Trans-Pacific Atmospheric Transport of Persistent Organic Pollutants and other Anthropogenic Semivolatile Organic Compounds to a High Elevation Site in the Pacific Northwest, U.S.A

Toby Primbs¹, David Schmedding², Glenn Wilson², Carol Higginbotham³, Staci Simonich⁴

¹Department of Chemistry, Oregon State University

²Department of Environmental and Molecular Toxicology, Oregon State University

³Department of Science, Central Oregon Community College, Bend, Oregon

⁴Department of Chemistry and Department of Environmental and Molecular Toxicology, Oregon State University

Introduction

Persistent organic pollutants (POPs) and other anthropogenic semivolatile organic pollutants (SOCs)may undergo long-range atmospheric transport, from Eurasian sources, and deposition to high elevations ecosystems in North America; with the potential of impacting these sensitive ecosystems¹⁻⁴. Air trajectories, combined with chemical measurements, show that transport across the Pacific can occur in as little as 5 to 10 days in the winter and spring seasons⁵. Direct contamination from Asia to the Pacific Coast of North America has been identified⁵⁻¹⁰. For more than a decade, the global atmospheric transport of POPs and other anthropogenic SOCs has been shown to cause surface contamination in remote locations¹ such as the Artic¹¹. Research investigating atmospheric transport of POPs and other anthropogenic SOCs, from Asia to the Pacific Coast of North America, is just beginning^{6-7,10}. High elevation sites may be in the free troposphere more often, and allow for more conclusive identification of trans-Pacific transport events. Additionally, further understanding of the trans-Pacific atmospheric transport of anthropogenic SOCs may have an impact on future treaties involving intercontinental transport of pollutants¹².

Atmospheric measurements of POPs and other anthropogenic SOCs were made at a high elevation site in the Pacific Northwest of the U.S. to further understand the trans-Pacific transport of SOCs. The primary objective of this preliminary study was to identify the differences between "background" concentrations of SOCs and trans-Pacific transport event concentrations of SOCs at this site.

Materials and Methods

High volume air sampling (~25 m³/hr for 24 hour periods) of both the gas and particulate phases began 20th April 2004 and is ongoing. The air sampling station is located on top of the summit building Mt Bachelor, Oregon, U.S.A. located in Oregon's Cascade Mountain Range (43.98°N, 121.69°W, ~2700 masl). The sampling media consists of two quartz fiber filters (Whatman) in series, for the collection of particle-phase analytes (the first filter) and for correction of sampling artifacts due to gas-phase sorption to the filter during sample collection (the second filter). Additionally, two polyurethane foam (PUF) plugs (Tisch Environmental) with XAD-2 resin (styrene divinylbenzene) (Supelco) in between the two plugs, was used for the collection of gas-phase analytes (first PUF and XAD-2) and the determination of potential analyte break-through (second PUF). The glass fiber filters were cleaned by heating at 350°C for 12 hours and the PUF plugs were cleaned by Accelerated Solvent Extraction (Dionex) with dichloromethane and ethyl acetate prior to use.

To date eighteen twenty-four hour samples have been collected, in addition to three field blanks. After sample collection, Accelerated Solvent Extraction was used to extract the analytes from the filters, PUF, and XAD-2. A Zymark Turbovap was used for solvent evaporation. Eighty one target analytes were selected for this project that represent emissions from combustion (polycyclic aromatic hydrocarbons), agricultural (pesticides), and industrial (polychlorinated biphenyls) sources. Both electron impact and electron capture negative ionization gas chromatographic (30 m J&W DB-5 GC column) mass spectrometry (GC/MS) were used in the SIM (selective ion monitoring) mode for the analysis to optimize instrument sensitivity. Instrument detection limits in electron impact and electron capture mode are on the order of 100 pg, while the instrument detection limits in the electron capture mode are on the order of 1 pg for chlorinated SOCs. Isotopically labeled compounds are used as surrogates and internal standards to quantify

EMV - Sources of POPs in the Pacific Rim

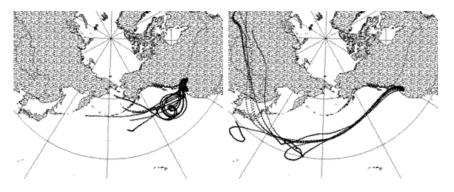
the concentration of the SOCs in extracts. Following chemical analysis of the samples, ten day back air trajectories were calculated using data from NOAA's Air Resources Laboratory (HYSPLIT). The trajectories were calculated every four hours for a twenty four hour period, and then imported into the ArcGIS program for spatial representation.

Other simultaneous atmospheric measurements are performed at Mt Bachelor Observatory by the Jaffe Group (University of Washington-Bothell) and Frontier Geosciences (Seattle, WA) and include: NO_x , CO, O_3 , aerosol light scattering (Nephelometer), Hg, and meteorology.

Preliminary Results and Discussion

Preliminary results for two of the eighteen samples collected to date are presented below. Figure 1 shows ten day back trajectories, one HYSPLIT trajectory every four hours for a twenty four hour sample. The sample collected on the 25-26 April has been described as a trans-Pacific transport event¹³. Jaffe et al. measured simultaneous increases in Hg, CO, O_3 , and sub-micron aerosol scattering during the 25 April event¹³. During this event there were no significant

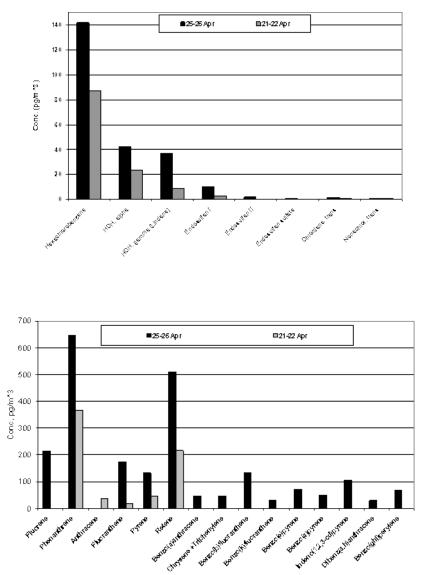
increases in NO_x , which can be used as an indicator for local pollution because of its short atmospheric lifetime¹³. Figure 1 also shows the back trajectories for the sample collected on 21-22 April 2004, which was not a trans-Pacific transport event.



21-22 April 2004 25-26 April 2004

Figure 1: Ten day back trajectories for the 24 hour samples collected on 21-22 April 2004 and 25-26 April 2004. The back trajectories were calculated using HYSPLIT and imported into ARC/GIS.

Figure 2 shows the concentration differences between the two samples for selected organochlorine compounds and polycyclic aromatic hydrocarbons (PAHs). Concentrations below represent the total concentrations (filters + PUF + XAD-2) and are recovery corrected, but not field blank corrected. The sample collected on the 25-26 April, during the trans-Pacific transport event, had elevated concentrations for HCB, HCHs, and endosulfans; as well as higher concentrations and numbers of PAHs than the non-trans-Pacific event. Additionally, higher molecular weight PAHs, in the "particulate phase", were measured in the sample collected on 25-26 April and not in the sample collected on 21-22 April.



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Figure 2: Concentrations of organochlorine pesticides (top) and polycyclic aromatic hydrocarbons (bottom). Elevated concentrations of most SOCs were measured in the sample collected during a trans-Pacific transport event (25-26-Apr) as compared to a non- trans-Pacific transport event (21-22 April).

In conclusion, elevated concentrations of most SOCs were measured in the sample collected on 25-26 April (trans-Pacific transport event) as compared to the sample collected on 21-22 April (non-trans-Pacific transport). Analysis of additional samples will assist in identifying additional differences between trans-Pacific events and non-trans-Pacific events at this high elevation site. Measurements of levoglucosan, a marker for biomass burning, will further assist in identifying combustion sources.

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References

- 1. Simonich S. L. and Hites R. A. (1995) Science. 269: 1851-1854.
- 2. Wania, F. a. M., D. (1996) Environmental Science & Technology. 30: 390A-396A.
- Grimalt, J. O.; Fernandez, P.; Berdie, L.; Vilanova, R. M.; Catalan, J.; Psenner, R.; Hofer, R.; Appleby, P. G.; Rosseland, B. O.; Lien, L.; Massabuau, J. C.; Battarbee, R. W. (2001) *Environmental Science & Technology*. 35: 2690-2697.
- Blais, J. M.; Schindler, D. W.; Muir, D. C. G.; Kimpe, L. E.; Donald, D. B.; Rosenberg, B. (1998) Nature. 395: 585-588.
- 5. Wilkening K. E., Barrie L. A. and Engle M. (2000) Science. 290: 65-+.
- Killin R. K., Simonich S.L., DeForest C.L. and Wilson G.R.(2004) Journal of Geophysical Research. 109: D25S15.
- 7. Harner T., Shoeib M., Kozma M., Gobas, F.A.P.C. and Li S.M. (2005) *Environmental Science & Technology*. 39: 724-731.
- 8. Jaffe D., Bertschi I., Jaegle L., Novelli P., Reid J.S., Tanimoto H., Vingarzan R. and Westphal D.L. (2004) *Geophysical Research Letters*. 31: L16106.
- 9. Jaffe D., Anderson T., Covert D., Kotchenruther R., Trost B., Danielson J., Simpson W., Berntsen T., Karlsdottir S., Blake D., Harris J., Carmichael G. and Uno I. (1999) *Geophysical Research Letters*. 26: 711-714.
- 10. Bailey R., Barrie L. A., Halsall C. J., Fellin P. and Muir D. C. G. (2000) Journal of Geophysical Research-Atmospheres. 105: 11805-11811.
- MacDonald R. W., Barrie L. A., Bidleman T. F., Diamond M. L., Gregor D. J., Semkin R. G., Strachan W. M. J., Li Y. F., Wania F., Alaee M., Alexeeva L. B., Backus S. M., Bailey R., Bewers J. M., Gobeil C., Halsall C. J., Harner T., Hoff J. T., Jantunen L. M. M., Lockhart W. L., Mackay D., Muir D. C. G., Pudykiewicz J., Reimer K. J., Smith J. N., Stern G. A., Schroeder W. H., Wagemann R. and Yunker M. B. (2000) Science of the Total Environment. 254: 93-234.
- 12. Holloway T., Fiore A. and Hastings M.G. (2003) Environmental Science & Technology. 37: 4535-4542.
- 13. Jaffe D., Prestbo E., Swartzenruber P., Weiss-Penzias P., Kato S.; Takami A., Hatakeyama S. and Kajii Y. (In Press Jan 2005) *Atmospheric Environment..*