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URANIUM AND THORIUM DECAY SERIES NUCLIDE ABUNDANCES IN MARINE PLANKTON

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IN MARINE PLANKTON

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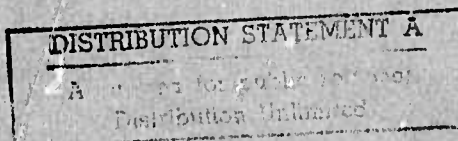New Haven, Connecticut 06520

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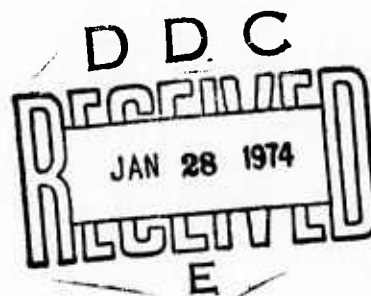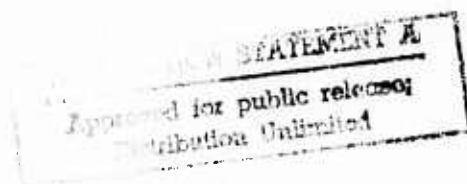
SUMMARY

A procedure for the analysis of marine plankton for selected members of the uranium and thorium decay series has been developed.

The Po^{210} and Pb^{210} concentrations of plankton when compared to surface sea water concentrations of these two nuclides can be used to determine the regional aerosol Pb^{210} flux to the oceans and the mean residence times of Po^{210} and Pb^{210} as they are removed by settling planktonic debris in surface waters of various regions of the world oceans.

The Po^{210}/Pb^{210} activity ratio in plankton reflects the ambient oceanic value which in turn is related to the productivity. The Th^{228}/Ra^{228} activity ratio of plankton yields similar results. As the Ra^{228} comes from shelf sediments free of its daughter, Th^{228}, the ratio of Th^{228}/Ra^{228} in the water also reflects distance from source of injection of the Ra^{228}.

The Ra^{226} concentration of plankton varies widely over the ocean but generally is higher in the phytoplankton-enriched samples. Its concentration can be used to assess the Ra^{228} concentration in plankton once the regional surface sea water ratio of Ra^{228}/Ra^{226} is known.

In regions of upwelling the deep water shows a deficiency of Po^{210} (and presumably Pb^{210}) relative to Ra^{226}. This is attributable to the large flux of particulates raining down from above in such highly productive regions.

The Th^{228} concentration of plankton permits an estimate of the maximum Th^{234} concentration in plankton. Pa^{234}, the 1.16 minute half life daughter of Th^{234}, is the major high energy γ emitter in plankton aside from potassium. A large γ "hot spot" is not expected from this source in plankton particles and is probably not a source of major background for towed scintillation detectors.

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I. AIM OF STUDY

The aim of this study has been to determine the concentrations of members of the uranium and thorium decay series in marine plankton over large areas of the Atlantic Ocean and to use this information in oceanographic problems. These radionuclides are partitioned in different ways between sea water and plankton and particulates in the ocean column, and this fact can be used to assist in the understanding of: (1) surface ocean circulation patterns, and (2) the sources and sinks of the nuclides in the oceans.

The accomplishment of these two goals also provides an opportunity for the assessment of the expected dosages in plankton of the three different types of radiation, α, β, and γ as a function of geography. In principle, although the γ activity in particles can be obtained by direct measurement of plankton, the short half lives of the major γ emitters, Po^{210} and Th^{234} (Pa^{234}), are best estimated from geochemical inferences of the sort derivable from this study.

II. PLAN OF STUDY

The study is divided into three major efforts: (1) the choice of
nuclides to be determined and the development of a scheme to analyze marine
plankton for these nuclides; (2) the collection of a suite of plankton
samples to be analyzed for these nuclides; and (3) the interpretation of
the results of these analyses.

The members of the U^{238}, U^{235}, and Th^{232} decay series are shown in
Table 1. The nuclides chosen for study on the basis of geochemical and
half-life arguments are the following: for the Th^{232} decay series, Th^{232},
Ra^{228}, and Th^{228}; for the U^{238} decay series, U^{238}, Th^{234}, U^{234}, Ra^{226},
Pb^{210}, and Po^{210}.

We actually were able to measure Th^{234} in only one sample because of
its short half life (24 days) and the normally long time lapse between
sample collection and analysis. We also made only a few measurements of
the Ra^{228} activity because of its low concentration. We were confident
that the measurement of the Ra^{226} activity would give us some information
on Ra^{228}, should we need it, based on surface sea water values of the $Ra^{228}/$
Ra^{226} activity ratios in the Atlantic that were being reported in the
literature by others at the time of our work.

The collection of the plankton samples was done primarily by others
and either shipped directly back to us or made available to us from collec-
tions already made. All the samples we report on are ones that were
analyzed sufficiently rapidly after collection to permit the determination
of unsupported Po^{210} (138 day half life).

The interpretation of the results is presented as a series of self-
contained reports, some of which have already been submitted for publication.

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Table 1: The uranium and thorium decay series.

	U-238 SERIES				Th-232 SERIES				U-235 SERIES			
Np												
U	U-238 4.51×10⁹ y	U-234 2.48×10⁵ y							U-235 7.13×10⁸ y			
Pa	Pa-234 1.18m								Pa-231 3.2×10⁴ y			
Th	Th-234 24.1 d	Th-230 7.5×10⁴ y			Th-232 1.39×10¹⁰ y	Th-228 1.9 y			Th-231 25.6 h	Th-227 18.6 d		
Ac						Ac-228 6.13h			Ac-227 22.0 y			
Ra		Ra-226 1622 y			Ra-228 6.7 y	Ra-224 3.64 d				Ra-223 11.1 d		
Fr												
Rn		Rn-222 3.825 d				Rn-220 54.5 s				Rn-219 3.92 s		
At												
Po		Po-218 3.05m	Po-214 1.6×10⁻⁴ s	Po-210 138.4 d		Po-216 0.158 s	Po-212 3×10⁻⁷ s			Po-215 1.83×10⁻³ s		
Bi			Bi-214 19.7m	Bi-210 5.0 d			Bi-212 60.5 m				Bi-211 2.16 m	
Pb		Pb-214 26.8 m	Pb-210 21.4 y	Pb-208 stable		Pb-212 10.6 h	Pb-208 stable			Pb-211 36.1 h	Pb-207 stable	
Tl							Tl-208 3.1 m				Tl-207 4.79 m	

Our analytical scheme for the determination of as many radionuclides of the uranium and thorium decay series of interest as possible was constrained by the fact that normally only about one gram of dry plankton was availab? for our work from any one location. The problem then was to develop techniques which were mutually compatible and provided the maximum accuracy of measurement for the expected low levels of radioactivity. Three areas of development were required to solve this problem:

(1) A high yield reliable method of chemical separation for the nuclides of interest had to be developed which could be done on single aliquot of plankton.

(2) Counting systems with the proper capabilities for low level counting of α and β radiation had to be established.

(3) Calibration of appropriate standards and spikes had to be effected to assure the accuracy of the measurements.

Although the development of each of these categories occurred simultaneously, they are separated in this report to feature the peculiar problems of each.

The normal "flow sheet" for the analysis of plankton from the moment we receive it in our laboratory to the final result is presented in the last section.

A. The details of the procedures

1. Chemical separation sequence

a. Polonium analysis

From the extensive study of Flynn (1968) it was evident that the polonium analysis should be performed first in the separation sequence because of the element's tendency to absorb on glassware. In addition, the volatility of the element at temperatures as low as 150°C suggested that it would be better to wet ash the plankton samples, and to use an artificial polonium isotope as spike. Po^{209} would have been preferred because of its halflife and α energy, but Po^{208} was chosen because it was commercially available.

Preliminary experiments with Po^{208} and Po^{210} in 1 $\overline{M}$ HCl solutions confirmed that polonium was plated quantitatively on Ag discs after 4 hr. at ∿ 80°C (Flynn, 1968). Analysis of a large plankton sample, half of which had been dry ashed at 600°C then spiked, the other half of which had been

spiked then wet ashed with HNO_3-$HClO_4$ mixture, showed that the former aliquot had lost 50% of its Po^{210}.

A problem with Fe^{3+} in plankton solutions, which caused discoloration of the Ag disc and a consequent loss of polonium α spectra resolution, was eliminated by reducing Fe^{3+} ion with $\sim$ 100 mg ascorbic acid before plating. To prevent polonium plating on both sides of the Ag disc, Teflon tape (initially a Teflon spray coating) was used to mask one side of the disc and the plate recessed (unmasked side up) in a small Teflon holder. Finally, the added ascorbic acid began to show signs of breakdown after 3 hours at 80°C, so this appeared a good compromise period between plating efficiency and good alpha resolution.

The polonium isotopes, Po^{208} (α, 5.11 MeV) and Po^{210} (α, 5.30 MeV) were readily resolved by α spectrometry.

b. Ra^{226} analysis

It was decided to perform two Ra^{226} analyses on each sample, one strictly to determine Ra^{226} after the polonium determination and one to ascertain whether there had been any loss of Ra^{226} (and consequently Ra^{228}) in the subsequent ion exchange procedures (i.e. using Ra^{226} as a tracer for Ra^{228}). The simplest method for Ra^{226} analysis is measurement of the α activity of Rn^{222} after a known storage time, when the fractional radioactive build-in with Ra^{226} can be calculated (Lucas, 1964).

In preliminary experiments using an apparatus similar to that of Bhat (1970), it was found that continuous flow bubbling of helium through standard solutions gave variable yields either because of incomplete removal of Rn^{222} from solution or incomplete trapping of Rn^{222} in the liquid nitrogen trap because of flow rate. This difficulty was overcome by installation of

a peristaltic pump which recirculated the helium repeatedly through the system. The ZnS(Ag) coated cells containing Rn^{222} in $\sim$ 38 cm Hg helium were counted at least 4 hr. after filling on a Teledyne-Isotopes Radon Counting System, Type 102, at which time radioactive equilibrium had been achieved by short lived α emitting daughters of Rn^{222}.

c. Uranium analysis

The first step in uranium analysis was performed by anion exchange after the Ra^{226} analysis at high acid molarity (8 $\overline{N}$ HCl). The subsequent solvent extraction and plating techniques are essentially those of Ku (1965, 1966). Uranium mounts were analysed by α spectrometry, and the principal α energies (U^{238}, 4.19 MeV; U^{234}, 4.77 MeV; U^{232}, 5.32 MeV) were readily resolved.

One problem which exists in uranium analysis is that the most suitable spike isotope is U^{232}. Unless freshly purified, this isotope is accompanied by its daughter, Th^{228} ($t_{1/2}$ = 1.91 yr), one of the nuclides of interest in this study. Thus if this spike is used, Th^{228} values for plankton are unobtainable. If Th^{230} spike is used instead U^{232}-Th^{228}, only the U^{234}/U^{238} activity ratio can be determined in a uranium analysis.

Spiked uranium analyses yielded chemical efficiencies of 50-70%.

d. Lead analysis

Lead was separated after uranium by anion exchange from 1.5 $\overline{M}$ HCl, following the method of Rama et al. (1962). Mounts for β^- counting to follow the radioactive build-in of Bi^{210} were prepared by mounting $PbCrO_4$. The chemical efficiency of separation was 65-90%.

e. Th analysis

Thorium separations were made by an anion exchange method from 7 $\overline{N}$ HNO_3

solution as described by Bhat (1970). The purified thorium was mounted for α spectrometry by the method of Ku (1966), and the principal α energies (Th^{232}, 4.01 MeV; Th^{230}, 4.68 MeV; Th^{228}, 5.42 MeV) were readily resolved. Chemical efficiencies from thorium analyses spiked with Th^{230} were 60-80%.

      f. Ra^{228} analysis

Ra^{228} was determined by chemical separation of its daughter Ac^{228} (β^-, $t_{1/2}$ = 6.13 hr) and following the decay of Ac^{228} (S. Krishnaswami, personal communication to D.P.K.) Ac^{228} was adsorbed on a $Fe(OH)_3$ precipitate, roasted and deposited as a slurry on a 3.3 x 1.1 cm. Lucite planchette. The planchette was then counted for decay of Ac^{228} on a Lal type flow gas counter. The chemical separation of Ac^{228} on $Fe(OH)_3$ and the physical transfer of $Fe(OH)_3$ to the planchette were assumed quantitative.

    2. Counting systems

      a. Alpha spectrometers

Two alpha spectrometers are used in this study, providing three counting channels, all with 450 mm^2 silicon surface barrier detectors. The dual system comprises two ORTEC 101-201 preamplifier-amplifier combinations fed to the halves of the memory of a TMC 400 channel analyzer. Background levels on the detectors of this system are too high in the Th^{228} peak region ($\sim$ 0.01 cpm) to be used in this study, and this spectrometer is used for polonium and uranium analyses only.

The second spectrometer has a new detector, and is used specifically for thorium analyses. This system consists of a Canberra #808 preamplifier, #816 amplifier, and #1461 biased amplifier, fed to a Nuclear Data 128 channel analyzer. Background in the Th^{228} peak region is 0.003 cpm.

The full width half maximum resolution of all three spectrometer

channels is in the range 60-80 keV on normal mounts counted for a few days.

b. Gas flow alpha proportional counter.

This system was used in the calibration of the Po^{208} spike, and routinely to give a quick indication of the level of activity on other alpha mounts. It consists of an NMC PCC 10A Proportional Counter Converter (2.25" diameter chamber) coupled to a TMC SG - 2A combined high voltage supply and scaler.

P-10 (10% CH_4 in Ar) is used as flow gas, and gives a background of $\sim$ 0.09 cpm on the alpha plateau at 1150 volts. This counter's α efficiency is 51% as determined by an Am^{241} source on stainless steel.

c. Gas flow beta proportional counter.

This counter is a Sharp LB-100 low level anticoincidence counting system, with a 1.25" diameter 80 $\mu g/cm^2$ Mylar window. It is used exclusively to monitor the growth of Bi^{210} (β^-, 1.16 MeV, 5.01 dy.) towards radioactive equilibrium with Pb^{210} (β^-, 0.015 MeV, 22 yr.) in lead mounts. Two counting windows are used, with a total background of 0.50 $\pm$ 0.01 cpm using P-10 as flow gas. Counting efficiency for Bi^{210} ($\sim$ 30 mg $PbCrO_4$, 5.2 mg/cm^2 Mylar filter for Po^{210} αs) is 28%.

d. Gas flow beta geiger counter.

This counter consists of a Lal-type detector and guard detector, with Sharp "Low beta" anticoincidence electronics. It is used exclusively to measure the decay of Ac^{228} (β^-, 1.11, 6.13 hrs.) in Ra^{228} analyses. The inherent counter background is 0.13 $\pm$ 0.01 cpm, operated in the geiger region and flowing Q gas (0.95% isobutane in He). Efficiency for Ac^{228} (20 mg. $(Fe(OH)_3$, 80 $\mu g/cm^2$ Mylar cover) is 32%.

e. Radon counting system.

This is a commercial system, a Teledyne Isotopes Model 102. The system has two independent counting channels for 125 ml. ZnS (Ag) detector cells. Typical detector backgrounds, rising slightly over a period of two years, are in the range 0.15-0.30 cpm.

3. Laboratory calibrations.

A Th^{230} spike solution, calibrated at 3.7 dpm/ml, was obtained from Lamont Doherty Geological Observatory. This spike was chosen as our primary reference, and the specific activity was assumed error free. Alpha spectrometry confirmed the solution free from Th^{232} and Th^{228}; therefore the spike was suitable for these isotopes in plankton analyses.

a. Aged Th^{232}-Th^{228} solution.

To calibrate the Ac^{228} chemical separation efficiency and the Lal-type counter efficiency for Ac^{228}, a Ra^{228} standard was required. Since none was commercially available, an aged $Th(NO_3)_4$ salt was dissolved in 8 $\overline{N}$ HNO_3 and standardized against the Th^{230} spike.

Runs with Th^{232}-Th^{228} solution alone. (Thorium isotopes separated by ion exchange, activity ratios determined by alpha spectrometry.)

	Th^{232}/Th^{228}	Th^{230}/Th^{232}	Th^{230}/Th^{228}
Run 1	0.975 + 0.014	0.120 + 0.004	0.123 + 0.004
Run 2	0.972 + 0.020	0.129 + 0.006	0.132 + 0.006
Run 3	0.995 + 0.020	0.102 + 0.005	0.102 + 0.005
Mean	0.981 + 0.011	0.117 + 0.003	0.119 + 0.003

Runs with 1 ml Th^{230} reference solution added to 2 ml Th^{232}-Th^{228} solution Y.

	Th^{232}/Th^{228}	Th^{230}/Th^{232}	Th^{230}/Th^{228}
Run 1	0.992 ± 0.017	0.324 ± 0.008	0.327 ± 0.008
Run 2	0.984 ± 0.023	0.325 ± 0.011	0.330 ± 0.011
Run 3	1.016 ± 0.024	0.327 ± 0.011	0.332 ± 0.011
Mean	0.997 ± 0.012	0.325 ± 0.006	0.326 ± 0.006

From the mean (Th^{228}/Th^{232}) activity ratios above, it is evident that the 4n radioactive series is close to secular equilibrium in the solution. The Th^{230} contaminant has a mean activity ratio of 0.118 ± 0.002 relative to Th^{232} and Th^{228}. Addition of 3.7 dpm Th^{230} spike to 2 ml of the solution causes this ratio to increase to 0.326 ± 0.004.

Then $(Th^{230}_{contaminant})/Th^{232} = 0.118 \pm 0.002$

and, in 2 ml solution Y,

$(Th^{230}_{contaminant} + Th^{230}_{spike})/Th^{232} = 0.326 \pm 0.004$

so specific activity of Th^{232} in solution $= 3.7/2 \ (0.208 \pm 0.004)$

$$= 8.9 \pm 0.2 \ \text{dpm/ml.}$$

Two aliquots of the $Th^{232}-Th^{228}$ solution were taken, the thorium isotopes separated by ion exchange, and Ac^{228} separated from the resultant solution containing Ra^{228}. The combined separation and counting efficiency for Ac^{228} was determined to be $31.4 \pm 1.8\%$ and $33.16 \pm 1.8\%$ (mean $32.3 \pm 1.3\%$), based on Ra^{228} specific activity of 8.9 ± 0.2 dpm/ml.

b. Aged $U^{232}-Th^{228}$ spike.

The history of this spike, also obtained from Lamont Doherty Geological Observatory, is well known (Kaufman, 1964; Ku, 1966). Extraction of uranium and thorium by ion exchange from the spike, followed by alpha spectrometric analysis, showed no thorium isotopes other than Th^{228} present, and only

U^{233} activity (= 0.024 U^{232} specific activity) besides U^{232}. This spike was used in uranium analyses of plankton samples, and was calibrated against the Th^{230} reference solution.

Runs with 1 ml Th^{230} reference solution added to 1 ml U^{232}-Th^{228} solution:

$$Th^{228}/Th^{230}$$

$$1.460 \pm 0.044$$

$$1.509 \pm 0.056$$

Mean $\qquad 1.485 \pm 0.036$

The mean value of the Th^{228}/Th^{230} activity ratio corresponds to a Th^{228} specific activity of 5.49 $\pm$ 0.13 dpm/ml. Since the purification of U^{232} in the spike was performed in 1950, transient equilibrium in the solution has been attained, corresponding to a Th^{228}/U^{232} activity ratio of 1.03. This yields a value of 5.33 $\pm$ 0.13 dpm/ml U^{232}, as of January, 1972.

   c. K120a uraninite solution.

This solution was obtained from R. Ku (University of Southern California) who had prepared it from a concordant uraninite in February, 1971. All the 4n + 2 series nuclides should be in secular equilibrium with the possible exception of Po^{210}, which could have volatilized during dissolution (Flynn, 1968). The solution was used to calibrate the Sharp proportional counter for Pb^{210} analyses. It itself was calibrated via the U^{232}-Th^{228} spike.

Runs with 1 ml U^{232}-Th^{228} spike added to 1 ml K120a.

	U^{234}/U^{238}	Mean U^{238}, U^{234}/U^{232}	Th^{230}/Th^{228}
Run 1	1.023 ± 0.028	0.974 ± 0.026	0.977 ± 0.031
Run 2	0.977 ± 0.024	0.920 ± 0.022	0.941 ± 0.026
Run 3	0.985 ± 0.032	0.941 ± 0.030	0.956 ± 0.023
Mean	0.995 ± 0.016	0.945 ± 0.015	0.958 ± 0.015

From the mean U^{234}/U^{238} activity ratio it is evident the $4n + 2$ radioactive series is in secular equilibrium in the K120a solution. The mean U^{238}, U^{234}/U^{232}) and Th^{230}/Th^{228} activity ratios correspond to specific activities of 5.04 ± 0.15 and 5.26 ± 0.15 dpm/ml (mean 5.15 ± 0.11 dpm/ml) for the $4n + 2$ series nuclides in the solution.

Aliquots of the K120a solution (1 ml, 2 ml and 5 ml) were used to calibrate the Sharp counter efficiency for Bi^{210}. The efficiency found was $28.3 \pm 0.9\%$ based on a Pb^{210} specific activity of 5.15 dpm/ml.

d. Rn^{222} extraction and counting efficiency.

The radon extract system used is described above. The combined physical extraction and counting efficiencies for Rn^{222} were determined by standards prepared from an Amersham Searle Ra^{226} solution, a Lamont Doherty Geological Observatory Ra^{226} standard and the K120a solution. The results for these standards in various counting vessels on both counting channels are shown below. Corrections are made to the raw data for detector background, Rn^{222} ingrowth from Ra^{226} during storage, and Rn^{222} decay from separation to the midpoint of counting.

Extraction and counting efficiencies of radon in the extraction
system and the detectors used.

Vessel	Standard	Channel A	Channel B
9	AS 2	93.5 ± 0.6	
9	LDGO	91.7 ± 0.5	92.5 ± 0.5
5	AS 2	89.6 ± 0.6	92.0 ± 0.6
6	AS 3	90.2 ± 0.7	90.4 ± 0.7
4	LDGO	96.4 ± 0.6	93.0 ± 0.9
3	AS 3	94.2 ± 0.9	93.5 ± 1.1
3	LDGO	91.2 ± 0.3	91.1 ± 0.5
7	K120a	91.9 ± 0.7	89.4 ± 0.7
6	AS 2	89.0 ± 0.8	91.9 ± 0.6
6	AS 3	94.6 ± 0.7	93.5 ± 0.5
3	LDGO	93.5 ± 0.3	
7	AS 2	93.8 ± 0.5	92.5 ± 0.5
5	LDGO	94.9 ± 0.5	96.0 ± 0.5
14	AS 2	89.0 ± 0.5	90.8 ± 0.4
9	AS 3	94.1 ± 0.5	91.2 ± 0.3
8	LDGO	94.3 ± 0.3	94.0 ± 0.4
6	K120a	91.5 ± 0.7	90.6 ± 0.6

The efficiency used in calculations from either channel was 92± 2%.

e. Po^{208} spike calibration.

The Po^{208} spike obtained from Amersham-Searle was calibrated after
plating on Ag discs on the PCC 10 A counter. The count rates of sources

plated for different times are given below.

Sample (1 ml Po^{208})	Plating Time (hours)	Count Rate (inc. background)
P3	3	1.57 ± 0.04
P24	3	1.59 ± 0.04
P21	16	1.61 ± 0.04
P20	4	1.69 ± 0.04
P22	4	1.64 ± 0.06
P24	4	1.67 ± 0.07
Mean of 4 hr. samples		1.67 ± 0.03
Counter Background		0.09 ± 0.01

The mean 4 hr. sample count rate less background (1.58 ± 0.03) corresponds to a specific activity of 3.1 ± 0.1 dpm/ml Po^{208} on 3/22/72. Three samples containing 1 ml K120a solution plus 1 ml Po^{208} spike yielded Po^{210}/Po^{208} ratios of 1.40 ± 0.05. 1.53 ± 0.05 and 1.48 ± 0.04 (mean 1.47 ± 0.03). With allowance for build-in in the time since preparation of the uraninite solution, this ratio should be 1.7 if no Po^{210} loss occurred in preparation or 1.4 if all Po^{210} was volatilized in preparation. Thus the value determined for the Po^{208} specific activity appears reasonable.

B. Flow sheet for the analysis of plankton

The plankton samples, usually frozen in seawater, are thawed, filtered on a Büchner funnel, washed with distilled water, and dried at 105°C. Some samples were obtained freeze dried: these were dried at 105°C. After homo-

genization in an agate mortar, a 200-400 mg aliquot of dried plankton was ashed at 600-700°C for 2 hr. and reweighed to give the fraction of inorganic material in the sample. (These ashed aliquots are reserved for neutron activation analysis at a future date.) The remainder of the plankton sample, usually 0.5-2 g, is taken for radiochemical analysis.

The sample is weighed and transferred to a Teflon dish, moistened with distilled water, and concentrated HNO_3 added slowly until effervescence ceases. Po^{208} and Th^{230} or U^{232}-Th^{228} spikes and Pb carrier are added, and the sample is treated with 25 ml HNO_3 and 5 ml. $HClO_4$ concentrated acids to destroy organic matter. The dry residue is again heated to dryness with 10 ml. concentrated HCl, and then leached with 2 x 12 ml. portions of 1 $\overline{M}$ HCl. The solid residue at this stage (usually only present if the sample is siliceous) is treated with 10 ml. 48% HF and a few drops of concentrated $HClO_4$ and heated to dryness. This second dry residue is converted to the chloride form by concentrated HCl, dissolved in a further 2 x 12 ml. 1 $\overline{M}$ HCl, and combined with the first leachates. All apparatus used to this stage is Teflon or polypropylene to avoid polonium absorption on the walls.

To the clear plankton solution in a 100 ml. Teflon beaker (50 ml., 1 $\overline{M}$ HCl), 100 mg. ascorbic acid is added to reduce any Fe^{3+} ion present. A 0.5" diameter Ag disc (0.005"thick), masked on one side with Teflon and recessed in a Teflon plug, is then immersed in the solution, and the solution heated at $\sim$ 80°C for 3 hr., constantly stirred by a Teflon paddle. This stirrer paddle goes through a heavy Teflon lid which reduces evaporation loss from the solution. Polonium plates spontaneously on the disc, which after washing with distilled water and acetone is ready for α spectrometric analysis.

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After the polonium separation, the solution is heated with 1 ml. each HNO_3 and $HClO_4$ added to destroy the ascorbic acid. The residue is dissolved in 50 ml. 8 $\overline{M}$ HCl and transferred to a radon bubbler vessel. Helium is passed through the solution to purge any radon initially present, and the vessel is then sealed and stored for at least 10 days before Ra^{226} analysis. At the end of this time, helium is passed through the solution in a closed pumping loop, and radon is condensed in a liquid nitrogen trap. At the end of circulation (20 min.), the excess helium is pumped off, the trapped radon is warmed up in vacuo and transferred to a pre-evacuated detector vessel with a slug of helium.

After Rn^{222} extraction, the solution is passed through a Dowex AG 1 x 8 anion exchange column (12 cm. x 1 cm., 100-200 mesh) preconditioned with 8 $\overline{M}$ HCl. Uranium isotopes are adsorbed by the resin, and after washing with 2 x 40 ml. 8 $\overline{M}$ HCl are eluted with distilled water. Any Fe^{3+} present is extracted from the uranium fraction in 8 $\overline{N}$ HCl by diisopropyl ether, the uranium is further purified by extraction to ethyl acetate from 4 $\overline{M}$ HNO_3/ saturated $Al(NO_3)_3$ solution, back extracted into distilled water and finally extracted as a TTA complex in benzene from a HNO_3 solution at pH 3. This complex is deposited and flamed on a 1" stainless steel disc for α spectrometric analysis.

The effluent from the uranium column is evaporated to dryness, dissolved in a minimum quantity of 6 $\overline{M}$ HCl, and diluted with distilled water to a 1.5 $\overline{M}$ HCl solution. This solution is passed through a Dowex AG 1 x 8 anion exchange column (12 cm. x 1 cm., 100-200 mesh) preconditioned with 1.5 $\overline{M}$ HCl. Lead isotopes are adsorbed on the column, and after washing with 2 x 30 ml. 1.5 $\overline{M}$ HCl are eluted with distilled water. The pH of the eluate

is adjusted to around 5, $PbCrO_4$ is precipitated by addition of excess Na_2CrO_4, and the pH readjusted to 5. The precipitate is filtered off, washed with distilled water, and dried at 110°C. The $PbCrO_4$ is mounted for β^- counting by deposition as an H_2O slurry on a tared 1" diameter Lucite planchette, dried and reweighed. A 5.2 mg./cm^2 Mylar film is glued over the planchette to filter Po^{210} α particles.

The effluent from the lead column is evaporated to dryness, the residue dissolved in 7 $\overline{M}$ HNO_3, and the solution passed through a Dowex AG 1 x 8 anion exchange column (12 cm. x 1 cm., 100-200 mesh) preconditioned with 7 $\overline{M}$ HNO_3. Thorium isotopes are adsorbed by the column, and after washing with 2 x 40 ml. 7 $\overline{N}$ HNO_3 are eluted with 6 $\overline{N}$ HCl. The eluate is taken to dryness, and the thorium isotopes extracted from 0.1 $\overline{N}$ HNO_3 solution as a TTA - benzene complex. This complex is mounted for α spectrometric analysis similarly to uranium.

The effluent from the thorium column is evaporated to dryness, dissolved in 250 ml. 1 $\overline{M}$ HCl, Fe^{3+} carrier added, and $Fe(OH)_3$ precipitated by ammonia in the presence of 10 mg. Ba^{2+} holdback carrier. The precipitate is discarded and the scavenged solution stored hot for ∿ 40 hours to remove Rn^{222} and its decay products from the solution and to allow Ra^{228} to develop a radioactive equilibrium activity of Ac^{228}. At the end of this period, Fe^{3+} carrier is again added and Ac^{228} adsorbed on the $Fe(OH)_3$ (20 mg.) precipitated from the solution. The precipitate is filtered, roasted and deposited as a slurry on a tared Lucite planchette for β^- counting. An 80 µg/cm^2 Mylar film is glued over the planchette when the precipitate is dry to prevent loss of material.

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IV RESULTS

A. Uranium and thorium decay series nuclides in plankton from the
    Caribbean.

B. The fates of Pb^{210} and Po^{210} in the ocean surface.

C. Pb^{210} in coastal waters of the eastern United States.

D. Ra^{226} in plankton from the Atlantic Ocean.

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    eastern South Pacific.

A. Uranium and thorium dec., series nuclides in plankton from

the Caribbean.

(Preliminary report)

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URANIUM AND THORIUM DECAY SERIES NUCLIDES IN PLANKTON

FROM THE CARIBBEAN

D. P. Kharkar, J. Thomson, K.K. Turekian, W.O. Forster

Introduction

The abundances of the members of the uranium and thorium decay series in the oceans can be used to understand both the dynamics of ocean circulation and the influence of particles in the water column on the distribution of elements in ocean water profiles and marine sediments. A major role is played by plankton in these studies both as indicators of surface water radionuclide abundances and as active agents modifying these abundances. We report in this paper a method of determining the abundance of several natural radionuclides in the same small plankton sample, together with data gathered over much of the Caribbean and the inferences drawn concerning the processes responsible for the observed distributions.

The samples were collected on two cruises during the Fall and Winter of 1971-1972 as previously reported by one of us (Forster et al., 1972). All the samples consist predominantly of calanoids and cyclopoids. This relative homogeneity may be expected to minimize effects of differential species uptake of the radionuclides. Figure 1 is an index map of the stations at which samples were obtained for this study.

Analytical Methods

The plankton samples were freeze dried on ship and stored in plastic vials. On arrival at Yale they were dried overnight at 105°C, and homogenized in an agate mortar. The available sample for radiochemical analyses was generally around 1 g, and was used in the following radiochemical procedure for the determination of U^{238}, U^{234}, Th^{232}, Ra^{228}, Ra^{226}, Pb^{210} and Po^{210}.

Sample dissolution

The samples were weighed and transferred to a Teflon dish, moistened with distilled water, and concentrated HNO_3 added until effervescence ceased. Po^{208} and Th^{230} or U^{232}-Th^{228} spikes and Pb carrier ($\sim$ 40 mg as $PbCrO_4$) were added, and the sample heated to dryness with 25 ml HNO_3 - 5 ml $HClO_4$. This residue was taken to dryness with 10 ml HCl, and then leached with 2 x 12 ml 1 $\overline{M}$ HCl. The remaining solid (generally siliceous) was treated with 10 ml HF and a few drops of $HClO_4$ and taken to dryness. This residue was again heated to dryness with HCl, and leached with 2 x 12 ml 1 $\overline{M}$ HCl. This procedure yielded a clear solution in 1 $\overline{M}$ HCl. All apparatus used to this stage was Teflon or polypropylene to prevent absorption of polonium.

Chemical separations

Fe^{3+} in the 1 $\overline{M}$ HCl plankton solution was reduced with $\sim$ 100 mg ascorbic acid (Francis et al., 1968), and polonium isotopes plated on to a 0.5" diameter Ag disc at 85°C for 3 hours (Flynn, 1968). Next the plankton solution was transferred to a bubbler vessel and purged of Rn^{222} with helium. The vessel was then sealed and stored for at least 10 days to develop Rn^{222} (Lucas, 1964). The Rn^{222} was transferred to a counting cell on an apparatus similar to that of Bhat (1970), with a peristaltic pump to recycle the helium carrier gas. Uranium, lead and thorium were then separated in that

sequence by anion exchange on Dowex Ag 1 x 8. U was separated from 8 $\overline{M}$ HCl solution, and further purified by solvent extraction as described by Ku (1965), (1966). Pb was separated from 1.5 $\overline{M}$ HCl solution, and precipitated as $PbCrO_4$ at pH 5 [Rama et al., 1961]. Th was separated from 7 $\overline{M}$ HNO_3 solution [Bhat, (1970)]. The solution remaining after the ion exchange steps contained only Ra^{228} of the isotopes of interest. Fe^{3+} carrier was added twice and precipitated as $Fe(OH)_3$ (20 mg). These precipitates were rejected and the solution stored warm at pH 1 in HCl for ~ 40 hours to allow Ac^{228} to develop from Ra^{228}. Ac^{228} was then scavenged on $Fe(OH)_3$, and the precipitate filtered off and roasted.

The purified U and Th fractions were mounted for α spectrometry by extraction of their thermoyltrifluoroacetone complexes in benzene from HNO_3 solutions at pH 3 and pH 1.5 respectively [Ku, (1966)]. Chemical yields for U and Th ranged from 50-70% and 60-80% respectively. $PbCrO_4$ was prepared for estimation of Pb chemical yield and β^- counting by mounting as a slurry on a 1" diameter tared Lucite planchette and was then dried and weighed. Pb yields ranged from 65-90%. The $Fe(OH)_3$ carrier for Ac^{228} was also mounted as a slurry on a 3.3 cm x 1.1 cm area on a rectangular Lucite planchette, the chemical separation being considered quantitative.

Counting prodedures

Po, U and Th mounts were counted by α spectrometry, using 450 mm^2 silicon surface barrier detectors with α resolutions around 75 KeV (f.w.h.m.) over count periods of days. The Ra^{226} daughter Rn^{222} (α, 3.823 dy) was counted in 125 ml ZnS(Ag) coated cells on a Teledyne Isotopes Type 102 radon counting system. The combined separation efficiency for Rn^{222} and counting efficiency for Rn^{222} and its daughter αs was 92%. Vessel back-

grounds ranged from 0.15 - 0.30 cpm. Pb^{210} was measured via the developed Bi^{210} activity (β^-, 5.01 dy.) on a Sharp LB-100 Lowbeta proportional system with a 1.25" diameter detector and 80 $\mu g/cm^2$ Au-Mylar window. The detection efficiency for Bi^{210}, with a 5.2 mg/cm^2 Mylar filter for Po^{210} αs, was 28% with a background of 0.5 cmp. Ra^{228} was determined via Ac^{228} (β^-, 6.13 hr.) decay (Moore, 1969) on a rectangular gas-flow Geiger counter (4.2 cm x 1.7 cm; Lal and Schink, 1960), with an anticoincidence guard and Sharp Lowbeta electronics. The combined chemical separation and counting efficiency for Ac^{228} was 32% with a background of 0.13 cpm.

Discussion

The concentration efficiency of plankton in extracting the radio-nuclides from sea water is highest for thorium and lowest for uranium (Table 2). Since the Th^{232} content of surface ocean water is so low (Kaufman, 1969) the Th^{232} concentration factor may be as much due to the trapping of thorium-rich particulates, as has been suggested for other plankton (Turekian, Katz and Chan, 1973), as adsorption or trapping of an ionic species. The other nuclides are undoubtedly present, at least initially, as ionic species and their relative concentration factors may be more realistic. Of these Po^{210} is most efficiently concentrated and uranium the least. The sequence is compatible with what is known about the chemical behavior of these nuclides, as expressed for example in the separation scheme described above.

In spite of the homogenous nature of the samples, the specific activities in Table 1 are variable, but patterns emerge when activity ratios of genetically coupled nuclides such as U^{234}/U^{238}, Po^{210}/Pb^{210} or Th^{228}/Ra^{228} are considered. It is these ratios which we use in an attempt to trace the Caribbean surface waters.

U^{234}/U^{238}: The scatter of U^{234}/U^{238} activity ratios is large because of the poor counting statistics derived from the small quantities of uranium. The average of all U^{234}/U^{238} activity ratio values, however, is 1.15, the value typical of sea water.

Po^{210}/Pb^{210}: The distribution of the Po^{210}/Pb^{210} activity ratio in the Caribbean plankton is shown in Figure 2. Lowest values occur in the south-east, the source of surface waters in the Caribbean. Indeed the Po^{210}/Pb^{210} map closely resembles Wüst's (1964) surface salinity map for the same region.

This source water at the southeast is the low salinity Guiana Current, coming along the Brazilian coast north of the Amazon. Its track is along a coastal area which may be presumed to be of relatively high productivity.

As shown by the pattern of the Po^{210}/Pb^{210} activity ratio (Figure 2) the relatively greater extraction of Po relative to Pb by plankton indicates that the source water to the Caribbean is from an area in which biological activity has stripped Po from the water. The gradual increase in the Po^{210}/Pb^{210} activity ratio away from the plume in the southeast implies a less efficient scavenging flux of Po^{210} by plankton throughout the Caribbean or a mixing with North Atlantic water with a low productivity history.

Th^{228}/Ra^{228}: Although only one Ra^{228} value is listed in Table 1, and that with a large error, it is possible to use the Ra^{226} data to obtain a fairly accurate estimate of the expected Ra^{228} concentration in the plankton if no fractionation from sea water occurs. The possibility of fractionation is fairly remote in that they are isotopes of an element that is readily soluble at the concentrations found in sea water. We can use the study of Ra^{228} abundances in surface waters of the Caribbean made by Kaufman et al. (1973) to obtain an activity ratio of Ra^{228}/Ra^{226} of 0.47 for Caribbean surface waters. Using this ratio we can obtain the Ra^{228} activities of the plankton samples by multiplying the Ra^{226} activities by this factor. Szabo (1966) obtained Ra^{226} values very similar to these reported here. This has been done in Table 3 where the measured Th^{228} activities are also given together with the attendant Th^{228}/Ra^{228} activity ratios.

Two features are evident in comparing Table 3 and the index map (Figure 1) showing the locations of the samples. First, the activity ratio of the four samples is <u>unity or less</u> whereas from the concentration factor in Table 2 we would expect a heavy bias towards Th^{228}, if the Th^{228}/Ra^{228} activ-

ity ratio were at equilibrium in the water column. This indicates that the source of the Ra^{228}, probably supplied to the Guiana Current by release from sediments on the Brazilian shelf from the mouth of the Amazon northward, is intense (as indicated by the high values of Kaufman et al., 1973) and that very little Th^{228} has had a chance to grow in or survive by the time this water reaches the Caribbean.

Second, there is a trend in the Th^{228}/Ra^{228} activity ratio pattern in the Caribbean plankton, supported by the Th^{228}/Ra^{228} activity ratio in surface sea water (Broecker et al., 1973). Although many more data are required the samples closest to the presumed site of the Ra^{228} migration into the surface water from shelf sediments along the north Brazilian coast have lower ratios than the most remote (northwestward) samples. We believe that this is consistent with the first feature mentioned as well as with the Po^{210}/Pb^{210} data discussed earlier. As the water penetrates into the Caribbean from the southeast, Th^{228} grows towards equilibrium with Ra^{228}. The data of Broecker et al. (1973) show the Guiana Current entering the Caribbean with a Th^{228}/Ra^{228} activity ratio around 0.05, which increases to 0.11 at the Yucatan Strait. If biological productivity in the Caribbean were high the efficient extraction of Th^{228} debris settling from the surface would frustrate this trend towards equilibrium. The fact that the Po^{210}/Pb^{210} and Th^{228}/Ra^{228} activity ratios show an increasing trend to the northwest indicates that the Caribbean water is less efficient at producing adsorption sites through biological productivity than the water just entering the Caribbean.

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Table 1: Concentration of radioactive nuclides in Caribbean plankton samples

Station	Date	Location	U^{238} dpm/g	U^{234}/U^{238}*	Th^{232} dpm/g	(Th^{228})ex dpm/g	Ra^{226} dpm/g	Ra^{228} dpm/g	Pb^{210} dpm/g	Po^{210} dpm/g	Po^{210}/Pb^{210}*
39	21 Nov 71	17°54'N, 66°55'W		1.17±0.05	0.04±0.01	0.07±0.02	0.29±0.02		4.6±0.3	90±4	20±2
41	22 Nov 71	15°15'N, 68°17'W	0.51±0.11	1.30±0.36			0.14±0.01		6.4±0.5	61±2	10±1
44	23 Nov 71	12°58'N, 70°4'W	0.40±0.03	1.04±0.10	0.07±0.02		0.28±0.02		4.4±0.4	68±3	15±2
47	24 Nov 71	12°9'N, 73°10'W		1.25±0.10	0.04±0.01	0.10±0.02	0.27±0.02		3.4±0.4	52±2	15±2
48	25 Nov 71	11°8'N, 76°28'W					0.15±0.01	0.17±0.12	3.1±0.3		
49	26 Nov 71	9°56'N, 76°20'W	0.30±0.03	1.00±0.12			0.13±0.01		2.5±0.2	64±2	26±2
51	29 Nov 71	11°50'N, 79°58'W		1.14±0.06	0.18±0.05	0.09±0.08	0.14±0.01		2.6±0.2	54±2	21±2
52	30 Nov 71	15°3'N, 81°21'W	0.30±0.02	1.25±0.09			0.16±0.01		2.8±0.3	73±2	26±2
54	1 Dec 71	17°52'N, 83°41'W					0.14±0.01		3.7±0.3		
57	2 Dec 71	18°39'N, 76°16'W		1.17±0.09	0.04±0.01	0.07±0.02	0.13±0.01		3.1±0.3	81±3	26±3
59	6 Dec 71	17°41'N, 73°22'W	0.56±0.04	1.06±0.13			0.15±0.02		6.2±0.5	101±4	16±2
65	11 Jan 72	16°51'N, 67°34'W					0.20±0.02		7.4±0.5		
66	21 Jan 72	17°53'N, 66°55'W					0.20±0.03		4.2±0.4	73±3	17±2
67	21 Jan 72	17°54'N, 66°55'W					0.63±0.04		3.4±0.4	71±3	21±2
68	22 Jan 72	15°15'N, 68°14'W					0.16±0.02		8.2±0.5	72±3	9±1
70	23 Jan 72	12°46'N, 70°11'W					0.33±0.02		1.2±0.2	31±1	26±4
75†	25 Jan 72	10°41'N, 65°28'W					0.84±0.04		2.3±0.3	74±1	32±4
77	26 Jan 72	11°36'N, 63°36'W					0.15±0.01		1.4±0.2	33±1	24±3
79†	26 Jan 72	11°40'N, 62°11'W					1.10±0.04		10.2±0.6	114±5	11±1

* Activity ratio

† All samples were taken with a 6 mesh net except Stations 75 and 79 (20 mesh).

)

Table 2: Concentrations of radionuclides in Caribbean plankton
relative to sea water

Nuclide	Average activity in dry plankton dpm/g	Surface Caribbean sea water dpm/l	Concentration factor. (liters of sea water equivalent to 1 gram of plankton)
Th^{232}	0.074	$\leqslant$ 0.000017	$\geqslant$ 4400
Po^{210}	70	0.072	970
Pb^{210}	4.3	0.11	39
Ra^{226}	0.29	0.06	4.9
U^{238}	0.41	2.4	0.17
Th^{228}	0.083	0.0042[*]	20

* From Broecker et al. (1973)

Table 3: The estimated Th^{228}/Ra^{228} activity ratio of Caribbean plankton

Station No.	Estimated* Ra^{228} dpm/g	Measured Th^{228} dpm/g	Activity ratio Th^{228}/Ra^{228}
39	0.14	0.07	0.50
47	0.13	0.10	1.30
51	0.066	0.09	0.73
57	0.061	0.07	0.87

* Estimated Ra^{228} is based on Ra^{226} and Ra^{228} specific activities of 8.5 and 4.0 dpm/100 Kg of sea water (Kaufman et al., 1973), resulting in an activity ratio of Ra^{228}/Ra^{226} of 0.47. The Ra^{226} concentrations in Table 1 are multiplied by 0.47 to arrive at the estimated Ra^{228} values.

Figure 1

Po²¹⁰/ Pb²¹⁰ ACTIVITY RATIOS
IN ZOOPLANKTON

JAN. 1972

NOV. 1971
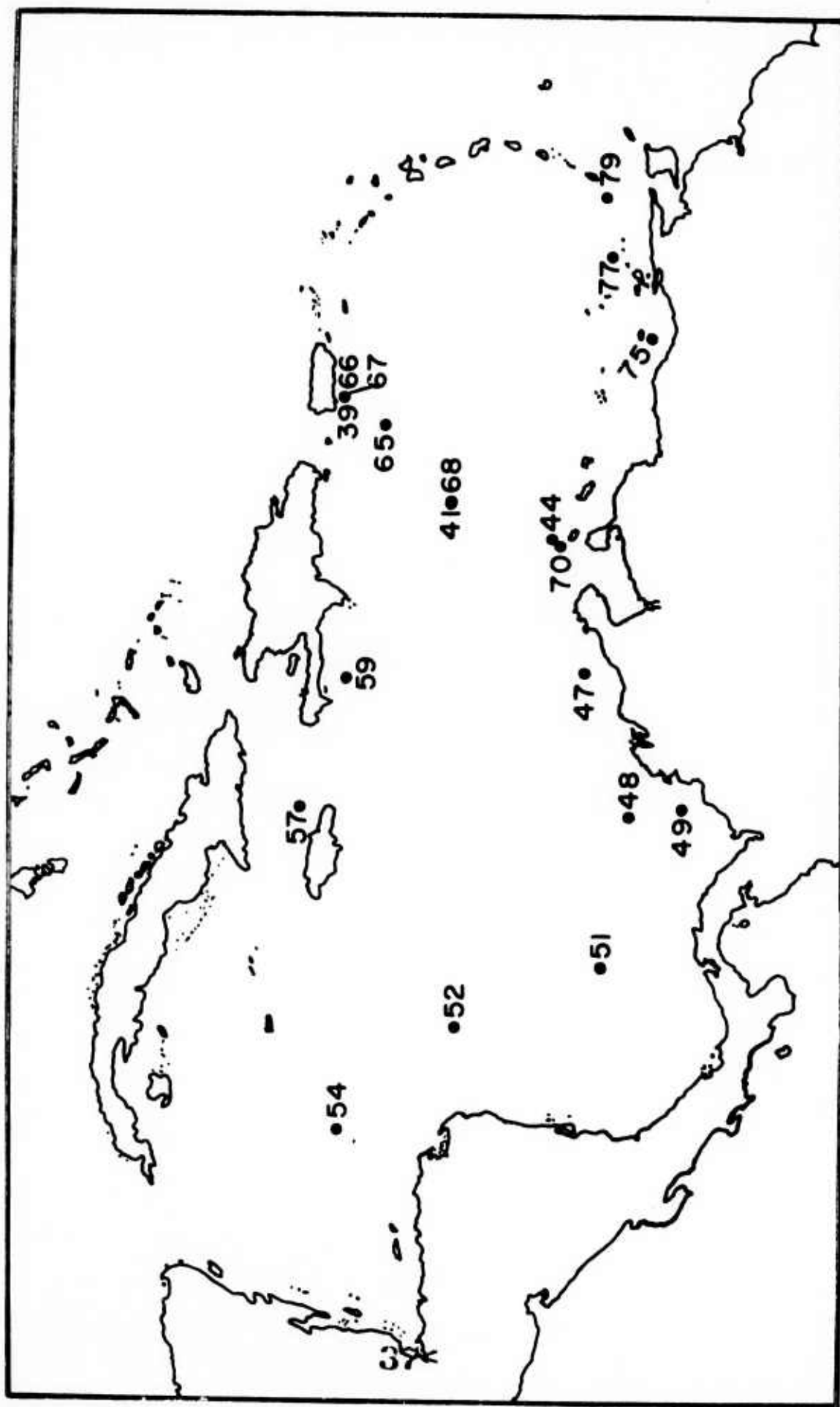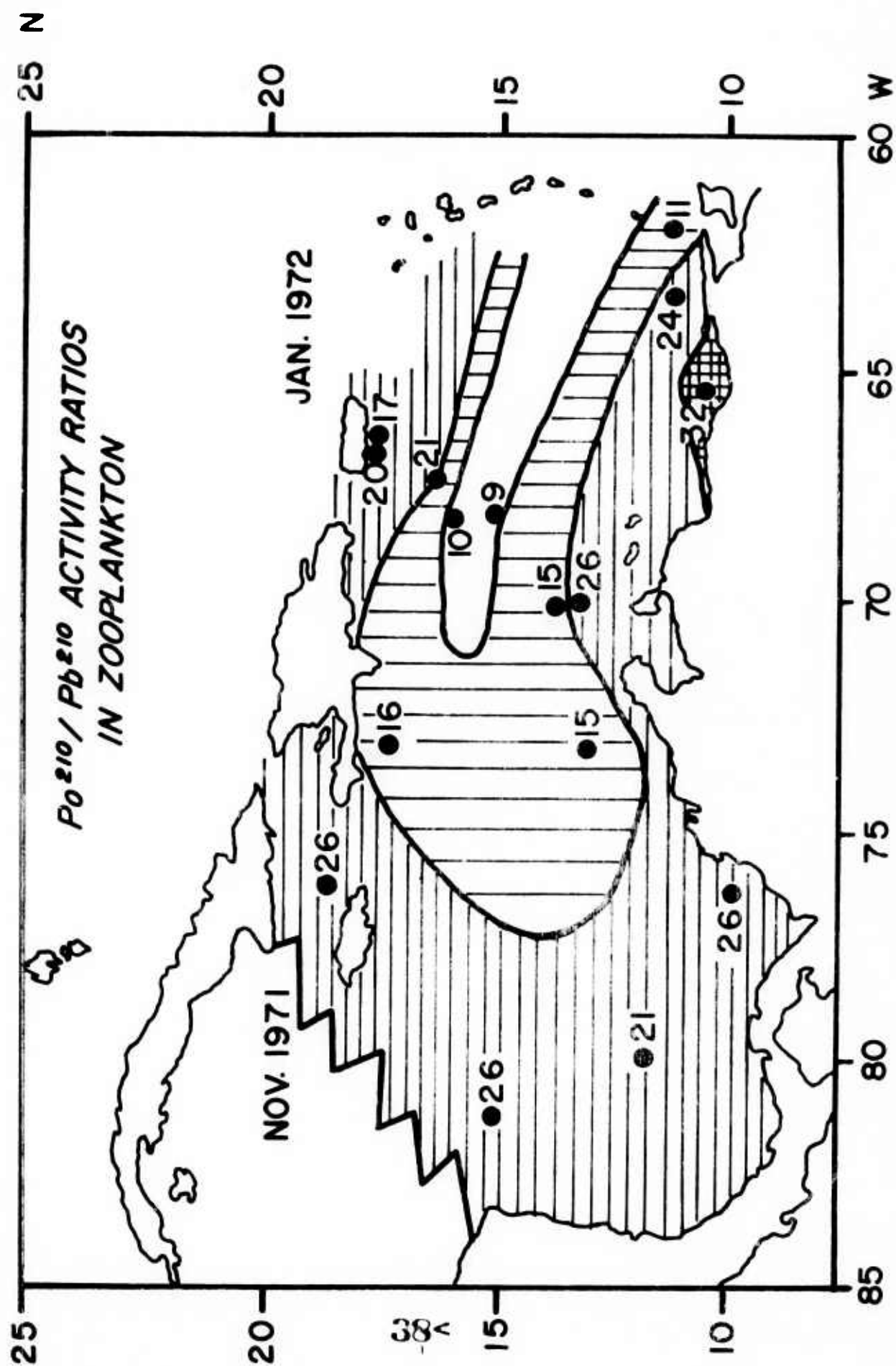
B. The fates of Pb^{210} and Po^{210} in the ocean surface.

(In press, <u>Journal de Recherches Atmosphériques</u>)

THE FATES OF Pb^{210} AND Po^{210} IN THE OCEAN SURFACE

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ABSTRACT

The concentration of Pb^{210} and Po^{210} in surface sea water is related to the atmospheric supply rate of Pb^{210} impressed on the supply from the decay of oceanic Ra^{226} on the one hand, and the relative removal fluxes of Pb^{210} and Po^{210} by particle transport to the deep water on the other. The Po^{210}/Pb^{210} activity ratio in marine zooplankton reflects the ratio in sea water which in turn reflects productivity. By using published and new values of Pb^{210} and Po^{210} concentrations in sea water and the partition coefficient of the Po^{210}/Pb^{210} ratio between plankton and surface sea water we are able to calculate the atmospheric flux of Pb^{210} at different oceanic sites. The mean residence times of Pb^{210} and Po^{210} in the mixed layer have also been calculated for these sites. It is proposed that a Po^{210} flux from the ocean surface to the atmosphere may supply at least some of the excess Po^{210} detected over continental areas.

Introduction

There is an excess of Pb^{210} in the surface waters of most of the open ocean over that expected from equilibrium with Ra^{226} by a factor of two to three. The source of this excess Pb^{210} is the atmosphere where Rn^{222}, supplied from the continents, decays to Pb^{210} and becomes part of the aerosol burden. By radioactive decay Pb^{210} (22 year half life) is transformed to Bi^{210} (5 day half life) and then to Po^{210} (138 day half life). The activities of Bi^{210} and Po^{210} in the atmosphere will depend on the mean residence time of aerosols. The Bi^{210}/Pb^{210} activity ratio in the atmosphere is higher than the Po^{210}/Pb^{210} activity ratio because of the approximately 5 day mean residence time of aerosols in the main part of the troposphere [1, 2].

The surface layer of the ocean attains a Pb^{210} activity which is the reflection of atmospheric supply rate, deep ocean supply rate (from Ra^{226} decay) and extraction rate to depth by adsorption on plankton and other particles.

In this paper we use the observed distribution of Pb^{210} and Po^{210} in plankton and sea water to determine the flux of Pb^{210} from the atmosphere to the ocean, the mean residence times of Pb^{210} and Po^{210} in the mixed layer of the oceans, and the Po^{210} flux from the ocean to the atmosphere.

The Pb^{210} and Po^{210} activities of plankton and ocean surface water

There have been several regional studies of the Pb^{210} and Po^{210} activities of marine plankton. Shannon et al. [3] have reported results off South Africa and Beasley et al. [4] have some results primarily from the Straits of Juan de Fuca in the eastern North Pacific. The levels reported

in both these papers are very similar to each other for zooplankton (Table 1). Only Shannon et al. have analyzed phytoplankton from the same region as the zooplankton and generally they find that although the Pb^{210} activities of both phytoplankton and zooplankton are the same, the phytoplankton contains markedly less Po^{210} than the zooplankton.

The samples we have analyzed are primarily zooplankton from various locations in the Atlantic Ocean (Table 1) and the Caribbean. We have reported on the Caribbean results elsewhere [5]. The Pb^{210} values of plankton obtained from the center of the Atlantic gyres and the Caribbean are higher than the values from the high productivity regions off the eastern United States which are more comparable to those of Beasley et al. [4] and Shannon et al. [3] from similarly high productivity regions.

Figure 1 is a representation of the distribution of the Po^{210}/Pb^{210} activity ratio in zooplankton in the Atlantic Ocean based on our data (Table 1 and the Caribbean results from [5]) and those of Shannon et al. [3].

The following features are accentuated in Figure 1: (1) Close to the eastern North American continent the Po^{210}/Pb^{210} ratios are low - generally less than 10. (2) The ratio increases abruptly from the coastal region to the oceanic side of the Gulf Stream and is highest at the center of the major gyre systems. (3) The Po^{210}/Pb^{210} ratios in the eastern Atlantic are low because of upwelling induced high productivity. (4) The equatorial region is intermediate between the low values of the highly productive margins of the basins and the high values typical of the low productivity regions of the interior of the gyres. (5) The waters north of the Gulf Stream are also low because of high productivity.

In Table 2 the data for the Po^{210} and Pb^{210} concentrations in associated sea water and zooplankton are given for several oceanic areas. The $(Po^{210}/Pb^{210})_{activity\ ratio-plankton}$ / $(Po^{210}/Pb^{210})_{activity\ ratio-seawater}$ ratio ranges between 16 and 25. Clearly, if zooplankton are responsible for the transport of Pb^{210} and Po^{210} from the surface waters to depth, then the efficiency of transport will be greater for Po^{210}. It is this fact combined with the very low Po^{210}/Pb^{210} activity ratios of atmospheric aerosols (about 0.1) that allows the possibility of calculating the fluxes through the mixed layer of the oceans.

The fluxes of Pb^{210} and Po^{210} through the oceanic mixed layer

If we consider a mixed layer in the oceans from 0 to 100 meters depth in which only vertical transport of Pb^{210} and Po^{210} occurs, we can write the steady state budget of Pb^{210} for one square centimeter of the ocean as:

$$R_{Ra} + R_{Pb} = \lambda_{Pb}N_{Pb} + k_{Pb}N_{Pb} \tag{1}$$

where R_{Ra} = rate of Pb^{210} supply from Ra^{226} decay in a volume 100 meter depth by one square centimeter (i.e. 10 liters)

R_{Pb} = rate (atoms per minute of Pb^{210} supply from atmospheric aerosols per cm^2 of ocean surface,

λ_{Pb} = decay constant for Pb^{210},

k_{Pb} = first order constant for unidirectional particulate transport of Pb^{210} from the mixed layer to depth,

N_{Pb} = total number of atoms per cm^2 of Pb^{210} in 100 meter of ocean (i.e. 10 liters).

similarly for Po^{210}:

$$\lambda_{Pb} N_{Pb} + R_{Po} = \lambda_{Po} N_{Po} + k_{Po} N_{Po} \qquad (2)$$

where:

R_{Po} = **rate** (atoms per minute) of Po^{210} supply from atmospheric aerosols per cm^2 of ocean surface,

λ_{Po} = decay constant for Po^{210},

k_{Po} = first order constant for unidirectional particulate transport of Po^{210} from mixed layer to depth,

N_{Po} = total number of atoms per cm^2 of Po^{210} in 100 meter of ocean (i.e. 10 liters).

To simplify we assume that R_{Po} is very small compared to $\lambda_{Pb} N_{Pb}$ since the activity of Po^{210} relative to Pb^{210} in aerosols is about 0.1 [1] and, as we shall see, the net R_{Po} may be very small compared to the particulate flux in the ocean column.

An estimate of R_{Ra} can be made based on the measured Ra^{226} activity in the surface water. We know from the data of Craig et al. [8] and unpublished data from our laboratory that deep water upwelling to form surface water can be depleted in Pb^{210} relative to Ra^{226}. We have chosen a Ra^{226} activity for 10 liters of water equal to 0.6 dpm [9] and arbitrarily assumed that 2/3 of this value is the standing crop of Pb^{210} from the supply to the surface of deep water. The Pb^{210}/Ra^{226} activity ratio may actually be less than this because of radon loss to the atmosphere.

With these approximations we can combine the equations for Pb^{210} and Po^{210} to obtain an expression relating the atmospheric Pb^{210} flux to the other parameters:

$$R_{Pb} = A_{Pb} \left[1 + \frac{1}{\alpha} \frac{\lambda_{Po}}{\lambda_{Pb}} \left(\frac{1}{(A_{Po}/A_{Pb})} - 1 \right) \right] - 0.4 \qquad (3)$$

where: A_{Pb} and A_{Po} are the activities in sea water of Pb^{210} and Po^{210} respectively, in dpm per cm^2 from the surface to a depth of 100 meters, and $\alpha = k_{Po}/k_{Pb}$.

Thus we can obtain an estimate of the atmospheric aerosol flux of Pb^{210} to different parts of the ocean if we know the values A_{Pb}, A_{Po} and α for the general area. If we take a large enough area we can ignore any horizontal fluxes as a first approximation. An estimate for α can be obtained for a region using the values for zooplankton and sea water as shown in Table 2. Generally in areas of high and average productivity the value of α will be assumed to be about 20. The values of α based on plankton values in the low productivity centers of the major ocean gyre systems may not be a true index of the Po^{210}/Pb^{210} activity ratio of the actual downward particulate flux. The flux is small and recycling in the nutrient depleted surface waters may yield an enhanced enrichment of Po in the surface material.

If we confine ourselves to the oceanic marginal areas (but not immediately coastal waters) we can calculate the atmospheric Pb^{210} flux and consequently the values of k_{Pb} and k_{Po} for a specific region from the available data. The reciprocals of the k_{Pb} and k_{Po} can then be taken as the mean residence times τ_{Pb} and τ_{Po}. These are listed in Table 3 for three large areas of the ocean for which sufficient data exist for such a calculation.

The most important observations are: (1) the Pb^{210} activity of surface water is not related to the Pb^{210} flux from the atmosphere, and (2) the mean residence times of Pb^{210} and Po^{210} in areas of high productivity are

shorter than in areas of low productivity.

Our results indicate that the deposition rate of Pb^{210} from the atmosphere is not expected to be constant at any one latitude. It is a function not only of the radon flux in the area from which the air mass arrives but also of the length of time the air mass takes to arrive at a particular geographic location and perhaps most important of all the efficiency of scavenging of Pb^{210} out of the air by aerosols and precipitation at different points along the route. We believe that our type of calculation using the Po^{210} and Pb^{210} activities provides both the best estimate of the Pb^{210} downward flux from the atmosphere to the ocean surface at each location and also the mean residence times of Pb^{210} and Po^{210} in the upper layer of the ocean. In this our calculations are different from those of Nozaki and Tsunogai [10] who hold the Pb^{210} flux constant along a latitude.

The possibility of a significant Po^{210} flux to the atmosphere

from the sea

Poet et al. [1] and Moore et al. [2] argue that there is an excess Po^{210} burden in the continental atmosphere above that permitted by the Bi^{210}-Pb^{210} calculation of atmospheric mean residence times of Pb^{210} and its daughters. If we assume that Bi^{210} and Pb^{210} activities in Boulder, Colorado measured by Poet et al. [1] define the first order aerosol downward removal flux constant (λ_R) we arrive at a value of 1.29×10^{-4} min^{-1}.

For the troposphere if there is a Po^{210} flux upward from the Earth's surface then for the steady state:

$$N_{Bi}\lambda_{Bi} + R_{Po\uparrow} = N_{Po}\lambda_{Po} + N_{Po}\lambda_R \qquad (4)$$

where: λ_{Bi} and λ_{Po} are the decay constants of Bi^{210} and Pb^{210} respectively,

N_{Bi} and N_{Po} are the atoms per unit volume of Bi^{210} and Pb^{210} respectively,

λ_R is the downward removal constant = 1.29×10^{-4} min^{-1}, and

$R_{Po\uparrow}$ is the upward flux of Po^{210} from the earth, equal to 4.57 $dpm/100$ m^3(STP).

If we assume that there is 0.8 m^3(STP) cm^2 of air in the troposphere then an upper value of $R_{Po\uparrow}$ in terms of the total troposphere per unit area is 0.037 atoms Po^{210} cm^{-2} min^{-1}. Poet et al. [1] and Moore et al. [2] argue that this upward flux may be ascribable to land derived soil type material wafted upwards with equilibrium activities of Pb^{210}, Bi^{210} and Po^{210}. We suggest that this flux could also be ascribed to Po^{210} derived from the ocean surface and transported to the continents as part of the marine aerosol burden.

We have no analyses of the postulated polonium-bearing particles released from the ocean surface. We can get an estimate of the flux of the presumed polonium carrier - organic material which provides the large surface necessary for efficient polonium adsorption from sea water - by considering plankton. The highest Po^{210} concentrations in plankton are found in the center parts of the warm water gyres of the oceans. A value of 150 dpm/g (dry weight basis) would represent an average of the high values from this region (Table 1). If this were a source of Po^{210} to the atmosphere and hence to the continents, it would imply a rate of mass of plankton-type material released to the atmosphere of 0.3 mg/cm^2/ year of ocean surface (since the ocean surface is twice the continental surface for which the deficiency was calculated). The actual specific activity of Po^{210} in the aerosol-forming material derived from the ocean

surface is not yet known but if it is higher than our assumed value, then this would diminish the assumed organic flux.

A test of the model of Po^{210} supply to the atmosphere should be possible by sampling oceanic air. Such air should have even a higher Po^{210}/Pb^{210} activity ratio than that found in continental air for the aerosol mean residence time calculated from the $Bi^{210}-Pb^{210}$ pair. Possible examples of this have been found in Hawaii [11] and in the Antarctic [12].

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Table 1: Pb^{210} and Po^{210} in zooplankton from the Atlantic Ocean

Sample	Location	Date	Source	Comments	Pb^{210} dpm/g dry wt.	Po^{210} dpm/g dry wt.	Po^{210}/Pb^{210} activity ratio
1 W-4	40°44'N 64°13'W	Mar 28 72	a	1900 GMT	0.38+0.05	4.4+0.8	20 ± 1
2 W-6	41°44'N 64°02'W	Mar 29 72	"	0630 GMT	0.23+0.01	4.5+0.3	21 ± 1
3 W12C	see comments		"	0745 to 1900 GMT for different tour Combination of 6 tours between 40°6.4'N 41°6.0'W and 42°53'N 58°30'W	0.56+0.09	2.2+0.8	30 ± 2
4 GOS 2	31°47'N 80°30'W	Feb 4 71	b	0-15m 6 mesh oblique tow	1.9 +0.2	-	-
5 " 3	31°41'N 80°12'W	Feb 5 71	"	0-30m	1.4 +0.6	95 ± 9	68 ± 30
6 " 6	31°18'N 78°27'W	Feb 6 71	"	0-20m	3.5 +0.8	196 ± 22	56 ± 14
7 AII60-25	32°58'S 30°31'W	Apr 13 71	"	300m Midnight tow	3.3 +0.5	97 ± 10	29 ± 5
8 -116	05°28'S 08°33'E	June 15 71	"	"	2.5 +0.1	17 ± 2	6.8+0.8
9 -118	02°50'S 08°05'E	June 16 71	"	"	4.4 +0.6	-	-
10 -121	00°26'N 17°23'W	June 28 71	"	"	1.2 +0.3	34 ± 4	28 ± 8
11 -122	00°10'S 34°31'W	July 3 71	"	"	5.0 +0.8	102 ± 9	20 ± 4
12 AII62-5	28°43'N 62°36'W	Oct 7 71	"	IDOE-17	6.1 +0.4	-	-
13 -6	28°37'N 62°28'W	Oct 7 71	"	IDOE-18	2.6 +0.1	86 ± 4	33 ± 2
14 -7	25°05'N 62°36'W	Oct 9 71	"	IDOE-20	1.9 +0.2	91 ± 6	48 ± 6
15 -13	35°57'N 64°41'W	Oct 16 71	"	IDOE-42 Sargassum	2.2 +0.4	164 ± 8	75 ± 14

Table 1 (cont.):

Sample	Location	Source	Date	Comments	Pb^{210} dpm/g dry wt.	Po^{210} dpm/g dry wt.	Po^{210}/Pb^{210} activity ratio
16 BF 1	33°44'N 75°28'W	c	Nov 6 72	1550 EDT 1/2 hour tow	0.4±0.2	33 ± 1	83 ± 41
17 " 2	34°18.4'N 75°33.5'W	"	Nov 6 72	2030 EDT 1 hour tow	1.3±0.1	30 ± 1	23 ± 2
18 BWP 1	39°45N 74°05'W	d	July 10 72	Barnegat Light,N.J.~2 mi. off shore	0.9±0.4	2.6±0.2	3 ± 1
19 2	"	"	July 10 72	"	1.0±0.8	3.6±0.3	3 ± 3
20 3	38°56'N 74°51'W	"	July 11 72	Cape May,N.J.	0.4±0.1	1.6±0.1	4 ± 1
21 4	38°19'N 75°04'W	"	July 12 72	Ocean City,Md.	0.4±0.1	3.3±0.1	8 ± 2
22 5	34°38'N 76°40'W	"	July 14 72	Beaufort, N.C. 4 mi. off shore	2.2±0.7	29 ± 1	13 ± 4
23 6	36°50'N 75°57'W	"	July 16 72	Virginia Beach,Va.~2 mi. off shore	0.8±1.0	7.3±0.4	9 ± 11

Source: a: Dr. A. Walton, Bedford Institute of Oceanography; b: Dr. G. Harvey, Woods Hole Oceanographic
Institution; c: Dr. R. Barber, Duke University Marine Station; d: J. Thomson and T. Eisensmith, Yale.

Table 2: The Po^{210} and Pb^{210} average concentrations in surface sea water, the Po^{210}/Pb^{210} activity ratios in plankton and sea water and the values of α

Region	Sea water				Plankton		
	dpm/1	dpm/1	Po^{210}/Pb^{210}*	Source	Po^{210}/Pb^{210}*	Source	α
Eastern South Atlantic	0.084	0.044	0.52	[3]	12	[3]	23
Caribbean	0.11	0.072	0.65	a	16	[5]	25
Eastern North Pacific	0.10	0.084	0.84	b	13	[4]	16
Western Pacific	0.092	0.063	0.68	[7]	-		-

* Activity ratio

$\alpha = (Po^{210}/Pb^{210})$ activity ratio-plankton $/ (Po^{210}/Pb^{210})$ activity ratio-sea water

Notes:

a Values obtained by present authors for a sample from Bermuda collected in March 1973.

b Po^{210} value from Folsom,T.R., Pillai, K.C. and Beasley, T.M. (1966) University of California; IMR-TR-922-66-A, B, C. cited in Beasley et al. [4]. Pb^{210} value from Rama et al. [6].

Table 3: Estimates of the atmospheric Pb^{210} flux (R_{Pb}) and the mean residence times of Pb^{210} and Po^{210} in surface waters from various oceanic regions. (α is assumed to be 20).

Region	Source of data	R_{Pb} (dpm cm^{-2}y^{-1})	τ_{Pb} (years)	τ_{Po} (years)
West Pacific	[7]	0.053	24	1.2
Eastern South Atlantic	[3]	0.10	9.4	0.41
Caribbean	This paper [5]	0.076	20	1

Figures

Figure 1: The Po^{210}/Pb^{210} activity ratio in zooplankton from the Atlantic Ocean. Data and locations in Table 1 and References [3] and [5].

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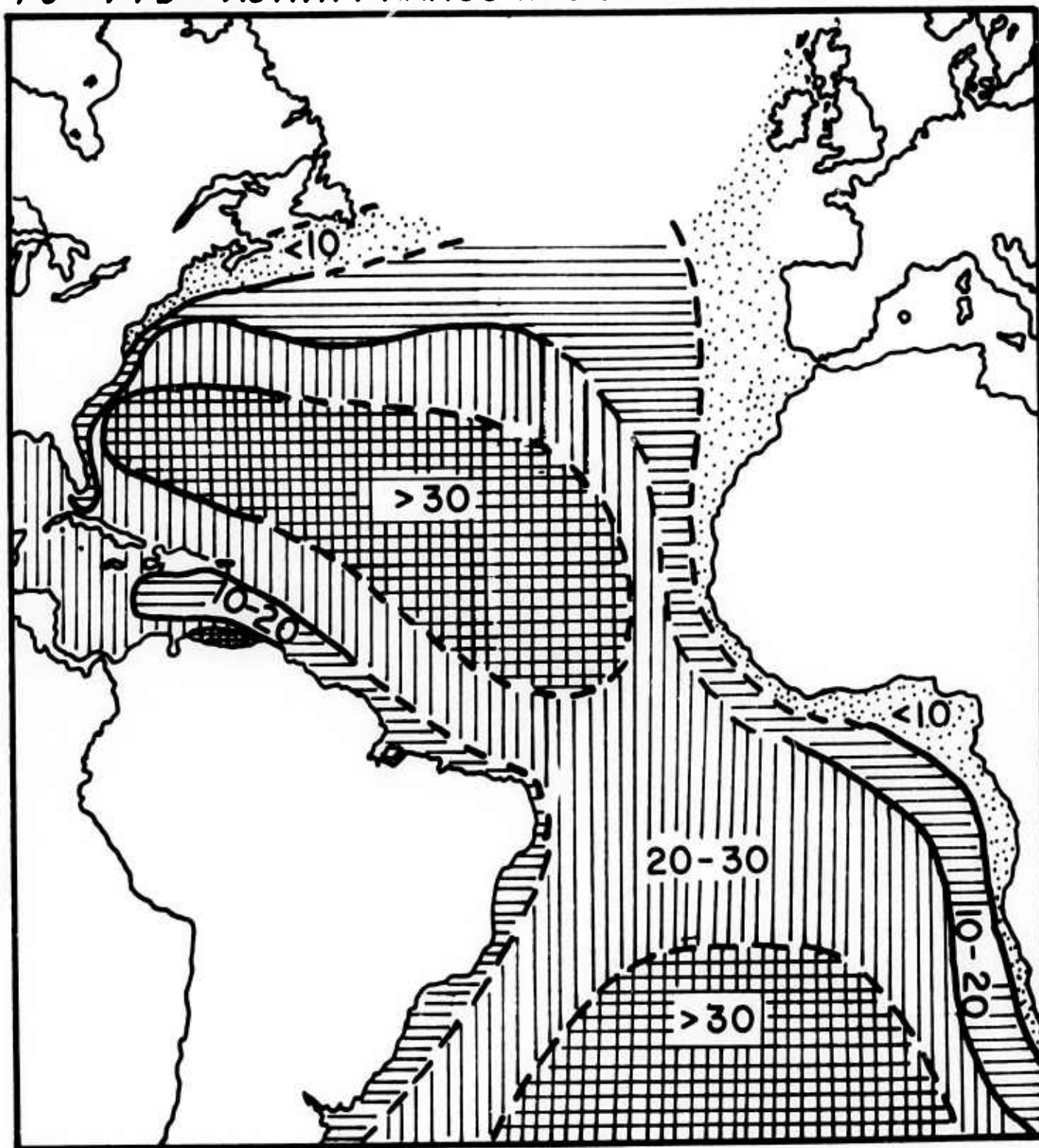
C. Pb^{210} in coastal waters of the eastern United States.

(To be submitted to <u>Nature</u>)

Pb^{210} IN COASTAL WATERS OF THE EASTERN UNITED STATES

J. Thomson and K. K. Turekian

In this paper we present data on the Pb^{210} activities in coastal waters of the eastern United States between Long Island Sound and Beaufort, North Carolina (Table 1). Coupling these data with the Pb^{210} and Po^{210} activities in plankton collected at the same time as the water, it is possible to estimate the atmospheric Pb^{210} flux to the ocean surface and the mean residence time of Pb^{210} in the mixed layer in the manner described by Turekian et al. (1974). In that work calculations were made for large areas of the ocean such as the eastern Caribbean, the western Pacific and eastern South Atlantic oceans in order to minimize the effects of time variation and horizontal fluxes. Coastal waters can be expected to show greater variability for both the Pb^{210} supply from the atmosphere and the productivity which determines the mean residence time of Pb^{210} in the surface ocean.

The sea water samples were transported to the laboratory where, without filtering, they were acidified to a pH of about 2. The samples sat for several months before processing so no attempt at measuring the initial Po^{210} in the water samples was made. Other experiments on coastal waters indicated that the particulates present in the water are mainly detrital and do not seriously influence the Po^{210} and Pb^{210} activities of the water phase on acidification. The measured Po^{210}/Pb^{210} activity ratio in plankton associated with the water samples analyzed for Pb^{210} can be converted to a Po^{210}/Pb^{210} activity ratio for the water by assuming that the Po^{210}/Pb^{210} activity ratio of plankton relative to that ratio in sea water is 20 as determined earlier for large oceanic areas (Turekian et al.,

1974).

With these data we calculate the atmospheric flux of Pb^{210} (R_{Pb}) to the ocean surface by the equation:

$$R_{Pb} = A_{Pb} \left[1 + \frac{1}{\alpha} \frac{\lambda_{Po}}{\lambda_{Pb}} \left(\frac{1}{A_{Po}/A_{Pb}} - 1 \right) \right] - 0.4$$

where A_{Pb} and A_{Po} are the activities of Pb^{210} and Po^{210} respectively in a volume of 1 cm surface by 100 meters depth (i.e. 10 liters), α is the concentration factor of Po^{210} relative to Pb^{210} and set at 20; and λ_{Po} and λ_{Pb} are the decay constants for Po^{210} and Pb^{210} respectively. The value of 0.4 represents the ocean water Ra^{226}-supported Pb^{210}.

The values for R_{Pb} in $dpm/cm^2/year$ are presented in Table 1. The value of R_{Pb} refers to an average value for an unspecified period prior to sampling and probably does not refer to an annual average rate. The important feature to note is that the samples south of Delaware Bay are about 5 to 10 times lower than the values to the north. Our interpretation of this observation is that, at least for the unspecified length of time to which the data speak, the air mass over the southern coast came from a more oceanic source and traversed more moist land (with low Rn diffusion) than the air mass over the northern coast. This is compatible with the patterns of air movement affecting the east coast of the U.S. The northern area receives air from the relatively arid interior U.S. and has been enriched in radon from which the Pb^{210} is ultimately derived. The farther south along the coast one goes the greater the marine air component, depleted in radon, that passes over the region.

We can also arrive at a value for the extraction constant, k_{Pb}, of

Pb^{210} from the surface waters by plankton at each station from the relation-ship:

$$R_{Pb} \text{ (atm)} + R_{Ra} = \lambda_{Pb} N_{Pb} + k_{Pb} N_{Pb}$$

Since we have assumed R_{Ra} is 0.4 atoms/cm^2/min for a 100 meter depth water column and R_{Pb} (atm) has been determined, the value of k_{Pb} can be obtained for each station. The reciprocal of k_{Pb} is τ_{Pb}, the mean residence time of Pb^{210} in the coastal water relative to extraction and removal by plankton. These values are also given in Table 1. The southerly stations show larger mean residence times than the northern stations. The largest mean residence time is for a sample taken most remotely from the coast and has the highest salinity of the samples studied. The τ_{Pb} can be taken as an index of pro-ductivity which can vary with time and location. The value of τ_{Pb} at any one station should be relatable to all the other factors observed to be indices of productivity. The value of τ_{Po} is determined by our choice of the value of $\alpha = 20$. It ranges from 0.06 for the Long Island Sound to 1 for the farthest off-shore sample at Beaufort. These low values are comparable to the mean residence times for Th^{228} determined by Broecker et al. (1973) in the western Atlantic closest to shore. This implies that Th^{228} and Po^{210} have similar modes of particulate transport out of the surficial bio-logically productive zone but Pb^{210} has a longer mean residence time resem-bling that of the nutrients.

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In press.

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Table 1:

Lat. & Long.	Salinity	Plankton dpm/g(dry wt) Pb^{210}	Plankton dpm/g(dry wt) Po^{210}	Po^{210}/Pb^{210} activity ratio	Assumed Po^{210}/Pb^{210} activity ratio ($\alpha=20$)	Sea water Measured dpm Po^{210}/l 13 months after collection	Sea water Corrected* Pb^{210} (dpm/l) for assumed Po^{210}/Pb^{210} ratio
Long Island Sound	25.4	0.8+0.4	1.5+0.1	1.9+0.9	0.095	0.043 +0.003	
Barnegat Light, N.Y.	28.8	0.9+0.4 } 1.0+0.8	2.6+0.2 } 3.6+0.3	3 +2	0.15	0.080 +0.005	
Cape May, N.J.	31.0	0.4+0.1	1.6+0.1	4 +1	0.20	0.090 +0.005	
Ocean City, Md.	29.1	0.4+0.1	3.3+0.1	8 +2	0.40	0.043 +0.003	
Virginia Beach, Va.	23.2	0.8+1.0	7.3+0.4	9 +11	0.45	0.032 +0.003	
Beaufort, N.C.	32.1	2.2+0.7	29 +1	13 +4	0.65	0.092 +0.005	

* Calculated Pb^{210} activity from Po^{210} measured 13 months after collection and the assumed Po^{210}/Pb^{210} activity ratio at time of collection.

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Location	Atmospheric flux of Po^{210} (R_{Pb}) (dpm/cm^2/y)	Mean residence time (τ_{Pb}) of Pb^{210} in water(years)	$\dfrac{Pb^{210}(\text{plankton})}{Pb^{210}(\text{seawater})}$	Mean residence time (τ_{Po}) of Po^{210} in water(years)
Long Island Sound	0.42	1.1	16	0.06
Barnegat Light, N.Y.	0.45	1.9	10	0.1
Cape May, N.J.	0.37	2.7	4	0.1
Ocean City, Md.	0.066	7.1	8	0.4
Virginia Beach, Va.	0.038	9.0	20	0.5
Beaufort, N.C.	0.069	20	20	1.

D. Ra^{226} in plankton from the Atlantic Ocean.

(Preliminary report)

Ra^{226} IN PLANKTON FROM THE ATLANTIC OCEAN

D. P. Kharkar, J. Thomson and K. K. Turekian

The average Ra^{226} concentration in marine plankton has been estimated to range over a factor of 100. Phytoplankton seems to be higher in Ra^{226} than zooplankton in the same waters as reported by Shannon and Cherry (1971) and there also appears to be a strong water mass effect in the region of study off South Africa. The phytoplankton from the marginal Agulhas current has about 10 times the activity of phytoplankton towards the center of the South Atlantic gyre.

Szabo (1967) reports values from the region of the Bahamas which, in general, are lower than the average zooplankton values of Shannon and Cherry. Our results (Table 1) cover a wider area of the oceans than either of these two above mentioned studies.

It is evident that the range of our data primarily on zooplankton encompasses the values of both Shannon and Cherry and Szabo. Although we must be cautious about generalizations even with this quantity of data, it appears that Shannon and Cherry's observations about the area of South Africa are generally applicable for the whole Atlantic and adjacent seas. In particular:

(1) Plankton from the low productivity areas of the oceans are generally lower than those from adjacent high productivity areas except in coastal waters where great variability can occur.

(2) Phytoplankton enriched samples and <u>Sargassum</u> are higher in Ra^{226} than associated zooplankton.

(3) The average of all samples of zooplankton from the normal or low

productivity regions is about 0.3 dpm Ra^{226}/g dry weight.

We are analyzing our samples for barium and silicon to establish what relationship these elements have to the concentration of Ra^{226} in plankton.

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Table 1: Ra^{226} in plankton from the Atlantic Ocean.

Sample No.*   Ra^{226} dpm/g dry wt.

A. Yale Results

1. Continental margin off Savannah, Georgia

GOS	2	1.7 ± 0.1
	3	3.3 ± 0.1
	6	2.2 ± 0.1

2. Continental margin off Beaufort, North Carolina

| BF | 1 | 0.16 ± 0.02 |
| BF | 2 | 0.17 ± 0.01 |

3. North Atlantic-Sargasso Sea

AII62	6	0.18 ± 0.01
	7	0.05 ± 0.01
	13 (Sargassum)	1.7 ± 0.1

4. North Atlantic - 40°W

W -	4	0.38 ± 0.05
	6	0.23 ± 0.01
	12C	0.56 ± 0.09

5. Equatorial Atlantic

AII60	116	0.19 ± 0.01
	118	0.27 ± 0.05
	121	0.05 ± 0.01
	122	0.26 ± 0.03

6. South Atlantic - 30°S

| AII60 | 25 | 0.95 ± 0.09 |

B. Averages of published results

1. Szabo (1967) - Bahamas   0.18

2. Shannon and Cherry (1971)

a.	South Atlantic - zooplankton	0.66
b.	South Atlantic - phytoplankton	2.2
c.	Agulhas Current - phytoplankton	17.

Table 1 (cont.)

Sample No.*	Ra^{226} dpm/g dry wt.
3. Kharkar et al. (1974) - Caribbean	
a. 20 mesh	0.20
b. 6 mesh	0.97

* The exact locations are given in Turekian et al. (1974).

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E. Po^{210} and Pb^{210} distribution in ocean water profiles from

the eastern South Pacific

(Preliminary report)

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Po^{210} AND Pb^{210} DISTRIBUTION IN OCEAN WATER PROFILES FROM THE EASTERN SOUTH PACIFIC: PRELIMINARY RESULTS

J. Thomson and K. K. Turekian

Introduction

In March 1972, we obtained sea water samples from the southeast Pacific NAVOCEANO cruise (the U.S.S. Bartlett, W. S. Moore, Chief scientist) to the high productivity upwelling region west of Peru. Samples from two profiles were received, one inside the upwelling area, and one to the northwest out of the upwelling. This provided an opportunity to study the Po^{210}/Pb^{210} activity ratio variation with depth in adjacent ocean areas with greatly different productivities. In addition, since Ra^{226} data already exist for the water column in this area (Chung and Craig, 1973) and additional data will be obtained by other groups participating in the NAVOCEANO cruise, the degree of disequilibrium in the $Ra^{226}-Pb^{210}-Po^{210}$ system may be investigated for different oceanic environments. Craig et al. (1973) showed disequilibrium for the Pb^{210}/Ra^{226} ratio in deep water of the North Pacific.

Analytical procedures

Aboard ship, water was transferred from the 30 liter Niskin bottles used for sampling into 1/2 gallon polyethylene bottles containing 10 ml concentrated HCl. (The 1/2 gallon bottles were new, and had been pre-cleaned with 6 $\overline{N}$ HCl, and 3 rinses of distilled water.) The resultant pH of storage was 1.2.

On arrival at the lab, the bottles were weighed. 1 ml Fe^{3+} carrier (10 mg/ml), 2 ml Pb carrier (39.52 mg as $PbCrO_4$/2 ml) and 1 ml Po^{208} spike ($\sim$ 0.24 dpm Po^{208}/ml) were added. The bottles were shaken and left to equilibrate, normally for several days. The samples were neutralized to pH 6 or 6.5 (Em 5-10 indicator sticks) with NH_3 gas, 5 ml Na_2CrO_4 solution (10 g/500 ml) was added, and the sample left overnight to settle. $Fe(OH)_3$ and $PbCrO_4$, carrying Po and Pb, were filtered off using 47 mm diameter, 0.4 μ Nuclepore filters in a Millipore apparatus with a plastic input funnel. Two filters were sometimes necessary to achieve reasonable filter speeds, about 40 minutes per sample. The precipitate was dissolved off the filters with a jet of 1 $\overline{N}$ HCl to a final volume of 50-70 ml in a 100 ml Teflon beaker. Approximately 100 mg ascorbic acid was added, a 1/2" diameter Ag disc (masked on one side with Teflon tape) added to the solution, and Po isotopes plated out at 85°C for 3 hours, stirred with a Teflon paddle. The disc was removed, washed with water and finally with acetone. The 1/2 gallon bottles were weighed empty to give the mass of water analyzed, 12 g being subtracted for the HCl added to each bottle. Each sample was counted for 1 week on a low background α spectrometer.

The solution remaining after plating was heated to dryness with 1 ml concentrated HNO_3 with a few drops of $HClO_4$ added. The residue was dissolved in 25 ml 8 $\overline{M}$ HCl and Fe (and U) removed from the solution on a Dowex Ag 1 x 8 anion exchange column (12 cm x 1 cm, 100-200 mesh). The effluent from the column and 2 x 40 ml 8 $\overline{M}$ HCl washes were heated to dryness. This residue was dissolved in 10 ml 6 $\overline{M}$ HCl, and distilled water added to bring the solution to 1.5 $\overline{M}$ HCl (40 ml). Pb was separated from the solution on a similar ion exchange column to that used in Fe separation, washed with

2×30 ml $1.5 \ \overline{M}$ HCl, and finally eluted with 2×40 ml distilled water. $PbCrO_4$ was precipitated from the eluate at pH 5 by addition of NaOH and excess Na_2CrO_4, filtered off, dried, and weighed into tared plastic vials. This gave the chemical efficiency for Pb, generally 75-90%.

The $PbCrO_4$ was dissolved in 5 ml 6 $\overline{M}$ HCl, 1 ml Po^{208} spike added, and the samples stored for a few months to develop Po^{210}. At the end of this time, the solutions were adjusted to 1 $\overline{M}$ HCl, and Po plated onto Ag discs as before. Pb^{210} activities were then calculated from the Po^{210} ingrowth, obtained by α spectrometry as before. The initial Po^{210} analyses were then corrected for ingrowth from this amount of Pb^{210} between collection and the first plating.

Two liter samples of doubly distilled water were treated analogously to the sea water samples to determine blanks for the procedure.

Results and discussion

The results to date are restricted to Po^{210} measurements uncorrected for potentially added Po^{210} from Pb^{210} decay between the time of collection and analysis. In the deeper waters where the Po^{210}/Pb^{210} activity ratio may be one no correction will be necessary. The surface values, where the ratio is generally less than one, without the Pb^{210} correction represent upper limits for the reported Po^{210} values. When sufficient time has elapsed to process the Pb^{210} separates, data will be available for the Po^{210}/Pb^{210} activity ratio at each depth as well as the corrected Po^{210} values.
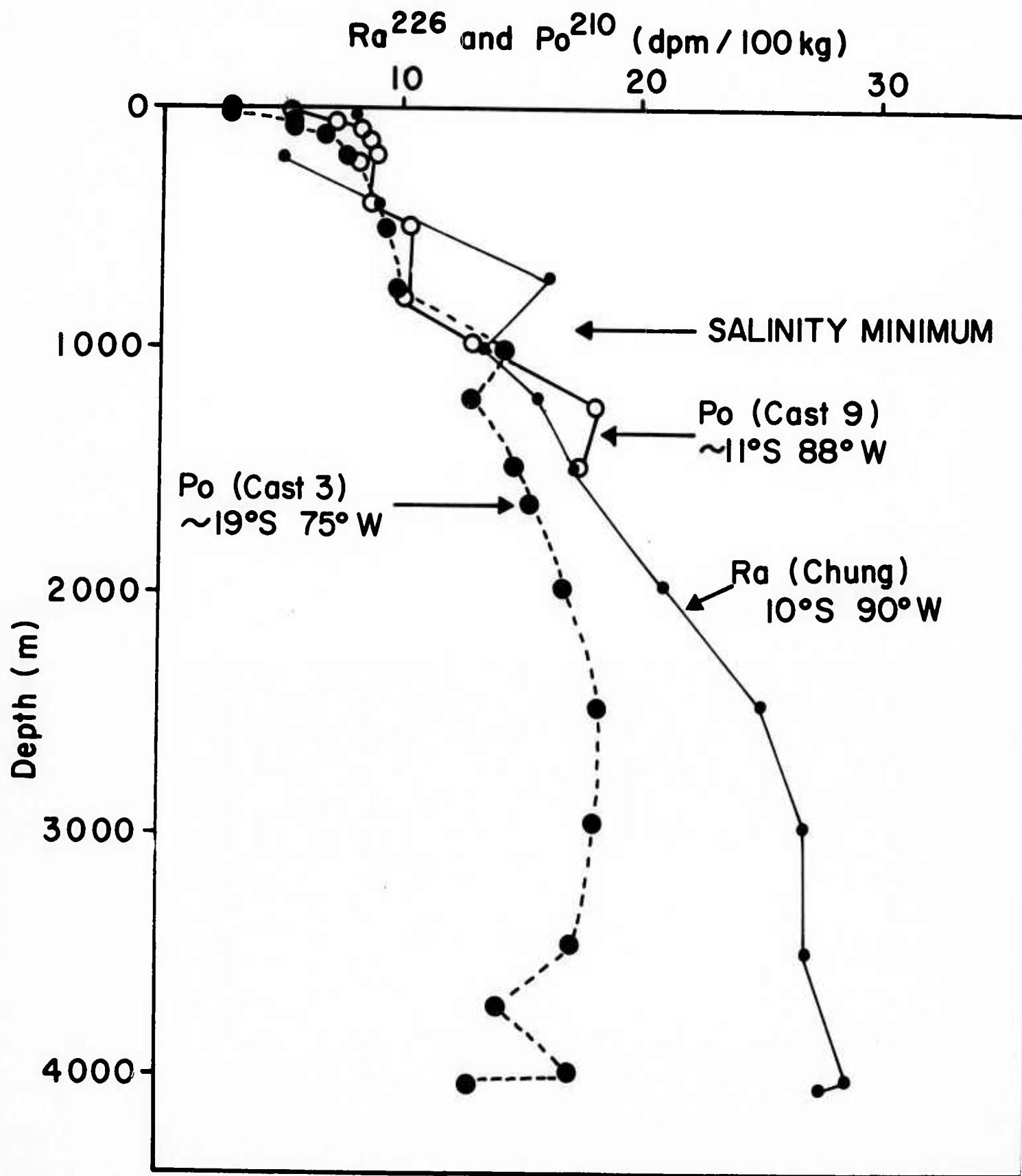
Figure 1 shows a plot of the uncorrected Po^{210} values as a function

of depth at the high productivity station (Cast 3) and the more normal productivity station (Cast 9). The Ra^{226} data for that general region are also plotted. It appears that in the region of Cast 9 the Po^{210}/Ra^{226} activity ratio below about 900 meters is at the equilibrium value whereas a marked deficiency of Po^{210} is found under the high productivity zone (Cast 3). This confirms the findings of Craig et al. (1973) with the constraint that we expect the greatest departure from equilibrium for the Pb^{210}/Ra^{226} system under regions of high productivity where the particle flux through the water column is expected to be the greatest.

References

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Figure showing vertical profiles of Ra^{226} and Po^{210} (dpm / 100 kg) versus Depth (m). Labels: SALINITY MINIMUM; Po (Cast 9) ~11°S 88°W; Po (Cast 3) ~19°S 75°W; Ra (Chung) 10°S 90°W.

V.   APPLICATION TO ARPA INTERESTS

We have shown in the previous section how we can use the relative con-
centrations of some of the members of the uranium and thorium decay series
in the following areas: (1) ocean surface circulation, (2) aerosol
derived Pb^{210} flux patterns over the oceans and the possible Po^{210} flux
from the ocean to the continents via marine aerosol transport, and (3) the
measure of the mean residence times of some of the radionuclides in the
surface ocean as a function of surface biological productivity.

In this section we review the relation of these studies to the problem
of interest to ARPA that initiated this program: can plankton provide a
high energy gamma ray source of high enough flux from natural radioactive
nuclides to be detected by towed scintillation crystal γ-ray detectors?

If we consider all the nuclides of Table 1 of Section II, the only
potential high energy γ-ray emitter that might be concentrated in plankton
is Th^{234}, which decays to Pa^{234} (1.18 minute half life) which then on
decay to U^{234} emits γ's as energetic as 1.6 Mev.

As we mentioned earlier it is difficult to obtain Th^{234} determination
unless the sample is returned immediately to the laboratory after shipboard
collection. It is possible, however, to obtain an idea of the maximum
Th^{234} concentration to be expected from a measurement of the Th^{228} concen-
tration in plankton and with a knowledge of the regional Th^{228} concentration
of surface sea water.

In major parts of the oceans away from coastal regions the Th^{228}/Ra^{228}
activity ratio is about 0.2 (Broecker et al., 1973). In the Atlantic
Ocean the average Ra^{228} activity in surface water is about 0.02 dpm/l;

hence the Th^{228} activity in 0.004 dpm/l. Because of the short half life of Th^{234} the Th^{234}/U^{238} activity ratios of open ocean water is about one (Bhat et al., 1969) and thus the Th^{234} activity equals about 2.4 dpm/l. The Th^{234}/Th^{228} activity ratio in Atlantic surface sea water is then about 600.

If the average excess Th^{228} activity of dry plankton is 0.1 dpm/g (Kharkar et al., 1974) and if this thorium were fully scavenged from the ocean by the plankton the Th^{234} activity of the dry plankton would be 60 dpm/g. The older the plankton the lower their value would be for the integrated plankton sample because of the decay of already entrapped Th^{234} in the aging plankton.

If the total γ activity of the Pa^{234} produced from the Th^{234} is 1% of the β activity which predominates, then a total of 0.6 dpm/g is that maximum γ radiation ascribable to Th^{234}.

Actually in upwelling regions and coastal waters where plankton thrive, the Th^{228} and Th^{234} activities of the sea water will actually be considerably less than the value we have used, and thus the activities in the plankton would be lower. Since the probability of encountering plankton patches would be greater in these highly productive areas it is clear that such encounters would not yield measurable γ hot spots on towed γ detectors.

REFERENCES

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Table 1: The gamma activity contributed by natural radionuclides in plankton (on a dry weight basis).

	Gamma activity (dpm/g)	Gamma energies
Potassium-40 (1)	2.6	1.46 Mev
Protactinium-234 (from Th^{234}) (2)	0.6	0.765 Mev $\sim$ 33% 1.00 Mev $\sim$ 67%
Polonium-210 (3)	0.001	0.80 Mev

(1) Assuming 1.3% K in dry zooplankton, K^{40} = 0.0118% of K and 11% of activity due to gammas emitted on the Ar electron capture branch to Ar^{40}.

(2) Assuming 60 dpm/g Th^{234} (thus Pa^{234}) activity in dry plankton based on calculation in text and a 1% activity due to gammas.

(3) Assuming 10^{-5} gammas for one alpha and a Po^{210} α activity of 100 dpm/g dry weight of plankton.