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#### Models of the distribution of <sup>210</sup>Pb in a section across the North Equatorial Atlantic Ocean

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#### ABSTRACT

The deficiency of <sup>210</sup>Pb relative to <sup>220</sup>Ra in the world's deep ocean is well documented, and the overall residence time of <sup>no</sup>Pb has been calculated to be about 15-100 years. It has been assumed, generally, that the removal mechanism is one of in situ adsorption on settling particles, but Bacon et al. (1976) suggested that a boundary scavenging process with diffusive and advective fluxes of <sup>210</sup>Pb from the interior ocean may be a significant factor. In this contribution we examine some two-dimensional models of 200Pb in a section across the North Atlantic Ocean at 15N. We show that satisfactory fits to the <sup>20</sup>Pb distribution may be obtained with (1) a model that includes both boundary scavenging and in situ adsorption with a constant adsorption rate constant or with (2) a model that has no boundary scavenging but allows the in situ adsorption rate constant to be a function of distance from the boundary. We have calculated the interior and boundary fluxes of 210 Pb required of each model and suggest that the boundary fluxes are of a magnitude to be compatible with Fe and Mn redox cycling in slope and shelf sediments but that the variations in the in situ adsorption flux are difficult to explain in terms of the known distributions of fine particles. We suggest that the boundary scavenging process is a function of the flux of Fe<sup>+2</sup> and Mn<sup>+2</sup> from anoxic sediments accompanied by rapid oxidation and precipitation in the boundary mixed layers.

The boundary fluxes calculated for model (1) amount to 2-8 dpm cm<sup>-2</sup> yr<sup>-1</sup> for slope and shelf sediments but only about 0.04 dpm cm<sup>-2</sup> yr<sup>-1</sup> for the deep ocean bottom boundary. The bottom boundary flux in the deep ocean is small and would not be detectable above the large particle flux of about 0.7 dpm cm<sup>-2</sup> yr<sup>-1</sup> contributed by biological removal from the ocean surface.

#### **1.** Introduction

Recent work on the distribution of <sup>210</sup>Pb in the oceans has been reviewed by Bacon *et al.* (1980a). The principal modes of supply of <sup>210</sup>Pb to the oceans are production within the water column, following the decay of <sup>220</sup>Ra, and deposition from the atmosphere. The atmospheric source derives from the decay of <sup>222</sup>Rn, a noble gas, which is produced from the decay of <sup>220</sup>Ra in continental areas and transported over the ocean (Turekian *et al.*, 1977). In open ocean areas, the atmospheric flux of <sup>210</sup> Pb gives rise to an excess of <sup>210</sup> Pb over <sup>220</sup>Ra that is a frequent feature of

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Figure 1. Station locations occupied during Cruise 32, F.S. Meteor and sampled for <sup>100</sup>Pb (from Bacon, 1977).

ocean surface waters. However, at depths below 500-1000 m, the  $^{210}Pb/^{226}Ra$  ratio is almost always less than one.

Estimates of the residence time of <sup>210</sup>Pb in ocean surface waters vary from about 0.5 years to 5 years, and most investigators agree that the rapid removal results, in some way, from biological activity even though the exact mechanism is not clear (Shannon *et al.*, 1970; Nozaki and Tsunogai, 1973; Bacon *et al.*, 1976; Nozaki *et al.*, 1976; Nozaki and Tsunogai, 1976).

Craig et al. (1973) first reported that <sup>210</sup>Pb and <sup>226</sup>Ra are not in equilibrium in the ocean deep water, and they showed relative deficiencies of 210Pb of 20-75% in both the Atlantic and Pacific Oceans. These observations have since been confirmed by a large number of measurements (Nozaki et al., 1973; Tsunogai et al., 1974; Applequist, 1975; Somayajulu and Craig, 1976; Bacon et al., 1976; Thomson and Turekian, 1976; Nozaki and Tsunogai, 1976; Bacon, 1977; Bacon et al., 1980a; Nozaki et al., 1980). It is generally assumed that <sup>210</sup>Pb is "scavenged" in the deep ocean by suspended particulate matter and subsequently eliminated from the water column by sinking. This was the view of Craig et al. (1973) who employed a vertical advection-diffusion model to calculate the deep water 210Pb flux in the Pacific Ocean. This calculation yielded a 54-year residence time for 210Pb in the deep sea. It was assumed that a minor fraction of the 210Pb occurs in particulate phases and that this residence time characterizes the transfer of 210Pb from dissolved to particulate form. Bacon et al. (1976) confirmed this assumption and showed that in the North Equatorial Atlantic less than 5% of the total 210Pb in the deep water resides on particles  $(>0.4\mu m)$ . However, these authors believed that, because of this low concentration of <sup>210</sup>Pb in particles, the particle sinking rates required to maintain the deep water



Figure 2. Dissolved <sup>210</sup>Pb (dpm 100 kg<sup>-1</sup>) in west-east section at about 15°-30°N in the Atlantic Ocean (data from Bacon, 1977).

<sup>210</sup>Pb flux are unreasonably high, and they suggested that a substantial fraction of the <sup>210</sup>Pb removal may occur directly at the sea floor by some kind of boundary scavenging mechanism. This hypothesis is consistent with the vertical gradients often observed, which show <sup>210</sup>Pb decreasing toward the sea floor. Bacon *et al.* (1976) showed that similar decreases occur as the sea floor is approached along horizontal planes. Nozaki *et al.* (1980) reporting on a substantial number of <sup>210</sup>Pb profiles in the Pacific Ocean, comment that both *in situ* adsorption and boundary scavenging may be involved in accounting for the <sup>210</sup>Pb deficiencies that they observe. It is generally assumed that increases in the particulate activity of <sup>210</sup>Pb with depth (or specific activity) provide prima facie evidence of the effect of an *in situ* adsorption process. This assumption is not necessarily true if the distribution of the particles carrying <sup>210</sup>Pb is controlled by horizontal diffusion and advection as well as by vertical settling.

The relative importance of *in situ* adsorption and boundary scavenging is not yet known. In this paper we examine some theoretical models for <sup>210</sup>Pb in an Atlantic Ocean section and attempt to define the model fluxes of <sup>210</sup>Pb that are required by different assumptions concerning the removal processes. The extent to which these fluxes may be explainable by known processes may assist in clarifying our current understanding or provide insight into experiments that would provide definitive answers.

The data that we model are derived from Bacon (1977). Figure 1 shows the location of stations occupied during Cruise 32 of the F. S. *Meteor*, and Figure 2 is a West-East section of dissolved <sup>210</sup>Pb (i.e., that passing through an  $0.4\mu$ m filter). The principal features of the <sup>210</sup>Pb distribution in this section are the high surface activities from the atmospheric flux, the deep maximum offset to the east, and the decreased activities close to the boundaries.

#### 2. Model considerations

The distribution of <sup>210</sup>Pb may be supposed as a balance between input and output processes modified by water motion. The simplest expression that can be used to model these processes in two dimensions is a diffusive model, with steady state assumed:

$$\frac{\partial C}{\partial t} = K_x \frac{\partial^2 C}{\partial x^2} + K_z \frac{\partial^2 C}{\partial z^2} + \lambda C_p - \lambda C - (F_o + F_1 e^{-\mu z})C = 0$$
(1)

where C is the concentration of dissolved <sup>210</sup>Pb, x and z are horizontal and vertical distances,  $K_x$  and  $K_z$  are horizontal and vertical eddy diffusion coefficients,  $C_p$  is the activity of the radioactive parent of <sup>210</sup>Pb, and  $\lambda$  is the decay constant of <sup>210</sup>Pb. The expression  $(F_o + F_1e^{-\mu z})$  describes *in situ* removal that is a combination of first order removal by adsorption  $(F_o)$  and by a biological uptake mechanism that decreases exponentially with depth. In equation (1) the term  $\lambda C_p$  defines the production of <sup>210</sup>Pb from its parent. For practical purposes the parent of <sup>210</sup>Pb in the ocean water column may be designated as <sup>220</sup>Ra and <sup>210</sup>Pb. The longest-lived radionuclides exist in the decay chain between <sup>220</sup>Ra and <sup>210</sup>Pb. The longest-lived of these intermediate products is <sup>222</sup>Rn with a half-life of 3.8 days. The loss terms in equation (1) are the radioactive decay of <sup>210</sup>Pb,  $\lambda C$ , and the *in situ* biological and adsorption removal terms.

In addition to the in situ processes, the distribution of <sup>210</sup>Pb is also assumed to be affected by fluxes at the ocean boundaries. The existence of an atmospheric flux to the ocean surface is well established (Turekian et al., 1977; Bacon et al., 1976) and this has been estimated to be about 0.5-1.5 dpm  $cm^{-2} yr^{-1}$ . The atmospheric flux is likely to be at a maximum in the western regions of the Atlanic north of 30°N latitude where the westerly winds carry continentally produced <sup>222</sup>Rn over the ocean. At these latitudes, Turekian et al. (1977) propose that the atmospheric flux of <sup>210</sup>Pb is about 1-1.5 dpm cm<sup>-2</sup> yr<sup>-1</sup> in the Western Atlantic decreasing to about 0.5 dpm cm<sup>-2</sup> yr<sup>-1</sup> in the Eastern Atlantic. Below 30°N the dominant tradewinds are known to carry continental air, from North Africa, over the ocean. Estimates of the 210Pb flux associated with the trades are not available, but it is unlikely that it differs greatly from the westerlies. However, the input from the east will certainly prevent the decreasing flux eastward as modeled by Turekian et al. (1977) at higher latitudes. In the absence of other information, we will assume that the atmospheric flux of <sup>210</sup>Pb to the ocean surface at the latitude of our section is constant at 0.6 dpm cm<sup>-2</sup>  $yr^{-1}$ , which is the value estimated by Bacon *et al.* (1976), using a box model on this same data set.

Fluxes of <sup>210</sup>Pb at the ocean sides and bottom are less well accepted. Bacon *et al.* (1976) first proposed such a flux in order to explain the close-to-boundary decreases in <sup>210</sup>Pb/<sup>220</sup>Ra activity ratios that are a consistent feature of most <sup>210</sup>Pb/<sup>220</sup>Ra pro-

1981]

files (either vertical or horizontal). In terms of our model the simplest expression to describe a boundary flux is given by

$$K_{i} \frac{\partial C}{\partial i} = \gamma (x, z)C$$
<sup>(2)</sup>

where *i* is either x or z and  $\gamma(x,z)$  can be thought of as a piston velocity describing the flux of <sup>210</sup>Pb into the boundary. It is not necessary that this piston velocity be the same at all ocean boundaries. Later we will demonstrate that our best model fit requires that the velocities for flux into the ocean sides must be substantially higher than the bottom piston velocities.

#### 3. Operation of the model

We have derived numerical solutions to equation (1) and consider an ocean section of dimensions 4000 km by 5 km divided into grid points separated by 200 km in the horizontal and 0.125 km in the vertical. The second order differentials were approximated by terms of the form

$$K_x \frac{\partial^2 C}{\partial x^2} = \frac{K_x}{x_0^2} (C_{(i,j-1)} - 2C_{(i,j)} + C_{(i,j+1)})$$
(3)

where  $x_0$  is the horizontal grid spacing (200 km). Boundary values were calculated by using equation (2) to calculate the point lying outside the boundary; for example at the left boundary with the boundary value being C(i,0) the relation

$$K_{x} \frac{\partial C}{\partial x} = \frac{K_{x}}{2x_{o}} (C_{(i,-1)} - C_{(k,+1)}) = \gamma(x,z)C_{(i,0)}$$
(4)

was used to calculate  $C_{(i,-1)}$  which was then substituted for the value  $C_{(i,f-1)}$  in equation (3). At the upper boundary, the relation used was

$$-K_z \frac{\partial C}{\partial z} = A \tag{5}$$

where A is the constant atmospheric flux.

In several model runs we have experimented with various values of  $K_x$  and  $K_z$ . Our best fit visual solution uses  $K_x = 5 \times 10^6$  cm<sup>2</sup> sec<sup>-1</sup> and  $K_z = 1$  cm<sup>2</sup> sec<sup>-1</sup> except at the vertical boundaries. Bacon *et al.* (1976), in their attempts to fit a onedimensional model to <sup>210</sup>Pb/<sup>220</sup>Ra horizontal profiles, showed that, if a constant horizontal eddy diffusion coefficient was applied, it was not possible to generate the steepness of the decline of the <sup>210</sup>Pb/<sup>220</sup>Ra ratio, with approach to the boundary, that was shown by the data. They showed that, if the value of  $K_x$  was determined according to Okubo's relationship (Okubo, 1971)

$$K_a = .0103l^{1.15} \tag{6}$$

(where  $K_a$  is the apparent eddy diffusion coefficient and l is a scale length in cm), then a much better fit was obtained for the ratio profiles. There is some conceptual difficulty in this approach because l in equation (6) is a scale length and not a distance. However, the physics of the diffusion process in the ocean is so poorly understood that it is not possible at this time to state that the apparent eddy diffusivity does not increase into the ocean interior. Clearly, our model will not tolerate a value of  $K_x = 0$  at the vertical boundaries, and we circumvent this problem by assuming a boundary region with a scale of about 50 m so that the value of  $K_x$  at the vertical boundaries is given by  $K_x = .0103 (5000)^{1.15} = 184.8 \text{ cm}^2 \text{ scc}^{-1}$ . With these values of  $K_x$  at the vertical boundaries, several model runs established that the results were very little different for the two cases in which 1) the values of  $K_x$  at the interior grid points were determined by  $K_x = .0103 (x \cdot .10^5)^{1.15} (x = 0 \rightarrow 2000 \text{ km}) \text{ or } 2)$  the values of  $K_x$  at the interior grid points were constant at  $K_x = 5 \times 10^6 \rightarrow 1 \times 10^7$ .

The model result given in Figure 3 was calculated with  $K_x$  constant at  $5 \times 10^{\circ}$ . The *in situ* production term  $\lambda C_p$  was inserted using the silicate distribution given in Figure 4 and the relationship between silica and radium concentrations used by Bacon *et al.* (1976).

$$Ra = 6.91 + 0.217Sil$$
 (7)

With these constants and the decay constant of <sup>210</sup>Pb of 0.0312 yr<sup>-1</sup>, a series of experimental model runs established that values approaching  $F_o = .007$  yr<sup>-1</sup>,  $F_1 = .3$  yr<sup>-1</sup> and  $\mu = 11$  km<sup>-1</sup> gave reasonable approximations to the <sup>210</sup>Pb distributions in the interior upper ocean. Subsequent model runs applied various values of  $\gamma(x,z)$  at the boundaries until a reasonable fit of the model to the data could be obtained for the whole system.

The fit demonstrated by Figure 3 has been obtained with

$$F_{o} = .007 \text{ yr}^{-1}$$

$$F_{1} = .3 \text{ yr}^{-1}$$

$$\mu = 11 \text{ km}^{-1}$$

$$\gamma(\text{west}) = 25 \text{ km yr}^{-1}$$

$$\gamma(\text{east}) = 5 \text{ km yr}^{-1}$$

$$\gamma(\text{bottom}) = .005 \text{ km yr}^{-1}$$
atmospheric flux = 0.6 dpm cm<sup>-2</sup> yr^{-1}
$$K_{z} = 1 \text{ cm}^{2} \text{ sec}^{-1}$$

$$K_{z}(\text{boundary}) = 184.8 \text{ cm}^{2} \text{ sec}^{-1}$$

$$K_{z}(\text{interior}) = 5 \times 10^{6} \text{ cm}^{2} \text{ scc}^{-1}$$

$$\lambda = .0312 \text{ yr}^{-1}$$

#### 4. Model results

The fit between the model and the data is quite good in both a qualitativetrend sense and in a quantitative sense. In fact, considering the fact that advec-





tion has been ignored, the fit is very good. It is likely that, with the exception of some upwelling in the eastern regions of the section that the principal advection may be the meridional circulation normal to the section. If the horizontal concentration gradients normal to the section are small, then we would expect that such advection would not have a marked effect on the distributions. Some effects of the meridional circulation are incorporated into the model because the silicate field has been used as the determinator of the radium field. The high silicate values around 1 km are the result of the penetration of high silicate waters associated with Antarctic Intermediate Water, while the silicate gradient in the bottom water results from the southward penetration of low silicate North Atlantic Deep Water associated with the western boundary deep flows.

The major features of the <sup>210</sup>Pb distribution are 1) the very low activities in the deep water toward the western boundary, 2) the steeply inclined isopleths in this region, 3) the penetration of a <sup>210</sup>Pb minimum of about 7 dpm/100l over 1000 km from the western boundary and about 400 km from the eastern boundary, 4) the <sup>210</sup>Pb maximum at 4-4.5 km which is offset to the east from the center of the section. and 5) surface values of about 20 dpm/100l, with the exception of an area between 20W and 32W. All of these features except the last are duplicated by the model. It is possible that this feature in the actual data is a transient feature of the upper ocean or that it represents an advective flux of low 210Pb surface water from regions in the Northeast Atlantic where the atmospheric flux is lower. Another discrepancy between the model and the data is that we cannot approach the deep maximum value of 14 dpm at 21W. Models with in situ adsorption or boundary adsorption terms set to duplicate that maximum do not give a satisfactory fit in other parts of the section. It would be possible to increase the model values in this region of the section by increasing the in situ production flux, but we have not allowed the derived 226Ra field to vary from that predicted by the 226Ra-Silicate relationship given earlier. It is worth noting that the maximum of 14.1 dpm/100l at Station 27 is only





a one-point maximum, but it is supported by a value of 13.0 dpm/100l at 4014 m at Station 23. The simple diffusive model does not replicate the complex small minima and maxima in the region between about 1 and 2 km. These may well be maintained by advection processes in regions where relatively important horizontal gradients may exist.

However, despite the discrepancies, the simple model, with boundary fluxes, gives an overall fit that is acceptable within the limits of our data set.

The *in situ* adsorption ( $F_o$ ) and biological removal ( $F_1$ ) terms invert into <sup>210</sup>Pb residence times of 143 yrs in the deep water and 3.3 yrs in the surface water with respect to *in situ* removal. The strong exponential applied to  $F_1$  gives a half-depth of removal of 63 meters, so the biological removal is dominant only in the upper 340 m of the water column. These residence times are, as expected, similar to those derived by Bacon *et al.* (1976).

It is of considerable interest and importance that the boundary piston velocities required to produce the model fit are different at each vertical boundary, and the bottom piston velocity is substantially smaller than that required at the side boundaries. We believe these differences are a function of the boundary removal process which will be discussed in more detail later.

#### 5. Lead-210 fluxes

An advantage of the model we have applied is that the boundary concentrations are determined as a function of all of the model parameters and thus we may use them to estimate the magnitude of the boundary fluxes. Table 1 gives an overall flux balance for the model. The data of Table 1 are in units of  $10^{10}$  dpm yr<sup>-1</sup> and apply to an ocean section of dimensions 4000 km × 5 km × 1 m. The *in situ* production flux was determined by vertical integration of the calculated radium profiles at each grid point and summation of the vertically integrated totals. SimpTable 1. Model <sup>210</sup>Pb Flux Balance (for section 4000 km × 5 km × 1 m) dpm × 10<sup>10</sup> yr<sup>-1</sup>.

Input	Output	
8.04		
2.40		
	5.73	(54.9%)
	1.29	(12.4%)
	2.65	(25.4%)
	0.40	(3.8%)
	0.21	(2.0%)
	0.16	(1.5%)
10.44	10.44	(100%)
	Input 8.04 2.40 10.44	Input Ou 8.04 2.40 5.73 1.29 2.65 0.40 0.21 0.16 10.44 10.44

son's rule was used to approximate the vertical integrals. Similar procedures established the *in situ* decay and the *in situ* biological and adsorption fluxes. The boundary fluxes were estimated by applying equation (2) with the calculated values of the boundary concentrations and the piston velocities. Subsequently the totals were derived by integration of the values at each of the boundaries over the length of the boundary.

From Table 1 it can be seen that, apart from radioactive decay, the most important removal flux is the biological uptake which, with the steep exponential decline, applies only to the upper few hundred meters of the water column. Of the remaining output fluxes, the boundary fluxes account for a total of about 7% of the removal while the *in situ* adsorption flux accounts for about 12%. Thus the two removal processes appear to be of a similar order of magnitude. The boundary fluxes of Table 1 give average unit fluxes of 42 dpm cm<sup>-2</sup> yr<sup>-1</sup>, 80 dpm cm<sup>-2</sup> yr<sup>-1</sup> and 0.04 dpm cm<sup>-2</sup> yr<sup>-1</sup> respectively for the east, west, and bottom boundaries. In considering these model fluxes as representatives of actual fluxes to the boundaries, it must be remembered that the model vertical boundaries of 5 km represent actual slope and shelf boundaries of dimensions 50 to 200 km or so. Thus the actual mean unit area fluxes would be a factor of 10 to 40 lower than the model fluxes, i.e., in the range of about 1 to 8 dpm cm<sup>-2</sup> yr<sup>-1</sup>.

It must be also remembered that the calculated model vertical boundary fluxes relative to other fluxes are somewhat dependent on the station locations on the section and the proximity of these stations to the boundaries. If there were stations located closer to the eastern boundary, particularly under the upwelling areas of the coast of north Africa, then further strong depletions of  $^{210}$ Pb may be observed that would increase the vertical boundary fluxes required to achieve a satisfactory solution to the data. Later in this paper, we argue that the boundary fluxes may be maximized in areas where the sediments are subject to high fluxes of organic matter. These arguments suggest that the calculated fluxes of 1 to 8 dpm cm<sup>-2</sup> yr<sup>-1</sup> should be toward the lower end of the observed fluxes into continental slope environments.

The magnitude of the bottom boundary flux required for reasonable conformance of the model is seen to be quite small. If we assume that the biological uptake flux represents a process of *in situ* loss from the surface into a large particle phase which sinks rapidly through the water column, then the vertical integral of that flux which amounts to about 0.66 dpm cm<sup>-2</sup> yr<sup>-1</sup> is very large compared to the 0.04 dpm cm<sup>-2</sup> yr<sup>-1</sup> calculated for the bottom boundary uptake flux. These considerations suggest that fluxes to the boundary which are significantly in excess of the atmospheric fluxes may occur on the continental slopes and shelves but, for the larger part of the ocean bottom, the increased flux due to boundary scavenging would not be detectable in the sediment inventories (Nozaki et al., 1977). It should be added at this point that excesses of <sup>222</sup>Rn over its parent <sup>226</sup>Ra are a frequent occurrence at near boundary locations (Broecker, 1965; Sarmiento et al., 1976). These excesses result from the input of 222Rn from bottom sediments where the 228Ra activities are relatively high. The decay of this excess 222Rn to 210Pb would increase the production term for <sup>210</sup>Pb in equation (1) for near boundary locations. However, assuming that all of this excess 222Rn is removed as 210Pb by the boundary uptake, the increase in the integrated fluxes to the boundaries would be only about 0.04 dpm cm<sup>-2</sup> vr<sup>-1</sup> (using an integrated bottom <sup>222</sup>Rn excess of about 1.2 dpm cm<sup>-2</sup>, Bainbridge et al., 1976).

#### 6. Alternate models

If boundary uptake of the <sup>210</sup>Pb does not occur, then another model that may account for the observed <sup>210</sup>Pb distribution can be derived by allowing  $F_0$  in equation (1) to be a function of x and z. If we assume that in near boundary locations the concentrations of particulate matter, and the fluxes of fine particulate matter, are higher than in the interior ocean then it is possible that the 210Pb removal by in situ adsorption could be increased by the greater availability of particle surfaces. It is well-known that strong nepheloid layers are a characteristic of the deep western boundary regions in the North Atlantic Ocean, particularly to the north and west of the Sargasso Sea but less so at the latitude of our 210Pb section (Biscaye and Eittreim, 1977). It is also known that surface biological productivity in the eastern regions of the North Atlantic, off the African coast, is substantially higher than in the interior ocean due to the upwelling processes that are characteristic of this region. Bishop et al. (1977) have demonstrated that the large particle flux, from the surface layers to the deep ocean, is substantially higher under these high productivity regions. While it is not clear that rapidly settling large particles may be effective in providing surfaces for the uptake of 210Pb, it is possible that the organic debris, which forms a substantial fraction of these particles, is very effective in sequestering 210Pb. Near bottom nepheloid layers are generally weak to nonexistent in the interior and eastern boundary regions of the Northern Subtropical Atlantic.



Figure 5. Model <sup>210</sup>Pb (dpm 100 kg<sup>-1</sup>) distribution resulting from a numerical solution of equation (1) with no boundary scavenging and variable *in situ* adsorption in the deep water.

Figure 5 shows the  $^{210}$ Pb distribution that results from a model using equation (1), but in which the boundary fluxes have been set to zero and the *in situ* adsorption flux is given by the relationship

$$F(x,z) = F_{o}(x) + F_{1}e^{-\mu z} + F_{2}e^{-\mu' (z_{m}-z)}$$
(8)

where  $F_1 = .3 \text{ yr}^{-1}$ ,  $\mu = 11 \text{ km}^{-1}$ ,  $F_2 = .055 \text{ yr}^{-1}$ ,  $\mu' = 11 \text{ km}^{-1}$ ,  $z_m$  is the total depth, i.e., 5 km.  $F_o$  decreases linearly from .15 yr<sup>-1</sup> at the western boundary to .004 yr<sup>-1</sup> at 1000 km, is constant at .004 yr<sup>-1</sup> to 3700 km, then increases linearly to .03 yr<sup>-1</sup> at the eastern boundary.

This relationship allows us to consider <sup>210</sup>Pb removal processes that are entirely in situ. The function F(x,z) increases from the interior toward all the boundaries. The vertical increases are confined by the large exponentials to the upper and lower few hundred meters of the water column, and the upper increase is similar to that used previously in accounting for the biological uptake; the lower increase may be supposed as that due to the adsorption of <sup>210</sup>Pb on particles resuspended from the bottom, and assumes that such resuspension is characteristic of all ocean areas. The horizontal increases are necessarily greater toward the western boundary and extend further into the section than the increases to the eastern boundary. While such a distribution of particles, to act as adsorbers, is not unreasonable at latitudes of 30-45N and in the bottom 2 km of the water column, the data of Eittreim et al. (1976) and Biscave and Eittreim (1977) do not support such large differences for latitudes of 15-20N. It should be noted that the fit of this model in Figure 5 to the data is equally as good as that of Figure 3, which includes boundary scavenging. However, it should also be noted that this fit can be obtained only by horizontal increases of  $F_{o}$  applied throughout the whole water column and that the magnitude of the increase from the interior to the western boundary is about a factor of 40. The data of Biscaye and Eittreim (1977) and Brewer et al. (1976) provide no evidence that increased particle concentrations toward the western boundary of the section could





Figure 6. Profiles of <sup>210</sup>Pb (dpm 100 kg<sup>-1</sup>) in the North Atlantic and Norwegian Sea. R.V. Knorr Cruise 54-6.

provide the increased *in situ* adsorption required of this model, particularly when such particles would be required throughout the whole water column. Accordingly, although an *in situ* adsorption model can be found to fit the <sup>210</sup>Pb distributions, the required variations in the rates of *in situ* removal do not seem to be reasonably explainable in terms of the known particle concentrations. It is possible that the quality of the particles with respect to adsorption of <sup>210</sup>Pb may change systematically as a boundary is approached, but there is no evidence of this other than, perhaps, under high productivity, upwelling areas. The western end of the section of Figure 5 is not such an area.

#### 7. Other evidence from deep water profiles of <sup>210</sup>Pb

Figure 6 shows two profiles of <sup>210</sup>Pb that we have measured from the North Atlantic Ocean and the Norwegian Sea, while Figure 7 gives a <sup>210</sup>Pb section off the continental shelf in the North Arabian Sea, determined from samples collected during *Atlantis II* Cruise 93. The data of Figure 6 is given by Spencer *et al.* (1980), while the North Arabian Sea data will be published later. We are currently determining the <sup>210</sup>Pb concentrations in several profiles from the Panama Basin. Preliminary <sup>210</sup>Po counts indicate that, in this area, <sup>210</sup>Pb is strongly depleted in the deep water. This strong depletion of <sup>210</sup>Pb relative to <sup>220</sup>Ra is evident at all of these locations, but is particularly pronounced in the North Arabian Sea and the Panama Basin. Bacon *et al.* (1980a) have argued that the decreasing <sup>210</sup>Pb/<sup>220</sup>Ra in the Labrador Sea, which is observed in progressing from Labrador Sea water to Iceland-Scotland Overflow water to Denmark Strait Overflow water, may well be a function of boundary proximity.





Figure 7. Section of <sup>no</sup>Pb (dpm 100 kg<sup>-1</sup>) in the North Arabian Sea, Persian Gulf region. R.V. Atlantis II, Cruise 93.

Strong depletions of <sup>210</sup>Pb are observed in the adiabatic deep water of the Norwegian Sea. Broecker et al. (1976) have shown that the high salinity North Atlantic surface water that flows northeastward into the Norwegian Sea has 228Ra activities of 7.5-9.5 dpm/100 kg. The low salinity surface water in the Greenland Sea has somewhat lower <sup>226</sup>Ra levels, about 6.6-8 dpm/100 kg. These <sup>226</sup>Ra concentrations may be compared with the <sup>210</sup>Pb concentrations of Station 70 in the Norwegian Sea (Fig. 6). The surface <sup>210</sup>Pb is clearly in excess of <sup>226</sup>Ra because of the atmospheric input of <sup>210</sup>Pb to the North Atlantic and the surface water residence times of about 2 years with respect to biological uptake and removal. The low salinity core at 350 m represents a core of surface water from the Greenland Sea that advects, around Iceland, into the Norwegian Sea. The minimum of <sup>210</sup>Pb in this core may be a function of decreased atmospheric fluxes at high latitudes and the lower 226Ra levels in the Arctic surface water. In the deep water, below 500 m, the <sup>210</sup>Pb activity decreases monotonically to the bottom where the <sup>210</sup>Pb is 70% depleted relative to <sup>228</sup>Ra. However, even at 1000 m a 30-40% depletion exists. The particulate <sup>210</sup>Pb activities at Station 70 are almost constant (at about 1 dpm/100/) with depth except for a slight increase in the low salinity layer at 350 m and in the near bottom sample. The adiabatic bottom water of the Norwegian Sea, with a salinity of 34.92% is formed by mixing and cooling of high salinity surface water from the North Atlantic with lower salinity Arctic surface water. This process probably takes place in the region of the Barents Sea, north of Norway. However, the overturn to the deep Norwegian Sea is much less than to the Greenland Sea, north of Iceland (the deep Norwegian Sea water has very low concentrations of fallout isotopes compared with the deep Greenland Sea, Peterson and Rooth, 1976), and the renewal time of the deep Norwegian Sea water probably approaches 100 years or so. The strong <sup>210</sup>Pb depletions in the deep water would indicate an overall removal residence time of <sup>210</sup>Pb of about 15 years. Such rapid removal, if it is being accomplished solely by *in situ* adsorption on particles, is not consistent with the almost constant particulate activities that exist in the deep water.

The northern Arabian Sea and the Panama Basin are areas of very high surface productivity, and it is likely that vertical particle fluxes, particularly the large particle fluxes, are also high. This increased particle flux may be in part responsible for the deficiencies of <sup>210</sup>Pb, but it is difficult to account for the shape of the <sup>210</sup>Pb distribution in the northern Arabian Sea without either a strong sink on the upper slope and shelf or a strong advective input of <sup>210</sup>Pb-rich bottom water. Such an input could exist, but there is no hydrographic evidence that it does.

We believe that this data, together with the model sections already discussed, provide support for the hypothesis that boundary scavenging is an important determinator of <sup>210</sup>Pb distributions in the deep ocean.

#### 8. The boundary scavenging mechanism

We propose that the most likely candidate for the boundary sink of <sup>210</sup>Pb is the redox cycling of Mn and Fe hydroxides associated with reducing sediment conditions. These occur predominantly in slope and shelf regions, particularly under high productivity zones where organic matter input is high.

That this process could be effective in the removal of <sup>210</sup>Pb from sea water is demonstrated by our results from the Cariaco Trench (Bacon et al., 1980b). The Cariaco Trench is a silled basin on the continental shelf north of Venezuela at about 10°30'N, 65W. It is approximately 1400 m deep and is separated from the Caribbean Sea by a sill that is at or about 150 m deep. Water above the sill depth exchanges freely with the open sea, while the deep water is isolated by the sill and by a strong density gradient that inhibits vertical mixing. The deep water below a depth of about 250 m is permanently anoxic (at least on a time scale of about 100 years, Deuser, 1973). Dissolved oxygen is completely depleted at about 250 m and from this depth down to 1400 m the concentration of H2S increases from zero to about 37  $\mu$ M/kg. A feature that is characteristic of the oxygen-H<sub>2</sub>S boundary is the redox cycling of Mn and Fe. This has been demonstrated by Spencer and Brewer (1971) and Spencer et al. (1972) for the Black Sea, a similar anoxic basin. Dissolved Mn+2 accumulates in the deep water following the reduction of particulate Mn+\* that settles across the O2/H2S boundary. This, in turn, establishes a diffusive flux of dissolved Mn+2 upward across the boundary, followed by oxidation, precipitation and



Figure 8. Dissolved and particulate Mn and dissolved and particulate <sup>210</sup>Pb profiles from the Cariaco Trench.  $O_z/H_2S$  transition region is that observed for the western Basin. Data from Bacon *et al.*, 1980b.

return to the deep water. Dissolved Fe<sup>+2</sup> also accumulates in the deep water and is subject to the same cycling.

The precipitation of the manganese and iron hydroxides, which is clearly evident in a thin layer just above the boundary, forms a powerful sink for <sup>210</sup>Pb (and other elements). Figure 8 shows particulate and dissolved manganese data together with particulate and dissolved <sup>210</sup>Pb data taken from the work of Bacon et al. (1980b). The depth range of the  $O_2/H_2S$  boundary is for the western basin of the Trench. In the eastern basin this boundary is slightly higher in the water column. This figure clearly shows the strong depletion of <sup>210</sup>Pb associated with the appearance of the thin zone of maximum particulate manganese. Following settling, reduction and dissolution of the Mn<sup>+4</sup>, the <sup>210</sup>Pb appears to be trapped in the deep water, probably associated with developing sulphide particulate phases. The maximum values for particulate Mn and <sup>210</sup>Pb are respectively about 2 µg kg<sup>-1</sup> and 3 dpm/100 kg giving a specific activity of <sup>210</sup>Pb of 1.5 × 10<sup>4</sup> dpm g<sup>-1</sup> Mn. Lewis (1977) has shown that the precipitation of Mn and Fe hydroxides in the Susquehanna River system provides a rapid scavenging of <sup>210</sup>Pb from solution, and Turekian (1977) stresses the importance of the redox cycling of Mn and Fe in the removal of reactive metals from estuarine and coastal waters.

Emerson et al. (1979) have shown that similar Mn and Fe cycling is taking place in the Saanich Inlet, a fjord in British Columbia, Canada, that has seasonally anoxic conditions in the deep water. Using carefully collected samples and very detailed

profiles across the  $O_2/H_2S$  boundary, these authors demonstrate that dissolved iron is oxidized and removed from the water very quickly; however, dissolved  $Mn^{+2}$ coexists with oxygen and is detectable in the water column up to 10 meters above the boundary. Further, they calculate the residence time for Mn in the oxic layer to be about 2-10 days which is more rapid oxidation and precipitation than would be expected from the extrapolation of abiotic laboratory oxidation rates to the ocean (Morgan, 1964). Emerson *et al.* (1979) also indicate that the oxidation rate of Mn in a biologically irrigated zone within the bottom sediments of Puget Sound gives a residence time for Mn<sup>+2</sup> with respect to oxidation of 2 to 5 days. Laboratory experiments suggest that the rapid oxidation is, in some way, catalyzed by bacteria.

These studies are most important, for they indicate not only that there is a substantive flux of  $Mn^{+2}$  and  $Fe^{+2}$  across the  $O_2/H_2S$  boundary, but also that the rates of oxidation are sufficiently rapid that virtually all of the  $Fe^{+2}$  will be lost by oxidation immediately at the boundary and that most of the  $Mn^{+2}$  will be lost by oxidation within a bottom mixed layer on a time scale of 2-10 days.

Fluxes of  $Mn^{+2}$ , amounting to 0.1 to 6.0 m moles  $m^{-2} d^{-1}$ , from the bottom sediments of Long Island Sound, have been reported by Aller (1980). If it is assumed that the Mn released from these sediments is oxidized and precipitated in the water column above the sediments on the time scale of 2-10 days and that the specific activity of <sup>210</sup>Pb in the precipitating MnO<sub>2</sub> approaches the 15 × 10<sup>4</sup> dpm g<sup>-1</sup> seen in the Cariaco Trench, then fluxes of <sup>210</sup>Pb to the sediments amounting to about 3-150 dpm cm<sup>-2</sup> yr<sup>-1</sup> could be accomplished.

The work of Lynn and Bonatti (1965), Bender (1971), Bischoff and Sayles (1972), Calvert and Price (1972), Murray and Gill (1978), Sawlan and Murray (1978) and Klinkhammer (1980) establishes that the diffusion of solubilized Fe and Mn upward and the reprecipitation in more positive Eh environments near the sediment water interface (or loss, if reducing conditions persist too close to the interface) are characteristic features of marine sediments in many locations.

Krishnaswami *et al.* (1973) have determined that the measured integrated deposition of excess <sup>210</sup>Pb in sediments from the Santa Barbara basin are about an order of magnitude greater than would be expected from the sum of the atmospheric flux and water column production. Similar high <sup>210</sup>Pb fluxes to coastal and upper continental slope sediments have been documented by Bruland (1974) and Shokes (1976). In these publications the authors explained the high fluxes by assuming an effective biological stripping process from ocean water advected over shelves. Recently, Bothner *et al.* (1981) have shown that the total sediment inventory of excess <sup>210</sup>Pb, in areas of recent mud deposition on the continental shelf off southern New England, is about a factor of 2 to 3 higher than could be generated solely by the atmospheric flux to this region. Such excesses over the atmospheric input should be a common feature of shelf and slope sediments, if our hypothesis is correct.

The literature data, discussed above, provides clear evidence that Mn+2 and Fe+2

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fluxes from sediments are a characteristic feature of many ocean sediments. Aller (1980) has shown that the  $Mn^{+2}$  flux to the overlying water is a function of the rate of supply of organic matter to the sediment, of the temperature and the organism activity (bioturbation, irrigation) within the sediment, but the average yearly production of  $Mn^{+2}$  is sufficient to scavenge trace metals from coastal waters at a rapid rate. In terms of the data we have presented in this paper, the very strong depletions of  $^{210}$ Pb in the Northern Arabian Sea and the Panama Basin are consistent with Aller's observations on the dependence of the  $Mn^{+2}$  flux on the supply of organic matter to the sediments. The upper slope and shelf regions of these locations, lying beneath highly productive surface waters, have extensive anoxic sediments, and it is reasonable to suppose that the rate of redox cycling of Mn and Fe is high.

The precipitation of Mn and Fe hydroxides is known to be a very effective mechanism for scavenging many elements. However, the extent to which such a process, operating at the ocean boundary, may be effective in the net removal of elements from the ocean will also depend on the chemistry of the scavenged elements in the reducing environment. Those elements that may be bound as insoluble sulphides, carbonates or perhaps by organic matter could be relatively immobile (e.g. perhaps Pb and other strongly sulphophile elements); others (such as Fe and Mn) could be mobilized and released to the sea water.

The rapid removal of <sup>228</sup>Th from coastal waters has been demonstrated by Broecker *et al.* (1973) and Li *et al.* (1979). Li (1979) has reported that <sup>239,240</sup>Pu residence times are also very short. Recently, Anderson (1981) has suggested that <sup>231</sup>Pa may be subject to boundary scavenging at a greater rate than <sup>230</sup>Th. The remobilization of several elements from sediments whether or not they were originally fixed by boundary scavenging has been documented. For example, the data of Noshkin and Wong (1979) and Bowen (1979) provide good evidence that Pu is being remobilized from sediments in the Pacific Ocean; Anderson (1981) suggests that <sup>230</sup>Th is released from sediments and Spencer *et al.* (1980) show that <sup>210</sup>Po is remobilized from shelf sediments in the North Sea.

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