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Comparison of Lichen, Conifer Needles, Passive Air Sampling Devices, and Snowpack as Passive Sampling Media to Measure Semi-Volatile Organic Compounds in Remote Atmospheres

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Abstract

A wide range of semi-volatile organic compounds (SOCs), including pesticides and polycyclic aromatic hydrocarbons (PAHs), were measured in lichen, conifer needles, snowpack and XAD-based passive air sampling devices (PASDs) collected from 19 different U.S. national parks in order to compare the magnitude and mechanism of SOC accumulation in the different passive sampling media. Lichen accumulated the highest SOC concentrations, in part because of its long (and unknown) exposure period, while PASDs accumulated the lowest concentrations. However, only the PASD SOC concentrations can be used to calculate an average atmospheric gas-phase SOC concentration because the sampling rates are known and the media is uniform. Only the lichen and snowpack SOC accumulation profiles were statistically significantly correlated ($r = 0.552$, $p\text{-value} < 0.0001$) because they both accumulate SOC present in the atmospheric particle-phase. This suggests that needles and PASDs represent a different composition of the atmosphere than lichen and snowpack and that the interpretation of atmospheric SOC composition is dependent on the type of passive sampling media used. All four passive sampling media preferentially accumulated SOC with relatively low air-water partition coefficients, while snowpack accumulated SOC with higher $\log K_{OA}$ values compared to the other media. Lichen accumulated more SOC with $\log K_{OA} > 10$ relative to needles and showed a greater accumulation of particle-phase PAHs.

Introduction

Passive air sampling is increasingly being recognized as an effective approach for measuring the relative concentrations of semi-volatile organic compounds (SOCs) in the atmosphere. Several types of natural media have been used to passively sample the atmosphere, including vegetation (1–6), soil (7, 8), and snowpack (9–11). Additionally, several types of

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Supporting Information Available

Details of the site and sample information, list of SOC measured and methods used, exposure periods, genus comparison, PAH concentration and profile, Tukey-Kramer honestly significant difference tests, and correlation coefficients are provided in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

manufactured media have also been used to measure the concentrations of SOC in air, including semi-permeable membranes (SPMDs) (12), polyurethane foam (PUF) disks (13), and Amberlite styrene divinylbenzene copolymer resin (XAD-based) passive air sampling devices (PASDs) (14). The selection of passive sampling media is important because the magnitude and mechanism of SOC scavenging from the atmosphere is dependent on the properties of the media and the physical-chemical properties of the SOC (15).

Previously, SOC accumulation in PUF and SPMDs (16), PUF, SPMDs, and soil (17), PUF and needles (18), XAD-based PASDs and soil (8, 19), lichen, PASDs, and soil (7), conifer needles, lichen, soil, and bark (20), conifer needles and soil (21), and lichen and conifer needles (15) have been compared. However, snowpack is increasingly being used to investigate SOC deposition to different locations (22) and no previous studies have directly compared lichen, conifer needles, PASDs, and snowpack collected from the same sites.

Vegetation is a useful passive air sampling media that naturally exists in temperate terrestrial ecosystems and contributes to food webs. Atmospherically derived SOC accumulate in terrestrial plants, including lichen and conifer needles, via wet and dry deposition. Additionally, gas-phase SOC can sorb to the waxy exterior of the foliage (23–25). Lichenized fungi, lacking barrier structures, absorb SOC directly into the thallus and, through wetting and drying cycles, accumulate pollutants in dynamic equilibrium with their availability in the air, canopy wash, and precipitation (26). SOC sorption in conifer needles occurs in the waxy surface (27). Accumulation in vegetation is dependent on the SOC physical-chemical properties, vegetation type, species, and plant surface area (5, 28, 29).

Man-made passive air samplers are manufactured uniformly and can be deployed for specific time periods in remote ecosystems where electrically powered active high-volume air samplers cannot be easily operated. Unlike vegetation and precipitation, PASDs can provide a quantitative assessment of SOC concentrations in the atmosphere because the uptake rates for some SOC have been determined (14). The XAD-based PASDs have a higher uptake capacity compared to the other manufactured samplers and is preferred for longer sampling periods of up to one year (14). Only gas-phase SOC are accumulated in the XAD-based PASD design (14).

Precipitation, specifically snow, efficiently scavenges both gas and particulate-bound SOC from the atmosphere (9–11, 30–32). During a snow event, gaseous SOC undergo sorption at the air-ice interface of the snow crystal whereas particulate-phase SOC can become trapped within the ice structure (11, 31).

The first objective of this research was to compare the magnitude of SOC accumulation in lichen, conifer needles, XAD-based PASDs, and snowpack samples collected from the same remote alpine and arctic sites in 5 Western U.S. national parks. The second objective was to determine if the different types of sampling media, collected from 19 remote alpine and arctic sites in Western U.S. national parks, preferentially accumulated different SOC from the atmosphere and if these differences were related to SOC physical-chemical properties. Differences in SOC accumulation in several lichen and conifer genera were also evaluated. This study provides mechanistic understanding that will aid future studies in selecting and using passive air sampling media.

Materials and Methods

Sampling

Lichen, needles, PASDs, and snowpack were collected from the same sites in five parks, including Emerald Lake in Sequoia, Mills Lake in Rocky, Hoh Lake in Olympic, Snyder

Lake in Glacier, and Wonder Lake in Denali (Figure 1). In addition, samples were collected from fourteen additional parks, but different sites within the parks, including Noatak, Gates of the Arctic, Katmai, Wrangell-St. Elias, Glacier Bay, Stikine LeConte, North Cascades, Mount Rainier, Crater Lake, Grand Teton, Yosemite, Great Sand Dunes, Bandalier, and Big Bend (Figure 1). The SOC concentration in needles has been shown to be a function of needle age (21, 33). For this reason, we only sampled 2-year old needles. The Supporting Information provides specific details of where, when, how and what species were collected (Table S1-S4), as well as the sampling details for PASDs and snowpack.

Analytical Method

The lichen and conifer needle analytical methods are described in detail in the Supporting Information. In brief, lichens and needles were ground, spiked with 28 isotopically-labeled surrogates (Tables S5 and S6) (34), and extracted using pressured liquid extraction (PLE). The lipid content of lichens and needles was measured gravimetrically by drying 2% of the extract by volume. The extract was purified with water extraction and silica solid-phase extraction (SPE) cartridges. For lichens, selected silica fractions were combined and analyzed directly for SOC. Conifer needle silica fractions underwent gel permeation chromatography (GPC) to remove additional interferences. Lichen and conifer needle fractions were concentrated with nitrogen to 0.2 mL and spiked with internal standards (34) prior to instrumental analysis. Laboratory blanks were prepared for every six lichen or conifer samples.

Lichen and conifer needle SOC concentrations are reported on a lipid basis. The SOC included in the study are lipophilic and partition to the lipophilic components of plant tissue (35). Normalizing the vegetation SOC concentrations to the lipid content more accurately accounts for variations in vegetation species than dry mass (23). The mean percent moisture and percent lipid for lichens were 33.3 ± 8.29 (% RSD) and 8.93 ± 0.98 (% RSD), respectively, and 55.9 ± 3.06 (% RSD) and 6.90 ± 3.69 (% RSD) for conifer needles, respectively.

For the PASDs, the retrieved XAD-2 was spiked with 28 isotopically-labeled surrogates (SI) (34) and extracted using PLE (36). The dry weight for the XAD-2 in each PASD was determined after extraction, averaged over all samples, and used to calculate the SOC concentration as ng/g XAD. The PASD extracts were concentrated with nitrogen to 0.2 mL and spiked with internal standards (34) prior to instrumental analysis.

The analytical method for the measurement of SOC in snowpack has also been described previously (34). In brief, snowpack samples were melted at room temperature for ~36 hours within the sealed collection bags, spiked with 28 isotopically-labeled surrogates, and extracted using two modified Speedisks (Mallinckrodt Baker, Phillipsburg, NJ) that contained hydrophobic and hydrophilic resins. The particulate phase and dissolved phase of the melted snow were not separated (30). Snowpack extracts underwent further cleanup with silica SPE and GPC (34). The snowpack extracts were concentrated to 0.2 mL and spiked with internal standards prior to instrumental analysis. Laboratory blanks were prepared with every set of two snowpack samples (9).

Instrumental Analysis

All lichen, conifer needle, PASD, and snowpack extracts were analyzed for SOC using an Agilent 6890 gas chromatograph (GC) with a $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$ DB-5 column (J&W Scientific, Palo Alto, CA) coupled to a 5793N mass spectrometer using either electron impact ionization (EI) or electron capture negative ionization (ECNI), depending on

the specific analyte. The GC temperature programs and ions monitored have been described elsewhere (34). The 65 SOC targets for analysis are listed in Tables S5 and S6.

Reported SOC concentrations were corrected for surrogate recovery and lab blank-subtracted. Sample-specific estimated detection limits (EDLs) were calculated using a representative sample from Rainier for lichen, needles, and PASDs and from Sequoia for snowpack following EPA-method 8280A (37) and are reported in Tables S5 and S6. The EDLs ranged from 0.004 to 35.78 ng/g lipid for lichen, from 0.013 to 56.42 ng/g lipid for needles, from 0.0002 to 0.206 ng/g for XAD, and from 0.0001 to 0.4 pg/g for snowpack. The sample SOC concentration was not reported if the sample blanks contained more than 33% of the sample SOC concentration or were below the estimated detection limits. The average recoveries of all surrogates were 68, 77, 74, and 55% (22, 34), for lichen, needles, PASDs and snowpack, respectively. For a listing of the analyte concentrations in each of the 379 samples measured in this study, see the WACAP database (http://www.nature.nps.gov/air/Studies/air_toxics/wacap.cfm).

Media Exposure Time Period

The approximate exposure time for each passive sampling media is listed in Table S7. Lichen exposure times could not be accurately determined because lichen age cannot be determined.

Although the PASDs were deployed at the same sites as lichen, conifer needles, and snowpack within the five parks, the PASD exposure period did not overlap with the lichen, conifer needles and snowpack exposure periods (Table S7). We have previously shown that, although the magnitude of SOC deposition in these parks varies from year-to-year, the relative contribution of each SOC to the total SOC concentration does not change significantly year-to-year (22). This indicates that the SOC sources to each park did not change significantly year-to-year within the time frame of this study (22). Based on this previous study, we assumed that the atmospheric SOC profiles did not vary significantly during the different media exposure time periods, allowing comparison of these non-overlapping datasets for the purposes of this work. Only the March 2003 and 2004 snowpack SOC concentrations were directly compared to the other passive sampling media SOC concentrations because they overlapped in exposure time period (Figures 2 and 3, Figures S1 and S2). However, the snowpack SOC concentrations from all years (including 2005) were used to investigate how SOC physical-chemical properties affected SOC accumulation in snowpack (Figure 4). Snowpack samples represent net SOC accumulation over the winter months through wet and dry deposition, as well as volatilization.

Results and Discussion

SOC Concentrations in the Different Media

The comparison of SOC concentrations in the different passive sampling media was limited to the five national parks (Denali, Olympic, Glacier, Sequoia and Rocky) where all four media were collected from the same sites. Mean concentrations of the most frequently detected current-use pesticides (CUPs) (dacthal, chlorpyrifos (sum of parent and oxon), endosulfans (sum of I, II, and sulfate), and γ -HCH) and historic-use pesticides (HUPs) (dieldrin, α -HCH, chlordanes (sum of *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, and *cis*-nonachlor), and HCB) are shown in Figure 2 for lichens (ng/g lipid), needles (ng/g lipid), PASDs (ng/g XAD), and snowpack (ng/g). The highest total pesticide concentrations (sum of the eight most frequently detected pesticides) were measured in *Platismatia glauca* lichen at Glacier (1,530 ng/g lipid). The highest total pesticide concentrations in needles, PASDs, and snowpack were at Sequoia (293 ng/g lipid, 2.0 ng/g XAD, and 6.01 ng/g, respectively)

(Figure 2). The pesticide concentrations were lowest in all four passive sampling media at Denali.

In general, of the four different passive sampling media, the individual pesticide concentrations were highest in lichen (Figure 2). This was the case for all of the most frequently detected pesticides at Sequoia, Olympic, and Glacier. However, some pesticide concentrations were higher in needles at Rocky and Denali than in lichen. This is likely because of lichen species differences among the parks. In Sequoia, Olympic, and Glacier, tree-dwelling lichens were present in the ecosystem and were collected. However, only rock lichen (*Xanthroparmelia*) was present in the Rocky ecosystems and only tundra lichen (*Masonhalea richardsonii*) was present in the Denali ecosystems. While the tree lichens accumulated SOC_s throughout the year, the rock and tundra lichen accumulated SOC_s for limited periods during the year because of snow cover and spring melt water. In Glacier and Sequoia, the dacthal, endosulfan I, endosulfan II, endosulfan sulfate, γ -HCH, α -HCH, *trans*-chlordane, and nonachlors concentrations in lichen were significantly higher than in the other passive sampling media (Tukey-Kramer Honestly Significant Difference (HSD), *p*-value < 0.05) (Table S9). However, in Denali, endosulfan sulfate, HCB and α -HCH concentrations were significantly higher in needles than in lichens. At Rocky and Olympic, the pesticide concentrations in lichens and needles were not statistically different.

The most frequently detected pesticides were measured in snowpack collected from each of the five parks, except *cis*-chlordane was not measured in any of the parks and *trans*-chlordane and endosulfan II were not measured in Denali. Snowpack HCB and γ -HCH concentrations at Denali were excluded from the data set due to high blank concentrations. All of the most frequently detected pesticides, except for dieldrin, were detected in the PASDs. However, PASD pesticide concentrations were up to three orders of magnitude lower than the other passive sampling media (Figure 2).

Figure S1 shows the mean PAH concentrations in lichens (ng/g lipid), needles (ng/g lipid), PASDs (ng/g XAD), and snowpack (ng/g) for the five parks where samples were collected from the same sites. The highest total PAH concentrations were measured in lichens, PASDs, and snowpack collected from Glacier (91,800 ng/g lipid, 2.82 ng/g XAD, and 0.549 ng/g, respectively) and in needles from Sequoia (301.3 ng/g lipid). In Glacier, all of the individual PAH isomer concentrations were significantly higher (*p* < 0.05) in lichens than in the other passive sampling media. We have previously shown that there are high atmospheric PAH concentrations in Glacier relative to the other parks (38). The lowest total PAH concentrations in lichen and snowpack were measured in Denali. PAHs were not detected in needles from Rocky and Olympic because the concentrations were below the detection limit. PAHs were not quantified in PASDs from Sequoia, Rocky, and Denali because the travel blank PAH concentrations for these parks were high. In general, the particulate phase PAHs (benzo[a]anthracene, chrysene/triphenylene benzo[b]fluoranthene, benzo[k] fluoranthene, benzo[e]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[ah]anthracene, and benzo[ghi]pyrene) were only detected in snowpack and the highest concentrations were measured in Glacier (Figure S1) (38).

Pesticide and PAH concentrations in different lichen genera were compared at the same sites because multiple lichen genera were present at the sites. However, the pesticide and PAH concentrations in different conifer genera could only be compared at the same parks because multiple conifer genera were only present within a park. The park name, lichen and conifer genera, and SOC concentration differences are listed in Table S8 and ranged from 1.2 to 71 times. Particulate-phase PAHs were only measured in the lichen genera *Hypogymnia* and *Letharia* at Glacier. Pesticide and PAH concentrations were generally higher in epiphytic lichen genera with textured (*Hypogymnia*) or wrinkled (*Platismatia*) lobes and filamentous

structure (*Letharia* and *Alectoria*) compared to smooth, dense rock lichens (*Xanthoparmelia*) and tundra lichens with smooth (*Masonhalea*) or leafy (*Flavocetraria*) lobes. In addition, the location of the lichen species in the ecosystem (above or below the snowline and rock lichen or epiphytic lichen) also affected exposure times and concentrations. The SOC concentrations in needles had the following order (after lipid normalization): *Tsuga* > *Pseudotsuga*, *Abies* > *Picea*, *Pinus*. This may indicate that flat, broad needles accumulated more SOC compared to narrow or rounded needles, with concentration differences of up to 71 times higher.

Preferential Accumulation of SOC in the Different Media

To compare lichen, conifer needle, PASD, and snowpack pesticide and PAH accumulation profiles statistically, the average percent contribution of each pesticide or PAH to the total pesticide (Σ Pesticide) or PAH (Σ PAH) concentration was calculated for each passive sampling media at the five parks where all four media were collected from the same sites. Figure 3 shows the mean pesticide profile for the most frequently measured pesticides by park and by media. In addition, the pesticide profiles in the different media were compared statistically using the Tukey-Kramer honestly significant different (HSD) test (Table S9) (39, 40). Relative to the other SOC, lichens and needles preferentially accumulated endosulfan sulfate at four of the five sites, PASDs preferentially accumulated HCB at four of the five sites, and snowpack preferentially accumulated dacthal at three of the five sites (Table S9).

To further compare the SOC accumulation profiles in the different passive sampling media, we looked for correlations between the mean SOC profiles (all pesticides and PAHs combined) in the different media (Table S10). Only the lichen and snowpack SOC profiles were significantly correlated ($r = 0.552$, $p\text{-value} \leq 0.0001$) (Table S10). This suggests that lichen and snowpack reflect a different atmospheric composition than needles and PASDs and that the interpretation of atmospheric SOC composition is dependent on the type of passive sampling media used.

Properties Governing Accumulation in the Different Media

The roles of the temperature-corrected air-water (K_{AW}) and octanol-air (K_{OA}) partition coefficients and the estimated atmospheric particulate phase fraction (Φ) of each SOC were investigated to understand how these properties influenced the accumulation of SOC in the different passive sampling media. The SOC K_{AW} values were estimated using Henrywin 3.10 (EPI Suite 3.12) and the temperature variation equations for Henry's Law constant, H (41), while the average monthly maximum temperature for the exposure period, at each sampling site, was estimated using PRISM (see Supporting Information) (42). The SOC log K_{OA} values were estimated using the site temperature-corrected K_{AW} values, divided by K_{OW} (estimated using KOWIN 1.67). K_{OW} was not corrected for site temperature because of its limited temperature dependence (43, 44). The fraction of each SOC in the atmospheric particulate phase is strongly influenced by SOC K_{OA} value and was calculated using the estimated K_{OA} values and the K_{OA} absorption model (43, 44) (see Supporting Information).

The influence of K_{AW} , log K_{OA} , and Φ on SOC accumulation in the different passive sampling media was investigated by calculating the frequency of detection of the different SOC (all individual pesticides and PAHs) in the 74 lichen samples, 83 needle samples, 36 PASD samples, and 30 snow samples that were collected from 19, 18, 19, and 8 parks, respectively (Figure 4). Approximately 80% of the SOC detected in lichens, needles, and PASDs, and approximately 98% of the SOC detected in snowpack, had K_{AW} values ranging up to 0.005 (Figure 4A). This indicated that all four passive sampling media preferentially accumulated SOC with relatively low K_{AW} values. The highest site

temperature-corrected K_{AW} values (>0.014) were for HCB and cis- and trans-chlordane at the warmest parks (Big Ben, Bandelier, and Sequoia).

Figure 4B shows that 25 to 54% of the SOC_s detected in all four sampling media had log K_{OA} values ranging from 8 to 10. SOC_s with log K_{OA} values between 11 and 12 also showed a relatively high frequency (20%) of detection in snowpack but not the other three media. This suggests that snowpack accumulated SOC_s with higher log K_{OA} values compared to the other media. Lichen accumulated more SOC_s with log K_{OA} > 10 relative to needles and showed a greater accumulation of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[e]pyrene, indeno[1,2,3-cd]perylene, dibenzo[ah]anthracene, and benzo[ghi]perylene relative to needles. PASDs accumulated only PAHs with log K_{OA} < 10 , which is consistent with previous studies (14).

Figure 4C shows that lichens, needles, and snowpack accumulated the widest range of SOC_s, including particulate phase SOC_s with Φ up to 83, 79, and 96% respectively. PASDs accumulated the narrowest range of SOC_s with Φ up to 7%. The frequency of detection for SOC_s with $\Phi > 20\%$ in lichens was 5.6 times higher than in needles, indicating that particle-bound SOC_s were detected more frequently in lichens than in needles. SOC_s with $\Phi > 80\%$ were detected in snowpack 36 times more frequently than in lichens. These results suggest that particulate phase SOC_s are accumulated in the following order: snowpack $>$ lichens $>$ needles and not accumulated in the XAD-based PASDs.

We have measured the net SOC concentration in the different passive sampling media after a lengthy (but typical) exposure period and environmental processes, including volatilization, photolysis, and biodegradation, likely occurred in each media to change the SOC concentration in the different sampling media over the sampling period. The proper selection of passive air sampling media is dependent on the study design; including the geographic location of the study (presence of vegetation, ambient temperature, and ease of access), the SOC_s of interest (vapor pressure and whether the SOC is present in the gas or particle phases), and the exposure time period of interest (season, as well as the duration and accuracy of knowing the exposure time period).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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FIGURE 1.

Map of U.S. national parks from which lichen, two-year old conifer needles, PASDs, and snowpack were collected. Letters after the park name indicate the media collected: “L” is lichen; “N” is needles; “P” is PASDs; “S” is snowpack. Parks with an asterisk indicate that lichen, needles, PASDs, and snowpack were collected from the same sites within the park.

FIGURE 2.

Mean concentrations of the 8 most frequently detected CUPS and HUPs in lichen (ng/g lipid), conifer needles (ng/g lipid), PASDs (ng/g XAD), and snowpack (ng/g) collected from the same sites, by park (A–E). Error bars represent the standard deviation among site replicates for lichen and needle samples within the same year ($n = 3$) and interannual replicates at the same site for snowpack ($n = 2$, except for Olympic where $n = 1$). The asterisk indicates the SOC was not detected for that media. Note the y-axis scale varies among graphs. Snowpack data includes the 2003 and 2004 snow accumulation periods.

FIGURE 3.

Mean percent of the total pesticide concentration for 8 of the most frequently detected CUPs and HUPs in lichen, conifer needles, PASDs, and snowpack collected from the same sites, by park (A–E). Error bars represent standard deviation among site replicates for lichens and needles within the same year ($n = 3$) and interannual replicates at the same site for snowpack ($n = 2$, except for Olympic where $n = 1$). The asterisk indicates the SOC was not detected for that media. Total pesticide concentrations for these 8 pesticides are shown for each media in parentheses. Snowpack data includes 2003 and 2004 snow accumulation periods.

FIGURE 4.

Frequency of detection for SOC classes within a range of K_{AW} (A), $\text{Log } K_{OA}$ (B), and percent particulate fraction (C) in lichen (74 samples), conifer (86 samples), PASDs (36 samples), and snowpack (30 samples) collected from 19, 18, 19, and 8 national parks, respectively. The asterisk indicates the SOC was not detected for that media.