# Outflow of Persistent Organic Pollutants and Other Semivolatile Organic Compounds from Asia in Spring 2004

Toby Primbs[1], David Schmedding[2], Staci Simonich[3]

[1]Department of Chemistry, Oregon State University
[2]Department of Environmental and Molecular Toxicology, Oregon State University
[3]Department of Chemistry and Department of Environmental and Molecular Toxicology, Oregon State University

## Introduction

Direct transport of air pollutants from Asia to the Pacific Coast of North America has been identified[1-6]. 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 seasons[1]. With the combination of observational data (which includes deposition of Asian dust in North America), direct measurements in the atmosphere, and computer modeling simulations, the evidence of Asian air pollutants transporting to the Pacific coast of North America is growing[1]. For more than a decade, the global atmospheric transport of persistent organic pollutants (POPs) and other anthropogenic semi-volatile organic compounds (SOCs) has been shown to cause surface contamination in remote locations[7] such as the Artic[8]. Research investigating atmospheric transport of SOCs, from Asia to the Pacific Coast of North America, is just beginning[2-3, 6]. Additionally, further understanding of the trans-Pacific atmospheric transport of anthropogenic SOCs may have an impact on future treaties involving intercontinental transport of pollutants[9].

To date, research investigating trans-Pacific transport has mostly taken place on the western coast of North America[2-3, 6]. The primary objectives of this research are to (1) identify the chemical composition of Asian air masses; (2) determine if different regions of Asia produce unique chemical compositions in their air masses; (3) begin to quantify the outflow of POPs and other anthropogenic SOCs from Asia (by making measurements of POPs and SOCs on the Island of Okinawa, Japan in the Spring of 2004). To our knowledge, this is the first research that has set out to look at the direct outflow of POPs and other anthropogenic SOCs in the direct vicinity of Asia, in relation to trans-Pacific transport.

## Materials and Methods

High volume air sampling (~25 $m^3$/hour for 24 hour periods) of both the gas and particulate phases was performed during a six week campaign from March 19 to May 1, 2004. The air sampling station, Hedo Point, Okinawa, Japan (28.8N, 128.2E, 60 masl) is located on the northwestern coast of the island. It is an established air monitoring site that has been described as remote, but influenced by the air masses from Asia[10]. The sampling media consisted 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$^o$C for 12 hours and the PUF plugs were cleaned by Accelerated Solvent Extraction (Dionex) with dichloromethane and ethyl acetate prior to use.

Eighteen samples were 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 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 the concentration of the SOCs in extracts. Following chemical analysis of the samples, ten day back air trajectories were calculated every four hours for a twenty four hour sample; this was done using NOAA's Air Resources Laboratory HYSPLIT model, and were then imported into the ArcGIS program for spatial representation.

Other simultaneous atmospheric measurements were performed during the sampling campaign by the Jaffe Group (University of Washington-Bothell), Frontier Geosciences, Tokyo Metropolitan University, and NIES (Tokyo, Japan) and included: volatile organic compounds, $NO_x$, CO, $O_3$, Aerodyne Aerosol Mass Spectrometer, aerosol light scattering (Nephelometer), Hg (speciation), and meteorology.

**Preliminary Results and Discussion**

Preliminary results for five of the eighteen samples are presented below. Concentrations below represent the total concentrations (filters + PUF + XAD-2) and are field blank and recovery corrected. The sample concentrations in Figures 1 and 2 are ordered from more "westerly" to more "northerly" back trajectories (left to right). Table 1 is a summary of the samples with their corresponding source region, sampling period, and the average temperature at the sampling site over the sampling period.

**Table 1:** Sample start day (2004) with its general corresponding source region as calculated from HYSPLIT and the average temperature at the sampling site over the sampling period.

| Start Day (JST) | Sampling Period (hr) | Avg. Site Temperature During Sampling (°C) | Source Region (HYSPLIT) |
|---|---|---|---|
| 22 March | 24 | 18 | Northerly/Japan |
| 1 April | 24 | 17 | Westerly/China |
| 4 April | 24 | 17 | Northwesterly/Korea/N. China |
| 19 April | 24 | 22 | Westerly/China |
| 29 April | 24 | 21 | Northerly/Japan |

Initial results of HCB, HCHs, and endosulfans showed that trajectories originating more from the west (out of China), were associated with higher concentrations (Figure 1). For example, Figure 1 shows the samples collected on the 19th of April (19-Apr) and the 1st of April (1-Apr) had the highest concentrations when compared to the other sampling days.

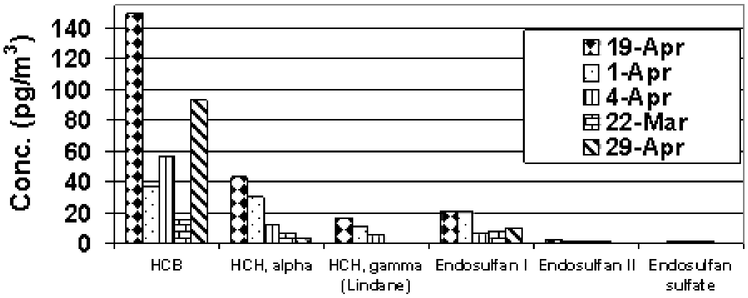

**Figure 1:** The bars are arranged from samples associated with more westerly trajectories to samples associated with more northerly trajectories.HCHs and endosulfans measured showed elevated concentrations which corresponded to trajectories from the west. HCB concentrations were elevated when associated with trajectories from the west, if similar site temperatures are compared.

Hexachlorobenzene (HCB) (a fungicide and byproduct of manufacturing) shown in Figure 1, had higher concentrations in samples that were associated with trajectories from the west, when a similar average daily temperature was compared. For example, the 19-Apr samples trajectories were of "westerly" origin (HCB conc. 149 $pg/m^3$, avg. temp.

22° C), while 29-Apr were of more “northerly” origin (HCB conc. 93 pg/m$^3$, avg. temp. 21° C). Conversely the 1-Apr samples trajectories were of “westerly” origin (HCB conc. 37 pg/m$^3$, avg. temp. 17° C), while 22-Mar were of more “northerly” origin (HCB conc. 16 pg/m$^3$, avg. temp. 18° C). The 4-Apr sample had HCB conc. 57 pg/m$^3$, avg. temp. 17° C, and its trajectories were more of a north-westerly origin. Thus, temperature may be an important factor in determining the outflow of HCB from Asia. PCBs were also measured in ranges of ~.1 to ~1 pg/m$^3$ for all of the samples except the 29th of April, in which PCBs were below the detection limit. The instrumental limit of detections, for the PCBs, ranged from 0.005 to 0.1 pg/m$^3$. The sample collected on 29-Apr was also unique because it contained the only detectable measurements of metribuzin (currently used on Okinawa) and heptachlor.

Figure 2 shows the results for the polycyclic aromatic hydrocarbons (PAHs) for the five samples. Again, the data are orientated in Figure 2 according to their association with trajectories from the west to north (left to right). The concentrations for the higher molecular weight PAHs (benzo(a)anthracene to benzo(ghi)perylene) are expanded in Figure 2 to better show the concentration differences. For the lower molecular weight (“gas phase”) PAHs (fluorene to retene) no distinct patterns set the samples apart; while the higher molecular weight (“particulate phase”) PAHs (benzo(a)anthracene to benzo(ghi)perylene) had higher concentrations in the samples corresponding to trajectories from the west.

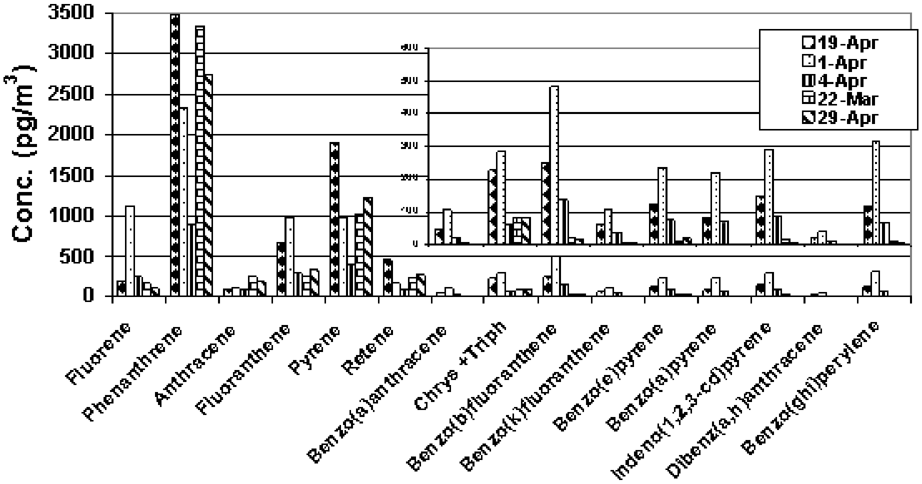

**Figure 2:**PAHs measured with their corresponding collection days. The higher molecular weight PAHs also showed higher concentrations for samples that corresponded to trajectories from the west. Bars are arranged from samples corresponding to trajectories from a westerly origin to a northerly origin.

In conclusion, long-range atmospheric transport is occurring to the island of Okinawa from Asia. Various pesticides, PCBs, and PAHs were measured in Okinawa and the samples that corresponded to trajectories more from the west, tended to have higher concentrations. Analysis of additional samples will provide further information into source regions and types. Furthermore, levoglucosan, an indicator for biomass burning, will be measured in the samples to further help identify biomass combustion sources. Finally, the Eurasian outflow of SOCs, using the CO/SOC enhancement ratio and CO inventory, will be calculated[11].

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