The Use of Vegetation to Study the Atmospheric Transport of Persistent Organic Pollutants to High Elevation Ecosystems in Sequoia National Park

Jill E Schrlau[1], Eli Moor[1], Lisa M Deskin[1], Linda Geiser[2], Staci L Simonich[3]

[1]Department of Chemistry, Oregon State University
[2]USDA - Forest Service, Corvallis, Oregon
[3]Department of Chemistry and Department of Environmental and Molecular Toxicology, Oregon State University

Introduction

The transport and deposition of persistent organic pollutants (POPs) and other semi-volatile organic compounds (SOCs) to higher elevation, remote ecosystems through the atmosphere has become an increasing concern. SOCs are transported through the atmosphere and into terrestial ecosystems based on persistence, subcooled vapor pressure changes with temperature, and interactions with lipids in foliage, soil and surface water.[1-3] Deposition of SOCs to vegetation occurs through wet and dry deposition.[4] Vegetation has been determined to be an important sink for SOCs because it covers approximately 80% of the earth's surface, has 6-14 times the surface area of the land, and has a wax (lipid) layer that promotes SOC accumulation.[5] The amount accumulated is dependent on the concentration of the SOC in the atmosphere and its octanol-air partition coefficient.[6] Vegetation has been used to biomonitor atmospheric SOC concentrations in previous studies using lichen, conifer needles, and bark.[7-10]

Lichen, conifer needles, and willow bark all have advantages and disadvantages as passive air samplers for POPs. Lichen has a long life span and can reflect 10-20 years of SOC concentration in the atmosphere. The disadvantage is that the exact age cannot be determined. Lichen can be sampled at higher elevations than conifer needles and willow bark. Analysis, however, requires a large amount of lichen and site abundance may be a limiting factor. Several studies have been conducted using lichen for the measurement of SOCs in the environment that will be useful for comparison of future data.[11-13] Conifer needles can be easily dated to 1 and 2 years by the growth pattern and thus can provide an average of SOC concentration for a short time scale. Sampling of needles is relatively easy except for harvesting needles of a particular age as this requires extra time and attention. Previous studies have been conducted using conifer needles collected from high elevation ecosystems.[7-9] Willow twigs can be easily aged by counting the rings of the twig from which it is removed from and can be greater than 10 years. The age of the wood, however, may not be the age of the bark due the bark flaking off over time. Willows are present at all the sites of interest all year long, grows at relatively high elevations and are easily sampled.[11] Willow bark has not been previously used in high elevation studies but tree bark, in general, has been used for a global study.[3]

The purpose of this study was to examine the differences between lichen (*Letharia vulpina*), conifer needles (*Pinus contorta*), and willow bark (*Salix alba*) with respect to matrix interferences and the number and concentration of SOCs detected at high elevation sites in Sequoia National Park. Although a greater percent lipid should accumulate a higher concentration of SOCs, it is theorized that this may also cause a higher level of matrix interferences increasing the level of detection during analysis. The vegetation with the greater number of SOCs detected at a higher concentration, as well as consideration of the ease of age determination and species location, will be sampled as part of the Western Airborne Contaminant Assessment Project (WACAP)[14]. WACAP assesses the deposition of atmospheric contaminants in western national parks to provide information on exposure, accumulation, impacts, and probable sources. Additionally, a comparison of SOC concentration from whole and ground lichen and conifer needles were performed to determine if grinding increased extraction efficiency.

Materials and Methods

Samples were collected from Sequoia National Park near Emerald Lake on August 24-26, 2003 (36.58 N, 118.67 W; 2800 masl). Samples were packed on ice during shipping and stored in a freezer at -20^{o}C. Aging of conifer needles took place on site and only 2 year samples were collected while willow bark was peeled from twigs that were later used for aging. For a lipid normalized comparison of SOC concentration, lichen and conifer needles were kept whole but willow bark was ground using a Büchi Mixer B-400 (Switzerland). The willow bark was separated into two age groups: 5.5 – 8 years old and 8.5 – 11 years old. The willow bark age was determined by counting the average number of rings on the ends of the willow stems.

Lichen, conifer needles, and willow bark samples with wet weights 20-50 g were extracted using an Accelerated Solvent Extraction System (ASE). Labeled surrogates were spiked onto the sample before being extracted twice with dichloromethane (DCM) under the following ASE conditions: pressure - 1500 psi, temperature - 100^{0}C, flush - 75%. The percent lipid for each extract was determined by weighing a dry aliquot equal to less than 1% of the total volume. Water extractions were performed two times and the solvent layer was dried with baked Na_2SO_4. The extracts were transferred to silica columns for additional clean-up. The lichen extracts were blown down to 300 µL, spiked with internal standards, and diluted 10 fold. The conifer needles and willow bark extracts required further clean-up using gel permeation chromatography (GPC). The GPC consisted of an Envirogel guard column and two Envirogel clean-up columns (Waters) with a pore size of 100Å. The conifer needles and willow bark extracts were blown down to 300µL, spiked with internal standards, and diluted 10 fold. The extracts were analyzed on electron capture negative ionization (ECNI) and electron impact (EI) gas chromatography/mass spectrometry (GC/MS) in SIM (selective ion monitoring) mode. Both GC/MS systems were Agilent 6890 GC with a DB -5MS column (J&W Scientific, 30 m) interfaced with Agilent 5973N MSD.

Results and Discussion

The lipid content and the length of time the vegetation was exposed to SOCs in the atmosphere were investigated. The percent lipid for lichen, conifer needles, and willow bark was determined to be 4.9%, 2.65% and 10.3%, respectively. Based solely on the percent lipid measurements, willow bark had the potential to store more SOCs, followed by lichen and conifer needles. The ages of lichen, conifer needles, and willow bark were greater than 10 years, 2 years, and 5.5 -11 years, respectively. Based solely on the length of exposure to the atmosphere, lichen had the potential to contain a higher concentration of SOCs, followed by willow bark and conifer needles.

The lipid normalized SOC concentrations detected in lichen, conifer needles, and willow bark are shown in Figure 1. The concentrations for the two age groups of willow bark were not statistically different so the data were combined. Figure 1 shows elevated concentrations of SOCs in lichen, specifically dacthal and Σ endosulfan . In addition, all of the SOCs listed in Figure 1 were measured in lichen but only five of the seven were measured in conifer needles and two of seven in willow bark. As previously discussed, lichen may contain a higher concentration and number of SOCs because of its length of exposure to the atmosphere. The fewer number of SOCs detected in willow bark may be attributed to matrix interferences which affected the identification of some SOCs.

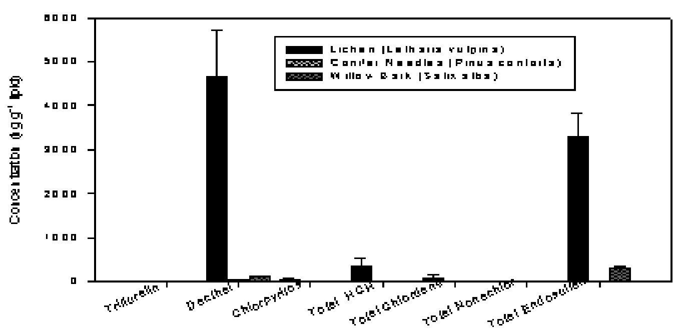

Figure 1: Comparison of SOC concentration (ng g^{-1} lipid) in lichen, conifer needles, and willow bark

The comparison of whole and ground conifer needles is shown in Figure 2. Ground conifer needles contained a highe concentration of all SOCs listed and gamma-HCH and PCB 153 were only detected in this sample. This indicates tha conifer needles should be ground prior to extraction. A comparison was also performed for lichen (data not shown) bu concentrations from both the whole and ground samples were similar.

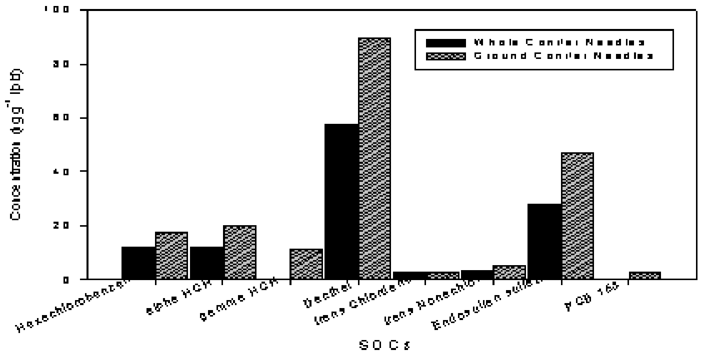

Figure 2: Comparison of SOC concentration (ng g^{-1} lipid) in whole and ground conifer needles

Based on the results above, the age of the vegetation, and growth regions, lichen and conifer needles were chosen as the vegetation to be sampled for the WACAP project. Willow bark was not selected because it had the lowest number and concentration of SOCs and aging the bark was not very reliable. Although lichen had a greater number and concentration of SOCs than conifer needles, the age of the conifer samples represented atmospheric concentration over the past 2 years while the lichen samples ranged to over a decade. Despite the inability to age lichen exactly, it may represent a decade of total environmental SOC deposition history to that ecosystem. The different growth patterns of lichen and conifer needles also made a good combination because lichen grow at higher elevations than conifers, allowing for higher elevation studies than possible with just conifers. At sites containing both types of vegetation, lichen and conifer needles will be sampled.

Acknowledgements

This work is part of WACAP (Western Airborne Contaminants Assessment Project), a collaborative venture between the National Park Service, the Environmental Protection Agency, the U.S. Geological Survey, Oregon State University, University of Washington, and the U.S.D.A. Forest Service. It was funded primarily through cooperative and interagency agreements with the National Park Service, and also included in -kind contributions from all of the project partners. Further information about WACAP can be found on the WACAP web site at: http://www2.nature.nps.gov/air/Studies/air_toxics/wacap.htm. This document has been subjected to appropriate institutional peer review and/or administrative review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This publication was made possible in part by grant number P30ES00210 from the National Institute of Environmental Health Sciences, NIH. Its contents are solely the responsibility of the authors and do not necessarily represent the official view of the NIEHS, NIH.

The authors would also like to thank Linda Geiser and the crew at the Forest Service for sample collection and Bethany Lund for sample preparation.

References

1. Wania, F. and D. Mackay. (1993). *Ambio*. 22: 10

2. Mackay and F. Wania. (1995). *Sci. Total Environ.* 25: 160-161.

3. Simonich, S.L. and R.A. Hites. (1995). *Science*. 269: 1851-1854.

4. Daly, G.L. and F. Wania. (2005). *Environ. Sci. Technol*. 39: 385-398.

5. Simonich, S.L. and R.A. Hites. (1994). *Nature*. 370:49-51.

6. Simonich, S.L and R.A. Hites. (1994) *Environ. Sci. Technol.* 28: 939-943.

7. Grimalt, J.O., F. Borghini, J.C. Sanchez-Hernandez, R. Barra, C.J. Torres Garcia, and S. Forcardi. (2004). *Environ. Sci. Technol. 38: 5386 – 5392.*

8. Kylin, H., E, Grimvail, and C. Östman. (1994). *Environ. Sci. Technol.* 28: 1320-1324

9. Davidson, D.A., A.C. Wilkinson, J.M. Blais, L.E. Kimpe, K.M. McDonald, D.W. Schindler. (2003). *Environ. Sci. Technol*. 37: 209-215.

10. Davidson, D.A., A.C. Wilkinson, L.E. Kimpe and J.M. Blais. (2004). *Enviro. Sci. Technol*. 23: 540-549.

11. Calamari, D., E. Bacci, S. Forcardi, C. Gaggi, M. Morosini, and M. Vighi. (1991) *Environ. Sci. Technology*. 25: 1489-1495.

12. Morosini, M., J.Schreitmuller, U. Reuter and K. Ballschmiter. (1993). *Environ. Sci. Technol*. 27: 1517-1523.

13. Muir, D.C.G., M.D. Segstso, P.M. Welbourn, D. Toom, S.J. Eisenreich, C.R.MacDonald and D.M. Whelpdale. (1993). *Environ. Sci. Technol*. 27: 1201-1210.

14. Landers, D. H.; Simonich, S. L.; Campbell, D. H.; Erway, M. M.; Geiser, L.; Jaffe, D.; Kent, M.; Schreck, C.; Blett, T.; Taylor, H. E. Western Airborne Contaminants Assessment Project Research Plan. **2003**, *Western Airborne Contaminants Assessment Project Research Plan.EPA/600/R-03/035. U.S. Environmental Protection Agency, Office of Research and Development, NHEERL, Western Ecology Division, Corvallis, Oregon. (http://www2.nature.nps.gov/air/Studies/air_toxics/wacap.htm).*

.