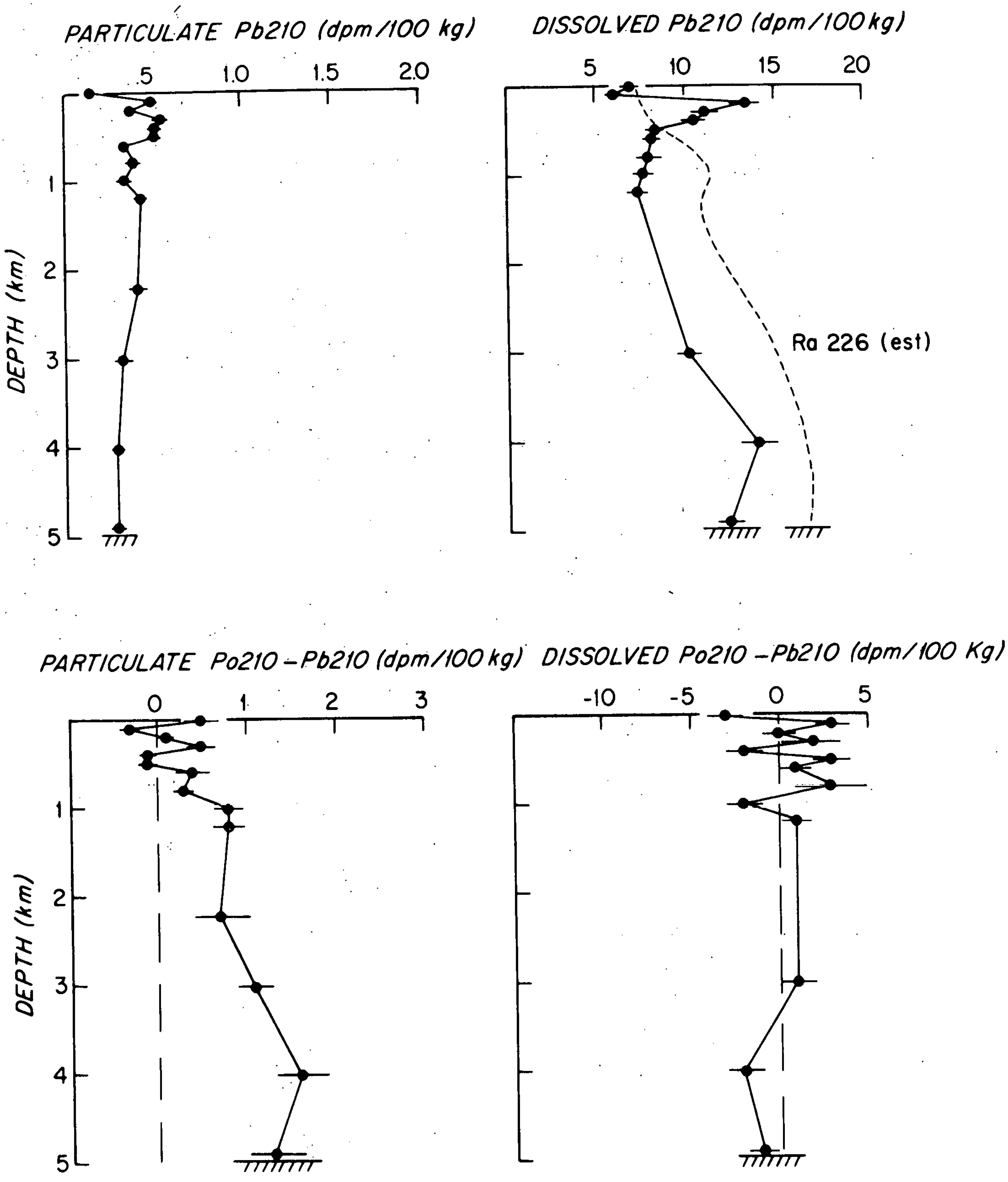
METEOR 32
STATION 22

Figure III.10



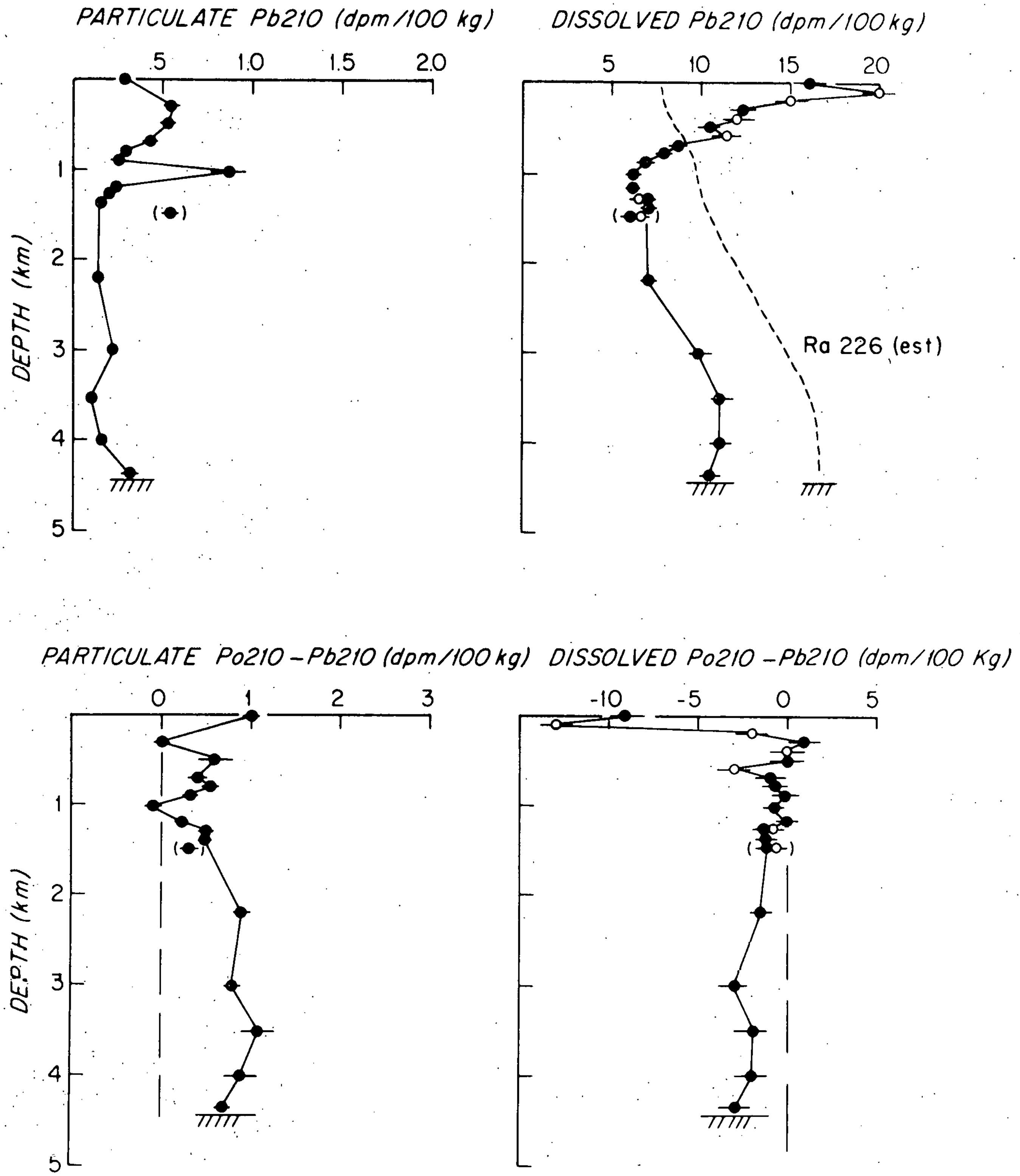
METEOR 32
STATION 23

Figure III.11



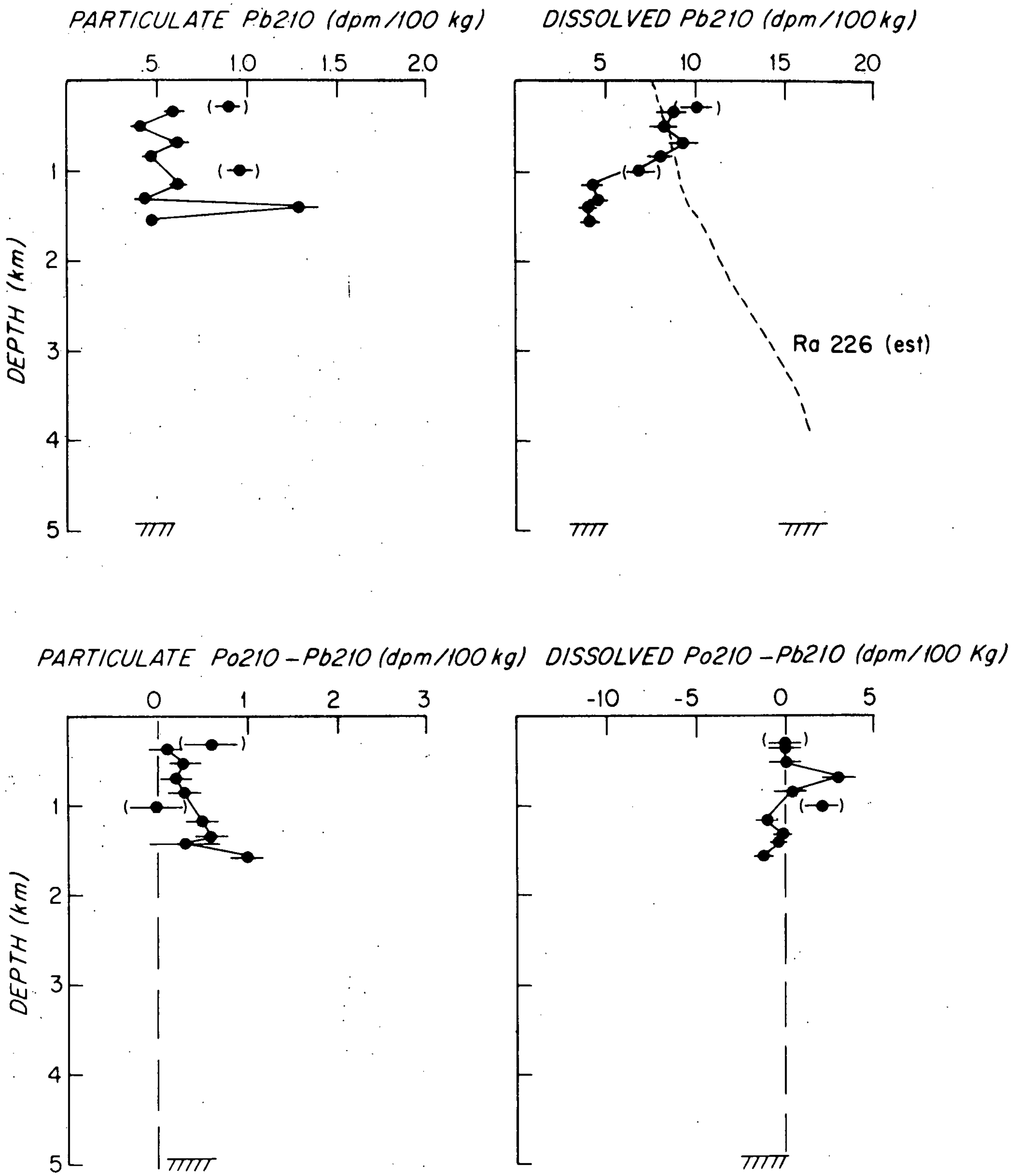
METEOR 32
STATION 27

Figure III.12



METEOR 32
STATION 32

Figure III.13



METEOR 32
STATION 34

Figure III.14

Figures III.15 and III.16. Vertical profiles of Pb-210 and Po-210 for Pacific GEOSECS stations. For GEOSECS 226 dissolved and particulate analyses were combined to give totals. Radium profiles are estimated as described in the text. The 3805-m results for GEOSECS 320, marked by parentheses, are uncertain due to sample leakage.

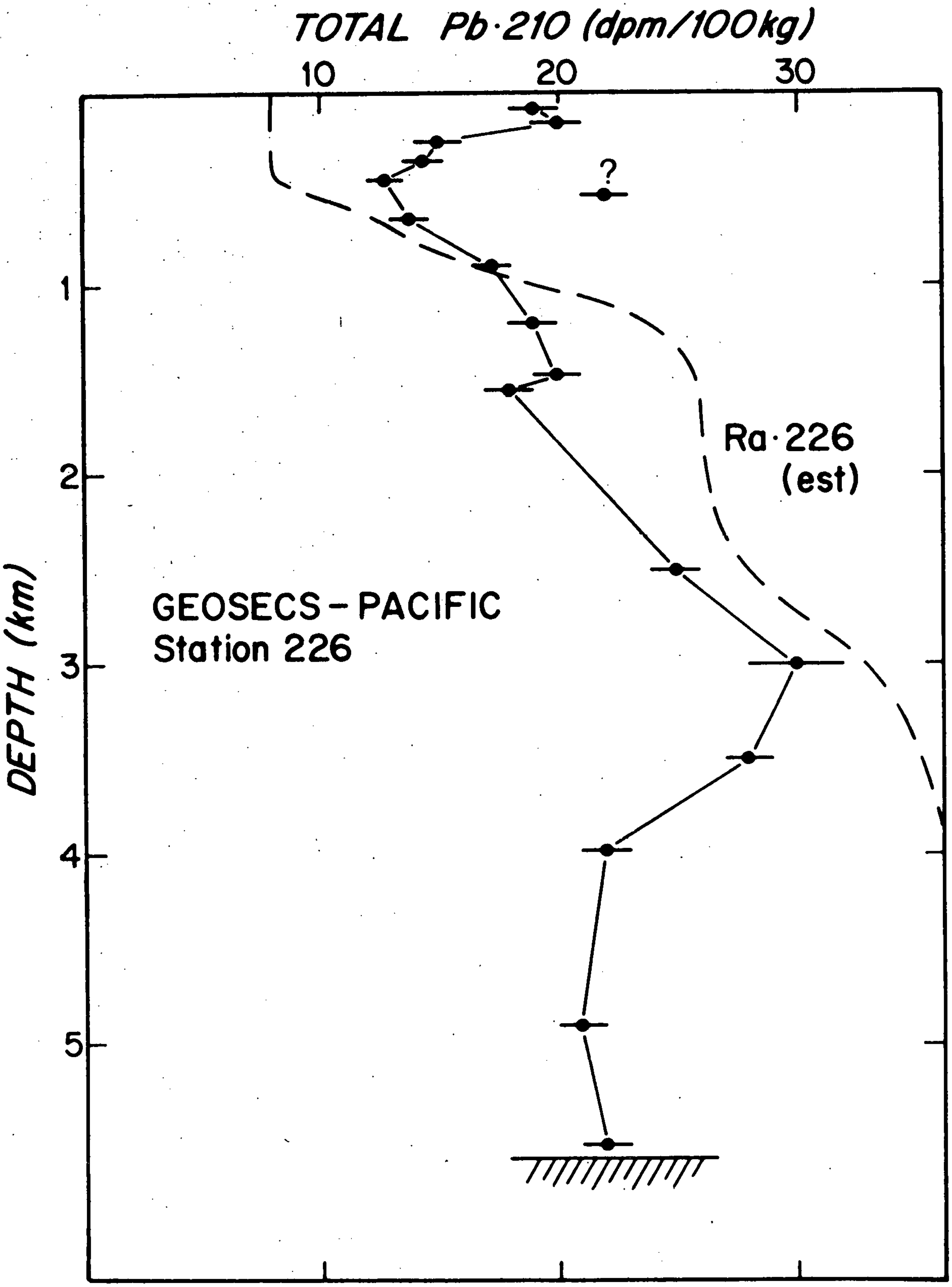


Figure III.15

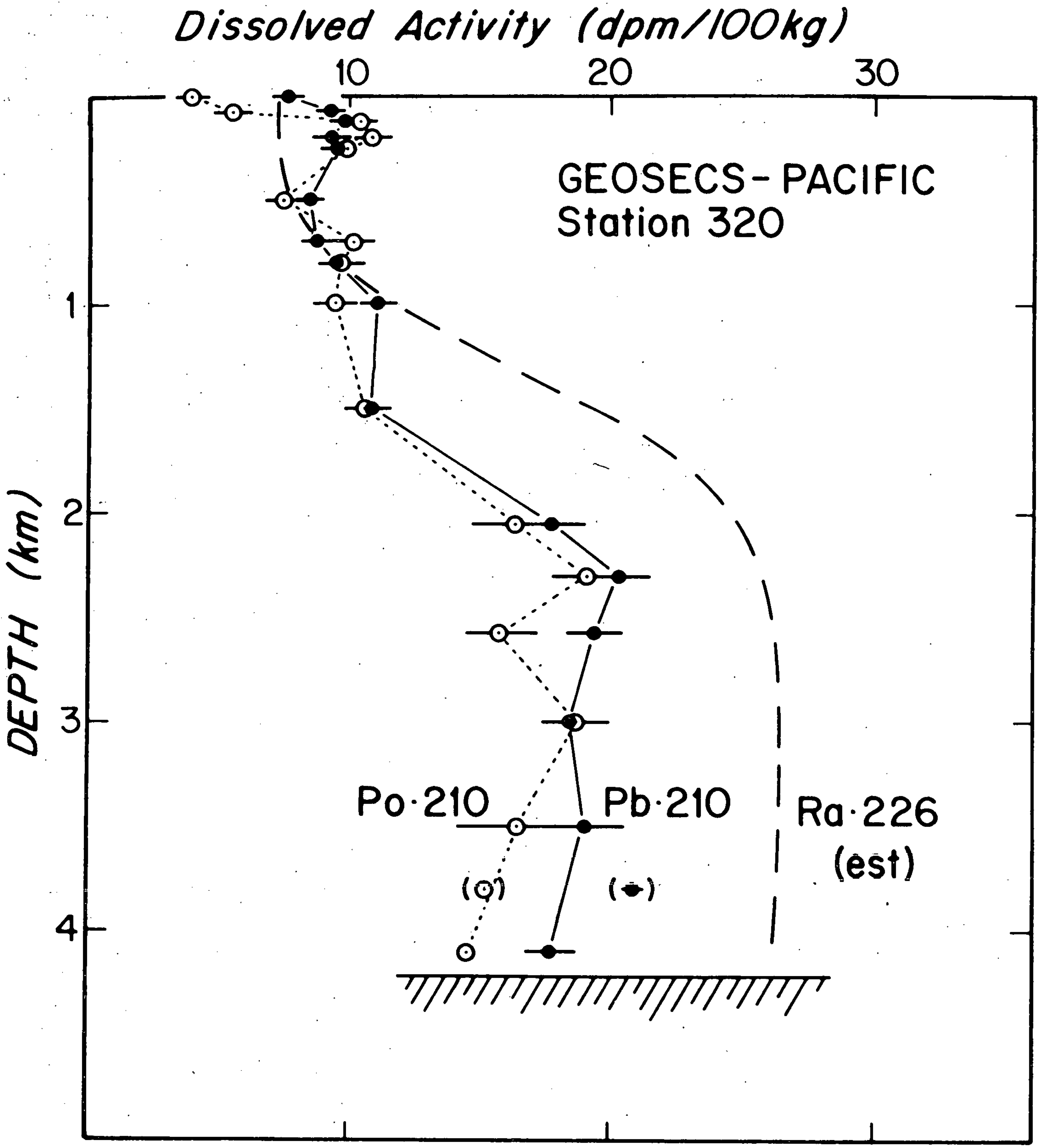


Figure III.16

CHAPTER IV

THE FATE OF PB-210 AND PO-210 IN THE UPPER LAYERS OF THE OCEAN

A. Introduction

Determinations of the Pb-210 concentration in sea water were first reported by Rama et al. (1961) and Goldberg (1963). These authors indicated that the principal supply of Pb-210 to the surface mixed layer of the sea is by deposition from the atmosphere following production by decay of Rn-222. On the basis of Pb-210 concentrations in rain water (Burton and Stewart, 1960; Blifford et al., 1952; Rama et al., 1961), they estimated a mean annual Pb-210 flux to the sea surface of 0.5 dpm/cm^2 and calculated a residence time for Pb-210 in the mixed layer of 2 years. A similarly short (10-y) residence time for stable lead in surface sea water was estimated by Tatsumoto and Patterson (1963).

Shannon et al. (1970) measured Pb-210 and Po-210 in surface waters and plankton collected around the Cape of Good Hope. It was found that Po-210/Pb-210 activity ratios in surface sea water are generally less than 1.0, indicating fast removal of Po-210. For Po-210 a residence time of 0.6 y was calculated; for Pb-210 a value of 5 y, in reasonable agreement with Rama et al. (1961), was obtained. Analyses of plankton showed it to be always enriched in Po-210 relative to Pb-210. The Po-210/Pb-210 activity ratio averaged 3.8 for three phytoplankton samples and 12.0 for eleven zooplankton samples. This preferential enrichment of Po-210 in plankton was given as an explanation for the more rapid turnover time of this nuclide in the mixed layer. Subsequent investigations have generally substantiated the above findings (Tsunogai and Nozaki, 1971; Nozaki and Tsunogai, 1973; Turekian _et al_., 1974; Kharkar _et al_., 1975).

The present investigation has provided information not heretofore available on the distribution of Pb-210 and Po-210 between dissolved and particulate phases and on the detailed vertical distribution of these nuclides in the upper part of the water column. In this chapter the relative amounts of Pb-210 and Po-210 in dissolved and particulate phases will be used to determine the residence times of these two nuclides in solution in the surface water and the residence time of particles that deliver the nuclides out of the mixed layer. Vertical distributions in the thermocline will be examined in an effort to determine the fate of Pb-210 and Po-210 following their removal from the mixed layer.

B. Pb-210 and Po-210 distributions

Analytical results have already been described in Chapter III, but a few of the more important observations will be repeated here. Table IV.1 summarizes data obtained from surface water samples collected during Meteor-32. Results vary widely from one station to the next, but it may be stated that the following conditions are nearly always found

TABLE IV.1

Analytical data for surface water, Meteor-32.

Samples were taken from depths of 6-8 m.

	Pb-210 (*)		Po-210 (*)		Po-210/Pb-210 (+)	
Station	Diss.	Part.	Diss.	Part.	Diss.	Part.
8	11.2	.31	11	1.6	.98	5.2
12	13.8	1.66	3.4	1.6	.25	1.0
15	20.8	.33	.2	1.6	.01	4.8
18	20.7	.54	5.0	1.4	.24	2.6
21	18	1.11	8	1.3	.44	1.2
22	16.9	--	2.2	--	.13	--
23	9.9	.22	4.3	1.0	.44	4.7
27	7.0	.16	4	.7	.57	4.4
32	15.6	.29	7.2	1.3	.46	4.5

(*) dpm/100 kg

(+) activity ratio

Estimated Ra-226 concentrations for surface waters range from 6.9-8.3 dpm/100 kg.

for surface waters in this region of the Atlantic:

1.) Pb-210 activities are in excess of Ra-226 activities, indicating the importance of deposition from the atmosphere.
2.) Po-210 is deficient relative to Pb-210.
3.) For both Pb-210 and Po-210, most of the activity is found in the dissolved phase.
4.) Suspended matter is enriched in Po-210 relative to Pb-210, as is plankton.

These findings were all expected on the basis of previous observations.

An unexpected trend is seen in the dissolved Pb-210 activities, which show a systematic decrease from west to east across the Atlantic (Me-32-15 through Me-32-27). Most of the Pb-210 in the mixed layer is derived from Rn-222 in the atmosphere, which is of continental origin. Because the prevailing winds in this region are from the east, the observed trend is one of decreasing concentration as the source is approached. This change in concentration is too large to be accounted for by differences in the mixed layer thickness, and it is unlikely that the decrease in Pb-210 concentration is a reflection of increased local productivity. Variations in the rate of surface primary production along the Meteor track appear to be small (Koblentz-Mishke, 1970). The fact that Po-210/Pb-210 activity ratios, which are expected to be inversely related to productivity (Turekian et al., 1974), do not show such a trend also argues against locally produced effects. The most probable explanation is that the low surface concentrations at the easternmost stations result from advection, in the North Equatorial Current, of water that has been biologically stripped of Pb-210 while resident off the northwest African coast, a well-known region of upwelling and high surface productivity. Sub-surface Pb-210 maxima observed at these stations (Me-32-23 and 27) may also arise from this effect and are not necessarily a result of *in situ* re-cycling of Pb-210.

Recent data of Koide *et al*. (1975) indicate that a significant fraction of the Pb-210 delivered from the atmosphere may occur in insoluble form, perhaps as much as 50%. A sample of atmospheric dust collected in Barbados contained 1.2 dpm Pb-210/mg. If similar material is deposited over the north equatorial Atlantic at a rate of .2 mg/ cm^2-y (Chester, 1972; Prospero and Carlson, 1972), the resulting Pb-210 flux would be 0.24 dpm/cm^2-y. This particular sample had been rinsed with distilled water prior to analysis, a procedure that was shown to release a sizable fraction of the Pb-210 (Koide *et al*., 1975), and the flux calculated here may be representative of the Pb-210 flux not readily dissolved in rain or on contact with the sea surface. The "insoluble" flux estimated above is not inconsistent with the total flux of 0.61 dpm/cm^2-y calculated in the section below on the basis of mass balance considerations and may provide an explanation for the variability in particulate Pb-210 concentrations shown in Table IV.1. An instantaneous pulse of atmospheric dust equivalent to 10% of the average annual input would increase the particulate Pb-210 concentration of a 100-m mixed layer by .24 dpm/100 kg, sufficient to double some of the amounts listed in Table IV.1. Betzer et al. (1974a) observed considerable patchiness in the distribution of total suspended matter concentrations of surface water in this region and suggested that periodic pulses in dust deposition could be responsible. An alternative explanation for the variability in particulate Pb-210 concentrations could, of course, be patchiness in the distribution of phytoplankton productivity. One would expect in this case, however, to find correlated variations in particulate Po-210 concentrations. In either case, the data strongly suggest the operation of processes that are not uniform with time.

C. Rates of removal and re-cycling of Pb-210 and Po-210

Because of the strong indications of advective and non-steady-state effects discussed above, it is unlikely that a simple treatment of data from individual stations will yield meaningful results. However, it is believed that by averaging the data over a large enough region these effects may be minimized and that a general picture of the processes controlling the mean distribution of Pb-210 and Po-210 in the upper layers of the sea can be developed.

The sub-surface distribution of Po-210 is shown in Figure IV.1, where activity differences have been plotted for Me-32 Stations 8-27. It is seen that within the upper 100 m of the water column nearly all of the data indicate a Po-210 deficiency. This is a zone of net removal of Po-210 from solution. Between the depths of 100 and 300 m,

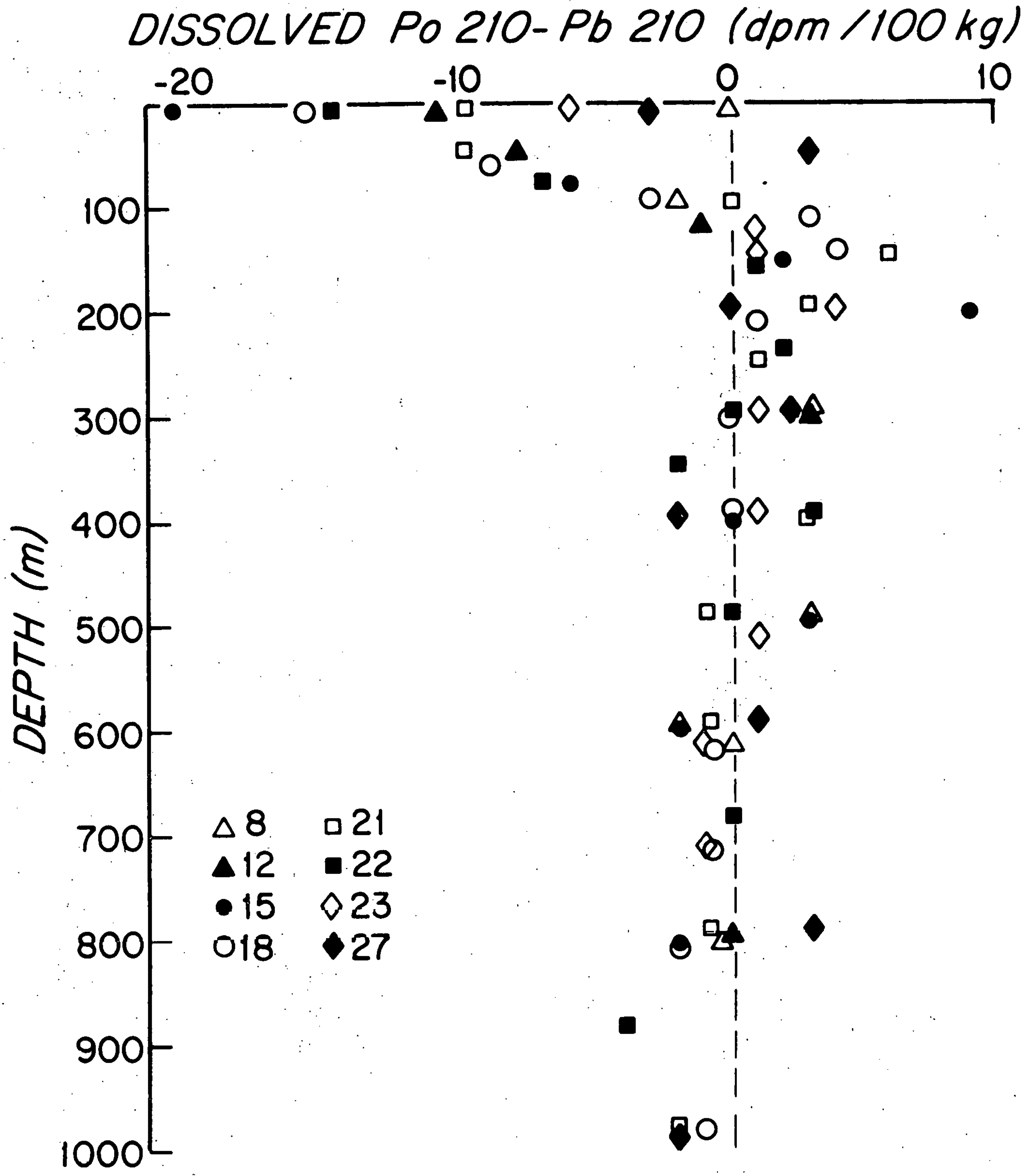


Figure IV.1 Vertical distribution of Po210-Pb210 activity differences in the upper layers of the tropical North Atlantic. All stations numbers refer to F/S Meteor Cruise 32.

a systematic Po-210 enrichment is found, indicating a net supply of Po-210 by processes other than radioactive decay. These two regions correspond approximately to the mixed layer and the thermocline in this region of the Atlantic. Because of the short radioactive turnover time of Po-210, these disequilibria are almost certainly a result of local processes.

The approach to be adopted is to compute numerical averages for all the data points in each of these two segments of the water column for all of the stations plotted in Figure IV.1. These stations lie between 14 and 22°N, and the structure of the water column is similar for all of them. Station 32 has been omitted, because it lies at a higher latitude and the mixed layer is considerably thicker. In Table IV.2 are listed standing crops of Ra-226, Pb-210 and Po-210 in each of the two layers considered. Also given are the same quantities calculated for other choices of the boundary depths. These quantities will be entered in the material balance calculations that follow. Throughout these calculations Ra-226, Pb-210 and Po-210 are designated by the subscripts 1, 2 and 3, respectively. Dissolved and particulate activities, A^d and A^p, are in units of dpm/cm^2 and are read directly from Table IV.2. These units are chosen so that fluxes for different reservoir sizes may be directly compared. Net rates of transfer between the dissolved and particulate phase are given by J in dpm/cm^2-y, which is taken to be positive when the net transfer is from the particulate to the dissolved phase. Removal of the nuclides in

TABLE IV.2

Inventories of Ra-226, Pb-210 and Po-210 in the surface layers of the North Equatorial Atlantic (Me-32-8, 12, 15, 18, 21, 22, 23, 27). Values are the arithmetic averages of all data points in the given depth intervals. Units are dpm/cm^2.

Depth interval (m)	A_1 Ra-226	A_2^d Pb-210(d)	A_2^p Pb-210(p)	A_3^d Po-210(d)	A_3^p Po-210(p)
0-50	.38	.74	.039	.25	.067
0-100	.76	1.46	.063	.77	.126
50-300	1.96	3.26	.120	3.45	.249
50-400	2.82	4.32	.161	4.58	.337
100-300	1.60	2.52	.106	2.94	.190
100-400	2.46	3.57	.143	4.07	.280

Decay constants used: Pb-210 -- 0.0312 y^{-1}
Po-210 -- 1.83 y^{-1}

particulate form is designated by the symbol P. Residence times are given by τ and always refer to the net sum of removal processes other than radioactive decay. As a first approximation we neglect fluid exchange across the boundaries. Numerical substitutions will be shown throughout so that the relative importance of each term in the material balance can be evaluated.

We consider first the material balance for dissolved Po-210 in the upper 100 m of the water column, and we have:

$$\lambda_3 A_2^{\,d} + J_3 = \lambda_3 A_3^{\,d} \qquad (1)$$

Equation (1) states that production of dissolved Po-210 by radioactive decay of Pb-210 in solution is balanced by radioactive decay and transfer of Po-210 to the particulate phase. On the basis of Po-210/Pb-210 ratios measured in air and rain water samples (Burton and Stewart, 1960; Lambert and Nezami, 1964; Poet et al., 1972), it can be estimated that the Po-210 flux from the atmosphere is approximately 10% of the Pb-210 flux and may be neglected in the present calculation. This assumption will be verified when the numerical value of the Pb-210 flux is estimated below. Moreover, Turekian et al. (1974) have suggested that a loss of Po-210 from the mixed layer across the sea surface may occur as a result of incorporation into organic-rich marine aerosols. Their suggestion has received some support in the data of Lambert et al. (1974). This loss of Po-210 may be sufficient to partly cancel the downward flux of Po-210 produced in the atmosphere. Therefore, transfer of Po-210 across the sea surface has been neglected. Substitution of numerical values from Table IV.2 in equation (1) gives

$$2.67 + J_3 = 1.41$$
$$J_3 = -1.26 \text{ dpm/cm}^2\text{-y}$$

The net flux J is negative, indicating that Po-210 is removed from solution to particles in the mixed layer. The residence time for Po-210 in solution is given by

$$\tau_3{}^d = A_3{}^d/-J_3 = 0.61 \text{ y} \qquad (2)$$

This result is in good agreement with the value of 0.6 y given by Shannon et al. (1970) and the range 0.41-1.21 y calculated for various oceanic regions by Turekian et al. (1974).

For particulate Po-210 we assume that supply by decay of particulate Pb-210 and by transfer from solution is balanced by radioactive decay and removal of particles from the mixed layer, and we write:

$$\lambda_3 A_2{}^p - J_3 = \lambda_3 A_3{}^p + P_3$$
$$0.12 + 1.26 = .23 + P_3 \qquad (3)$$
$$P_3 = 1.15 \text{ dpm/cm}^2\text{-y}$$

The residence time for particulate Po-210 is

$$\tau_{Po}{}^p = A_3{}^p/P_3 = .11 \text{ y} \qquad (4)$$

We note that this time is much shorter than the residence time of Po-210 in the dissolved phase.

If it is assumed that Pb-210 is removed from the mixed layer by particles having a residence time similar to those that carry Po-210, it is possible to determine the flux of particulate Pb-210 from the mixed layer:

$$P_2 = (A_2{}^p/A_3{}^p)\ P_3 \qquad (5)$$
$$= (0.063/0.126)\ (1.15) = .58 \text{ dpm/cm}^2\text{-y}$$

The assumption adopted here was first suggested by Turekian et al. (1974), who used activity ratios measured in zooplankton, rather than total suspended matter, as an indication of the relative downward fluxes for the two nuclides.

Constructing a material balance for particulate Pb-210 and entering the above value for P_2, we have

$$-J_2 = \lambda_2 A_2{}^p + P_2$$
$$= 0.002 + 0.58 \qquad (6)$$
$$J_2 = -0.58 \text{ dpm/cm}^2\text{-y}$$

Finally the dissolved Pb-210 balance is considered, the unknown term here being the rate of input from the atmosphere, I_a, which, for the moment, we consider to be soluble:

$$\lambda_2 A_1 + I_a + J_2 = \lambda_2 A_2{}^d$$
$$0.02 + I_a - 0.58 = 0.05 \qquad (7)$$
$$I_a = 0.61 \text{ dpm/cm}^2\text{-y}$$

The residence time of Pb-210 in solution is

$$\tau_2{}^d = A_2{}^d/-J_2 = 2.5 \text{ y} \qquad (8)$$

In equation (7) we have neglected the effect of radon escape across the sea surface, which would reduce the rate of Pb-210 production by decay of Ra-226 by about 25% (Broecker and Peng, 1971). Because the radioactive production term is very small, however, the error introduced is insignificant. Estimates of the Pb-210 residence time in the mixed layer and the rate of Pb-210 delivery from the atmosphere given above are in good agreement with those of other authors cited in the introduction. Calculations similar to those made here were made by Turekian et al. (1974), who obtained much lower estimates of the atmospheric delivery rate (0.05-0.10 dpm/cm^2-y) and longer Pb-210 residence times (9.4-24 y). The difference lies in their use of Po-210/Pb-210 ratios in zooplankton, which are commonly a factor of 5 higher than in total suspended matter. Reconsideration of the problem (Kharkar et al., 1975) led them to conclude that zooplankton is not a reliable indicator of relative fluxes out of the mixed layer, and an atmospheric delivery rate of 0.75-1.0 dpm/cm^2-y appears to them to be the estimate most consistent with available data (Kharkar et al., 1975; K. K. Turekian, personal communication).

We now consider the possibility, as indicated previously by the data of Koide et al. (1975), that Pb-210 delivered from the atmosphere enters the sea surface in particulate form. For dissolved Pb-210 in the mixed layer, we assume no soluble input, and we may omit I_a and determine J_2:

$$\lambda_2 A_1^d + J_2 = \lambda_2 A_2^d \qquad (9)$$

$$J_2 = 0.05\text{-}0.02 = 0.03 \text{ dpm/cm}^2\text{-y}$$

Here J_2 becomes positive, indicating a net transfer of Pb-210 from particles to solution, as required to maintain the dissolved Pb-210 excess observed in the mixed layer. The material balance for particulate Pb-210 is then used to determine the atmospheric input:

$$I_a - J_2 = \lambda_2 A_2{}^p + P_2$$
$$I_a - 0.03 = 0.002 + 0.58 \qquad (10)$$
$$I_a = 0.61 \text{ dpm/cm}^2\text{-y}$$

The estimate of I_a remains essentially unchanged.

We may now consider the sub-surface layer between 100 and 300 m, which is a region of net release of Po-210 to solution. For dissolved Po-210 we have:

$$\lambda_3 A_2{}^d + J_3 = \lambda_3 A_3{}^d$$
$$4.61 + J_3 = 5.38 \qquad (11)$$
$$J_3 = 0.77 \text{ dpm/cm}^2\text{-y}$$

The flux of Po-210 released from particles in this region, J_3, represents 67% of the flux leaving the surface mixed layer. This percentage will be referred to as the re-cycling efficiency. A similar calculation for Pb-210 gives:

$$\lambda_3 A_1{}^d + J_2 = \lambda_2 A_2{}^d$$
$$0.050 + J_2 = 0.079 \qquad (12)$$
$$J_2 = 0.029 \text{ dpm/cm}^2\text{-y}$$

The amount of Pb-210 re-cycled is small, and a re-cycling efficiency of about 5% is indicated. Even this value may be overestimated, because we have neglected sub-surface delivery of Pb-210 by vertical or horizontal mixing processes.

The results obtained from the above calculations are summarized in Table IV.3 along with results for different choices of the boundary depths. There is some dependency on the choice of reservoir size,

TABLE IV.3

Results of box-model calculations for north equatorial Atlantic

		Residence times in upper reservoir			% re-cycled	
Reservoir thickness (m)	I_a (dpm/cm^2-y)	τ_{Pb}^{d} (y)	τ_{Po}^{d} (y)	τ_{Po}^{P} (y)	Pb	Po
0-50, 50-300	.51	1.4	.27	.08	8	41
0-50, 50-400	.51	1.4	.27	.08	9	55
0-100, 100-300	.61	2.3	.61	.11	5	67
0-100, 100-400	.61	2.3	.61	.11	6	79

but the effects are not large enough to significantly alter the conclusions, which are summarized below.

D. Summary and conclusions

The major conclusions arising from the above material balance considerations may be summarized as follows:

1.) The most important source of Pb-210 in the surface mixed layer is the deposition of Pb-210 produced in the atmosphere by radon decay. For the tropical North Atlantic this delivery is calculated to be approximately 0.6 dpm/cm^2-y, a value that is independent of the assumed form, dissolved or particulate, in which the Pb-210 is delivered. Only at very high latitudes does production from Ra-226 decay in the mixed layer appear to become significant relative to delivery of Pb-210 from the atmosphere (Lambert and Nezami, 1965). Escape of Rn-222 from the sea surface is generally not an important consideration in the Pb-210 material balance, because little of the Pb-210 in surface water is formed _in situ_.

2.) Polonium-210 in the mixed layer is supplied principally by _in situ_ decay of Pb-210. The flux of Po-210 activity from the atmosphere should be about 10% of the Pb-210 flux or 0.06 dpm/cm^2-y. This value is small compared with rates of Po-210 turnover within the mixed layer. The hypothesis of Turekian _et al_. (1974) may allow for partial cancellation of this flux by escape of Po-210 across the sea surface.

3.) Residence times of Pb-210 and Po-210 in surface sea water are about 2 y and 0.5 y, respectively. The residence time of Pb-210 is short compared to its radioactive mean life, and only a small fraction (about 5%) of the total removal of Pb-210 in the mixed layer results from radioactive decay. For Po-210 the residence time is comparable to the radioactive mean-life, and approximately half of the Po-210 atoms produced in the mixed layer are lost by decay, the other half being removed by biological or chemical processes.

4.) Particles bearing Po-210 in the mixed layer are replaced in approximately 0.1 y. It is tempting to interpret this residence time in terms of simple gravitational settling of individual particles at an average velocity of about 500 m/y, but significant losses of particles may also occur as a result of consumption by grazers and subsequent incorporation into rapidly sinking fecal pellets. The mean residence time of Po-bearing particles is considerably shorter than the mean residence time of Po-210 in solution, suggesting that removal from the mixed layer is controlled by processes of incorporation of this nuclide into particles and that retention of particles in the mixed layer is not a significant limitation on the overall removal rate.

5.) About 50% or more of the Po-210 removed from the mixed layer is re-cycled at depths less than 400 m. Figure IV.1 shows a slight tendency toward more negative Po-210-Pb-210 activity differences between 400 and 1,000 m and suggests that additional re-cycling of Po-210 occurs within this depth interval. It is possible that virtually all of the Po-210 leaving the mixed layer,allowing for losses by decay, is re-cycled within the upper 1,000 m of the water column. This rapid release of Po-210 from particles is somewhat surprising for an element that otherwise displays extreme instability in sea water. Polonium (IV) is the stable oxidation state in oxygenated solutions and at neutral or alkaline pH is readily hydrolyzed and associates with available surfaces. A bivalent oxidation state is also known (Figgins, 1961). Possibly polonium undergoes reduction during biological fixation and is subsequently released in a metastably reduced form. Alternatively, Po (IV) may be released as a soluble organic complex from which it is only slowly released as a free ion to solution.

6.) The behavior of Pb-210 is in marked contrast to that of Po-210, its re-cycling efficiency being less than 10%. Comparison of Pb-210 and tritium profiles of Östlund et al. (1974) in this region suggests that excess Pb-210 in the thermocline may be supplied almost entirely by local vertical mixing or by horizontal spreading along isopycnal surfaces. Because transport by mixing was not considered in the material balance calculations above, the re-cycling efficiency for Pb-210 may be overestimated. In any case, it appears that most of the Pb-210 introduced at the surface is incorporated into particles that enter the deep sea with little or no subsequent release to solution. A rapid delivery of Pb-210 from the sea surface to the sediments is consistent with the conclusion of Chow and Patterson (1962) that the distribution of stable lead isotopes in sediments is inconsistent with large-scale mixing of lead from different continental sources.

CHAPTER V

DEEP-SEA SCAVENGING OF PB-210 AND PO-210

A. Introduction

Lead-210 concentrations in deep-ocean water were first measured by Rama et al. (1961), who concluded that they were essentially in secular equilibrium with Ra-226 concentrations that had been reported at that time. Later measurements by Craig et al. (1973), however, demonstrated that Pb-210 and Ra-226 are not generally in secular equilibrium, relative Pb-210 deficiencies of 20-75% being found in deep water of both the Atlantic and Pacific. Subsequent investigations (Tsunogai et al., 1974; Applequist, 1975; this thesis, Chapter III) have confirmed these findings.

To explain this state of radioactive disequilibrium, one must postulate a deep-sea sink at which Pb-210 is removed in a time comparable to its radioactive mean-life (32 y), and it is generally presumed that Pb-210 is continuously removed from solution as a result of "scavenging" by suspended particulate matter and subsequently eliminated from the water column by sinking. Thus Craig et al. (1973), using a vertical advection-diffusion model, calculated a 54-year residence time for Pb-210 with respect to in situ chemical removal from solution. Tsunogai et al. (1974) estimated a mean sinking rate for Pb-210 of about 30 m/y. Both calculations were based on measurements of total Pb-210 in unfiltered sea water and involved implicit assumptions concerning the distribution of Pb-210 between dissolved and particulate phases. Craig _et al_. (1973) assumed that insignificant amounts of Pb-210 are contained in the particulate phase, and their model implies that Pb-210 removal from the deep sea is controlled by relatively slow adsorption followed by rapid sinking of particles. The calculation of Tsunogai _et al_. (1974), on the other hand, implies that transfer from solution is rapid, that Pb-210 exists largely in particulate form and that removal is controlled by particle sinking rate.

The present investigation was aimed at further understanding the mechanism of Pb-210 removal by scavenging. It appeared that knowledge of the distribution of Pb-210 between dissolved and particulate phases was of critical importance, and such information has been obtained throughout the water column for six stations in the Atlantic. Partial information has also been obtained from several additional stations at which the water column was sampled only to mid-depths or at which particulate activities were not measured. Analytical results have been presented in Chapter III.

In the case of Po-210, there appear to be no published measurements for deep-ocean water, probably because of the short half-life of this nuclide and the expectation that it should be in secular equilibrium with Pb-210. However, polonium is known to be a highly reactive element and to have a strong tendency at neutral or alkaline pH to become associated with available surfaces (Figgins, 1961). Therefore, the possibility that measurable Po-210/Pb-210 disequilibria might exist in the deep sea was also investigated.

B. Removal of Pb-210 from the deep sea

To explain sub-equilibrium concentrations of Pb-210, it is necessary to postulate processes other than radioactive decay that remove Pb-210 from the deep sea, and it is this non-radioactive rate of removal that we wish to estimate. We begin by considering the dissolved Pb-210 profiles shown in Figures III.5-III.16. As pointed out in Chapter IV, unsupported Pb-210 delivered from the atmosphere penetrates to appreciable depths in the water column, presumably by a combination of physical mixing and particle transport with dissolution. The influence of this source, however, appears to become small as depths of 500-1,000 m are approached (generally in the lower part of the thermocline), and Pb-210 profiles frequently pass through minima at these depths. In defining the deep water column, therefore, we shall take this level as the upper boundary and assume that the net diffusive exchange across it is negligibly small. (In applying their advection-diffusion model to Pb-210 and Ra-226 profiles from the Pacific, Craig et al. (1973) showed that Pb-210 losses across the upper and lower boundaries were insignificant relative to the inferred rates of removal within their mixing regime. Such a model, however, is inappropriate in the Atlantic, and in treating the dissolved Pb-210 data we adopt what is essentially a box-model approach.) The lower boundary of the deep water column is set at the sea floor.

The principal source of Pb-210 in the deep sea is the in situ decay of Ra-226, and rates of production from this source are calculated by integrating Ra-226 profiles over the height of the deep-water column. Integrations were performed simply by dividing the water column into intervals defined by the mid-points between sampling depths and weighting each data point according to the depth interval it represented. Integrated Ra-226 and Pb-210 activities are given in Table V.1 for all stations at which both dissolved and particulate Pb-210 were measured throughout the water column. Also listed in Table V.1 are similar results for two Pacific GEOSECS stations, based on data of Applequist (1975). Rates of Pb-210 production from Ra-226 are given, in activity units, by $\lambda_2 A_1$, where λ_2 is the Pb-210 decay constant (0.0312 y^{-1}) and A_1 is the Ra-226 activity. These rates vary from 1.2-1.9 dpm/cm^2-y for the Atlantic stations and are about twice as high for the Pacific, where Ra-226 concentrations are higher.

Two additional sources of Pb-210 in the deep sea need to be considered: 1) release from particles sinking from the surface and 2) generation near the sea floor by decay of excess Rn-222. Because of the short residence time of Pb-210 in the mixed layer, the flux of particulate Pb-210 entering the deep water reservoir is approximately equal to the rate of atmospheric Pb-210 deposition at the sea surface. This flux was estimated in Chapter IV to be approximately 0.6 dpm/cm^2-y for the tropical North Atlantic. It was also seen in Chapter IV that

TABLE V.1

Integrated Ra-226 and Dissolved Pb-210 Activities For the Deep Water Column, Rates of Pb-210 Removal by Processes Other than Radioactive Decay, and Apparent Residence Times, τ .

Station	Depth range (m)	Dissolved Pb-210 (dpm/cm^2)	Ra-226 (dpm/cm^2)	Removal Rate (dpm/cm^2-y)	τ (y)
Me-32-12	990-4880	17.4	45.9	.89	20
Me-32-15	700-5003(*)	19.8	49.9	.94	21
Me-32-18	666-3820	23.5	37.5	.44	54
Me-32-23	451-4940	45.4	61.1	.49	93
Me-32-27	887-4950	42.8	58.1	.48	90
Me-32-32	960-4440	31.1	47.7	.52	60
+ GEOPAC 201	984-4720	66.6	119.3	1.64	41
+ GEOPAC 314	977-4580	55.2	89.4	1.07	52

(+) Based on data from Applequist, 1975.

(*) The two bottom samples at this station were taken within the nepheloid layer, and the lower boundary is taken above this level. For all other stations, the lower boundary is set at the sea floor.

re-dissolution of Pb-210 in the thermocline is insignificant, and by extrapolation we assume that this conclusion also holds for the deep ocean. There is no way to verify this assumption, because the deep-water disequilibrium reflects only the net effect of supply and removal processes, and is always in a direction indicating net removal of Pb-210 from solution. However, the assumption is not of crucial importance in the discussion that follows, because, in evaluating the in situ scavenging hypothesis, we are concerned principally with the net effects.

The standing crop of excess Rn-222, maintained by the flux of unsupported Rn-222 from the sediments, ranges from 0.2-20 dpm/cm^2 (Broecker et al., 1968) and produces Pb-210 at rates ranging from 0.006-0.6 dpm/cm^2-y. Radon fluxes tend to be highest in regions of low sedimentation rate, and the highest values measured by Broecker et al. (1968) are from the Pacific. A typical value for Pb-210 production from excess Rn-222 in the Atlantic is 0.1 dpm/cm^2-y.

Because release of Pb-210 from particles and production from excess Rn-222 appear to be relatively small, we shall assume that all of the Pb-210 in the deep sea is derived from in situ decay of Ra-226. Lead-210 decay in solution is given by $\lambda_2 A_2$, where A_2 is the dissolved Pb-210 activity, and the difference $\lambda_2 A_1 - \lambda_2 A_2$ is the rate of removal of Pb-210 from solution by processes other than radioactive decay. Calculated values of this removal rate are given in Table V.1 along with apparent residence times given by $A_2/\lambda_2 (A_1-A_2)$. These residence times are in fair agreement with the value of about 40 y estimated by

Craig et al. (1973) for the Atlantic and their value of 54 y for the Pacific, but significant differences between stations are apparent, as will be discussed below.

C. In situ scavenging of Pb-210

The removal rates listed in Table V.1 represent fluxes of Pb-210 from solution that must be accounted for by processes other than radioactive decay. If it is assumed that this removal is maintained entirely by in situ scavenging, at the rates given in Table V.1, then it should be possible to estimate particle sinking rates from particulate Pb-210 profiles. For simplicity we assume that Pb-210 is transferred at a constant rate R (dpm/m^3-y) from solution to particles. Actually, according to the in situ scavenging hypothesis, the divergence of Ra-226 and Pb-210 profiles toward the bottom implies that the rates of scavenging increase somewhat with depth, but we shall use the average rate obtained by dividing the profile integrations of Table V.1 by the height of the water column. Particles are assumed to sink at a constant rate S (m/y). The rate of change of particulate Pb-210 concentration P with depth z (positive downward) is given by

$$dP/dz = R/S - \lambda_2 P/S \qquad (1)$$

The first term on the right-hand side of equation (1) is the rate of gain by transfer from solution, and the second term is the rate of loss due to radioactive decay. Setting $z=0$ and $P=P_0$ at the upper boundary, we have the solution

$$R-\lambda_2 P = (R-\lambda_2 P_0)\ \exp(-\lambda_2 z/S) \qquad (2)$$

As z becomes large in equation (2), P must approach the limiting value R/λ_2, for which radioactive decay is just balanced by transfer from solution.

It is clear that for Pb-210 deficiencies to be maintained in the deep sea by in situ scavenging, dP/dz must be positive; i.e., for any segment of the water column, the total Pb-210 increment due to transport by sinking must be negative. Of the six complete particulate Pb-210 profiles from the Atlantic (Me-32-12, 15, 18, 23, 27, 32), only one (Me-32-18) shows a significant increase in activity with depth. This anomalous station is located close to the Mid-Atlantic Ridge and will be discussed below. For the other five profiles, it is possible that positive gradients exist but are simply not detectable. For this to be the case, however, high sinking velocities would be required, because R is always much greater than $\lambda_2 P$ [see equation (1)], when R is assumed to account for all of the Pb-210/Ra-226 disequilibrium. Table V.2 indicates how large these sinking velocities must be to account for the observed profiles. Equation (2) has been fit to the particulate Pb-210 profiles and 2σ confidence limits on the settling velocity have been calculated. A typical case is illustrated in Figure V.1, where profiles to be expected for other settling velocities are also drawn for the same initial condition. Because the gradients are so small, and in some of the cases even slightly negative, it is generally possible only to assign lower limits to the apparent sinking

TABLE V.2

Results of Pb-210 Sinking Velocity Calculations

Station	R (dpm/m^3-y)	S (m/y)	2σ limits (m/y)	No. of Observations	Spurious Points Discarded
Me-32-12	2.29	11,000	> 3,100	9	None
Me-32-15	2.18	--	>14,000	4	1813 m
Me-32-18	1.38	380	250-790	11	None
Me-32-23	1.09	--	> 6,600	11	None
Me-32-27	1.17	--	--	6	None
Me-32-32	1.49	6,800	> 2,600	8	1034,1477 m
(+) GEOPAC 201	4.40	2,200	1,500-3,900	9	None
(+) GEOPAC 314	2.96	1,600	970-4,200	13	None

(+) Based on data from Applequist, 1975.

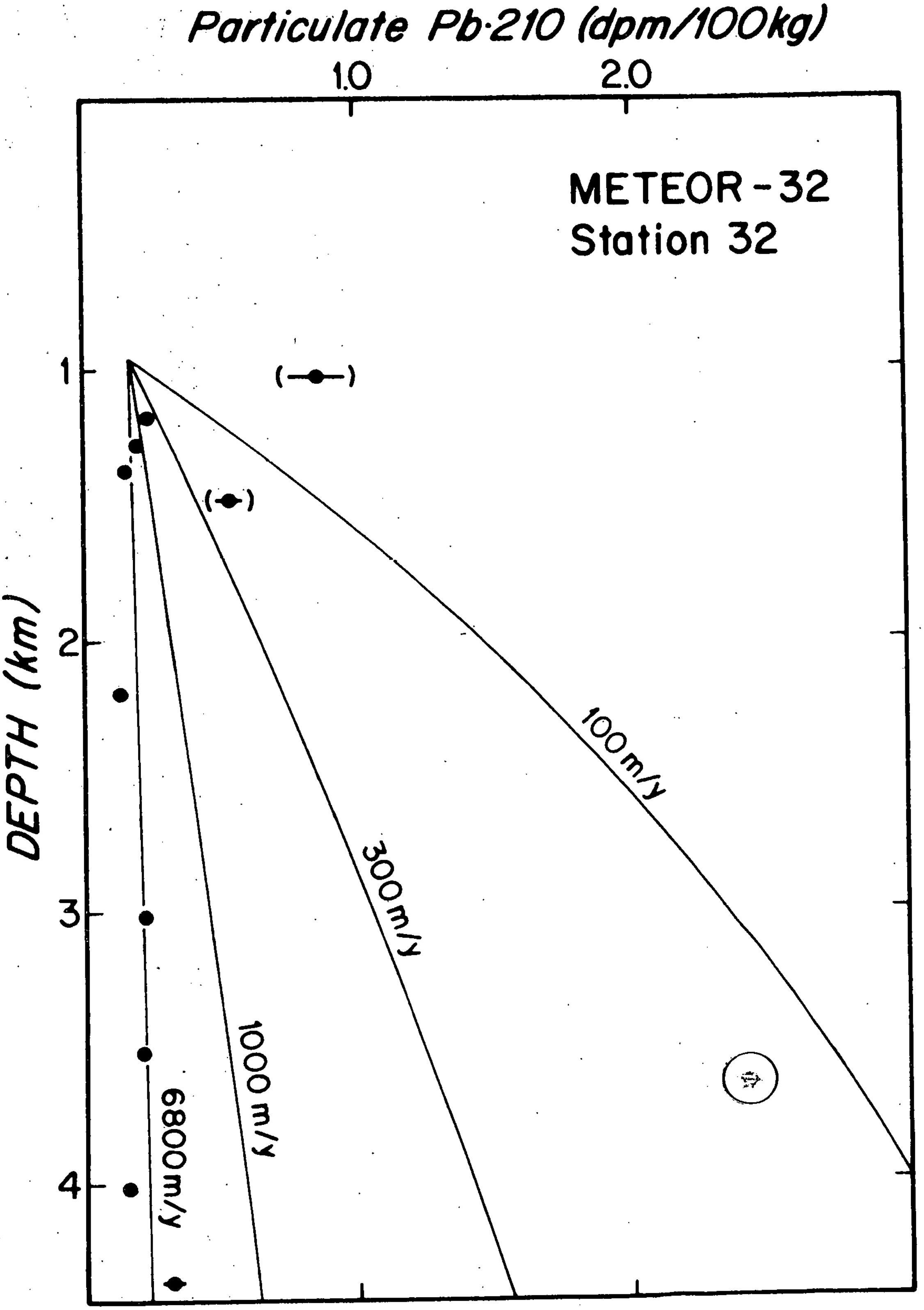


Figure V.1. Particulate Pb-210 profile showing fit of equation (2). The best fit to the data is given by the 6800 m/y curve. Other curves result from substitution of other values for S with P_0 held constant. The two points in parentheses were omitted in determining the best fit.

rate. It is clear, however, that settling velocities of several thousands of meters per year must be invoked if Pb-210 removal is to be maintained by particulate flux alone.

The settling velocities given in Table V.2 are about an order of magnitude larger than those estimated for other radioactive tracers. Noshkin and Bowen (1972) modelled the distribution of fallout Pu-239 in the water column and sediments of the Atlantic and achieved a good fit by assigning various fractions of the plutonium activity to particles sinking at rates of 70-390 m/y. It was assumed that all of the plutonium activity in the water column is in the particulate phase. Their case is not strictly analogous to that of Pb-210 in the deep sea, because the input of plutonium and its association with sinking particles occurs at the surface rather than at depth.

A more comparable example is that of the thorium isotopes, Th-234 and Th-230, produced throughout the water column by decay of dissolved U-238 and U-234. Recent measurements of particulate Th-234 and Th-230 by D. Lal (unpublished report) indicate that approximately 10% of the Th-234 activity in the deep water is contained in particles collected on cotton-fiber filters (pore-size not reported). This distribution suggests very rapid removal of thorium from solution by suspended particles, the residence time of thorium in solution being on the order of one year, and it further implies that virtually all of the Th-230 activity should be in the particulate phase (if scavenging by particles is irreversible). As expected, particulate Th-230 activity shows an increase with depth, and from its rate of increase one may estimate a sinking velocity of about 400 m/y. This estimate probably represents an upper limit for comparison with data obtained with 0.4-micron Nuclepore filters, because the efficiency of Lal's filters is probably lower.

If the sinking velocities calculated in Table V.2 are unreasonably high, then an alternative explanation for the near-zero vertical gradients observed in particulate Pb-210 profiles must be sought. In applying equation (2) we have assumed that R, the rate of solution-to-particle transfer, is defined by the extent of the dissolved Pb-210/Ra-226 disequilibrium, and in this case R is always much greater than $\lambda_2 P$ (i.e., particulate Pb-210 activities account for only a small fraction of the dissolved Pb-210/Ra-226 activity difference). As noted above in the discussion of equation (1), particulate Pb-210 activities should tend to approach a limiting value for which $R=\lambda_2 P$. This is the condition for which uptake from solution is compensated by radioactive decay, and it is here suggested that such a condition may already have been reached in the Atlantic by particles entering the deep sea. If this is the case, then it is possible to calculate the rate of in situ scavenging from the average particulate Pb-210 activity in the deep water. Values of R calculated in this manner are given in Table V.3 and compared with those determined earlier by considering the dissolved Pb-210/Ra-226 differences. When in situ scavenging fluxes are estimated in this way, 90-95% of the dissolved Pb-210/Ra-226 disequilibrium remains

TABLE V.3

Rates of in situ Pb-210 scavenging calculated by two different methods

	From dissolved Pb-210/Ra-226 disequilibrium (as in Tables V.1 and V.2)		From R = λP (ave)	
Station	R(dpm/m^3-y)	τ(y)	R(dpm/m^3-y)	τ(y)
Me-32-12	2.29	20	.23	200
Me-32-15	2.18	21	.094	490
Me-32-18	1.38	54	--	--
Me-32-23	1.09	93	.072	1400
Me-32-27	1.17	90	.11	960
Me-32-32	1.49	60	.066	1400

unaccounted for, and an additional sink for Pb-210 in the deep sea must be sought.

We have so far not considered the possibility that particulate Pb-210 may be partially supported by Ra-226. There appear to be no published measurements of particulate Ra-226 in deep water, but the few values given in the report by Lal are in the range 0.01-0.04 dpm/100 kg and thus do not exceed 20% of the particulate Pb-210 concentrations. If allowance were to be made for this additional contribution, estimates of R would be even further reduced.

D. Lead-210 scavenging at the sediment-water interface

It was noted by Craig et al. (1973) that some of the lowest Pb-210 concentrations in their Pacific profile occur near the bottom where large quantities of excess Rn-222 also are present, and they suggested that rapid scavenging of Pb-210 must occur in this region. A similar effect has been noted in Chapter III for the Atlantic profiles, which consistently show a greater extent of disequilibrium as the sea floor is approached. Craig et al. (1973) also pointed out, however, that the influence of such boundary scavenging only extends upward, by vertical mixing, to a height of about 1,000 m from the bottom. Within their mixing regime (1791-4100 m, 200 m above the bottom), less than 5% of the Pb-210 removal could be accounted for by vertical mixing across the boundaries, and it was concluded that the remainder must be accounted for by in situ scavenging and radioactive decay. What is not considered in a vertical model such as theirs is that, if boundary scavenging is effective to heights of 1,000 m from the bottom, then it may also be of importance at appreciable distances from lateral boundaries.

Let us consider the case in which Pb-210 is scavenged at some topographic boundary, such as a continental margin or mid-ocean ridge, and allow for in situ production from Ra-226 decay and consumption by transfer to suspended particles. Neglecting the effects of advection, we have, at steady-state,

$$-K_H\, \partial^2 A_2/\partial x^2 + \lambda_2 A_1 = (\lambda_2+k)A_2 \qquad (3)$$

where K_H is the horizontal eddy diffusivity, and k is the rate constant for in situ scavenging (assumed to be first-order). As x approaches infinity, the activity ratio A_2/A_1 is determined solely by the rate of in situ scavenging and approaches the value λ_2/λ_2+k. With the additional boundary condition that $A_2=A_{2,0}$, and for A_1 constant, we have the solution

$$\frac{\lambda_2}{\lambda_2+k} - \frac{A_2}{A_1} = \left(\frac{\lambda_2}{\lambda_2+k} - \frac{A_{2,0}}{A_1}\right) \exp\left(-\sqrt{\frac{\lambda_2+k}{K_H}}\, x\right) \qquad (4)$$

Figure V.2 is a plot of A_2/A_1 versus distance to the nearest topographic boundary. The need to consider sources of Pb-210 other than Ra-226 decay as well as the effects of local scavenging at the bottom has been avoided by including data only from depths greater than 1,000 m below the surface and greater than 1,000 m above the bottom. Distances were determined by plotting station locations on a bathymetric chart and measuring distances to the nearest contours at

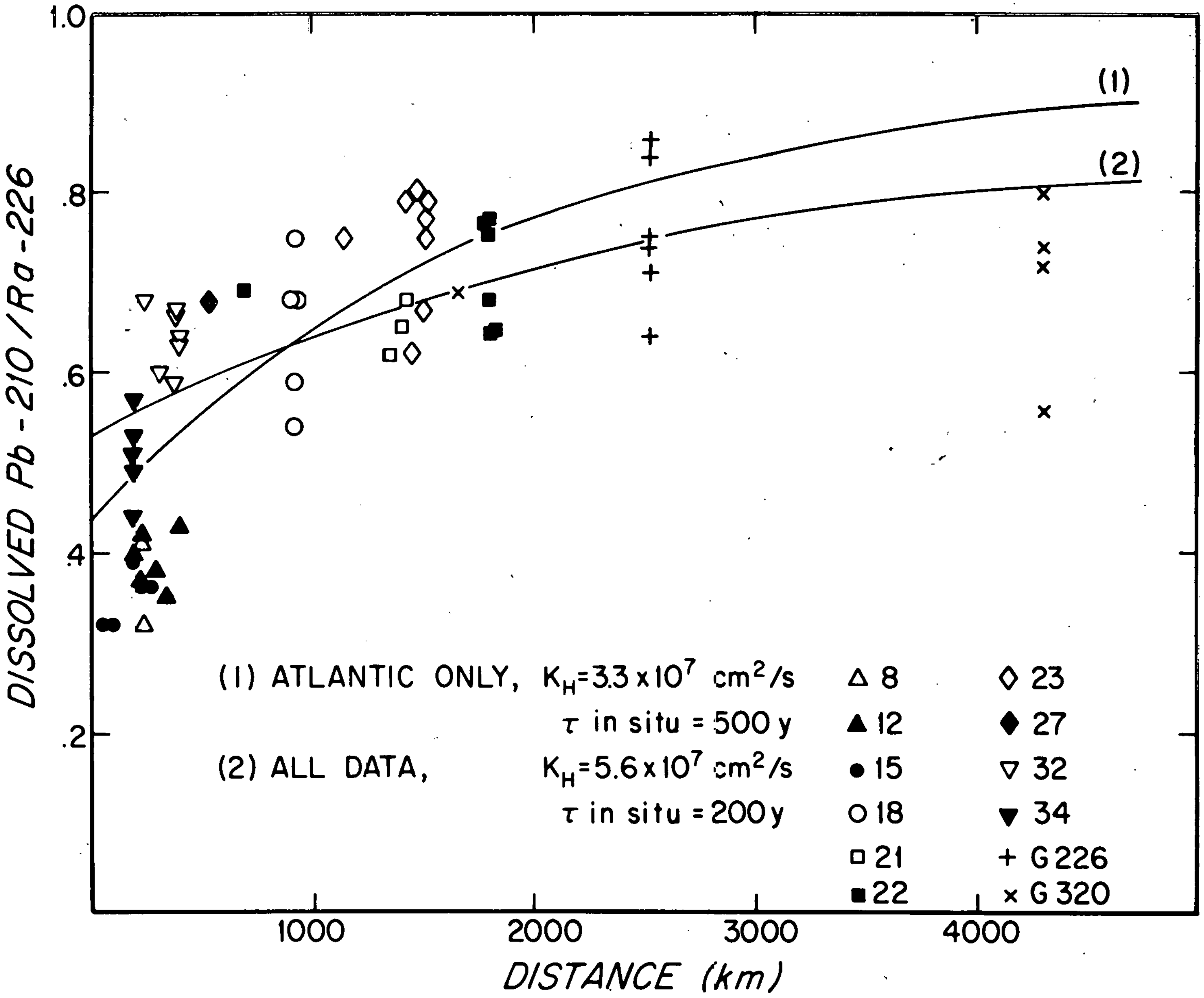


Figure V.2. Horizontal distribution of the Pb-210/Ra-226 activity ratio. With increasing distance from lateral boundaries, the ratio increases; i.e., the apparent Pb-210 residence time becomes longer. The curves are the best fits of equation (4). Samples within 1,000 m of the surface and bottom are omitted.

1,000-m intervals. Interpolations were performed for intermediate sampling depths. The figure clearly shows a significant correlation between the Pb-210/Ra-226 activity ratio (i.e., the apparent Pb-210 residence time) and horizontal distance from the assumed Pb-210 sink.

The curves drawn in Figure V.2 were obtained by adjusting K_H and k in equation (4) until the best fit was obtained. For this purpose it must be assumed that, at any depth, the Ra-226 concentration does not vary along a horizontal line between a given station and its nearest intersection with the sea floor. This assumption and the use of the activity ratio A_2/A_1 allow data from different regions to be compared on the same diagram. For the Atlantic data, the best fit was obtained for $K_H=3.3\times10^7$ cm^2/s and k=0.002/y. When the Pacific data were included, K_H increased to 5.6×10^7 and k increased to 0.005. These values for k correspond to residence times for Pb-210 with respect to in situ scavenging of 500 and 200 years and are in reasonable agreement with residence times calculated in Table V.3 from the Atlantic particulate Pb-210 data. The implication is that most of the Pb-210 removal flux may be carried by mixing to a remote sink at the sea floor, and the rates of horizontal eddy diffusion required to maintain this transport do not appear unreasonably large. Most estimates of K_H lie in the range 10^6-10^8 cm^2/s (Sverdrup et al., 1942). Kuo and Veronis (1973), for example, achieved reasonable success in modelling the world-ocean oxygen distribution by adopting the value $K_H = 6\times10^6$ cm^2/s.

The observation that Pb-210/Ra-226 ratios decrease as topographic boundaries are approached has been interpreted as evidence that scavenging at the sea floor is a major mechanism for removing Pb-210 from the deep sea. Broecker *et al*. (1973) have suggested a similar possibility in the case of thorium. In surface water Th-228/Ra-228 activity ratios showed a positive correlation with distance from the nearest 100-fm contour in much the same way that Pb-210/Ra-226 ratios in the deep sea have been seen to correlate with distance from the nearest appropriate contours. Because most of the samples showing very low Th-228/Ra-228 ratios were taken from nearshore, however, it was not possible to rule out the effects of higher productivity or higher suspended loads in these locations. In making the present interpretation regarding Pb-210 scavenging in the deep ocean, we are not faced with quite this same problem, but it is still necessary to consider the possibility that the trend shown in Figure V.2 may be caused by factors other than boundary scavenging.

We consider first of all the possibility that sampling of different water masses might coincidentally lead to the correlation shown in Figure V.2. Because of the short radioactive and chemical turnover times for Pb-210, it seems unlikely that Pb-210/Ra-226 ratios measured at depth would reflect the initial ratios acquired while the water mass was resident at the surface. It may be argued, however, that differences in the quantity or nature of the suspended load among various water masses might lead to variations in the rate of *in situ* scavenging and that, if a given water mass were sampled with greater frequency at one station than at another, a spurious correlation might result. In Figure V.3 data from Figure V.2 have been re-plotted with points identified according to depth, in 500-m intervals, rather than station number. It may be seen that the trend followed by all of the data points is also followed within any depth interval.

It is unlikely that biological activity should control the rate of Pb-210 scavenging in the deep sea, but K. K. Turekian (personal communication) has suggested the possibility of an indirect control by overlying surface productivity. Increasing the rate of surface production would increase the rate of supply of biogenic particles to the deep water, where *in situ* scavenging might consequently be accelerated. When locations of the Meteor and GEOSECS stations used in constructing Figure V.2 are compared with the global distribution of phytoplankton productivity (Koblentz-Mishke, 1970), it is seen that they are all from regions of low to moderate productivity. It is true that both of the Pacific GEOSECS stations, showing some of the lowest apparent rates of Pb-210 removal, are from some of the least productive areas, but Me-32-12 in the Caribbean, with a very low Pb-210/Ra-226 ratio, is from an area of comparably low surface productivity. During the Meteor crossing of the Atlantic, strong gradients in the rate of surface production were not crossed, but one would expect a general trend of increasing productivity in moving from west to east as the west African coastal upwelling region was approached. Apparent rates of Pb-210 removal actually decrease in

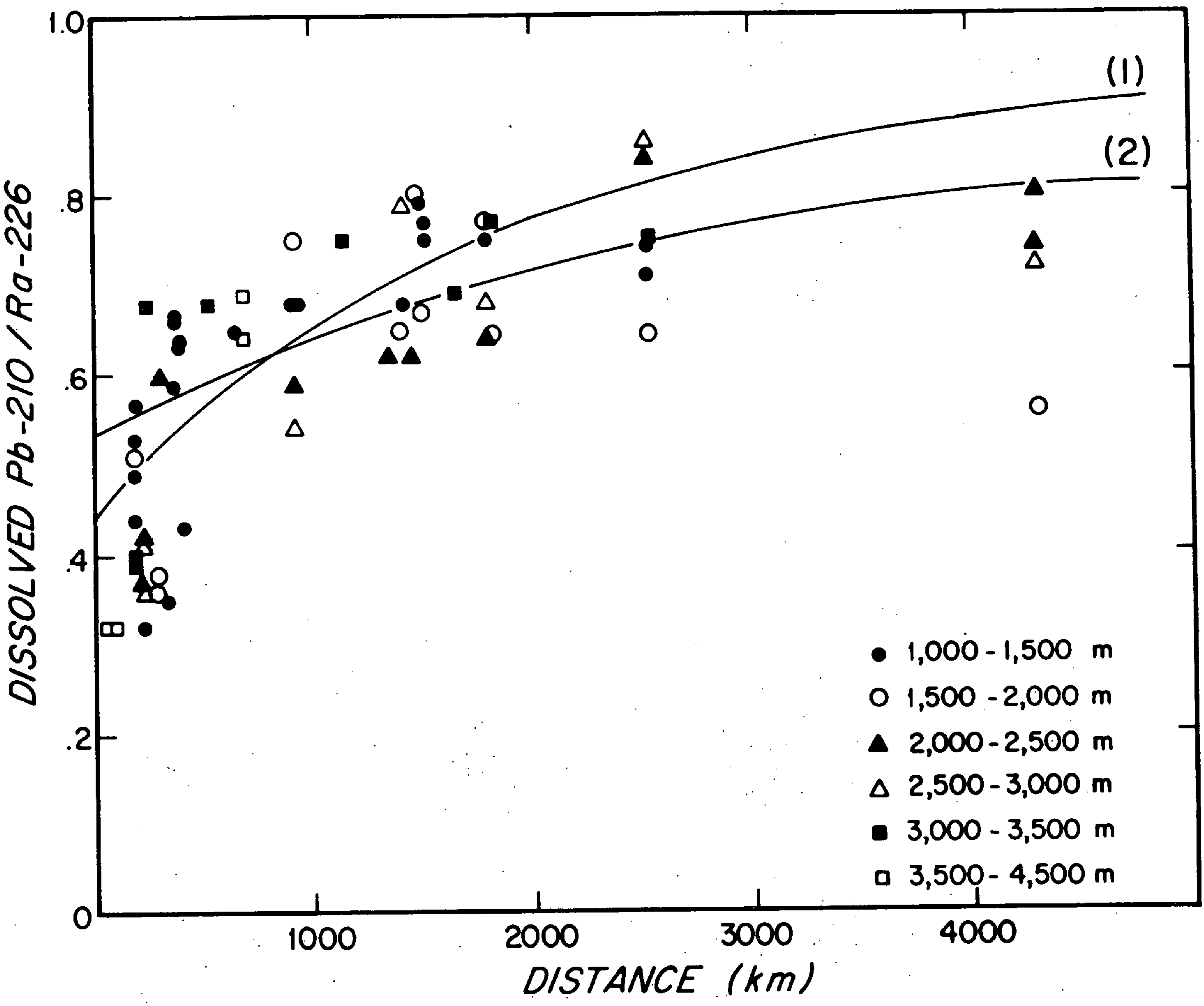


Figure V.3. Same as Figure V.2, with points identified as to sampling depth.

this direction (compare Me-32-15, 18, 21, 22, 23). This trend is also opposite to what one would expect if increasing rates of supply of wind-blown dust from the north African deserts were to increase the rates of in situ scavenging in the deep water. It is not necessarily implied that rates of particle supply or production at the surface are unimportant in controlling the rates of deep scavenging for some elements, but these factors do not seem to be important in the particular case of Pb-210. It should be further pointed out in this connection, however, that it has been difficult to correlate increased surface productivity locally with increased concentrations at depth of such variables as particulate organic carbon (Menzel, 1975) or total suspended matter. Data from GEOSECS indicate that distinct particle maxima in the interior of the deep ocean occur only in association with recent convective overturn (Brewer et al., 1975). In most regions the standing crop of particles at depth and the surface area available for reaction may be relatively independent of local supply at the surface.

The relatively rapid scavenging of Pb-210 at the sea floor that we have inferred from our data seems to require special explanation. A 4,000-m water column lying above one square meter of sediment surface contains approximately 40 g of suspended solid. With a specific surface area of 20 m^2/g, typical of sediments (Volchok and Kulp, 1956), particles in suspension ought to be more "reactive" than the sea floor, at least on the basis of available surface area for reaction. It appears necessary then to postulate processes unique to the sea floor in order to account for preferential Pb-210 removal at that site, and it is suggested that co-precipitation of Pb-210 with manganese and iron oxides forming at the interface might be such a process. The extent to which manganese may be precipitating in the water column is not known, but it seems likely that the major site is at the sea floor. In anoxic basins it is known that manganese does precipitate in the water column just above the O_2-H_2S interface (Spencer and Brewer, 1971), and preliminary results from the Cariaco Trench (M. P. Bacon, unpublished data) strongly suggest an association of Pb-210 with manganese in this region. Chow and Patterson (1962) have measured the distribution of lead in marine sediments and indicate a strong and widespread association of lead and manganese. Betzer _et al_. (1974b) reported high concentrations of particulate iron in samples collected close to the Mid-Atlantic Ridge crest, and similar anomalies have been found by R. Chesselet (unpublished report). Such anomalies could be the result of precipitation from the iron-rich solutions suggested to be leaking into the water column from volcanically active areas (Zelenov, 1964) and leading to the formation of metalalliferous sediments (Dymond _et al_., 1973). If this interpretation is correct, then the particulate Pb-210 profile at Me-32-18, near the Mid-Atlantic Ridge, which shows an anomalous maximum at about 3200 m, may provide further evidence that Pb-210 is rapidly co-precipitated by newly formed precipitates. An alternative explanation is that this maximum represents Ra-226 enrichment in the particulate matter sampled. In the absence of Ra-226 analyses for these samples, the question cannot be resolved, but in either case, this region is a promising one for future investigations.

E. Scavenging of Po-210

The behavior of Po-210 in the deep sea is markedly different from that of Pb-210 with respect to its rate of association with suspended particles. In Chapter III it was pointed out that, although there is considerable scatter in the data, Po-210 shows a slight deficiency in the dissolved phase, averaging about 12%. A corresponding enrichment in the particulate phase is found in nearly all of the samples. These observations can only be attributed to rapid in situ scavenging of Po-210 from solution. A value of about 4 years may be calculated for the mean residence time of Po-210 in the deep sea with respect to removal from solution.

It is of interest to examine whether this rapid transfer to particulate matter leads to any detectable net removal of Po-210 from the water column. In Table V.4 are listed integrated vertical profile activities for total Pb-210 and Po-210, obtained by summing dissolved and particulate analyses. These integrations have been performed over the entire water column. The mean difference is +1.2 dpm/cm^2 with a standard deviation of 2.0 dpm/cm^2. This difference is in the direction of Po-210 enrichment but is not significantly different from zero. The water column as a whole appears to be nearly in secular equilibrium. Although removal of Po-210 from solution is rapid, as indicated by its

TABLE V.4

Integrated total Pb-210 and Po-210 profile activities, surface to bottom. Units dpm/cm^2

Station	Pb-210	Po-210	Po-Pb
12	31	31	0
15	32	40	+8
18	34	34	0
23	52	53	+1
27	54	59	+5
32	45	39	-6
		Mean	+1±2

distribution between dissolved and particulate phases, the mean sinking velocity of Po-210 in particulate form is not large enough to maintain a total Po-210/Pb-210 disequilibrium throughout the water column. This lack of any significant total disequilibrium makes the sinking velocity essentially indeterminate. One can, however, rule out the possibility that significant amounts of Po-210 in the deep sea associate with particles having residence times very much less than 4 years.

F. Summary and conclusions

Measurements of the distribution of dissolved Pb-210 have been compared with the reported distribution of Ra-226, and a pronounced radioactive disequilibrium in the deep sea has been observed, thus confirming the findings of Craig _et al_. (1973). Concentrations of excess Pb-210 in the particulate phase, however, account for only a small fraction (5-10%) of the Pb-210 deficiency in the dissolved phase, and increases in the particulate Pb-210 concentration with depth are not generally observed. To account for Pb-210 removal by _in situ_ scavenging alone requires that very rapid particle sinking rates be invoked, and it is suggested that much of the Pb-210 removal occurs by scavenging at the sediment-water interface. This conclusion is supported by the observation that Pb-210/Ra-226 activity ratios decrease as the sea floor is approached in both vertical and horizontal directions. It appears that chemical processes unique to the sea floor must be invoked, and it is suggested that Pb-210 removal occurs as a result of association with newly formed precipitates of manganese and iron oxides. The existence of a strong boundary sink for Pb-210 implies that rates of in situ reaction calculated from vertical advection-diffusion models can be seriously over-estimated. This consideration may apply generally for constituents having a boundary source or sink.

In contrast to Pb-210 with a residence time of several hundred years with respect to in situ scavenging, Po-210 displays a markedly different behavior, its residence time in solution being on the order of 4 years. Both elements are highly "reactive" in that they both have short residence times in the water column (<100 y), but they follow distinctly different pathways in being removed to the sediments. A similar kind of separation on a short time scale appears to operate for Th-230 and Pa-231 (Ku and Broecker, 1969).

CHAPTER VI

CONCLUDING REMARKS

Results of the present investigation support the following observations or conclusions from earlier work:

1.) Excess Pb-210, maintained by flux from the atmosphere, is present in the surface mixed layer of the sea.
2.) Lead-210 in the mixed layer is incorporated into particles, presumably as a result of biological activity, on a time-scale of about 2 years.
3.) Polonium-210 in the mixed layer is ordinarily deficient with respect to its equilibrium concentration, and its residence time is about 0.6 y.
4.) Particulate matter in the mixed layer, like plankton, is enriched in Po-210.
5.) Disequilibrium between Ra-226 and Pb-210 in the deep sea is a worldwide phenomenon and indicates removal of Pb-210 in a time comparable to its radioactive mean-life.

The following represent new observations or interpretations that differ from those of other authors:

1.) Surface-water residence times calculated for Pb-210 and Po-210 characterize their net rate of transfer from the dissolved to the particulate state. It may be that the rate of removal of these nuclides from the mixed layer is controlled by their net rate of incorporation by plankton and is not appreciably limited by retention of particles in the mixed layer.

2.) The population of particles bearing Po-210 in the mixed layer is replaced about 10 times per year. Interpretation of particle residence times in this region in terms of settling velocities is probably not appropriate. Removal of particles by filter-feeders and subsequent formation of fecal pellets, which sink very rapidly, may be as important as sinking of individual small particles. The effects of these two processes cannot be separated with the available data.

3.) Polonium-210 removed from the mixed layer is efficiently (50-100%) re-cycled within the upper several hundred meters of the water column. This conclusion is based on the presence of unsupported Po-210 in the thermocline at several stations in the tropical North Atlantic.

4.) The presence of excess Pb-210 in the thermocline can be explained as the result of physical transport, and re-cycling of Pb-210 at these depths appears to be negligible. By extrapolation one may speculate that re-cycling in the deep sea is also insignificant, but verification is not possible because of the operation of processes in the deep sea that rapidly remove Pb-210 from solution.

5.) Dissolved Pb-210 produced in the deep sea by radioactive decay of its parent is removed principally at the sediment-water interface, presumably by incorporation into authigenic phases, and its distribution in the water column is controlled by mixing processes. Scavenging by suspended particles in the water column appears to be of lesser importance.

6.) Polonium-210, in contrast to Pb-210, is rapidly scavenged by suspended material in the deep sea. Its residence time in solution is approximately 4 years. Because of the slow settling velocity of most particulate matter in the deep sea, the residence time of Po-210 in the water column is much longer than the radioactive mean-life, and no disequilibrium for <u>total</u> Po-210/Pb-210 in the water column can be detected.

It is appropriate to consider here the significance of the above conclusions with respect to marine geochemical studies in general. The detailed distribution of Pb-210 and Po-210 in dissolved and particulate phases in several vertical profiles has revealed that processes such as biological fixation, re-dissolution at depth, abiotic scavenging and scavenging at the sea floor are important in controlling the rates of removal of these nuclides and their rates of cycling in the sea. To suggest that the above-named processes might be important is hardly an innovation, but to demonstrate that they actually operate at certain rates, in specific cases, has not been an easy task. A recent review of marine chemistry (Goldberg <u>et</u> <u>al</u>., 1971) contains a classification of the chemical elements based upon our current understanding of how they behave in the sea. Only 59 elements were even classified.

Of these, 27 were in the "conservative" category, having concentrations in sea water roughly proportional to salinity. Of the remaining 32, only 4 elements could be said to have well-developed and readily described variability in concentration, as a function of depth, ocean basin, or both. From the results of more recent work, it may be possible to add a few additional elements to this category, but there is still a large group of elements for which even total concentrations in sea water are highly uncertain, let alone the pathways they follow in the ocean. This group consists largely of elements referred to as reactive, which are, almost by definition, present at very low abundances in sea water, and progress in understanding their behavior has been retarded by the familiar problems of analysis and sample contamination (Brewer and Spencer, 1970). These problems were avoided in the present study by selecting tracers for which the contamination potential is minimal and for which very sensitive analytical techniques are available. The use of a number of the natural decay series radionuclides is also recommended by the fact that they are supplied to the oceans at accurately known, or measurable, rates by decay of their parent nuclides. Therefore, their rates of transport within the oceans can be easily quantified.

Lead and polonium belong to the large group of so-called "reactive" elements in sea water which are typified by residence times in the ocean of less than 1,000 years (Goldberg, 1965), and it was one of the principal intentions of this investigation, when it was begun, to learn more about how the removal of these elements is controlled. In the two cases chosen for investigation, it has been possible to reach some important conclusions, but the contrasting behavior of Pb-210 and Po-210 warns against the formation of hasty predictions concerning the behavior of other reactive elements. Both nuclides are subject to rapid removal from the oceans, but each follows a different pathway. (Removal of Po-210 from the water column could not be detected,but this is a consequence of its very rapid radioactive turnover time. It was demonstrated that this element is rapidly attached to particles, most of which are removed in less than 100 years.)

Such a separation on a short time scale has also been indicated for Th-230 and Pa-231 (Ku and Broecker, 1969), two other highly reactive nuclides, which are produced in the water column by decay of uranium isotopes. One is tempted to put aside temporarily the foregoing admonition against categorization and to speculate that Th-230 and Pa-231 are separated in the deep water column in much the same way that Pb-210 and Po-210 are separated. The particulate Th-234 data of Lal (unpublished report, 1975) indicate that thorium very rapidly becomes attached to particles in the water column, as does Po-210. It is frequently assumed that Pa-231 behaves in the same way, but this has not been demonstrated. Perhaps Pa-231 is more stable in solution and follows a pathway similar to that of Pb-210. There has been speculation that Pa-231 may be stabilized in sea water by fluoride ion (Antal, 1966), and Pa-231 is known to be enriched relative to

Th-230 in some authigenic phases (Bernat and Goldberg, 1969; Ku and Broecker, 1969).

A more direct application of the results of this investigation is in the consideration of the marine geochemistry of stable lead. One must, of course, recognize the fact that stable lead is introduced at the sea surface, while Pb-210 is supplied throughout the water column by radioactive decay of its parent. Moreover, detailed predictions would require the assumption that Pb-210 and stable lead are introduced at the surface in the same chemical form. This assumption has not been tested. Whatever their similarities or differences might be at the point of introduction, however, it can be stated that both Pb-210 and stable lead are rapidly removed from the mixed layer. Tatsumoto and Patterson (1963) calculated a 10-y residence time for stable lead based on measured concentrations in surface water and their estimates of lead input rates. This estimate is probably somewhat too high, because later measurements of stable lead in surface sea water gave lower concentrations (Chow and Patterson, 1966). It may be reasonably expected that, following a residence of a few years in the mixed layer, both stable lead and Pb-210 would be transported to the deep sea in similar types of particles, and that no significant amounts would dissolve at depth. If there is no appreciable supply of dissolved stable lead in the deep sea, then the question of scavenging at the boundary versus the water column is irrelevant in considering the transport of stable lead to the sediments. The overall transit time for lead between the surface and the sea floor cannot be precisely evaluated. One might, to arrive at a possible upper limit, interpret the particle residence time in the mixed layer in terms of a 500 m/y sinking velocity (see Chapter IV). This would give a transit time of about 8 years. Lead isotope distributions in sediments are not consistent with appreciable mixing of isotopes from different continental sources (Chow and Patterson, 1962), and a more rapid transit via fecal pellets may be required (McCave, 1975).

A further note should be added concerning estimates of the mean oceanic residence time of lead, given in a number of published tables, which are on the order of several thousand years, in disagreement with estimates from Pb-210 measurements. These figures were based on rates of accumulation of lead in sediments given by Chow and Patterson (1962) and on a value of 20-30 ng/kg for the stable lead concentration of sea water (Tatsumoto and Patterson, 1963; Chow and Patterson, 1966). It has recently been suggested (C. C. Patterson, personal communication) that the true stable lead concentrations in deep ocean water are less than 1 ng/kg and that the higher results reported earlier were simply a measure of sample contamination. Concentrations this low would lead to greatly reduced estimates of the stable lead residence time, in closer agreement with the Pb-210 data.

Any investigation of the sort presented here is necessarily incomplete and leads to the suggestion that further work be done. One of the principal conclusions of this thesis is that the Pb-210/Ra-226 disequilibrium in the deep water is maintained largely by removal of Pb-210 at the boundaries and is not significantly driven by in situ scavenging processes. One of the major arguments which led to this conclusion is that vertical fluxes required to satisfy the in situ scavenging hypothesis cannot be maintained by particles sinking at reasonable speeds. This argument is based on the interpretation of vertical profiles of particulate Pb-210 concentration. A more direct test of the in situ scavenging model could be made with sediment traps placed at two or more depths in the deep water column. At any depth in the water, one would expect to receive a flux of Pb-210 originating at the surface, even in the absence of in situ scavenging at depth. This flux would be roughly equal to the local delivery rate of Pb-210 from the atmosphere, and it would be the background flux against which increments resulting from deep scavenging would have to be detected. In the North Atlantic the flux at the sea floor would be approximately twice as large as this background if all of the Pb-210 removal from the deep water occurred in particles. Greater sensitivity to the effects of in situ scavenging could be achieved in such an experiment in the South Pacific, where the atmospheric production of Pb-210 is lower and where Ra-226 concentrations in the deep water are higher.

Additional mapping of the horizontal distribution of Pb-210 in the deep ocean would be desirable. In particular, reliable samples from points far removed from lateral boundaries, such as in the North Pacific, are needed.

Specific regions of interest for more intensive study are suggested by Pb-210 data from the nepheloid layer of the western North Atlantic and by the anomalous mid-depth maximum in the particulate Pb-210 profile near the Mid-Atlantic Ridge. In both cases there are indications that Pb-210 may be rapidly scavenged in the water column by particles occurring in these regions, but this must be verified by measurements of both Ra-226 and Pb-210 in the particulate matter.

Identification of the site at which Pb-210 is removed from the oceans, as well as the rate, is by no means a trivial problem. If it could be verified that Pb-210 is not appreciably affected by *in situ* chemical processes and is removed from solution only at ocean boundaries (both sea surface and sea floor), then it could be stated that the behavior of Pb-210 approaches that of a radioactive conservative tracer, as defined by Craig (1969), and potential applications of Pb-210 as a tracer of mixing processes could be considered.

Further investigations utilizing the distribution of Po-210 in the water column might be profitable but should be preceded by attempts to improve the precision of the analyses. The major limitation in the present study was the unavoidable time delay between sampling and analysis. Also significant improvements in both Po-210 and Pb-210 analyses could be made by substituting Po-209 for the Po-208 tracer. With improved precision the possibility that Po-210/Pb-210 ratios in the deep water show systematic variations could be further examined.

References

Antal, P. S. (1966) Diagenesis of thorium isotopes in deep-sea sediments. Limnol. Oceanogr., 11, 278-292.

Applequist, M. D. (1975) Lead-210 in the deep sea: Pacific Ocean investigations. Unpublished M. S. dissertation, University of California, San Diego.

Beasley, T. M. (1969) Lead-210 production by nuclear devices. 1946-1958. Nature, 224, 573.

Bernat, M. and E. D. Goldberg (1969) Thorium isotopes in the marine environment. Earth Planet. Sci. Lett., 5, 308-312.

Betzer, P. R., K. L. Carder and D. W. Eggimann (1974a) Light scattering and suspended particulate matter on a transect of the Atlantic Ocean at 11°N. In: Suspended Solids in Water (ed. R. J. Gibbs) Plenum Press.

Betzer, P. R., G. W. Bolger, B. A. McGregor and P. A. Rona (1974b) The Mid-Atlantic Ridge and its effect on the composition of particulate matter in the deep ocean. (Abstract) Trans. Am. Geophys. Un., 55, 293.

Bhat, S. G., S. Krishnaswamy, D. Lal, Rama and W. S. Moore (1969) Th^{234}/U^{238} ratios in the ocean. Earth Planet. Sci. Lett., 5, 483-491.

Blifford, I. H., L. B. Lockhart, Jr. and H. B. Rosenstock (1952) On the natural radioactivity in the air. J. Geophys. Res., 57, 499-509.

Boyle, E. and J. M. Edmond (1975) Determination of transition metals in aqueous solution by APDC chelate co-precipitation. A.C.S. Series, in press.

Brewer, P. G. (1975) The distribution of particulate matter in the Atlantic Ocean. Earth Planet. Sci. Lett., in press.

Brewer, P. G. and D. W. Spencer (1970) Trace element intercalibration study. W.H.O.I. Ref. No. 70-62.

Broecker, W. S., J. Cromwell and Y.H.Li (1968) Rates of vertical eddy diffusion near the ocean floor based on measurements of the distribution of excess ^{222}Rn. Earth Planet. Sci. Lett., 5, 101-105.

Broecker, W. S., A. Kaufman and R. Trier (1973) The residence time of thorium in surface sea water and its implications regarding the rate of reactive pollutants. Earth Planet. Sci. Lett., 20, 35-44.

Broecker, W. S., Y. H. Li and J. Cromwell (1967) Radium-226 and radon-222: concentration in Atlantic and Pacific Oceans. Science, 158, 1307-1310.

Broecker, W. S. and T. H. Peng (1971) The vertical distribution of radon in the BOMEX area. Earth Planet. Sci. Lett., 11, 99-108.

Burton, W. M. and N. G. Stewart (1960) Use of long-lived natural radioactivity as an atmospheric tracer. Nature, 186, 584-589.

Chester, R. (1972) Geological, geochemical and environmental implications of the marine dust veil. In: The Changing Chemistry of the Oceans (eds. D. Dyrssen and D. Jagner) Nobel Symposium, 20, Wiley-Interscience, pp. 291-305.

Chow, T. J. and C. C. Patterson (1962) The occurrence and significance of lead isotopes in pelagic sediments. Geochim. Cosmochim. Acta, 26, 263-308.

Chow, T. J. and C. C. Patterson (1966) Concentration profiles of barium and lead in Atlantic waters off Bermuda. Earth Planet. Sci. Lett., 1, 397-400.

Craig, H. (1969) Abyssal carbon and radiocarbon in the Pacific. J. Geophys. Res., 74, 5491-5506.

Craig, H., S. Krishnaswami and B.L.K. Somayajulu (1973) Pb^{210}-Ra^{226}: radioactive disequilibrium in the deep sea. Earth Planet. Sci. Lett., 17, 295-305.

Cranston, R. E. and D. E. Buckley (1972) The application and performance of microfilters in analyses of suspended particulate matter. Unpublished manuscript, Report BI-R-72-7, Bedford Institute of Oceanography, Dartmouth, Nova Scotia.

Dymond, J., J. B. Corliss, G. R. Heath, C. W. Field, E. J. Dasch and H. H. Veeh (1973) Origin of metalliferous sediments from the Pacific Ocean. Geol. Soc. Am. Bull., 84, 3355-3372.

Edmond, J. M. (1970) Comments on the paper by T. L. Ku, Y. H. Li, G. G. Mathieu and H. K. Wong, "Radium in the Indian-Antarctic Ocean south of Australia". J. Geophys. Res., 75, 6878-6883.

Feely, H. W. and H. Seitz (1970) Use of lead 210 as a tracer of transport processes in the stratosphere. J. Geophys. Res., 75, 2885.

Figgins, P. E. (1961) The radiochemistry of polonium. NAS-NRC Nuclear Science Series, 3037, 68 pp.

Flynn, W. W. (1968) The determination of low levels of polonium-210 in environmental materials. Anal. Chim. Acta, 43, 221-227.

Goldberg, E. D. (1954) Marine geochemistry I. Chemical scavengers of the sea. J. Geol., 62, 249-265.

Goldberg, E. D. (1963) Geochronology with lead-210. In: Radioactive Dating, Int'l. At. En. Agency, Vienna, pp. 121-131.

Goldberg, E. D. (1965) Minor elements in sea water. In: Chemical Oceanography, v.1 (eds. J. P. Riley and G. Skirrow) Academic Press, pp. 163-196.

Goldberg, E. D., W. S. Broecker, M. G. Gross and K. K. Turekian (1971) Marine chemistry. In: Radioactivity in the Marine Environment, NAS-NRC, pp. 137-146.

Gorsuch, T. T. (1959) Radiochemical investigations on the recovery for analysis of trace elements in organic and biological materials. Analyst, 84, 135-173.

Israel, H. (1951) Radioactivity of the atmosphere. In: Compendium of Meteorology. Am. Met. Soc., Boston, pp. 155-161.

Jaworowski, Z. (1966) Temporal and geographic distribution of Radium D (Lead-210). Nature, 212, 886-889.

Junge, C. E. (1963) Air chemistry and Radioactivity. Academic Press, New York.

Kharkar, D. P., J. Thomson, K. K. Turekian and W. O. Forster (1975) Uranium and thorium decay series nuclides in plankton from the Caribbean. Limnol. Oceanogr., in press.

Koblentz-Mishke, O. J., V. V. Volkovinsky and J. G. Kabanova (1970) Plankton primary production of the world ocean. In: Scientific Exploration of the South Pacific (ed. W. S. Wooster) NAS, Washington, pp. 183-193.

Koide, M., J. J. Griffin and E. D. Goldberg (1975) Records of plutonium fallout in marine and terrestrial samples. J. Geophys. Res., 80, 4153-4162.

Krauskopf, K. B. (1956) Factors controlling the concentrations of thirteen raremetals in sea water. Geochim. Cosmochim. Acta, 9, 1-32B.

Ku, T. L. and W. S. Broecker (1969) Radiochemical studies on manganese nodules of deep-sea origin. Deep-Sea Res., 16, 625-637.

Ku, T. L., Y. H. Li, G. G. Mathieu and H. K. Wong (1970) Radium in the Indian-Antarctic Ocean south of Australia. J. Geophys. Res., 75, 5286-5292.

Kuo, H. H. and G. Veronis (1973) The use of oxygen as a test for an abyssal circulation model. Deep-Sea Res., 20, 871-888.

Lambert, G. and M. Nezami (1965) Importance des retombees seches dans le bilan du plomb 210. Ann. Geophysique, 21, 245-251.

Lambert, G., J. Sanak and B. Ardouin (1974) Origine marine des exces de polonium 210 dans la basse atmosphere Antarctique. J. Rech. Atmos., 8, 647-648.

McCave, I. N. (1975) Vertical flux of particles in the ocean. Deep-Sea Res., 22, 491-502.

Martell, E. A. and H. E. Moore (1974) Tropospheric aerosol residence times: a critical review. J. Rech. Atmos., 8, 903-910.

Matsumoto, E. (1975) ^{234}Th-^{238}U radioactive disequilibrium in the surface layer of the ocean. Geochim. Cosmochim. Acta, 39, 205-212.

Menzel, D. W. (1974) Primary productivity, dissolved and particulate organic matter, and the sites of oxidation of organic matter. In: The Sea, v. 5 (ed. E. D. Goldberg) Wiley-Interscience, pp. 659-678.

Moore, H. E., S. E. Poet and E. A. Martell (1973) ^{222}Rn, ^{210}Pb, ^{210}Bi and ^{210}Po profiles and aerosol residence times versus altitude. J. Geophys. Res., 78, 7065-7075.

Noshkin, V. E. and V. T. Bowen (1972) Concentrations and distributions of long-lived fallout radionuclides in open ocean sediments. IAEA Symposium on Interaction of Radioactive Constituents of the Marine Environment, Seattle, July 1972.

Nozaki, Y. and S. Tsunogai (1973) Lead-210 in the North Pacific and the transport of terrestrial material through the atmosphere. Earth Planet. Sci. Lett., 20, 88-92.

Östlund, H. G., H. G. Dorsey and C. G. Rooth (1974) GEOSECS North Atlantic radiocarbon and tritium results. Earth Planet. Sci. Lett., 23, 69-86.

Peirson, D. H., R. S. Cambray, and G. S. Spicer (1966) Lead-210 and polonium-210 in the atmosphere. Tellus, 18, 427-433.

Poet, S. E., H. E. Moore and E. A. Martell (1972) Lead 210, bismuth 210, and polonium 210 in the atmosphere: accurate ratio measurement and application to aerosol residence time determination. J. Geophys. Res., 77, 6515-6527.

Prospero, J. M. and T. N. Carlson (1972) Vertical and areal distribution of Saharan dust over the western Equatorial North Atlantic Ocean. J. Geophys. Res., 77, 5255-5265.

Rama, M. Koide and E. D. Goldberg (1961) Lead-210 in natural waters. Science, 134, 98-99.

Shannon, L. V., R. D. Cherry and M. J. Orren (1970) Polonium-210 and lead-210 in the marine environment. Geochim. Cosmochim. Acta, 34, 701-711.

Sheldon, R. W., T.P.T. Evelyn and T. R. Parsons (1967) On the occurrence and formation of small particles in sea water. Limnol. Oceanogr., 12, 367-375.

Sill, C. W. and D. G. Olson (1970) Sources and prevention of recoil contamination of solid-state alpha detectors. Anal. Chem., 42, 1596-1607.

Somayajulu, B.L.K. and H. Craig (1973) Pb-210 and Ra-226 in Atlantic and Pacific deep water (abstract). Trans. Am. Geophys. Un., 54, 299.

Spencer, D. W. and P. G. Brewer (1971) Vertical advection diffusion and redox potentials as controls on the distribution of manganese and other trace metals dissolved in waters of the Black Sea. J. Geophys. Res., 76, 5877-5892.

Stumm, W. and J. J. Morgan (1970) Aquatic Chemistry. Wiley-Interscience, 583 pp.

Sverdrup, H. U., M. W. Johnson and R. H. Fleming (1942) The Oceans. Prentice-Hall, 1087 pp.

Szabo, B. J., F. F. Koczy and G. Ostlund (1967) Radium and radiocarbon in Caribbean waters. Earth Planet. Sci. Lett., 3, 51-61.

Tatsumoto, M. and C. C. Patterson (1963) The concentration of common lead in sea water. In: Earth Science and Meteorites (eds. J. Geiss and E. D. Goldberg). North-Holland Publ. Co., Amsterdam, pp. 74-89.

Tsunogai, S. and Y. Nozaki (1971) Lead-210 and polonium-210 in the surface water of the Pacific. Geochem. J., 5, 165-173.

Tsunogai, S., Y. Nozaki and M. Minagawa (1974) Behavior of heavy metals and particulate matters in sea water expected from that of radioactive nuclides. J. Oceanogr. Soc. Japan, 30, 251-259.

Turekian, K. K., Kharkar, D. P. and J. Thomson (1974) The fate of Pb^{210} and Po^{210} in the ocean surface. J. Rech. Atmos., 8, 639-646.

Volchok, H. L. and J. L. Kulp (1956) The ionium method of age determination. Geochim. Cosmochim. Acta, 11, 219-246.

Weller, R. I., E. C. Anderson and J. H. Barker, Jr. (1965) Radioactive contamination of contemporary lead. Nature, 206, 1211-1212.

Wilkening, M. H. and W. E. Clements (1975) Radon 222 from the ocean surface. J. Geophys. Res., 80, 3828-3830.

Zelenov, K. K. (1964) Iron and manganese in exhalations of the submarine Banu Wuhu volcano (Indonesia). Doklady Akad. Nauk SSSR, 155, 94-96.

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The distribution of Pb-210 and Po-210 in dissolved (<0.4 micron) and particulate (>0.4 micron) phases has been measured at ten stations in the tropical and eastern North Atlantic and at two stations in the Pacific. Both radionuclides occur principally in the dissolved phase. Unsupported Pb-210 activities, maintained by flux from the atmosphere, are present in the surface mixed layer and penetrate into the thermocline to depths of about 500 m. Dissolved Po-210 is ordinarily present in the mixed layer at less than equilibrium concentrations, suggesting rapid biological removal of this nuclide. Particulate matter is enriched in Po-210, with Po-210/Pb-210 activity ratios greater than 1.0, similar to those reported for phytoplankton. Box-model calculations yield a 2-y residence time for Pb-210 and a 0.6-y residence time for Po-210 in the mixed layer. These residence times are considerably longer than the time calculated for turnover of particles in the mixed layer (about 0.1 y). At depths of 100-300 m, Po-210 maxima occur and unsupported Po-210 is frequently present. Calculations indicate that at least 50% of the Po-210 removed from the mixed layer is recycled within

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3. Removal

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Comparison of the Pb-210 distribution with the reported distribution of Ra-226 at nearby GEOSECS stations has confirmed the widespread existence of a Pb-210/Ra-226 disequilibrium in the deep sea. Vertical profiles of particulate Pb-210 were used to test the hypothesis that Pb-210 is removed from deep water by *in situ* scavenging. With the exception of one profile taken near the Mid-Atlantic Ridge, significant vertical gradients in particulate Pb-210 concentration were not observed, and it is necessary to invoke exceptionally high particle sinking velocities (>10 m/d) to account for the inferred Pb-210 flux. It is proposed that an additional sink for Pb-210 in the deep sea must be sought. Estimates of the dissolved Pb-210/Ra-226 activity ratio at depths greater than 1,000 m range from 0.2 to 0.8 and reveal a systematic increase, in both vertical and horizontal directions, with increasing distance from the sea floor. This observation implies rapid scavenging of Pb-210 at the sediment-water interface and is consistent with a horizontal eddy diffusivity of 3-6 x 10^7 cm^2/s. The more reactive element Po, on the other hand, shows evidence of rapid *in situ* scavenging. In filtered sea water, Po-210 is deficient, on the average by ca.10% relative to Pb-210; a corresponding enrichment is found in the particulate phase. Total inventories of Pb-210 and Po-210 over the entire water column, however, show no significant departure from secular equilibrium, and reliable estimates of particle sinking rates cannot be made.

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6.

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15. Supplementary Notes

16. Abstracts

The distribution of Pb-210 and Po-210 in dissolved (<0.4 micron) and particulate (>0.4 micron) phases has been measured at ten stations in the tropical and eastern North Atlantic and at two stations in the Pacific. Both radionuclides occur principally in the dissolved phase. Unsupported Pb-210 activities, maintained by flux from the atmosphere, are present in the surface mixed layer and penetrate into the thermocline to depths of about 500 m. Dissolved Po-210 is ordinarily present in the mixed layer at less than equilibrium concentrations, suggesting rapid biological removal of this nuclide. Particulate matter is enriched in Po-210, with Po-210/Pb-210 activity ratios greater than 1.0, similar to those reported for phytoplankton. Box-model calculations yield a 2-y residence time for Pb-210 and 0.6-y residence time for Po-210 in the mixed layer. These residence times are considerably longer than the time calculated for turnover of particles in the mixed layer (about 0.1 y). At depths of

17. Key Words and Document Analysis. 17a. Descriptors

1. Pb-210/Po-210
2. Distribution
3. Removal

100-300 m, Po-210 maxima occur and unsupported Po-210 is frequently present. Calculations indicate that at least 50% of the Po-210 removed from the mixed layer is recycled within the thermocline. Similar calculations for Pb-210 suggest much lower recycling efficiencies.

17b. Identifiers/Open-Ended Terms

Comparison of the Pb-210 distribution with the reported distribution of Ra-226 at nearby GEOSECS stations has confirmed the widespread existence of a Pb-210/Ra-226 disequilibrium in the deep sea. Vertical profiles of particulate Pb-210 were used to test the hypothesis that Pb-210 is removed from deep water by <u>in situ</u> scavenging. With the exception of one profile taken near the Mid-Atlantic Ridge, significant (over)

17c. COSATI Field/Group

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vertical gradients in particulate Pb-210 concentration were not observed, and it is necessary to invoke exceptionally high particle sinking velocities (>10 m/d) to account for the inferred Pb-210 flux. It is proposed that an additional sink for Pb-210 in the deep sea must be sought. Estimates of the dissolved Pb-210/Ra-226 activity ratio at depths greater than 1,000 m range from 0.2 to 0.8 and reveal a systematic increase, in both vertical and horizontal directions, with increasing distance from the sea floor. This observation implies rapid scavenging of Pb-210 at the sediment-water interface and is consistent with a horizontal eddy diffusivity of 3-6 x 10^7 cm^2/s. The more reactive element Po, on the other hand, shows evidence of rapid *in situ* scavenging. In filtered sea water, Po-210 is deficient, on the average, by ca. 10% relative to Pb-210; a corresponding enrichment is found in the particulate phase. Total inventories of Pb-210 and Po-210 over the entire water column, however, show no significant departure from secular equilibrium, and reliable estimates of particle sinking rates cannot be made.