Influence of Asian and Western United States Agricultural Areas and Fires on the Atmospheric Transport of Pesticides in the Western United States

Toby Primbs[1], **Glenn Wilson**[2], **David Schmedding**[2], **Carol Higginbotham**[3], and **Staci Massey Simonich**[1,2,*]

[1]Department of Chemistry, Oregon State University, Corvallis, Oregon

[2]Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon

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

Abstract

Historic and current use pesticides (HUPs and CUPs), with respect to use in the United States and Canada, were identified in trans-Pacific and regional air masses at Mt. Bachelor Observatory (MBO), a remote high elevation mountain in Oregon's Cascade Range located in the United States, during the sampling period of April 2004 to May 2006 (n=69), including NASA's INTEX-B campaign (spring 2006). Elevated hexachlorobenzene (HCB) and α-hexachlorocyclohexane (α-HCH) concentrations were measured during trans-Pacific atmospheric transport events at MBO, suggesting that Asia is an important source region for these HUPs. Regional atmospheric transport events at MBO resulted in elevated dacthal, endosulfan, metribuzin, triallate, trifluralin, and chlorpyrifos concentrations, with episodic increases in concentration during some spring application periods, suggesting that the Western U.S. is a significant source region for these CUPs. Endosulfan I, γ-HCH, and dacthal concentrations were significantly positively correlated (p-value < 0.05) with increased air mass time in Western U.S. agricultural areas. Elevated γ-HCH concentrations were measured at MBO during both trans-Pacific and regional atmospheric transport events, including regional fire events. In addition to γ-HCH, elevated Σchlordane, α-HCH, HCB, and trifluralin concentrations were associated with fires in Western North America due to revolatilization of these pesticides from soils and vegetation. Trans-chlordane/cis-chlordane and α-HCH/γ-HCH ratios were calculated and may be used to distinguish between free tropospheric and regional and/or Asian air masses.

*Corresponding Author, staci.simonich@orst.edu, v: (541)737-9194, f: (541)737-0497.

Introduction

Evidence of trans-Pacific atmospheric transport of combustion byproducts (e.g. CO) and semivolatile organic compounds (SOCs), including pesticides, is growing (1–7) and the outflow of SOCs from Asia was recently reported (8). Coupling measurements of pesticides in trans-Pacific air masses on the West Coast of North America with measurements in Asian air masses, near Asian source regions (8), may result in the identification of unique molecular markers for specific Asian source regions based on regional pesticide use patterns.

Previous research investigating the trans-Pacific atmospheric transport of pesticides has focused primarily on organochlorine pesticides (2–4). Using aircraft measurements in Western Canada, Harner et al. measured elevated α-hexachlorocyclohexane (α-HCH) concentrations in the mid-troposphere due to trans-Pacific atmospheric transport (3). However, Harner et al. reported no significant increase in α-HCH concentrations were measured at a ground based site (3). In addition, Bailey et al. measured increasing concentrations of α and γ HCHs in Western Canada with increasing air mass time in Asia (2). Killin et al. reported increased concentrations of some current-use and historic-use pesticides (CUPs and HUPs) in trans-Pacific transport events; however, HCHs were not detected (4).

Pesticides may enter the atmosphere during application (e.g. spray drift), wind erosion of soil particles containing sorbed pesticides, and/or volatization from historically contaminated soils (9–11). Once in the atmosphere, pesticides may be transported far from their source regions to remote locations such as the Arctic and/or high elevation ecosystems (11,12). In addition, mid-latitude mountains serve as local areas of convergence for SOCs (13) and regional agricultural pesticide usage has been reported to have an impact on remote high elevation mountains in the Western U.S. (10,11). The objectives of this research were: (1) to measure current and historic use pesticides (CUPs and HUPs), with respect to the United States and Canada, in trans-Pacific and regional air masses at a remote, high elevation mountain site in the Western U.S.; (2) to determine the source regions of these CUPs and HUPs; and (3) to identify differences and similarities in the pesticide composition of regional Western U.S., trans-Pacific, and Asian air masses. The incomplete combustion byproduct (polycyclic aromatic hydrocarbons), industrial (polychlorinated biphenyls), and consumer use (fluorotelomer alcohols) SOC composition of these air masses has been reported elsewhere (7,14).

Experimental

Chemicals

The pesticides and pesticide degradation products measured in this study included trifluralin, hexachlorobenzene (HCB), α- and γ-hexachlorocyclohexane (α-HCH and γ-HCH), metribuzin, dacthal, chlorpyrifos, chlorpyrifos oxon, trans and cis chlordane (TC, and CC), trans and cis nonachlor (TN and CN), endosulfan I and II, endosulfan sulfate, and dieldrin. A matrix interferant prevented the measurement of heptachlor. A complete list of targeted

pesticides, including those not detected, isotopically labeled standards used for quantification, and solvents has been previously reported (8,15).

Sampling Site

Figure 1 shows the location of Mt. Bachelor Observatory (MBO) (43.98°N 121.69°W, 2763 m above sea level) in Oregon's Cascade Range (1,5–7,16) and the percent cropland in each county in Western North America (17). Air sampling was conducted at the summit building and access to the site was limited during extreme weather and lift maintenance. Other simultaneous measurements included: submicron aerosols (nephelometer), reactive gaseous mercury, particulate-phase mercury, Hg^0, NO, NO_x, CO, O_3, Rn, meteorology, and water vapor mixing ratio conducted by the Jaffe group (University of Washington-Bothell) (1,5,6,16).

Sample Collection, Extraction, and Analysis

Sixty-nine SOC air samples were collected from the 19th of April 2004 to the 13th of May 2006 at MBO using a modified high volume air sampler (Tisch Environmental, Cleves, OH) over 24 hour periods (~644 m^3 air sampled) (7). The sampling dates, site temperature, wind speed, and wind direction for the samples collected are reported elsewhere (7). Thirty-five air samples were initially collected over the first two year sampling period (April 2004 to March 2006) and an additional thirty-four samples were collected in spring 2006 (April-May 2006) in conjunction with NASA's Intercontinental Transport Experiment (INTEX-B) (18). The predominant wind direction on the days sampled was from the west-northwest and west (7).

The sample collection, extraction, and analysis for these samples have been reported previously (7). Quartz fiber filters (Whatman, England) were used to collect the particulate-phase and polyurethane foam (PUF) (Tisch Environmental, Ohio) coupled with polystyrene divinyl benzene (XAD-2) (Supelco, Pennsylvania) in a PUF-XAD-PUF sandwich was used to collect the gas-phase. ASE (Dionex, California) cleaning and extraction has been previously reported in detail (7,8). Sample analysis was conducted using gas chromatographic mass spectrometry (GC/MS) in selective ion monitoring (SIM) mode with both negative chemical ionization (NCI) and electron impact (EI) ionization modes (8,15). Additional information on sample collection, extraction and analysis is provided in supporting information.

Back Trajectories and Data Analysis

Ten-day air mass back trajectories were calculated using NOAA's ARL HYSPLIT 4.0 model (FNL) (19). Back trajectories were calculated at three elevations above model ground level (1300, 1500, and 1700 m), every three hours, over the twenty-four hour sampling period (including start and stop time) to determine the air mass time spent in designated source regions for a total of 27 trajectories per sample. MBO's elevation is ~1400 m above model ground level in the HYSPLIT model, thus three elevations were selected (16). The trajectories were imported into ArcGIS (ESRI, Redlands, California) for spatial representation and S-PLUS version 7.0 (Insightful, Seattle, Washington) was used for statistical analysis.

Results

Identification of Air Mass Source Regions

Regions with intensive agriculture in the Western U.S. were identified based on the percent cropland on the county scale (17) and 1997 estimated current use pesticide usage maps (20). Figures 1A and 1B show the agricultural source regions (solid boxes) used to assess trans-Pacific and regional atmospheric transport of pesticides to MBO. The potential source regions in the Western U.S. included: Eastern Oregon/ Washington, Western Oregon, and Central California (Figure 1B). In Asia, two source regions were identified: the first was a more agriculturally intensive area including China, the Koreas, and Japan (Asia); and the second was Eastern Russia (Siberia) with less agricultural intensity (Figures 1A) (2). These boxes extend into the Pacific Ocean because of the outflow plumes from Asia (7,8) and the large trajectory uncertainties (21).

Figure S1 shows the USGS 1997 estimated pesticide usage maps in kilograms per $1° \times 1°$ cell for the CUPs (dacthal, endosulfan, trifluralin, chlorpyrifos, triallate, and metribuzin) and trajectories for samples with elevated CUP concentrations (20). The 2002 estimated agricultural pesticide usage was recently reported by the USGS, however this data is not yet available in GIS format (20). In general, the 1997 usage maps are very similar to the 2002 maps for the CUPs discussed herein (20). Lindane (γ-HCH), a CUP used as a seed treatment, is not represented in the usage maps shown in Figure S1 because its use was not included in the USGS estimates. However, Washington and Oregon states both hold active labels for lindane as a seed treatment (22).

Source region impact factors (SRIFs), the percentage of time a sampled air mass back trajectory spent in a designated source region compared to the total trajectory time, were calculated using ten-day back trajectories. Details of the SRIF calculations are reported elsewhere (7,8). Figure S2 shows the air mass SRIFs for the different agricultural source regions and Figure S3 shows the percent of the air mass SRIF from the individual source regions.

Pearson correlation coefficients were calculated using the individual pesticide concentrations (measured from 2004 to 2006 at MBO) and the air mass SRIFs to assess if changes in concentration were significantly correlated with air mass time in agricultural source regions. If a source region had a significant impact on the pesticide concentration at MBO, then a significant correlation may exist. Conversely, if multiple source regions had a significant impact on the pesticide concentrations at MBO, then a significant correlation may not exist. In addition, if increased pesticide concentrations occurred sporadically due to episodic transport events, such as a spring time application of CUPs or revolatilization due to forest and/or agricultural fires, a significant correlation may not exist. Meteorological influences, including temperature and water vapor mixing ratio, on SOC concentrations at MBO are discussed in the supporting information.

Historic Use Pesticides

Figure 2 shows the temporal profile of CUP and HUP air concentrations over the sampling period at MBO. HUPs were more frequently detected than CUPs; where HUP frequency of

detection in air masses (FOD%) was HCB (100%) and α-HCH (100%) > chlordanes (including nonachlors) (~80%) > dieldrin (7%). The concentration ranges of HUPs were: HCB (18 to 94 pg/m^3); α-HCH (2 to 43 pg/m^3); trans-chlordane (<DL to 5 pg/m^3); cis-chlordane (<DL to 3 pg/m^3); trans-nonachlor (<DL to 2 pg/m^3); and dieldrin (<DL to 4 pg/m^3). Table S4 shows the estimated atmospheric and soil half lives of the detected HUPs.

α-HCH—Technical HCH was a source of γ-HCH and was the primary source of α-HCH to the environment (23). Technical HCH use in the U.S. and Canada were cancelled in 1978 and 1971, respectively (24). Although technical HCH was banned in China in 1983 (25), the facilities that produced technical HCH were not shut down until 2000 (26). Recent measurements of Asian air masses showed that elevated α-HCH concentrations were associated with increased air mass time in China (8).

At MBO, the α-HCH concentrations were significantly positively correlated (p-value < 0.05) with HCB, γ-HCH, trifluralin, Σgas-phase PAH, Σparticulate-phase PAHs, and retene concentrations (Table S3). The significant correlations between α-HCH concentrations and concentrations of SOCs that are markers for Asian air masses (Σparticulate-phase PAHs) (7,8), in addition to markers for regional fires (Σgas-phase PAHs and retene) (7), suggests that both trans-Pacific atmospheric transport and fires result in elevated α-HCH concentrations at MBO. The α-HCH concentrations were not significantly correlated with SOC markers (e.g. ΣFTOHs) for urban areas in the Western U.S (7,14). The highest α-HCH concentrations at MBO were measured during a trans-Pacific transport event on 25–26 April 2004 (Figure 2 and S2). Eckhardt et al recently reported elevated HCH, DDT, and PCB concentrations in air masses associated with fires, suggesting the increased concentrations were due to volatization from previously contaminated soils and vegetation (27). In addition, elevated PCB concentrations were measured in air masses at MBO that were associated with regional fire events (7). Increased α-HCH concentrations were measured at MBO on 11–12 July 2004 in an air mass that passed over a fire event in Alaska (Figure 2A).

WV data was available for 53 of the 69 samples and the 53 samples were divided into two groups, those greater than and those less than the measured median WV (2.52 g/kg). The α/γ HCH ratio in air samples corresponding to a WV greater than the median, n=26 (wet, boundary layer air) were compared to the ratio in samples corresponding to a WV less than the median n=27 (dry, free tropospheric air) using a Students t-test. A significantly higher (p-value, 0.01) α/γ HCH ratio was measured in the free tropospheric air (average ratio (±standard error) of 5.2 ± 0.8) compared to the boundary layer air (2.9 ± 0.3). Furthermore, the α/γ HCH ratio was significantly negatively correlated with WV (p-value < 0.05). The α-HCH isomer has a 25% longer atmospheric lifetime than the γ-HCH isomer based on reaction with the OH radical (28) and this may explain the difference in the measured ratios.

The average (±standard error) α/γ-HCH ratio measured near Asia in Spring 2004 was 2.5 ± 0.2 (8). In Summer 2002, Qiu et al. reported an α/γ-HCH ratio of 1.0 to 2.1 in China (29), and in Summer 2003, Lammel et al. reported a ratio of 1.6 to 2.9 in China/Korea (30). During a relatively fast (i.e. ~5–6 days) trans-Pacific atmospheric transport event from Asia to MBO (25–26 April 2004) (1), a ratio of 1.5 was measured, which is similar to Asian measurements (Figures 1 and S4A). During periods of increased air mass time over the

Pacific Ocean and Siberia (e.g. 9–10 Jan 2005, 6–7 Feb 2005, 15–16 April 2006, 8–9 May 2006, and 12–13 May 2006) and during spring 2006, the α/γ HCH ratio at MBO (5.6 ± 0.9) was similar to the α/γ HCH ratio (5.2 ± 0.8) in the upper troposphere (Figure S4A and Figure S3). Shen et al reported annual average α/γ HCH ratios for sites in Western Canada (average ($\pm$standard error) of 5.2 ± 0.7), with the ratio dropping significantly (to 0.2) at sites near the Canadian Prairies due to the use of lindane (γ-HCH) as a seed treatment (31). During periods of relatively fast (<10 days) trans-Pacific transport and/or regional transport at MBO, the ratio was lower (2.9 ± 0.3) and was reflective of impacts from agricultural regions in both the U.S. and in Asia (Figure S4A and Figure S3).

HCB—HCB use as a fungicide was canceled in the U.S. and Canada in 1984 and 1972, respectively (24). However, HCB is an industrial byproduct, combustion byproduct, and contaminant in pesticides (32). The major source of HCB to the atmosphere is thought to be volatization from past uses (32). However, elevated HCB concentrations have been associated with Chinese air masses (8).

Elevated HCB concentrations were measured at MBO during late spring and summer, and when the source region was identified as Asia (e.g. 25–26 April 2004) (Figure 2 and S2). HCB concentrations were significantly positively correlated (p-value < 0.05) with α-HCH, γ-HCH, Σchlordane, trifluralin, ΣPCB, Σgas-phase PAH, Σparticulate-phase PAH, and retene concentrations, and were negatively correlated with chlorpyrifos concentrations (Table S3). Elevated HCB concentrations were measured in air masses influenced by fires in Alaska and Canada (11–12 July 2004), as well as Western Oregon (9–10 August 2005) (7) (Figure 2B).

Dieldrin—Dieldrin was used as a pesticide and is a degradation product of aldrin. Dieldrin uses in the U.S. were limited to use as a termiticide in 1974, followed by cancellation in 1987. Dieldrin was only detected in the spring 2006 MBO samples, on 11–12 April, 12–13 April, 29–30 April, 10–11 May, and 11–12 May, and dieldrin concentrations were not significantly correlated (p-value > 0.05) with other measured SOC concentrations. On 11–13 April 2006, the air masses were associated with Central California; whereas on 29–30 April and 10–12 May 2006 the air masses were associated with Western Oregon (Figure S2).

Chlordane—Following major cancellation in the U.S. in 1983, chlordane use was limited to subterranean termites from 1983 to 1988 (33). In a global passive air sampling study, some of the highest concentrations of chlordane were measured in California (34). Increased chlordane concentrations have also been associated with urban areas, compared to rural areas (34,35).

The Σchlordane concentrations at MBO were significantly positively correlated (p-value < 0.05) with HCB, γ-HCH, Σendosulfan, trifluralin, ΣPCB, Σgas-phase PAH, retene, and levoglucosan concentrations (Table S3). Elevated chlordane concentrations were measured in air masses that had spent considerable time in Central California; including air masses sampled on 24–25 April 2005, 7–8 May 2005, 12–13 May 2005, 27–28 May 2005, 4–5 April 2006, and 12–13 April 2006 (Figure 2 and S2). The chlordane concentrations at MBO were lower in trans-Pacific air masses and in free tropospheric air masses that had spent

significant time over Siberia or the Pacific Ocean (Figure S2). Significantly decreasing trans-chlordane concentrations (p-value < 0.05) were associated with increasing air mass time over Siberia.

The highest Σchlordane concentrations at MBO were measured in the 9–10 August 2005 air mass that was impacted by regional fires and elevated concentrations were measured in the 11–12 July 2004 air mass that passed over fires in Alaska and Canada (7). The statistically significant positive correlation between Σchlordane concentrations and Σgas-phase PAH, levoglucosan, and retene concentrations provide further evidence that fires result in revolatilization of chlordanes stored in soils and vegetation.

A significantly higher (p-value, 0.02) trans-chlordane/cis-chlordane (TC/CC) ratio was measured in boundary layer air (1.39 ± 0.1), compared to free tropospheric air (0.87 ± 0.05), at MBO (Figure S4B). The technical chlordane used in North America has been reported to have a TC/CC ratio of 1.0–1.26 (2,12,36). TC is more susceptible to photodegradation than CC and should result in a lower TC/CC ratio (< 1.0) (2,12). This may be the reason the free tropospheric ratio is less than the boundary layer ratio.

The trans-chlordane/trans-nonachlor (TC/TN) ratio is also shown in Figure S4C. This ratio could not be calculated in air masses that spent a significant amount of time over the Pacific Ocean and Siberia (e.g. 9–10 Jan 2005, 6–7 Feb 2005, and 12–13 May 2006) because the chlordanes were below the detection limit. The TC/TN ratio was significantly positively correlated (p-value, 0.006) with the TC/CC ratio, indicating that increases in both ratios are indicative of shorter transport times from the boundary layer of the Western U.S. to MBO.

Current-Use Pesticides

Figure 2 shows the temporal variation in the CUP concentrations at MBO. The most frequently detected CUPs in air masses (FOD%) were γ-HCH (90%) > endosulfan I (80%) and dacthal (75%) > trifluralin (36%) > chlorpyrifos (26%) > metribuzin (9%) and triallate (7%). The FOD% for the degradation products chlorpyrifos oxon and endosulfan sulfate was 6% and 30%, respectively. Metribuzin and triallate were only detected in spring 2006 samples.

The concentrations of CUPs were: dacthal (<DL to 352 pg/m^3); endosulfan I (<DL to 255 pg/m^3); endosulfan II (<DL to 33 pg/m^3); endosulfan sulfate (<DL to 4 pg/m^3); γ-HCH (<DL to 29 pg/m^3); chlorpyrifos (<DL to 6 pg/m^3); chlorpyrifos oxon (<DL to 58 pg/m^3); metribuzin (<DL to 7 pg/m^3); triallate (<DL to 36 pg/m^3); and trifluralin (< DL to 2 pg/m^3) (Figure 2). CUP concentrations were generally low in winter, with sporadic increases in concentration in the spring, summer, and fall likely due to seasonal applications (Figure 2). Table S4 shows the estimated atmospheric and soil half lives of the detected CUPs. In general, CUPs have shorter estimated atmospheric and soil half lives than HUPs.

γ-HCH—Lindane, which is primarily γ-HCH, has been used as an organochlorine insecticide in warehouses, for public health purposes, and as a seed treatment (33). Sources of γ-HCH include both current uses (lindane) and historic uses (as part of technical HCH). In 2004, use of γ-HCH as a seed treatment in Canada was banned (37). Active labels, for use

as a seed treatment, were in effect during the MBO sampling periods in the western states of Washington and Oregon (22). However, there were no active registrations of γ-HCH in California, British Columbia, or Alaska (22). Lindane continues to be produced and used in Asia (38) and increased γ-HCH concentrations have been associated with Chinese air masses (8).

At MBO, the γ-HCH concentrations were significantly positively correlated (p-value < 0.05) with HCB, α-HCH, Σchlordane, trifluralin, Σendosulfan, ΣPCBs, Σparticulate-phase PAH, Σgas-phase PAH, retene, and levoglucosan concentrations (Table S3). The correlations between γ-HCH concentrations and markers for trans-Pacific atmospheric transport (particulate-phase PAHs) (7), in addition to markers for biomass combustion (retene and levoglucosan) (7), suggest that both trans-Pacific transport and regional fires lead to elevated γ-HCH concentrations (7). The highest concentrations of γ-HCH were measured during a trans-Pacific transport event on 25–26 April 2004 (Figure 2A). The second highest concentrations of γ-HCH were measured on 9–10 August 2005, in an air mass that was influenced by fires in Western Oregon, and a moderate increase in γ-HCH concentrations was also measured in the air mass collected on 11–12 July 2004 that was influenced by fires in Alaska and Canada (Figure 2A) (7). Elevated γ-HCH concentrations were also measured in air masses that had elevated Eastern Oregon/Washington SRIFs (7–8 September 2005, 23–24 April 2006, and 4–6 May 2006) (Figure 2A) and increasing concentrations were significantly positively correlated (p-value < 0.05) with increasing air mass time over Eastern Oregon/Washington. These findings suggest that γ-HCH source regions to MBO include Asia, regional fires, and Eastern Oregon/Washington.

Dacthal—Dacthal (DCPA), a pre-emergent current use herbicide that is used as a weed control for annual grasses and broad-leaved weeds in turfs, ornamentals, vegetable and fruit crops, has a soil half life of 16–86 days (39) and an estimated atmospheric lifetime of 24 days (40). Dacthal undergoes atmospheric transport (11,41) and is used intensively in Eastern Oregon/Washington and Central California (Figure S1) (42). Dacthal concentrations at MBO were significantly positively correlated (p-value < 0.05) with only Σendosulfan concentrations (Table S3) and dacthal use areas in the Western U.S. overlap with endosulfan use areas (Figure S1). Increased dacthal concentrations at MBO occurred in mid to late spring (Figure 2), likely coinciding with application periods, and periods when air masses spent considerable time over Eastern Oregon/Washington (19–20 June 2004; 27–28 May 2005; 22–26 April 2006; and 4–6 May 2006) (Figures 2 and S2). Increasing dacthal concentrations at MBO were significantly positively correlated (p-value < 0.05) with increasing air mass time over Eastern Oregon/Washington.

Endosulfan—Endosulfan is a broadly used current use insecticide and technical endosulfan is 70% endosulfan I and 30% endosulfan II (43). Endosulfan I and II have been previously measured in air samples collected from rural and urban sites in British Columbia (3). In addition, endosulfan is used in agriculture throughout the Western U.S. (Figure S1C) and British Columbia, Canada (34,42). Significant positive correlations (p-value < 0.05) existed between Σendosulfan concentrations and dacthal, γ-HCH, Σchlordane, ΣPCB, and retene concentrations at MBO (Table S3). Increased endosulfan concentrations were

measured during the spring and summer and during periods when air masses spent considerable time over Eastern Oregon/Washington (19–20 June 2004; 13–14 Mar 2005; 7–8 September 2005; 22–24 April 2006; and 4–6 May 2006) (Figure 2 and S2). Increasing endosulfan I concentrations were significantly correlated (p-value < 0.05) with increasing air mass time over Eastern Oregon/Washington.

Decreasing endosulfan sulfate concentrations were significantly correlated (p-value < 0.05) with increasing air mass time over Asia, while increasing concentrations were associated with increasing air mass time over Siberia. Air masses that spent increased time in Siberia were often associated with high pressure systems that directed the air mass through Eastern Oregon/Washington. For example, the highest endosulfan sulfate concentrations were measured on 19–20 June 2004. This air mass spent a considerable amount of time in Siberia and also passed through Eastern Oregon/Washington (Figure S3).

To further investigate the endosulfan source regions to MBO, the ratio of endosulfan I concentrations to the sum of endosulfan I and II concentrations was calculated. This ratio was calculated to compare the measured ratio to the ratio for current applications (i.e. the ratio of the technical product) and to compare potential atmospheric lifetime differences between Asian and regional source regions. The endosulfan I/(endosulfan I + endosulfan II) ratios were calculated in boundary layer and free tropospheric air using the median WV as a divider. No significant difference (p-value > 0.05) existed between the ratios, with a free tropospheric average ($\pm$standard error) of 0.90 ± 0.01 and boundary layer average ($\pm$standard error) of 0.88 ± 0.02. During spring 2004, the ratio measured in Asian air masses was similar to these ratios, with an average ($\pm$standard error) of 0.92 ± 0.01 (8).

Endosulfan II was not detected in winter samples and, thus, a winter time ratio could not be calculated. During periods of increased air mass time over the Pacific Ocean and Siberia, endosulfans were not detected (e.g. 9–10 Jan 2005, 6–7 Feb 2005, and 12–13 May 2006) and the endosulfan I/ (endosulfan I + endosulfan II) ratio was similar during periods of increased air mass time over Asia and the Western U.S (Figure S4D).

Trifluralin—Volatization of trifluralin, a current use selective pre-emergence herbicide, after application can be significant, with loss of ~18% applied (44). The majority of the use of trifluralin in the Western U.S. is in California, with some use in Washington and Oregon (Figure S1F) and its estimated atmospheric half life is on the order of hours (40). Significant positive correlations (p-value < 0.05) existed between trifluralin concentrations and HCB, α-HCH, γ-HCH, Σchlordane, Σgas-phase PAH, ΣPCB, retene, and levoglucosan concentrations (Table S3). Elevated trifluralin concentrations were measured in air masses that spent considerable time in all designated Western U.S. source regions; Western Oregon SRIFs (21–22 April 2004, 25–26 April 2004, 10–11 May 2004, 9–10 August 2005, and 27–29 April 2006), Eastern Oregon/Washington SRIFs (7–8 Sept 2005), and Central California SRIFs (May 2005, 4–5 April 2006) (Figure 2 and S2). Elevated trifluralin concentrations were indicative of regional transport and not trans-Pacific transport.

Significant positive correlations (p-value < 0.05) between NO concentrations and trifluralin concentrations existed (Table S2); suggesting trifluralin may be associated with highly

populated agricultural regions in the Western U.S., such as Central California. Figure S1F shows the trajectories for the 4–5 April 2006 sample over Central California, which is both agriculturally intensive and highly populated. Correlations between trifluralin concentrations and biomass combustion marker (retene and levoglucosan) concentrations suggest increased trifluralin concentrations are associated with fires. The highest concentrations of trifluralin were measured on 9–10 August 2005, in an air mass that had passed over fires in Western Oregon (Figure 2C) (7).

Triallate and Metribuzin—Triallate and metribuzin were detected only in the spring 2006 samples at MBO. Both triallate and metribuzin have relatively short estimated atmospheric half lives (on the order of hours) (40).Volatization of triallate, a pre-emergent current use herbicide (33), after application is ~21% (44). Triallate use in the Western U.S. is primarily located in Eastern Oregon/Washington (Figure S1E) and elevated triallate concentrations were measured in air masses with elevated SRIFs in this region (22–25 April 2006) (Figure S2). These measurements are consistent with where triallate is used (Figure S1) and its spring time application.

Metribuzin use in the Western U.S. is primarily located in both Oregon and Washington, with some use in Central California (Figure S1D). Metribuzin, a current use triazine herbicide (33), concentrations were elevated on 6–7 April 2006, 18–19 April 2006, and 4–6 May 2006 (Figure 2). These sampled air masses were influenced by either Eastern Oregon/ Washington or by Southern Oregon/Northern California.

Chlorpyrifos—Chlorpyrifos, a current use organophosphate insecticide, is one of the most frequently used pesticides in U.S. homes for roach and termite control (45). It has been previously reported to be detected more frequently in urban areas than agricultural areas (9). Chlorpyrifos concentrations at MBO were significantly negatively correlated (p-value < 0.05) with HCB (Table S3) and significantly positively correlated with NO concentrations (p-value < 0.05) (Table S2). The correlation between NO and chlorpyrifos concentrations indicate increased concentrations of chlorpyrifos are associated with highly populated regions in the Western U.S., such as Central California. Elevated chlorpyrifos concentrations were measured during periods of increasing air mass time over Central California (4–5 April 2006) and E. Oregon/Washington (13–14 March 2005 and 22–24 April 2006), reflecting the broad use of chlorpyrifos in Western U.S. urban and agricultural areas (Figure 2 and S2).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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A) Asian Source Regions
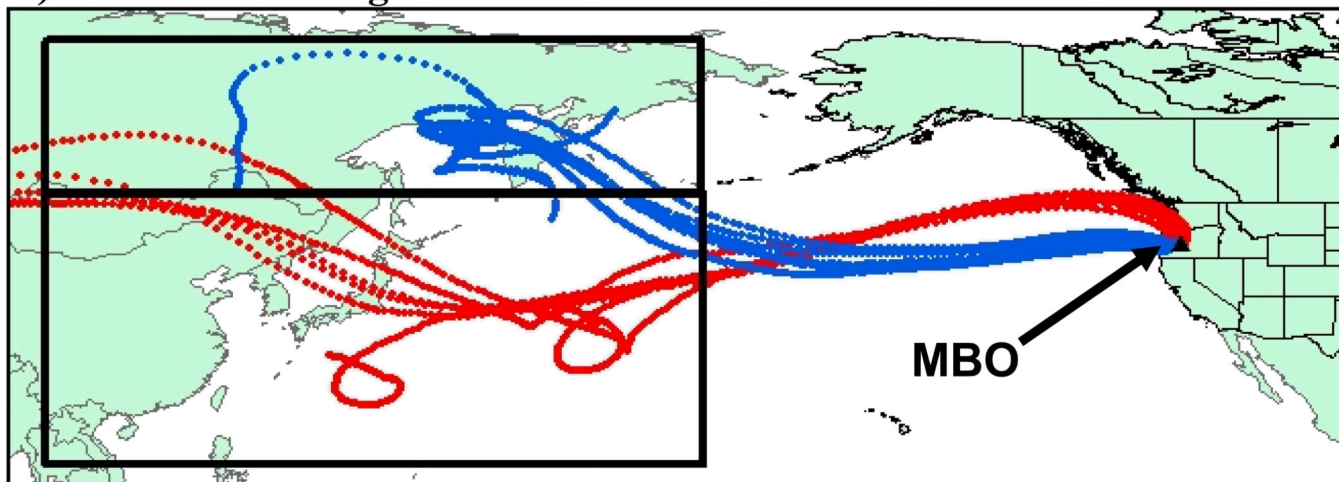
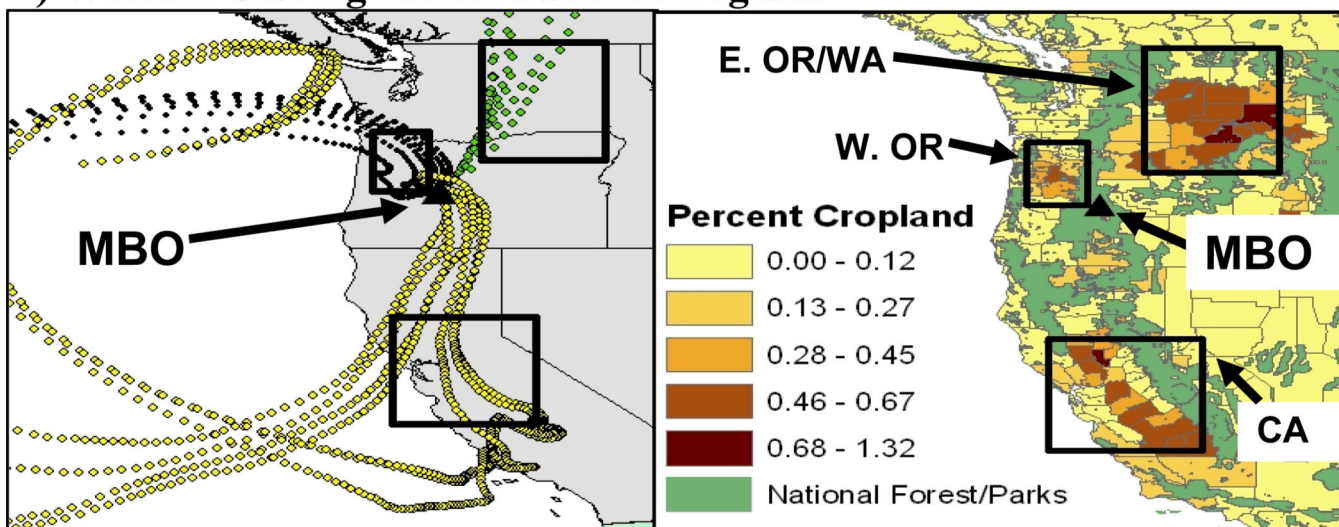## B) Western U.S. Agriculture Source Regions

Figure 1.
MBO, black triangle, (43.98° N 121.69° W, 2.7 km a.s.l.) is located in Oregon's Cascade Range. **A** Asia and Siberia source regions (boxes) with respect to MBO. Example trajectories 25–26 April 2004 (red, Asia) and 12–13 May 2006 (blue, Siberia). **B** Western Oregon (W. OR), Eastern Oregon/Washington (E. OR/WA), and Central California (CA) agriculture source regions (boxes). Example trajectories 4–5 April 2006 (yellow, Central California), 13–14 March 2005 (green, Eastern Oregon/Washington), and 28–29 April 2006 (black, Western Oregon). Also shown is the percent cropland on the county level (17) and national parks/forests in Western North America.
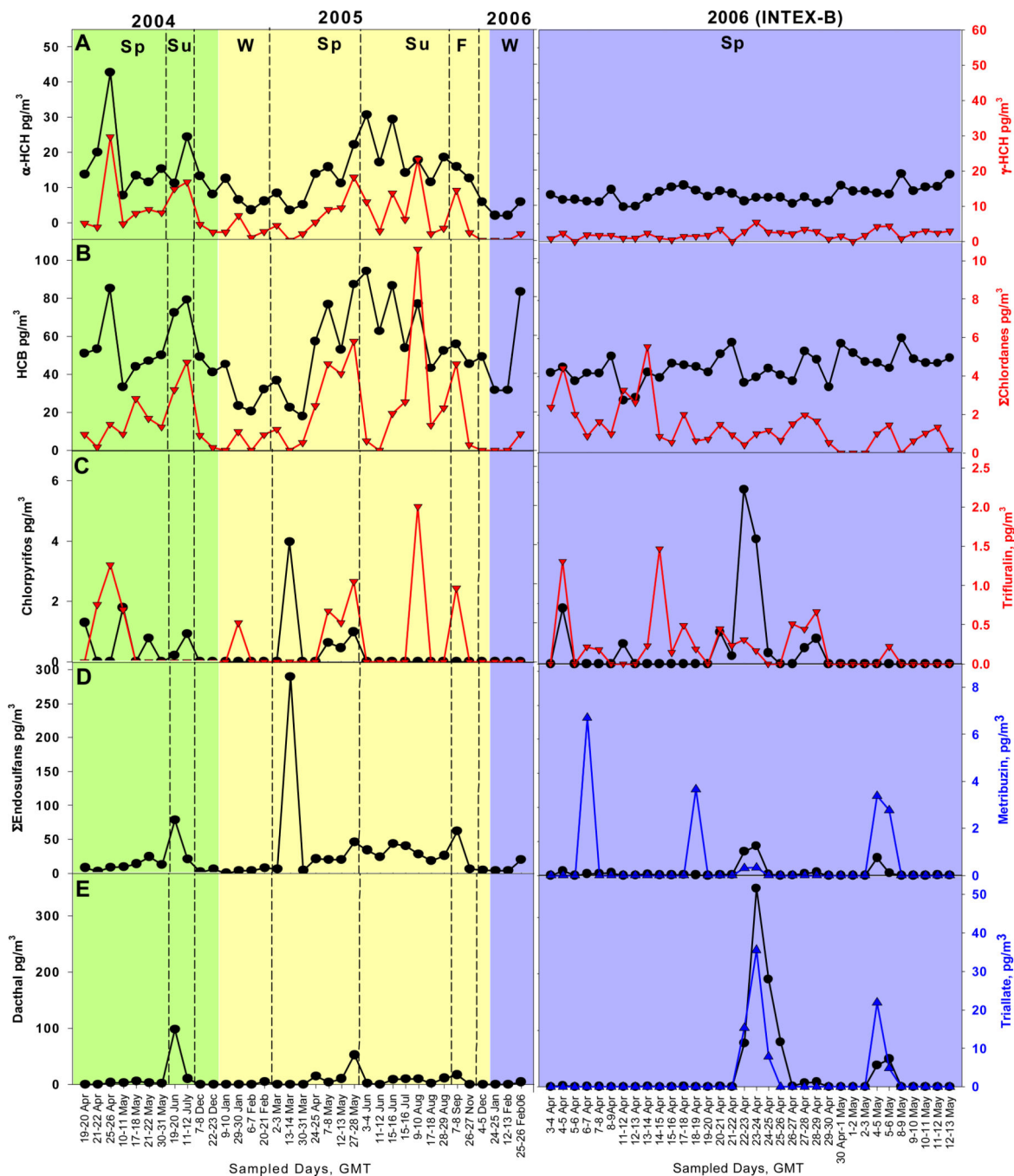
Figure 2.
Pesticide concentrations 2004–2006. **A** α-HCH (black, circle) and γ-HCH (red, triangle). **B** HCB (black, circle) and Σchlordanes (red, triangle). **C** chlorpyrifos (black, circle) and trifluralin (red, triangle). **D** Σendosulfans (black, circle) and metribuzin (blue, triangle). **E** dacthal (black, circle) and triallate (blue, triangle). Metribuzin and triallate (blue) were only detected in the spring 2006 samples. Winter (W) (Dec. Jan., Feb.), Spring (Sp) (Mar., Apr.,

May), Summer (Su) (June, July, Aug.), Fall (F) (Sept., Oct., Nov.) are separated by dashed lines. Background colors designate different years.