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Variability in Pesticide Deposition and Source Contributions to Snowpack in Western US National Parks

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Abstract

Fifty-six seasonal snowpack samples were collected at remote alpine, sub-arctic, and arctic sites in eight Western US national parks during three consecutive years (2003–2005). Four current-use pesticides (CUPs) (dacthal (DCPA), chlorpyrifos, endosulfan, and γ -hexachlorocyclohexane (HCH)) and four historic-use pesticides (HUPs) (dieldrin, α -HCH, chlordane, and hexachlorobenzene (HCB)) were commonly measured at all sites, during all years. The mean coefficient of variation for pesticide concentrations was 15% for site replicate samples, 41% for intra-park replicate samples, and 59% for inter-annual replicate samples. The relative pesticide concentration profiles were consistent from year to year but unique for individual parks, indicating a regional source effect. HUP concentrations were well-correlated with regional cropland intensity when the effect of temperature on snow-air partitioning was considered. The mass of individual CUPs used in regions located one-day upwind of the parks was calculated using air mass back trajectories and this was used to explain the distribution of CUPs among the parks. The percent of the snowpack pesticide concentration due to regional transport was high (>75%) for the majority of pesticides in all parks. These results suggest that the majority of pesticide contamination in US national parks is due to pesticide use in North America.

INTRODUCTION

Semi-volatile organic contaminants (SOCs), including some pesticides, are known to volatilize from source regions and undergo atmospheric transport to remote locations (1). Cold condensation enhances dry deposition, particle deposition, and scavenging by snow and rainfall (2–3), resulting in the transfer of SOC from the atmosphere to terrestrial and aquatic ecosystems in alpine (4) and polar regions (5). This is of concern because of potential toxicological threats these compounds pose to sensitive species, especially when

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SUPPORTING INFORMATION AVAILABLE

This file contains detailed information about analytical methods, snow sampling, variability analysis, cropland and CUP usage data, back trajectory generation, and trajectory clustering. Tables contain site information, concentrations, fluxes, regional pesticide indicators, an example calculation for USAGE+WIND, and physical properties. Figures show park locations, back trajectory maps, frequency of analyte detection, CV interquartile ranges for pesticide concentrations and flux, and example regression plots. Supporting information is available free of charge via the internet at <http://pubs.acs.org>.

biomagnification occurs (6–8). Moreover, potential risks exist for indigenous people and subsistence food consumers that rely on fish and meat from cold ecosystems.

Seasonal snowpack has been identified as a useful matrix for measuring the atmospheric deposition of pesticides, and other SOC_s, in cold ecosystems during the snow-accumulation period (5,9–13). The seasonal snowpack typically lasts at least six months in mid-latitude alpine, sub-arctic, and arctic regions. Snowpack SOC concentrations have been used to investigate their sources in national parks in the western US (11,14–15) and in the Norwegian Arctic (16), as well as their input to aquatic ecosystems during snowmelt (17).

However, snowpack SOC concentrations in replicate samples from the Italian Alps had higher than expected variability (12), significant changes in pesticide concentrations have been observed during snowpack metamorphosis (16,18–20), and significantly different snowpack SOC concentrations were measured in samples collected from the same site during two consecutive years in Alberta (17). Variability snowpack SOC concentrations may be due to changing environmental factors and/or concentrations in the atmosphere. Because of the growing interest in using seasonal snowpack to understand SOC sources to and distribution and fate in remote ecosystems, it is important to characterize and understand this variability. Additionally, approaches for using the snowpack to investigate the sources of SOC_s in remote ecosystems need refinement, especially when snowpack is collected over a wide geographical area where temperatures, and therefore snow-air partitioning, can change significantly.

We measured current-use pesticides (CUP_s), historic-use pesticides (HUP_s), and their degradation products in seasonal snowpack samples, collected annually over three consecutive years (2003–2005) from remote alpine, sub-arctic, and arctic ecosystems in eight US national parks. The first objective of this research was to quantify and compare the variability in snowpack pesticide concentrations and flux in site replicate, intra-park replicate, and inter-annual replicate samples. The second objective was to compare pesticide concentration profiles among the parks in order to understand the similarities and differences in potential sources. The third objective was to identify source regions by combining results from an extensive atmospheric modeling study of the parks (21–22), documented pesticide use (23), and calculated temperature effects on snow-air partitioning.

EXPERIMENTAL SECTION

Sample Sites

Seasonal snowpack samples were collected from 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 during March and April of 2003, 2004, and 2005 (Supporting Information (SI) Table S1 and Figure S1). Samples were also collected at Olympic NP in 2004 and at N. Cascades NP in 2005. Further information about park and site selection and detailed maps are provided by Landers et al. (22). The snow-accumulation period extended from October or November to April at all parks. Although the aim was to use the same sampling sites each year, a lack of snow at prescribed sites prevented this in four cases during which samples were collected from nearby, higher-elevation sites (see SI for details). Initial results from the 2003 sampling campaign were previously described (11).

Snow Sampling Method

Full-depth snowpack samples were collected near the time of 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. Further details can be found in a previous publication (11) and in the SI.

Analytes and Analytical Method

The target analyte list was composed of 47 pesticide and pesticide degradation products and included amide, organochlorine, organochlorine sulfide, phosphorothioate, thiocarbamate, triazine, and other miscellaneous insecticides and herbicides. The analytical method has been described elsewhere (11,24) and further details are provided in the SI.

Variability Analysis

The variability in snowpack pesticide concentration was assessed using three different analyses and calculated for the eight most frequently detected pesticides. Site variability in pesticide concentration was assessed using the coefficient of variation (CV) (standard deviation divided by the mean multiplied by 100) for replicate samples collected at the same time, from the same snow pit. Intra-park variability was assessed using the CV of snowpack pesticide concentrations at different sites, within a park, and collected within a few days of each other. Inter-annual variability was assessed using pesticide concentrations from 11 sites that were sampled during three consecutive years (2003, 2004, and 2005). Further details are provided in the SI.

The Kruskal-Wallis one-way analysis of variance on ranks with the Dunn/Bonferroni method (25) was used to test for statistically significant differences ($p < 0.05$) among CVs for different replicate types, pesticides, and parks. Mann-Whitney rank sum t-tests (25) were used to test for statistical differences ($p < 0.05$) in cases where two groups were compared. Statistical analysis was conducted with SigmaPlot (Chicago, IL) Version 11.0.

Indicators of Regional Pesticide Use

Three indicators of regional pesticide use (Table S3) were used in our analysis. The first was the area of cropland within 150 km of the center of a park (CROPLAND); which is the same as cropland intensity (11) except not expressed as a percentage. CROPLAND potentially represents a source influence from both historic and current pesticide use because agricultural soils act as a continuing source of persistent HUPs (26), and most likely CUPs, to the atmosphere. The second was the mass of specific CUPs used on agricultural land located within 150 km of parks (USAGE) (11). CUP application rates vary somewhat year to year; therefore, the USAGE parameter is an approximate application rate and indicates the quantity of CUPs that may be volatilizing from agricultural soils in which CUPs have accumulated due to past and present usage. The third indicator was the mass of individual CUPs used on agricultural land located within the region one-day upwind of the park's perimeter (the park's one-day airshed) (USAGE+WIND). Literature references and details about cropland and CUP usage data are provided in the SI.

To calculate USAGE+WIND, one-day air mass back trajectories were determined for each day from 1998 to 2005, for each park, using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model with the National Center for Environmental Prediction (NCEP) data grid (21–22). Using a non-hierarchical clustering algorithm, trajectories were grouped with respect to distance, altitude, and direction to form trajectory clusters representing the six main atmospheric transport pathways at each park (Figure S2) (21–22). The tear-drop shaped regions associated with each cluster represent the horizontal standard deviation of all trajectories within a cluster. Percent membership (Figure S2) was defined as the percentage of trajectories associated with a given cluster, during a given time period, and was calculated for the winter seasons of our study. For example, 15% of Glacier's 1-day air mass back trajectories during the 2002-03 winter season were associated with cluster A, which represented relatively slow air masses from the southwest (Figure S2). To obtain the USAGE+WIND indicator for each park, the CUP usage within an air mass cluster was multiplied by the associated mean %membership (for the three winters of this

study) for that cluster. This was repeated for each cluster and the values for the six clusters were summed for each park. The percent contribution of pesticide mass associated with each cluster was also calculated. An example calculation is shown in Table S4.

Temperature-Normalized Snowpack Concentrations

Assuming equal air concentrations and no other significant influencing factors, snowpack concentrations will be higher at colder temperatures due to the effects of temperature on air-snow partitioning (2). To investigate differences in our measured pesticide snowpack concentrations due to differences in air concentration (without the effect of temperature variability playing a role), we transformed measured snowpack concentrations, $C_{\text{snow(M)}}$, to temperature-normalized snowpack concentrations, $C_{\text{snow(N)}}$, using the following equations.

$$C_{\text{snow(N)}} = C_{\text{snow(M)}} \frac{C_{\text{snow(N)}}}{C_{\text{snow(M)}}} \quad (1)$$

$$C_{\text{snow(N)}} = C_{\text{snow(M)}} \frac{C_{\text{air}} \text{SSA} \rho_w K_{\text{SA(normalization T)}}}{C_{\text{air}} \text{SSA} \rho_w K_{\text{SA(actual T)}}} \quad [\text{ref.}(2)] \quad (2)$$

$$C_{\text{snow(N)}} = C_{\text{snow(M)}} \frac{K_{\text{SA(normalization T)}}}{K_{\text{SA(actual T)}}} \quad (3)$$

$$\frac{K_{\text{SA(normalization T)}}}{K_{\text{SA(actual T)}}} = e^{\frac{\Delta H_{\text{ads}} + RT_{\text{av}}}{R} \left(\frac{1}{\text{actual T}} - \frac{1}{\text{normalization T}} \right)} \quad [\text{ref.}(27)] \quad (4)$$

$$C_{\text{snow(N)}} = C_{\text{snow(M)}} e^{\frac{\Delta H_{\text{ads}} + RT_{\text{av}}}{R} \left(\frac{1}{\text{actual T}} - \frac{1}{\text{normalization T}} \right)}, \quad (5)$$

where $C_{\text{snow(N)}}$ is the predicted snowpack concentration at a given mean winter air temperature, C_{air} is the pesticide concentration in air, SSA is the snow surface area ($\text{m}^2 \text{ g}$), ρ_w is the density of water (g m^{-3}), K_{SA} is the snow surface-air partition coefficient (m) (at specified temperature), T_{av} is the mean of the actual and normalization temperatures (T), and ΔH_{ads} is the enthalpy of the air-snow sorption reaction (kJ mol^{-1}). For this exercise, we assumed that SSA and ρ_w were constants, allowing their cancelation in equation 2.

ΔH_{ads} was assumed to be similar to the enthalpy of adsorption to the liquid water surface (ΔH_{IA}) (2) and was calculated from:

$$\Delta H_{\text{IA}} (\text{kJ/mol}) = -5.07 \ln K_{\text{IA}} (15^\circ \text{C}) - 107. \quad [\text{ref.}(28)] \quad (6)$$

K_{IA} is the interfacial adsorption coefficient on the liquid water surface and is calculated at 15°C from the poly-parameter linear free energy relationship:

$$\text{Log } K_{\text{IA}} = 0.635 \text{ Log } L^{16} + \Sigma \beta_2^H + \Sigma \alpha_2^H - 8.47, \quad [\text{ref.}(29)] \quad (7)$$

where L^{16} is the gas-hexadecane partition coefficient, $\Sigma \beta_2^H$ is the summation hydrogen bond basicity, and $\Sigma \alpha_2^H$ is the summation hydrogen bond acidity (Table S5).

RESULTS AND DISCUSSION

Pesticide Concentration and Flux Variability

Of the 47 target analytes, 16 were detected in snowpack samples (Figure S3). These chemicals have not been used or produced in the national parks in this study; thus, their presence indicates that they are persistent enough to undergo atmospheric transport to remote ecosystems. Although γ -HCH is no longer registered for use in the US (30) and has recently been listed by the Stockholm Convention (31), it is considered a CUP herein because it was used as a grain crop seed treatment in the US during the sampling period of this study (32) and it wasn't phased out in Canada until the end of 2004 (33). Therefore, γ -HCH may have been used during the summers of 2002, 2003, and 2004, just prior to our spring sampling. The frequency of detection of individual pesticides and degradation products in the snowpack samples ranged from 5% to 98% (Figure S3). Eight of the sixteen detected analytes were found in at least 90% of samples. With the exceptions of triallate in Rocky and Glacier and p,p' -DDE in Sequoia in 2003, all detected analytes were found in all parks.

The concentrations of the most frequently detected CUPs, i.e. dacthal, chlorpyrifos (sum of parent and oxon), endosulfan (sum of I, II, and sulfate), and γ -HCH, and the most frequently detected HUPs, i.e. dieldrin, α -HCH, chlordane (sum of trans-chlordane, cis-nonachlor, and trans-nonachlor), and HCB are listed in Table S2. The fluxes for these eight pesticides are shown in Table S6. Pesticide flux (ng/m^2) is the concentration of pesticide measured in the melted snowpack sample (ng/m^3) multiplied by the snow depth in water equivalents (m) (SWE) for a specific winter season. SWE, which depends on site characteristics such as climate, elevation, and aspect, ranged from 0.042 to 2.0 m at our sites (Table S1). Although snowpack pesticide concentrations (assuming equilibrium), pesticide flux estimates the total quantity of pesticide delivered to an ecosystem during the snow-accumulation period.

The mean site variability, i.e. mean CV for all pesticides in site replicates ($n = 61$, see SI), was 15% and the interquartile range (25) was 6–20% (Figure 1). The site variability in snowpack pesticide concentration was grouped by pesticide (Figure 1) and by park (Figure S4) to determine if variability was influenced by physiochemical properties of the pesticides or by environmental factors that may vary among parks; no statistically significant differences were observed. A previous study in the Italian Alps measured site variability for 13 pesticides using triplicate snowpack samples. Our calculations, using their data, indicate that site variability was 45%, with an interquartile range of 10–60% (12), which was significantly higher than site variability in our study.

The mean intra-park variability, i.e. mean CV for all pesticides in intra-park replicates ($n = 138$), was 41% and the interquartile range was 14–60% (Figure 1). The mean intra-park variability was 2.7 times higher than, and significantly different from, site variability. There were no significant differences in intra-park variability among pesticides (Figure 1) or parks (Figure S4). The mean inter-annual variability, i.e. mean CV for all pesticides in inter-annual replicates ($n = 85$), was 59% and the interquartile range was 29–78% (Figure 1). In the seven cases in which sampling sites were exactly the same over the three years (see SI), the mean inter-annual variability was 52% and the interquartile range was 32–74%,

indicating that minor changes in sampling location among years had minimal effects on results. The mean inter-annual variability was 3.5 to 3.9 times higher than site variability and significantly different from both site and intra-park variability. Intra-park variability was significantly higher at Noatak/Gates than at Glacier (Figure S4). No other significant differences in intra-park variability were observed.

Site, intra-park and inter-annual variability were also calculated using pesticide flux (Table S6). Concentration- and flux-based site variability were the same because the SWE values were the same for site replicates (Table S1, Figure S5). The mean flux-based intra-park variability for all pesticides was 57%, while inter-annual variability was 70% (Figure S5). Flux-based intra-park variability was significantly higher than concentration-based variability due to the variation in SWE, in addition to concentration. However, the flux- and concentration-based inter-annual variabilities were not significantly different.

Pesticide Concentration Profiles

The sum of concentrations for the eight most frequently detected pesticides was calculated for each park and for each year. The percent of each pesticide that made up the total pesticide concentration was then calculated for each case; these percentages were then used to create pesticide concentration profiles for each park and year (Figure 2). Pesticide concentration profiles reveal consistent patterns year to year, within a park, even though the total pesticide concentration varied. For example, the total pesticide concentration in Sequoia was ~2.4 times higher in 2005 than 2004 but the pesticide concentration profiles were similar (Figure 2A). This suggests that the processes influencing the magnitude of pesticide deposition vary from year to year but that the geographical sources of pesticides generally do not. The pesticide profiles are also useful for identifying anomalies. For example, dieldrin concentrations were relatively high in Sequoia in 2003 (Figure 2A) and chlorpyrifos concentrations were relatively high in Glacier in 2005 (Figure 2F).

Pesticide concentration profiles were also unique for each park (Figure 2). For example, Sequoia's profile (Figure 2A) was dominated by the CUPs dacthal, chlorpyrifos, and endosulfan (in that order), while Rocky's profile (Figure 2B) was dominated by dacthal and endosulfan, with very little chlorpyrifos. These unique profiles indicate that the pesticide sources to each park are different and that regional differences, in both past and current pesticide use, influence the distribution of pesticides deposited to a park.

Influence of Regional Pesticide Use

The relationship between the 2003 snowpack logarithm₁₀-transformed (log) pesticide concentrations and a variety of factors that could hypothetically influence these concentrations was previously described (11). Those results indicated that regional cropland intensity (i.e. CROPLAND) and USAGE were more influential in explaining the variation in snowpack CUP and HUP concentrations in the individual parks than site temperature, latitude, elevation, or snowpack particulate matter (11).

Here, we conducted correlation analysis between CROPLAND and the mean of intra-park replicate log concentrations for the 2003, 2004, and 2005 snowpack samples (Figure S6). Results for HCB are not discussed due to inconsistent trends in 2003 and 2004 and lack of detection in 2005, which may be due to its low affinity for snow (Table S5) and potential to revolatilization from the snowpack (20). Log transformation was used because overall, correlations were better and showed less curvature (25) with mean log-transformed concentrations than mean concentrations. Correlations with CROPLAND were significant for dacthal and endosulfan for all three year but were not significant for the other pesticides (Figure S6). Correlation plots indicated that pesticide concentrations at Denali and Noatak/

Gates, where CROPLAND is zero, were sometimes as high as those in other parks and that, with the exception of dacthal and chlorpyrifos, concentrations at Noatak/Gates were consistently higher than those at Denali (by 6.5 times on average). Example regression plots are shown in Figure S7.

As reported previously for the 2003 data (11), log snowpack pesticide concentrations were not correlated with mean winter air temperatures (an example regression plot is shown in Figure S8). Pesticide concentrations in inter-annual replicates were also not correlated with SWE, particulate matter, or air mass back trajectory %membership (Table S1, Figure S2) during different years.

Nonetheless, we hypothesized that the colder air temperatures in the Alaskan Parks (Denali and Noatak/Gates) (Table S1) could be responsible for the relatively high snowpack pesticide concentrations at these specific parks. To test this hypothesis, we transformed measured snowpack concentrations, $C_{\text{snow(M)}}$, to temperature-normalized snowpack concentrations, $C_{\text{snow(N)}}$, using -6.5°C as the normalization temperature (see Experimental Section). A temperature of -6.5°C was selected because it was the mean winter air temperature at all parks; however, the choice of temperature had no effect on the results of our correlation analysis because the relationship between temperature-normalized concentrations at different sites is the same at any specified temperature.

The correlation coefficients were higher for the regression of CROPLAND with mean log temperature-normalized concentrations than with mean log concentrations for all pesticides except dacthal and endosulfan (which were already well-correlated with CROPLAND) (Figure S6). Improved correlation occurred because temperature normalization lowered the pesticide concentrations at Alaskan parks relative to those at other parks (Figure S7), indicating that the air concentrations in the Alaska parks were much lower than those at other parks. This result supports our hypothesis that relatively cold temperatures at the Alaskan parks caused enhanced air-to-snowpack partitioning of pesticides and that the distribution of pesticides among the parks in this study can be explained by regional source contributions if the effect of temperature on partitioning is taken into account.

To better understand the influence of regional pesticide sources on the distribution of CUPs among the parks in this study, we also performed correlation analysis between mean log temperature-normalized concentrations and both USAGE and USAGE+WIND (Figure 3). For comparison, correlation coefficients using mean log concentrations are shown in Figure S6; however, all correlation results discussed after this point were conducted with log temperature-normalized concentrations. Mean correlation coefficients for dacthal, which has an atmospheric half-life of ~24 days (34), were significant for regressions with CROPLAND and USAGE+WIND but not with USAGE (Figure 3). The correlation was not significant with USAGE because relatively high dacthal concentrations were measured at Glacier and N. Cascades but dacthal usage was minimal within 150km of these parks (Figure S9). The correlation was significant with USAGE+WIND because dacthal usage is relatively high in the one-day air sheds of Glacier and N. Cascades (Figure S9). These results indicate that dacthal concentrations in these parks are better explained by its usage within regions 1-day upwind from parks than by usage within 150 km of the parks. Our analysis (Table S4) also enables us to determine that the large majority (~72%) of the dacthal in Glacier's one-day airshed is associated with cluster F, representing southern Washington and central Oregon (Figure S2). Approximately 92% of the dacthal in the N. Cascades one-day air shed is associated with cluster D, representing central Washington (Figure S2).

Correlation coefficients for chlorpyrifos, which has an atmospheric half-life of ~1 day (35), were not significant for CROPLAND, significant in 2003 (but not in 2004 or 2005) for

USAGE, and significant in all years for USAGE+WIND (Figure 3). Lack of significance with CROPLAND occurred because chlorpyrifos use (Table S3) is much higher around Sequoia than around the other parks even though Sequoia's cropland intensity is similar to several other parks (Table S3).

For endosulfan, which has an atmospheric half-life of ~1 day (35), the pattern in correlations coefficients was similar to that of dacthal. The correlations with CROPLAND and USAGE +WIND were significant but not with USAGE (Figure 3). Endosulfan was not well-correlated with USAGE because endosulfan use near Glacier and Rocky was relatively low (Table S3) even though the measured endosulfan concentrations in these parks were moderately high compared to the other parks (Table S2). However, endosulfan was used in the one-day airshed of Glacier (SI Table 3), with the majority (~66%) being associated with cluster F, representing southern Washington and central Oregon (SI Figure 2). Endosulfan usage was also relatively high in Rocky's one-day airshed, with the majority (~64%) being associated with cluster F, representing southern Idaho and eastern Oregon (SI Figure 2).

Percent Regional Transport

We also calculated the regional transport contribution (%RT) for each pesticide, at each of the non-Alaskan parks, for each year (Figure 4). This was done by first calculating the global background concentration, which we defined as the mean temperature-normalized pesticide concentration in the Alaskan Parks (Denali and Noatak/Gates), where there was no regional pesticide use (Table S3). The global background concentration was then subtracted from each park's mean temperature-normalized pesticide concentration for a given year and multiplied by 100. The %RT was generally >75% (Figure 4) with the only exceptions being at Rainier in 2005 for γ -HCH, dieldrin, α -HCH, and chlordanes. %RT values reported here are generally higher than those we previously reported (11) due to the use of temperature-normalized pesticide concentrations in the Alaska parks. We believe that this is a more accurate approach. These results suggest that the majority of pesticide contamination in western US national parks is due to pesticide use in North America.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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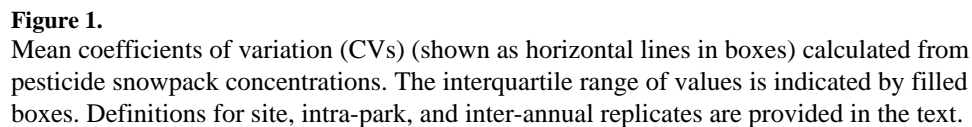
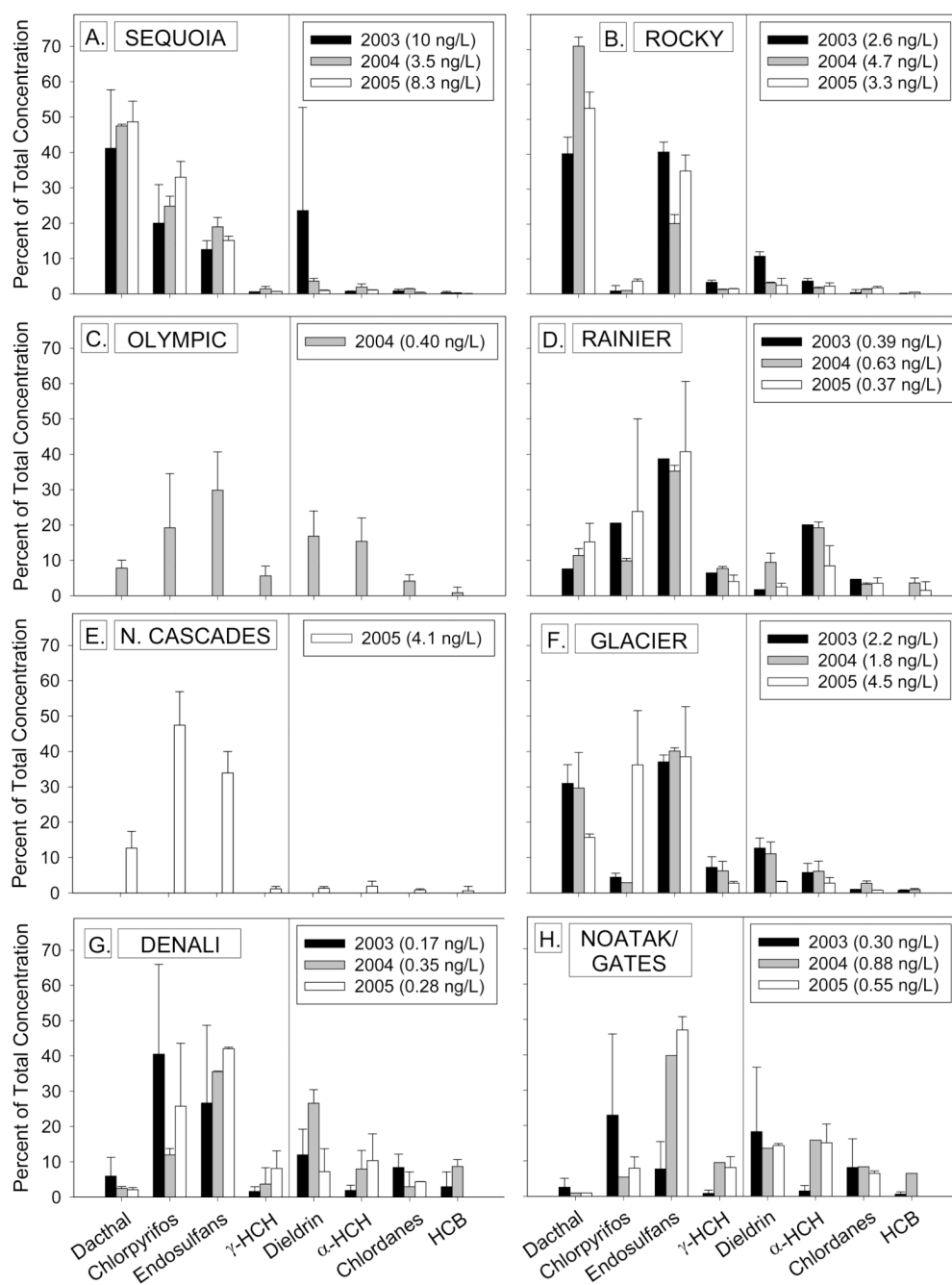


Figure 1. Mean coefficients of variation (CVs) (shown as horizontal lines in boxes) calculated from pesticide snowpack concentrations. The interquartile range of values is indicated by filled boxes. Definitions for site, intra-park, and inter-annual replicates are provided in the text.

**Figure 2.**

Pesticide concentration profiles for the eight most commonly detected pesticides in snowpack at each park. Bars represent the mean percent of the total concentration (i.e. the sum from the eight most commonly detected pesticides); error bars represent standard deviation among intra-park replicates. Total concentrations (mean of intra-park replicates) are listed for each year in parentheses.

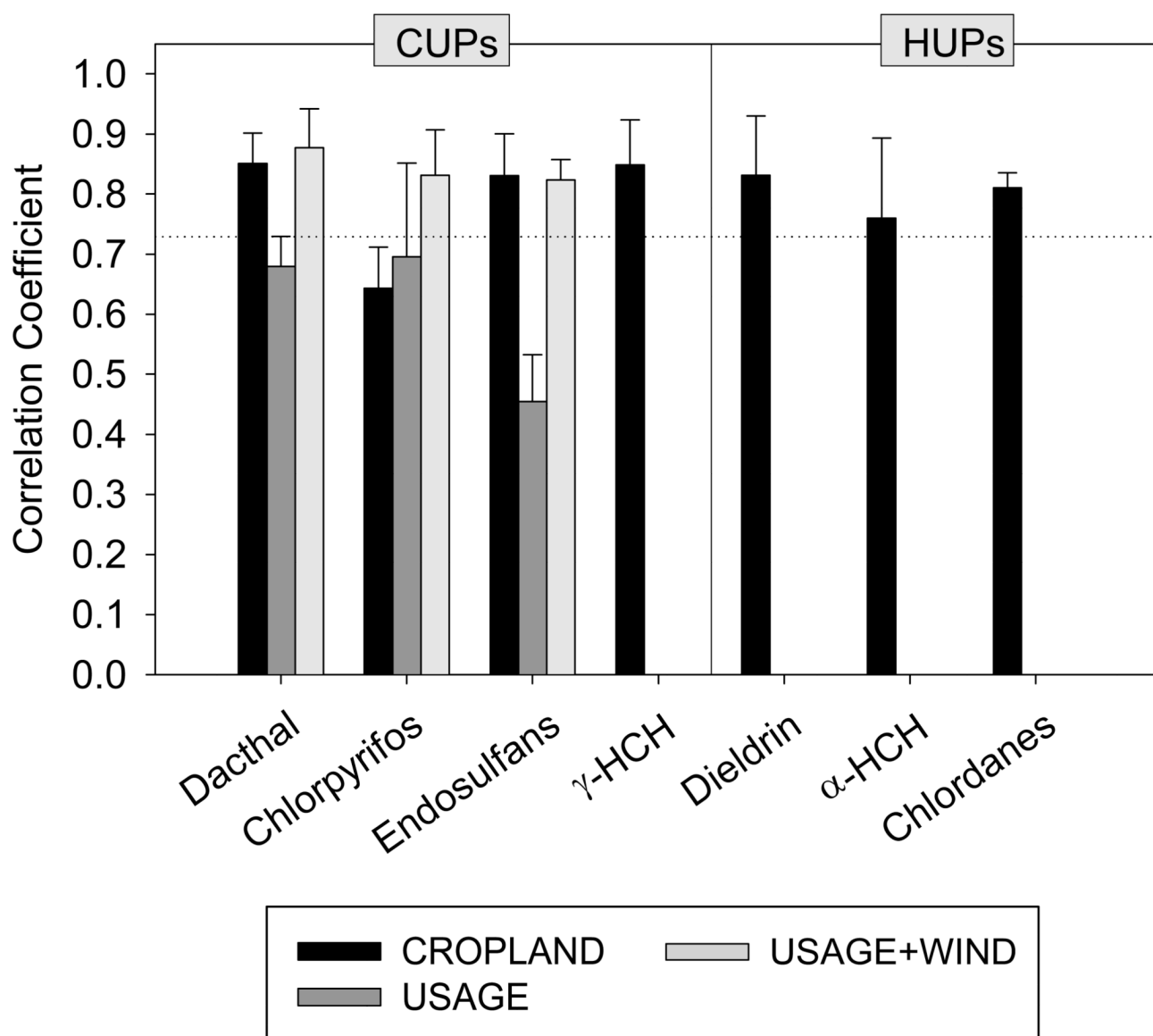


Figure 3.

Correlation coefficients for the regression of mean (intra-park replicate) log temperature-normalized concentrations with indicators of regional pesticide source intensity (definitions are provided in the text). Bars represent mean values calculated using snowpack samples from 2003, 2004, and 2005; error bars represent standard deviation. The dotted horizontal line indicates the significance threshold at $p < 0.05$ for 5 degrees of freedom (7 individual parks).

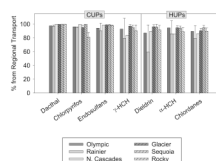


Figure 4.

Percent of total concentration due to regional transport (%RT). Bars represent mean values calculated for 2003, 2004, and 2005; error bars represent standard deviation. The percentage due to the global background signal, or long-range transport, can be estimated by subtracting %RT from 100. The global background signal was defined as the mean temperature-normalized concentration in the Alaskan Parks (Denali and Noatak/Gates).