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Osmium isotopes and silver as tracers of anthropogenic metals in sediments from Massachusetts and Cape Cod bays

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Abstract—High concentrations of osmium (Os) and silver (Ag) and low $^{187}Os/^{186}Os$ ratios in Boston sewage make these elements sensitive tracers of the influence of sewage on marine sediments in Massachusetts and Cape Cod bays. Pristine marine sediments have Ag concentrations more than 200 times lower than sewage sludge, Os concentrations 10–40 times lower, and $^{187}Os/^{186}Os$ ratios six times higher. Surface sediments from both Massachusetts and Cape Cod bays exhibit both high Ag concentrations and low $^{187}Os/^{186}Os$ ratios indicating the influence of sewage particles on marine sediments in this region extends some 70 km from the point of sewage release. In detail, the distribution of Os and Ag do not support a model of simple physical mixing of sewage particles with normal marine sediments. Deviations from the mixing model may be the result of fractionation of Os and Ag in the marine environment, and [or] independent temporal variations in the Os and Ag content of the waste stream. The results of this investigation suggest that osmium isotopes may be widely applicable as tracers of the influence of sewage on sediments in estuarine environments and that subtle variations in the isotopic composition of Os in the waste stream may help constrain the sources of Os and other metals delivered to the environment.

1. INTRODUCTION

In order to directly compare two tracers of anthropogenic metal distribution in the estuarine environment, we report the results of a study of osmium isotopic variations in sediments from Boston Harbor, Massachusetts Bay, and Cape Cod Bay, in conjunction with complementary silver data (Bothner et al., 1993). Osmium isotopic variations in Long Island Sound sediments have been attributed to the influence of anthropogenic Os and were shown to be consistent with a model of physical mixing of anthropogenic and naturally occurring Os (Esser and Turekian, 1993a). Here we extend this work by comparing osmium isotopic variations in marine sediments to variations in Ag concentrations in the same samples. This dataset allows two independent tracers of anthropogenic metals to be compared and provides a means testing whether two component physical mixing models can explain the distribution of both anthropogenic metals. In addition, this study of anthropogenic Os in sediments from Massachusetts and Cape Cod Bays covers a much wider area than has previously been investigated, allowing an assessment of the geographic extent of anthropogenic Os impact. Very recent work in Chesapeake Bay has provided additional evidence of anthropogenic osmium in coastal deposits (Adelson et al., 1995), indicating that anthropogenic shifts in osmium isotopic composition are common proximal to developed coastlines.

Levels of Ag in municipal wastes (average 25 $\mu g/g$: Sung et al., 1986) are typically enriched more than two hundred-fold relative to the Ag concentrations commonly found in pristine marine sediments, making Ag one of the most sensitive indicators of the influence of sewage particles in the marine environment. The high concentration of Ag in sewage sludge is likely to be the result of Ag use in photography, x-ray applications, and electronics.

An isotopic contrast between Os carried by pristine coastal sediments and Os used in commercial and industrial applications provides an independent means of tracing the distribution of anthropogenic metals. Variations in osmium isotopic composition result from ^{187}Re decay to ^{187}Os (half-life ≈ 45 billion years). Typical crustal materials have relatively high Re/Os ratios, giving rise to large $^{187}Os/^{186}Os$ ratios over geologic time ($^{187}Os/^{186}Os$ ratios between 8 and 11: Ravizza and Turekian, 1992; Esser and Turekian, 1993b). In contrast, the ultramafic rocks from which Os is mined for medical and industrial uses have low Re/Os ratios; consequently, $^{187}Os/^{186}Os$ ratios remain low in these rocks ($^{187}Os/^{186}Os \approx 1$; Hart and Kinloch, 1989). Thus, the addition of unradiogenic anthropogenic Os to coastal sediments lowers $^{187}Os/^{186}Os$ below typical radiogenic crustal values, providing an isotopic finger print of anthropogenic metals.

Using isotopic data to infer the presence of anthropogenic metals is more definitive than using metal concentration data alone. Natural processes can act to locally elevate metal concentrations above average crustal concentrations in the absence of significant anthropogenic inputs. These natural metal enrichments complicate efforts to distinguish pristine environments from those having only subtle enrichments in anthropogenic metals. Size sorting, chemical diagenesis, and bioconcentration are examples of natural processes that can locally enrich marine sediments in various trace metals. Heavy isotopes, such as the isotopes of Pb (Flegal and Stukas, 1987) and Os, are not effectively fractionated in the natural environment due to their small fractional mass difference. Consequently, osmium isotopic variations in recently deposited sediments can only arise as a result of mixing of two or more isotopically distinct sources of Os.

Lead isotopes have been used to trace the distribution and source of anthropogenic Pb with great success (Sturges and Barrie, 1987; Flegal et al., 1989a). However, because Pb pollution is extremely far reaching in the marine environment and is dominated by atmospheric transport (Flegal et al., 1989b; Hamelin et al., 1990), lead isotopic variations are not well suited to tracing a point source of pollution in the coastal marine environment. Although little is known about the pathways by which anthropogenic Os is delivered to the marine environment data, all work to date in this area indicates municipal sewage is a major source of anthropogenic Os (Esser and Turekian, 1993a; this study). Thus, osmium isotopes may be unique isotopic tracers of sewage distribution in the coastal marine environment.

2. STUDY AREA

Plans to relocate Boston's present sewage-effluent outfall 16 km seaward of its present location at the mouth of Boston Harbor have motivated a comprehensive examination of the influence of previously released sewage on the Massachusetts Bay region and of the mechanisms of dispersal and transport of this material (Geyer et al., 1992; Butman and Signell, 1993). During the past several decades, the principal source of both suspended solids and metals to the Massachusetts Bay region was discharge of sewage sludge and waste waters from municipal treatment facilities, mainly within Boston Harbor (Menzie-Cura and Associates, 1991). All release of sewage sludge to the region stopped in December 1991. Damming of local rivers draining into Boston Harbor and Massachusetts Bay renders rivers a minor source of sediment to this region, thus increasing the relative importance of anthropogenic inputs and redistribution within the study area (Knebel, 1993). Prevailing southerly current from the Gulf of Maine (Butman et al., 1992) may also supply fines advected from regions north of the study area.

In general, the estuarine part of the system is a trap for fine-grained sediment, while the open shelf is extensively winnowed and displays irregular bottom topography, reflecting a complex pattern of sediment deposition and erosion (Knebel, 1993). Prevailing currents may also transport some portion of the fine-grained sediment southward along the coast into Cape Cod Bay (Geyer et al., 1992). The heterogeneous character of sediment deposition patterns and varied mechanisms of sediment transport complicate efforts to delineate the geographic extent and pattern of pollutant distribution in Massachusetts and Cape Cod Bays. Radiochemical data collected as part of the investigation of transport and accumulation of sediments in Massachusetts and Cape Cod Bays attest to complexity of sedimentation in this region (Wade et al., 1989; M. H. Bothner, unpubl. data). The details of these studies will be reported and interpreted elsewhere, however, we will refer to preliminary results of this work as they are needed to constrain interpretation of the Ag and Os data.

3. SAMPLES

As part of an effort to document the geographic extent of sewage influence on Massachusetts and Cape Cod Bay sediments, sediment cores were taken in 1992 during operations aboard the R/V *Argo Maine* at a series of stations in this region (Fig. 1). Cores up to 60 cm in length were recovered by using a hydraulically damped gravity corer that minimizes disturbance of material at the sediment water interface. The least disturbed of four replicate cores were extruded vertically and sampled with noncontaminating titanium tools, taking care to trim and discard sediment in contact with the core barrel. A single sediment sample, initially collected for organic geochemical analysis, from Fort Point Channel in Boston Harbor was also analyzed.

Two samples of sewage sludge were analyzed to define the chemical character of the metal source. One sample was archived sludge collected in 1980 from the Deer Island treatment facility, one of Boston's two major sewage treatment facilities. The second sample was collected in 1994 from the Massachusetts Water Resources Authority Fore River site. This sample contained sludge from both the Deer Island and Nut Island treatment facilities. Since 1991, all of metropolitan Boston's sewage sludge has been dewatered and pelletized at the Fore River Site. The sample used in this study was collected prior to dewatering and was dried to constant weight at 85°C in the laboratory.

4. METHODS

At a shore-based laboratory, wet sediment samples were homogenized and dried to constant weight at 70°C. Dried samples were ground with an agate mortar and pestle prior to chemical analyses. Details of the sample preparation and methods for the complete textural and chemical analysis of these samples are given elsewhere (Bothner et al., 1986, 1993). Here we discuss only the procedures for the analysis of Ag and Os.

For the silver analyses, samples were completely dissolved by using perchloric, nitric, and hydrofluoric acids. The resulting solutions were subject to an organic extraction to isolate Ag. Analyses of Ag were performed by graphite furnace atomic absorption spectrometry. The details of the methods employed are described by Aruscavage and Campbell (1979).

For Os analyses, sediment and sludge decomposition and Os preconcentration was achieved by nickel sulfide (NiS) fire assay (Hoffman et al., 1978). Sample sizes ranged from 0.9–2.0 g for sediment analyses and from 0.3–0.5 g for sludge analyses. The NiS bead separated from the fusion glass was dissolved in hot 6.2 N hydrochloric acid (HCl). The HCl insoluble residue from the NiS bead was dissolved in a 4 N sulfuric acid solution with CrO_3, and Os was distilled as the volatile osmium tetroxide (Luck, 1982). Final purification of Os prior to loading on a platinum (Pt) filament was accomplished by ion exchange on a single resin bead.

Osmium isotopic analyses were performed by negative thermal ion mass spectrometry (Creaser et al., 1991; Volkening et al., 1991). The procedures employed in this study are briefly reviewed here; details are reported elsewhere (Hauri and Hart, 1993). Osmium, as the hexabromide, was loaded onto a platinum filament and heated to a dull glow under vacuum in order to reduce Os to the metal. Approximately 10 μg of barium nitrate were loaded onto the Os deposit following reduction. Osmium was measured as OsO_3^- ions on NIMA-B, a solid source, magnetic sector mass spectrometer with 9″ radius, using an electron multiplier. Atom ratios were calculated from the measured OsO_3^- ion beam intensities by using an iterative algorithm that corrects for instrumental mass fractionation. Reported $^{187}Os/^{186}Os$ ratios were calculated from measured $^{187}Os/^{192}Os$ ratios by using $^{186}Os/^{192}Os = 0.03907$ (Luck and Allegre, 1983). Concentrations of samples spiked with ^{190}Os were calculated from measured $^{190}Os/^{188}Os$ ratios. Precision of $^{187}Os/^{186}Os$ ratio measurements ranged from ±0.3–0.8%.
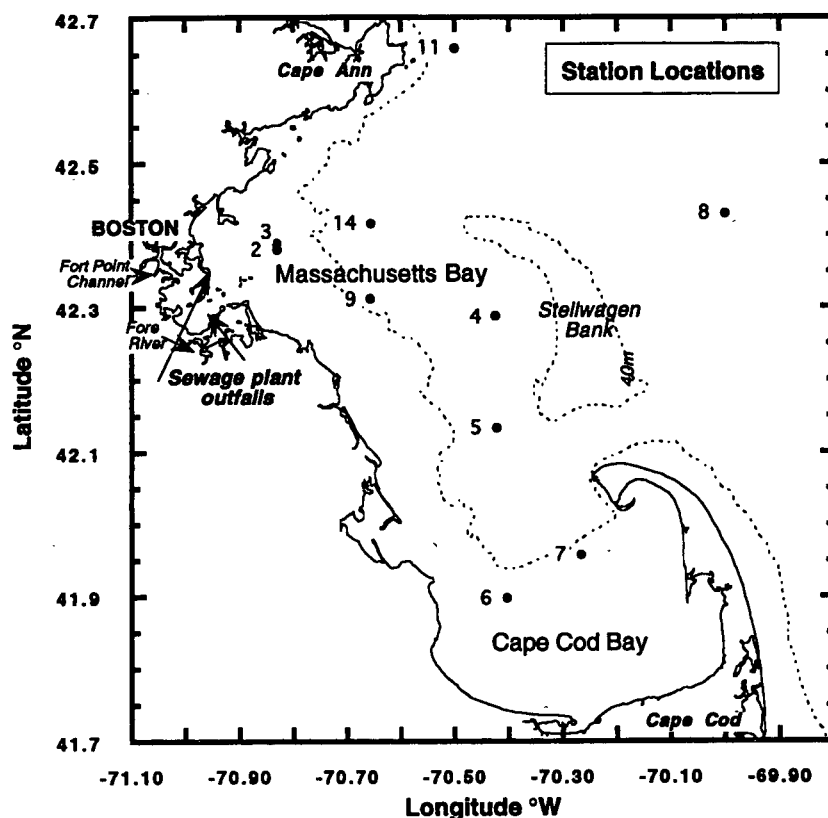
FIG. 1. Sampling locations occupied during a cruise in May 1992 aboard the R/V Argo Maine. Data from stations 4, 5, 6, 7, and 8 are presented in this study.

The Os blank was dominated by Os associated with the fusion reagents. For each analysis, the same mass of fusion reagents was used regardless of sample mass, and the procedural blank was 4 pg Os with a ^{187}Os/^{186}Os of 9.2. For low concentration samples, blank Os comprised no more than 8% of total analyte and for all samples averaged 3.5% of the total analyte. For samples having low ^{187}Os/^{186}Os ratios, blank corrections shifted the reported isotope ratios by a maximum of 3%. Blank corrections to the ^{187}Os/^{186}Os ratio of other samples was typically less than 1%.

5. RESULTS

5.1. Sludge Analyses

Results of Boston sludge analyses (Table 1) demonstrate that the Os carried in the municipal waste stream is isotopically similar to Os from Bushveld ores (Hart and Kinloch, 1989) and New Haven sludge (Esser and Turekian, 1993a). The ^{187}Os/^{186}Os ratios carried in the waste stream are much lower than the estimated range (^{187}Os/^{186}Os between 10 and 11) in average upper crustal material (Esser and Turekian, 1993b). Thus, the sludge analyses confirm that the isotopic composition of Os carried in the Boston municipal waste stream is distinct from ambient crustal Os. This isotopic contrast provides the basis for applying osmium isotopes as tracers of sewage particles in sediments of Boston Harbor, Massachusetts Bay, and Cape Cod Bay. The concentration of silver in the 1980 Deer Island sludge sample is 55 μg/g.

5.2. Sediments Analyses

Station 8 was chosen as a control site for the Ag study because it is sheltered from Boston sewage discharge by Stellwagen Bank, a prominent bathymetric high situated directly between this site and Boston Harbor (Fig. 1). Silver concentrations measured in sediments from this station are

Table 1. Os analyses of Boston sewage sludge. Both blank corrected and uncorrected values are given below. Values in parentheses are uncorrected for procedural blanks. Reported uncertainties in the uncorrected data are ± 2 sigma values based on counting statistics. New Haven sewage and Bushveld ores data are shown for comparison.

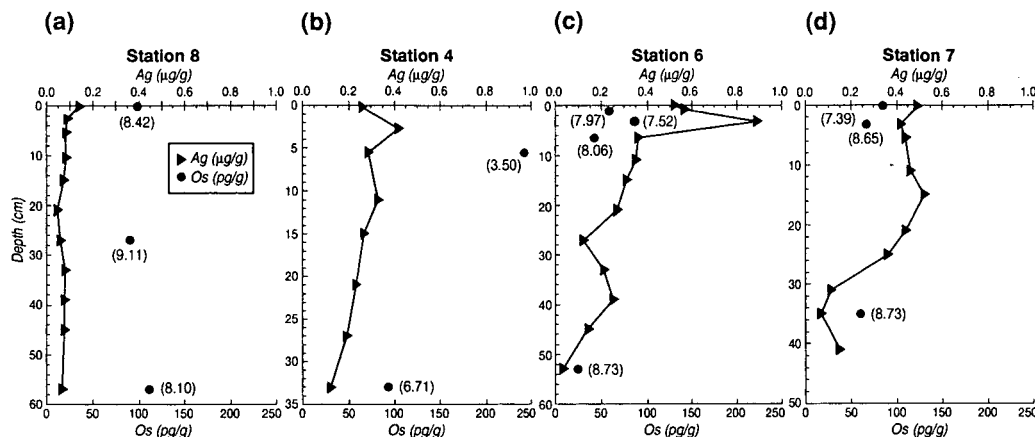|	Os (ng/g)	^{187}Os/^{186}Os
Deer Island Sewage Sludge, Boston 1980	4.01 (4.02)	1.42 (1.445 ± 0.008)
Sewage Sludge from Boston 1994	1.31 (1.32)	1.27 (1.315 ± 0.005)
Boulevard Treatment Plant, New Haven 1972 (Esser and Turekian 1993)	0.57	1.53 ± 0.03
Bushveld Ores (Hart and Kinloch 1989)	—	1.413 - 1.509 (range; n = 38)

FIG. 2. Vertical profiles of Ag concentration and Os concentration are displayed for stations 8 (a), 4 (b), 6 (c), and 7 (d). In each panel sample $^{187}Os/^{186}Os$ ratios are given in parentheses adjacent to the corresponding Os concentration. Station 8, a control station in the Ag study, defines background Ag concentrations at 0.1 $\mu g/g$. $^{187}Os/^{186}Os$ ratios throughout this core are between 8.1 and 9.1, high relative to Boston sewage, and provide a measure of the osmium isotopic composition of local pristine sediments. At other stations, near surface sediments exhibit high Ag and Os concentrations, as well as low $^{187}Os/^{186}Os$ ratios, relative to deep sediments, indicating the presence of an anthropogenic metal component in Massachusetts and Cape Cod Bays. Note data from all stations are plotted on the same scale.

in general slightly less than 0.1 $\mu g/g$ (Fig. 2a), similar to the concentration of Ag in average crustal material (Shaw et al., 1986). The distribution of Ag in cores from Stations 4, 6, and 7 (Fig. 2b–d) shows that highest Ag concentrations occur in near surface sediments from Cape Cod Bay (Stations 6 and 7), reaching five to eight times background concentrations. At depth in all cores, Ag concentrations drop to near background levels.

Surface sediment Ag concentrations can be as low as 0.04 $\mu g/g$ proximal to the mouth of Boston Harbor (Fig. 3). However, if Ag concentrations are recalculated based on the mass of the clay fraction in each sample to account for textural variations, the normalized Ag concentrations in adjacent sandy and muddy locations are similar, and a pattern of high Ag concentrations close to Boston Harbor becomes apparent. These results indicate that dilution by a coarse, metal-poor component is an important factor controlling bulk sediment Ag concentrations. However, regardless of normalization, Ag concentrations are anomalously high at Stations 6 and 7 in Cape Cod Bay which are approximately 70 km away from Boston Harbor.

A subset of sediment samples was selected for osmium isotope analysis in order to determine whether an osmium isotopic signature indicative of anthropogenic metals could be identified. Cores containing appreciable amounts of sand were not studied so that problems associated with extreme metal dilution by coarse clastics could be avoided. Osmium data from analyses of sediments from Stations 4–8 and data from a single analysis of a sample from Fort Point Channel in Boston Harbor are given in Table 2. Osmium concentrations range from 22–286 pg/g and $^{187}Os/^{186}Os$ ratios vary between 2.95 and 8.73. High Os concentrations and low $^{187}Os/^{186}Os$ occur in Boston Harbor and Stellwagen Basin (Station 4). As expected, $^{187}Os/^{186}Os$ ratios measured at Station 8,

the control station chosen for the silver study, and deep samples from Stations 6 and 7 in Cape Cod Bay are indistinguishable from values measured in pristine coastal sediments (Fig. 4), and are uninfluenced by anthropogenic Os. Osmium concentrations of these unimpacted sediments are variable (22–108 pg/g) but bracket the estimated Os concentration of average crustal material (50 pg/g: Esser and Turekian, 1993b). In Massachusetts and Cape Cod Bays (Stations 4, 6, and 7) near surface sediment samples have consistently lower $^{187}Os/^{186}Os$ ratios, and higher Os concentrations than deep samples from the same core (Fig. 2b–d). Thus, the general distribution of Os is similar to the Ag distribution.

6. DISCUSSION

6.1. Comparison of Silver and Osmium Data

Both the Os and the Ag data indicate that discharge of sewage into Boston Harbor has affected sediments in Cape Cod Bay, roughly 70 km away. In the case of Ag, this interpretation is based on the elevated concentrations in near surface sediments, relative to the control station, and a correlation in surface sediments between the concentrations of Ag and *Clostridium perfringens,* a bacterium spore found in sewage sludge (Bothner et al., 1993; Keay et al., 1993; Hill et al., 1993). For Os, surface sediments from Cape Cod Bay exhibit both elevated concentrations and shifts to lower $^{187}Os/^{186}Os$ ratios relative to deep samples from the same core. We interpret the low $^{187}Os/^{186}Os$ ratios (7.39 between 0 and 0.5 cm depth at Station 7; 8.06–7.52 between 1 and 7 cm at Station 6) as evidence of a component of sewage-derived osmium in the sediment. At Station 6 (Fig. 2c), a maximum in Ag concentration coincides with a maximum in Os concentration and a minimum in $^{187}Os/^{186}Os$ ratio,
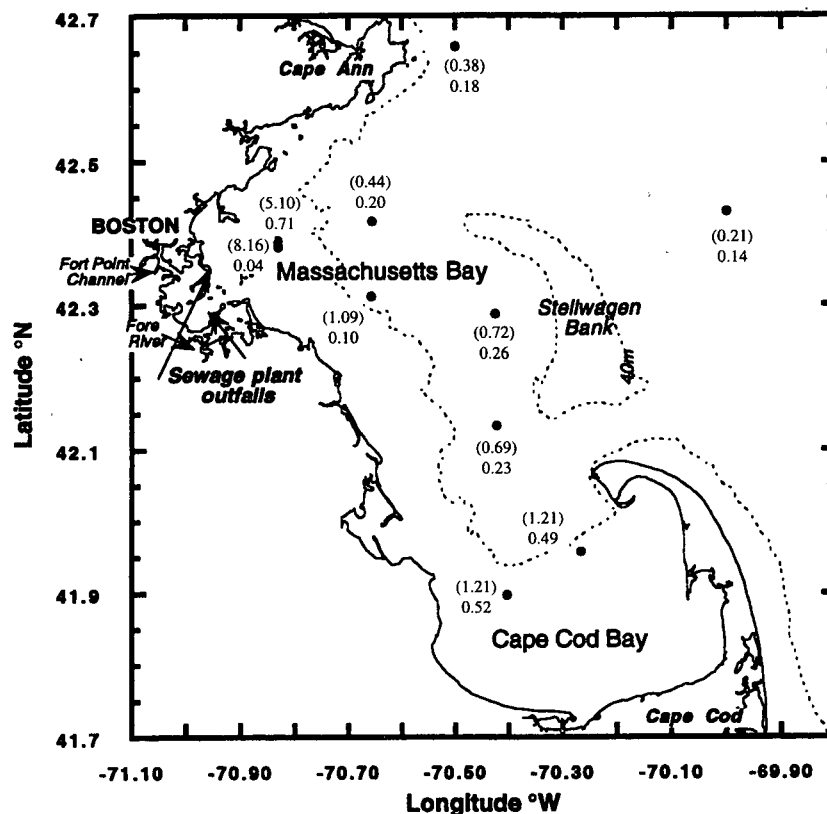
FIG. 3. Bulk Ag concentrations, and normalized Ag concentrations (divided by weight percent clay in the sample) in surface (0–0.5 cm) collected at ten locations are shown. Normalized Ag data are given in parentheses. Note that the lowest unnormalized Ag concentration (0.042 μg/g) occurs near the mouth of the harbor. This sample is 97.8% sand and the low concentration of Ag is clearly a textural effect. Normalized Ag reveal a pattern of highest Ag concentrations closest to Boston Harbor. However, high Ag concentration in Cape Cod Bay persist even when Ag concentration are normalized to mud fraction to account for textural variations.

suggesting that the silver maximum is the product of anthropogenic Ag rather than natural concentration of ambient Ag.

In several instances Os and Ag do not display coherent patterns of variation. At Station 5 (Table 2), 2.5–3 cm depth, Ag concentrations are four times background values (0.39 μg/g) while $^{187}Os/^{186}Os$ is 8.65, within the range measured at Station 8, the unimpacted site east of Stellwagen Bank. Similarly, at Station 7 (Fig. 2d) the sediment $^{187}Os/^{186}Os$ ratio increases to background levels just below the sediment-water interface ($^{187}Os/^{186}Os = 8.68$ at 3 cm depth), but Ag concentrations remain above 0.3 μg/g to a depth of 26 cm. Thus, some sediment samples that are clearly enriched in Ag show no shift in osmium isotopic composition. In Stellwagen Basin (Station 4; Fig. 2b), low $^{187}Os/^{186}Os$ ratios and high Os concentrations persist to a depth of 34 cm, but Ag concentrations drop to nearly background levels (0.15 μg/g) at this depth. These specific examples illustrate that separate interpretations of the Os data and the Ag data would create disparate impressions of the magnitude of the anthropogenic metal impact in both space and time.

6.2. Two Component Mixing Models

In order to better understand the nature of the discrepancies between Ag and Os as tracers of anthropogenic metals,

we compare the measured variations in Ag concentration, Os concentration, and $^{187}Os/^{186}Os$ ratios measured in Cape Cod Bay and Massachusetts Bay sediments to those predicted by a simple two component physical mixing model. A similar model was used by Esser and Turekian (1993a) to interpret the osmium isotopic variations in Long Island Sound sediments impacted by human activity. The model is constructed under the assumption that all variations in Ag concentrations, Os concentrations, and $^{187}Os/^{186}Os$ ratios arise as a result of mixing pristine marine sediments (Ag: 0.1 μg/g; Os: 58 pg/g; $^{187}Os/^{186}Os$: 8.65) with traces of particulate sewage sludge (Ag: 55 μg/g; Os: 4000 pg/g, and $^{187}Os/^{186}Os$: 1.4). A description of the equations governing the model is presented elsewhere (Ravizza et al., 1991). The choice of the mixing endmembers is based on analysis of 1980 Deer Island sewage sludge for the sewage endmember and deep sediment from Station 7 in Cape Cod Bay for the pristine sediment endmember.

Osmium data from Station 8 was not used to define the pristine sediment endmember in the mixing model because Os concentrations of these sediments were higher than deep sediments from Cape Cod Bay Stations 6 and 7. Figure 5 illustrates that sediments from Station 8 tend to contain a larger fraction of clay than sediments from Massachusetts

Table 2. Os and Ag data from Boston Harbor, Massachusetts Bay, and Cape Cod Bay Sediments. Both blank corrected and uncorrected Os data are given below. Values in parentheses are uncorrected for procedural blanks. Reported uncertainties in the uncorrected data are ± 2 sigma values based on counting statistics. Organic carbon data are from Bothner et al. (1993). The uncertainties associated with the Ag analyses are approximately ± 7%.

Sample	Organic Carbon %	Ag (µg/g)	Os (pg/g)	$^{187}Os/^{186}Os$	$^{187}Os/^{188}Os$
Core AM-92 8-S3 (Station 8)					
0 - 0.5 cm	1.7	0.14	94 (97)	8.42 (8.451 ± 0.063)	1.010
26 -28 cm	1.5	0.06	88 (90)	9.11 (9.121 ± 0.026)	1.093
56-58 cm	1.5	0.07	108 (111)	8.10 (8.122 ± 0.034)	0.972
Core AM-92 7-S2 (Station 7)					
0 -0.5 cm	2.6	0.49	81 (85)	7.39 (7.466 ± 0.040)	0.887 ·
3.0 - 3.5 cm	2.4	0.42	64 (67)	8.65 (8.681 ± 0.024)	1.038
34-36 cm	1.9	0.07	58 (60)	8.68 (8.701 ± 0.071)	1.042
Core AM-92 6-S1 (Station 6)					
1.0 -1.5 cm	1.9	0.56	56 (58)	7.97 (8.013 ± 0.025)	0.956
3.0 - 3.5 cm	2.4	0.89	84 (86)	7.52 (7.560 ± 0.024)	0.902
6.0 - 7.0 cm	1.4	0.36	40 (42)	8.06 (8.109 ± 0.024)	0.967
52 -54 cm	0.56	0.03	22 (24)	8.73 (8.766 ± 0.044)	1.048
Core AM-92 5-S1 (Station 5)					
2.5 -3.0	2.7	0.39	79 (83)	8.62 (8.648 ± 0.032)	1.034
Core AM-92 4-S3 (Station 4)					
5.0 - 6.0 cm	2.4	0.29	238 (242)	3.50 (3.578 ± .008)	0.420
32 - 34 cm	1.8	0.12	91 (93)	6.71 (6.761 ± 0.018)	0.805
Fort Point Channel Boston Harbor 7.0 - 9.0 cm	5.1	6.7	286 (288)	2.95 (3.018 ± 0.015)	0.354

and Cape Cod Bays. Further these sediment do not exhibit the same correlation between organic carbon content a grain size as the other stations. We suggest that this enrichment in the clay fraction may represent a detrital component derived from outside the region, delivered to Station 8 by prevailing southerly currents from the Gulf of Maine (Butman et al., 1992). The presence of an additional source of mineral detritus at Station 8 may also be reflected in the greater variability in pristine sediment $^{187}Os/^{186}Os$ ratios at this site relative to deep samples from Stations 6 and 7 in Cape Cod Bay.

The results of the model calculations and the measured variations in the sediments are presented in Fig. 6. ^{192}Os and Ag concentration variations (Fig. 6a) in samples from Cape Cod Bay (Stations 6 and 7) have slopes similar to the physical mixing trend. In interpreting this plot it is important to note that the slope of the mixing line is approximately equal to the Os/Ag ratio in the sewage endmember, and subtle shifts in the assumed pristine sediment endmember have the effect of translating the intercept of the line without significantly affecting the slope. Thus, the Station 6 and 7 trends are displaced from the mixing line as a result of local variability in Os concentration of pristine sediments. The

Station 4 data require an unreasonably low Ag/Os ratio in the sewage endmember to accommodate the physical mixing model. The position of the Station 4 data, well below the physical mixing trend in the $^{187}Os/^{186}Os$ vs. Ag plot (Fig. 6b), is another manifestation of the same problem.

Comparing the relationship between $^{187}Os/^{186}Os$ and Ag (Fig. 6b) predicted by the mixing model to the Cape Cod Bay data (Stations 6 and 7) shows that the hyperbolic trend produced by the mixing model does not fit the data; samples consistently exhibit higher $^{187}Os/^{186}Os$ than predicted. Estimates of the weight percent sewage in sediment samples provide a more intuitive means of expressing the discrepancy between the results of physical mixing models based on Os and Ag. Based on Ag data alone, a simple physical mixing model indicates sewage particles account for approximately 1.5% of the sediment by weight in the 3.0–3.5 cm sample from Station 6, the sample with the highest Ag concentration in the dataset. In contrast, estimates based on the osmium isotopic composition and Os concentration data from the same sample indicate between 0.3% and 0.6% sewage particles, respectively.

The failure of the mixing model is also apparent in Fig. 6c, a conventional osmium isotope mixing diagram. While
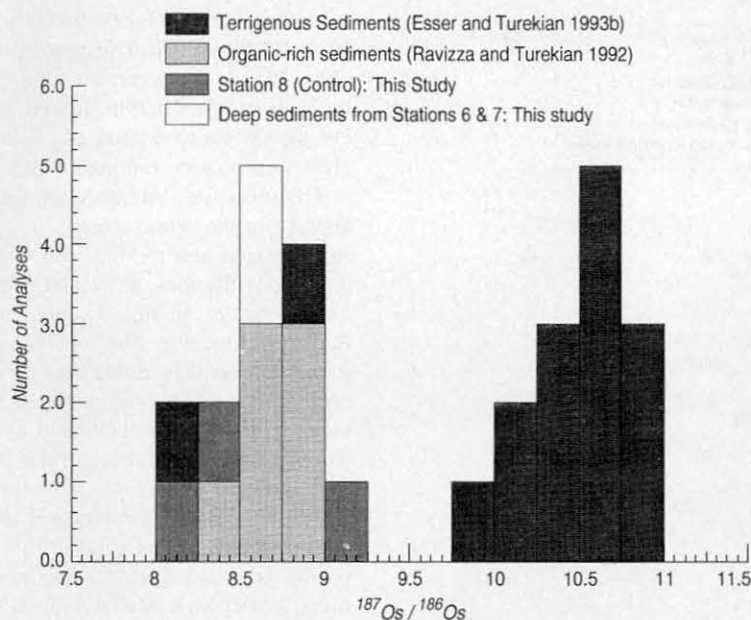
FIG. 4. Histogram of $^{187}Os/^{186}Os$ ratios which demonstrates that the osmium isotopic composition of sediments from the control station (Station 8) and deep sediments from Cape Cod Bay (Stations 6 and 7) is similar to that of pristine organic-rich coastal sediments, but is depleted in ^{187}Os relative to most terrigenous sediment samples.

the Station 6 data define a linear trend on this plot, as is expected for physical mixing, the slope of the mixing line and the inferred $^{187}Os/^{186}Os$ for the anthropogenic endmember differ dramatically from the physical mixing trend calculated by using the sludge data to define the anthropogenic endmember. In the case of the Station 4 Os data, there is reasonable agreement between the physical mixing model and the data indicating that physical mixing can explain the Os data but not the Ag data at this station. Again, comparing Os- and Ag-based estimates of weight percent sewage particles highlights the discrepancy between quantitative estimates of sewage influence calculated from these two chemical tracers. Osmium isotope and concentration data indicate between 4.5 and 3.2% sewage particles, while the Ag data

suggests sewage accounts for slightly less than 0.4% of the sediment mass.

It is important to note that the deviations from the mixing model presented in Fig. 6 cannot be eliminated by renormalizing sediment Ag and Os concentrations to eliminate dilution effects associated with a metal poor coarse fraction. To demonstrate this the mixing model presented above was recast in terms of organic carbon normalized Ag and Os concentrations using the organic carbon data in Table 2. Note that organic carbon and grain size are correlated in these sediments (Fig. 5). The results did not yield a better fit to the physical mixing model and are, therefore, not shown here. This is also clearly illustrated in a plot of $^{187}Os/^{186}Os$ vs. $Ag/^{192}Os$ (Fig. 7). Both variables in this plot are independent of any concentration normalization scheme because they are ratios. As before, the data do not conform to the trend predicted by the physical mixing model.

There are several plausible explainations for the poor fit between the data and the physical mixing model. Here we consider three different explainations which potentially play a role in creating the observed discrepancies between the data and the model: (1) different discharge histories of Os and Ag to the waste stream; (2) fractionation of Os from Ag in the marine environment; and (3) additional sources of anthropogenic Os to the marine environment. Each of these is considered below.

6.3. Different Discharge Histories of Osmium and Silver to the Waste Stream

Commercial and industrial uses of Ag and Os are not closely related. The principal applications of Ag are in the photographic and electronic industries, while consumption
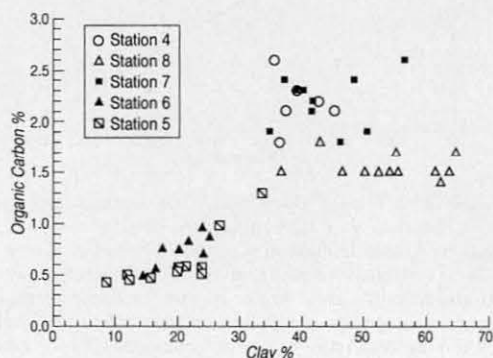

FIG. 5. Organic carbon content and grain size, as indicated by clay content, are correlated in sediments from Stations 4, 5, 6, and 7. Data from Station 8 deviate from this trend, displaying finer grain size for a similar organic carbon content.
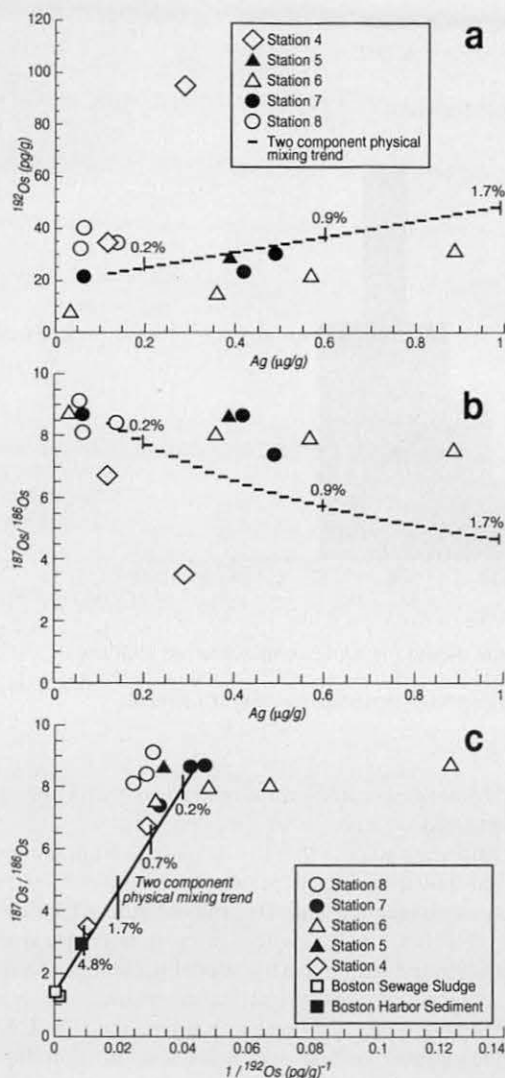
FIG. 6. Plots of ^{192}Os concentration vs. Ag concentration (a), ^{187}Os/^{186}Os vs. Ag concentration (b) and ^{187}Os/^{186}Os vs. the reciprocal of ^{192}Os concentration (c). The trends expected for simple physical mixing of normal marine sediments with 1980 Boston sewage sludge are shown as dashed lines. Assumed endmember ^{187}Os/^{186}Os ratios and Os and Ag concentrations are given in the text.

of anthropogenic Os. Preliminary evidence of this alleged temporal bias is clear in the depth profiles from Station 7 (Fig. 2d). In the sediment sample from 3.0–3.5 cm depth the silver concentration is well above background values, but the Os concentration and ^{187}Os/^{186}Os are indistinguishable from pristine sediment.

The proposed differences in time release histories of Os and Ag in the waste stream, in conjunction with sediment resuspension and mixing, can explain the deviation of the data from Stations 5, 6, and 7 from the two component mixing model. In Fig. 7, data from these sites plot above the 2 component mixing line indicating that the Ag/Os ratio of the sediments is higher than predicted by the model based on the ^{187}Os/^{186}Os ratio of the samples. Physical mixing of older sediments, contaminated by Ag but not by Os, with recent sewage particles, similar to the sludge analyzed in this study, would result in sediments displaced from the trend predicted by the physical mixing model as indicated schematically by the solid arrows in Fig. 7. The Station 6 profile exhibits coincident maxima in Os and Ag concentrations, as well as a related minimum in ^{187}Os/^{186}Os ratio. We speculate that this horizon may have been produced by a storm event which deposited sediments resuspended from near by Boston Harbor. Focused redeposition in this region of Cape Cod Bay following a storm event would supply an admixture of recent and older contaminated sediment producing local maxima in both Ag and Os concentration, as well as Ag/Os ratios lower than contemporaneous sewage. Radiochemical data from this and other cores also provide evidence of physical mixing of sediments in Cape Cod Bay by bioturbation and [or] resuspension. Apparent ^{210}Pb accumulation rates (1 to 0.5 cm/yr) which exceed long-term ^{14}C

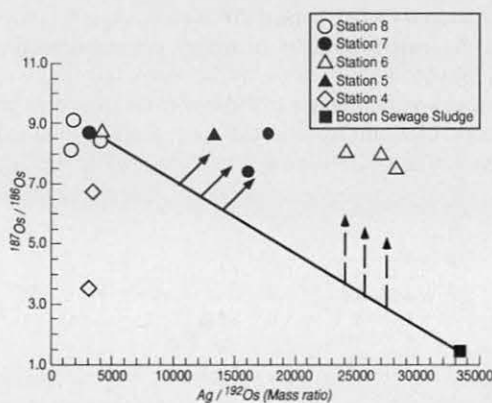of Os is mainly related to research applications, microscopy, and chemical manufacturing (Smith et al., 1974). Therefore, it is possible that the inadequacy of the physical mixing model is partly the result of variations in the composition of the waste stream through time. Disposal of fixative solutions containing OsO$_4$, used in the preparation of tissue samples for electron microscopy, is likely to be the major source of anthropogenic Os to the estuarine environment (Esser and Turekian, 1993a). Thus, because this use of Os is highly specialized and is a recent technological development, the high concentrations of Os in the waste stream should have become common more recently than high Ag concentrations. Therefore, it is reasonable to expect that the impact of anthropogenic Ag on marine sediments will predate the impact

FIG. 7. Plot of ^{187}Os/^{186}Os vs. Ag/^{192}Os demonstrates that the poor fit of the data to a two component mixing model is not a consequence of variable dilution of a trace metal-poor, coarse component. Both variables plotted are ratios, and are, therefore, invariant upon normalization to grain size or organic carbon content. Points above the two component physical mixing trend could be explained either by mixing with older sediment, contaminated by Ag but not by Os (solid arrows) or by chemical exchange between sorbed anthropogenic Os and more radiogenic dissolved Os (dashed arrows). Points below the physical mixing trend require either an anthropogenic metal source with very low Ag/Os ratio or diagenetic Os addition to these sediments.

rates by roughly an order of magnitude, and nearly constant and nonzero $^{239,240}Pu$ activities (0.07–0.04 dpm/g) attest to the vigor of physical mixing in these sediments. Thus, the sediment mixing scenario proposed above seems plausible in light of these radiochemical data. However, mixing old contaminated sediment with recent sewage and pristine marine sediments cannot explain the low Ag/Os ratios measured in sediments from Station 4.

6.4. Fractionation of Osmium and Silver in the Marine Environment

Isotopic exchange between dissolved and particulate Os, and fractionation of Os from Ag can also be invoked to explain the poor agreement between the physical mixing model and the sediment data. Although knowledge of the marine chemistry of Os is very limited, current understanding of this element suggests that Os and Ag will be fractionated from one another in the marine environment. Silver liberated to the Massachusetts Bay-Cape Cod Bay region is likely to remain associated with sewage particles because Ag is very particle reactive both in the open ocean (Martin et al., 1983) and in coastal waters (Sanudo-Wilhelmy and Flegal, 1992; Smith and Flegal, 1993). In addition, Ag is strongly bound to biomass (Harris and Ramelow, 1990) and the organic portion of sewage sludge (Chapman et al., 1988). In contrast, speciation calculations based on chemical equilibria indicate the stable form of Os in oxic seawater is anionic ($H_3OsO_6^-$: Palmer et al., 1988). By analogy to other metals that occur in seawater as oxyanions (V and Mo), Os is expected to be much less particle reactive than Ag and to have a longer oceanic residence time.

Based on the above argument, the discrepancy between the physical mixing model and the Cape Cod Bay data (Stations 6 and 7), could also be attributed to desorption of anthropogenic Os from sewage particles and exchange with Os dissolved in ambient seawater which has higher $^{187}Os/$ ^{186}Os ratios. Schematically such an exchange model would displace the data from the physical mixing trend along the vertical dashed arrows in Fig. 7. Aqueous fractionation of Os from Ag could also be invoked to explain the low Ag/ Os ratios at Station 4 which plot above the mixing lines in Fig. 6a and below the mixing line in Figs. 6b and 7. In this case, diagenetic addition of dissolved anthropogenic Os without accompanying Ag would be required. While there is not direct evidence demonstrating fractionation of Os from Ag, the fact that the anthropogenic Os signature at Station 4 appears to penetrate more deeply than Ag contamination does strongly suggest diagenetic remobilization. Isotopic analyses of dissolved and particulate Os in coastal waters would allow processes such as diagenetic Os enrichment and osmium isotopic exchange in the water column to be examined directly.

6.5. Additional Sources of Anthropogenic Osmium

The Ag/Os ratios of samples from Station 4 are much lower than in the sewage sludge analyzed. Although sewage particles are likely to be the major source of anthropogenic

Os released to the coastal environment, an additional source of anthropogenic Os which did not carry significant amounts of Ag could account for the low Ag/Os ratios at Station 4. This would eliminate the need to call upon diagenetic Os enrichment, discussed above, to explain these data.

Elevated concentrations of other platinum group elements (PGEs) in sewage (Lottermoser and Morteani, 1993; Lottermoser, 1994) suggest that use of Os as OsO_4 may not be the only important source of Os to the waste stream. Osmium associated with other, more commonly used PGEs may also be important. Specifically Pt, Pd, and Rh use in association with automobile catalytic converters may result in incidental release of Os. Catalytic converters are known to release between 1.2 μg Pt/km (Hill and Mayer, 1977) and 2–40 ng/ km (Konig et al., 1992) and roadside dust can contain up to 680 ppb Pt and 280 ppb Pd (Hodge and Stallard, 1986). The possible magnitude of Os release by catalytic converters is unexplored. In metropolitan Boston, many street sewers are drained into municipal sewage treatment facilities, but by-pass the facility during heavy rain storms. It is possible that release from storm sewers may constitute an anthropogenic metal source with low Ag/Os ratios relative to sludge. However, the high Ag/Os ratio from the Fort Point Channel sample within Boston Harbor does not support this contention.

The contrast between the $^{187}Os/^{186}Os$ ratios of 1980 and 1994 sludge (Table 1) suggests that Os the source of anthropogenic Os is changing with time. The Os used in the United States for microscopy applications is derived exclusively from South African sources (pers. commun., Electron Microscopy Sciences). New Haven and Boston sewage from 1972 and 1980 ($^{187}Os/^{186}Os$ = 1.53 and 1.42, respectively) fall close to the range of South African Os (1.509–1.413 for Bushveld ores: Hart and Kinloch, 1989). However, 1994 sewage has a significantly lower $^{187}Os/^{186}Os$ (1.27). This value is below the Bushveld range, but similar to the $^{187}Os/$ ^{186}Os of PGE deposits hosted in Siberian flood basalts ($^{187}Os/$ ^{186}Os ranges from 1.35–1.27 in samples with Os > 100 ppb: Walker et al., 1994). At present the supply of Russian PGEs to the United States and their specific uses are not well constrained. As this becomes better documented, osmium isotopic contrasts between different PGE sources may provide a means of better constraining the various pathways by which PGEs are introduced to the environment.

7. SUMMARY AND CONCLUSIONS

The $^{187}Os/^{186}Os$ ratio of Boston sewage sludge (1.42–1.27) is six times lower than in nearby marine sediments, which are unimpacted by human activity (9.1–8.1). The Os concentration of sludge is ten to forty times higher than in pristine marine sediments. These contrasts in osmium isotopic composition and concentration indicate that osmium isotopes can be used as a sensitive tracer of the influence of sewage sludge on sediments from Massachusetts and Cape Cod Bays. A previous investigation has yielded similar results (Esser and Turekian, 1993a). Together these studies suggest that high concentrations of anthropogenic Os are characteristic of municipal sewage in general and that os-

mium isotopes can be employed as tracers of sewage dispersal in a wide variety of estuarine environments.

Silver is another sensitive indicator of the influence of sewage on sediments in the Massachusetts Bay region. Comparison of Os and Ag data show that surface sediments from both Massachusetts and Cape Cod Bays have Ag concentrations above background levels and $^{187}Os/^{186}Os$ ratios below background levels. We interpret these chemical signatures as evidence of the influence of sewage particles carrying unradiogenic Os and high Ag concentrations. In detail, however, the distribution of Os and Ag do not support a model of simple physical mixing of sewage particles with normal marine sediments. Deviations from the mixing model are likely to be the result of independent temporal variations of the Os and Ag content of the waste stream and possibly fractionation of Os and Ag in the marine environment.

Subtle variations in the osmium isotopic composition of sludge over time give some indication that the source of Os delivered to the waste stream may be changing. The $^{187}Os/^{186}Os$ of 1980 sludge is indistinguishable from Bushveld ores, while 1994 sludge is similar to Siberian ores. The cause for this shift in osmium isotopic composition of sludge is not clear at present. Future studies of osmium isotopic variations in the waste stream may help define the source and delivery mechanisms of PGEs and other anthropogenic metals in the waste stream.

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