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A procedure for independently estimating blanks and uncertainties for measured values of ^{90}Sr and ^{137}Cs concentrations in the Atlantic Ocean

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ABSTRACT

A procedure has been developed for independently estimating blanks and measurement uncertainties for measured values of ^{90}Sr and ^{137}Cs concentrations in the Atlantic Ocean. The procedure depends on delineation of a region in the Atlantic Ocean which has never contained measurable quantities of these fission products. Such a region is defined. A simple model, with supporting data, is used to show that reported ^{137}Cs inventories in deep ocean sediments could have accumulated without ever raising concentrations of ^{137}Cs in this tracer-free volume above minimum detectable limits. Several examples are presented to show that the use of the procedure results in a substantial improvement in the quality of ^{90}Sr and ^{137}Cs data. The method is applicable to any laboratory that has determined ^{90}Sr and ^{137}Cs concentrations in samples collected from within the tracer-free volume.

1. Introduction

Measurements of concentrations of the soluble fallout radioisotopes ^{90}Sr ($T_{1/2} = 29.0$ y) and ^{137}Cs ($T_{1/2} = 30.2$ y) have been carried out in the subsurface and surface Atlantic Ocean for more than 20 years. This interval includes the periods of most rapid introduction of these isotopes, between 1957 and 1965. These data comprise a unique body of information for studying processes that influence the exchange of water between the surface and subsurface ocean. The data are particularly important since almost no subsurface tritium or ^{14}C data were collected in the Atlantic during the six critical years between 1957 and 1964. Hence, ^3H and ^{14}C cannot provide any information about the early oceanic history of the major bomb tracer input. During the period 1957 through 1964, concentrations of ^{90}Sr (and a small number of ^{137}Cs concentrations) were measured in samples from 68 vertical profiles collected by the Woods Hole Oceanographic Institution (WHOI).

The usefulness of soluble fission product data has been hampered by disagreement about concentrations in the deep ocean (for example, Volchok, *et al.*, 1971, p. 68,

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69). We have developed what we feel is a simple, systematic procedure that for the Atlantic Ocean essentially eliminates this disagreement. The procedure results in an estimate of a blank value (the deep ocean blank—DOB) and the corresponding measurement uncertainty for a laboratory during a given period of time that is independent of the laboratory's own blank and uncertainty estimates. These independent estimates are derived from samples taken from a region of the ocean which appears never to have contained measurable concentrations of ^{90}Sr and ^{137}Cs .

The procedure has been applied to ^{90}Sr and ^{137}Cs concentrations measured at WHOI and by associated contractor laboratories. Several examples illustrating the effectiveness of this procedure are presented. A model is presented which accounts for measured ^{137}Cs concentrations in the sediments without requiring measurable concentrations of ^{137}Cs in deep ocean water.

In a companion paper, Kupferman, Livingston, and Bowen (1979) have estimated the total inventory of ^{90}Sr and ^{137}Cs in the North Atlantic Ocean in 1972 using DOB corrected data and compared this value with estimates of the amounts of these isotopes introduced by direct fallout and by other inputs.

2. The deep ocean blank procedure

While the procedure is a simple one, its use is critically dependent on delineating the region which has no measurable fission product concentration. This requires a large number of precise, high quality analyses taken throughout a large portion of the ocean over a reasonably short period of time. The 1972-73 Atlantic GEOSECS (Geochemical Ocean Sections) cruises and other WHOI cruises during 1972 provided these data. To establish that this portion of the deep ocean was always without measurable concentrations, certain ancillary data such as WHOI analyses of ^{90}Sr and ^{137}Cs concentrations in deep ocean sediment cores were also required.

The procedure for establishing the ^{90}Sr and ^{137}Cs free region is as follows. 1972-73 Atlantic Ocean water analyses were examined. Samples south of 50N and below 1000 m were the prime focus of attention. The salinity of each sample and also the water structure at the station were carefully examined for any evidence that the large volume water samplers had leaked or pretripped so that data from such events could be excluded. The ^{90}Sr and ^{137}Cs concentrations were plotted by laboratory and depth range (the ranges used were: deeper than 3000 m, 3000-2000 m, and 2000-1000 m) on charts of the Atlantic Ocean. These data along with information on the hydrographic structure of the Atlantic Ocean and GEOSECS tritium values (Ostlund *et al.*, 1976) were used to delineate a volume which we call the tracer free volume (TFV), which did not appear to have received a measurable amount of ^{90}Sr or ^{137}Cs from the surface ocean. This volume in 1972 was below 2000 m and south of 30N in the northern hemisphere and includes the Caribbean Sea and was below 1000 m and north of 40S in the southern hemisphere. We did not consider the Gulf of Mexico or the Mediterranean Sea in defining the TFV. We have been very conservative

Table 1. WHOI 1972 Low Activity Subsurface Values (concentrations in dpm/100 l).

Location	Depth(m)	N	⁹⁰ Sr			¹³⁷ Cs			
			$\overline{\alpha}$ $\overline{{}^{90}\text{Sr}} \pm \text{SD}^\beta$	$\overline{\text{LU}}^{\alpha, \gamma}$	$\frac{\text{SD}^\delta}{\sqrt{N}}$	$\overline{\alpha}$ $\overline{{}^{137}\text{Cs}} \pm \text{SD}^\beta$	$\overline{\text{LU}}^{\alpha, \gamma}$	$\frac{\text{SD}^\delta}{\sqrt{N}}$	
NA	>3000	8	0.10 ± 0.50	0.36	0.18	13	-0.12 ± 0.34	0.37	0.09
SA	"	8	0.15 ± 0.60	0.38	0.21	9	-0.27 ± 0.39	0.39	0.13
NA	2000 to 3000	1	0.2 ^η	0.2 ^η		2	-0.5 ± 0.30	0.35	0.20
SA	"	2	0.75 ± 0.50	0.40	0.35	4	-0.10 ± 0.22	0.35	0.11
NA ^ε	1000 to 2000	11	0.85 ± 0.84	0.30	0.25	12	0.59 ± 0.79	0.46	0.23
SA	"	5	-0.04 ± 0.31	0.39	0.14	5	-0.06 ± 0.40	0.40	0.18
TFV ^ζ		24	0.15 ± 0.50	0.37	0.10	33	-0.17 ± 0.35	0.38	0.06

NA = Equator to 30N

SA = Equator to 40S

^α Overbar indicates mean value.

$$^\beta \text{ Standard deviation} \equiv \sqrt{\frac{\sum(x-\bar{x})^2}{N-1}}$$

^γ $\overline{\text{LU}}$ stands for mean laboratory counting uncertainty.

$$^\delta \frac{\text{SD}}{\sqrt{N}} \equiv \text{Standar error of the mean.}$$

^ε Not included in calculating deep ocean blanks.^ζ TFV (tracer free volume) includes all regions shown in this table with the exception of NA 1000 to 2000m.^η Individual analysis values and uncertainties are generally reported to the nearest 0.1 dpm/100 l. We have in this table carried an extra decimal place in quantities representing combinations of individual values.

in our specification of the TFV requiring consistency of ^{90}Sr , ^{137}Cs and tritium results, and appropriate hydrographic structure. There are undoubtedly other volumes (for example, see tritium results of Weiss *et al.*, 1976) that have not received measurable ^{90}Sr and ^{137}Cs from the surface ocean but that we have not included.

Table 1 shows statistical summaries for WHOI ^{90}Sr and ^{137}Cs values from the TFV, and also from the 1000 to 2000 m layer north of the equator which was not included in this volume. A comparison of mean values with the standard error of the mean $\left(\frac{\text{SD}}{\sqrt{N}}, \text{SD} = \text{standard deviation} = \sqrt{\frac{\sum(x-\bar{x})^2}{N-1}} \right)$ shows that this layer contained significant fission product concentrations. It is of interest to note that the standard deviations of the values from within the TFV are close to the means of the (one sigma) laboratory counting uncertainties reported by WHOI (see bottom line of Table 1). This is to be expected if samples contained identical concentrations of ^{90}Sr and of ^{137}Cs , and if the laboratory counting uncertainties approach the overall uncertainties in the measurement process. (It is customary in many laboratories engaged in the measurement of fission product radioactivity for the laboratory counting uncertainty or quantities closely related to it to be used as an estimator of the uncertainty in the total measurement process.) The ^{137}Cs mean value in the TFV is slightly below zero, while the ^{90}Sr mean value is slightly greater than zero. These deviations from zero are substantially smaller than the mean laboratory counting uncertainties; however, the ^{137}Cs concentration is also significantly less than zero compared to the standard error of the mean, indicating a slight overestimate of the analytical blank value during this period at WHOI.

All WHOI and WHOI contractor data from within the TFV from samples collected during the years 1957 through 1972 were examined. The mean values of all analyses used are listed by year of collection and laboratory in the left-hand column labeled DOB in Table 2. Also listed are the number of analyses, the standard deviation, the mean of the laboratory counting uncertainties and the standard error of the mean.

Not all analyses in the TFV were used for calculating the values listed in Table 2. Values whose laboratory counting uncertainties were greater than twice the mean laboratory counting uncertainty were excluded whenever four or more other values were available. Values that differed from the mean of the remaining values by more than three standard deviations were also excluded. The total number of analyses excluded was less than 20. 224 ^{90}Sr and 84 ^{137}Cs values were used to obtain the values shown in Table 2.

The present mean value for the total inventory of ^{137}Cs in deep Atlantic Ocean sediments is less than 2 millicuries/km² (mCi/km²) (Noshkin and Bowen, 1973; Livingston and Bowen, to be published). The inventory varies somewhat with latitude. The ^{90}Sr inventory is typically 1/3 to 1/4 of this value. A 1000 m layer of water containing a uniform fission product concentration of 1 dpm/100 l contains

a total inventory of 4.5 mCi/km². Since the mean depth of the Atlantic Ocean is about 4000 m, a comparison of the earlier mean concentration values in Table 2 with the essentially zero 1972 WHOI values strongly implies that the waters in the TFV could not have lost to the sediments the concentrations reported earlier. Thus values from samples collected within the TFV should always have been zero, within experimental uncertainty. Nonzero values are an indication of contamination introduced at some stage(s) of the collection-measurement process. A model presented in the section addressing transport through the tracer free volume shows that the amounts presently found in the sediments could have accumulated without ever raising the concentrations in the TFV above detectable limits for the sample sizes (typically 60 l) that were analyzed.

We therefore conclude that the mean values in Table 2 are independent estimates of blank values and that the standard deviations are independent estimates of the entire uncertainty in the measurement process, from sample collection to reporting of results. We will henceforth refer to the mean values as deep ocean blanks (DOBs).

During the whole analytical period under discussion, both contractor laboratories and WHOI, in addition to regular series of reagent blanks, analyzed, systematically, samples of Coney Island well water or of a Devonian oil-well brine from New Mexico, the first of which provided a blank for ¹³⁷Cs only, and the second, blanks for both ⁹⁰Sr and ¹³⁷Cs (Bowen *et al.*, 1974). As discussed by Bowen (1978), however, these samples contained very substantial concentrations of natural uranium- or thorium- daughter radionuclides, and either involved disproportionate amounts of some reagents for the larger number of clean-up steps required, or led to erroneously high blank values. They did not, also, provide a good test of a laboratory's container clean-up procedure, to be discussed later. For those reasons, it is not surprising that use of these "natural blanks" did not result in data that satisfactorily reflected each laboratory's actual performance blank.

A glance at Table 2 will show that for certain years, some laboratories analyzed only a few, or no, samples from within the TFV. It is also apparent that for a given laboratory, DOB values over a several year period are relatively stable when viewed in terms of the standard deviations of these values or mean laboratory counting uncertainties. Since the one year period is arbitrary, we have combined, on the right-hand side of Table 2, values from periods with relatively stable DOB values for a given laboratory. This was done by averaging all of the individual analysis values for the period. When we mention DOB values, it is to these combined values that we will be referring, unless otherwise noted. For WHOI ¹³⁷Cs, the years 1967-69 were without samples in the TFV. The DOB appeared to change significantly during this period. We arbitrarily assigned a DOB value equal to the mean of the preceding and following periods. These years are distinguished by an "M" in the column denoting the number of analyses.

To apply a DOB correction, the DOB value for the laboratory and period is sub-

Table 2. Deep Ocean Blanks (DOB, SD, \overline{LU} and AU in dpm/100 l).

Lab & Year	^{90}Sr						DOB and AU values to be used for periods indicated	
	\overline{N}	\overline{DOB}	\overline{SD}	\overline{LU}^{α}	$\frac{SD}{\sqrt{N}}$	\overline{AU}^{β}	\overline{DOB}^{β}	$\overline{AU}^{\beta,\gamma}$
WHOI 57	3	0.7	0.2	1.4	0.1		0.7	
58	1	2.4		0.2				
59								
60								
61	4	2.3	0.8	0.7	0.4	0.4	2.9	1.4
62	1	1.5		1.4				
63	14	3.6	2.4	1.8	0.6	1.6		
64	7 ^s	2.2	0.9	0.5	0.3	0.8		
65	2	-0.4	0.3	0.5	0.2			
66	5	0.9	0.8	0.3	0.4	0.7		
67							0.7	0.6
68	13	0.6	0.7	0.3	0.2	0.7		
69								
70	6	0.9	0.8	0.6	0.3	0.4		
71	4	0.2	0.3	0.6	0.1		0.2	
72	24	0.2	0.5	0.4	0.1			
TW 64	1	-0.9		1.3				
65								
66	1	1.1		0.3				
67								
68	6	1.3	1.8	1.0	0.7	1.5	1.1	1.3
69								
70	2	1.2	0.6	0.5	0.5			
71	7	0.6	1.0	0.8	0.4	0.6		
72	66	0.9	0.8	0.5	0.1	0.7	0.8	0.7
HN 63	4	1.4	0.8	0.5	0.4	0.7	1.4	0.7
64	3	0.5	0.2	0.7	0.1			
65	3	0.2	0.3	0.5	0.2		0.4	
66	4	0.4	0.8	0.6	0.4			
TE 63	1	1.2		1.3				
64								
65	1	1.5		0.8			1.7	
66								
67	2	2.3	0.8	0.7	0.6	0.4		
68	6	1.6	1.3	1.0	0.5	0.8		
CN 65	1	0.5		0.1				
66	8	0.6	0.2	0.7	0.1		0.6	

Table 3. Comparison of Duplicate Sample Values. Samples Collected on Cruise of Erika Dan, 1962 (^{90}Sr , DOB, AU and difference values in dpm/100 l).

	Depth (m)	Lab	$^{90}\text{Sr}^a$	DOB	AU	Corrected ^{90}Sr	Differences Between Duplicates (WHOI- Contractor Lab)	
							Uncor- rected	DOB Cor- rected
Station 374	1082	W	5±4	2.9	±1.4	2.1±4.2		
59°23'N, 26°01'W		HN	1.2±0.8	1.4	±0.7	-0.2±1.1	3.8	2.3
Total Depth 2456 m	1961	W	5±1	2.9	±1.4	2.1±1.7		
IV-17-62		HN	0.6±0.6	1.4	±0.7	-0.8±1.0	4.4	2.9
	2378	W	2±1	2.9	±1.4	-0.9±1.7		
		CN	0.9±0.3	0.6		0.3±0.3	1.1	-1.2
Station 295	1004	W	12±2	2.9	±1.4	9.1±2.4		
59°32'N, 59°45'W		CN	6±0.6	0.6		5.4±0.3	6	3.7
Total Depth 1498 m								
III-21-62	1479	W	3±1	2.9	±1.4	0.1±1.7		
		HN	2.9±0.8	1.4	±0.7	1.5±1.1	0.1	-1.4
Station 237	1979	W	2±2	2.9	±1.4	-0.9±2.4		
57°40'N, 48°06'W		HN	2.8±0.6	1.4	±0.7	1.4±0.9	-0.8	-2.3
Total Depth 3396 m								
II-26-62	3281	W	5±2	2.9	±1.4	2.1±2.4		
		HN	4.3±0.4	1.4	±0.7	2.9±0.8	0.7	-0.8

Summary

Mean Laboratory		Mean Sample		Difference Between Duplicates; Mean, Standard Deviation, Standard Error of the Mean.	
Uncertainty (dpm/100 l)		Uncertainty (dpm/100 l)		(dpm/100 l)	
WHOI	Other	WHOI	Other	Uncorrected	DOB Corrected
±1.9	±0.6	±2.4	±0.8	2.2, ±2.5, ±0.9	0.5, ±2.4, ±0.9

^a Number of significant figures entered as they appear on data sheets.

tracted from an uncorrected analysis value. Here it is important to note that we have assigned DOBs on the basis of time of collection rather than time of analysis. The normal analysis schedule for samples was that alternate samples in each profile were analyzed as a first group and finished within 12 to 18 months of collection; when greater detail appeared desirable, the remaining samples were analyzed, mostly by a different laboratory, and finished within no less than 12 to 18 months. The actual analysis time of samples collected in a given year, then, commonly stretched over at least a three-year period following collection, and often longer. In this circumstance, the time of analysis of a sample could be a relevant parameter in determining the DOB correction to be applied. However, time of analysis is correlated with the time

of collection and it has not been possible to distinguish clearly between contamination occurring at the time of collection and at the time of analysis particularly for earlier periods when typically only a limited number of values from the TFV were available. Indeed, for at least a certain subset of this data it is apparent that the two possible sources of contamination are not clearly distinguishable even in theory. Intercomparisons, especially between WHOI, HN and the Atomic Energy Commission's Health and Safety Laboratory, some of which are summarized in Table 3, convinced WHOI that care in removing surface contamination before opening the shipping containers was a vital step in reducing blanks and that inadequate attention to this step accounted for systematically high values by some WHOI analysts and by some contractor laboratories. In these cases, contamination at the time of collection and at the time of analysis cannot be considered to be independent. Given these circumstances, we feel that applying the DOB correction by laboratory and period of collection is most reasonable. As will be seen in section 3, the DOB procedure as specified is effective in erasing irregularities between data sets produced by two or more laboratories and in improving the quality of data.

To correct an analysis value for a year before a laboratory's earliest DOB value, its earliest DOB value in Table 2 should be used. We have found analysis results by these laboratories, from samples collected outside of, but close to, the boundaries of the TFV, with fission product concentrations comparable to those shown in the table during these early years and believe that it is reasonable to use this procedure.

For some periods, as can be seen from Table 2, the standard deviation associated with the yearly DOB value considerably exceeded the mean laboratory counting uncertainty. In such cases we feel that the standard deviation provides a more realistic estimate of the uncertainties in the measurement process for the set of samples than do laboratory counting uncertainties. Here a better estimate of the uncertainty in an individual sample value to which a DOB correction is to be applied is composed of a combination of its laboratory counting uncertainty and a quantity called the additional uncertainty (AU) which is associated with the particular DOB. We will call this combination of AU and laboratory counting uncertainty the sample uncertainty (SU). We define the AU as the quantity that combined with the mean laboratory counting uncertainty of the DOB samples by propagation of errors is equal to the SD of these samples. With this definition the AU is

$$\text{AU} = \{(\text{SD})^2 - (\text{mean laboratory counting uncertainty})^2\}^{\frac{1}{2}} \quad (1)$$

and the SU is defined as

$$\text{SU} = \{(\text{laboratory counting uncertainty})^2 + (\text{AU})^2\}^{\frac{1}{2}} \quad (2)$$

The advantage of using an SU defined in this way instead of simply using the SD in place of individual laboratory counting uncertainties is that an SU cannot be smaller than a laboratory counting uncertainty, as can be seen from equation 2,

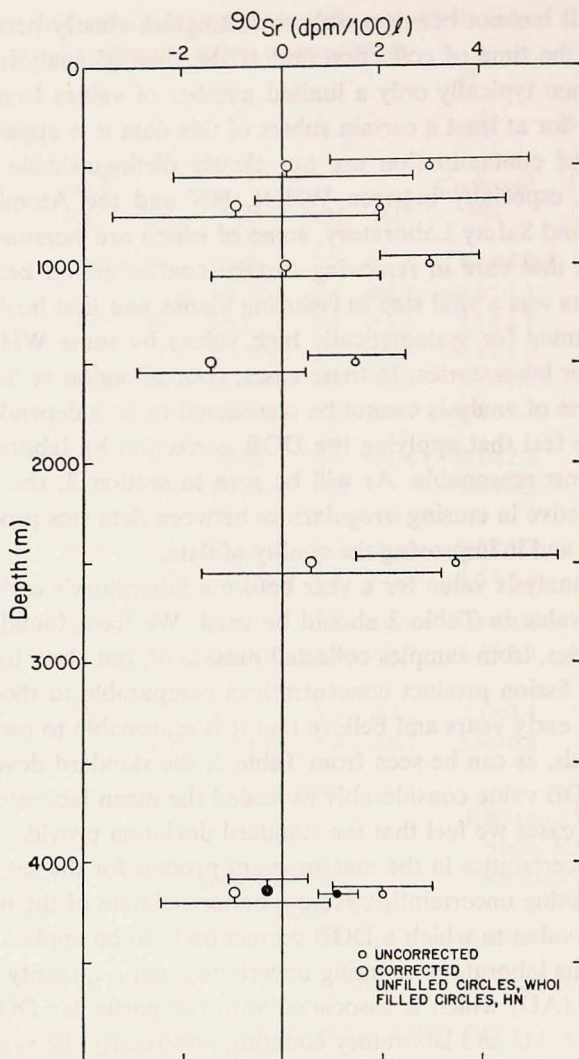


Figure 1. Uncorrected and DOB Corrected ^{90}Sr Concentrations at Crawford 91, Station 1503, 21 April 1963, $16^{\circ}00'\text{N}$, $60^{\circ}12'\text{W}$, Depth Approximately 4500 m.

while an SD can. This feature is important since the laboratory counting uncertainty represents a lower limit to the uncertainty associated with a measured value.

We feel that the use of AU's will result in significantly improved estimates of uncertainty in those cases where they are about equal to or larger than the mean laboratory counting uncertainty. Where relevant, AU's which have been calculated from all individual analysis and laboratory counting uncertainty values for a period have been listed with the DOB's on the right-hand side of Table 2. The uncertainties in

all values that have been adjusted by the DOB procedure will be called sample uncertainties whether or not it has been necessary to apply equation (2).

3. Effectiveness of the deep ocean blank procedure

If the DOB procedure is effective, this effectiveness should manifest itself in at least two ways. It should result in an improvement in the agreement between sample values obtained at different laboratories. It should also result in improved ⁹⁰Sr and ¹³⁷Cs depth profiles, that is, profiles that are consistent, within experimental uncertainty, with what we know about the structure of the ocean.

Table 3 shows values obtained on all duplicate samples (seven pairs) collected on a cruise of the Erika Dan in the winter of 1962. The WHOI laboratory analyzed one of each pair, the other was analyzed by the contractor laboratory shown. These samples were all collected north of 57N and are from some of the earliest WHOI profiles in this region. The duplicates all contain relatively low concentrations of ⁹⁰Sr and were all therefore useful for checking the DOB procedure. For samples with high concentrations, systematic differences and statistical variations of a few percent in estimates of counting or extraction efficiency could overwhelm the differences due to differing DOBs.

In Table 3 are shown the appropriate DOB and AU values, the corrected values and sample uncertainties, and the differences between duplicate values before and after correction. Note that for the corrected values the mean difference is less than the standard error of the mean, while for the uncorrected values the mean difference is more than twice the standard error of the mean.

Figure 1 shows a vertical profile of ⁹⁰Sr concentration from samples collected in 1963 in a region where recent WHOI ⁹⁰Sr and ¹³⁷Cs and University of Miami tritium data indicate the absence of significant concentrations of these tracers below 500 m. At this station, samples below 2000 m are in the TFV and were used in determining the DOBs used in correcting this profile (the corrected values are shown by the larger circles). Since only two of the 27 samples used to obtain the WHOI DOB and only one of four contractor samples are in this profile, we feel that even the samples below 2000 m are relatively independent indicators of the effectiveness of the DOB procedure.

We have calculated the total inventories of ⁹⁰Sr in the water column below 500 m using the corrected and uncorrected mean ⁹⁰Sr concentrations. They are -7.0 ± 4.8 mCi/km² and 41.5 ± 6.0 mCi/km², respectively. The uncertainties shown were estimated using the standard error of the mean of the ⁹⁰Sr concentrations, in each case.

The corrected inventory value shows that there was no significant inventory of ⁹⁰Sr in the water column below 500 m, as we would expect from recent measurements in the water column, the inventory in the sediments, and our knowledge of the circulation and water structure in this area.

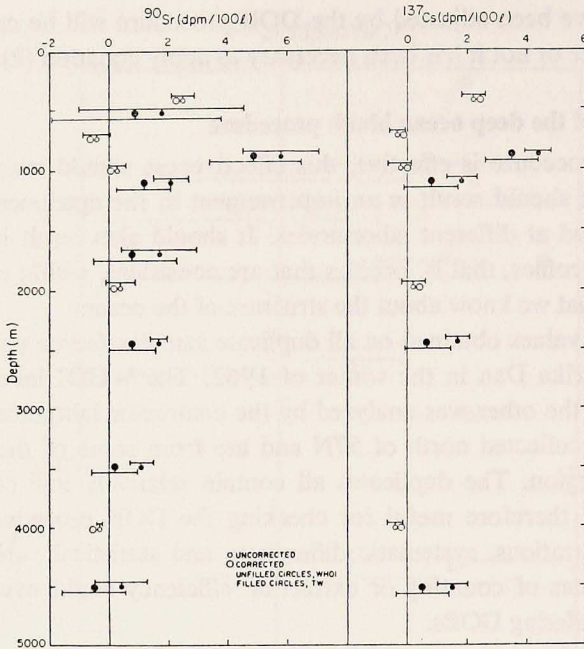


Figure 2. Uncorrected and DOB Corrected ^{90}Sr and ^{137}Cs Concentrations at Knorr 30, Station 37, 13 October 1972, $12^{\circ}01.5'\text{N}$, $51^{\circ}00.0'\text{W}$, Depth 5073 m.

A profile taken in 1972 (GEOSECS Station 37) in the same general region is shown in Figure 2. Both ^{90}Sr and ^{137}Cs analyses (from the same water sample) are shown where available.

Tritium analyses at this station again do not indicate significant tritium concentrations below 500 m. This was not one of the better soluble fission product stations, from the standpoint of contractor analysis (filled circles). A tritium analysis within 45 m of the values at 894 m (taken on a different cast) did not indicate significant concentrations of tritium (Ostlund *et al.*, 1976). Such unexplained high values were found a number of times for this contractor in 1972, as with other contractors in other years. The values shown are almost certainly spurious. We have included them here because both the ^{90}Sr and ^{137}Cs values were high. Where only one of the isotope values is off, it is simple to detect the error from a comparison with neighboring values in the profile or from the highly anomalous $^{137}\text{Cs}/^{90}\text{Sr}$ value, a value which is normally close to 1.45 (Bowen *et al.*, 1974). A contractor ^{137}Cs value at 3472 m (6.0 ± 0.6 dpm/100 l) has been discarded as erroneous on the basis of these criteria.

While the DOB correction brings all of the contractor points in Figure 2 into substantially better agreement with the WHOI (and tritium) analyses, it is clear that in this profile the contractor DOBs undercorrect by about 0.6 dpm/100 l both for ^{90}Sr and ^{137}Cs . We feel that this is undesirable but acceptable since most of the cor-

Table 4. ¹³⁷Cs on Filters. (All samples collected from surface water).

Filter Number	Date	Location	S(‰)	Total Depth(m)	Volume Filtered (l)	¹³⁷ Cs (dpm/100 l)
49	10/26/74	39°57.0'N, 73°16.3'W	33.156	73	462	0.03±0.03 ^α
53	10/24/74	39°29.4'N, 71°30.6'W	34.867	3630	757	0.1±0.2 ^β
55	10/23/74	39°53.2'N, 71°57.2'W	33.865	112	745	-0.01±0.03 ^α

^α At WHOI, chemical extraction, purification and beta counting.

^β At UD, nondestructive gamma ray spectrometry of entire filter.

NOTE: We are indebted to H. Feely and G. Kipphut for providing us with these filters.

rected contractor values are within their sample uncertainties of zero. The agreement could probably be improved for 1972, in view of the large number of values in the TFV by this contractor, through subdividing the ocean into eastern and western subregions. Values on the eastern side seem to be somewhat lower on the average for this contractor than those on the western side.

The DOB values for WHOI are so small in 1972 that it is hard to see any clear-cut improvement from applying the DOB procedure. For two out of four ⁹⁰Sr and three out of four ¹³⁷Cs values, the DOB corrections bring the values closer to zero. It should also be noted that 21 out of 26 of the corrected values deeper than 500 m in Figures 2 and 3 are within their sample uncertainty of zero, their expected value, while only 8 of 26 uncorrected values are within their laboratory counting uncertainty of zero. On the basis of this and other similar evidence, we are convinced that the DOB and AU corrections bring about a substantial improvement in the quality of the entire data set.

4. Transport through the tracer free volume

Since the mean inventory of ¹³⁷Cs in open ocean sediments is about 2 mCi/km² (⁹⁰Sr is several times less, but clearly present), it is important to find a process that could transport this material from the ocean surface to the sediments, and yet not result in measurable concentrations of ⁹⁰Sr and ¹³⁷Cs in the TFV. It has been suggested that ¹³⁷Cs is associated with particles sinking at high speeds (Noshkin and Bowen, 1973). The tracer must also be regarded as not susceptible to transfer by isotope exchange to the solution through which it sinks (Bowen, 1977). If a model is formulated assuming that typical sinking rates of these particles are 500 m/yr (Bowen, personal communication) and that this process has been transporting ¹³⁷Cs to the sediments at a constant rate since 1960, the time that surface concentrations in the North Atlantic were at substantially the same level that they are at present,

then for an ocean 4000 m deep, a mean concentration of ^{137}Cs on particulates of 0.05 dpm/100 l would have transported 2 mCi/km² to the sediments. Laboratory counting uncertainties in Table 2 show that this concentration would have been considerably below minimum levels of detection.

There is some evidence that this estimated concentration is not unrealistically low, and that ^{137}Cs is being continuously transported downward by rapidly sinking particles. Table 4 shows ^{137}Cs concentrations obtained from filters collected for us in surface shelf and slope waters off the northeastern United States by H. Feely and G. Kipphut of Lamont Doherty Geological Observatory, in 1974. The filters had an effective pore size of 0.3 μ . At the time, typical ^{137}Cs concentrations in the region were 30 dpm/100 l. As can be seen, there were no detectable concentrations of ^{137}Cs on the particulates for limits of detection that are in the neighborhood of concentrations estimated by our simple model.

Table 5 shows the results of nondestructive gamma ray analysis of two sediment trap samples (these samples and the supporting data were obtained from W. Gardner and G. Rowe of WHOI) from a mooring on the lower continental rise off the northeastern United States. The upper sediment trap was outside of the nepheloid layer. Only the material in the upper trap evidenced significant ^{137}Cs activity. The ^{137}Cs deposition rate estimated from this sample, if assumed uniform since 1960, results in sediment inventories in reasonable agreement with those found in WHOI cores from this area. Particle sinking rates determined for this sample are the same order of magnitude as those assumed in our model.

While the results presented in these tables are not from the waters of the deep ocean, they are clearly consistent with the simple transport model we have presented.

5. Conclusions and closing statement

The simple procedure outlined results in a significant improvement in the quality of ^{90}Sr and ^{137}Cs seawater analysis values. It has been tested on WHOI and WHOI contractor analyses but is applicable to any laboratory that has analyzed samples from within the tracer free volume prior to 1973. Ocean circulation processes may be expected to alter the TFV. Thus future measurements of ^{90}Sr , ^{137}Cs and tritium in the vicinity of the 1972 boundaries will be particularly important for examining the extent of these changes and the nature of the processes that cause them.

It is of interest to note that the DOB procedure will facilitate interlaboratory comparisons even when it is known that actual concentrations in a given well-sampled region are *not* equal to zero. So long as the standard error of the mean of each laboratory's mean value for its samples from this region is small with respect to differences between the various laboratories' mean values, the procedure can be used as an independent measure of the difference between actual performance blanks in cases where the mean values are only a few times greater than the standard errors.

Table 5. ¹³⁷Cs in Sediment Trap Samples. (Collected May 1976 at 38°19N, 39°37W, total depth 3755 M, collecting area of traps 494 cm²).

Height Above Bottom (m)	Collection Time (days)	Total Dry Weight of Sample (mg)	¹³⁷ Cs ^β Activity (dpm)	Estimated Total Transport at Rate	Suspended Particle Load		Mean Settling Velocity (m/y) ^γ
				Measured, Since 1960 (mCi/km ²)	Height Above Bottom (m)	Concen- tration (ug/l)	
518	15.8	188.5	1.2±0.4	4.1±1.4	501	22.5	3920
118	15.8	354.0 ^α	0.7±0.8	2.4±2.7	101	71.8	2300 ^δ

^α Plus weight of isopod found in trap but not included in sample counted.

^β By non-destructive gamma ray spectrometry at WHOI.

^γ Mean settling velocity = $\frac{\text{total weight of sample}}{\text{suspended particle concentration} \times \text{collection area} \times \text{collection time}} \times \text{conversion factor}$. Conversion factor, for units in this table, is 3.65×10^9 . It should be noted that mean settling velocity calculated in this way, without consideration of particle size spectra of trapped material or of suspended material is strictly order of magnitude. For further discussion, see Gardner, 1977.

^δ Calculated from total weight of sample excluding weight of isopod.

NOTE: We are indebted to W. Gardner and G. Rowe for providing these samples and all data except for ¹³⁷Cs activities. Further discussion of geological properties of these samples may be found in Gardner, 1977.

When mean values are many times greater, differences between means may also, or predominantly, reflect differences in such variables as extraction efficiency and standardization.

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