Atmospheric Deposition of Current-Use and Historic-Use Pesticides in Snow at National Parks in the Western United States

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The United States (U.S.) National Park Service has initiated research on the atmospheric deposition and fate of semi-volatile organic compounds in its alpine, sub-Arctic, and Arctic ecosystems in the Western U.S. Results for the analysis of pesticides in seasonal snowpack samples collected in spring 2003 from seven national parks are presented herein. From a target analyte list of 47 pesticides and degradation products, the most frequently detected current-use pesticides were dacthal, chlorpyrifos, endosulfan, and γ-hexachlorocyclohexane, whereas the most frequently detected historic-use pesticides were dieldrin, α-hexachlorocyclohexane, chlordane, and hexachlorobenzene. Correlation analysis with latitude, temperature, elevation, particulate matter, and two indicators of regional pesticide use reveal that regional current and historic agricultural practices are largely responsible for the distribution of pesticides in the national parks in this study. Pesticide deposition in the Alaskan parks is attributed to long-range transport because there are no significant regional pesticide sources. The percentage of total pesticide concentration due to regional transport (%RT) was calculated for the other parks. %RT was highest at parks with higher regional cropland intensity and for pesticides with lower vapor pressures and shorter half-lives in air.

Introduction

There is mounting evidence that pesticides and other semi-volatile organic compounds (SOCs) are accumulating in remote high-elevation and high-latitude ecosystems throughout the world (1−3). The presence of pesticides in remote ecosystems is of concern because many pesticides are carcinogenic or estrogenic (4) and, therefore, pose potential threats to sensitive aquatic and terrestrial ecosystems, and to humans that consume biota from them (2, 5). The sequence

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of processes resulting in the transport of SOCs to these remote "cold" regions of the earth are (a) volatilization from relatively warm source locations, (b) atmospheric transport, and (c) wet or dry deposition upon encountering decreased air temperatures (1). The tendency for SOCs to preferentially partition to surfaces as temperatures decrease is known as "cold condensation" and has been observed with temperature gradients on both global (6) and regional (7, 8) scales. Although pesticide deposition has been reported in the Sierra Nevada Mountains in California (9−11) and in the Rocky Mountains in Colorado (12), little is known about the occurrence, distribution, or sources of pesticides in alpine, sub-Arctic, and Arctic ecosystems in the Western U.S.

The U.S. National Park Service, which has a legal mandate to protect the ecosystems under its jurisdiction (13, 14), initiated the Western Airborne Contaminants Assessment Project (WACAP) in 2002 with the general objective of gaining information about atmospherically transported pesticides and other SOCs in its high-elevation and high-latitude national parks, which are located in the Western U.S. (15). While SOCs are being quantified in a number of environmental matrices, this article focuses on pesticides in seasonal snowpack samples collected from WACAP sites in 2003. The seasonal snowpack is an important medium because it contains an integrated record of atmospheric deposition during the snow-accumulation period. Moreover, snow is an efficient scavenger of both particle-bound and gas-phase pesticides from the atmosphere (3, 16) and snowfall provides the majority of the annual precipitation in alpine, sub-Arctic, and Arctic ecosystems in the Western U.S. The fate of pesticides in an aging or melting snowpack varies according to the physical and chemical properties of the specific pesticide, the properties of the snowpack, and climatological conditions (17). Modeling results predict temporary pulses of increased pesticide concentrations in air, water, and soil during spring snowmelt (17).

Three specific objectives of WACAP were addressed by the work described herein. The first was to quantify and document the distribution of pesticides, if present, in seasonal snowpack samples from seven national parks in the Western U.S. The target analyte list was composed of 47 pesticides and pesticide degradation products and included both current-use and historic-use pesticides (defined here as those that are and are not currently registered as pesticides in the U.S., respectively). The second objective was to investigate potential factors that may influence the distribution of pesticides in national parks in the Western U.S. The investigated factors were latitude, mean winter air temperature, elevation, particulate matter, and two indicators of regional pesticide use (cropland intensity and current-use pesticide application within given radii of parks). The third objective was to estimate the percentage of total concentration due to regional sources versus long-range sources for each of the most frequently detected current and historic-use pesticides detected at each park.

Experimental Section

Sample Sites. Seasonal snowpack samples were collected at Sequoia National Park (NP), Rocky Mountain NP, Mount Rainier NP, Glacier NP, Denali NP, Noatak National Preserve, and Gates of the Arctic NP and Preserve (Figure 1). Although the WACAP research plan (15) prescribes sampling at Olympic NP, seasonal snowpack samples were not collected there in 2003 due to the lack of snow at sampling time. One to three sites were selected for sampling at each park for a total of 13 sites. Site information is provided in Supporting Informa-
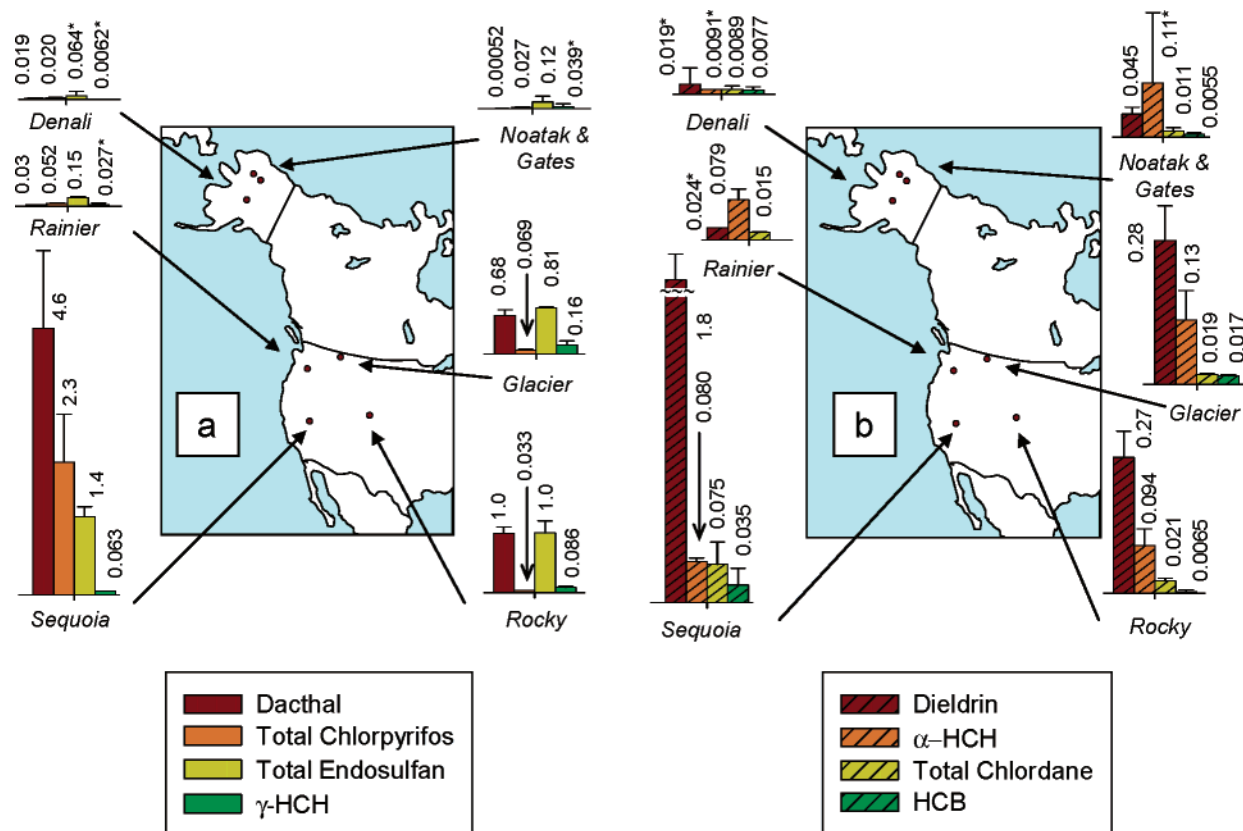
FIGURE 1. Mean pesticide concentrations (ng/L) in seasonal snowpack samples at all sites within a given park for the four most frequently detected (a) current-use pesticides and (b) historic-use pesticides. Mean concentrations are provided above bars; note the difference in scale between (a) and (b). Error bars denote standard deviation for concentrations measured at all sites within a given park; note that error bars are not always large enough to be observed at the scale depicted here. Asterisks indicate that one or more of the concentrations used to determine the average was below the method detection limit and was, therefore, replaced by one-half of the method detection limit (see SI Table 2).

tion (SI) Table 1. Snowpack sampling sites are located in or near lake catchments where WACAP water, sediment, fish, and vegetation sampling occurs because a future objective is to evaluate the exchange of SOCs between ecosystem components. The snow accumulation period extended from October or November 2002 to April 2003 at all parks.

Snow Sampling Method. Seasonal snowpack samples were collected in open areas on north-facing slopes located at least 200 m from potential sources of contamination (e.g., roadways, snowmobile trails, or aircraft landing zones). Sampling was conducted in March and April of 2003, near the time of annual maximum snow accumulation but before the onset of spring melting. Snowpits were excavated to the ground and a vertical column of snow was cut from the pit face. For each sample, ~50 kg of snow were collected in six solvent-rinsed 60 × 60-cm polytetrafluoroethylene (PTFE) bags using solvent-rinsed polycarbonate resin shovels. Filled PTFE bags were wrapped in low-density black polyethylene bags to minimize light exposure and high-density polypropylene bags for protection. Samples were shipped to the laboratory on dry ice and stored at −20 °C until analysis. Replicate samples were collected at Emerald Lake in Sequoia and Lake Irene in Rocky (SI Table 1). Field blanks were collected at Lake Irene in Rocky, Alta Vista in Rainier, and Wonder Lake in Denali by pouring VOC/pesticide-grade water (EMD Chemicals, Gibbstown, NJ) over sampling shovels and collecting it in PTFE bags. Thereafter, field blanks were treated identically to snowpack samples.

Analytical Method. The target analyte list was composed of 47 pesticide and pesticide degradation products and included amide, organochlorine, organochlorine sulfide, phosphorothioate, and thiocarbamates pesticides, as well as

triazine herbicides. A detailed description of the analytical method and the target analyte list is provided elsewhere (*18*). In brief, snow samples were removed from the freezer at the time of analysis and allowed to melt in the dark, without heat, for ~36 h in sealed PTFE bags. Once melted, a methanol solution containing 16 isotopically labeled pesticides, for use as recovery surrogates, was spiked into the sample. Target analytes were extracted from melted snow using solid-phase extraction disks that were prepared in-house by combining hydrophobic and hydrophilic 1-g divinylbenzene Speedisks from Mallinckrodt Baker (Phillipsburg, NJ) (*18*). Efforts were not made to separately analyze dissolved-phase and sorbed-phase pesticides because their phase distribution in the snowpack is not maintained when the snow is melted (*19*). Thus, concentrations reported herein are for total pesticide concentrations in snow, i.e., the sum of pesticides in the dissolved and sorbed phases. Gel permeation and silica gel adsorption chromatography were performed to remove matrix interferants. The final extract was spiked with an ethyl acetate solution containing four isotopically labeled internal standards. Analyte separation, detection, and identification were performed on Agilent (Palo Alto, CA) 6890N gas chromatographs equipped with Agilent DB-5MS 30 m × 0.25 mm × 0.25 μm columns and 5973N mass selective detectors. Approximately one-half of the target analytes were quantified using electron impact ionization while the other half were quantified using electron capture negative ionization (*18*).

Target analyte loss was corrected for surrogate recovery by using target analyte to surrogate response ratios in calibration curves. The mean recovery over the entire analytical method for all surrogates in all samples was 55%, which is similar to that reported previously for this method

(*18*). A laboratory blank was included with every set of two snowpack samples. Laboratory blanks were generated by spiking designated extraction disks with surrogate solution and then following all elution and cleanup steps. Snowpack concentrations reported herein were calculated by subtracting the mass of target analyte in a laboratory blank from that in corresponding snowpack samples. On average, analyte mass in laboratory blanks was 3% of that in corresponding snowpack samples for the concentrations reported in SI Table 2. Concentrations are not reported for cases in which the mass in the laboratory blank exceeded 33% of that in the sample; those cases are designated in SI Table 2. On average, concentrations in field blanks were 15% of those in corresponding snowpack samples. In correlation analyses, nondetects were replaced by concentrations representing one-half of the estimated method detection limits. Estimated method detection limits for specific pesticides are provided elsewhere; values ranged from 0.20 to 120 pg/L for the 47 target pesticides (*18*).

Particulate Matter Concentration. Particulate matter in seasonal snowpack samples was captured during extraction by the polypropylene mesh screens and glass fiber filters (0.2−2 μm) in the extraction disks. The mass of particulate matter in a sample was determined by drying (105 °C) and weighing the extraction disk before and after the extraction procedure. Particulate matter concentration in milligram per liter (SI Table 1) was calculated for each sample by dividing the particulate matter mass by the volume of melted snow.

Indicators of Regional Pesticide Use. Regional cropland intensity was defined as cropland area as a percentage of total land area within a given radius of a park (SI Figure 1). U.S. data was for 2002 (*20*), whereas data for the Canadian province of Alberta (used for Glacier) was for 2001 (*21*). The quantity of specific current-use pesticides (dacthal, divide as chlor-pyrifos, and endosulfan) applied within a given radius of a park was calculated from data for 1997 (*22*); similar data was not available for Canada. Cropland and pesticide-use data were provided on a per county basis. Cropland and pesticide-use distributions within counties were adjusted to account for the fact that there is no cropland in U.S. national parks nor on U.S. national forest land and for the fact that the pesticide-use database did not include pesticide uses on either of these land classifications. In cases where there was no available data (i.e., cropland data for British Columbia and pesticide-use data for British Columbia and Alberta), the acreage representing the area with no data was subtracted from the total number of acres in the circle.

Results & Discussion

Pesticide Concentration and Deposition. The current-use pesticides detected in seasonal snowpack samples at national parks in this study were dacthal (DCPA), chlorpyrifos, endosulfans (I and II), γ-hexachlorocyclohexane (γ-HCH) (lindane), trifluralin, and triallate. Additionally, endosulfan sulfate, which is a degradation product of endosulfan I and II, and chlorpyrifos oxon, which is a degradation product of chlorpyrifos, were detected. Although none of the detected current-use pesticides were identified as persistent organic pollutants (POPs) by the 2001 Stockholm Convention on POPs (*23*), their presence in remote ecosystems implies that they are persistent enough to undergo transport to remote ecosystems in national parks. To the best of our knowledge, γ-HCH, which was used in Sequoia NP from 1960 to 1978, is the only current-use pesticide that we detected that has been used in the parks in this study. Concentrations for the most frequently detected pesticides, i.e., dacthal, total chlorpyrifos (parent and oxon), total endosulfan (I, II, and sulfate), and γ-HCH, are provided in SI Table 2; their mean concentrations at individual parks are mapped in Figure 1a. Concentrations of trifluralin and triallate, which were

detected in less than one-half of the samples, ranged from 0.00094 to 0.021 ng/L and from 0.030 to 0.62 ng/L, respectively.

Mean concentrations were highest at Sequoia for all of the most frequently detected current-use pesticides and generally followed a decreasing trend in Rocky, Glacier, Rainier, and the Alaskan parks (Denali, Noatak, and Gates of the Arctic) (Figure 1a). Notable was the high mean concentration for total chlorpyrifos in Sequoia, which was ~30 times higher than at the park with the next highest concentration (Glacier). In contrast, smaller incremental changes in concentrations were observed among parks for the other current-use pesticides. Chlorpyrifos oxon was detected only in Sequoia where its concentrations represented 57%, 28%, and 8.6% of the total chlorpyrifos in the Pear Lake and Emerald Lake replicate samples, respectively. On the other hand, endosulfan sulfate was detected at all but one site (with the exception being Wonder Lake in Denali). The percentage contribution of endosulfan sulfate to the total endosulfan concentration ranged from 4% to 57% with the mean value being 24%.

The historic-use pesticides detected in seasonal snowpack samples at national parks in this study were dieldrin, α-HCH (a component of technical HCH), three components of technical chlordane (trans-chlordane, cis-nonachlor, and trans-nonachlor), and hexachlorobenzene (HCB). In addition to being a historic-use pesticide, HCB has been and is currently emitted to the environment as a byproduct of industrial processes and as a trace contaminant in some current-use pesticides (*24*). p,p′-dichlorodiphenyldichloro-ethene (DDE) also was detected but only at the three sites in Sequoia. The mean concentration of DDE at the Sequoia sites was 0.11 ng/L and the relative standard deviation was 16%. DDE is a degradation product of dichlorodiphenyl-trichloroethane (DDT), a historic-use pesticide, and an impurity in dicofol (*25*), a current-use pesticide. Dicofol is used in California (*22*) and has been measured in the San Joaquin River in California (*26*). In 1987, the U.S. Environmental Protection Agency (EPA) set the upper limit for DDT in dicofol at 0.1%; however, higher percentages were permitted prior to that (*27*).

The presence of historic-use pesticides in snow at the national parks in this study indicates that they are undergoing atmospheric transport and deposition to remote ecosystems despite being banned as pesticides in the U.S. for several decades. To the best of our knowledge, none of these pesticides have ever been used in the parks in this study. Concentrations for the four most frequently detected pesticides, i.e., dieldrin, α-HCH, total chlordane, and HCB, are provided in SI Table 2; their mean concentrations at individual parks are mapped in Figure 1b. The mean concentrations for dieldrin, total chlordane, and HCB were highest at Sequoia (Figure 1b). The highest α-HCH concentration in the study was measured at Burial Lake in Noatak; however, α-HCH was not detected at the other Alaskan sites (Figure 1b; SI Table 2).

Pesticide deposition for the most frequently detected current-use and historic-use pesticides is provided in SI Table 3. Pesticide deposition (ng/m^2) is defined here as the concentration of the pesticide measured in melted snow (ng/m^3) multiplied by the snow depth in water equivalents (m) (SWE) at the selected site. SWE, which depends on site characteristics such as climate, elevation, and aspect, varied by a factor of ~30 times between the sites in this study (SI Table 1). Deposition has important ecological relevance because it reflects the total quantity of pesticide delivered to an ecosystem during the snow-accumulation period. On the other hand, snowpack concentration may be a better indicator of mean air concentrations during the snow-accumulation period. Comparison between concentration
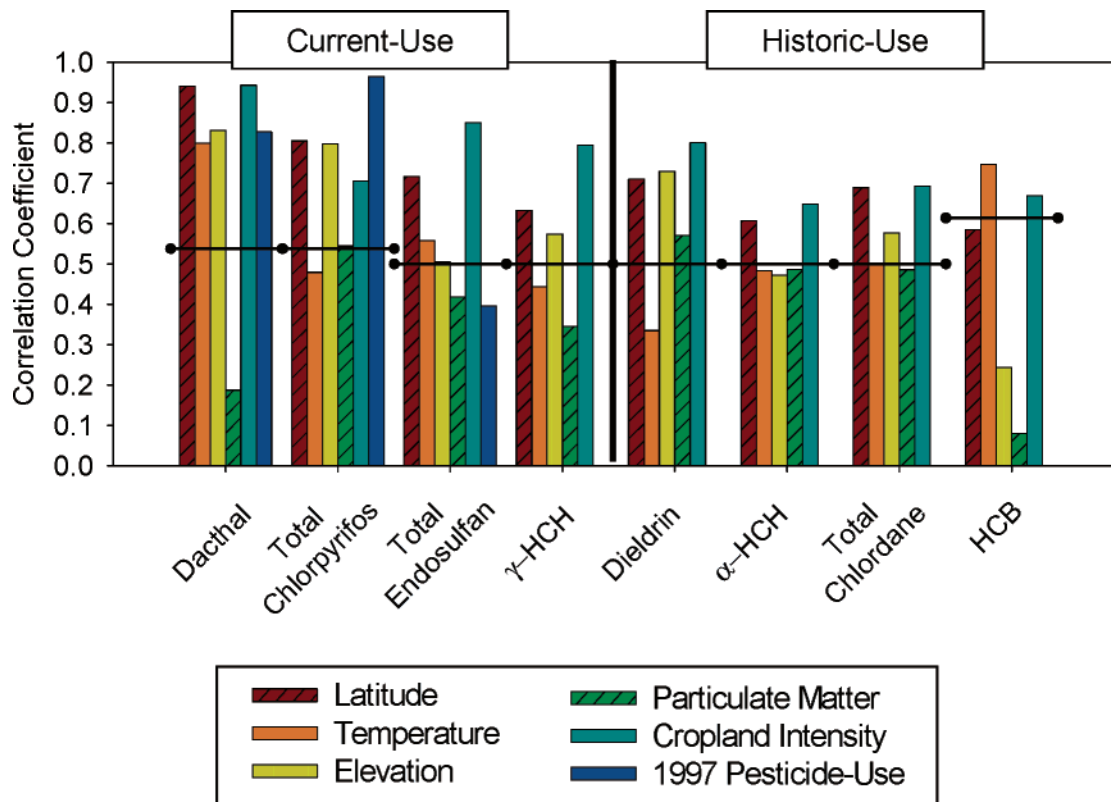
FIGURE 2. Correlation coefficients for log pesticide concentration with latitude, mean winter air temperature, elevation, particulate matter concentration, regional cropland intensity within 150 km, and the quantity of specific current-use pesticides applied within 150 km of each park in 1997. Correlation coefficients for 1997 pesticide use are only provided for pesticides that were used within 150 km of the parks in 1997 (i.e., dacthal, chlorpyrifos, and endosulfan). Diagonal lines through bars indicate negative correlation while solid bars indicate positive correlation. Horizontal lines indicate statistical significance at $p < 0.05$.

(SI Table 2) and deposition (SI Table 3) reveals the importance of snowfall quantity on the delivery of contaminants to an ecosystem. For example, deposition (ng/m^2) was ~1200 times greater than the concentration (ng/L) at Alta Vista in Rainier (where SWE was relatively high) whereas deposition was only ~42 times higher at McLeod Lake in Denali (where SWE was relatively low).

Correlation with Latitude, Temperature, Elevation, and Particulate Matter. Figure 1 and SI Table 2 indicate that the concentrations of current-use and historic-use pesticides tend to decrease with latitude. To investigate this relation, correlation analysis was conducted between logarithm (log) pesticide concentration and latitude. An example regression plot (for dacthal) is shown in SI Figure 2a. Correlation coefficients for latitude were negative for all of the most frequently detected pesticides and were statistically significant at $p < 0.05$ for all pesticides except HCB (Figure 2). Although the relation between SOC concentration and latitude has been investigated in several previous studies (6, 28, 29), latitude itself does not control pesticide distribution. Rather, latitude was used as a surrogate for temperature or source intensity in those studies. To directly assess the influence of temperature on pesticide distribution at our sites, correlation analysis was conducted between log pesticide concentration and mean winter (November 2002 through March 2003) air temperature (SI Table 1). An example regression plot (for dacthal) is shown in SI Figure 2b. Correlation coefficients for temperature were positive in all cases although only significant at $p < 0.05$ for dacthal, total endosulfan, total chlordane, and HCB (Figure 2). Of most interest to this investigation is the observation that pesticide concentrations decreased with decreasing temperature, which signifies that cold condensation is not the dominant

factor influencing pesticide distributions among the sites in this study.

The relation between log pesticide concentration and site elevation was investigated and an example regression plot (for dacthal) is shown in SI Figure 2c. Correlation coefficients were lower relative to those with latitude for all of the most frequently detected pesticides except dieldrin (Figure 2). Additionally, correlation coefficients were positive in all cases; i.e., log pesticide concentrations increased with site elevation. However, it is critical to note that mean winter air temperature increases with elevation (although not with statistical significance) at our sites because the highest-elevation sites (e.g., Sequoia and Rocky) are located at the lowest latitudes (SI Table 1). Thus, increases in pesticide concentration with elevation among the sites in this study cannot be attributed to cold condensation. Daly and Wania reviewed previous investigations into the relation between pesticide concentration and elevation and noted that proximity to sources may be more important than elevation when sample sites are not located along a single mountain slope (1).

Correlation analysis was conducted between log pesticide concentration and the concentration of particulate matter in snowpack samples based on the hypothesis that pesticides may be associated with particulate matter, such as dust from agricultural fields, in the atmosphere. An example regression plot (for dacthal) is shown in SI Figure 2d. Correlation coefficients for this analysis were low compared to those for latitude for all of the most frequently detected pesticides (Figure 2). Moreover, pesticide concentrations decreased with increasing particulate matter because particulate matter concentrations were generally highest at the highest-latitude parks (SI Table 1). Thus, particulate matter concentration did not play an important role in controlling the distribution

of pesticides among the sites in this study. Latitude was negatively correlated with temperature and elevation at $p < 0.01$, whereas the relation between latitude and particulate matter was positive but not statistically significant. Correlation coefficients describing the relation between log pesticide deposition and latitude, mean winter air temperature, elevation, and particulate matter concentration (SI Figure 3) were generally similar to those obtained using log pesticide concentration (Figure 2).

Correlation with Indicators of Regional Pesticide Use. Correlation analyses implied that neither cold condensation nor particulate matter played a dominant role in determining the distribution of pesticides among the sites in this study because the highest pesticide concentrations were found at the warmest temperatures, elevations, and latitudes and at the sites with the lowest concentrations of particulate matter. Therefore, we investigated the potential role that pesticide sources associated with regional agriculture might play in influencing observed pesticide distributions. Correlation analyses between log pesticide concentration and two indicators of regional pesticide use were conducted. The first was cropland intensity, defined as cropland area as a percentage of total land area within a given radius of a park. The second indicator was the quantity of a current-use pesticide applied within a given radius of a park. Although pesticide-application data is highly specific for current-use pesticides, cropland intensity data is useful because it potentially represents land-use associated with both past and present pesticide application (historic and current-use pesticides). Past agricultural practices cannot be ignored because many historic-use pesticides persist in agricultural soils and continue to volatilize from them (30). Cropland intensity in the vicinity of the parks in this study did not vary significantly between 1950 and 1990 (31).

A radial area of influence was selected because air masses from different wind directions are likely to influence the snowpack during the 6-month snow-accumulation period. Additionally, diurnal upslope/downslope wind patterns are important in mountain systems (1) and are likely to transport contaminated air to high elevations from all directions. Regional cropland intensity was calculated for radial distances of 75 km, 150 km, and 300 km. The atmospheric travel times for these distances (with a mean wind speed of 6 km/h) are 12.5, 25, and 50 h, respectively, and represent the low end of the range of half-lives in air for the selected pesticides (SI Table 4). Correlation coefficients describing the relation between log pesticide concentration and cropland intensity within each of the radial distances were calculated (SI Figure 4a). An example regression plot (for dacthal with 150 km) is shown in SI Figure 2e. For total chlorpyrifos, total chlordane, and HCB, the optimal distance (defined here as the distance at which the correlation coefficient was highest) was 75 km; for dacthal, total endosulfan, γ-HCH, and dieldrin, it was 150 km; and for α-HCH, it was 300 km. When correlation coefficients were calculated using log pesticide deposition, optimal distances were the same as those for log pesticide concentration for all pesticides except γ-HCH (SI Figure 4b). Correlations for both sets of data indicated statistical significance at $p < 0.05$ between pesticide half-life in air (SI Table 4) and the optimal radial distance (if HCB was excluded). Because the optimal radial distance was best at 150 km for the largest number of pesticides, it was used for further analysis. From this point forward, regional cropland intensity refers to that calculated with a radial distance of 150 km unless otherwise noted.

Correlation analysis indicated that both log pesticide concentrations (Figure 2) and log pesticide depositions (SI Figure 3) were positively correlated with regional cropland intensity at $p < 0.05$ for all of the most frequently detected current and historic-use pesticides. For the current-use pesticides, this implies that they are at least persistent enough to travel to cold ecosystems within proximity of application sites and that current regional use is important in dictating their distribution at remote sites. For the historic-use pesticides, this implies that past agricultural practices continue to influence their distribution in national parks in the Western U.S. This influence is likely due to volatilization from historically contaminated agricultural soils (30). Note that the half-lives for the most frequently detected pesticides are longer in soil than in air (SI Table 4). In a study designed to investigate the distribution of organochlorine chemicals in European mountains, the potential effects of cold condensation and source proximity confounded each other because the coldest sites were located closest to suspected source regions (32). This was not the case in our study because the coldest sites were located farthest from the source regions (SI Table 1).

Correlation analysis was conducted between log pesticide concentrations of current-use pesticides (dacthal, total chlorpyrifos, and total endosulfan) and the quantities of these pesticides applied in 1997 within 150-km radii of the parks (Figure 2). An example regression plot (for dacthal) is shown in SI Figure 2f. Identical analysis was conducted with log pesticide deposition (SI Figure 3). For dacthal and total chlorpyrifos, correlation coefficients were positive and statistically significant at $p < 0.05$ (for analysis with both concentration and deposition), providing further evidence that regional pesticide use influenced their distribution at these parks. The correlation was not statistically significant at $p < 0.05$ for total endosulfan (for analysis with both concentration and deposition). Correlation analysis was not conducted for γ-HCH because there was no record of its application within 150 km of the parks in this study in the 1997 pesticide-use database (22); however, that database does not include pre-plant seed treatments. The U.S. EPA's September 2002 Reregistration Eligibility Decision document states that γ-HCH is registered for use as a seed treatment for barley, corn, oats, rye, sorghum, and wheat (27). Thus, usage of γ-HCH as a seed treatment on one or more of these crops may have occurred within 150 km of the national parks in this study. Although γ-HCH has been used heavily in the Canadian prairie provinces (33, 34), all uses in Canada were phased out between 2001 and 2004 (35). Thus, our snowpack samples were collected during the Canadian phase-out period.

α-HCH and HCB. The distributions of the more-volatile pesticides, namely α-HCH and HCB, merit additional attention because their distributions over large latitudinal ranges have been investigated in several previous studies. In tree bark (6) and surface soil (36) samples from around the world, α-HCH and HCB concentrations increased with latitude. In contrast, α-HCH and HCB concentrations in air were relatively uniform across the U.S. and Canada (29, 37). A third trend was observed in our study where α-HCH and HCB concentrations in snow decreased with latitude (38). Differences in distribution patterns between matrixes may be attributed to their varying capabilities to retain volatile pesticides. Although snow is efficient at scavenging contaminants from the atmosphere (3, 16), α-HCH and HCB are more likely to be retained by lipid-rich tree bark and soil than by lipid-deficient snow. For example, rapid volatilization of α-HCH and HCB from fresh snow was observed in the Norwegian Arctic (39). It is possible that more-rapid volatilization occurred at the higher-latitude sites in our study than at the lower-latitude sites due to differences in wind ventilation. Wind ventilation, which enhances the transfer of SOCs from snow to air and affects snow surface area, is maximized when the snowpack depth is minimal and the exposure to wind is maximal (3, 17). At our high-latitude
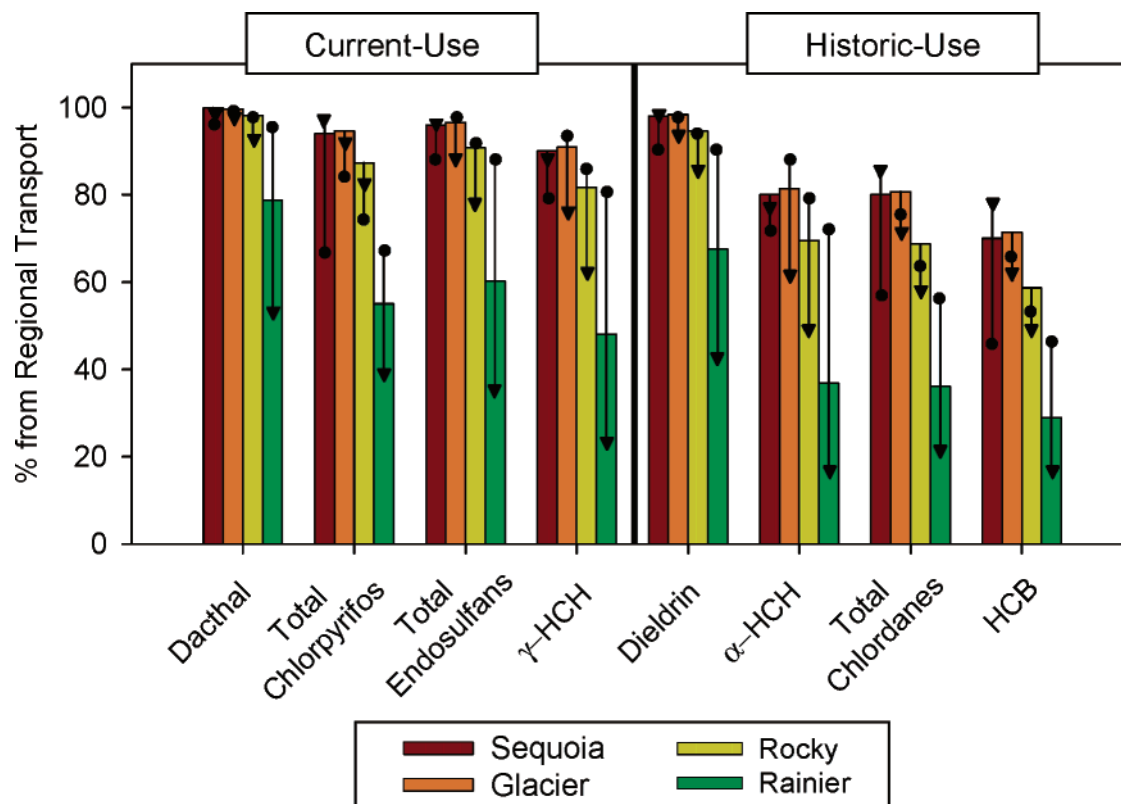
FIGURE 3. Percentage of total pesticide concentration due to regional transport (%RT) where "regional" is defined as 150 km (bars), 75 km (triangles), and 300 km (circles). The percentage due to long-range transport can be estimated by subtracting %RT from 100. %RT was assumed to be zero for the Alaskan parks (Denali, Noatak, and Gates).

sites, snowpack depths were relatively low (SI Table 1) and wind exposure was particularly high.

Regional Versus Long-Range Transport. The relative importance of regional versus long-range (or global background) sources in influencing pesticide concentrations in the national parks in this study was investigated. Percent pesticide concentration due to regional transport (%RT) was estimated for each pesticide at each park. This was accomplished by assuming that pesticide concentrations due to long-range sources are the same at all parks and that observed variations between parks are due entirely to contributions from regional sources. Although this assumption is simplistic, it is a useful approximation that facilitates initial investigation into regional versus long-range source apportionment. Based on this assumption, the y-intercept of the regression line for log pesticide concentration with regional cropland intensity represents the pesticide concentration due to long-range transport. In other words, where regional cropland intensity is zero (e.g., at the Alaskan parks), pesticide deposition must be due entirely to long-range transport. %RT for a pesticide at a given park was calculated by subtracting the concentration representing long-range transport (as determined by the y-intercept) from the total (regional plus long-range) concentration at the park (as determined from the regression line) and then dividing that value by the total concentration and multiplying by 100. For example, the calculated concentration due to long-range transport for dacthal was 0.011 ng/L (SI Figure 2e). The total concentration of dacthal at Rocky, where cropland intensity within 150 km (SI Table 1), was 0.58 ng/L (SI Figure 2e). Thus, the %RT for dacthal at Rocky was 98%. %RT was calculated using regional cropland intensity values where "regional" was defined as 75 km, 150 km, and 300 km (Figure 3). %RT was not significantly different when calculated using deposition rather than concentration (data not shown).

%RT was highest at parks with higher regional cropland intensity (Sequoia, Glacier, and Rocky) (SI Table 1) and for pesticides with relatively low vapor pressures and shorter half-lives in air (e.g., dacthal and dieldrin) (SI Table 4). %RT was lowest at parks with lower regional cropland intensity (Rainier and the Alaskan parks) (SI Table 1) and for pesticides with higher vapor pressures and longer half-lives in air (e.g., α-HCH and HCB) (SI Table 4). At Sequoia, Glacier, and Rocky, %RT was greater than 50% for all compounds at all radial distances. %RT varied the most at Rainier (Figure 3) because regional cropland intensity varied more with radial distance at Rainier than at the other parks.

Our results suggest that both current-use and historic-use pesticides are currently undergoing deposition via snow to remote high-elevation and high-latitude ecosystems in national parks in the Western U.S. Clearly, regional U.S. and Canadian agricultural practices, both past and present, play a significant role in contributing to the accumulation of pesticides in the seasonal snowpack. However, a more detailed analysis of the source regions (both regional and long-range) through in-depth air trajectory analysis is needed, using pesticide snowpack accumulations over several years, to better determine the relative contribution of regional and long-range sources to national parks. Finally, detailed information on the fate and effects of pesticides, and other anthropogenic SOCs, in remote high-elevation and high-latitude ecosystems in U.S. national parks is needed.

Note Added after ASAP Publication

A typographical error appeared in the Regional Versus Long-Range Transport section in the version published ASAP on April 15, 2006; the corrected version was published April 25, 2006.

Supporting Information Available

Site information, concentration and deposition values, physical-chemical properties for selected pesticides, a U.S. cropland map, correlation plots for an example pesticide (dacthal), correlation coefficients for deposition with each investigated factor, and correlation coefficients between concentration/deposition and regional cropland intensity defined using different radii. This material is available free of charge via the Internet at http://pubs.acs.org.

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