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Recent Changes in Platinum Group Element Concentrations and Osmium Isotopic Composition in Sediments from an Urban Lake

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Automobile catalyst emissions have resulted in the occurrence of elevated Pt, Pd, and Rh concentration in the urban and roadside environment. We investigate the chronology of platinum group elements (PGE) accumulation in dated sediments from an urban lake near Boston, MA. Chronological profiles demonstrate that Pt, Pd, and Rh concentrations increased following the introduction in catalysts with accumulation rates 6−16 times larger in 1992−2002 than prior to the introduction of catalysts. Ratios of these elements closely match their ratios in catalysts, providing further evidence of an automobile source. Iridium and Ru accumulation in sediments also increased following the introduction of catalysts, and while past Os contamination is associated with leather tanning, recent changes in the isotopic composition of Os indicate another anthropogenic source for this element. The PGE have similar geochemical properties and are difficult to separate from one another, and therefore, we suggest that automobile catalyst emissions also result in increasing environmental concentrations of Ir, Ru, and Os, which occur as impurities in catalysts. An automobile catalyst source of Ir and Os is supported by elevated concentrations of these elements in a tunnel dust sample.

Introduction

The increasing use of platinum group elements (*1*) has resulted in increasing interest in their environmental behavior (*2*−*9*). Among the PGE, platinum, palladium, and rhodium have attracted most of the attention as a result of their extensive use in automobile exhaust catalysts. Automobile catalysts, introduced in the United States in 1975, are now also mandated in the European Unio. Platinum, Pd, and Rh are the main active components in automobile catalysts, and it has been demonstrated that these three metals are released during vehicle operation (*10*−*13*), resulting in elevated concentrations in the urban and roadside environment (*3*, *4*, *6*, *8*, *14*−*18*). Increasing levels of Pt, Pd, and Rh have also been reported in remote environments (*19*), stressing the need to understand the dispersion of the emitted PGE.

Few environmental studies have considered the other three PGE, Ir, Ru, and Os, although their use is also increasing (*1*). Iridium and Ru are used by chemical and electrochemical industries and in electronics (*1*). Iridium has been used in automobile catalysts (*1*) but to a lesser extent than Pt, Pd, and Rh, and elevated Ir concentrations have been measured in the roadside environment (*7*, *8*).

Osmium has a limited number of uses, the largest single use being as fixative and stain in the preparation of tissue thin sections for optical and electron microscopy (*20*). Elevated osmium concentrations have been reported in coastal and estuarine sediments, and distinctive isotopic compositions have supported the conclusion that anthropogenic Os input into the environment is occurring (*5*, *20*−*22*). The radioactive β^--decay of ^{187}Re (half-life of 41.6 Gyr) results in the production of ^{187}Os. The isotopic composition of a sample (measured here as ^{187}Os/^{188}Os) therefore depends on its Re/Os concentration ratio and its age. The high (i.e., radiogenic) ^{187}Os/^{188}Os of $\sim 1.05 \pm 0.23$ characteristic for the eroding continental crust reflects its old mean age and relatively high Re/Os compared to the Earth's mantle (*23*). Commercial Os is mined from mantle-derived PGE deposits with low Re/Os concentration ratio and, consequently, low (i.e., unradiogenic) ^{187}Os/^{188}Os of ∼0.1−0.2 compared to that of the crust (*5*, *20*−*22*). A recent study on sediments from Massachusetts Bay, Cape Cod Bay, and Boston Harbor reports background Os concentrations in the range 22−108 pg g^{-1} and ^{187}Os/^{188}Os of 0.972−1.093, whereas contaminated sediments from Boston Harbor have an Os concentration of 286 pg g^{-1} and a ^{187}Os/^{188}Os of 0.354 (*5*).

We present evidence for recent changes in Pt, Pd, Os, Ru, and Ir accumulation rate and osmium isotopic composition in sediments from the Upper Mystic Lake. The lake, which is located in a highly urbanized watershed, provides an excellent record of industrial and traffic-related pollution in the area (*3*, *24*, *25*). Elevated platinum concentrations in recent Upper Mystic Lake sediments have been attributed to automobile catalysts (*3*). The determination of PGE concentration changes and accumulation rates may provide a further understanding of PGE transport on a regional scale and help determine the source of PGE in the environment.

Experimental Section

Sampling Site. Sediment cores were collected in the Upper Mystic Lake, North of Boston, MA (*3*, *24*−*29*). The Upper Mystic Lake receives the entire flow of the Aberjona River (0.78 m^3 s^{-1}), which drains the Aberjona watershed, and also has two minor inlets (0.037 m^3 s^{-1}) (*25*). The watershed is heavily developed, covering an area of 67 km^2 with residential communities embedded within commercial and industrial areas. Population density exceeds 1100 inhabitant km^{-2}, and a 1.8-fold population growth has occurred since 1950 (*29*). Industrial activity has been important since the early 19th century and was dominated by leather tanning and chemical industries until the mid-20th century. Metal-contaminated sediments occur throughout the watershed as a result of historical chemical waste discharge to waterways (*26*, *29*). Automobile traffic is also believed to be an important source of heavy metals in the watershed, which has an estimated 65 000 passenger cars and a dense network of urban roadways, including Interstate Routes 93 and 95.

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TABLE 1. Reported PGE Concentrations and ^{187}Os/^{188}Os Ratio in Sediment Cores and the BCR 723 Reference Material. Missing Concentrations for Rh and Ru Correspond to Values for Which Standard Deviations Were Larger than 20% (see Experimental Section)

sample	depth (cm)	age estimate (calendar year)	Os (pg g^{-1})	^{187}Os/^{188}Os	Pd (ng g^{-1})	Pt (ng g^{-1})	Rh (ng g^{-1})	Ru (ng g^{-1})	Ir (pg g^{-1})
core 1 01	1	2002	149	0.803	19.0	19.0			615
core 1 03	5	1999	111	0.945	17.1	14.4	2.8	0.7	275
core 1 05	9	1996	92	1.139	21.5	16.3	3.1	1.7	128
core 1 07	13	1992	81	1.291	22.3	20.8	4.2		180
core 1 09	17	1987	74	1.248	21.7	24.6	1.3	0.3	200
core 1 11	21	1981	146	0.741	4.5	6.0			447
core 1 13	25	1974	112	1.097	23.2	4.7	8.9		124
core 1 15	29	1967	395	0.3606	4.1	2.2	1.3	0.2	225
core 1 17	33	1959	98	1.233	2.2	1.7	0.9	0.2	125
core 2 01	1	2002	154	0.651	21.9	12.0		4.8	124
core 2 02	3	2001	88	0.958	24.4	11.2	2.1		228
core 2 03	5	1999	95	1.177	23.3	19.5	3.5	0.4	120
core 2 04	7	1998	170	0.778	26.3	25.0	3.5	1.4	168
core 2 05	9	1996	107	1.289	24.9	29.5	3.2	0.4	155
core 2 06	11	1994	105	1.171	25.2	26.8	2.6	0.5	97
core 2 07	13	1992	96	1.220	26.4	21.9	2.2		130
core 2 08	15	1989	102	1.180	12.2	13.5	1.6	3.2	124
core 2 09	17	1987	98	1.292	12.2	8.0	1.6	0.3	162
core 2 10	19	1984	112	1.136	19.0	9.8			527
core 2 11	21	1981	118	1.117	13.9	5.0			170
core 2 12	23	1978	138	1.017	36.4	3.5			143
core 2 13	25	1974	121	0.992	16.1	1.5	4.3	0.9	89
core 2 14	27	1971	193	0.685	6.1	0.9	1.0		82
core 2 16	31	1963	114	1.079	9.5	2.5	0.7		162
core 2 18	35	1955	105	1.074	2.0	1.3			56
core 2 20	39	1948	71	1.439	5.4	3.7		0.2	151
core 2 a	69	1890	162	2.095	4.7	1.5			110
core 2 b	71	1886	154	2.207	2.7	1.7	0.2		145
core 2 c	73	1882	56	1.92	1.6	1.0	0.2	0.2	71
BCR 723			1206	0.2707	6.6	97	15		956

The Upper Mystic Lake is a 0.58 km^2 dimictic, eutrophic kettlehole lake with a 0.35 km^2 main basin and two shallow embayments with a combined area of 0.23 km^2. The main basin, where sediment cores were collected, has a mean depth of 13 m, a maximum depth of 25 m, and a volume of 5.4×10^6 m^3, while the two smaller basins have a combined volume of 0.3×10^6 m^3. The lake is typically thermally stratified from April to November, while it is totally or partially covered with ice in January and February (*27*). The lake is an efficient settling basin for suspended particles, having an average residence of water of 100 days (*25*), and the historical record of trace element accumulation, which is preserved in sediment cores from this lake, is highly resolved and remarkably reproducible from one sediment core to another (*3*, *25*). The sediments generally have a relatively constant and high organic content (20−40%), although organic matter is not believed to have a major influence on heavy metal profiles (*25*).

Sediment Core Collection. Sediment cores were collected from the deep center of the Upper Mystic Lake by freeze coring, a technique which has been demonstrated to provide relatively undisturbed lake sediment cores (*3*, *24*, *25*). The corer consists of a squared tubing with three sides of Extren polymer and one side of aluminum and a sharp edge at the bottom (*25*). The corer is filled with a slurry of ethanol and crushed dry ice and dropped into the sediments. Sediments in contact with the aluminum plate freezes, and the corer is recovered after 15 min with frozen sediment attached to it. The sediment slab is then removed from the corer, wrapped in plastic foil, and placed in a cooler filled with dry ice. Two cores are used is this study: core 1 was collected on May 8, 2002 and core 2 on October 3, 2002. Both cores were approximately 80 cm long. On return to the laboratory, cores were sliced into 2 cm using an electrically heated tungsten wire and dried in an oven at 103 °C. Wet and dry weights and wet volume were measured, and sediment samples were stored in PET containers at room temperature until analysis.

Dating. The sediment cores used in this study are part of a set of cores for which dating has been described in detail by Rauch and Hemond (*3*). Dates were inferred from ^{210}Pb accumulation rates. ^{210}Pb activities obtained by γ-counting (GL2020 Detector with Series 40 multichannel analyzer, Canberra Industries, Meriden, CT) at 10 depths in core 2 and at seven depths in an independent core collected in May 2002 were used to estimate sediment accumulation rates (expressed as thickness increment per year) using the constant input concentration model assuming a constant yearly deposition of ^{210}Pb. Accumulation rates were corrected for changes in water content at different depths, resulting in increased thickness per year at the top of core due to higher water content in the upper samples (*3*). Both cores provided similar accumulation rates with a difference of less than 5% between the cores. Accumulation rates ranged from 1.8 cm year^{-1} at the top of the core to 0.5 cm year^{-1} at the bottom. Date estimates for the analyzed core sections are provided in Table 1.

Visual laminations and the profile of elements with a known history were used to verify the accuracy of our dating. Laminations, which were assumed to represent annual marks, appear at several depths in the cores. Increasing distance between lamina at the top of the core agreed well with accumulation rates obtained from ^{210}Pb data.

The occurrence of arsenic and chromium in the Aberjona watershed has been attributed to sulfuric acid and pesticide production and leather tanning, respectively, and concentration maxima in Upper Mystic Lake sediments have been reported for 1916 and 1925, respectively. Remobilization of the contamination, likely by waste moving activities in the watershed, has also resulted in an As peak in 1964 and a Cr peak in 1959 (*25*). The As and Cr profiles obtained for three cores collected in 2002 were in good agreement with maxima in 1963 for both As and Cr and elevated concentrations in the early 20th century (*3*).

Accumulation rates and ^{210}Pb activities obtained here were compared in detail with data from a previous study on Upper Mystic Lake sediment cores (*25*) and accumulation rates estimated as mass increments per year. The dates presented here were considered suitably accurate for the investigation of automobile catalyst-related pollution, as maximum spread between the different dating strategies used in the comparison were <1 year for the top 10 cm (1995), <2 years at 20 cm (1982), and <15 years at 70 cm (1888) (*3*).

Sample Preparation and Analysis. Samples were prepared by NiS fire assay and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS), as described by Ravizza and Pyle (*30*) and Hassler et al. (*31*). Analysis was done on a sector field ICP-MS instrument (ELEMENT, ThermoFinnigan, Bremen, Germany) equipped with a desolvating nebulizer (MCN-6000, Cetac, Omaha, NE).

Sediment samples were ground in an agate mortar, weighted, and spiked with a mixed PGE spike enriched in ^{99}Ru, ^{105}Pd, ^{190}Os, ^{191}Ir, and ^{198}Pt. Samples were prepared by NiS fire assay, which uses the high affinity of PGE for sulfide, resulting in the preconcentration of PGE and the removal of most interfering elements. The obtained sulfide bead is then dissolved under reducing conditions in 6.2 N HCl at ~150 °C. The solution containing insoluble PGE-rich particles is filtered through a 0.45 μm cellulose filter. The filter paper is then transferred to a Teflon vial and digested in 1 mL of concentrated HNO_3. To fully dissolve the PGE-rich particles and oxidize Os to volatile OsO_4, the closed Teflon vial is heated to ~100 °C for about 90 min. After chilling the vial in ice water and diluting the solution 5-fold with Millipore water, the Teflon lid is replaced with a two-port cap, one end of which is connected to the Ar supply and the other to the ICP-MS torch. When Ar is bubbled through the solution, volatile OsO_4 is carried with the Ar stream into the plasma, allowing the determination of Os and its isotopic composition. Complementary PGE concentrations are determined by ICP-MS in the liquid residue after it is taken to dryness and redissolved in 5% HNO_3.

Osmium, Pt, Pd, Ir, and Ru concentrations were calculated using two isotope ratios each to check for consistency. Concentrations generally agree within a few percent of each other, except for Ru. Ruthenium concentrations are not listed when the standard deviation of the two results is larger than 20%. Rhodium is monoisotopic, and therefore, isotope dilution analysis is not possible for this element. Rhodium concentrations were calculated using the spikes for Pt and Pd, and four concentrations were obtained as two isotope ratios were used for each element. Rhodium concentrations were removed when the standard deviation was larger than 20%. For the determination of the isotopic composition of Os, data were corrected for instrumental mass bias using a geometric three-dimensional procedure using a linear fractionation law (*32*).

Approximately 200 mg of a tunnel dust standard reference material (BCR 723) with certified Pd, Pt, and Rh concentrations of 6.0 ± 1.8, 81.3 ± 2.5, and 12.8 ± 1.2 ng g^{-1} (presented as average ± half width of 95% confidence interval), respectively, was analyzed. Measured concentrations (Table 1) agreed relatively well with certified values. Good agreement between Pt concentrations obtained by microwave-assisted *Aqua regia* leach and quadrupole ICP-MS analysis and the present study provided a further, favorable assessment of the quality of Pt measurements. Additional details of analytical blanks as well as accuracy and precision of the analytical method have recently been summarized by Peucker-Ehrenbrink et al. (*33*).

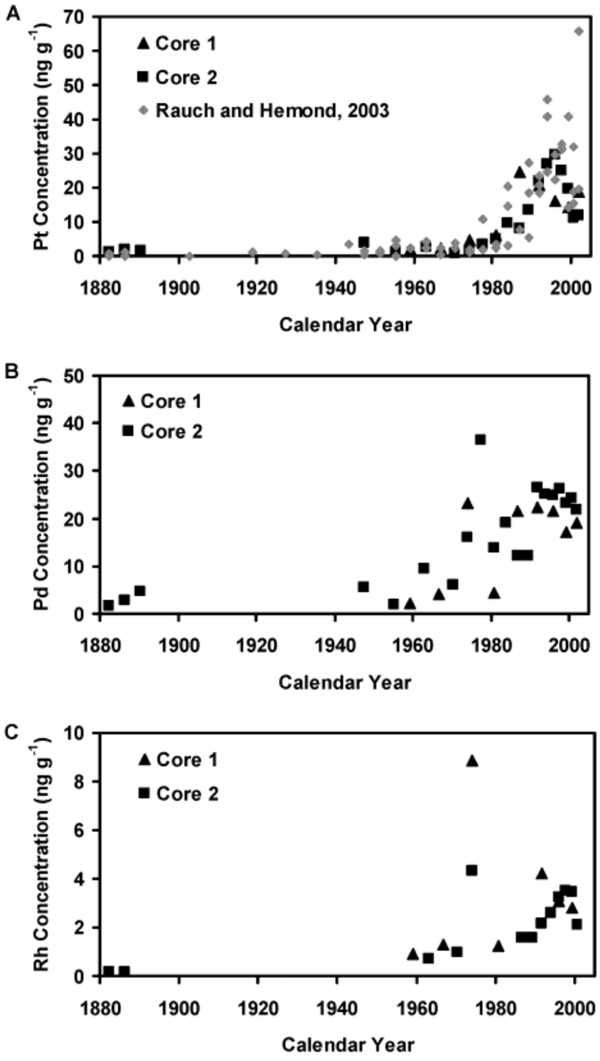

FIGURE 1. Platinum (A), palladium (B), and rhodium (C) concentration profiles in sediment cores from Upper Mystic Lake. Platinum profiles include concentrations reported by Rauch and Hemond (*3*).

Data are presented in the text as mean ± standard deviation. Comparison of data groups was performed using the *t*-test on the logarithm of concentrations (the logarithm was applied to obtained equal variances). Assumptions of normal distribution and equal variances were checked and the Mann−Whitney U-test was used when the assumption of equal variances could not be satisfied. Trends were estimated as linear regressions in the logarithm mode. Chronological sections for Pt, Pd, and Rh were determined by fitting linear regressions to the increasing period defined as 1975−*x*, 1975 being the year of introduction of catalysts and *x* was varied from 1990 to 2000. The breakpoint was defined as the year *x* after which a consistent decrease of the slope was observed.

Results and Discussion

Platinum, Palladium, and Rhodium. PGE concentrations changes were observed in both cores between 1880 and 2002 (Figure 1). Platinum concentrations obtained in this study are similar to those reported by Rauch and Hemond (*3*) for Upper Mystic Lake sediment cores (Figure 1a). In the present study, Pt concentrations were 1.4 ± 0.3, 2.1 ± 1.0, and 20 ± 6 ng g^{-1} for pre-1940, 1940−1975, and 1992−2002. For the same periods, Rauch and Hemond reported concentrations of <0.5−1.2, 2.3 ± 1.3, and 29 ± 13 ng g^{-1}, respectively (*3*).

Background Pt concentrations in deep Upper Mystic Lake sediments (Table 1) were higher than the 0.6 ± 0.3 ng Pt g^{-1} reported background for the nearby Massachusetts Bay (*9*) and the 0.510 ng Pt g^{-1} estimate for the eroding Upper Continental Crust (*23*), possibly due to the lithological composition of the drainage basin or transport mechanisms favorable to an enrichment of Pt in Upper Mystic Lake sediments.

For statistical analysis on Pt concentrations, the data set of Rauch and Hemond (*3*) and concentrations in Table 1 were combined. The combined dataset has 80 data points, including 47 values corresponding to dates after 1975. Platinum concentration was found to be significantly higher after the introduction of catalysts than before (*t*-test, $p = 0.05$). A simple linear regression model was applied to the logarithm of Pt concentrations as independent variable and the year as explanatory variable to determine if there is a significant trend before and after the introduction of PGE containing catalysts. Three sections were considered: (1) 1940−1975, (2) 1975−1994, and (3) 1994−2002. No significant trend was found when using the complete data set for 1940−1975 and 1994−2002 with $R^2 = 0.001$ and 0.04, respectively, although data for cores 1 and 2 indicate a decrease for the latter period. These periods are interpreted as having constant platinum levels equal to the mean of the measurements, i.e., 2.3 ± 1.3 and 25 ± 10 ng g^{-1}, respectively. A significant linear trend ($R^2 = 0.64$, $p < 0.001$) was obtained in the logarithm mode for the period 1975−1995, and Pt concentration in this period could be described by eq 1.

$$[\mathrm{Pt}_i] = e^{0.131\times \mathrm{Year}_i - 258.523} \qquad (1)$$

Background Pd concentration in deep Upper Mystic Lake sediments was 3.0 ± 1.6 ng g^{-1}. Palladium concentration in the Upper Continental Crust has been estimated to be 0.520 ng g^{-1}, and measured background concentration in nearby Massachusetts Bay is 0.6 ± 0.3 ng g^{-1} (*9*). Higher concentration in Upper Mystic Lake sediment may be the result of local conditions, e.g., elevated Pd concentration in the surrounding bedrock or favorable transport mechanisms. Palladium concentration remained below 10 ng g^{-1} until 1974, after which higher Pd concentrations were found in sediments. Palladium concentration increased from 2.1 ± 1.0 ng g^{-1} in 1945−1974 to a plateau at 21 ± 7 ng g^{-1} in 1992−2002. While the size of the data set does not allow the determination of trends, concentrations were significantly higher after 1974 than before (*t*-test, $p = 0.05$). The trend follows closely the trend for Pt with a good correlation between the two elements, except for a sharp peak in 1974−1978 (Figure 1B). As in the case of Pt, Pd concentration plateaus after 1992 and the observed decrease after 1992 was not found to be significant ($R^2 = 0.21$, in the logarithm mode).

A background Rh concentration of 0.174 ± 0.019 ng g^{-1} was measured in samples corresponding to the 1890s, higher than the reported 0.06 ng g^{-1} concentration estimate for the eroding continental crust (*34*). A baseline concentration of 1.1 ± 0.3 ng g^{-1} was measured for 1959−1987 with a peak concentration in 1974 matching the observed Pd peak. Rhodium concentration increased from 1989 until 1995, when it reached a plateau with a nonsignificant decrease since 1995 ($R^2 = 0.36$, in the logarithm mode). The delayed increase compared with Pt and Pd can be attributed to the later introduction of Rh in automobile catalysts. Concentrations in 1995−2002 were significantly higher than before 1974 (*t*-test, $p = 0.05$).

Palladium and Rh are the only PGE with elevated concentrations in 1974−1978. Rhodium was introduced in catalysts in the early 1980s, indicating a noncatalyst origin for these high PGE levels. The presence of the Pd−Rh peak in two independent cores argues against sample contamination, and it is not clear what the source of these metals is. The most likely explanation is industrial contamination, although we have no independent evidence that such a contamination occurred at the time.

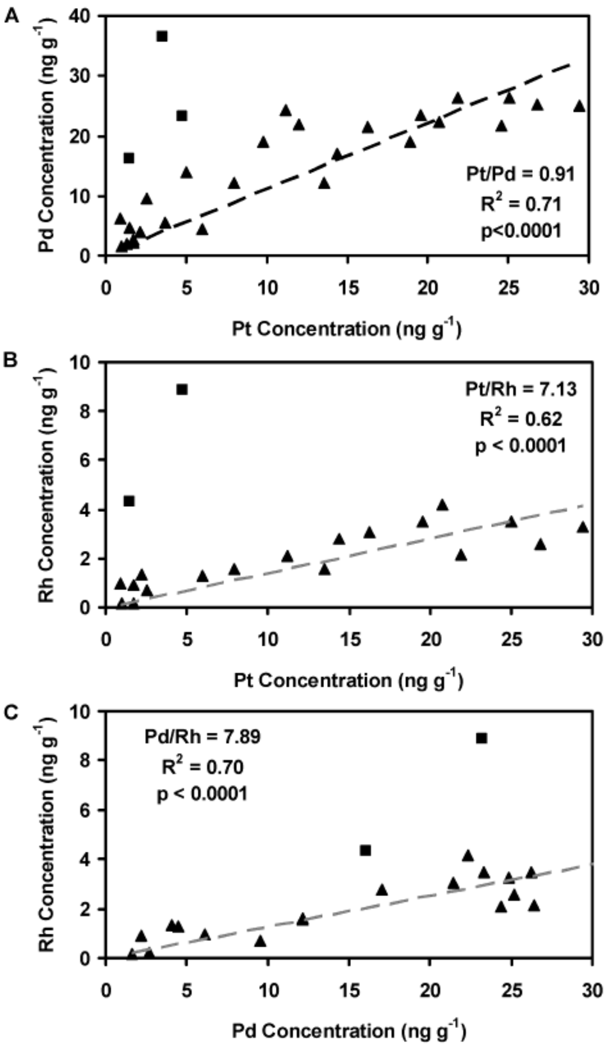

FIGURE 2. Pt−Pd (A), Pt−Rh (B), and Pd−Rh (C) plots. The dashed line shows the correlation (intercept set to 0). The data for 1974 and 1978 (square) were considered as outliers.

Not considering Pd and Rh data for 1974 and 1978, a good correlation was found between Pt, Pd, and Rh concentrations (Figure 2), despite differences in the onset of increasing concentration. The ratio between these elements has been used to identify catalyst as the source of PGE in the environment (*8*, *15*, *19*, *35*). Ratios in automobile catalysts have recently been estimated to be in the range 1−2.5, 4−9, and 5−16 for Pt/Pd, Pd/Rh, and Pt/Rh, respectively (*8*). The ratios found in this study are within these ranges, although slightly lower for Pt/Pd, providing a further indication that catalysts are the major source of Pt, Pd, and Rh in Upper Mystic Lake sediments. Platinum and Rh are expected to have relatively low solubilities in the aquatic environment, and therefore, these elements have relatively unfractionated ratios compared to the catalyst source. The lower Pt/Pd value might be the result of the relatively higher mobility that has been reported for Pd (*36*, *37*).

Deviation from the 0.91 Pt/Pd ratio does not follow any clear temporal trend. Early oxidation catalysts used on model years 1975−1980 vehicles contained both Pt and Pd, typically in a 5/2 ratio (*38*). Rhodium was introduced in the early 1980s with the introduction of three-way catalysts. These

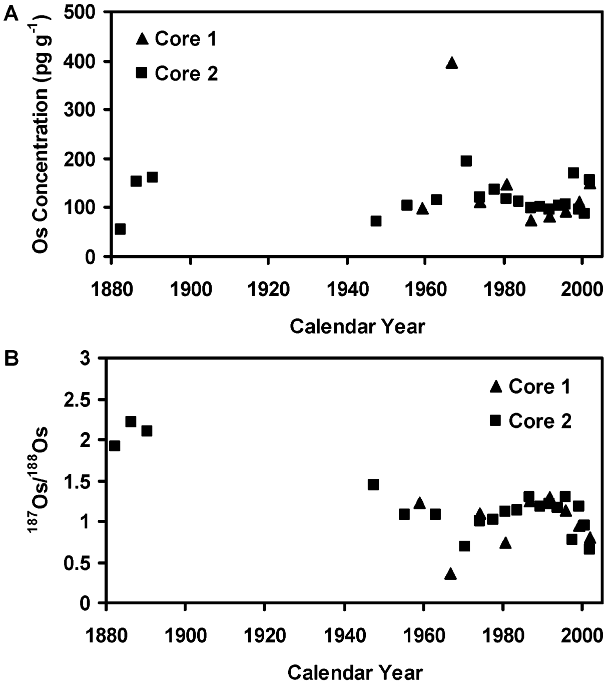

FIGURE 3. Osmium concentration profile (A) and ^{187}Os/^{188}Os ratio (B) in Upper Mystic Lake sediment cores.

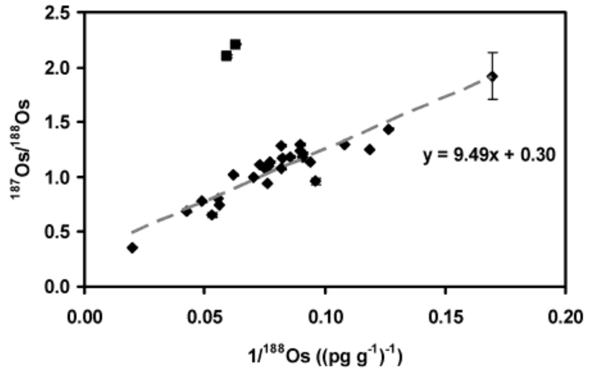

FIGURE 4. Plot of ^{187}Os/^{188}Os vs 1/(^{188}Os concentration) for Upper Mystic Lake sediments. The dashed line shows the correlation (R^2 = 0.87, $p < 0.0001$). The data for 1886 and 1890 (squares) were considered as outliers.

catalysts typically had a higher Pt loading than Pd throughout the 1980s (*38*), but lower market price for Pd and technological developments encouraged car manufacturers to use a higher Pd loading (*1*, *38*). The shift to Pd triggered an increase of its price, leading some car manufacturer to shift back to higher Pt loading (*1*). Currently, Pt/Pd/Rh, Pt/Rh, Pd/Rh and Pd-only formulations are use in commercial catalysts (*39*). Changes in the Pt/Pd ratio in catalysts were not observed in Upper Mystic Lake sediments.

Increasing PGE concentrations that follow PGE ratios in automobile catalysts (Figure 2) are together clear evidence that automobile catalysts are the primary source of PGE catalysts in the environment of the Upper Mystic Lake.

Osmium. Changes in osmium concentration and isotopic composition (^{187}Os/^{188}Os) were observed in both core 1 and core 2 (Figure 3). There is a good correlation between 1/^{188}Os and ^{187}Os/^{188}Os with higher concentrations corresponding to lower isotopic ratios, except for two background samples corresponding to 1886 and 1890 (Figure 4).

Samples corresponding to 1880−1890 have an average Os concentration of 0.12 ± 0.06 ng g^{-1} and an average ^{187}Os/^{188}Os of 2.07 ± 0.15. Osmium concentration in the eroding continental crust has been estimated at 0.031 ng Os g^{-1} with an average ^{187}Os/^{188}Os of 1.05 ± 0.23 (*23*). Background sediment concentrations in the range 0.088−0.108 ng g^{-1} have been reported for nearby Massachusetts and Cape Cod Bays with a ^{187}Os/^{188}Os in the range 0.972−1.093 (*5*). Preindustrial sediments from the Long Island Sound have approximately 0.040 ng Os g^{-1} and a ^{187}Os/^{188}Os of 1.06 (*22*). The relatively high background Os concentration is caused by the two outliers in Figure 4, but the high ^{187}Os/^{188}Os indicates that these are indeed background concentrations. It is unlikely that these high concentrations result from smaller sediment accumulation rates for the period, and they may therefore be the results of a higher input of bedrock material. The more radiogenic nature of the local background relative to the average eroding continental crust is consistent with the occurrence of Precambrian to Paleozoic felsic, intermediate and mafic igneous, and metasedimentary bedrock in the watershed.

Osmium concentrations during the period 1947−1963 were 0.097 ± 0.019 ng g^{-1} for a ^{187}Os/^{188}Os ratio of 1.21 ± 0.17. Changes in concentration and isotopic composition may be related to chromium tanning in the watershed from ca. 1900 to 1925. Chromium is produced from ultramafic ores, which have mantle characteristics such as a low ^{187}Os/^{188}Os and high PGE concentrations (*21*). The relationship between elevated Cr and Os is further supported by a sharp Os peak in 1967 with a maximum concentration at 0.395 ng g^{-1} for a ^{187}Os/^{188}Os of 0.361, which matches within dating uncertainties a Cr peak associated with the remobilization of an old contamination by waste moving activities in the 1960s (*3*, *25*). The peak shape indicates that Os is relatively immobile in Upper Mystic Lake sediments, a higher mobility would have resulted in a broader peak.

From 1974 to 1996, Os concentration and ^{187}Os/^{188}Os remained relatively constant at levels similar to those in 1947−1963 with 0.107 ± 0.020 ng g^{-1} and 1.14 ± 0.15, respectively. However, a small increase corresponding to 1996−2002 appears at the top of the core. The cause of this change is not clear. Biomedical research facilities have been suggested as the major source of anthropogenic Os because of its use as fixative and stain for optical and electron microscopy (*20*). However, a biomedical source is unlikely in the area. Automobile catalysts have been suggested as another possible anthropogenic source of Os (*5*). It is interesting to note that the highest Os concentration and the lowest ^{187}Os/^{188}Os were measured in the tunnel dust standard reference material. Automobile traffic is expected to be the principal source of metals in tunnel dust, and the results therefore suggest that automobile traffic potentially represents a major source of anthropogenic Os to the environment. The lake may receive catalyst-derived PGE from either surface runoff or sewer overflow during heavy storm events, and input of PGE into the lake has been demonstrated, with catalysts as a likely source (*3*). It can therefore be hypothesized that Os present as impurity in catalysts is released during vehicle operation and accumulates in Upper Mystic Lake sediments.

Ruthenium and Iridium. Chronological changes in Ir and Ru concentrations are presented in Figure 5. Background Ir and Ru concentrations were 0.11 ± 0.04 and 0.190 ng g^{-1}. Iridium and Ru concentrations of 0.022 and 0.210 pg g^{-1} were estimated for the Upper Continental Crust (*23*).

No clear trend could be found for these metals. Iridium and Ru concentrations remained at background level throughout the studied period, although higher concentrations were observed in a few recent samples (Figure 5), with Ir concentrations up to 0.6 ng g^{-1} and Ru concentrations up to 4.8 ng g^{-1}. These high values indicate that there are small anthropogenic sources of these metals in the watershed. The large variability observed after 1975 (Figure 5) is likely to be caused by Ir and Ru being present in a few particles.

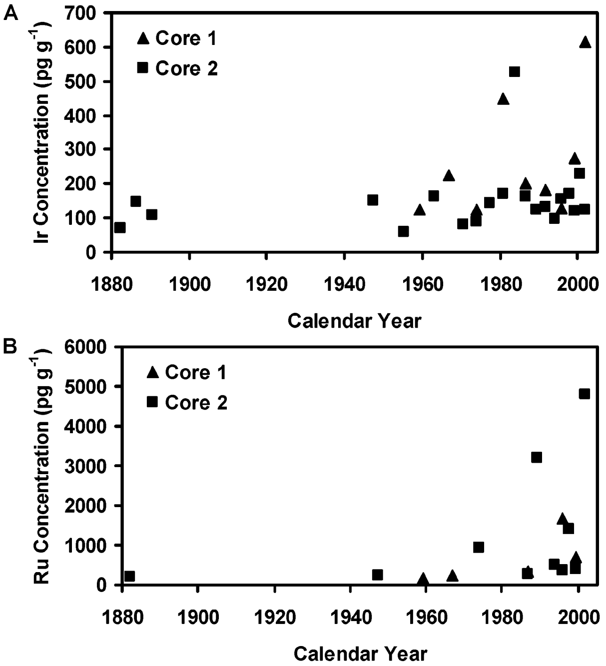

FIGURE 5. Iridium (A) and ruthenium (B) concentration profiles in sediment cores from Upper Mystic Lake.

TABLE 2. PGE Accumulation Rates for 1948−1971 and 1992−2002 (presented as mean ± standard deviation). Accumulation Rates for Os Do Not Include Values for the 1967 Peak

element	accumulation rate (μg m^{-2} year^{-1}) 1948−1971	accumulation rate (μg m^{-2} year^{-1}) 1992−2002
Pt	0.6 ± 0.3	9 ± 5
Pd	1.2 ± 0.6	10 ± 4
Rh	0.22 ± 0.06	1.3 ± 0.4
Os	0.029 ± 0.008	0.045 ± 0.017
Ir	0.034 ± 0.015	0.069 ± 0.018
Ru	0.055 ± 0.017	0.5 ± 0.5

Iridium has been used in some automobile catalysts formulations (*1*), and elevated Ir concentrations have been reported in the roadside environment (*7*). Ruthenium is used in electrode coatings and electronic components and as catalyst in the production of chemicals (*1*). While no report on the use of Ru in automobile catalysts could be found in the literature, decreasing Ru concentration with increasing distance from a road in Germany and elevated Ru concentration in an Austrian tunnel dust sample have been reported, indicating an automobile source (*7*). On this basis, we suggest here that the elevated Ir and Ru concentrations measured in some Upper Mystic Lake sediment samples are the result of automobile catalyst emission, with Ir present as catalysts component or impurity and Ru present as impurity.

Accumulation Rates. Rates of PGE accumulation for 1948−1971 and 1992−2002 are given in Table 2. Sediment focusing that may increase sediment accumulation at the deep part of lake was not considered in the calculation of accumulation rates. A higher mean accumulation rate was found for all PGE for the latter period. The increase was found to be significant for Pt, Pd, and Rh (*t*-test, $p = 0.05$) with 16-fold, 8-fold, and 6-fold increases, respectively. Platinum, Pd, and Rh deposition rates 2 m from a busy road in Germany have been reported to be 2.2−6.2, 0.2−1, and 0.3−1.5 μg m^{-2} year^{-1}, respectively (*40*). PGE deposition is expected to decrease rapidly with increasing distance from the road, and the relatively high accumulation rates for the lake despite a lower exposure to traffic than at the German study site indicate that the lake integrates PGE deposition in the watershed and stormwater is the main source of PGE in Upper Mystic Lake, with direct atmospheric deposition playing a relatively minor role. The 9-fold and 2-fold increases of Ru and Ir accumulation were also found to be significant despite the large relative variability (Ru, *t*-test; Ir, Mann−Whitney U-test, $p = 0.05$). Only Os accumulation was not found to have significantly increased between 1948−1971 and 1992−2002.

Elevated concentrations and accumulation of Pt, Pd, and Rh in Upper Mystic Lake sediments appear linked to the use of PGE-containing automobile catalysts. Platinum, palladium, and rhodium accumulation reach a plateau in the 1990s following the stabilization of the number of cars equipped with catalysts with accumulation rates 6−16-fold the pre-catalyst accumulation rate. The separation and purification of individual PGE is difficult owing to their geochemical similarities, especially in large-scale industrial processes, and the occurrence of nonlabeled Pt, Pd, or Rh impurities has been reported in commercial catalysts (*41*) and their emissions (*12*). We therefore suggest that Ru and Ir, present as impurities in catalysts, are released from automobile catalysts resulting in elevated accumulation of these metals in Upper Mystic Lake sediments. Past osmium contamination is attributed to Cr emissions by the leather tanning industry in the watershed, and automobile catalysts may further contribute to a recent ^{187}Os/^{188}Os decrease associated with a small concentration increase. While Pt, Pd, and Rh concentrations appear to have stabilized, it is important to further monitor these metals and assess their environmental relevance. Investigations on PGE should also include Ir, Ru, and Os for which available data are sparse.

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