Trans-Pacific Atmospheric Transport of Persistent Organic Pollutants to the Olympic Peninsula of Washington, USA

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Introduction

The global atmospheric transport and deposition of pollutants has been recognized to cause contamination in remote locations such as the Arctic, and the high mountains of Europe.[1,2,3] There have been many reports that show that trans-pacific transport has occurred and that anthropogenic compounds, such as CO and O_3 are being transported from Asia.[4,5] However, few studies have looked at the trans-Pacific transport of persistent organic pollutants and other anthropogenic semi-volatile organic compounds (SOCs).[2,6,7,8] Results from these studies suggest that certain anthropogenic SOCs, depending on their atmospheric lifetimes, make good molecular markers.[8] The use of SOCs as molecular markers has the potential to distinguish between Asian and North American sources, such as combustion, agriculture, and biomass burning sources.

Long range atmospheric transport of SOCs occurs in both the gas and particle phases of the atmosphere. A Hi-volume air sampler was used to collect SOCs in both phases of the atmosphere at Cheeka Peak Observatory, which is on the Northwest tip of the Olympic Peninsula in the state of Washington. Cheeka Peak is a well-established site for research on trans-Pacific atmospheric transport, because of measurements of ozone, carbon monoxide, and mercury made by Dan Jaffe and his research group since 1997. [4, 5]

The objectives of this research are to study SOC trends over different years at Cheeka Peak Observatory, and to use this data to distinguish between trans Pacific and non-trans Pacific events at this site. We believe SOCs can also be used to distinguish between different source types at CPO, such as fossil fuel combustion, biomass burning, agriculture, and industrial sources.

Materials and Methods

SOCs were sampled using a high volume air sampler located at Cheeka Peak Observatory from March 15th to May 30th 2002 and from January 28th to June 18th, 2003. The Hi-volume air sampler (Tisch Environmental) has a brushless motor that pulls air underneath the hood through two quartz fiber filters and a two PUF (polyurethane foam) system. The flow rate of the air sampler was 14 m^3/hour and, over a 48 hour sampling period, approximately 670 m^3 of air was sampled.

The PUF and quartz fiber filters were extracted using Accelerated Solvent Extraction (ASE) where pressure conditions reached 1500psi and a temperature of 100^{o}C. The PUF were spiked with labeled surrogates and extracted using two cycles of a 75:25 hexane:acetone mixture, and the quartz fiber filters were extracted using one cycle of dichloromethane and one cycle of ethyl acetate. The samples were then concentrated with nitrogen gas to a volume of 300uL and spiked with internal standards. The extracts were analyzed for a large list of SOCs with a wide range of atmospheric half-lives (hours to months) using gas chromatography mass spectrometry (GC-MS) with both electron impact ionization (EI) and electron capture negative ionization (ECNI) in SIM mode. The surrogate recoveries ranged from about 60-100% and the method detection limit for (EI) analytes was approximately 1.67pg/m^3 and 16.7fg/m^3 for the (ECNI) analytes.

There were 83 different analytes of interest that can be grouped into three categories. These are the polycyclic aromatic hydrocarbons (PAHs), pesticides, such as organophosphates, organochlorines, and triazines, and polychlorinated biphenyls (PCBs).

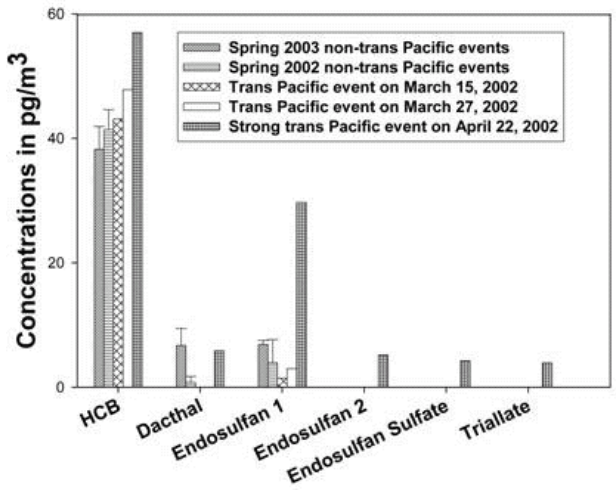
Results and Discussion

From March 15-May 30th 2002, three trans-Pacific events were identified based on increased concentrations of CO and aerosols, HYSPLIT back trajectories, the GEOS-CHEM global model, and Principal Component Analysis of the SOC data.[7] These sampling periods were: March 15-16 2002, March 27-28 2002, and April 22-23 2002. During the Spring of 2003 no trans Pacific events were identified from the samples taken. However during the summer of 2003, two samples indicated trans Pacific transport of biomass burning emissions in Siberia had occurred. These sampling periods were: June 2-4 2003 and June 16-18 2003.

Figure 1 compares the pesticide concentrations measured in Spring 2002 and Spring 2003. The results for 2003 are also shown

from January to June of both PAHs and pesticides in Figures 2 and 3.

Figure 1. Pesticides Spring 2002 vs. 2003



The first two bars in the graph represent the average concentrations of the non-trans Pacific events of Spring 2003 and Spring 2002. The following three bars represent the three trans Pacific events of 2002. The strong trans Pacific event on April 22, 2002 showed an increase in the concentrations of endosulfan 1, heptachlor, dacthal, trans-nonachlor, cis-nonachlor, and mirex. In addition, this was the only day that endosulfan II, endosulfan sulfate and triallate were measured.

Figure 2. Pesticide concentrations measured in 2003

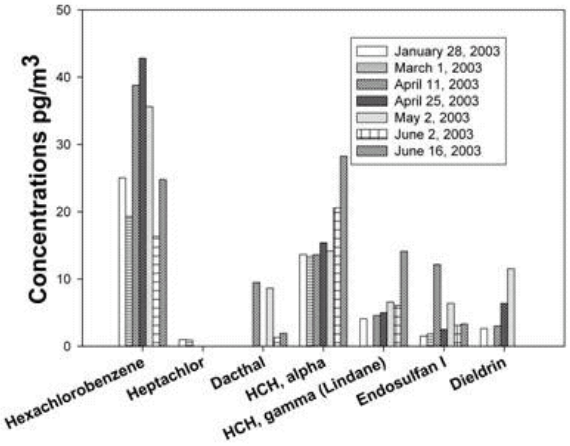


Figure 2 shows the seasonal trends of the pesticide concentrations during 2003 from January to June. Trans Pacific transport of biomass burning emissions in Siberia occurred during two of the sampling periods. (June 2-4, 2003 and June 16-18 2003) During these dates, we measured increased concentrations of alpha HCH compared to the rest of the year.

Figure 3. PAH concentrations measured in 2003

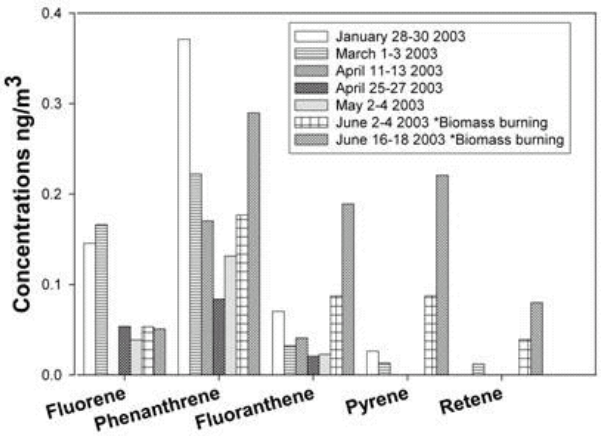


Figure 3 shows the seasonal trends of the gas-phase PAH concentrations during 2003. The two sampling periods influenced by biomass burning on June 2-4, 2003 and June 16-18, 2003 show increased concentrations of some PAHs, most notably retene, a biomarker for wood combustion.

Conclusion

Elevated concentrations of certain SOCs were observed at CPO during the trans Pacific events of 2002. Increased concentrations of retene were measured at CPO in the summer of 2003 during Siberian biomass burning events. In the future, other tracers for biomass burning emissions, including the biogenic SOC, levoglucosan, will be investigated. Also, the analysis of additional samples during subsequent years will help us to understand the trans Pacific transport of SOCs during different seasons and under different environmental conditions.

Acknowledgements

We thank Dan Jaffe and laboratory at University of Washington-Bothell, the National Science Foundation-CAREER Grant (ATM-0239823) and the National Institute of Environmental Health (NIH) (P30ES00210) for financial support and the Makah Tribal nation for the collection of air samples.

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