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Sources and Deposition of Polycyclic Aromatic Hydrocarbons to Western U.S. National Parks

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Abstract

Seasonal snowpack, lichens, and lake sediment cores were collected from fourteen lake catchments in eight western U.S. National Parks and analyzed for sixteen polycyclic aromatic hydrocarbons (PAHs) in order to determine their current and historical deposition, as well as to identify their potential sources. Seasonal snowpack was measured to determine the current wintertime atmospheric PAH deposition; lichens were measured to determine the long-term, year around deposition; and the temporal PAH deposition trends were reconstructed using lake sediment cores dated using ²¹⁰Pb and ¹³⁷Cs. The fourteen remote lake catchments ranged from low-latitude catchments (36.6° N) at high elevation (2900 masl) in Sequoia National Park, CA to high-latitude catchments (68.4° N) at low elevation (427 masl) in the Alaskan Arctic. Over 75% of the catchments demonstrated statistically significant temporal trends in ΣPAH sediment flux, depending on catchment proximity to source regions and topographic barriers. The ΣPAH concentrations and fluxes in seasonal snowpack, lichens, and surficial sediment were 3.6 to 60,000 times greater in the Snyder Lake catchment of Glacier National Park than the other 13 lake catchments. The PAH ratios measured in snow, lichen, and sediment were used to identify a local aluminum smelter as a major source of PAHs to the Snyder Lake catchment. These results suggest that topographic barriers influence the atmospheric transport and deposition of PAHs in high-elevation ecosystems and that PAH sources to these national park ecosystems range from local point sources to diffuse regional and global sources.

INTRODUCTION

The U.S. National Parks contain exceptionally diverse ecosystems with unique plant and animal species (1) and U.S. government regulations, such as the Organic Act, Clean Air Act, Wilderness Act, and the National Environmental Policy Act, have instated the U.S

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Supporting Information Available Detailed information about the sample sites, radionuclide activity, PAH composition for each site, doubling times, half-lives, ratios of select PAHs, PCA scores and loadings, and the physical and chemical limnological characteristics of each lake site. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Department of the Interior's National Park Service as steward of U.S. National Parks (2). In 2002, the U.S. National Park Service initiated the Western Airborne Contaminant Assessment Project (WACAP) to investigate the deposition of semi-volatile organic compounds (SOCs), including polycyclic aromatic hydrocarbons (PAHs), to remote ecosystems in western U.S. National Parks (2,3).

PAHs are produced from the incomplete combustion of fossil fuels and biomass decay/burning and some PAHs pose risks to human and ecosystem health because of their toxicity (4,5). Hafner et al 2005 reported that atmospheric PAH concentrations are positively correlated with human population density (5). PAHs are deposited to remote high-elevation and/or high-latitude ecosystems via air-surface exchange, dry deposition and/or wet deposition in the form of snow and rain (6-8). As a result of colder temperatures in these ecosystems, PAH degradation and revolatilization to the atmosphere is decreased, potentially resulting in elevated concentrations (6).

The objectives of this study were to 1) determine the spatial and temporal PAH distribution patterns using PAH concentrations and fluxes measured in seasonal snowpack, lichen, and sediment cores collected from 14 U.S. national park lake catchments and 2) identify potential PAH sources to these remote ecosystems using the PAH profile and isomer ratios.

EXPERIMENTAL SECTION

Lacustrine Catchments

From 2003 to 2005, sediment cores were collected from oligotrophic lakes in Sequoia National Park (Sequoia) (Pear Lake and Emerald Lake), CA, Rocky Mountain National Park (Rocky) (Lone Pine Lake and Mills Lake), CO, Olympic National Park (Olympic) (Hoh Lake and PJ Lake), WA, Mt. Rainier National Park (Rainier) (Golden Lake and LP19), WA, Glacier National Park (Glacier) (Snyder Lake and Oldman Lake), MT, Denali National Park (Denali) (Wonder Lake and McLeod Lake), AK, Gates of the Arctic National Park and Preserve (Gates) (Lake Matcharak), AK, and Noatak National Preserve (Noatak) (Burial Lake), AK (Figure S1) as part of WACAP. Lichen and sediment cores were collected from Sequoia and Rocky in 2003, Noatak, Gates, and Denali in 2004, and Glacier, Rainier, and Olympic in 2005. Lake location, physical and chemical limnological characteristics, the ratio of these characteristics within a national park, and site description are provided in Table S1 and Figure S1. In 2003 and 2004, seasonal snowpack samples were collected from each lake catchment (12). However, there was insufficient seasonal snowpack accumulation in Olympic for sample collection (9).

Analytes, Surrogates, and Internal Standards Measured

The PAHs measured included acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), retene, benzo[a]anthracene (BaA), chrysene and triphenylene (CT), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA), and benzo[ghi]perylene (BghiP). The isotopically-labeled recovery surrogates included d_{10} -fluorene, d_{10} -phenanthrene, d_{10} -pyrene, d_{12} -triphenylene, d_{12} -benzo[a]pyrene, d_{12} -benzo[ghi]perylene. The isotopically-labeled internal standards were d_{10} -acenaphthene, d_{12} -benzo[k]fluoranthene, and d_{10} -fluoranthene. All standards were acquired from the EPA repository or purchased from Chem Services Inc (West Chester, PA), Restek (Bellefonte, PA), Sigma-Aldrich Corp (St. Louis, MO), or AccuStandard (New Haven, CT).

Sample Collection and Analysis

Snow and sediment samples were collected and analyzed by GC/MS as previously described (9-11). Briefly, seasonal snowpack (50 kg) was collected at the end of the snow accumulation season (March or April) into polytetrafluoroethylene bags from a snow pit. Snow samples were extracted using a modified hydrophobic/hydrophilic Speedisk (10). Sediment and lichen samples were extracted using accelerated solvent extraction (11). PAHs were isolated and matrix interferences were removed using gel permeation chromatography, followed by silica gel chromatography and analyzed by GC/MS using previously published methods (9-11). A complete description of the methods used for the three matrices is provided in the Supporting Information. PAH concentrations below the quantification limit were assigned zero values. Focusing factors (FF) were calculated for each sediment core in order to correct for sediment focusing. These details are provided in the Supporting Information.

PRISM

The Parameter-elevation Regressions on Independent Slopes Model (PRISM) was used to estimate the average annual total precipitation and annual maximum temperature for each lake catchment from 1971-2000, at 800×800 m resolution (Table S1) (12). PRISM was designed to incorporate digital elevation models and station data to account for orographic precipitation effects and has been used throughout the Pacific Northwest and Colorado (12,13).

RESULTS AND DISCUSSION

PAH Spatial Distribution

Previous studies have shown a significant positive correlation between atmospheric PAH concentrations and human population density (5,14,15). However, there was no correlation between seasonal snowpack or lichen Σ PAH concentration and population density within 150 km of the eight parks we studied (Figure S16). Figure S16 shows that Glacier, and the Snyder Lake catchment in particular, was an outlier due to relatively high PAH concentrations and moderate surrounding population density. This suggests that additional PAH sources may be responsible for the relatively high PAH deposition in the Snyder Lake Catchment.

The 2003 seasonal snowpack Σ PAH flux is shown in Figure 1 for all fourteen lake catchments. In Glacier, the Snyder Lake catchment snowpack Σ PAH flux was 7.7 times higher than the Oldman Lake catchment and 40 to 60,000 times higher than the other twelve WACAP lake catchments (Figure 1). The lowest seasonal snowpack Σ PAH fluxes were all measured in Alaska at Wonder Lake catchment in Denali ($0.005 \mu\text{g m}^{-2} \text{y}^{-1}$), McLeod Lake catchment in Denali ($0.03 \mu\text{g m}^{-2} \text{y}^{-1}$), and Lake Matcharak catchment in Gates ($0.1 \mu\text{g m}^{-2} \text{y}^{-1}$). The difference in the PAH profile among the 14 lake catchments was investigated using the 2003 and 2004 seasonal snowpack samples (Figure S17). The most frequently detected PAHs were PHE, FLA, PYR, retene, BbF, BkF, BeP, BaP, IcdP, and BghiP. This provides evidence that snow is an efficient scavenger of both gas-phase and particle-phase PAHs.

The seasonal snowpack PAH profiles in Burial Lake and Lake Matcharak catchments in Noatak and Gates were significantly different from both Wonder Lake and McLeod Lake catchments in Denali (Figure S17). This may suggest that the Noatak and Gates sites are impacted by different PAH sources than the Denali sites. In 2003 at Alert, an Canadian Arctic site, higher atmospheric PAH concentrations were measured during December and January (16). The higher PAH concentrations during the winter months was attributed to increased frequency of long-range atmospheric transport events and increased PAH

emission from East Asia, Northern Europe, and North America (16). Burial Lake catchment had a snowpack Σ PAH flux similar to Sequoia, Rocky, and Rainier (Figure 1) and was ~40 times higher than the Σ PAH flux measured in Lake Matcharak. Burial Lake may be impacted to a greater extent by winter long-range atmospheric transport than Lake Matcharak.

The lichen Σ PAH concentrations were normalized to lichen lipid content to account for possible accumulation difference between the nine different lichen species collected across the eight national parks/preserves (Figure 1). Similar to seasonal snowpack, lichen Σ PAH concentrations were highest in the Snyder Lake catchment in Glacier, second highest in Oldman Lake catchment in Glacier, and lowest in the Alaskan lake catchments (Figure 1). The most frequently detected PAHs in the lichen samples were FLO, PHE, FLA, PYR, retene, CT, and BaA.

Surficial sediment Σ PAH focus-corrected fluxes ranged four orders of magnitude and only McLeod Lake in Denali had surficial sediment concentrations below the quantification limit (Figure 1). Similar to seasonal snowpack flux and lichen concentrations, the Snyder Lake surficial sediment Σ PAH flux in Glacier was 3.6 to 3400 times higher than the other thirteen lake catchments, followed by Mills Lake in Rocky and Oldman Lake in Glacier (Figure 1) (2,11). The lowest surficial sediment Σ PAH fluxes were measured in the Alaskan lakes. The Lake Matcharak surficial sediment Σ PAH focus-corrected flux was ~17 times higher than Burial Lake. This trend is the opposite of the snowpack Σ PAH flux measurements and suggests that the snowpack Σ PAH flux may vary significantly year to year at these Alaskan sites. The surficial sediment PAH profile varied among the western U.S. National Parks however, the most frequently detected PAHs were FLA, PYR, BaA, CT, BbF, BkF, BeP, and BaP (Figure 2).

PAH Temporal Trends and Sources

Using a linear least-squares regression model, eleven of the fourteen sediment cores had statistically significant ($p < 0.05$) temporal trends in Σ PAH flux (Figure 2 and S18). Six of the eleven sediment cores demonstrated Σ PAH flux half-lives (decreasing flux with time), ranging from 15.3 to 28.3 yrs, and five cores demonstrated Σ PAH doubling times (increasing flux with time), ranging from 10.5 to 112.6 yrs.

The arctic lakes, Burial Lake and Lake Matcharak, both had Σ PAH doubling times, but different rates of increase (Figure S18). Lake Matcharak had the highest Σ PAH doubling time (10.5 ± 0.01 yrs) of all of our sites. In contrast, the Σ PAH flux in Wonder Lake in Denali had a half-life of 15.3 ± 0.02 yrs. In addition, the Alaskan arctic catchments (Burial Lake and Lake Matcharak) and the Denali catchments (Wonder Lake and McLeod Lake) had significantly different sediment core PAH profiles. The Burial Lake sediment core PAH profile was composed of both low and high molecular weight PAHs, including ACY, ACE, PHE, B[b]F, and B[ghi]P, while the Lake Matcharak sediment core PAH profile was dominated by low molecular weight PAHs, primarily PHE and FLA (Figure 2D). In Lake Matcharak, the PHE flux represented ~75% of the Σ PAH flux. However, it was only detected in the top four intervals dating back to the early 1970s (Figure 2).

The differences in temporal Σ PAH deposition and PAH profiles further suggest that these sites may be exposed to different PAH sources (Figure 2 and S18). One-day air mass back trajectory clusters were calculated for Gates and Noatak, as well as Denali, using the National Oceanic and Atmospheric Administration's ARL HYSPLIT 4.0 model (FNL) (3). The Gates and Noatak clusters extended to the west over eastern Russia, while their clusters to the east extend over parts of the Prudhoe Bay oil fields (2). The Prudhoe Bay oil fields are the largest oil fields in North America and began production in 1977 (17). The Denali

clusters did not overlap significantly with the Gates or Noatak clusters and extend over more populated areas of Alaska (2).

Rocky, Rainier, and Glacier each had one lake catchment sediment core that showed an increase in PAH focus-corrected flux overtime (22.6, 62.3, and 48.9 yrs, respectively) and a lake catchment sediment core that showed a decrease (28.3, 15.4, and 46.8 yrs, respectively) (Figure S18). The spatial and temporal variation in SOC deposition within a park has been shown to be dependent on the proximity of the site to source regions and topographic barriers (11).

Rainier and Olympic are both less than 100 km from Seattle's metropolitan area where more than 3 million residents live with 150 km of these national parks (Figure S1). Olympic is located west of Seattle, while Rainier is located southeast of Seattle (Figure S1). In Olympic, Hoh Lake is located on the northwest Pacific Coast side, while PJ Lake is located on the northeast Puget Sound side. These two Olympic lakes are separated by only ~30 km and 50 m elevation (Table S1). However, the Hoh Lake and PJ Lake surficial sediment Σ PAH focus-corrected fluxes were $0.5 \mu\text{g m}^{-2} \text{y}^{-1}$ and $23 \mu\text{g m}^{-2} \text{y}^{-1}$, respectively (Figure 1). PJ Lake has received, on average over the past ~50 years, ten times higher Σ PAH deposition than Hoh Lake (Figure 2). This may be because PJ Lake is on the side of the Olympic range closest to the Seattle metropolitan area and closest to the PAH emissions from nearby ship traffic in the Strait of Juan de Fuca (18).

The PAH profile of coal, gasoline and diesel combustion sources have been identified (19). The PAH profile for the Seattle metropolitan area is dominated by 3-ring PAHs, primarily PHE and FLA, because these are the primary PAH emitted from vehicular traffic (19). The Rainier annual snowpack PAH profiles, from both Golden Lake and LP19 catchments, were very similar and were dominated by higher-molecular weight PAHs (5 and 6 ring PAHs) (Figure S17E). This suggests that the Seattle metropolitan area is not the only source of PAHs to Rainier and may include emissions of higher molecular weight PAHs from a coal-fired power plant ~85 km west of Rainier and/or trans-Pacific transport (20). The Golden Lake sediment Σ PAH half-life was 15.4 ± 0.01 yrs from 1951 to 2005 ($r^2=0.86$, $p<0.01$), while the LP19 lake doubling time was 48.8 ± 0.01 yrs from 1903 to 2000 ($r^2=0.90$, $p<0.001$) (Figure S18E). This difference suggests that Rainier is impacted by multiple PAH sources and/or potential seasonal sources.

PAH Deposition in Glacier

Based on the sediment record over the past ~50 years, Snyder Lake in Glacier (located west of the Continental Divide) has received, on average, 8.5 times higher Σ PAH deposition than Oldman Lake in Glacier (located east of the Continental Divide) (Figure 2). In addition, the Snyder Lake surficial sediment Σ PAH flux ($185 \mu\text{g m}^{-2} \text{y}^{-1}$) was approximately 5.3 times higher than Oldman Lake ($35 \mu\text{g m}^{-2} \text{y}^{-1}$) (Figure 1). The Snyder Lake sediment Σ PAH half-life was 46.8 ± 0.01 yrs from 1967 to 2005 ($r^2=0.87$, $p<0.01$), while the Oldman Lake sediment doubling time was 48.9 ± 0.01 yrs from 1906 to 2005 ($r^2=0.90$, $p<0.001$) (Figure S18G). In addition, the Glacier Σ PAH concentrations in seasonal snowpack and lichens and surficial sediment flux were a factor of 7.7, 32.8, and 5.3 higher, respectively, in the Snyder Lake catchment relative to the Oldman Lake catchment (Figure 1).

PAHs are deposited in Glacier from both anthropogenic and biogenic incomplete combustion sources. Potential PAH sources to Glacier include 208,000 people living within 150 km of Glacier (21), approximately 2,000,000 park visitors driving approximately 500,000 automobiles each year, biomass burning, aluminum smelting operation, and oil and natural gas drilling operations (Figure S19) (1). The relatively modest population surrounding Glacier does not account for the high PAH concentrations measured in the

Snyder Lake and Oldman Lake catchments (Figure S16). The doubling time of the population growth within 150 km of the west side of the Continental Divide (accounting for ~78% of the total population surrounding Glacier) was 78 years from 1960 to 2000 (21). The population increase on the west side of the Continental Divide does not explain the decrease in Σ PAH flux in Snyder Lake sediment. Visitors travel through Glacier during the summer months on the Going-to-the-Sun Road which is approximately 5 and 20 km from Snyder and Oldman lakes, respectively. Because the seasonal snowpack accumulates between October and April when Going-to-the-Sun Road is closed, PAH emissions from automobiles can be eliminated as a major source to Glacier's seasonal snowpack. In addition, recreational snowmobiling is prohibited in Glacier (22).

In order to investigate potential PAH emissions from biomass burning, the MODIS Web Fire Mapper was used to visually identify high biomass burning time periods in Glacier from 1999 to 2005 (23). This program uses satellite images of mid-infrared radiation from fire emissions and a unique algorithm to identify fires (23). During the 1999 to 2005 time period, fires burned in Glacier only during the summer months. The magnitude and number of fire events in Glacier varied widely from year to year, with the greatest fire intensity from 2001 to 2006 occurring during the summer of 2003, after seasonal snowpack accumulation (23). These data suggest that large-scale biomass burning did not significantly contribute to the PAH concentrations in Glacier's seasonal snowpack.

Oil and gas wells have been drilled in southwest Alberta, Canada, located within 150 km of Glacier on the east side of the Continental Divide, since the 1920s (24). Waste gases from these wells are flared for safety reasons during well testing (24). In 2000, approximately 5,300 gas flares were operational in Alberta and PAH concentrations in air near the flares were similar to large-scale industrial areas (25). Since 1983, the number of oil and gas flares in Alberta has increased from 3,600 to 15,700, with a doubling time of 9.5 yrs ($r^2=0.72$, $p<0.001$) (26). Three hundred and fifty well rigs were located within 150 km of Glacier in June 2007 and 97% of these were located east of the Continental Divide (26). The increase in the number of oil and gas flares overtime may explain, in part, the Σ PAH flux doubling time (48.9 ± 0.01 yrs) measured in Oldman Lake. The difference in PAH temporal deposition trends between Snyder lake (half-life of 46.8 ± 0.01 yrs) and Oldman lake (doubling time of 48.9 ± 0.01 yrs) may be due to differences in PAH source regions and the Continental Divide serving as a topographic barrier.

A dam-powered Söderberg aluminum smelter became operational in Columbia Falls, MT in 1955 (27). The smelter resides on the Flathead River, approximately 10 km southwest of Glacier on the west side of the Continental Divide and approximately 45 km southwest of Snyder Lake (Figure S19 and S20). The outflow from Snyder Lake forms a tributary to the Flathead River. Söderberg aluminum smelters can be significant local sources of hydrogen fluoride and PAHs (28,29) because of the use of coal tar in the smelting process. According to U.S. EPA records, this smelter released, on average, ~65 tons of hydrogen fluoride per year from 1999 to 2004 and, on average, ~14 tons of PAH per year from 1999 to 2005 (30).

In 1970, fluoride concentrations were measured in foliage, collected in a radial pattern centered on the aluminum smelter, and used to produce fluoride concentration isolines that extended up the valley toward Snyder Lake (31) (Figure S20). This previous study suggests that fluoride emissions from the smelter were transported and deposited in the Snyder Lake catchment. These same upslope winds likely also transported and deposited PAH emissions from the smelter to the Snyder Lake catchment.

The individual PAH ratios have been used to identify PAH sources in the environment (32-34). The $IcdP/(IcdP+BeP)$, $IcdP/(IcdP+BghiP)$, and $FLA/(FLA+PYR)$ ratios remain

fairly constant from emission to deposition in the environment because these higher molecular weight PAHs are typically sorbed to atmospheric particles and have similar physical and chemical properties (32,35,36). Uncertainty in this source tracking technique includes overlap in the PAH profile of multiple emission sources (32). The IcdP/(IcdP+BeP) ratio from gasoline combustion in motor vehicles is 0.74 (33) (Figures S21A and S22) and the IcdP/(IcdP+BghiP) ratio from the combustion of wood is 0.64 ± 0.07 (Figures S21B and S22) (32). The ratio of IcdP/(IcdP+BeP) and IcdP/(IcdP+BghiP) from the combustion of pine wood in a fireplace is 0.53 and 0.54, respectively (Figure S21) (37). In addition, Söderberg aluminum smelters emit an IcdP/(IcdP+BeP) ratio, IcdP/(IcdP+BghiP) ratio, and FLA/(FLA+PYR) ratio of 0.39, 0.42, and 0.58, respectively (Figures S21 and S22) (29,38). It is important to acknowledge that PAH ratios do not provide definitive identification of sources. However, in a weight of evidence approach, these ratios can be used to help identify and/or dismiss potential sources.

The 2003 Snyder Lake catchment Σ PAH snow flux ($310 \mu\text{g m}^{-2} \text{y}^{-1}$) was 7.7 times higher than the Oldman Lake catchment flux ($40 \mu\text{g m}^{-2} \text{y}^{-1}$) (Figure 1). In addition, the 2003 Snyder Lake seasonal snowpack IcdP/(IcdP+BeP) and IcdP/(IcdP+BghiP) ratios were 0.40 and 0.43, while the same ratios in Oldman Lake seasonal snowpack were 0.49 and 0.54, respectively (Figures S21 and S22). The 2003 and 2004 Snyder Lake catchment snowpack PAH ratios were similar to the ratios calculated from the Söderberg aluminum smelter emissions, while the Oldman Lake catchment snowpack PAH ratios were similar to the ratios calculated from petroleum combustion and pine wood combustion in residential fireplaces (Figures S21 and S22). The retene flux, a marker for softwood combustion, in the 2003 Oldman Lake snowpack ($1.5 \mu\text{g m}^{-2} \text{y}^{-1}$) was similar to Snyder Lake catchment ($1.2 \mu\text{g m}^{-2} \text{y}^{-1}$). The retene flux is likely the result of wood combustion for heating and/or manufacturing (23).

The Snyder Lake 2004 snowpack Σ PAH flux ($100 \mu\text{g m}^{-2} \text{y}^{-1}$) was approximately 33% of the 2003 Σ PAH flux ($310 \mu\text{g m}^{-2} \text{y}^{-1}$). In March 2003, after the 2003 snow accumulation period, the operation of the aluminum smelter reduced from 60% to 20% capacity (39). In 2002, the aluminum smelter emitted 15.1 tons of PAHs to the atmosphere (operating at 60% capacity) and, in 2004, the smelter emitted 5.0 tons of PAHs (operating at 20% capacity) (30). The reduction in smelter operation over this time period is consistent with the reduction in PAH emissions reported to USEPA and the reduction in Σ PAH flux in the Snyder Lake seasonal snowpack. This suggests a direct link between smelter operations and the Snyder Lake snowpack Σ PAH flux. In addition, the Snyder Lake seasonal snowpack IcdP/(IcdP+BeP) ratio remained fairly constant from 2003 to 2004 (Figure S21A) but the IcdP/(IcdP+BghiP) ratio increased from 0.43 (in 2003) to 0.49 (in 2004) (Figure S21B). The increase in the IcdP/(IcdP+BghiP) ratio from 2003 to 2004 may be the result of the smelter emissions contributing less to the overall PAH burden in the Snyder Lake catchment due to reduced smelter operations.

In 2004 in Glacier, *Platismatia glauca* was sampled in the Snyder Lake catchment, while *Letharia vulpine* was sampled in the Oldman Lake catchment. These lichens were collected < 3 km from the Going-to-the-Sun Road and were exposed to PAH sources in both summer and winter. The IcdP/(IcdP+BeP) ratio in the Snyder Lake catchment lichen was 0.41, which closely matched the 2003 Snyder Lake snowpack IcdP/(IcdP+BeP) ratio (0.40) and the Söderberg aluminum smelter emissions (0.39) (Figure S21A). BeP was not detected in Oldman Lake catchment lichens and, therefore, the IcdP/(IcdP+BeP) ratio could not be calculated.

The 1893 Snyder Lake sediment core interval, which was prior to the aluminum smelter becoming operational, had IcdP/(IcdP+BeP) and IcdP/(IcdP+BghiP) ratios of 0.49 and 0.55,

respectively (Figure S21). After the aluminum smelter became operational in 1955, the Snyder Lake sediment core IcdP/(IcdP+BeP) ratio dropped to 0.35 ± 0.05 and the IcdP/(IcdP+BghiP) ratio dropped to 0.48 ± 0.05 . The Snyder Lake surficial sediment IcdP/(IcdP+BeP) and IcdP/(IcdP+BghiP) ratios were 0.38 and 0.50, respectively (Figure S21). In the Oldman Lake sediment core, IcdP was only detected in the 1906 and 2005 intervals. In the 1906 Oldman Lake sediment interval, the IcdP/(IcdP+BeP) and IcdP/(IcdP+BghiP) ratios were 0.66 and 0.50, respectively, while the surficial sediment ratios were 0.45 and 0.51, respectively (Figure S21). In addition, the Snyder Lake sediment core retene flux was not correlated with the Σ PAH, BeP, IcdP, or BghiP flux in the same sediment core ($p > 0.05$). However, these fluxes were correlated in the Oldman Lake sediment core ($p < 0.05$). This suggests that PAH emissions from biomass burning were not a major source of PAHs to the Snyder Lake catchment (Figure S23).

The individual PAH fluxes in all WACAP lake sediment cores were compared using Principal Component Analysis (PCA) (S-PLUS version 7.0, Insightful, Seattle, WA) (Figure S24). To account for the scaling sensitivity of the multivariate analysis, the individual PAH fluxes were standardized by subtracting their mean flux and dividing by the standard deviation of the individual PAH flux (40). The PCA results showed that PC1 and PC2 accounted for 64.4% and 9.6% of the total variance, respectively. The PCA score plots (PC1 versus PC2) show that the sediment intervals can be divided into two different clusters (Figure S24). All of the Snyder Lake sediment core intervals prior to the aluminum smelter becoming operational in 1955 formed one cluster, while all of the other WACAP sediment core intervals, including the 1898 Snyder Lake interval, formed a separate and distinct second cluster (Figure S24). The PCA loadings also indicated a difference in the PAH composition of the two different clusters, with higher molecular weight PAHs dominating in the post-1955 Snyder Lake cluster (Figure S24). Together, the changes in the seasonal snowpack Σ PAH flux with smelter operation over time, the PAH ratios, and the PCA results suggest that the aluminum smelter's PAH emissions have contributed to Snyder Lake catchment's total PAH load since it began operation in 1955. This conclusion is supported by known smelter PAH emission ($\sim 14 \text{ tons } \text{y}^{-1}$), as well as regional airflow patterns mapped out by fluoride measurements (Figure S20) (30).

PAH Source Apportionment in Glacier National Park

PAH ratios can be used to estimate the contribution of different sources to the Σ PAH concentration or flux (41). However, a highly accurate assessment of the different source contributions is difficult because the individual PAH are emitted from multiple combustion source types. The PAH source apportionment can be further complicated because some PAH sources are seasonal, such as automobile traffic through the park in summer and the combustion of wood in residential homes for heating in the winter. Nevertheless, PAH source apportionment can provide direction for further studies.

In order to estimate the relative contributions of different PAH sources to Glacier, we assumed that, during the winter months when "Going-to-the-Sun Road" was closed, automobile traffic through the park was 0% (relative to summer) and wood combustion from home heating was 100% (relative to summer). The 2003 (when the smelter was operating at 60% capacity) Snyder Lake catchment snowpack IcdP/(IcdP+BeP) and IcdP/(IcdP+BghiP) ratios were slightly higher than the same ratios measured from aluminum smelter emissions (29,38), but less than the same ratios measured from wood combustion in residential fireplaces (Figure S21) (37). This suggests that both of these sources contribute PAHs to the Snyder Lake catchment in winter. Using a simple numerical solution x and $x-1$ algebraic equation (where x = fraction from the smelter and $x-1$ = fraction from local fireplaces) and the IcdP/(IcdP+BeP) and IcdP/(IcdP+BghiP) ratios measured from an aluminum smelter, residential fireplaces, and in the 2003 Snyder Lake catchment snowpack (smelter operating

at 60% capacity), we roughly estimate that approximately 92% of the PAHs in the 2003 Snyder Lake snowpack originated from the smelter and approximately 8% originated from wood combustion. Using the same simple numerical solution for the 2004 Snyder Lake snowpack (smelter operating at 20% capacity), we roughly estimate that approximately 71% of the PAHs in the 2004 Snyder Lake snowpack originated from the smelter and approximately 29% originated from wood combustion.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

The 2003 snowpack ΣPAH flux, lichen ΣPAH concentration ($\mu\text{g}/\text{g}$ lipid), and surficial sediment ΣPAH focus-corrected flux for all WACAP lake catchments. Snowpack samples were not collected at Hoh Lake and PJ Lake because of reduced snowpack. nd indicates not detected and nm indicates not measured because samples were not available for collection. Lichen and sediment samples were collected from Emerald, Pear, Mills, and Lone Pine Lake in 2003, McLeod, Wonder, Matcharak, and Burial Lake in 2004, and LP19, Golden, Hoh, PJ, Oldman, and Snyder in 2005.

Figure 2. Lake sediment core PAH focus-corrected flux ($\mu\text{g m}^{-2} \text{y}^{-1}$) profiles. Dashed lines (—) indicate when the local smelter became operational in 1955 on the west side of Glacier National Park.