EVIDENCE OF DEPOSITION OF ANTHROPOGENIC POLLUTANTS IN REMOTE ROCKY MOUNTAIN LAKES

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Abstract. Thirteen trace elements, the PAH flouranthene and PCBs were measured in the sediments of four remote high altitude lakes in Rocky Mountain National Park. PCBs were found in the sediments of all four lakes providing substantial evidence of anthropogenic inputs, most likely through atmospheric transport. The results were less certain, but still suggestive as to the anthropogenic origins for the elements As, Cd, Pb, and Sb and the PAH fluoranthene. Several of these elements, as well as fluoranthene and the PCBs, were found to be elevated in surface sediments compared to samples taken at greater depths, inferring that loadings of these substances into Rocky Mountain National Park region have increased with time.

1. Introduction

Recently there has been an increased interest in assessing the transfer and dispersal through the atmosphere of toxic and potentially toxic trace substances released during the combustion of fossil fuels. These substances include elements such as As, Cd, Hg, Pb, and Se and organics such as polycyclic aromatic hydrocarbons (PAHs) (Comm. on Natural Resources and the Nat'l Res. Council, 1981). Several studies have been focused on measurements of trace element deposition in lakes located in areas thought to be affected by acid precipitation in the eastern U. S. (Heit *et al.*, 1981; Galloway and Likens, 1979; Davis *et al.*, 1980) and Scandinavia (Davis *et al.*, 1980; Norton and Hess, 1980). Although there has been recent evidence of acid precipitation in the western U.S., notably in the high altitude remote areas of California (Tonnessen and Harte, 1980; Liljestrand and Morgan, 1978) and the Rocky Mountains of Colorado (Lewis and Grant, 1980), little information is available on whether these areas are also receiving anthropogenic inputs of potentially toxic trace substances.

In this study we measured several trace elements, polychlorinated biphenyls (PCBs), and the PAH fluoranthene in surface sediments from lakes located in remote areas of Rocky Mountain National Park. The purpose of this investigation was to assess whether this region is in fact receiving elevated loadings of trace substances known to have toxic or potentially toxic effects on aquatic biota and or on human health, and whether further studies are warranted to determine the origin and depositional history of these trace elements.

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2. Sampling Sites and Methods

Sediment samples were collected from four high altitude lakes in Rocky Mountain National Park during September 1981. Lake Louise (elevation 3365 m) and Lake Husted (elevation 3380 m), are both located in the Mummy Range in the northeastern corner of the park. They are both in the drainage area at the head of the north fork of the Big Thompson River in a cirque valley and are fed by glacial meltwater as well as precipitation.

Lake Haiyaha (elevation 3109 m) is a cirque lake at the head of Chaos Creek, a tributary of the south fork of the Big Thompson River. Ice fields and precipitation are the only sources of input. The fourth lake sampled, The Loch (elevation 3109 m), is a shallow basin in the middle of a valley. It is fed by streams coming from Longs Peak, Andrew and Taylor Glaciers. The watershed of The Loch is the largest of the lakes sampled (859 ha). The other watershed sizes are 107 ha for Husted, 404 ha for Haiyaha, and 111 ha for Louise. The watersheds of all four lakes are underlain by Precambrian granitic material including granite, gneiss, and schist. None of these lakes are directly affected by any point sources of pollution, such as dwellings or sewage. There are no roads near the lakes; they can only be reached by hiking several kilometers.

It should be noted that some silver mining occurred near Rocky Mountain National Park from 1879–1893. Most notably in the vicinity of the now defunct ghost-town site of Lulu City. However, leaching from mine-tailings is not considered to be a potential source of contamination since all such activity was limited to the north fork of the Colorado River drainage basin, which excludes the four lakes studied. No smelter was built in the vicinity of the park so that atmospheric inputs associated with local sources of mining are also not considered to be a significant source of anthropogenic input (Kaye, 1983).

All of the samples were collected with a 2.5 cm diameter modified Hongve-Davis gravity corer lowered from a rubber raft. The top 2 cm of several cores were combined in order to provide enough sediment for multiple-element and organic-compound analyses.

3. Analytical Methods

3.1. TRACE ELEMENTS

Digestion of the samples for Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sr, Tl, V, and Zn was performed by weighing from 0.3 to 2.5 g dry weight of sample into a 125 mL flat bottom flask, adding 5 to 10 mL of double distilled HNO_3 and refluxing the sample for 4 hr. The digestate was allowed to cool, and then it was quantitatively transferred to a 25 or 50 mL flask with deionized water (prepared using a Millipore Milli–Q water purification system). Concentrated HCl was added to give an HCl final concentration of 1%. This was done to prevent Hg from plating out on the walls of the digestate storage bottles. The sample was then transferred to prewashed linear polyethylene bottles.

For As and Se analyses, sediment samples were leached with 1 : 1 HNO_3 : perchloric acid to fumes of perchloric acid and then diluted to 25 or 50 mL with deionized water. For Sb analyses, samples were digested with a 6 : 3 : 1 HNO_3 : H_2SO_4 : perchloric acid mix to H_2SO_4 fumes. Beryllium was analyzed from HNO_3 reflux digestates.

The analysis of the samples was performed by either atomic absorption techniques or by inductively coupled argon plasma emission spectroscopy (Heit *et al.*, 1980a). The elements Be, Pb, and Tl were measured by flame atomic absorption and/or flameless (graphite furnace) techniques. Mercury was analyzed using a cold vapor technique. Mercury is reduced to its elemental state as a vapor in the presence of stannous chloride, and hydroxylamine sulfate is passed through an unheated absorption cell and the absorbance is then measured. Thallium was analyzed using a graphite furnace. The atomic absorption instrumentation used was a Perkin–Elmer 305B spectrophotometer with an HGA 2100 furnace, and background correction was performed using a deute-

TABLE I

Analytical quality control

Element	Average accuracy (%)	Precision (%)
As	104	21
Be	101	14
Cd	100	<1
Cu	110	2
Fe	103	1
Hg	94	13
Ni	137	5
Pb	99	5
Sb	152	24
Se	117	25
Tl	n.d.	13
V	106	2
Zn	108	2
PAH		
Fluoranthene	130	<1
PCB		
Trichlorobiphenyl		16
Tetrachlorobiphenyl		41
Pentachlorobiphenyl	n.d.	47
Hexachlorobiphenyl		56
Heptachlorobiphenyl		39
Octachlorobiphenyl		n.d.

Explanatory Notes:

accuracy: measured conc./expected conc. × 100

precision: coefficient of variation between replicates ($\sigma/\bar{X} \times 100$); 4–6 replicate analyses.

n.d.: not determined or not detected.

rium lamp. Antimony, As, and Se were analyzed by hydride generation in conjunction with graphite furnace atomic absorption. Analyses of the remaining metals were performed using a Jarrell–Ash Model 800 Series Atom-Comp inductively coupled argon plasma spectrometer.

Quality control results are shown in Table I. Precision and accuracy results were obtained from analysis of an Environmental Measurements Laboratory (EML) reference sediment and National Bureau of Standards (NBS) standard reference material 1645, river sediment. As shown in Table I, the precision values were excellent ($< 10\%$) for Cd, Cu, Fe, Ni, Pb, Sr, V, and Zn; the values were good (11 to 19%) for Be, Hg, and Tl; and were acceptable (20 to 30%) for As, Sb, and Se. The accuracy was excellent ($100 \pm 10\%$) for almost all of the elements, with the exception of Se for which accuracy was good ($100 \pm 20\%$) and the accuracy was poor for Sb and Ni ($100 \pm > 30\%$). However, the data for these latter two elements were not corrected, since precision was excellent for Ni and acceptable for Sb.

It should be noted that attempts were made to analyze Al and Sc through HNO_3 digestion. However, subsequent results performed at our laboratory indicated that only a portion of these metals could be recovered in this manner and that a total digestion technique such as HF dissolution or a Paar Bomb is required. Hence, results for these elements are not reported.

3.2. POLYCYCLIC AROMATIC HYDROCARBONS

Sediment samples were dried by extraction with methanol in a Soxhlet apparatus and further extracted with 4 : 1 methylene chloride : methanol (v/v). The combined extracts were washed with water to remove the methanol and the resultant methylene chloride extract was dried over granular anhydrous sodium sulfate and concentrated using a Kuderna-Danish (KD) apparatus.

The concentrated extract was cleaned up by activated alumina chromatography. An initial petroleum ether fraction (F1) was discarded to remove long-chain nonpolar interferences. A 10% methylene chloride in petroleum-ether fraction (F2) was collected and was found to contain PCBs. A 100% methylene chloride fraction and a 100% ethyl ether fraction was combined (F3) and found to contain PAHs. The (F3) fraction was spiked with nonadecylbenzene as an internal standard and analyzed by gas chromatography (GC) with a flame ionization detector (FID) using an SE–52 glass capillary column.

Standard solutions containing known concentrations of key PAHs were periodically analyzed to determine response factors for each of the compounds. Identifications were made on the basis of retention indices using phenanthrene, chrysene and indeno(c,d) pyrene as reference points. Recoveries of the PAHs were monitored by determining the recoveries of two surrogate standards (9-phenylanthracene and 9,10-diphenylanthracene), which were added to each sample prior to extraction. Representative sediment samples were analyzed by gas chromatography – mass spectrometry (GC–MS) to confirm identifications made on the basis of retention index measurements and to identify unknown compounds.

Precision and accuracy results were obtained from analysis of an EML reference sediment. Of the PAHs analyzed, only fluoranthene was measured with both acceptable accuracy (100 ± <30%) and precision (<30%) and hence only these data are reported. Difficulties with the other PAHs measured may have resulted from the rather small sample sizes analyzed, mostly 10 to 18 g dry weight. Nevertheless, fluoranthene may be used as a surrogate compound for most of the other parental PAHs, e.g., those without side chains, since it has been shown that this compound is usually the most abundant combustion-related PAH present in sediments (Laflamme and Hites, 1978; Heit and Tan, 1979) and that the other PAHs are significantly correlated with its distribution in sediments (Heit *et al.*, 1981). It should be noted that the alkylated homologues of several of the PAH, $C_{15}H_{12}$, $C_{16}H_{14}$, and $C_{17}H_{12}$ were analyzed for but not detected in the sediments.

3.3. POLYCHLORINATED BIPHENYLS

The 10% methylene chloride in petroleum ether fraction (F2) was spiked with 4-bromobiphenyl as an internal standard and analyzed by GC with an electron capture detector (ECD) using an SE-52 glass capillary column. Standard solutions containing known concentrations of selected PCBs were periodically analyzed to determine response factors for each of the standard compounds. Response factors for the other PCBs were determined by FID versus ECD response. Identifications were made on the basis of retention time.

No certified reference material is yet available for assessing the accuracy of PCB analyses in sediment. In lieu of this, recovery efficiencies shown below were ascertained from spiked process blanks and a reference sediment. In general the average recoveries were excellent although there was variation (Table II). No PCBs were detected in the process blanks and unspiked reference sediment.

TABLE II

PCB recovery

Compound	% Recovery	
	Spiked process blanks	(Reference) representative sediment
Trichlorobiphenyl	101 ± 8	100 ± 14
Tetrachlorobiphenyl	98 ± 6	96 ± 9
Hexachlorobiphenyl	105 ± 39	114 ± 50
Octachlorobiphenyl	105 ± 23	98 ± 34

Because the compound selected for use as a surrogate standard (4,4′-dibromobiphenyl) did not elute with the PCBs, we were not able to directly determine the recoveries for the lake sediments and instead had to rely upon the data from the spiked process blanks and reference sediments. In addition, the levels of PCB isomers detected in several of the samples were < 10 ppb and therefore very close to the detection limits achieved for these compounds. The value of the data for these samples may not be in the quantification of the various PCB isomers as much as in the fact that they were detected in the samples.

Precision values were ascertained from replicate analyses of blind duplicates and the results are shown in Table I. Precision was good for the trichlorobiphenyls, but not for the remaining isomers. However, considering the very low levels of these PCBs in the sediments, generally < 50 ng g^{-1} dry weight, we believe these results to be reasonable.

4. Results and Discussion

Surface (0 to 2 cm) sediment concentrations of 13 trace elements, PAH-fluoranthene and PCBs are shown for the four lakes in Table III. In addition, concentrations for subsurface sediments are presented for Lakes Husted and Louise; such sediment was not collected for The Loch and Haiyaha. Unfortunately, because of difficulties with the coring apparatus the exact depth of this subsurface sediment is unknown. Nevertheless, as shown in Table III, about half of the trace elements, fluoranthene and all of the PCBs were lower in concentration in the subsurface samples.

In the following paragraphs each group of trace substances measured is discussed in relationship to (a) the concentrations observed relative to other areas, and (b) their significance as indicators of anthropogenic deposition.

4.1. TRACE ELEMENTS

None of the lakes had consistently higher elemental concentrations in their sediments. For example, Cd was highest in concentration in Husted; Ni and Tl in The Loch; As, Be, Cu, Fe, Se, and V in Haiyaha; and Hg, Pb, Sb, and Zn in Louise. Although there was some variation in elemental concentrations among the lakes, none of the elements differed by levels greater than an order of magnitude. The percent variation among the four lakes was in general < 50, with the exception of As (84) and Fe (67) – due to significantly higher concentrations of these two elements in Haiyaha.

A comparison of the surface sediment concentrations in the four Rocky Mountain lakes with concentrations reported in the literature for other lakes (Heit *et al.*, 1980, 1981; Galloway and Likens, 1979; Goldberg *et al.*, 1981) (Table IV) shows that the concentrations measured here are not exceptionally high and in fact are generally lower for several of the elements. For example, none of the Rocky Mountain Lakes have metal concentrations as high as those found in Standley Lake, CO (Heit *et al.*, 1980), a lake which appears to have received industrial runoff, or Southern Lake Michigan (Goldberg *et al.*, 1981), which is in an area described as having intensive agricultural and industrial activities. Rather, the levels in the Rocky Mountain Lakes more closely approach the concentrations found in remote high altitude Adirondack Lakes, where some elemental inputs have been ascribed to atmospheric deposition (e.g., Pb) (Comm. on Natural

TABLE III

Concentrations of trace substances in Rocky Mountain Lake sediments

	Lake Husted		Conc. ratio[b] surface/ subsurface	Lake Louise		Conc. ratio[b] surface/ subsurface	L. Haiyaha surface conc.	The Loch surface conc.
	Surface conc.	Depth conc.		Surface conc.	Depth conc.			
Element[a]								
As	2.5 ± 0.2	0.79 ± 0.05	3	2.5 ± 0.3	1.0	3	8.4 ± 0.2	1.4 ± 0.2
Be	3.9 ± 1.0	2.7 ± 0.9	1	5 ± 3	7.4	1	9.3 ± 1.1	7.4 ± 1.3
Cd	0.70 ± 0.04	0.32 ± 0.07	2	0.5 ± 0.3	0.09	6	0.34 ± 0.03	0.32 ± 0.05
Ca	26 ± 1	12 ± 2	2	34.1 ± 0.1	26.5	1	54 ± 5	47 ± 6
Fe	1.6 ± 0.04	1.1 ± 0.1	1	2.4 ± 0.1	1.9	1	6.2 ± 0.9	2.3 ± 0.3
Hg	0.03 ± 0.01	0.03	1	0.065 ± 0.007	0.05	1	0.05 ± 0	0.04 ± 0.01
Ni	9.6 ± 0.2	4.2 ± 0.8	2	10 ± 0	9.0	1	12.3 ± 0.6	18 ± 2
Pb	28 ± 2	10 ± 7	3	43 ± 0	13.7	3	26 ± 2	14 ± 2
Sb	0.38 ± 0.03	0.14 ± 0.02	3	0.44 ± 0.08	0.16	3	0.32 ± 0.04	0.19 ± 0.04
Se	1.8 ± 0.1	0.9 ± 0.2	2	1.2 ± 0.1	0.76	2	1.8 ± 0.4	1.1 ± 0.3
Tl	0.13 ± 0.02	0.14 ± 0.02	1	≤0.25	≤0.2	1	0.20 ± 0.07	0.27 ± 0.16
V	27.3 ± 0.1	15 ± 3	2	35 ± 6	32.8	1	55 ± 6	43 ± 3
Zn	117 ± 2	80 ± 13	1	125 ± 3	155.0	1	72 ± 4	95 ± 9
PAH[c]								
Fluoranthene	110 ± 40	55 ± 2	2	375 ± 110	30	13	96 ± 6	80 ± 30
$C_{17}H_{12}$	n.d.	n.d.		n.d.	n.d.		n.d.	n.d.
PCB[c]								
Trichlorobiphenyl	142	7	20	51	8	6	31 ± 9	21 ± 4
Tetrachlorobiphenyl	194	12	16	142	15	9	70 ± 40	40 ± 20
Pentachlorobiphenyl	95	7	14	60	6	10	30 ± 20	15 ± 11
Hexachlorobiphenyl	74	4	19	40	6	7	20 ± 16	15 ± 14
Heptachlorobiphenyl	31	n.d.	n.d.	16	1	16	9 ± 1	5 ± 4
Octachlorobiphenyl	4	n.d.	n.d.	4	n.d.	n.d.	2 ± 1	2 ± 1
$\sum$PCB	540	30	18	310	36	9	160 ± 90	98 ± 54

n.d. = not detected.

[a] Concentrations in $\mu g\, g^{-1}$ dry weight except Fe ($mg\, g^{-1}$).

[b] Cultural Enrichment Factor (15) = surface sediment concentration ÷ subsurface sediment concentration (rounded to nearest whole number).

[c] Concentrations in $ng\, g^{-1}$ dry weight.

TABLE IV

Comparison of trace substance concentrations in Rocky Mountain Lakes with concentrations in other lake sediments

Element	Range or average concentration (μg g^{-1} dry)					
	Rocky Mtn.[b]	Sagamore[c]	Woods[c]	Woodhull[d]	Standley[e]	Michigan[f]
A. *Surface Sediments*						
As	1.4 – 8.4	5.3 ± 0	13 ± 4	10	11 ± 5	–
Be	3.9 – 9.3	5.1 ± 0.1	5.7 ± 0.2	–	2 ± 1	–
Cd	0.32– 0.70	1.5 ± 0.1	2.6 ± 0.0	2.5	2 ± 1	1.9
Cu	26 – 54	8.7 ± 0	15 ± 1	18	200 ± 20	130
Fe[a]	16 – 62	–	–	28	–	40
Hg	0.03– 0.07	0.38 ± 0.01	0.46 ± 0.11	–	0.5	–
Ni	9.6 – 18	6.4 ± 0.6	11.0 ± 0.1	10	38 ± 12	32
Pb	14 – 43	53 ± 4	138.0 ± 8.0	160	210 ± 20	110
Sb	0.19– 0.44	–	–	3.0	–	–
Se	1.1 – 1.8	1.6 ± 0.1	4.6	–	0.04	–
Tl	0.13– 0.27	10.0 ± 0.8	5.8 ± 0.1	–	1.0	–
V	27 – 55	105 ± 0	114 ± 1	39	120 ± 10	90
Zn	72 –125	139 ± 1	345 ± 8	16	1200 ± 200	300

PAH	Range or Concentration (ng g^{-1} dry)				
	Rocky Mtn.[b]	Sagamore[c]	Woods[c]	Coburn Pond[l]	L. Superior[l]
Fluoranthene	80–375	80–460	300–1200	100–600[g]	80–90[g]

PCB	Range of Concentration (ng g^{-1} dry)					
	Rocky[b] Mountain	Puget[h] Sound	Lake[i] Ontario	Lake[j] Michigan	Hudson[j] River	Conn.[j] River
$\sum$PCB	98–540	12–640	120	40	n.d.–6700	n.d.–3500

Resources and the Nat'l Res. Council, 1981; Heit *et al.*, 1981) and/or leaching from the watersheds (e.g., Zn) (Kahl *et al.*, 1982).

It should be noted that while several of the elements measured in the Rocky Mountain Lakes are similar in concentration to the levels found in subsurface layers of the Adirondack sediment, there are some exceptions. For example, the range of concentrations of As, Be, Cu, Ni, and Se approach or exceed those found in the surface sediments of Sagamore, Woodhull and Woods Lakes.

Although its use can be misleading due to the local natural depletion or enhancement of particular elements, a comparison of the ratios of element concentrations found in a particular sediment with the estimated concentrations of the elements in the crust of the earth (Clarke Values) or in the major rock types in the area in which the sample was collected (here granitic) may provide information on the sources of trace elements (Heit

Table IV (continued)

Element	Range of Average Concentration ($\mu g\ g^{-1}$ dry)					
	Rocky Mtn.[b]	Sagamore[c]	Woods[c]	Woodhull[d]	Standley[e]	Michigan[f]
B. *Sub-Surface Sediments*[k]						
As	0.8– 1.0	1.0	1.3	6.2	13 ± 5	–
Be	2.7– 7.4	4.4	4.3	–	8 ± 7	–
Cd	0.09– 0.32	0.6	0.6	0.5	16 ± 4	0.2
Cu	12– 27	5.7	0.9	6	370 ± 2	60
Fe[a]	11– 24	–	–	18	–	25
Hg	0.03– 0.05	0.2	0.2	–	0.7	–
Ni	4.2– 9.0	6.6	5.3	10	40 ± 10	20
Pb	10– 14	4.2	5.8	15	370 ± 30	70
Sb	0.14– 0.16	–	–	1.2	–	–
Se	0.8– 0.9	0.8	1.6	–	0.2	–
Tl	0.14– 0.30	11.0	5.7	–	2.5	–
V	15– 33	97	99	30	120 ± 8	80
Zn	80–125	81	54	75	3400 ± 500	50

PAH	Range of Concentration ($ng\ g^{-1}$ dry)				
	Rocky Mtn.[b]	Sagamore[c]	Woods[c]	Coburn Pond[l]	L. Superior[l]
Fluoranthene	< 100	10–40	10–25	< 10[g]	20[g]

n.d. = not detectable.

[a] Fe concentration in $mg\ g^{-1}$ dry.

[b] This paper.

[c] From Heit *et al.* (1981).

[d] From Galloway and Likens (1979).

[e] From Heit *et al.* (1980b).

[f] From Goldberg *et al.* (1981).

[g] Pyrene concentrations used in lieu of fluoranthene concentrations.

[h] From Pavlow and Dexter (1979).

[i] From Haile *et al.* (1975).

[j] From Nisbet (1976).

[k] Lowest concentration reached in sub-surface sediment.

[l] From Gschwend and Hites (1982).

et al., 1981). A variety of terms have been used to describe such an approach to evaluating geochemical data. Among these is the concept of the enrichment factor (EF), which is defined by the following equation:

$$EF = (X/Y)_{\text{sample}}/(X/Y)_{\text{crustal material}}$$

where X is the concentration of the element of interest and Y is the concentration of an element representative of crustal material. Aluminum, Fe, and Sc are elements that are representative of crustal material (Heit *et al.*, 1981; Galloway and Likens, 1979). For this study we have used Fe as a comparative 'marker' element. The enrichment factor may be interpreted as follows. If an element exists in its crustal ratio (EF = 1) this implies that the main source of the element is the earth's crust. Any ratios other than EF = 1 are assumed to be due to local geological conditions, anthropogenic inputs or both. For example if the ratio EF is > 1, additional sources of input besides average surface crustal sources are indicated; while an EF < 1 may be interpreted as an indication of local depletion in a particular element.

The EFs for each element of interest, based upon the average concentration of iron in igneous rock, are given in Table V. By this method of comparison it can be clearly seen that the sediment in the majority of the lakes had elevated levels of several of the elements including As, Be, Cd, Pb, Sb, Se, and Zn. It should be remembered, however, that this type of analysis is subject to misinterpretation if the natural levels of elements in the area measured differ greatly from their average concentrations in crustal igneous rock. This in fact may be the case for two of the elements which appear to be enriched, namely Be and Se. We make this statement based upon a comparison of the ratios of the surface sediment concentrations of the elements to that of their concentrations in the subsurface sediment. This ratio, also known as the Cultural Enrichment Factor (CEF) (Robins and Edington, 1977), is shown on Table III for Lakes Louise and Haiyaha. This ratio may be interpreted as follows: Ratios < 1 suggest a decrease in elemental input compared to the deeper sediment; ratios ~ 1 indicate no changes in input, and ratios > 1 suggest enhanced inputs; the greater the ratio the greater the relative change of input with time.

While EF values (Table V) were between 3 and 6.4 for Be; and 33 and 128 for Se; the CEF (Table III) values were 1 for Be; and only 2 for Se, a substantial difference.

TABLE V

Trace element enrichment factors for Rocky Mountain Lake sediments

Element	Avg conc.[a] Igneous Rock ($\mu g\ g^{-1}$ dry)	Enrichment Factor (EF)			
		L. Haiyaha	L. Husted	The Loch	L. Louise
As	1.8	4.2	5.5	1.9	3.3
Be	2.8	3.0	5.0	6.4	4.2
Cd	0.2	1.5	12	3.9	5.8
Cu	55	0.9	1.7	2.1	1.5
Fe	56[b]	1[c]	1[c]	1[c]	1[c]
Hg	0.08	0.6	1.3	1.2	1.9
Ni	75	0.2	0.5	0.6	0.3
Pb	12.5	1.9	8.1	2.7	12
Sb	0.2	1.5	6.8	2.3	5.2
Se	0.05	33	128	54	57
Tl	0.45	0.4	1.0	1.5	<1.1
V	135	0.4	0.7	0.8	0.6
Zn	70	0.9	6.0	2.4	4.2

[a] Values from Bowen (1966).

[b] $mg\ g^{-1}$ dry.

[c] Fe enrichment factor = 1 by definition.

The use of the CEF would thus suggest that the unexpectedly high EF values for these two elements are due primarily to a natural elevated background level rather than to anthropogenic deposition. Some investigators have in fact reported that the Rocky Mountains contain soils and rocks with high levels of Se (Callahan *et al.*, 1979; Fisher, 1975). It should be noted that we are not excluding the possibility of some Se anthropogenic input since the CEF was 2 for both Lakes Husted and Louise.

Those elements which showed EF and CEF ratios > 1 in both Haiyaha and Louise included As, Cd, Pb, Sb. Interestingly, these elements are among those found to be elevated in surface sediments in cores taken from remote Adirondack lakes where their origins are ascribed to anthropogenic sources (Heit *et al.*, 1981; Galloway and Likens, 1979). Based upon these preliminary results, we will in the future take sediment cores from these lakes or from other lakes situated nearby so that a chronology of trace element fluxes into this region can be determined and possible origins such as the atmospheric transport and deposition from urban, industrial and automotive sources can be evaluated.

4.2. POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons may be formed by both natural and anthropogenic processes. These include high temperature (> 700 °C), incomplete combustion and diagenesis from organic precursors (Heit *et al.*, 1981). Our data indicate, however, that the PAH, fluoranthene, in the four lakes was produced primarily by combustion. We base this conclusion on the ratio of the parental, e.g., without side chains, fluoranthene to its alkyl homologues $C_{17}H_{12}$. Ratios of the parental PAH to alkylated homologues which are > 1 have been shown to be indicative of high temperature combustion (Hites *et al.*, 1977). Ratios that are < 1 have been shown to be typical of PAHs produced by diagenetic or biogenetic processes (Heit *et al.*, 1981). $C_{17}H_{12}$ values are not shown in Table III, because in none of the samples measured was $C_{17}H_{12}$ detectable (i.e. < 50 ng g^{-1}). Since the average concentration of surface sediment measured in the four lakes ranged from 80 to 375 ng g^{-1} (see Table III), the ratio of fluoranthene/$C_{17}H_{12}$ clearly has to be > 1, suggesting a combustion origin in all four lakes.

It is quite difficult to evaluate whether the major source of the fluoranthene is from natural combustion such as forest fires or anthropogenic combustion such as from industry or power generation. However, the fact that the CEF ratios were > 3 in both Lakes Husted and Louise (Table III) suggests that the loadings of fluoranthene into these lakes have increased with time.

A comparison of the fluoranthene concentrations in the surface sediments of Rocky Mountain Lakes with data reported elsewhere in the literature is shown in Table IV. Again, as was the case for the trace elements, the levels measured here were not exceptional in that they were similar to the range of values reported for remote high altitude lakes in the Adirondacks (Sagamore and Woods) (Heit *et al.*, 1981), a lake in rural Maine (Coburn Mountain Pond) (Gschwend and Hites, 1982), and a remote station on Lake Superior (Gschwend and Hites, 1982). It should be noted that for all of these lakes, it is believed that the PAHs entering these sites are atmospherically transported, and are combustion produced and most likely originate from anthropogenic sources. While this hypothesis cannot be proven for the Rocky Mountain Lakes until chronologically dated sediment cores are taken, it is surmised that the similar trends of fluoranthene in the sediment of Lakes Louise and Husted, coupled with the similarity in concentrations found in other lakes believed to receive anthropogenic deposition, indicate that this hypothesis can be applied to high altitude lakes of the Colorado Rocky Mountains.

4.3. POLYCHLORINATED BIPHYENYLS

Although some halogenated organic hydrocarbons can in fact be produced in nature by biogenesis, PCBs cannot – they are solely produced by anthropogenic processes. They were first made in 1929 and were commercially produced in the 1930's with major increases in their use during the World War II period. In 1973 their production was restricted by the U.S. Environmental Protection Agency, however they are long-lived and persist in the environment (Boyle and Highland, 1979). Since they are only produced by commercial processes, their occurrence may be taken as proof of the presence of anthropogenic pollution. Because we have found PCBs present in all four remote lakes (Table III), there is no doubt that anthropogenic pollutants have been deposited in these lakes. Furthermore, they must have been atmospherically transported since no local discharge sources of anthropogenic pollution are present. We cannot from our data suggest a source for these pollutants other than long distance transport. Possible sources may be Denver to the southeast, Salt Lake City to the west or fallout from global transport of pollutants (Atlas and Giam, 1981).

As far as the composition of the PCBs in the sediment of the four lakes is concerned, it appears that most of the isomers were tetrachlorobiphenyls with approximately equal amounts of trichloro and pentachlorobiphenyls. Although comparisons were not made with authentic PCB mixtures, in Table VI we compare the percent composition of chloride isomers in various commercial PCB mixtures, Arochlors, with the composition found in the four Rocky Mountain lakes. Arochlor 1254 and 1260 are among those PCB mixtures present in these lakes based upon the relatively large amount (13 to 17%) of hexachlorobiphenyl and detectable levels of heptachlorobiphenyl (3 to 6%) and octachlorobiphenyl (< 1 to 2%) found in the sediments. We cannot assess from these data from which of several possible arochlors the tetrachlorobiphenyl and trichlorobiphenyl components result. It is sufficient to state, however, that the PCB mixtures detected in the four Rocky Mountain lakes include those associated with both relatively light isomeric mixtures of Arochlors such as 1242 and heavier Arochlors such as those mentioned above. It should also be noted that the majority of the isomers detected in the lakes (> 60%) were composed of trichloro and tetrachlorobiphenyls. These results are in general agreement with Atlas and Giam (1981) whose data suggest differential rates of removal of PCB isomers from the atmosphere with rainfall and dry deposition scavenging of heavier isomers occurring at a greater rate than that of lighter compounds.

Finally, in Table IV we compare the concentrations of PCBs found in the sediments of the four Rocky Mountain lakes with values reported elsewhere. Unfortunately,

TABLE VI

Percent composition of PCB isomers

		Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8
Arochlor 1221[a]		3	n.d.	n.d.	n.d.	n.d.	n.d.
Arochlor 1232[a]		24	15	0.5	n.d.	n.d.	n.d.
Arochlor 1016[a]		57	21	1	n.d.	n.d.	n.d.
Arochlor 1242[a]		40	32	10	0.5	n.d.	n.d.
Arochlor 1248[a]		23	50	20	1	n.d.	n.d.
Arochlor 1254[a]		n.d.	16	60	23	1	n.d.
Arochlor 1260[a]		n.d.	n.d.	12	46	35	6
Rocky Mountain Lakes[b]							
Husted	(surface)	26	36	18	14	6	< 1
	(depth)	23	40	23	13	n.d.	n.d.
Louise	(surface)	16	46	19	13	5	1
	(depth)	22	42	17	17	3	n.d.
Haiyaha	(surface)	19	44	19	13	6	1
The Loch	(surface)	21	40	15	15	5	2

[a] Data from Webb and McCall (1973).
[b] This paper.
n.d. = not detected.

comparative information was not available for PCB levels in remote lakes. Nevertheless, it appears that the concentrations of PCBs in the Rocky Mountain Lakes were typical of levels found elsewhere, Puget Sound (Pavlow and Dexter, 1979), Lake Ontario (Haile *et al.*, 1975), and Lake Michigan (Nisbett, 1976) excepting severly contaminated sites such as the Hudson River and the Connecticut River (Nisbett, 1976).

5. Conclusions and Recommendations

Evidence is presented here which indicates that the remote high altitude lakes in the Rocky Mountain National Park have received inputs of anthropogenic pollutants. The results are unequivocal for PCBs, but less certain for the trace elements As, Cd, Pb, and Sb, and for the polycyclic aromatic hydrocarbon, fluoranthene. Furthermore, the absence of local sources of pollution suggests that the trace substances measured have been transported and deposited into the lakes by atmospheric processes.

The levels of these trace substances in the surface sediments of the four lakes are typical of values reported elsewhere in the literature for other remote lakes and rural aquatic systems, but are far lower in concentration than the levels found in severely polluted aquatic systems.

Sediments taken at depth have lower concentrations of several of the elements, PCBs and fluoranthene than do surface sediments. From this we infer inputs have increased recently compared to earlier times.

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