THERMOCLINE VENTILATION OF ANTHROPOGENIC LEAD IN THE WESTERN NORTH ATLANTIC

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Abstract. Massive industrial aerosol emissions from North America have over the past century overwhelmed the natural distribution of lead in the western North Atlantic thermocline. The resultant features to 2000-m depth have been mapped near Bermuda for the year 1984. Since earlier reported measurements have largely been rejected on grounds of sample contamination, the twentieth-century evolution of anthropogenic Pb in the oceanic water column is unknown. Coupling of the 1984 water column Pb distribution to historical records in reef-building corals and tracer-derived thermocline ventilation rates (Jenkins, 1980) has permitted a model reconstruction of Pb penetration into the Sargasso Sea. The model is constrained by three distinct Pb distributions (Pb concentration, stable Pb isotopes, and 210Pb) with adjustable scavenging and regeneration parameters to account for nonconservative behavior. The results of the model substantiate the importance of lateral isopycinal ventilation while pointing out the necessity of dissolved-particulate exchange (i.e., scavenging of the order of 70 years in the deep thermocline; minimum regeneration of 10% particulate Pb between surface and 1700 m). Residual discrepancies between model isotopic predictions and observations below 800 m are likely due to a combination of the following factors: (1) presence of nonradiogenic background Pb in intermediate depth waters, (2) geographic variability in North American industrial source signatures, (3) Mediterranean Pb inputs of European origin, and (4) along-isopycnal mixing effects.

1. Introduction

Over most of the last century, the distribution of Pb in the upper waters of the western North Atlantic has been controlled by industrial inputs of North American origin. Evidence for this is contained in the skeletal Pb content of reef-building corals near Bermuda (Shen and Boyle, 1987). Direct detection of anthropogenic Pb in the Atlantic Ocean was first accurately reported by Schaeule and Patterson (1983) only 5 years ago. Since this time, Boyle et al. (1986) have attempted to document the Sargasso Sea's response to changing Pb inputs from the atmosphere. Rapid changes in the thermocline distribution of Pb are possible because ventilation time scales at these depths are brief relative to the history of Pb inputs. Jenkins [1980, 1987] and Serdane [1983] computed characteristic ventilation times of 10–50 years for the main thermocline of the Sargasso Sea and Beta Triangle region of the North Atlantic based on modeled 210Pb and 214Pb distributions. Additionally, the residence time of Pb with respect to particulate removal ranges from only about 2 years in surface waters to several decades deeper in the thermocline (Craig et al. [1973], Noszai et al. [1976], Bacon et al. [1976], and many others). Owing to this particle reactivity and an alkyl Pb flux which has been greatly curtailed over the past 2 decades, the distribution of Pb in the upper waters of the North Atlantic is in a state of rapid transition. Mapping of systematic changes in the mixed layer and upper thermocline, however, requires frequent sampling in order to gauge natural oceanic variability, which exists on very short temporal and spatial scales.

As a chemical tracer, Pb possesses properties both akin to and distinct from those of other transient tracers. Historical emissions of Pb roughly resemble those of O2 and chlorofluorocarbons. The physicochemical reactivity of Pb, however, is closer to that of bomb-test plutonium. Adaptation of lateral thermocline ventilation schemes based on model 210Pb ages must therefore consider particulate transfer processes for this nonconservative tracer. Since Pb ores exist as heterogeneous mixtures of four stable isotopes, industrial source variability allows for an additional time-dependent constraint. If used can be made of this second label, some of the complexities inherent in using a nonconservative tracer can be offset.

A first attempt at reconstructing the accumulation of industrial Pb in the Sargasso Sea was reported earlier [Boyle et al., 1986]. In this model, the input history of Pb was assumed proportional to U.S. alkyl Pb consumption, and thermocline ventilation time scales were those estimated by Jenkins [1980]. In successfully reproducing the general features of measured Pb concentration profiles, this study reconfirms the importance of lateral transport along isopycnal surfaces. Model refinements incorporating scavenging and regeneration, however, could not be uniquely specified. This was ascribed to uncertainties in the assumed Pb input history and possible geographic variability in Pb fluxes over outcropping winter waters. This paper attempts to refine our previous conclusions by incorporating two additional model constraints. These consist of the actual depositional history of industrial Pb near Bermuda

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Paper number 89JC03161.
0148-0227/88/88JC-03161$05.00

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as recorded by the coral Diploria strigosa, and complementary tracer systematics made possible by measurements of stable Pb isotopic ratios.

2. Methods

Nearly all of the seawater and trapped particles described in this work were collected 30 km southeast of Bermuda at station "S" (32°2'N, 64°30'W). The coral Pb concentration and isotopic records were produced from a 120-year core of Diploria strigosa growing on the seaward side of North Rock, a reef tract 14 km north of Bermuda (32°29'N, 64°48'W). Discussion of sampling and analytical methods is divided into these areas for clarity: seawater, corals, and particles.

2.1. Seawater

Sampling and analytical techniques for Pb concentration measurements in seawater are given by Boyle et al. [1986]. The dissolved Pb concentration profiles used throughout this paper are from this earlier work.

Sample collection and measurement techniques for Pb isotopes are subject to similar (and possibly more severe) contamination problems. To date, only one stable Pb isotopic determination has been reported for Atlantic waters by Ng et al. in 1979 [Schaule and Patterson, 1981]. Surface waters analyzed in the present study were collected either by pole sampling [Boyle et al., 1981] or underway pumping [Boyle et al., 1982]. The foremost difficulty, however, lies in sampling of subsurface waters in volumes sufficient for mass spectrometry. Samples allocated for Pb isotopic analysis were pooled from the residuals of 250-mL samples collected for concentration determination using the circulating "vane samplers" [see Boyle et al., 1986]. Sample sizes ranged from 300 mL to 1 L yielding 4-25 mg Pb, depending on sample depth and volume. Sample preconcentration was performed by ion exchange chromatography on 1-M Chelex 100 resin beds (200-400 mesh; Na⁺ form) in polyethylene columns. Acidified samples were neutralized to pH 7-8 using purified HNO₃ immediately before Chelexing. Samples were eluted with 0.5N HNO₃. Additional purification of the Chelexed fractions (primarily to remove calcium) was effected by anion exchange chromatography of Pb⁺⁺⁺⁺ species on Bio-Rad AGI-X8 resin (200-400 mesh) [see Shen and Boyle, 1988]. Net chromatographic recoveries ranged from 70% to 90%. The estimated total Pb blank was 235 pg, and isotopic ratio corrections were applied to subsurface seawater determinations on 10 mg or less total Pb.

Pb isotopic ratios were determined on a 12-inch magnetic sector solid source mass spectrometer (S. R. Hart, Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology). Samples were loaded in phosphoric acid and silica gel to enhance ionization efficiency [Cameron et al., 1969]. Whenever signal strength permitted, 60-100 sets of 206/204, 207/204, and 208/204 ratios were collected. Measurement error (95% confidence limits) is estimated at ± 0.001 for reported 206/207Pb ratios (±0.002 for determinations on 5 mg or less total Pb) to allow for variable mass fractionation and blank correction uncertainties. Measurements of National Bureau of Standards SRM-981 Pb standard gave the following ratios:

206/204Pb = 16.906 ± 0.016
207/204Pb = 15.448 ± 0.015
208/204Pb = 36.546 ± 0.030

These values result in a mass discrimination coefficient of 0.0010/amu relative to the Pb ratios reported by the NBS [Catanzaro et al., 1968]. Note that the isotopic ratios reported in this paper are uncorrected values.

2.2. Corals

Sample recovery, x-ray radiography, cleaning, and analysis of corals for skeletal Pb content are described fully by Shen and Boyle [1988]. Sample sizes for isotopic analysis ranged from 300 to 3000 mg crushed coral yielding 20-30 mg purified Pb. Cleaning techniques used were the same as described for determination of skeletal concentrations. Pb purification was by anion exchange chromatography. Generally, three passes through fresh AG1-X8 resin reduced calcium concentrations to acceptable levels. As Ca begins to ionize within the upper range of Pb ionization temperatures, thus contributing to signal suppression, instability, and/or fractionation, it is desirable to remove as much of this interferent as possible. Estimated total blank levels achieved for coral isotopic determinations were 50-100 pg or 0.1-0.3% of sample weights. Blank corrections to coral Pb isotopic ratios were insignificant at the 1% level of precision accorded 206/207Pb determinations.

2.3. Sediment trap particles

The most difficult sampling task of all was acquisition of uncontaminated particles settling at various depths in the water column. The purpose of these collections was to elucidate the dissolved-particle Pb exchange process via isotopic measurements. Miniature trace-element sediment traps were fabricated from 18" x 3" OD (2-13/16" ID) polycarbonate (Lexan) cylinders solvent bonded to Millipore filtration funnels (47-mm filter size). Entry baffles were constructed from 3" x 5/8" OD polycarbonate tubes bonded together in a honeycomb arrangement. Traps were deployed at three depths (100, 400, and 860 m), supported by polycarbonate crossframes (4-foot span) designed to hold four traps each. Normally, one trap per cross frame was used as a blank, leaving a capture area of 3 x 37 cm² or 111 cm² per collection depth. The free-drifting trap array was connected with 1/2-inch polypropylene line and weighted with 125 lbs. of anchor chain. Floation was provided by two 16-inch-diameter glass spheres (Benthos). A 25-m string of fisherman's floats terminated by a spar buoy, radar reflector, and strobe enabled visual and radar tracking of the array over several days of station work.

In spite of extreme precautions, including acid-leaching and deployment of traps covered and filled with distilled water, filter blanks averaged 5 ng Pb per trap. Since total capture masses ranged only from 2 to 20 mg Pb per depth, the high blank prohibited total filter digestion. Instead, filters were shaken and scraped to release
atmospheric Pb releases to the Sargasso Sea in the
nineteenth century, resulting from American indus-
trialization. The gradual buildup in the early
twentieth century is repeated after 1940 as a con-
sequence of alkyl Pb combustion in automobiles.
Post-1970 phasing-out of leaded fuels in the
United States is reflected by a dramatic decline in
coral Pb concentrations at Bermuda, which re-
turned to levels similar to those experienced in
the 1920s and 1930s. For use as an industrial Pb
source function, the coral data is best inter-
preted as a record of surface ocean concentrations
near Bermuda. Conversion of skeletal Pb
concentrations to dissolved concentrations is straightfor-
ward. The coral:seawater Pb distribution coefficient
($K_{dp}$ = Pb/Ca)$_{coral}$/(Pb/Ca)$_{seawater}$) for the
species Diploria strigosa has been estimated to be
2.3 [Shen and Boyle, 1987]. Thus a skeletal Pb
content of 100 nmol/mol Ca would be equivalent to
a dissolved Pb concentration of 435 pn.

The Pb concentration profile of Figure 2a ex-
hibits strong seasonal variability in the upper
200 m of the water column, a broad maximum cen-
tered near 350 m, and gradually diminishing concen-
trations with increasing depth. Short-term
variations in the upper ocean (up to 3235)
are caused by seasonal buildup and erosion of the
mixed layer and thermocline and by weather effects
as discussed by Boyle et al. [1986]. Such high-
frequency changes are filtered out in the coral
record, which is based on annual band determina-
tions. Several mechanisms can be invoked to ex-
plain the subsurface Pb maximum. Regeneration
of particulate Pb could result in a similarly shaped
profile, given suitable scavenging and decomposi-
tion parameters. Alternatively, the profile could
result simply from passive ventilation of the upper
thermocline with increasingly depleted surface
waters reflecting the post-1970 phasing-out of lead-
ed gasoline in the United States. A third possi-
bility also driven by passive ventilation would
require that density surfaces within the maximum
outcrop at latitudes which receive especially
heavy industrial fallout. The potential density
($ho$) of the waters in question is about 26.6.
This density surface outcrops in winter near 40$^\circ$N,
which is centrally located with respect to the
flow path of U.S. aerosol emissions and winter
rainfall. The lower portion of the stable Pb pro-
file in Figure 2a reflects reduced penetration of
Pb, probably caused by longer ventilation time
scales. At 1600 m, Jenkins [1980] estimates a
ventilation time of 100 years, which approaches the
time since significant industrial discharges of
Pb began.

3. Data

3.1. Lead Concentrations: The Historical Record
and Modern Vertical Distribution

Stable Pb concentrations in coral aragonite
from North Rock, Bermuda, and in seawater at sta-
tion S are shown in Figures 1a and 2a. The coral
chronology documents the inception of significant
captured particles into clean Teflon beakers.
Particles were then digested in concentrated HBr
and purified as per the coral Pb isotope proce-
dure. Analytical blank corrections were relative-
ly large in two of five cases (4206/207Pb =
0.003–0.004) owing to small sample sizes. It
occurred to us that standard full-scale sediment
traps might circumvent contamination effects by
virtue of their large capture volume. Three mea-
surements of material from W. Deuser's PAPFLUX Ber-
muda time series, however, yielded anomalously low
206/207Pb ratios (1.164–1.176). According to
the coral record, Pb of this composition has never
before existed in the western North Atlantic.
Lead concentrations in the sediment trap spits of
approximately 100–500 ppm also indicate sample
contamination. Jickells et al. [1984] reported Pb
levels in the range 40–100 ppm.

3.2. Lead Isotopes: The Historical Record
and Modern Vertical Distribution

Measurements of stable Pb isotopic ratios in
D. strigosa and at station S are presented in Fig-
ures 1b and 2b. Corresponding 204, 206, 207, and
208 ratios can be found in Tables 1 and 2. Figure
1b confirms a nineteenth century industrial per-
turbation of oceanic Pb by exhibiting a departure
from the background 206/207Pb ratio as deter-
mined from pelagic sediments and manganese nodules
by Chow and Patterson [1962]. Less radiogenic Pb
resulting from industrial emissions (e.g., steel,
lead, copper, zinc, coal, etc.) caused 206/207Pb
ratios to fall gradually toward 1.184 by 1934.
This progression, however, was reversed after 1940, when alkyl Pb exhausts became a prominent source, suggesting use of more radiogenic ores, possibly of Mississippi Valley origin. Curtailment of leaded gasoline after 1970 is reflected by a return of the isotopic signal toward earlier (1930s) values. Very recent Pb isotopic source signatures (1983-1986) are based on 11 measurements of surface waters at station S as shown in Figure 3 (accompanying data are presented in Table 3). Seasonal isotopic variability in the surface layer is very pronounced, as has been observed for Pb concentrations [Boyle et al., 1986]. Over the course of a year, these high-frequency variations are averaged sufficiently to allow smooth annual progressions as witnessed by the coral record. Although several rainfall isotopic measurements (see Figure 3 and Table 4) fall significantly below concurrent mixed layer $^{206}/^{207}$Pb values, they are consistent with the observed decline in surface $^{206}/^{207}$Pb over 1983-1986. A simple mixing calculation which assumes (1) a 1.25-year Pb residence time in surface waters, (2) a constant rain $^{206}/^{207}$Pb = 1.98, and (3) no net loss or accumulation of Pb in the mixed layer over 1983-1986, predicts $^{206}/^{207}$Pb ratios for July 1984, 1985, and 1986 of 1.197, 1.191, and 1.186, respectively. These values fall very close to the observed trend.

The contemporary vertical distribution of Pb isotopes at station S is shown in Figure 2b. This profile is the first of its kind in the Atlantic Ocean; one other vertical Pb isotopic distribution has been reported by Flegal et al. [1986] in the North Pacific. The resemblance to the concentration profile of Figure 2a is largely coincidental. The isotopic profile depicts higher values of $^{206}/^{207}$Pb in the upper 500 m which reflect the fact that inputs since 1970 have been relatively radiogenic. Deeper $^{206}/^{207}$Pb values to 1500 m range from 1.190 to 1.195 and are indicative of older inputs from earlier this century. At still greater depths where industrial Pb is expected to comprise a smaller proportion of total Pb, one might expect the isotopic signal to eventually converge with the background field. If preindustrial $^{206}/^{207}$Pb at 1700 m resembles that of surface water and sediments ($\approx 1.214$), it becomes apparent that the 1984 measurement at this depth

<table>
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<th>Year</th>
<th>$^{206}/^{207}$Pb</th>
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TABLE 2. Lead Isotopic Composition of Subsurface Water (Station S, Bermuda, January-September 1984)

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<th>Weighted Average Depth</th>
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<th>Pb, ng</th>
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<td>2.060</td>
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diverges from expectation. However, the vertical distribution of natural Pb may be a function of depth and water mass provenance. Later, we will look more closely at the possible influence of background Pb in intermediate waters on the present-day isotopic profile.

A more informative way of viewing the contemporary vertical distribution of Pb isotopes in light of historical inputs is provided in Figure 4. If use is made of a second Pb isotope (preferably the most abundant one, 206Pb), it is seen that pre- and post-World War II fluxes of Pb isotopes define two distinct trends on a 206Pb/207Pb versus 208Pb/206Pb plot. The vertex defines a radiogenic minimum near 206/207Pb = 1.180 and 208/206Pb = 2.075. The seawater data from Figure 4b plot closely along the 1940-to-present-day trend, with deeper samples reflecting older isotopic values. An interesting aspect of the dissolved Pb distribution is how little prealkyl Pb inputs appear to have influenced deeper isotopic signatures; i.e., a single-path evolution from 1934 on would largely account for the observed isotopic ratios to 1700 m. This concern will be raised again in modeling discussions. A final point in connection with the 206/207Pb versus 208Pb/206Pb plot involves the locus of surface ocean Pb compositions since 1983. Inclusion of the data in Figure 3 (not shown) yields an array nearly identical to the 1934-1974 coral trend. Thus movement along this isotopic pathway over the last 50 years appears to have been controlled almost exclusively by growth and elimination of alkyl Pb fuel additives. It follows that the composition and volume of nonalkyl Pb emissions from the United States have probably not changed dramatically over the last several decades. At the present time, with alkyl Pb usage levels at an all-time low, bulk Pb aerosols in the United States probably lie close to the nonradiogenic vertex of the 206/207Pb versus 208Pb/206Pb isotopic array.

3.3. Lead-210

In addition to the complementary stable Pb concentration and isotopic constraints, use can be made of a third vertical Pb distribution: 210Pb. Since there are no significant anthropogenic sources of 210Pb, the distribution displayed in Figure 4c can be considered at steady state.

TABLE 3. Lead Isotopic Composition of Sargasso Sea Surface Water (Station S, Bermuda, 1983-1986)

<table>
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<tr>
<th>Collection Date</th>
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</tr>
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<td>Dec. 1984</td>
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<td>2.043</td>
<td>18.73</td>
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<td>38.26</td>
</tr>
<tr>
<td>March 1985</td>
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<td>2.034</td>
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<td>15.61</td>
<td>38.22</td>
</tr>
<tr>
<td>Aug. 1985</td>
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<td>2.062</td>
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</tr>
<tr>
<td>Oct. 1985</td>
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<td>2.059</td>
<td>18.60</td>
<td>15.68</td>
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</tr>
<tr>
<td>Jan. 1986</td>
<td>1.190</td>
<td>2.052</td>
<td>18.76</td>
<td>15.76</td>
<td>38.49</td>
</tr>
</tbody>
</table>

Fig. 3. Ratios of 206Pb to 207Pb in Sargasso Sea surface waters (Station S, June 1983 through January 1986) and Bermuda rain samples (rain samples furnished by T. M. Church, University of Delaware).
Scatter in the seasonal depth profiles in excess of analytical error, however, suggests that the ocean is relatively noisy to depths approaching 2000 m. Similar variability in the stable Pb concentration data of Figure 2a can be linked to measured offsets in temperature and salinity [Boyle et al., 1986]. Nevertheless, the Pb "steady state" profile will be of particular importance in constraining Pb inputs in model runs which allow for geographic variability in winter-time fluxes.

4. A Ventilated Thermocline Model for Stable Pb

The model selected calls exclusively on lateral transport of Pb rather than vertical exchange, except via scavenging and regeneration. Jenkins [1980] demonstrated that a vertical model incorporating either fixed or depth-dependent diffusivities of 1-10 cm/s could not geologically evolve oceanic distributions of 210Pb and 226Ra simultaneously. Required vertical diffusivities of 1-10 cm/s are over an order of magnitude greater than those normally encountered. This suggests that transport of a conservative tracer within the thermocline by cross-isopycnal exchange is probably less than 10% of the total transport. Further evidence of the importance of lateral advection now exists in distributions of radionuclides in the glacial Ocean [Cochran et al., 1987] and Pacific Pb-Ra measurements [Gargett et al., 1986]. In outlining isopycnal ventilation rates near Bermuda, Jenkins employed an open-ended box model in which injected tracers mix instantaneously. This is a valid approximation in the upper thermocline; however, for 210Pb > 226Ra, lateral gradients in Pb may become significant, resulting in spatially variable ventilation rates [Bermant, 1983].

In applying the continuum box model concept and Pb ventilation rates to Pb, a number of simplifying assumptions can be made: (1) Pb and 210Pb deposition are coupled geographically; (2) scavenging is first order with respect to concentration; (3) 226Ra Pb regeneration is proportional to the apparent oxygen utilization rate (AOU), and consequently, Pb regeneration is proportional to the product of the 226Ra regeneration rate and the surface water Pb/226Ra ratio; (4) regenerated Pb bears a mixed layer isotopic signature. Assumption 1 is discussed by Boyle et al. [1986]. Though not strictly founded, assumption 2 has been commonly invoked in the absence of better information [e.g., Craig et al., 1973]. Originally, Pb scavenging was defined relative to particulate removal only; however, boundary scavenging effects [Bacon et al., 1976] are absorbed in the same term for the purposes of this model. Assumption 3 draws from the close relationship between particulate organic matter and Pb removal [Jickells et al., 1984; Moore and Dymond, 1981]; however, actual regeneration rates and mechanisms are unknown. The validity of assumption 4 again, has not been strictly tested, but the very brief residence time and high concentration of Pb in the mixed layer suggest that it is a good approximation. Furthermore, because of deep seasonal overturn, the upper several hundred meters of the Sargasso Sea are

<table>
<thead>
<tr>
<th>TABLE 4. Lead Isotopic Composition of Bermuda Rain</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Collection Date</strong></td>
</tr>
<tr>
<td>Nov. 9, 1982</td>
</tr>
<tr>
<td>May 29, 1983</td>
</tr>
<tr>
<td>May 29, 1983 (replicate)</td>
</tr>
<tr>
<td>Nov. 6, 1983</td>
</tr>
</tbody>
</table>
relatively uniform with respect to Pb (see Figures 1a and 1b). Therefore particle signatures from the upper thermocline are not very different from those originating in surface waters. The mechanisms responsible for Pb transport must therefore satisfy three chemical distributions simultaneously: Pb concentration, stable Pb concentration, and stable Pb isotopes. The governing expressions are:

\[ \frac{dC_{\text{ox}}(z,t)}{dt} = -k_1C_{\text{ox}}(z,t) + k_2R(z)C_{\text{ox}}(z,t) + \frac{A_{226}(z)}{A_0(0)} \frac{(A_{226}(z) - A(z,t))}{t(z)} \]  

(1)

\[ \frac{dA(z,t)}{dt} = -k_1A(z,t) + k_2R(z)A(z,t) + \frac{A_{226}(z)}{A_0(0)} \frac{(A_{226}(z) - A(z,t))}{t(z)} \]  

(2)

\[ \frac{dC_{\text{regen}}(z,t)}{dt} = \frac{C_{\text{regen}}(z,t)}{C_{\text{regen}}(z,t) + C(z,t)} \cdot -I(z,t)/t(z) \]  

(3a)

\[ \frac{dC(z,t)}{dt} = \frac{C(z,t)}{C_{\text{regen}}(z,t) + C(z,t)} \cdot I(z,t)/t(z) \]  

(3b)

where

- \( C(z,t) \) concentration of stable Pb at depth \( z \) and time \( t \) (pm);
- \( C_{\text{ox}}(z,t) \) concentration of stable Pb in surface waters for depth \( z \) at time \( t \) (pm);
- \( C_{\text{regen}}(z,t) \) regenerated particulate Pb at depth \( z \) and time \( t \) (pm/yr) given by \( k_2R(z)C_{\text{ox}}(z,t) \), activity of \( 210\text{Pb} \) at depth \( z \) and time \( t \) (dpm/100 kg) (A(\( z \)) reaches steady state within 100 years);
- \( A_0(z) \) activity of \( 210\text{Pb} \) in surface waters for depth \( z \) (dpm/100 kg);
- \( A_{226}(z) \) activity of \( 226\text{Ra} \) at depth \( z \) (dpm/100 kg);
- \( I(z,t) \) isotopic composition of Pb at depth \( z \) and time \( t \) (dimensionless);
- \( \lambda_0(t) \) isotopic composition of Pb in surface waters at time \( t \) (dimensionless);
- \( t(z) \) helium-tritium ventilation age for depth \( z \) (in years);
- \( k_1 \) first order scavenging constant (per year);
- \( k_2 \) Pb regeneration rate multiplier (dpm/100 kg/mL/L);
- \( R(z) \) source of Pb at depth \( z \) (dpm/L/yr);
- \( \lambda \) \( ^{210}\text{Pb} \) decay constant (per year).

The first terms in (1) and (2) and the entire expression in (3a) signify that the time rate of change of each tracer is proportional to the difference between the winter outcrop value and the value at depth, scaled to the ventilation rate for that depth. The mathematical formulation does not distinguish between eddy diffusion and advective transport, both of which are probably responsible for communication between surface ocean and interior. The principal adjustable parameters are the scavenging and regeneration rate constants, \( k_1 \) and \( k_2 \). Adjustment of winter source water \( ^{210}\text{Pb} \) and Pb concentrations (A(\( z \)) and \( C_{\text{ox}}(z,t) \)) to allow for latitudinal variability provides a third free parameter. As is required by assumption (1), changes in \( C_{\text{ox}}(z,t) \) occur in direct proportion to changes in \( A_{\text{ox}}(z,t) \) deduced from fitting of the steady state 226Ra profile. No provision is made for geographic variability in stable Pb isotope delivery. Concentrations of \( 226\text{Ra} \) are estimated from dilute measurements as per Boyle et al. [1986] using the correlation of Broecker et al. [1976]. The steady state mixed layer Pb concentration is assumed equal to the measured average, 15.46 dpm/100 kg (omitting highly variable measurements in the extreme surface layer). This value corresponds to a steady state atmospheric flux of 0.76 dpm/cm²/yr assuming a mixed layer thickness of 100 m and a residence time of 2 years. Turekian et al. [1983] estimated an average flux of 0.69 dpm/cm²/yr based on monthly mean measurements at Bermuda. Apparent oxygen utilization rates used are those of Jenkins [1980]. Values of adopted model parameters are summarized in Table 5.

Input functions for stable Pb and Pb isotopes (\( C_{\text{ox}} \) and \( \lambda_0 \)) consist of polynomial fits to the corresponding records recovered from D. strigosa at North Rock, Bermuda (Figures 1a and 1b). Post-1983 Pb concentrations are based on multiple surface seawater determinations which declined from 128 pm in 1984 toward 90 pm in 1986 (K. A. Boyle, 1988 unpublished data). Post-1980 206/207Pb values are from Figure 3. To facilitate model computations incorporating a wide variety of constraints, a finite difference scheme was used rather than exact solutions to the differential equations [Boyle et al., 1986]. The model is initiated in the year 1980 assuming negligible background Pb everywhere but the surface, and it is stepped through time to 1986 in 0.1-year increments.

### Table 5. Model Parameter Values

<table>
<thead>
<tr>
<th>Depth, m</th>
<th>( a_0 ) (yr)</th>
<th>226Ra* (dpm/100 kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>26.4</td>
<td>0.459</td>
</tr>
<tr>
<td>400</td>
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</tr>
<tr>
<td>500</td>
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<tr>
<td>750</td>
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<tr>
<td>950</td>
<td>27.5</td>
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</tr>
<tr>
<td>1100</td>
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</tr>
<tr>
<td>1400</td>
<td>27.7</td>
<td>0.021</td>
</tr>
<tr>
<td>1700</td>
<td>27.8</td>
<td>0.0078</td>
</tr>
</tbody>
</table>

*From Jenkins [1980].
**From Boyle et al. [1986].

4.1. Conservative Evolution

In the simplest possible model, Pb is conservative (no scavenging or particulate regeneration), and winter source waters are assigned the same
Fig. 5. Conservative evolution with pure physical ventilation of thermocline and no winter source water adjustment. (a) Model steady state $^{210}$Pb distribution compared to measurements. Isopycnal outcrop $^{210}$Pb activity, $A_0$, is constant with latitude (or, effectively, depth). Note how the model overestimates $^{210}$Pb below 700 m. (b) Model-generated twentieth-century $^{207}$Pb concentration evolution. The source function is based on the coral reconstruction of Figure 1a. (c) Model 1984 $^{207}$Pb concentration profile compared to measurements. Note that the model predicts too much $^{207}$Pb below thermocline as with $^{210}$Pb in Figure 5a. (d) Model-generated twentieth-century $^{208}$Pb isotope evolution. The source function is based on the coral reconstruction of Figure 1b. (e) Model 1984 $^{208}$Pb isotope profile compared to measurements. Note large discrepancies below 700 m.
Wind patterns, however, differ markedly between the North Pacific and North Atlantic. Because the wintertime low-pressure cell in the high latitude North Atlantic lies further north than in the North Pacific (Tchernia, 1980), North American westerlies appear capable of delivering a more latitudinally uniform Pb flux. In the absence of actual wintertime measurements, however, source water “tuning” in all subsequent scenarios will be based upon fitting the steady state Pb distribution at station 5.

The results of the best fit Pb source variation model are shown in Figure 6. The model has been forced to the average measured Pb value in each depth interval. Required surface ocean Pb boundary conditions (Figure 6a) remain near 15 dpm/100 kg down to 600 m but fall off to near 5 dpm/100 kg at 1700 m. When applied to the stable Pb model, these severe source corrections overcompensate for the excesses observed in the simple conservative model and result in a predicted Pb deficiency between 800 and 1700 m. At the same time, relatively minor positive adjustments (1-10x) at 400, 500, and 600 m cause a pronounced subsurface maximum to appear in the stable Pb profile. The source tuning effect is amplified in this portion of the water column because Pb concentrations here are highest. Since the model is initialized with no Pb below the mixed layer, the isotopic evolution (Figures 6d and 6e) reflects a pure coral-dictated end member and therefore remains unchanged.

Though the general features of the Pb concentration model are clearly correct, discrepancies below 800 m and discordant isotopic predictions reveal that a conservative model cannot satisfactorily account for all three Pb distributions. Even relaxing the Pb-Pb coupling assumption would do nothing to affect the Pb isotope model predictions unless a vertical exchange mechanism were introduced.

### 4.3 Scavenging With Source Tuning

Inclusion of a scavenging term in the model significantly alters the source corrections required to fit the measured Pb vertical distribution (Figure 7a). Setting $k_i = 0.01 \text{ yr}^{-1}$ (corresponding to a Pb residence time of 100 years with respect to scavenging removal), surface Pb boundary conditions for the deepest isopycnals approximate 12 dpm/100 kg. This is close to the average value of 11.2 dpm/100 kg reported by Mon et al. [1978] for Labrador Sea waters at 90 to 100 m depth. One-hundred years is also consistent with the range of reported deep water Pb residence times [Thomson and Turekian, 1976; Craig et al., 1973; Nakaz and Tsunogai, 1976]. This refinement shifts the 1986 model Pb profile (Figure 7c) very nearly within the range of measured values. Discrepancies remain at 400-600 m (predicted excess) and 1700 m (predicted deficit). In the absence of end member mixing (no preexisting Pb at depth), simple scavenging does not result in a redistribution of Pb isotopes; thus the isotopic evolution (Figures 7d and 7e) again remains unchanged from previous schemes. The enhanced source water adjustment and isotopic deviation at 1700 m suggest that these waters are flushed more rapidly than is indicated by Jenkins’ H-He ventilation age estimate of 150 years.
Conservative Evolution + Source Tuning

Fig. 6. Same as Figure 5 but with source water concentration adjustments based on fit to steady state 210Pb. Note severe changes required of $A_0(z)$ and consequent underspecification of 1984 Pb concentration below 750 m. The 206/207Pb ratio is not changed from conservative model.
Fig. 7. Nonconservative evolution (1) including scavenging and source tuning to $^{210}\text{Pb}$. Particulate scavenging rate constant $k_1$ is proportional to $\text{Pb} \cdot 100$ years. Source water concentrations are adjusted based on fit to steady state $^{210}\text{Pb}$. Note improved agreement between 1984 Pb concentration profile and observations. $^{206}/^{207}\text{Pb}$, however, remains unchanged.
Before considering chemical mechanisms which would alter the isotopic distribution, it is useful to explore in greater detail the sensitivity of the concentration model to an additional refinement. The model represented by Figure 8 slightly relaxes the Pb fit between 400-600 m (3-1.4X shift) since within this depth interval, the stable Pb response is highly sensitive to source adjustments and the profile is not well constrained. The subsurface maximum remains (Figures 8b and 8c) but is greatly moderated. The isotopic progression is as before.

4.4. Scavenging, Regeneration, and Source Tuning

In order to influence the isotopic distribution of Pb in the Sargasso Sea, a mean of vertical exchange or nonuniform mixing of Pb along isopycnal surfaces is necessary. The most obvious mechanism which accomplishes this is particulate Pb regeneration.

In the model shown in Figure 9, a 210Pb regeneration rate multiplier of 2 dpn/100 kg/ml. 02/g/L is selected, corresponding to a 2% Pb regeneration efficiency of 1%/2 throughout the water column to 1700 m. On the basis of 210Pb profiles from the north equatorial Atlantic, Bacon et al. (1976) estimated a recycling efficiency of about 8% for 210Pb between 50 and 400 m. To offset deepwater increases in Pb concentration due to regeneration, Pb k1 is increased to 0.015 yr-1 (corresponding to a 67-year Pb residence time). Adjustments to source water 210Pb concentrations (Figure 9a) are more severe than in the simple scavenging model; however, they are still within reason. A large discrepancy at 1700 m exists as before.

The direction of the resultant shift in deepwater isotopic signatures (Figure 9a) is as desired, although the magnitude of the shift is not quite large enough to accord with the data. Displacement of deep waters toward lower 206/207Pb ratios as a result of regeneration is expected on the basis of the historical coral record (Figure 1b). Since flushing times for waters below 900 m are greater than 50 years, Pb in these waters would be expected to possess a relatively old isotopic signature in the absence of regeneration (206/207Pb = 1.200-1.205). By introducing a regeneration term at all depths in the model (proportional to A0UR), more recent source signatures (206/207Pb = 1.190 between 1920 and 1960) act to drive the deepwater ratios toward lower values. The effect, however, is reversed after 1960 as fallout 206/207Pb ratios climb back toward higher, more radiocarbon values. This explains why the model curve for 1960 (Figure 9b) falls toward lower 206/207Pb relative to 1984 in deep waters. Although a dramatic redistribution of Pb isotopes is achieved, the stable Pb concentration profile changes very little as a result of regeneration. The reason is that Pb added by regeneration at a given depth is compensated both by increased scavenging and reduced Pb introduced by ventilation (as dictated by 210Pb tuning). All of these terms are first order with respect to the source water concentration, C, as seen in equation (1). If a 12% net recycling efficiency improves the isotope fit so substantially, a greater degree of regeneration might be expected to yield an even better fit to the data. Selecting a regeneration rate multiplier of 3.5 dpn/100 kg/ml. 02/g/L (net recycling efficiency of 20% to 1700 m; k1 adjusted to 0.025), however, leaves the 1984 206/207Pb profile largely unaltered. Much the same happens if the assumed recycling proportionality to A0UR is abandoned and regeneration in the deep thermocline is arbitrarily enhanced. A point of diminishing returns has been reached insofar as adjusting subsurface isotopic signatures through addition of surface Pb. Further enhanced regeneration accomplishes little and pushes the limit of credibility with regard to observed scavenging and regeneration behavior and source variability of 210Pb.

Application of this final model run in a predictive capacity is attempted in Figure 10, where Pb concentration and isotopic model depth distributions have been extrapolated to the year 2000. These predictions are based on a reduced but constant industrial flux of Pb from 1987 onward, marked by a surface ocean concentration of 85 PM and 208/207Pb ratio of 1.180. The magnitude of the 16-year offsets indicated by the model are likely to be more accurate than the absolute concentrations and isotopic ratios predicted for the year 2000.

5. Evidence for Particulate Pb Regeneration

Evidence of a particulate transfer mechanism was sought directly via isotopic measurements of particles collected in trace-element-clean, free-drifting sediment traps. Samples collected on two deployments (August 1984 and March 1985) from 100-, 400-, and 860-m depths were barely abundant enough to allow measurement of Pb isotopic ratios (Figure 11 and Table 6). Curiously, the data from the two deployments are contradictory. In August 1984, a sample from 860 m possessed the same 208/207Pb ratio as particles collected at 100 m. This suggests that particles do not continuously accumulate Pb as they transit the water column. Loss of original Pb picked up from the mixed layer, though, may occur without altering the isotopic state of the particles. Thus the August 1984 particulate Pb isotope distribution is at least consistent with the requirements of a regeneration model. Analyses of March 1985 samples, on the other hand, suggest the diametrically opposed situation. From these data, one might conclude that falling particles exchange Pb rapidly and continuously so as to approach isotopic equilibrium with surrounding waters, throughout the water column. The observed ratio at 90 m differs markedly from the 1984 determination but can be accounted for by rapid changes in the surface ocean as seen in Figure 1. A continuous exchange process like that suggested by the March 1985 data would also shift modeled 208/207Pb ratios in the desired direction, but the net effect would be very small. Additional measurements are needed to characterize the particulate Pb exchange process more clearly. Standard large-scale trap deployments, however, will probably not serve unless careful attention is directed toward contamination control (see section 2.3).

6. The Pb Isotopic Discrepancy below 800 m: Contributing Factors

The residual discrepancy between the observed and modeled Pb isotopic distribution with depth may be attributable to several factors.
Fig. 5. Nonconservative evolutions (T1) including scavenging and source tuning to P. N. W. 2000. The process of Pb scavenging substantially modifies the magnitude of the 1984 model Pb sub-surface maximum. The 206/207Pb ratio is again, unaffected.
**Fig. 9.** Nonconservative evolution including scavenging + regeneration + source tuning to $^{210}$Pb. The regeneration rate constant $k_2 = 2.0$ giving a net recycling efficiency of 12% through the upper 1700 m (regeneration is assumed proportional to NO3). The scavenging rate constant $k_3$ is adjusted slightly (corresponding to 67 years $t_g$) to compensate. Source water concentrations are adjusted according to fit to steady state $^{210}$Pb profile. Note the dramatic shift in the 1984 model $^{206}/^{207}$Pb distribution resulting from Pb regeneration.
Fig. 10. (a) Predicted Sargasso Sea Pb concentrations for the year 2000 relative to the 1984 modeled profile (see section 4.4). Measured 1984 Pb distribution is included for reference. (b) Predicted 206/207Pb isotopic ratios for the year 2000 relative to the 1984 modeled profile (see section 4.4). Measured isotopic distribution in 1984 is included for reference.

1. One possible modification of the model which would emphasize deepwater isotopic adjustment would be incorporation of background Pb at depth. Although deep waters (1000-2000 m) could hardly have been expected to support more than 15 pM Pb (the pre-industrial surface value estimate based on D. steiropora) (Shen and Boyle, 1987), this concentration would be sufficient to modify the contemporary isotopic signature in these waters which presently contain only 50-75 pM total Pb. In adopting a background Pb isotopic signature, one approach would be to estimate a value from Chow and Patterson's (1962) survey of pelagic sediments and manganese nodules (206/207Pb = 1.208-1.218). However, since we are concerned with intermediate water and not surface water (from which most sedimented Pb is presumably derived), it might be more appropriate to seek out a particular weathering source signature; continental leads supplying the Labrador Sea might be more realistic. Since much of eastern Canada and Greenland is Archean in age, crustal weathering would be expected to release relatively nonradiogenic Pb (206/207Pb = 1.0) (Russell and Farquhar, 1960, Moorabath et al., 1981). This is precisely the type of signature needed to shift the model isotopic profile toward lower values of 206/207Pb. For example, if the present day Pb inventory at 1400 m includes a 10% background component, a natural 206/207Pb signature of 1.13 would remove the model discrepancy. The weakness in this argument lies in the absence of measurements in this range throughout most of the world's ocean basins. Chow and Patterson's (1962) lead isotopic survey of Atlantic and Pacific pelagic sediments showed that despite regional heterogeneities, 206/207Pb rarely falls below 1.190. Thus, if a nonradiogenically-labeled North Atlantic deepwater mass does exist, it cannot be a major source of sedimented Pb.

2. A second consideration about which little is known is the spatial variability of isotopic fluxes from anthropogenic sources. Unlike Pb con-


TABLE 6. Lead Isotopic Composition of Settling Particles Caught by Sediment Traps (Station S and F, Bermuda)

<table>
<thead>
<tr>
<th>Collection Date</th>
<th>Trap Type</th>
<th>Depth (m)</th>
<th>206/207 Pb</th>
<th>208/206 Pb</th>
<th>206/204 Pb</th>
<th>207/204 Pb</th>
<th>208/204 Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feb. 1979</td>
<td>Deuser 3200*</td>
<td>1.164</td>
<td>2.094</td>
<td>18.21</td>
<td>15.64</td>
<td>38.13</td>
<td></td>
</tr>
<tr>
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<td>Deuser 3200*</td>
<td>1.171</td>
<td>2.083</td>
<td>18.25</td>
<td>15.59</td>
<td>38.01</td>
<td></td>
</tr>
<tr>
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<td>2.081</td>
<td>18.57</td>
<td>15.79</td>
<td>38.65</td>
<td></td>
</tr>
<tr>
<td>Aug. 1984</td>
<td>Shen</td>
<td>90</td>
<td>1.203</td>
<td>2.038</td>
<td>18.77</td>
<td>15.60</td>
<td>38.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400*</td>
<td>1.223</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>860</td>
<td>1.202</td>
<td>2.040</td>
<td>19.02</td>
<td>15.83</td>
<td>38.81</td>
</tr>
<tr>
<td>March 1985</td>
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<td>90</td>
<td>1.191</td>
<td>2.052</td>
<td>18.73</td>
<td>15.73</td>
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<td></td>
<td></td>
<td>860</td>
<td>1.196</td>
<td>2.047</td>
<td>19.70</td>
<td>15.83</td>
<td>38.22</td>
</tr>
</tbody>
</table>

*Samples contaminated.

Concentration boundary conditions which can be tuned against steady state Pb, no constraints exist for tuning of isotopic boundary conditions. Boyle et al. [1986] have proposed mapping the distribution of source water concentrations of Pb and Pb0 along winter isopycnal overturns. This will provide a critical new constraint on the Pb concentration tracer. Mapping of Pb isotope distributions will be performed concurrently, but corrections will prove difficult to extrapolate backward in time. Sturges and Barrie [1987] have recently confirmed that a gradient exists in isotopic ratios of contemporary emissions between the United States and Canada. Between 1984 and 1986, Canadian atmospheric particles from Ontario bore relatively monodisperse Pb/Pb* ratios of 1.14-1.16 as compared to northern U.S. signatures of 1.19-1.23. This offset is also in the sense required to improve the isotopic model predictions in the deep thermocline; however, it is difficult to assess how large these differences have been historically and how long they have persisted.

Over the depth range 1000-1600 m at Bermuda (oz = 27.6-27.8), a potentially important Pb source not addressed in the model is Mediterranean Overflow Water (MOW). The difficulty in incorporating this component is that virtually nothing is known about the history of Pb accumulation in the deep Mediterranean. Nevertheless, we can try to estimate the influence of European Pb delivered through this pathway using very recent information. First, it is necessary to state several crude assumptions.

a. The contemporary isotopic composition of European Pb based on several observations over the Mediterranean and Cape Verde Basin is 100/207Pb = 1.152 [Maring et al., 1987; R. Hanellin, personal communication, 1988]. Assume that this has been constant over the last century. b. The contemporary dissolved Pb concentration in MOW is about 100 pM [Ruiz-Pino et al., 1988] versus 60 pM at depths of 1000-1600 m in the Sargasso Sea. Assume that this proportion has been constant over the last century and that scavenging losses in MOW en route to Bermuda are small.

c. Over most of the last century, 206/207Pb at 1000-1600 m in the Sargasso Sea has been 1.195 ± 0.005. Use this ratio to estimate the magnitude of a shift imposed by European Pb.

If we allow that the contribution of MOW (salinity = 38.45/oo) [Bryden and Stommel, 1982] to deep thermocline waters at Bermuda (salinity = 35.0/oo) causes a maximum salinity increase of 0.109/oo, 206/207Pb is shifted by -0.02 to 1.193. The magnitude of such a correction is significant but insufficient to reconcile the residual discrepancy between the observed and modeled Pb isotope distributions. The unusually nonradiogenic Pb observed at 1700 m (actually integrated over 1571-1971 m) remains anomalous unless a proportionally larger influx of European Pb is specified over this interval.

Separate from its injection via MOW, it should be pointed out that European Pb deposited directly into the eastern Atlantic basin may also comprise a component of the Pb inventory near Bermuda. However, since gyre recirculation of this source to outcropping isopycnals is relatively inefficient, the net contribution at depth is likely to be small.

A fourth mechanism not incorporated into the ventilated thermocline model is mixing along isopycnal surfaces. Such a model basis would call for lateral advective/diffusive transport and acknowledge the existence of concentration and isotopic gradients along isopycnals, particularly in deeper waters (oz>26.8). In a general sense, this type of model should reduce the role of newer inputs at the surface boundary, since these will require a finite time to travel laterally. In Jenkins' continuum box model, new inputs are instantaneously and uniformly absorbed along the entire length of an isopycnal surface. In terms of the stable Pb isotope problem, a deep basin of very recent Pb inputs (206/207Pb from 1965-1984 = 1.195 ± 0.005) should allow the model output to match the measured Pb isotope distribution more closely.

A final possible variation of the model pertains to the applicability of assumed ventilation rates based on 3H and 3He distributions and the possibility of time dependency. Soney and Jenkins [1987] have pointed out that ventilation rates calculated from a transient tracer field are dependent on the nature of the tracer's boundary condition. In the case of 3H versus 3He time scales, 3H-based ventilation rates often exceed 3He-based values owing to the dependence of gaseous 3H on relative rates of air-sea gas exchange and mixed layer subduction. Since the surface boundary behavior of Pb is expected to resemble that of 3H and assumed ventilation time scales are con-
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xistent with \(^{206}\)Pb-based estimates, there should be no problem with the model treatments previously discussed. In the event that a systematic error does exist, however, it is worth noting that uniformly faster or slower ventilation cannot in itself change a predicted \(\text{Pb}\) isotope distribution. To accomplish this, ventilation rates must change as a function of time.

Jenkins [1982] inferred decadal variations in Sargasso Sea water mass renewal rates in examining historical records of salinity back to 1950. Reconstructed renewal rates along shallow isopycnals (2000 m) near Bermuda show a maximum twofold increase near 1968. Incorporation of this observation in the stable \(\text{Pb} - ^{207}\text{Pb}\) model, however, results in little change in either concentration or isotope distributions. In the deeper water column, where the modeled \(\text{Pb}\) isotope distribution suffers most, temporal variations in ventilation rates are expected to be small. To test the non-conservative model's sensitivity to such changes should they actually occur, the conditions outlined in section 4.4 were rerun assuming hypothetically doubled ventilation rates between 1925 and 1960 (years chosen to maximize injection of non-radiogenic \(\text{Pb}\)). On average, discrepancies between model and observations are reduced by about 30% relative to the scavenging/regeneration result of Figure 9. This is a relatively minor improvement for such an extreme change in ventilation parameters. This test case illustrates that in order to accomplish a match to the data through variable ventilation, rate changes must occur in the proper sense, at the necessary depths, at very opportune times. The model's relative insensitivity to changes in renewal rates and the low likelihood of such changes in the deep thermocline suggest that this mechanism has probably not substantially influenced the vertical distribution of \(\text{Pb}\).

7. Conclusions

While application of stable \(\text{Pb}\) as a chemical tracer poses considerable sampling and measurement difficulties, several unique aspects of this tracer element warrant consideration in future tracer studies. The geochronological cycle of natural \(\text{Pb}\) has been disrupted for over 100 years. As a result, contemporary \(\text{Pb}\) levels in the upper waters of the North Atlantic are almost wholly anthropogenic. The exact evolution of industrial perturbations can be reconstructed from reef-building corals, thus providing detailed regional input histories. The correlation is binary in natural \(\text{Pb}\) concentrations as well as isotopic states are measurable in seawater, corals, and ocean particles. Additionally, \(\text{Pb}\) provides a well-characterized, steady state, chemical analogue. Inclusion of a coral-based input history and \(\text{Pb}\) isotope measurements has allowed us to extend an earlier analysis of \(\text{Pb}\) accumulation in the Sargasso Sea [Boyle et al., 1986] based on \(^{210}\text{Pb}\) and \(^{226}\text{Ra}\) ventilation rates of Jenkins [1980]. These new constraints have revealed a number of new insights:

1. Simple conservative models based on \(^{210}\text{Pb}\) ventilation rates cannot account simultaneously for observed profiles of stable \(\text{Pb}\) and \(^{210}\text{Pb}\). At best, only one concentration distribution can be satisfied at a time through coupled adjustment of \(^{210}\text{Pb}\) and \(^{210}\text{Pb}\) fluxes to wintertime outcropping isopycnals. The measured distribution of \(206/207\text{Pb}\) cannot be reproduced by any conservative scheme.

2. Particulate scavenging of \(\text{Pb}\) is a vital element of the \(\text{Pb}\) and \(^{210}\text{Pb}\) concentration evolution in the thermocline. However, in the absence of vertical mixing of \(\text{Pb}\) or local gradients along isopycnal surfaces, the observed isotopic distribution cannot be reproduced by a simple scavenging model.

3. Moderate regeneration (12%) of particulate \(\text{Pb}\) of surface origin (assumed proportional to \(\text{AOBR}\)) is capable of shifting modeled \(206/207\text{Pb}\) in the required sense while preserving realistic \(\text{Pb}\) and \(^{210}\text{Pb}\) distributions and source variability. Thus recycling of scavenged \(\text{Pb}\) is identified as a second key component of the oceanic \(\text{Pb}\) geochemical cycle.

4. Residual inconsistencies between modeled and observed isotopic distributions at depth may be partly attributable to a significant background \(\text{Pb}\) inventory of relatively nonradiogenic origin. A second potentially important but poorly understood consideration relates to spatial variability of \(\text{Pb}\) isotopic fluxes to winter source waters. European \(\text{Pb}\) delivered by Mediterranean Overflow and gyre recirculation represents an additional possible source term. However, until more historical information on the accumulation and isotopic composition of this source is available, its influence on the western North Atlantic cannot be specified. Finally, mixing along deeper isopycnal surfaces over finite rather than instantaneous time scales should also improve model accuracy.

Acknowledgments. The authors extend their gratitude to E. R. M. Druffel and S. M. Griffin, who furnished the coral samples; to W. G. Deuser for sediment trap samples; to S. R. Hart for permitting us to use his mass spectrometer; and to T. M. Church for supplying rain samples from Bermuda. Discussions with B. Hamelin and A. Le Huray are gratefully acknowledged. W. J. Jenkins, R. V. Anderson, and two anonymous reviewers are thanked for their insightful comments and suggestions. This study was supported by NSF grant OCE82-18583. Lamont-Doherty Geological Observatory contribution 4359.

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(Received February 20, 1988; revised June 6, 1988; accepted May 11, 1988.)