

Current and Historical Deposition of PBDEs, Pesticides, PCBs, and PAHs to Rocky Mountain National Park

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An analytical method was developed for the trace analysis of 98 semivolatile organic compounds (SOCs) in remote, high-elevation lake sediment. Sediment cores from Lone Pine Lake (west of the Continental Divide) and Mills Lake (east of the Continental Divide) in Rocky Mountain National Park, CO, were dated using ²¹⁰Pb and ¹³⁷Cs and analyzed for polybrominated diphenyl ethers (PBDEs), organochlorine pesticides, phosphorothioate pesticides, thiocarbamate pesticides, amide herbicides, triazine herbicides, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) using this method. SOC deposition profiles were reconstructed, and deposition half-lives and doubling times were calculated, for U.S. historic-use pesticides (HUPs) and current-use pesticides (CUPs) as well as PBDEs, PCBs, and PAHs. Sediment records indicate that the deposition of CUPs has increased in recent years, while the deposition of HUPs has decreased since U.S. restriction, but has not been eliminated. This is likely due to the revolatilization of HUPs from regional soils, atmospheric transport, and deposition. Differences in the magnitude of SOC sediment fluxes, flux profiles, time trends within those profiles, and isomeric ratios suggest that SOC deposition in high-elevation ecosystems is dependent on regional upslope wind directions and site location with respect to regional sources and topographic barriers.

Introduction

Semivolatile organic compounds (SOCs) are ubiquitous throughout the environment due to anthropogenic activities and have the potential to accumulate in polar and mountainous regions (1–8). SOC can undergo atmospheric long-range transport via large-scale winds (2, 3, 5–7, 9). In mountainous regions, diurnal winds have the potential to transport SOC from lower-elevation source regions to higher elevations (3). The U.S. Environmental Protection Agency has also classified certain SOC as persistent, bioaccumulative, and toxic (PBT) chemicals (10). Due to the potential

for transport and deposition of these PBT SOC to sensitive remote ecosystems, the Western Airborne Contaminant Assessment Project (WACAP) was developed to study the atmospheric deposition of SOC to high-elevation and high-latitude lake catchments in eight national parks throughout the western U.S. from 2003 to 2005 (11).

Hageman et al. (7) showed that regional cropland intensity (cropland area as a percentage of total land area) within a 150 km radius of western national parks, including Rocky Mountain National Park, is significantly correlated with log snowpack concentrations of dacthal, Zendosulfans (endosulfan I, II, and endosulfan sulfate), γ -HCH, and dieldrin. The same study estimated that 50 to 98% of the pesticides in the Rocky Mountain 2002–2003 snowpack was due to regional sources (7). This was attributed to revolatilization of pesticides from soils, atmospheric transport, and deposition. Westerly winds predominate in the Colorado Rocky Mountains (12). However, atmospheric deposition of nitrogen, in the form of NO_x and NH₃, has been shown to originate from fossil-fuel combustion and agriculture sources in major metropolitan areas <150 km east of Rocky Mountain (Denver, Boulder, and Fort Collins) and is linked to summer diurnal mountain winds (12).

Lake sediments preserve the chronology of SOC deposition to lake catchments, and radiometric dating of an undisturbed sediment core permits reconstruction of the historical deposition (13–16). The objectives of this research were to develop and validate an analytical method for quantifying 98 SOC in sediment, to quantify SOC in sediment from two high-elevation lake catchments located on either side of the Continental Divide in Rocky Mountain National Park, to reconstruct the history of SOC deposition, and to identify possible SOC source regions to the two Rocky Mountain National Park lakes.

Materials and Methods

Sediment cores were collected from the deepest point in each lake during the ice-free summer using an UWITEC gravity corer containing an 86 mm internal diameter polycarbonate core tube. Sediment cores were collected in September 2003 from Lone Pine Lake (3024 masl, 40.22° N, 105.73° W) and Mills Lake (3030 masl, 40.29° N, 105.64° W) in Rocky Mountain National Park. Lone Pine Lake, located west of the Continental Divide, and Mills Lake, located east of the divide, are ~1150 m lower in elevation than the Continental Divide and are approximately 10 km apart. The complete details of the sample collection, lake bathymetry, and coring site locations from both lakes are shown in the Supporting Information (Figure S1).

Each sediment interval was homogenized to a uniform color and texture using a Teflon spatula, and an aliquot (1–5 g) was removed and freeze-dried to determine the percent moisture. The remainder of the sediment sample was stored at –20 °C for SOC analysis. Aliquots of the freeze-dried sediment were used for the analyses of total carbon, total organic carbon, ²¹⁰Pb, ¹³⁷Cs, ²²⁶Ra, and ²⁴¹Am. Further details of the physical and elemental analytical methods, together with plots of the fallout radionuclide activities vs depth, are presented in the Supporting Information (Figures S2 and S3).

For SOC analysis, sediment samples were allowed to thaw in sealed glass jars, ground with sodium sulfate, and extracted using a pressurized liquid extraction. Interferences were removed from the sediment extract using a 20 g silica solid-phase extraction cartridge and gel permeation chromatography. The sediment extracts were analyzed for target SOC

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by gas chromatographic mass spectrometry, using both electron impact ionization and electron capture negative ionization with selective ion monitoring as described in detail by Usenko et al. (6) and Ackerman et al. (17). The precision and accuracy of the entire analytical method was validated in triplicate using NIST SRM1941b marine sediment that was collected from Baltimore Harbor (18, 19). Complete details of the methods used for extraction, cleanup, instrumental analysis, quantification, and validation as well as chemicals, standards, and solvents are presented in the Supporting Information.

Results and Discussion

Method Validation. Analyte recoveries over the entire analytical method were measured with triplicate spike and recovery experiments using sediment from Waldo Lake (Table S1). Target SOC concentrations were spiked at 12–36 ng g⁻¹ ww sediment and were corrected for background concentrations in the sediment. The average SOC recoveries and percent relative standard deviations (%RSD) for the entire analytical method were 60.3 and 8.5%, respectively. While the recoveries varied among the SOCs, no significant correlation between recovery and octanol–water partition coefficient was observed.

The concentrations of 35 SOCs were measured in three ~2.0 g (dry wt) samples of SRM1941b using this analytical method. NIST certified values, with 95% confidence intervals, for 27 of the 35 measured SOCs (14 polycyclic aromatic hydrocarbons (PAHs), 6 polychlorinated biphenyls (PCBs), and 7 organochlorine pesticides) were used to determine the accuracy of the analytical method. The average percent difference and %RSDs of our measured concentrations and the certified concentrations were 16.8 and 23.6%, respectively, and the percent difference ranged from 0.0% (PCB 187, phenanthrene, *p,p'*-DDD, *p,p'*-DDE, benzo[*b*]fluoranthene) to 55.4% (*cis*-nonachlor) (Table S1, Supporting Information). We measured average concentrations and %RSDs for PBDE-47, PBDE-99, and PBDE-100 in SRM1941b of 1.3 ng/g and 4.8%, 0.56 ng/g and 0.7%, and 0.85 ng/g and 0.9%, respectively (Table S1).

Sedimentation Rate and Focusing Factors. Total ²¹⁰Pb activity in the Lone Pine Lake core reached equilibrium with the supporting ²²⁶Ra at a depth of 11.5 cm (Figure S2, Supporting Information). Unsupported ²¹⁰Pb (calculated by subtracting ²²⁶Ra activity from total ²¹⁰Pb) declines more or less exponentially with depth, suggesting relatively uniform sedimentation accumulation during the past 100 years or so. ²¹⁰Pb dates were calculated using the constant rate of supply (CRS) model, because the ²¹⁰Pb and ¹³⁷Cs plots suggest that the sediment records may have been influenced by a moderate degree of mixing. Small corrections were made to account for this possibility. The resulting chronology placed 1963 at 4.5 cm, in reasonably good agreement with the depth suggested by the ¹³⁷Cs record (Figure S2b, Supporting Information). The mean dry mass sedimentation rate in Lone Pine Lake for the past century was calculated to be 0.014 g cm⁻² year⁻¹, with a mean volumetric rate of 0.09 cm year⁻¹.

In the Mills Lake core, equilibrium between the total ²¹⁰Pb activity and the ²²⁶Ra activity was reached at a depth of 12.0 cm (Figure S3, Supporting Information). The unsupported ²¹⁰Pb record can be divided into two distinct parts. In the top 4 cm of the core, there is no net decline; below 4 cm it declines rapidly, and more or less exponentially with depth. These data may indicate either fairly intensive mixing of the surficial sediments or a recent substantial increase in the sedimentation rate. Comparison with the ¹³⁷Cs record suggests that the latter is more likely. Dates calculated using the CRS model place 1963 at 6.25 cm, in good agreement with the depth indicated by the well-resolved peak in the ¹³⁷Cs/²¹⁰Pb activity ratio (Figure S3b). Although the ¹³⁷Cs

profile does not have a clearly defined peak, dilution caused by rapid changes in the sedimentation rate affects both radionuclides, and the normalized ¹³⁷Cs profile provides an alternative means of identifying the 1963 depth. It should also be noted that the rapid increase in activity between 8.5 and 7 cm suggests that all sediments above 7 cm post-date the period of greatest fallout in the early 1960s. The CRS model results indicate episodes of accelerated sedimentation in Mills Lake in the early 1960s and again during the 1990s. The mean sedimentation rate for the past 80 years was calculated to be 0.024 g cm⁻² year⁻¹ (0.14 cm year⁻¹).

To compare the SOC fluxes measured in Lone Pine Lake to Mills Lake cores, dry weight sediment concentrations (ng g⁻¹ dw) were multiplied by the mass sedimentation rate (g cm⁻² year⁻¹) and divided by the unitless focusing factors (FF) to arrive at the focus-corrected flux (ng m⁻² year⁻¹). All SOC sediment fluxes are reported in focus-corrected flux. FF were derived from the ratio of measured/expected unsupported ²¹⁰Pb inventories in the core (18). Because the lakes are only 10 km apart and at similar latitudes and elevations, we assumed that the atmospheric ²¹⁰Pb flux was the same at both lakes and that the expected ²¹⁰Pb inventory supported by this flux was 3200 Bq m⁻² (19.2 dpm cm⁻²) (20). The FF of the Lone Pine Lake core site was 1.87 and that of the Mills Lake core site was 1.48 (Table S2, Supporting Information).

SOC Sediment Flux. Current-Use Pesticides (CUPs). The focus-corrected sediment SOC concentrations and fluxes are provided in Table S3. The CUPs and their degradation products measured in Rocky Mountain sediment included *Σ*endosulfans (endosulfan I, II, and endosulfan sulfate) and dacthal. The *Σ*endosulfan flux profile, which was primarily comprised of endosulfan sulfate, has steadily increased in both Lone Pine Lake and Mills Lake sediment since U.S. introduction of technical endosulfan in 1954, reaching a maxima in the surficial sediments (2003) (Figure 1B). The doubling time of *Σ*endosulfan in Lone Pine Lake and Mills Lake was 19.1 ± 0.004 years (*r*² = 0.92, *p* < 0.001) and 12.8 ± 0.005 years (*r*² = 0.93, *p* < 0.001), respectively (Figure S4B and Table S4, Supporting Information). The surficial *Σ*endosulfan flux at Lone Pine Lake (86 ng m⁻² year⁻¹) was significantly different from (*p* < 0.01, two-sided *t*-test) and approximately 6 times lower than that at Mills Lake (500 ng m⁻² year⁻¹). Throughout both sediment cores, the endosulfan sulfate flux was ~10 times higher than the endosulfan I and II flux (Figure 1B).

The dacthal surficial sediment flux in Lone Pine Lake (5.1 ng m⁻² year⁻¹) was significantly different from (*p* < 0.01, two-sided *t*-test) and lower than that at Mills Lake (19.5 ng m⁻² year⁻¹) (Figure 1D). The doubling time for dacthal in Lone Pine Lake was not calculated because the dacthal flux was not correlated with sediment interval year (Figure S4D). The doubling time of dacthal in Mills Lake, since introduction in 1955, was 30.7 ± 0.02 years (*r*² = 0.64, *p* < 0.02) (Figure S4D and Table S4, Supporting Information).

The SOC focus-corrected fluxes of sediment intervals that overlapped by date were examined to compare differences in SOC deposition between the two lake catchments over time (2003, 1990, 1987, 1974, and 1954) (Table S5, Supporting Information). The higher fluxes (by a factor of 1.5 to 6.4) of *Σ*endosulfan and dacthal in Mills Lake relative to those of Lone Pine Lake (Table S5) suggest that Mills Lake has consistently received a greater flux of these SOCs over the past ~50 years (Table S5). A comparison of these measured fluxes to other remote locations could not be made because of the lack of *Σ*endosulfan and dacthal flux measurements in the literature.

Historic-Use Pesticides (HUP). The major constituents of technical chlordane (*trans*-chlordane (TC), *cis*-nonachlor (CN), and *trans*-nonachlor (TN)) were detected in both lake sediment cores; however, *cis*-chlordane, heptachlor, and

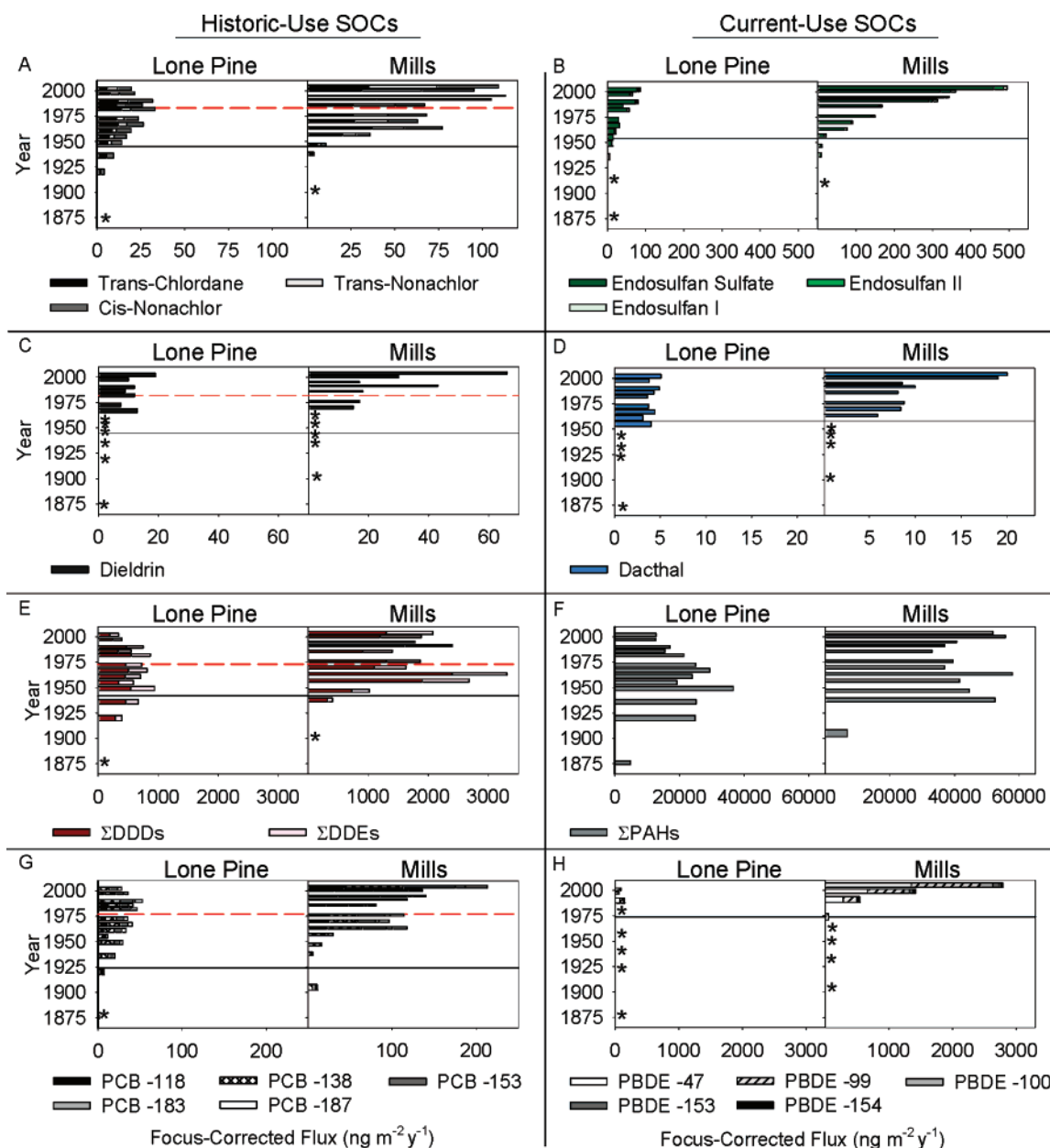


FIGURE 1. Focus-corrected flux ($\text{ng m}^{-2} \text{year}^{-1}$) profiles of current and historic-use SOC in Lone Pine Lake (west) and Mills Lake (east) sediment cores. Solid lines (—) indicate U.S. registered use date, dashed lines (---, red) indicate U.S. restriction date, and * marks indicate below method detection limit.

heptachlor epoxide were not detected (21). Technical chlordane was used as an insecticide in the U.S. from 1948 to 1979 but only for termite control from 1979 to 1988 (22). The TC, CN, and TN fluxes in Lone Pine Lake increased from the time of technical chlordane introduction until restriction, with a doubling time of 27.5 ± 0.01 years ($r^2 = 0.92$, $p < 0.01$) (Figure S4A, Supporting Information). TC, CN, and TN fluxes in Lone Pine Lake peaked in the early 1980s and have been declining, with a half-life of 28.5 ± 0.01 years, since 1982 ($r^2 = 0.80$, $p < 0.03$) (Figure S4A).

In general, the TC, CN, and TN fluxes in Mills Lake increased from U.S. introduction until U.S. restriction, with a doubling time of 10.9 ± 0.02 years ($r^2 = 0.76$, $p < 0.03$) (Figure S4A, Supporting Information), and there is no evidence of a decline in the flux of these SOC in Mills Lake after U.S. restriction. Over the past 50 years, Mills Lake received a greater flux (by a factor of 2.3 to 6.0) of TC than Lone Pine Lake (Table S5, Supporting Information).

The ratio of TN/(TN+CN) for Lone Pine Lake and Mills Lake sediment averaged 0.05 ± 0.50 and 0.06 ± 0.32 ,

respectively, and were statistically different from each other ($p < 0.01$, two-sided t -test) (Figure S5A, Supporting Information). This same ratio in technical chlordane was 0.78 (21). Ratios lower than 0.78 suggest that TN has undergone more degradation than CN. The TN/(TN + CN) ratios in Lone Pine Lake and Mills Lake sediment decreased with time ($r^2 = 0.49$ and 0.53, respectively, $p < 0.03$), and the slopes of the regressions were not statistically different from each other ($p = 0.22$) (Figure S5A). This suggests that, in both sediment cores, TN was preferentially degraded over CN at a similar and constant rate. The difference in chlordane isomeric ratios between the two cores cannot be attributed to differences in sediment degradation rates and may reflect differences in microbial degradation in the different soils to which they were originally applied in the eastern lowlands and western lowlands, respectively.

Dichlorodiphenyltrichloroethane (DDT) was detected in sediments from both lakes. This SOC, which was heavily restricted in the US in 1972, undergoes reductive dechlorination to DDD under anoxic conditions and dehydrochloro-

mination to DDE under oxic conditions (23, 24). *o,p*-DDT and *p,p'*-DDT were not detected in either core. However, *o,p*-DDD + *p,p'*-DDD (Σ DDDs) and *o,p*-DDE + *p,p'*-DDE (Σ DDEs), the major degradation products of technical DDT, were detected (Figure 1E).

In Lone Pine Lake sediment, Σ DDD and Σ DDE fluxes increased from the time of technical DDT's widespread U.S. use (1942) to U.S. restriction (1972), with a doubling time of 46.3 ± 0.01 years ($r^2 = 0.76$, $p < 0.05$) and peaked in the early 1980s (Figure S4E, Supporting Information) (10). Since 1980, the flux of Σ DDD and Σ DDE in Lone Pine Lake has declined with a half-life of 16.0 ± 0.01 years ($r^2 = 0.81$, $p < 0.03$) (Figure S4E). Σ DDD and Σ DDE were detected in two sediment samples dating prior to 1940 (Figure 1E), which was before the widespread use of technical DDT in the U.S. (22). This irregularity in the sediment core may be attributed to downward molecular diffusion, bioturbation, and/or sediment smearing during sampling (25). Despite this irregularity, the reconstructed profiles for Σ DDD and Σ DDE in Lone Pine Lake are consistent with technical DDT introduction and restriction in the U.S.

The Σ DDD and Σ DDE fluxes in Mills Lake also increased from the time of U.S. introduction of technical DDT, reaching a maximum in the mid 1960s (Figure 1E). Over the last 45 years, the deposition of Σ DDD and Σ DDE has been fairly constant in Mills Lake and has not shown a statistically significant decrease since U.S. restriction in 1972 (Figure S4E, Supporting Information). Over the past 50 years, Mills Lake received a greater flux (by a factor of 2.5 to 6.1) of Σ DDD and Σ DDE than Lone Pine Lake (Table S5, Supporting Information). In addition, the ratios of Σ DDE/ $(\Sigma$ DDE + Σ DDD) in Lone Pine Lake and Mills Lake were statistically different from each other ($p < 0.02$, two-sided *t*-test) (Figure S5B, Supporting Information) and may reflect different relative contributions from different source regions.

In 1999, Mills Lake was cored, dated, and analyzed for *p,p'*-DDE and *p,p'*-DDD (8). Three sediment intervals dating after 1940 were analyzed (~1944, ~1970, and ~1990). However, the reconstructed *p,p'*-DDE and *p,p'*-DDD profiles were not corrected for sedimentation rate or sediment focusing (8). This sediment profile showed *p,p'*-DDE and *p,p'*-DDD concentrations peaking in 1970 and decreasing in 1990 (8). This core, as well as the two cores in this study, showed higher concentrations of *p,p'*-DDD than *p,p'*-DDE, suggesting that DDT is degrading under anoxic conditions (Figure 1E) (26).

Dieldrin was measured in sediment intervals from both lakes after U.S. introduction in 1949 (Figure 1C). The dieldrin flux was not correlated with time interval in either lake (Figure S4C, Supporting Information). The maximum dieldrin flux was in the surficial sediment of both lakes, and the flux of dieldrin to Mills Lake has been greater (by a factor of 2.0–3.5) than that of Lone Pine Lake over the past 30 years (Table S5, Supporting Information). From 1946 to 1982, dieldrin was manufactured at the Rocky Mountain Arsenal, which is located in Denver (10).

The focus-corrected concentrations ($\text{ng g}^{-1} \text{ dw}$) of Σ DDE + Σ DDD and the major constituents of technical chlordane in Lone Pine Lake and Mills Lake surficial sediment were similar to surficial sediment concentrations ($\text{ng g}^{-1} \text{ dw}$) measured in the remote sub-Arctic lakes located in the Canadian Yukon territory (27).

Polycyclic Aromatic Hydrocarbons. Σ PAH fluxes in Lone Pine Lake sediment peaked around 1949 ($36\,600 \text{ ng m}^{-2} \text{ year}^{-1}$) and have decreased over time to $12\,800 \text{ ng m}^{-2} \text{ year}^{-1}$ in 2003 (Figure 1F). From 1967 to 2003, the Σ PAH flux in Lone Pine Lake decreased, with a half-life of 28.3 ± 0.01 years ($r^2 = 0.94$, $p < 0.01$) (Figure S4F, Supporting Information). However, the deposition of Σ PAH to Mills Lake increased, with a doubling time of 22.6 ± 0.01 years ($r^2 =$

0.88 , $p < 0.01$) from 1987 to 2003 (Figure S4F). This may be the result of increased population east of the Continental Divide (including the Denver metro area), which has increased from 1985 to 2003 with a doubling time of 32.9 years (28). The Σ PAH flux was greater (by a factor of 1.6 to 4.1) in Mills Lake than Lone Pine Lake throughout the sediment cores (Figure 1F and Table S5, Supporting Information). In addition, the BaP/(BaP + BeP) and FLA/(FLA + PYR) ratios calculated for Mills Lake and Lone Pine Lake sediment cores were statistically different ($p < 0.05$ and $p < 0.02$, respectively) (Figure S5, Supporting Information).

The surficial sediment Σ PAH flux measured in Lone Pine Lake and Mills Lake is similar to that measured in high-elevation lake catchments in Europe, which ranged from approximately $38\,000 \text{ ng m}^{-2} \text{ year}^{-1}$ to $130\,000 \text{ ng m}^{-2} \text{ year}^{-1}$ and did not include ACY, ACE, FLO, ANT, or DahA (Table S3, Supporting Information) (14). The Σ PAH flux measured at the Rocky Mountain sites and the European sites were approximately an order of magnitude lower than the surficial sediment Σ PAH flux measured in Michigan inland lakes (29).

Polychlorinated Biphenyls. The sediment cores from both lakes contained PCB 118 (penta), PCB 138 (hexa), PCB 153 (hexa), PCB 183 (hepta), and PCB 187 (hepta). The Σ PCB flux increased from U.S. introduction (1929) to U.S. restriction (1977) in Lone Pine Lake. However, there was no significant correlation between Σ PCB flux and time interval in Lone Pine Lake (Figure S4G, Supporting Information). The Σ PCB flux in Lone Pine Lake peaked around 1990 ($53 \text{ ng m}^{-2} \text{ year}^{-1}$) and has since declined slightly ($35 \text{ ng m}^{-2} \text{ year}^{-1}$). The ratio of PCB congeners in Lone Pine Lake remained fairly constant throughout the sediment profile (Figure 1G).

From 1938 to 1974, the Σ PCB flux to Mills Lake increased with a doubling time of 8.3 ± 0.01 years ($r^2 = 0.90$, $p < 0.01$) to $114 \text{ ng m}^{-2} \text{ year}^{-1}$ in 1974 (Figure 1G and Figure S4G, Supporting Information). After U.S. restriction in 1977, the Σ PCB flux in Mills Lake continued to increase, but at a slower rate, with a doubling time of 13.6 ± 0.01 years ($r^2 = 0.86$, $p < 0.01$), reaching a maximum flux in the surficial sediment of $213 \text{ ng m}^{-2} \text{ year}^{-1}$ (Figure 1G and Figure S4G, Supporting Information). The ratio of the five PCB congeners was relatively constant throughout the core (Figure 1G). As with CUPs, HUPs, and Σ PAHs, the Σ PCB flux to Mills Lake has been greater (by a factor of 2.0 to 6.5) than that to Lone Pine Lake over the past 50 years (Table S5, Supporting Information). Because of the limited number of PCB congeners measured, it is difficult to compare these measured fluxes with other remote sites.

Polybrominated Diphenyl Ethers. Of the 31 PBDEs measured (Table S1, Supporting Information), only PBDE-47, PBDE-99, PBDE-100, PBDE-153, and PBDE-154 were detected in both sediment cores. The Σ PBDE flux in Mills Lake was highest in the surficial sediment ($2790 \text{ ng m}^{-2} \text{ year}^{-1}$) and increased with a doubling time of 5.4 ± 0.001 years ($r^2 = 0.99$, $p < 0.001$) since U.S. introduction in 1977 (Figure S4H, Supporting Information). The two most abundant PBDE congeners in the Mills Lake sediment (PBDE-47 and PBDE-99) were also the most abundant PBDE congeners in the penta formulation, representing >87% of the Σ PBDE flux to Mills Lake. The relative ratios of the PBDE congeners were fairly constant throughout the Mills Lake core (Figure 1H). PBDEs were only detected in three sediment intervals in Lone Pine Lake and were at or below the quantitation limit. The Σ PBDE flux to Mills Lake was 3–24 times greater than that to Lone Pine Lake (Table S5, Supporting Information). In addition, Σ PBDEs had the highest flux of any organohalogen SOC in Mills Lake surficial sediment (Figure 1H).

The Σ PBDE doubling time in Mills Lake is similar to doubling times for Σ PBDEs (tri- through heptaBDEs) in Lake Michigan and Lake Erie (Table S4, Supporting Information) (30). While the PBDE inputs to Lake Michigan and Lake Erie

are due to both atmospheric inputs and industrial and domestic wastewater discharge, the inputs to Mills Lake are due to atmospheric inputs only. The PBDE-47 flux measured in the surficial sediment of Mills Lake was 2–3 orders of magnitude greater than that measured in surficial sediment throughout the Canadian Arctic (31).

Physical and Chemical Limnological Characteristics. Lake catchment area, elevation, hydraulic residence time (HRT), primary productivity, and total organic carbon are characteristics that may influence the measured SOC fluxes. However, the differences in these characteristics between the two lakes are relatively small (a factor of 0.61 to 2.2) (Table S2, Supporting Information) in comparison to the SOC focus-corrected flux difference (a factor of 1.5 to 24) and are likely not responsible for the observed difference in SOC sediment fluxes. Lake catchment size does not explain the SOC sediment flux difference because the Mills Lake catchment is 30% smaller than the Lone Pine Lake catchment (Table S2) (32). In addition, the HRT of Mills Lake is slightly shorter (3.3 days) than that of Lone Pine Lake (4.4 days) (Table S2). Total nitrogen, total phosphorus, chlorophyll α , and turbidity show that both Mills and Lone Pine Lakes are considered oligotrophic lakes (33). Both lakes exhibit similar productivity as measured by water concentrations of nitrogen, phosphorus, chlorophyll α , and nephelometric turbidity units (Table S2) (32). The total organic carbon concentration in the two sediment cores was also similar (Table S5, Supporting Information).

Previous studies have shown that the distribution of some SOC in mountain regions is strongly temperature-dependent (1, 34). However, the average annual maximum air temperature for the Lone Pine Lake and Mills Lake catchments from 1971 to 2000 on an 800 \times 800 m grid was 7.7 and 7.4 $^{\circ}$ C, respectively (Table S2, Supporting Information) (35). This small temperature difference is likely not responsible for the observed differences in SOC flux.

Mills Lake and Lone Pine Lake have upstream lakes that were included in the lake catchment calculations (Table S2) and may affect the transport of SOC. However, Mast et al. reported that concentrations of *p,p'*-DDE and *p,p'*-DDD in the surficial sediments (0–3 cm) of Mills Lake and Black Lake were very similar (8). Black Lake is located east of the Continental Divide, approximately 2 km upstream of Mills Lake. This suggests that SOC are not preferentially accumulating in Mills Lake due to transport from Black Lake.

Source Regions. Mills Lake and Lone Pine Lake are only 10 km apart, so their distance from source regions is very similar (Figure S1, Supporting Information). However, because these two lakes are on opposite sides of the Continental Divide and approximately 1150 m below the peak elevation, they may receive SOC from different source regions and/or to varying degrees. An east vs west distinction of the Continental Divide difference in total N deposition has been previously shown in Colorado's Front Range (12). Lone Pine Lake and Mills Lake, on the east and west sides of the Continental Divide, receive upslope winds that originate from the western and eastern lowlands, respectively (3, 36). Similar agricultural and urban sources exist on both sides of the Continental Divide. However, the magnitude of emissions is higher on the east side of the Continental Divide (37, 38), which may explain the increased SOC sediment fluxes in Mills Lake relative to those of Lone Pine Lake. A value of 98% of the population within a 150 km radius from Rocky Mountain National Park resides east of the Continental Divide (38). The population in the Colorado counties just east of Rocky Mountain National Park has risen at an exponential rate over the last century (39). In 1997, 92% of the cropland intensity within a 150 km radius of Rocky Mountain National Park was on the east side of the Continental Divide (40). In

addition, 100% of the 1997 dacthal and endosulfan use was also on the east side (41).

Atmospheric PAH concentrations have been shown to be positively correlated with population density (42, 43), and PBDEs are widely used in consumer and commercial products linked to urban areas (30). Like PAHs and PBDEs, PCBs have urban sources (44). The greater Σ PBDE, Σ PAH, and Σ PCB fluxes in Mills Lake relative to those of Lone Pine Lake (Figure 1 and Table S5, Supporting Information) are consistent with the above-mentioned population distribution. The Σ PAH flux in Lone Pine Lake has decreased over the past \sim 35 years (Figure 1F), while the Σ PAH flux in Mills Lake has not. In addition, the Σ PCB flux in Mills Lake has been increasing over the past 15 years, even after the restriction of PCBs in 1977, and the Σ PCB flux in Lone Pine Lake has not. Σ PBDE, Σ PCB, and Σ PAH fluxes and trends within these sediment profiles suggest that the two lake catchments may be receiving SOC from different source regions and/or different magnitudes. Like PBDEs, PCBs, and PAHs, differences in CUP and HUP doubling times, half-lives, and fluxes between the two lakes may be the result of differences in SOC emission-source strengths between the western lowlands and the eastern lowlands.

Snow SOC Concentration, Flux, and Load. The majority of the pesticides in remote Rocky Mountain National Park lake catchments arrive via atmospheric transport from regional sources (7) and are deposited in the form of rain (8), snow (7, 8), and dry deposition. During the winter months, the dominant form of precipitation is snow, which is associated with westerly air masses (8, 12), and snow is an efficient scavenger of SOC from the atmosphere (8, 45–47). To understand the deposition of SOC via annual snowpack, SOC were measured in snow samples, collected in April 2003, from both Mills Lake and Lone Pine Lake catchments (7). In 2003, the Mills Lake snow concentrations of dacthal, *trans*-chlordane, and Σ PAH were not statistically different than those of Lone Pine Lake ($p > 0.05$, using a two-sided *t*-test); however, the Σ endosulfan and dieldrin concentrations were 1.4–1.6 times higher in Mills Lake (Table S5, Supporting Information). In a different study of the same Front Range area, from 1992 to 1997, snow concentrations of NH_4^+ showed no difference between sites east and west of the Continental Divide (12).

By multiplying the snow SOC concentrations (ng m^{-3}) by the snow depth in snow–water equivalents (SWE) (cm), we calculated the SOC snow flux ($\text{ng m}^{-2} \text{ year}^{-1}$) (7). The ratio of the Mills Lake to Lone Pine Lake SWE in the 2003 snow samples was 2.3. In 2003, the Σ endosulfan, dacthal, TC, dieldrin, and Σ PAH snow flux to Mills Lake catchment was greater than that of Lone Pine Lake by a factor of 2.2–4.3 (Table S5, Supporting Information).

The ecosystem SOC load from snow for 2003 was calculated by multiplying the snow flux by the lake catchment area (Table S5, Supporting Information). The ratio of the Mills Lake to Lone Pine Lake catchment area was 0.71 (Table S2, Supporting Information). The SOC, which consistently had higher fluxes in Mills Lake 2003 surficial sediment, also had higher snow fluxes and ecosystem loads (by a factor of 1.6–3.1) during the 2003 snow accumulation season (Table S5). This suggests that the difference in SOC sediment flux between the two lakes may be partially explained by SOC snow flux and load. In addition, the 2003 lake water concentrations of Σ endosulfans and dacthal, which were collected at the same time as the sediment cores, were greater in Mills Lake than those of Lone Pine Lake by factors of 4.0 and 1.5, respectively (Table S5).

Precipitation Rates. During the late spring and summer months, rain is the dominant form of precipitation to Rocky Mountain National Park, and air masses arrive from the south and east (8). The deposition of SOC in the summer months

was measured in Lone Pine Lake and Mills Lake catchments. However, in 2002, it was determined that ~85% of the annual atmospheric CUP deposition to Bear Lake occurred via rain during the summer months (8). Bear Lake resides on the east side of the Continental Divide, 3 km north and ~135 m lower in elevation than Mills Lake. In addition, a significant portion of Lock Vale catchment's total N deposition occurred during the summer from upslope winds originating from the east (12). The Loch Vale catchment resides on the east side of the Continental Divide, 1.5 km north and ~130 m higher in elevation from Mills Lake. These previous studies emphasize the potential importance of SOC deposition to Rocky Mountain National Park during the summer months as well as the potential for SOC to undergo atmospheric transport to Rocky Mountain National Park from source regions to the east.

Because there is no long-term measured precipitation data for Mills Lake and Lone Pine Lake, the parameter-elevation regressions on independent slopes model (PRISM), was used to estimate the average annual precipitation to Lone Pine Lake and Mills Lake from 1971 to 2000 on an 800 × 800 m grid (35). The annual average precipitation rates for the Lone Pine Lake and Mills Lake catchments from 1971 to 2000 were 97.6 cm/year and 107.1 cm/year, respectively (Table S2, Supporting Information). For the years that correspond to the five paired sediment intervals (2003, 1990, 1987, 1974, and 1954), a 2 × 2 km grid was used to estimate the average annual precipitation rate because the 800 × 800 grid data was only available from 1971 to 2000. The total precipitation estimates for April through September (summer) and October through March (winter) in these years were similar (Table S5). Over the five paired sediment intervals, the average summer and winter precipitation lake catchment ratios were 0.97 and 1.0, respectively. The model estimated a slight increase in precipitation at Mills Lake during the 2002–2003 (October thru March) winter season, with a Mills Lake/Lone Pine Lake precipitation ratio of 1.1 (Table S5, Supporting Information). The PRISM data suggests that differences in long-term summer, winter, and annual precipitation do not account for differences in historical SOC deposition to the two lakes.

The significant differences in the current and historical deposition of PBDEs, CUPs, HUPs, PCBs, and PAHs to Mills Lake and Lone Pine Lake were not explained by differences in lake catchment characteristics or precipitation and were partially explained by snow SOC flux and load. This suggests different relative contributions from SOC source regions to the two lakes. Similar to atmospheric N deposition in this region, a majority of the SOC deposition to the Mills Lake catchment may arrive via upslope winds from the east in the warm summer months when SOC source strengths are highest. This is counter to prevailing westerly winds, suggesting that lake catchment location with respect to topographic barriers, such as the Continental Divide, influences SOC deposition in high-elevation ecosystems.

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Supporting Information Available

Detailed information about the chemicals used, sample collection, physical and elemental analysis, SOC extraction, isolation and recoveries, quantification and validation, PRISM, and analysis and quality control; information about sample sites, radionuclides fallout, doubling times, half-lives, and ratios of select contaminants vs depth is also provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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