Trans-Pacific and Regional Atmospheric Transport of Polycyclic Aromatic Hydrocarbons and Pesticides in Biomass Burning Emissions to Western North America

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Abstract

The trans-Pacific and regional North American atmospheric transport of polycyclic aromatic hydrocarbons (PAHs) and pesticides in biomass burning emissions was measured in air masses from April to September 2003 at two remote sites in western North America. Mary's Peak Observatory (MPO) is located in Oregon's Coast Range and Cheeka Peak Observatory (CPO) is located on the tip of the Olympic Peninsula in Washington State. During this time period, both remote sites were influenced by PAH and pesticide emissions from forest fires in Siberia and regional fires in Oregon and Washington State. Concurrent samples were taken at both sites on June 2 and August 4, 2003. On these dates, CPO had elevated gas phase PAH, alpha-hexachlorocyclohexane and retene concentrations (p<0.05) and MPO had elevated retene, particulate phase PAH and levoglucosan concentrations due to trans-Pacific transport of emissions from fires in Siberia. In addition, during the April to September 2003 sampling period, CPO and MPO were influenced by emissions from regional fires that resulted in elevated levoglucosan, dacthal, endosulfan and gas phase PAH concentrations. Burned and unburned forest soil samples collected from the regional forest fire area showed that 34 to 100% of the pesticide mass was lost from soil due to burning. These data suggest that the transPacific and regional atmospheric transport of biomass burning emissions results in elevated PAH and pesticide concentrations in western North America. The elevated pesticide concentrations are likely due to re-emission of historically deposited pesticides from the soil and vegetation during the fire event.

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Introduction

Biomass burning, including forest fires, produces atmospheric pollutants such as particulate matter, carbon monoxide, mercury, volatile organic compounds (VOCs), and semi-volatile organic compounds (SOCs) (1–5). Because biomass burning emissions are expected to increase significantly with global warming, the effect that biomass burning emissions have on the global radiation budget, the production of greenhouse gas emissions, and air quality has become a growing concern (6).

The air quality of western North America is influenced by biomass burning emissions from both regional and trans-Pacific atmospheric transport (4, 5, 7). In addition, during some periods of trans-Pacific atmospheric transport, the concentrations of carbon monoxide and ozone in western North America increase and sometimes exceed air quality standards (7).

During the summer of 2003, large-scale biomass burning occurred throughout Siberia, with the most intense fires occurring from May to early June and during the month of August (8). Approximately 18.9 million hectares of land were burned during the entire 2003 fire season in Russia, and, on average, approximately 8 to 10 million hectares burn there each year (7). In the summer of 2003, elevated concentrations of carbon monoxide and $PM_{2.5}$ had a significant impact on air quality in western North America and were linked to two separate trans-Pacific events of Siberian fire emissions (7, 8). On June 6, 2003, the U.S. EPA's 8-hour standard for ozone was exceeded in Enumclaw, WA (55 km southeast of Seattle) and, during the first week of August in 2003, the 24-hour average PM2.5 standard was exceeded in Seattle, WA (7, 8). During these time periods, we measured polycyclic aromatic hydrocarbons (PAHs) and pesticides concurrently in air masses at both Cheeka Peak Observatory (CPO), a remote site located on the Olympic Peninsula of Washington, and at Mary's Peak Observatory (MPO), a remote site located in Oregon's Coast Range. The two sites are located approximately 500 km from each other and have an elevation difference of 769 m. Concurrently sampling at these two remote sites provide a unique opportunity to investigate the spatial and altitudinal variation of PAH and pesticide concentrations in trans-Pacific and regional air masses. In addition to these trans-Pacific event time periods, PAHs and pesticides were also measured at these two sites from April to September 2003 in air masses influenced by several regional fires. The objectives of this research were to measure PAH and pesticide concentrations in trans-Pacific and regional air masses influenced by biomass burning events and to assess the influence that these fire events have on their concentrations in western North America.

Experimental Section

SOCs

Eighty-four targeted SOCs, including polycyclic aromatic hydrocarbons (PAHs) and historic and current-use pesticides, were measured in hi-volume air samples (9). These SOCs span several orders of magnitude in vapor pressure; exist in both the gas and particle phases of the atmosphere, and their atmospheric half-lives range from hours to months. Twenty-seven isotopically labeled surrogates and four internal standards, which spanned the full mass range of the target analytes, were used to recovery correct and quantify the SOC

concentrations over the entire analytical method (9). A complete list of the SOC standards, their manufacturers and storage conditions have been previously reported (10).

Sampling Sites

Air samples were collected from two remote sites located in western North America. Mary's Peak Observatory (MPO) (44.5°N, 123.6°W, 1249 m) is the highest peak in Oregon's coast range, while Cheeka Peak Observatory (CPO) (48.3°N, 124.6°W, 480 m) is a coastal site located on the tip of the Olympic Peninsula in Washington State (Figure S.1). The annual precipitation at both MPO and CPO is ~250 cm (11) and the predominant wind direction at both sites is westerly (from the Pacific Ocean).

CPO is a well-established site for the study of trans-Pacific atmospheric transport to the United States and is located ~240 km West of Seattle and 3 km from the Pacific Ocean (7, 8, 12–15). Previous studies have identified that, during westerly flow, this site is primarily influenced by clean marine air masses and Asian air masses containing anthropogenic emissions (12, 14, 15). MPO is located ~26 km from the Pacific Ocean and ~30 km west of the agriculturally intensive Willamette Valley and Interstate 5 (Figure S.1). Concurrently sampling at CPO and MPO provide a unique opportunity to investigate the spatial and altitudinal variation of PAH and pesticide concentrations in trans-Pacific and regional air masses.

Sample Collection

From April to September 2003, twenty-one high volume air samples were collected at MPO and CPO (Table S.1). During this time period, seven 48-hour air samples and 2 field blanks were collected at CPO using a modified hi-volume air sampler (Tisch Environmental, Cleves, OH). At CPO, an 11cm diameter sampling head with two quartz fiber filters (QFFs) (Whatman, Maidstone England) was used to collect the particulate phase SOCs and two 5.5 cm diameter polyurethane foam (PUF) plugs w ere used to collect the gas phase SOCs. This sampler had an average flow rate of approximately 14 m^3/hour and, during a 48-hour period, an average of 650 m^3 of air was sampled.

At MPO, eleven 48-hour and three 24-hour air samples, as well as 2 field blanks, were collected using a modified hi-volume air sampler (Tisch Environmental, Cleves, OH) (Table S.1). At MPO, a 20.3cm by 25.4 cm rectangular sampling head with a QFF was used to collect the particulate phase SOCs and two 6.5 cm diameter PUF plugs, with ~50 grams of Amberlite XAD-2 resin (Supelco, Bellefonte, PA) placed between the two PUF plugs was used to collect the gas phase SOCs. In a 48 hour sampling period, ~ 2500m^3 of air was sampled and, in a 24 hour sampling period, ~900m^3 of air was sampled. The sampling flow rate decreased when the sampling period changed from 48 to 24 hours because the brush motor (higher flow rate) was replaced with a brushless motor (lower flow rate). The air sampling media was pre-cleaned before deployment in the field. Details of the cleaning procedure and solvents used have been previously reported (9, 16).

A composite soil sample was collected from an un-burned (100 m^2) and burned (100 m^2) area in the Deschutes National Forest, located 6 miles west of Sisters, Oregon at the edge of the area burned by the B&B complex forest fire. The burned and unburned areas were

adjacent to each other but separated by a two lane road which stopped the forest fire. Each composite soil sample consisted of 7 random surface (20 cm deep) samples for each 100 m^2 area.

Information on the methods used for measuring SOCs and the quality assurance/quality control procedures used are given in the supporting information.

Air Mass Back Trajectory Calculation and Satellite Image Analysis

10-day air mass back trajectories were calculated using NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) to assess potential source regions (17). For each sampling period, a 10-day back trajectory was calculated every 4 hours at the site elevation and location and at 8 points located in a 1° by 1° grid surrounding the site. This resulted in approximately 162 trajectories calculated for each sampling period. At CPO and MPO, trajectories were calculated at the site elevations of 500 m and 1249 m, respectively. HYSPLIT data was imported into ArcGIS and was used to calculate the percent of time the trajectory spent in the boundary layer (below 1000 m) and above the boundary layer (above 1000 m) for each sample.

The Moderate Resolution Imaging Spectroradiometer (MODIS) flies onboard NASA satellites and collects global fire activity in a 1° by 1° grid (18). The Navy Aerosol and Analysis Prediction System (NAAPs) model estimates smoke emissions based on satellite and MODIS fire product data (19). The MODIS fire detects, the NAAPs model, and the 10-day air mass back trajectories were used to help determine the location of both the regional and Siberian fires during the sampling periods.

Results

Identification of Air Mass Source Regions and Biomass Burning events

HYSPLIT back trajectories were used to calculate source region impact factors (SRIFs) for each air mass sampled at MPO and CPO. The SRIF was calculated by determining the percentage of time the back trajectories spent in a given source region compared to the total trajectory time, and details of these calculations are reported elsewhere (4, 5, 16). The defined source regions included agriculturally intensive areas in the Western U.S., including Eastern Washington, the Willamette Valley in Oregon, and the Central Valley in California (Figure S.1) (4). Two other potential source regions in Asia and Siberia were identified and used to assess the influence of these source regions on the SOC concentrations in the sampled air masses (4). The SRIFs for each sampling date are listed in Table S.1. The SRIFs do not add up to 100% because they do not account for the significant time the trajectories spent over the Pacific Ocean. However, during trans-Pacific transport, Asian dust and smoke plumes may be present over the Pacific Ocean. In order to account for this, the percentage of time the air mass trajectories spent over the Pacific Ocean as opposed to continental land was calculated (Table S.1).

Levoglucosan, a combustion byproduct of cellulose that exists in the particulate phase in the atmosphere, is often used as a molecular marker for biomass burning emissions (20–23) The levoglucosan concentrations measured at both sites are listed in Table S.2A. For sampling

dates that had elevated levoglucosan concentrations (greater than 10,000 pg/m^3) or NAAPs model images that indicated smoke emissions, air mass back trajectories and satellite images were used to determine the fire locations. The NAAPs model images for the concurrent CPO and MPO sampling start dates of June 2 (Figure S.2A) and August 4 (Figure S.2B) show smoke emissions from large scale fires burning in Siberia being transported across the Pacific Ocean to the west coast of North America. The NAAPs model images also indicated that CPO was influenced by Siberian biomass burning emissions during the June 16 sampling period (Figure S.2C) and MPO was influenced by regional fire emissions in Eastern Oregon during the September 4 sampling period (Figure S.2D).

To determine if biomass burning emissions influenced individual air samples, the following were considered; (1) the levoglucosan concentration in the air sample was elevated (greater than 10,000pg/m^3) (2) the smoke emissions estimated by the NAAPS model passed over the sampling site, and (3) the 10-day air mass back trajectories for the sample passed near MODIS fire detects.

Polycyclic Aromatic Hydrocarbons

Siberian Fires—During the June 2–4 concurrent sampling at CPO and MPO, elevated particulate phase PAH concentrations were measured at MPO, while elevated gas phase PAH concentrations were measured at CPO (Figure 1A and Table S.2AB). Previous studies have shown that elevated particulate phase PAH concentrations are associated with transPacific air masses at Mt. Bachelor Observatory (MBO), which is located at 2800m in Oregon's Cascade Range (5), while elevated gas phase PAH concentrations were measured in trans-Pacific air masses at CPO (15). A recent study has measured the emissions and outflow of PAHs from forest fires in China and Russia (24).

To determine if the sampled air mass represented the boundary layer or tropospheric air, the HYSPLIT back trajectories were used to calculate the amount of time the air mass time spent above (>1000 m) or below (<1000 m) the boundary layer in the 10 days prior to sampling (Table S.1). In the June 2 air masses, 96% of the trajectory time was spent above the boundary layer prior to reaching MPO, while only 68% of the trajectory time was spent above the boundary layer prior to reaching CPO (Table S.1). At CPO, the concentrations of retene, a biomarker for the incomplete combustion of soft wood (2), fluoranthene, and pyrene were elevated (p-value < 0.05) in the June 2 air mass, while, at MPO, the levoglucosan concentration was elevated (>10,000 pg/m^3). However, the levoglucosan concentration at CPO was below the detection limit. Levoglucosan is particle bound and water-soluble and the relatively wet boundary layer air mass at CPO may partly explain the loss of levoglucosan at CPO. In addition, the average relative humidity CPO and MPO during the June 2 sampling was 79% and 60%, respectively. Due to CPO's higher relative humidity and closer proximity to the Pacific Ocean, fog formation is greater at CPO than at MPO. Fog is an efficient scavenger of SOCs and may explain the removal of levoglucosan and particle bound PAHs from the sampled air mass at CPO.

The NAAPs model images indicate that, during the June 2 concurrent sampling, smoke plume from Siberian fires crossed the Pacific Ocean and passed over CPO and MPO (Figure S.2A). In addition, Figure 1A shows the air mass back trajectories for the June 2 concurrent

sampling at CPO and MPO overlaid onto MODIS 10-day fire start images. The MODIS images are generated by satellite data over 10-day periods and the image shown in Figure 1A represents the June 1–10 time period. In Figure 1, each red dot represents a fire that burned during the 10-day period, while the yellow dots indicate areas of more intense burning (18). By comparing the MPO and CPO trajectories in Figure 1A and the SRIFs given in Table S.1, it is clear that the MPO air mass spent more time over the Siberian and Asian source regions (13.2%) than the CPO air mass (1.4%). This indicates that, during the June 2 concurrent sampling, MPO was influenced to a greater extent by Siberian biomass burning emissions than CPO. This, along with different site characteristics, such as relative humidity and elevation, may explain the different observations at CPO and MPO.

The ratios of individual PAH isomers have been used for source apportionment by comparing the PAH ratio of the combustion source to the PAH ratio measured in air (15, 25, 26). It has been previously reported that the use of PAH ratios can be misleading for source identification when the PAHs have significant differences in physical chemical properties (25). However, Zhang et al reported that the Indeno[1,2,3-cd]pyrene (IcdP) (26) and Benzo[ghi]perylene (BghiP) (27) ratio can be accurately used for source identification because of their similar properties. During the June 2 concurrent sampling, the ratio of indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene +benzo[ghi]perylene) was 0.65 at MPO. This PAH ratio for wood combustion is 0.64 ± 0.07 (26), suggesting that the MPO air mass contained biomass burning emissions from the Siberian fires. The same PAH ratio could not be calculated in the concurrent June 2 CPO air mass or the CPO and MPO concurrent August 4 air masses because the concentrations of both indeno[1,2,3-cd]pyrene and benzo[ghi]perylene were below the detection limits (Table S.2A).

Similar to the June 2 concurrent sampling, during the August 4 concurrent sampling, MPO had elevated particulate phase PAH concentrations and CPO had elevated gas phase PAH concentrations compared to the rest of the 2003 samples (Figure 1B). A previous study reported low total aerosol scattering/carbon monoxide concentration ratios during the August 4 time period at CPO and the affect of precipitation in transit to CPO was explored to explain this low ratio (8). The HYSPLIT model indicated that relatively low precipitation, 1.4 mm at CPO and 15.1 mm at MPO, fell along the 10-day air mass back trajectory of the June 2 sampled air mass. However, for the August 4 sampled air mass the precipitation that fell in transit was 9.5 mm at CPO and 38.6 mm at MPO. Because wet deposition is a primary removal mechanism of submicron aerosols from the atmosphere, precipitation in transit across the Pacific Ocean may explain why the particulate phase PAH concentrations in the August 4 air mass were lower than the June 2 air mass at CPO and MPO (Figure 1). The NAAPs model image for the August 4 concurrent sampling confirms the influence of Siberian biomass burning emissions at CPO and MPO (Figure S.2B).

Principal component analysis (PCA) was used to further evaluate the differences in PAH profiles in the CPO and MPO air masses. Individual PAH concentrations were normalized to total PAH concentrations in each air sample to allow direct comparison of the PAH profile between samples. Centered log ratio transformation was then performed on normalized concentrations to avoid negative bias and closure (28). The PCA biplot in Figure S.3 confirms that the June 2 and August 4 air masses sampled concurrently at MPO and CPO

contained different PAH profiles even though both air masses were influenced by the same Siberian biomass burning emissions. The PCA biplot indicates that the CPO (10S and 17S) and MPO (8S) air masses influenced by the Siberian biomass burning emissions had elevated pyrene and retene concentrations.

Regional Fires—Fluorene concentrations were elevated at CPO in the April 11 air mass compared to the rest of 2003 and it was the only sampled air mass at CPO that was from an easterly rather than westerly direction (Table S.1 and S.2 and Figure S.3). The atmospheric lifetime of fluorene is relatively short (22 hours) (29), suggesting that this CPO air mass may have been influenced by local sources.

From August 19 to September 26, approximately 90,789 acres of U.S. National Forest burned in the Oregon Cascade Range located 150 miles east of MPO (referred to as the B&B complex fire). An air mass was sampled at MPO on September 4–6, during one of the most intense periods of burning. The predominant wind direction at MPO during this time period was from the southwest (Table S.1). However, the NAAPs model image shows that smoke emissions from this forest fire influenced a large portion of Oregon (Figure S.2D). This air mass had elevated concentrations of all gas phase PAHs, including anthracene and retene, and levoglucosan (Table S.2). The relatively high anthracene concentrations in this air mass, along with its relatively short atmospheric half-life of 1.5 hours (29), confirms that this air mass was influenced by a regional combustion source and the elevated retene and levoglucosan concentrations suggest it was the B&B complex fire.

Pesticides

Siberian Fires—The fate of pesticides in fires depends on their physical chemical properties and the temperature of the fire (30). At temperatures greater than 500°C, most pesticides thermally degrade (30). However, under smoldering conditions (300°C to 600°C), pesticides volatilize to the atmosphere (30). Experiments on the combustion of insecticide treated wood showed that stable pesticides with higher vapor pressures, such as gamma-HCH (lindane), volatilized under smoldering conditions and 43% of the gamma-HCH was recovered in the smoke stream (30). For pesticides with lower vapor pressures, such as chlorpyrifos, 28% was recovered in the smoke stream under smoldering conditions (30). When gamma-HCH and chlorpyrifos were burned at temperatures greater than 500 °C, both pesticides thermally degraded (30). Because the physical chemical properties of gamma HCH are similar to its isomer alpha-HCH, it is possible that alpha-HCH, and other SOCs, volatilizes from soil and vegetation during biomass burning.

The highest dieldrin concentrations at CPO were measured in the June 2, June 16, and August 4 air masses (Table S.3). At CPO, the dieldrin concentration was significantly correlated with alpha and gamma HCH, fluoranthene, pyrene, and retene concentrations (Table S.5). The NAAPs model indicated these three CPO air masses were influenced by the trans-Pacific transport of Siberian biomass burning emissions (Figure S.2). The highest dieldrin concentrations at MPO were measured in the Sept. 21 air mass. On this day, air mass back trajectories and elevated particulate phase PAH concentrations indicated

influence from trans-Pacific transport at MPO. This suggests that dieldrin, banned in the U.S in 1987, was transported during these trans-Pacific events to CPO and MPO.

Dieldrin use in China has not been reported however, dieldrin has been measured in sediments from Lake Taihu and in air in Beijing and Qingdao (27, 31–33). Dieldrin was also measured in air on Okinawa, Japan, a site located downwind of Asian source regions, but no single Asian source region could be identified (16). The CPO and MPO data suggest that dieldrin undergoes trans-Pacific transport to the west coast of North America.

The alpha-HCH concentration was also elevated at CPO in the June 2, June 16, and August 4 air masses that were influenced by the Siberian biomass burning emissions (Figure 1 and Table S 3). Technical HCH (containing alpha-HCH and gamma-HCH) was banned in the U.S in 1974, in China in 1983, and in the former Soviet Union in 1990 (34). Emission inventories for alpha-HCH have been developed for both China and the former Soviet Union based on production and usage in these countries (35–37). From these inventories, it is evident that most of the land burned in Siberia during the summer of 2003 had minimal direct use of alpha-HCH (36, 37). However, the burned area in Siberia was near the areas of intense alpha-HCH use in China and the Soviet Union and was likely a receptor region for these alpha-HCH emissions for many years (38).

At CPO, alpha-HCH concentrations were significantly ($p < 0.05$) positively correlated with dieldrin concentrations and negatively correlated with dacthal concentrations. Dacthal (or DCPA) is a current use pesticide in the U.S. These correlations suggest that the elevated alpha-HCH and dieldrin concentrations at CPO are due to trans-Pacific transport, while the elevated dacthal concentrations are due to regional transport. The alpha to gamma-HCH ratio did not appear to be indicative of trans-Pacific or regional atmospheric transport (Table S.3). In addition, this ratio was not correlated with SOC concentrations at MPO or CPO (Table S.4 and S.5).

Regional Fires—The highest CPO concentrations of dacthal and endosulfan I, both current use pesticides, were in the April 11 easterly air mass (Table S.3). Pesticide use maps show dacthal and endosulfan use in Eastern Washington on wheat (39). Because the air mass back trajectories passed over Eastern Washington and the highest concentration of levoglucosan at CPO was measured in this air mass, it is likely that the April 11 air mass was influenced by agricultural field burning in Eastern Washington. The most prevalent agricultural burning of wheat fields (89% of the total acres burned in Washington) occurs in April and May and also in September and October (40). Also, the dacthal concentration at CPO was significantly negatively correlated with the alpha-HCH concentration, providing further evidence that the dacthal at CPO was from regional, and not trans-Pacific, sources.

The highest dacthal and endosulfan sulfate concentrations at MPO were measured in the Sept. 4 air mass that was influenced by the B&B complex fire (Table S.3). The concentration of dacthal and endosulfan sulfate at MPO were significantly positively correlated with each other and gas-phase PAH concentrations. In addition, the PCA biplot of normalized, centered log ratio transformed pesticide concentrations confirms the elevated dacthal concentrations in the Sept. 4 air mass at MPO (Figure S.3B). This suggests that these

current use pesticides were volatilized and transported to MPO during regional fire events, including the B&B complex fire.

Pesticide Loss from Soil Due to Forest Fires

Composite forest soil samples from a burned and unburned area of the B&B complex forest fire discussed above were collected and analyzed to investigate the potential loss of SOCs from soil due to re-emission and/or degradation from a forest fire. The pesticides with elevated concentrations in air masses influenced by the Siberian and regional biomass burning emissions, dieldrin, alpha-HCH, dacthal, and endosulfan sulfate, had concentrations in burned forest soil that were decreased by 100%, 97%, 90%, and 97%, respectively, compared to unburned forest soil (Figure 2, Table S.6). These four pesticides also had some of the highest concentrations in unburned soil among the pesticides measured (Figure 2, Table S.6). Other pesticides measured in the unburned forest soils included trifluralin, HCB, gamma-HCH, heptachlor, chlorpyrifos oxon, heptachlor epoxide, trans-chlordane, trans-nonachlor, and endosulfan II. Their losses from forest soil ranged from 34 to 100% (Figure 2, Table S.6). The losses of PCBs from forest soil ranged from 80 to 85% (Figure 2, Table S. 6). However, the PCB concentrations in unburned forest soil were significantly lower than the dieldrin, alpha-HCH, and endosulfan sulfate concentrations. These results confirm that pesticides and other SOCs may re-volatilize and/or degrade during biomass burning.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

References

1. Friedli HR, Radke LF, Prescott R. Mercury emissions from the August 2001 wildfires in Washington State and an agricultural waste fire in Oregon atmospheric mercury budget estimates. Global Biogeochemical Cycles. 2003; 17(2):1–8.

2. Simoneit BRT, Rogge WF, Mazurek MA, Standley LJ, Hildemann LM, Cass GR. Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion. Environ Sci Technol. 1993; 27(12):2533–2541.

3. Eckhardt S, Breivik K, Mano S, Stohl A. Record high peaks in PCB concentrations in the Arctic atmosphere due to long-range transport of biomass burning emissions. Atmospheric Chemistry and Physics Discussions. 2007; 7:6229–6254.

4. Primbs T, Wilson G, Schmedding D, Higginbotham C, Massey Simonich Staci. Influence of Asian and Western United States Agricultural Areas and Fires on the Atmospheric Transport of Pesticides in the Western United States. Environ Sci Technol. 2008; 42(17):6519–6525. [PubMed: 18800524]

5. Primbs T, Piekarz A, Wilson G, Schmedding D, Higginbotham C, Field J, Simonich SM. Influence of Asian and Western United States Urban Areas and Fires on the Atmospheric Transport of Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls, and Fluorotelomer Alcohols in the Western United States. Environ Sci Technol. 2008; 42(17):6385–6391. [PubMed: 18800505]

6. Penner JE, Dickinson RE, O'Neill CA. Effects of Aerosol from Biomass Burning on the Global Radiation Budget. Science. 1992; 256(5062):1432. [PubMed: 17791612]

7. Jaffe D, Bertschi I, Jaegle L, Novelli P, Reid JS, Tanimoto H, Vingarzan R, Westphal DL. Long-range transport of Siberian biomass burning emissions and impact on surface ozone in western North America. Geophysical Research Letters. 2004; 31(16)

8. Bertschi IT, Jaffe DA. Long-range transport of ozone, carbon monoxide, and aerosols to the NE Pacific troposphere during the summer of 2003: Observations of smoke plumes from Asian boreal fires. Journal of Geophysical Research-Atmospheres. 2005; 110(D5)

9. Primbs T, Genualdi S, Simonich S. Solvent Selection for Pressurized Liquid Extraction of Polymeric Sorbents Used in Air Sampling. Environmental Toxicology and Chemistry. 2008; 27(2008):1267–1272. [PubMed: 18220448]

10. Usenko S, Hageman KJ, Schmedding DW, Wilson GR, Simonich SL. Trace analysis of semivolatile organic compounds in large volume samples of snow, lake water, and groundwater. Environmental Science & Technology. 2005; 39(16):6006–6015. [PubMed: 16173557]

11. Anderson HG. Growth Form and Distribution of Vine Maple (Acer Cirinatum) on Marys Peak, Western Oregon. Ecology. 1969; 50(1):127–130.

12. Jaffe D, Anderson T, Covert D, Kotchenruther R, Trost B, Danielson J, Simpson W, Berntsen T, Karlsdottir S, Blake D, Harris J, Carmichael G, Uno I. Transport of Asian air pollution to North America. Geophysical Research Letters. 1999; 26(6):711–714.

13. Jaffe D, Anderson T, Covert D, Trost B, Danielson J, Simpson W, Blake D, Harris J, Streets D. Observations of ozone and related species in the northeast Pacific during the PHOBEA campaigns 1. Ground-based observations at Cheeka Peak. Journal of Geophysical Research-Atmospheres. 2001; 106(D7):7449–7461.

14. Jaffe D, McKendry I, Anderson T, Price H. Six 'new' episodes of transPacific transport of air pollutants. Atmospheric Environment. 2003; 37(3):391–404.

15. Killin RK, Simonich SL, Jaffe DA, DeForest CL, Wilson GR. Transpacific and regional atmospheric transport of anthropogenic semivolatile organic compounds to Cheeka Peak Observatory during the spring of 2002. Journal of Geophysical Research-Atmospheres. 2004; 109(D23)

16. Primbs T, Simonich S, Schmedding D, Wilson G, Jaffe D, Takami A, Kato S, Hatakeyama S, Kajii Y. Atmospheric Outflow of Anthropogenic Semivolatile Organic Compounds from East Asia in Spring 2004. Environ Sci Technol. 2007; 41(10):3551–3558. [PubMed: 17547177]

17. Draxler, RR.; Rolph, GD. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model. NOAA Air Resources Laboratory; Silver Spring, MD: 2003. http://www.arl.noaa.gov/ready/hysplit4.html

18. Descloitres, J. MODIS Rapid Response System Global Fire Maps. http://rapidfire.sci.gsfc.nasa.gov/firemaps/

19. NRL Monterey Aerosol Page. http://www.nrlmry.navy.mil/aerosol/

20. Simoneit BRT, Schauer JJ, Nolte CG, Oros DR, Elias VO, Fraser MP, Rogge WF, Cass GR. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmospheric Environment. 1999; 33(2):173–182.

21. Simoneit BRT. Biomass burning - A review of organic tracers for smoke from incomplete combustion. Applied Geochemistry. 2002; 17(3):129–162.

22. Simoneit BRT, Elias VO. Detecting organic tracers from biomass burning in the atmosphere. Marine Pollution Bulletin. 2001; 42(10):805–810. [PubMed: 11693634]

23. Simoneit BRT, Elias VO, Kobayashi M, Kawamura K, Rushdi AI, Medeiros PM, Rogge WF, Didyk BM. Sugars - Dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter. Environmental Science & Technology. 2004; 38(22):5939–5949. [PubMed: 15573592]

24. Yuan H, Tao S, Li B, Lang C, Cao J, Coveney R. Emission and outflow of polycyclic aromatic hydrocarbons from wildfires in China. Atmospheric Environment. 2008; 42:6828–6835.

25. Zhang XL, Tao S, Liu WX, Yang Y, Zuo Q, Liu SZ. Source Diagnostics of Polycyclic Aromatic Hydrocarbons Based on Species Ratios: A Multimedia Approach. Environ Sci Technol. 2005; 39(23):9109–9114. [PubMed: 16382931]

26. Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry. 2002; 33(4):489–515.

27. Lammel G, Ghim YS, Grados A, Gao HW, Huhnerfuss H, Lohmann R. Levels of persistent organic pollutants in air in China and over the Yellow Sea. Atmospheric Environment. 2007; 41(3):452–464.

28. Christensen J, MacDuffee M, Yunker MB, Ross P. Hibernation-Associated Changes in Persistent Organic Pollutant (POP) Levels and Patterns in British Columbia Grizzly Bears (Ursus arctos horribilis). ES&T. 2007; (41):1834–1840.

29. Brubaker WW, Hites RA. OH Reaction Kinetics of Polycyclic Aromatic Hydrocarbons and Polychlorinated Dibenzo-p-dioxins and Dibenzofurans. J Phys Chem A. 1998; 102(6):915–921.

30. Bush, PB.; Neary, DG.; McMahon, CK. Fire and Pesticides: A Review of Air Quality Considerations. Fire and Forest Ecology: Innovative Silviculture and Vegetation Management; Tall Timbers Fire Ecology, Tall Timbers Research Station; Tallahassee, FL. 2000; Tallahassee, FL: Tall Timbers Research Station; 2000. p. 132-136.

31. Regionally Based Assessment of Persistent Toxic Substances. Global Environmtal Facility. 2002. http://www.chem.unep.ch/pts/regreports/C&NE%20Asia%20full%20report.pdf

32. Peng XZ, Zhang G, Zheng LP, Mai BX, Zeng SW. The vertical variations of hydrocarbon pollutants and organochlorine pesticide residues in a sediment core in Lake Taihu, East China. Geochemistry-Exploration Environment Analysis. 2005; 5:99–104.

33. Wang X, Li X, Cheng H, Xu X, Zhuang G, Zhao C. Organochlorine pesticides in particulate matter of Beijing, China. Journal of Hazardous Materials. 2007; 155(1–2):350–357. [PubMed: 18280031]

34. Willett KL, Ulrich EM, Hites RA. Differential Toxicity and Environmental Fates of Hexachlorocyclohexane Isomers. Environ Sci Technol. 1998; 32(15):2197–2207.

35. Li YF, Cai DJ, Shan ZJ, Zhu ZL. Gridded usage inventories of technical hexachlorocyclohexane and lindane for china with 1/6 degrees latitude by 1/4 degrees longitude resolution. Archives of Environmental Contamination and Toxicology. 2001; 41(3):261–266. [PubMed: 11503061]

36. Li YF, Cai DJ, Singh A. Technical hexachlorocyclohexane use trends in China and their impact on the environment. Archives of Environmental Contamination and Toxicology. 1998; 35(4):688–697. [PubMed: 9776788]

37. Li YF, Zhulidov AV, Robarts RD, Korotova LG. Hexachlorocyclohexane use in the former Soviet Union. Archives of Environmental Contamination and Toxicology. 2005; 48(1):10–15. [PubMed: 15657800]

38. Tsydenova O, Batoev V, Weissflog L, Klaus-Dieter W. Pollution of the Lake Baikal Basin: Organochlorine Pesticides. Chemistry for Sustainable Development. 2003; 11:349–352.

39. U.S. Geological Survey. Pesticide National Synthesis Project. http://ca.water.usgs.gov/pnsp/pesticide_use_maps_1997

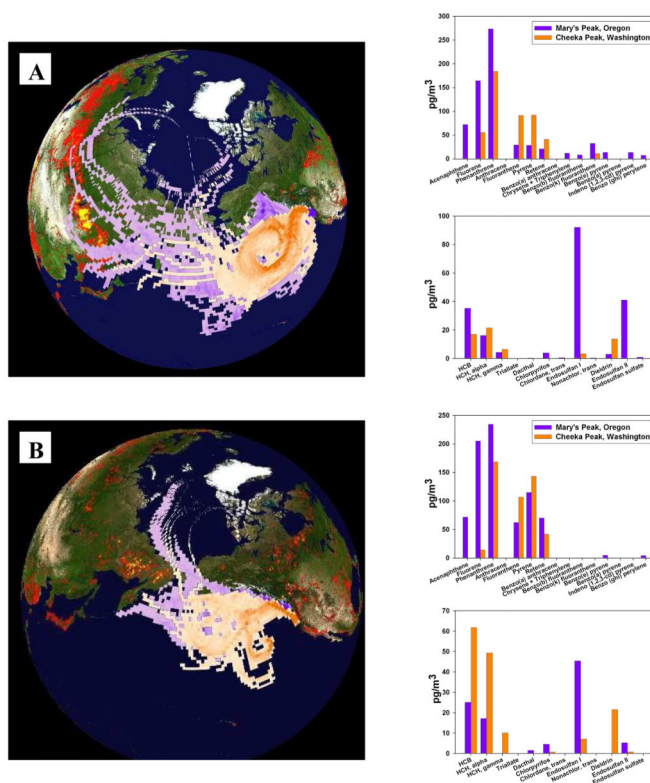40. 2003 Annual Report - Washington State Agricultural Burning Program. 2003. http://www.ecy.wa.gov/pubs/0402013.pdf

Figure 1.
MODIS 10-day fire detects overlaid with 10-day air mass back trajectories and corresponding PAH and pesticide concentrations measured at MPO (purple) and CPO (orange) for the concurrent sampling on A) June 2, 2003 and B) August 4, 2003. Smoke plumes extended across the Pacific Ocean to Western North America. (Figure SI.2 A and B).
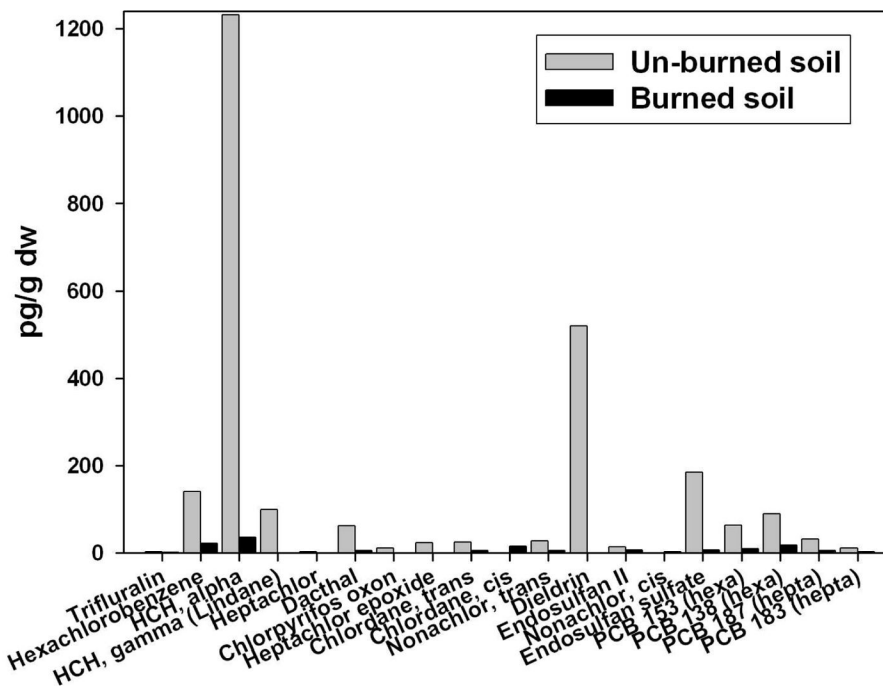
Figure 2.
Concentrations of pesticides and polychlorinated biphenyls (PCBs) (pg/g dry weight) in burned and un-burned forest soil collected from the B&B complex forest fire in the Deschutes National Forest, Oregon.