Supporting Information

Manuscript Title:

Influence of Asian and Western U.S. Agricultural Areas and Fires on the Atmospheric Transport of Pesticides in the Western U.S.

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Sample Collection, Extraction, and Analysis

Details of the Sample Collection, Extraction, and Analysis have been previously reported *(7)*. In brief, previously baked (12 hours at 350°C) quartz fiber filters (QFFs) (Whatman, England) followed by previously ASE (Dionex, California) extracted XAD-2 (Supelco, Pennsylvania) resin, sandwiched between two ASE extracted 1½ " x 3 " polyurethane (PUF) (Tisch Environmental Cleves, OH) plugs, were used for collection of SOCs. This sampling train was used to collect both the particulate (QFFs) and gas phase (PUF-XAD-PUF) SOCs. Sampling media was transported to the sampling site on ice and stored in a freezer located at the summit of MBO. After sampling the samples were stored in the site freezer, transported back to the lab on ice where they were stored in a freezer till extraction. Just before extraction, samples were brought to room temperature in sealed containers. Samples were spiked with isotopically labeled standards before extraction and ASE extracted. Following extraction on the ASE, samples were concentrated to 300 µL using a combination of a Turbovap II (Caliper Life Sciences, Massachusetts) and a micro N_2 stream concentrator.

Sample analysis was conducted using gas chromatographic mass spectrometry (GC/MS) in selective ion monitoring (SIM) mode with both electron capture negative ionization (ECNI) and electron impact (EI) ionization modes *(7,8,15)*. Instrumental limits of detection ranged from 0.01 to 6.7 pg/µL *(15)*. Limits of quantification, defined as the lowest standard used in the calibration curves, ranged from 0.25 to 75 pg/µL *(8)*. Estimated method detection limits, calculated using EPA method 8280A, ranged from 0.39 to 114 pg/m^3 for the GC/MS-EI and 0.0001 to 4.6 pg/m^3 for the GC/MS-NCI *(8,46)*. Only peaks with signals three times the peak to peak noise were reported. Details of all quantifying and qualifying ions monitored have been previously reported

for the targeted analytes *(15)*. All target analytes were quantified from isotopically labeled internal standards (surrogates) added prior to extraction *(8,15)*.

Recoveries ranged between 48 to 95% over the entire analytical method. Four travel blanks, traveled to the field in sealed containers and treated in the same manner as the samples, were collected. All targeted pesticides were less than the quantitation limit in the travel blanks showing that lab and travel contamination was not an issue. Thirteen field blanks, traveled to the field installed in the sampler with the motor off, were collected. Pesticides were detected in QFF (HCB, γ-HCH, chlordanes, endosulfans, trifluralin, dacthal, and chlorpyrifos) and PUF/XAD-2 (HCB, dacthal, and chlorpyrifos) field blanks above the quantitation limit. For these SOCs the limit of detections were defined as the average field blank concentration (n=13), plus three times the standard deviation *(3)*. SOC concentrations were blank corrected. The bottom PUF plug was used to assess if breakthrough occurred and was analyzed separately in half of the samples. The percentage of SOC concentration measured on the bottom PUF to the total gas-phase concentration plug was less then 1%. No correction for breakthrough was made.

Meteorological Influences

Only chlorpyrifos concentrations at MBO were significantly positively correlated (p-value < 0.05) with wind speed and no pesticide concentrations were significantly correlated (p-value > 0.05) with wind direction (sine and cosine of the wind direction).

Pesticide volatization during application and/or after application from soils is a major route of pesticide entry to the atmosphere and is dependent on temperature *(47)*. To assess the potential impact of temperature on pesticide concentrations, the Clausius-Clapeyron equation was used *(8,48,49)* and MBO site temperatures below 273 K were replaced with 273 K *(7,49)*. Table S1 shows the statistically significant slope parameters (p-value < 0.05) for log HCB, α-HCH, γ-

HCH, trans-chlordane, cis-chlordane, trans-nonachlor, trifluralin, dacthal, and endosulfan I concentrations versus 1000/T. These slopes were similar to previous studies *(48)* and the variability in pesticide concentrations at MBO are, in part, explained by temperature.

Weiss-Penzias et al. previously reported using the water vapor mixing ratio (WV) at MBO as a good indicator for distinguishing between boundary layer (wet) and free tropospheric (dry) air masses *(5)*. In addition, increased O_3 concentration in MBO air masses was attributed to influence from the free troposphere *(5)*. Anticyclonic systems, associated with subsiding air masses in the Pacific Northwest of North America, were frequently associated with air mass back trajectories that passed over the relatively dry high desert and agriculturally intensive source region in Eastern Oregon/Washington (Figure S1E). Thus, in addition to decreased WV in air masses being associated with increased impact from the free troposphere, decreased WV was also associated with impact from the Eastern Oregon/Washington source region.

For the entire MBO dataset (2004-2006), the Σchlordane concentrations were significantly correlated (p-value < 0.05) with both WV (positive correlation) and O_3 (negative correlation) concentrations (Table S2A). This suggests that chlordane sources to MBO are located in the boundary layer of Western North America. The HCB and γ-HCH concentrations were significantly positively correlated (p-value < 0.05) only with WV (Table S2A). The chlorpyrifos concentrations were significantly correlated (p-value < 0.05) with both WV (negative correlation) and O_3 (positive correlation) (Table S2A). This suggests that elevated concentrations of chlorpyrifos at MBO may be due to either trans-Pacific transport or agricultural uses in Eastern Oregon/Washington. Chlorpyrifos has a relatively short estimated atmospheric half life (on the order of hours) *(40)*, thus elevated concentrations were likely associated with regional sources in Eastern Oregon/Washington.

In the spring 2006 data set only, statistically significant positive correlations (p-value < 0.05) existed between WV and metribuzin concentrations, indicating increased metribuzin concentrations were associated with boundary layer air. The Σendosulfan and α-HCH concentrations were significantly correlated (p-value < 0.05) with WV (negative correlation) and O_3 (positive correlation) concentrations, suggesting their concentrations are higher in the free tropospheric air masses. Higher concentrations of α-HCH in the mid troposphere, compared to ground based sites, have been attributed to Asian sources *(3)* and may be due to trans-Pacific transport. Endosulfan is used in Asian countries, however, in general, endosulfan air concentrations are higher in the Pacific Northwest of North America than in Asia *(34)*. Like chlorpyrifos, these correlations suggest that elevated concentrations of endosulfans at MBO may be due to either trans-Pacific transport or agricultural uses in Eastern Oregon/Washington.

References

(46)   Method 8280A, E.P.A. The analysis of polychlorinated dibenzop-dioxins and polychlorinated dibenzofurans by high-resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS). http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8280a.pdf.

(47)   Rice, C. P.; Nochetto, C. B.; Zara, P. Volatilization of Trifluralin, Atrazine, Metolachlor, Chlorpyrifos, alpha-Endosulfan, and beta-Endosulfan from Freshly Tilled Soil *J Agr Food Chem* **2002**, *50*, 4009-4017.

(48)   Wania, F. H., J-E.; Lei, Y.; Mackay D. Temperature Dependence of Atmospheric Concentrations of Semivolatile Organic Compounds *Environ. Sci. Technol.* **1998**, *32*, 1013-1021.

(49)   Carlson, D. L.; Hites, R. A. Temperature dependence of atmospheric PCB concentrations *Environ Sci Technol* **2005**, *39*, 740-747.

Table S1: Slopes (±standard error), p-value, and R^2 for the correlation of log pesticide concentration (pg/m^3) versus 1000/T(K). NS (not significant), p-value > 0.05.

Analyte*	slope	p-value	R^2
HCB	-1.5 ± 0.4	0.0002	0.21
α-HCH	-1.9 ± 0.6	0.002	0.15
TC	-3.3 ± 0.8	0.0003	0.24
CC	-2.7 ± 0.9	0.004	0.28
TN	-3.1 ± 0.7	0.0001	0.30
Trifluralin	-3.3 ± 0.9	0.003	0.37
γ-HCH	-4.7 ± 1.0	< 0.0001	0.30
Dacthal	-7.9 ± 2.9	0.01	0.14
Chlorpyrifos	NS	0.2	0.10
Endosulfan I	-4.7 ± 1.7	0.009	0.14
Endosulfan II	NS	0.5	0.02
Endosulfan Sulfate	NS	0.2	0.10

*Only pesticides measured in >10% of the samples are shown, others were not statistically significant.

Table S2: Correlation coefficients (R) (p-value < 0.05) between pesticide concentrations and CO, water vapor (WV), NO, and O_3 concentrations. **(A)** 2004-2006 data and **(B)** spring 2006 data only. NS (not significant), p-value > 0.05. NA (not available), only detected spring 2006.

A) 2004-2006

	CO	WV	NO	O_3
HCB	NS	0.28	NS	NS
α-HCH	NS	NS	NS	NS
γ-HCH	NS	0.35	NS	NS
Σchlordanes	NS	0.40	NS	-0.30
Chlorpyrifos	NS	-0.68	NS	0.51
Trifluralin	NS	NS	0.56	NS
Σendosulfans	NS	NS	NS	NS
Metribuzin	NA	NA	NA	NA
Dacthal	NS	NS	NS	0.29
Triallate	NA	NA	NA	NA

B) Spring 2006 (INTEX-B)

|	CO	WV	NO	O_3
HCB	NS	NS	NS	NS
α-HCH	NS	-0.45	NS	0.46
γ-HCH	-0.47	NS	NS	NS
Σchlordanes	NS	NS	NS	-0.43
Chlorpyrifos	NS	NS	0.86	NS
Trifluralin	NS	NS	0.67	NS
Σendosulfans	NS	-0.54	NS	0.46
Metribuzin	NS	0.83	NS	NS
Dacthal	NS	NS	NS	NS
Triallate	NS	NS	NS	NS

Table S3: Significant correlation coefficients (R) (p-value <0.05) between SOC concentrations: Σgas-phase PAHs (Σgas-PAHs), Σparticulate-phase PAHs (Σpart-PAHs), ΣPCBs, HCB, α-HCH, γ-HCH, Σchlordanes (Σchlord), chlorpyrifos (chlorp), trifluralin (trif), endosulfans (endos), metribuzin (metr), dacthal (dac), triallate (triall), retene (ret), and levoglucosan (lev). PAHs, retene, levoglucosan, and PCBs have been discussed in detail elsewhere *(7)*. NA (not applicable). Dieldrin concentrations were not correlated with other SOC concentrations.

|	Σgas-PAHs	Σpart-PAHs	ΣPCBs	HCB	α-HCH	γ-HCH	Σchlord	Chlorp	Trif	Σendos	Metr	Dac	Triall	Ret	Lev
Σgas-PAHs	NA		0.61	0.66	0.52	0.61	0.50		0.44					0.71	0.33
Σpart-PAHs		NA		0.47	0.81	0.65									
ΣPCBs	0.61		NA	0.43		0.65	0.80		0.62	0.51				0.65	0.63
HCB	0.66	0.47	0.43	NA	0.78	0.67	0.37	-0.50	0.49					0.45	
α-HCH	0.52	0.81		0.78	NA	0.76			0.49					0.36	
γ-HCH	0.61	0.65	0.65	0.67	0.76	NA	0.55		0.62	0.53				0.57	0.35
Σchlord	0.50		0.80	0.37		0.55	NA		0.60	0.36				0.46	0.43
Chlorp				-0.50				NA							
Trif	0.44		0.62	0.49	0.49	0.62	0.60		NA					0.50	0.69
Σendos			0.51			0.53	0.36			NA		0.36		0.38	
Metr											NA				
Dac										0.36		NA			
Triall													NA		
Ret	0.71		0.65	0.45	0.36	0.57	0.46		0.50	0.38				NA	0.35
Lev	0.33		0.63			0.35	0.43		0.69					0.35	NA

Table S4: Estimated pesticide atmospheric and soil half lives *(25)*.

| Pesticide	Estimated Atmospheric Half Lives, h	Estimated Soil Half Lives, h
HCB	951	8640
HCHs	1830	8640
Chlordanes	50.6	8640
Nonachlors	45.8	8640
Dieldrin	27.8	8640
Chlorpyrifos	2.8	8640
Trifluralin	10.7	8640
Endosulfans	31.3	8640
Metribuzin	14.1	1800
Dacthal	582	2880
Triallate	7.7	2880
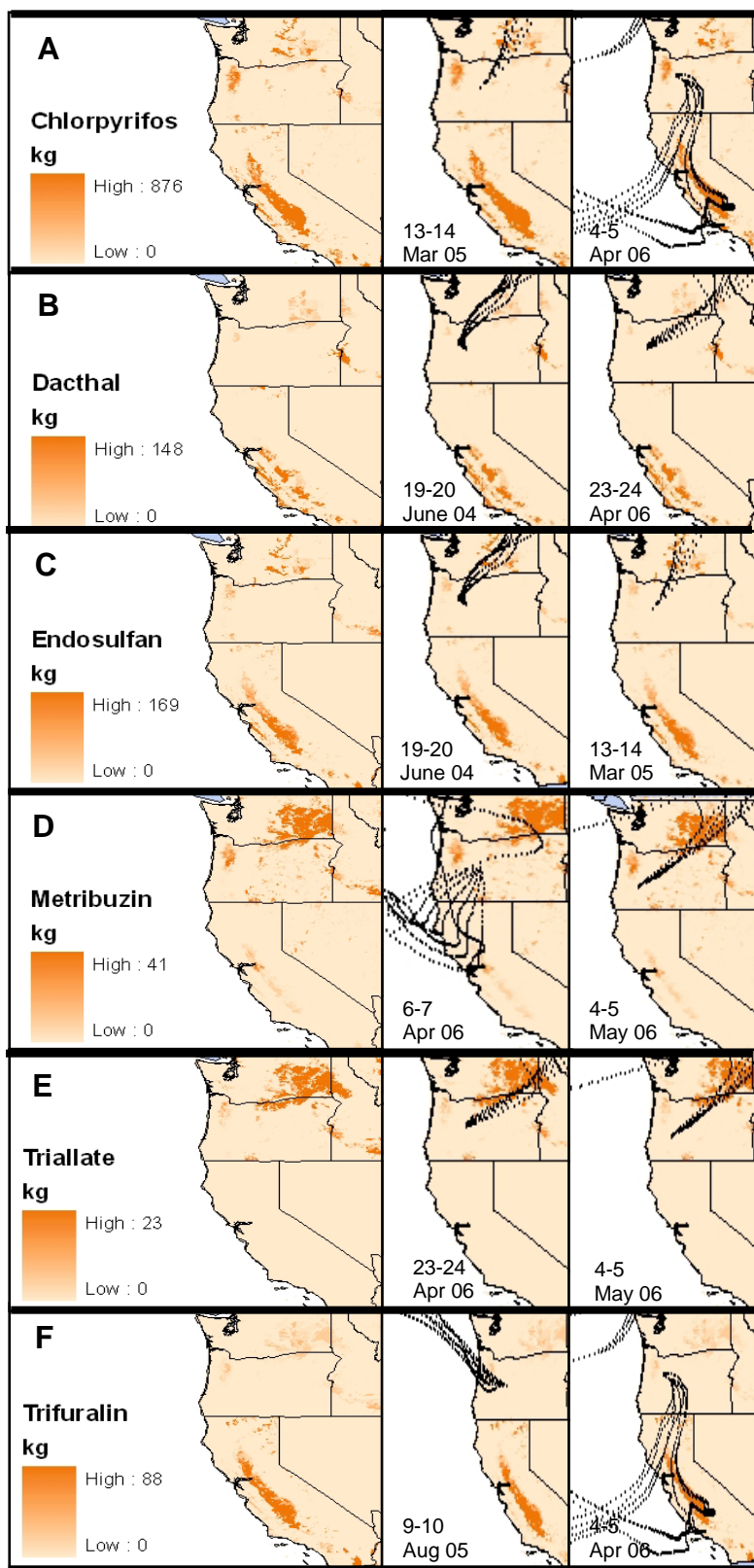
Figure S1: 1997 agricultural current-use pesticide usage maps in kilograms per 1° x 1° grid cell for (A) chlorpyrifos, (B) dacthal, (C) endosulfan, (D) metribuzin, (E) triallate, and (F) trifluralin; in addition to example trajectories of samples with elevated concentrations overlaid on the usage *(20)*.
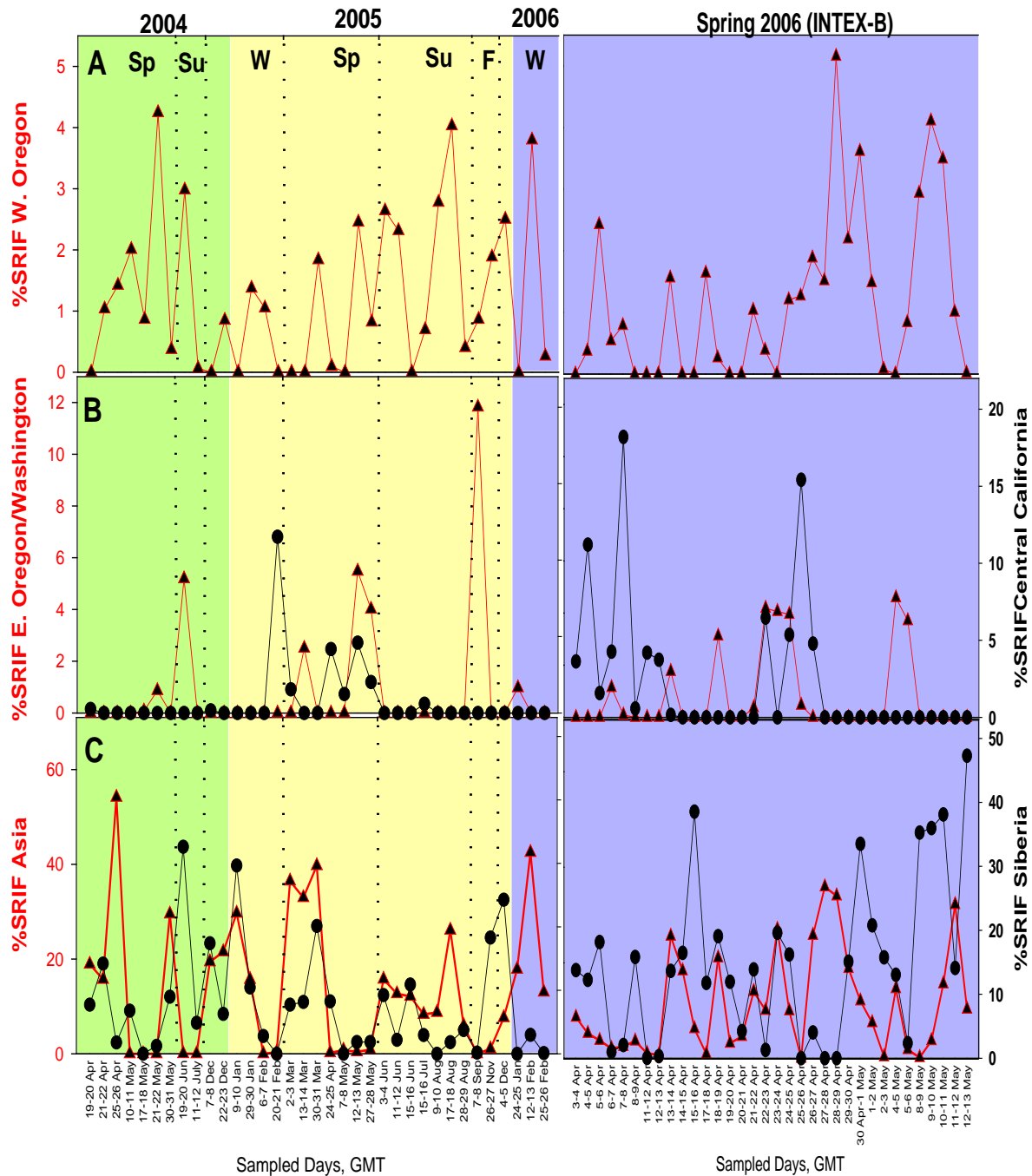
Figure S2: Source region impact factors (SRIFs) for: **(A)** Western Oregon (red, triangles); **(B)** Eastern Oregon/Washington (red, triangles) and Central California (black, circles); **(C)** Asia (red, triangles) and Siberia (black, circles). Winter (W) (Dec. Jan., Feb.), Spring (Sp) (Mar., Apr., May), Summer (Su) (June, July, Aug.), Fall (F) (Sept., Oct., Nov.) are separated by dashed lines. Background colors designate different years.
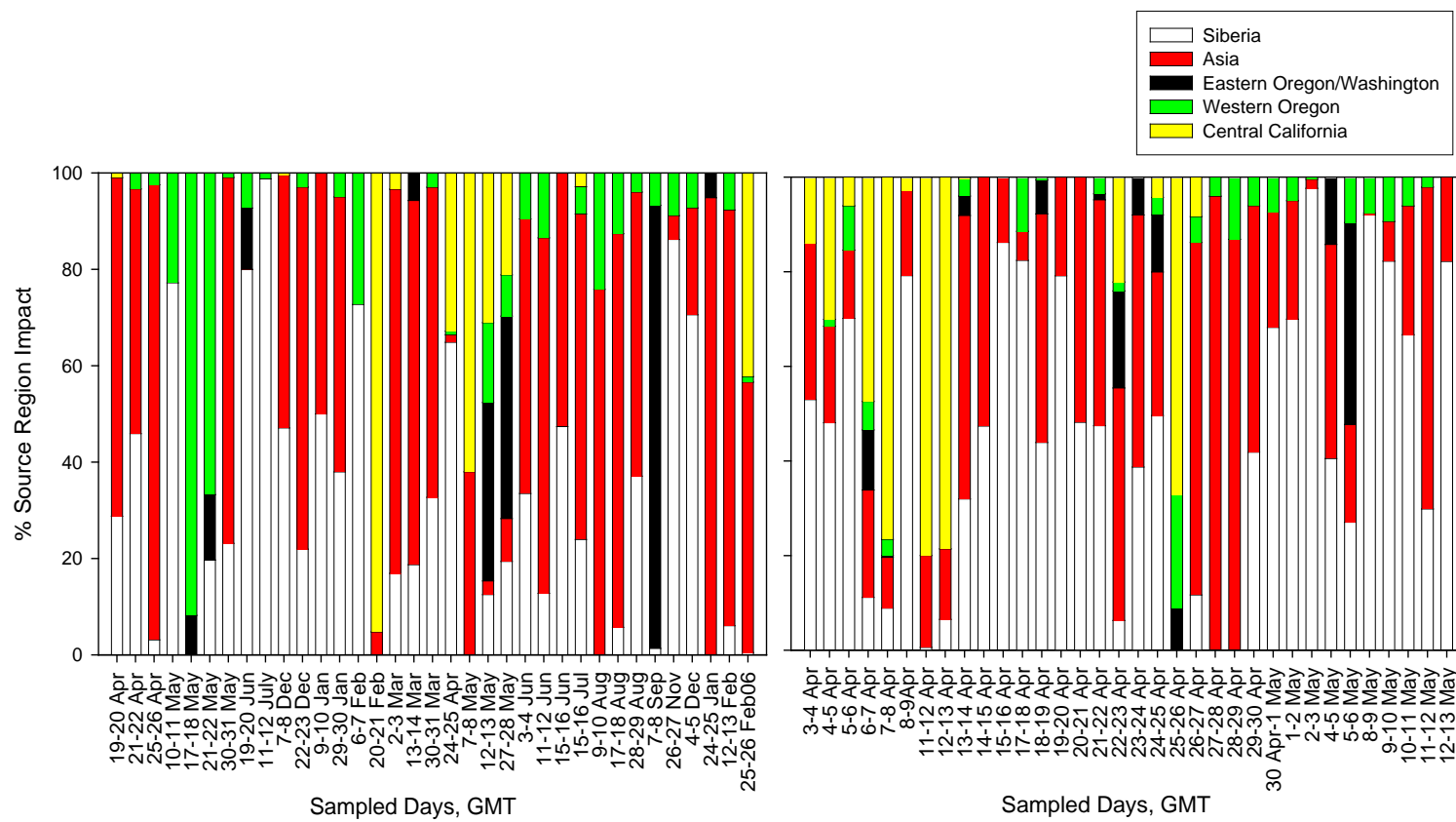
Figure S3: Percent of source region impact factor from Siberia, Asia, E. Oregon/Washington, W. Oregon, and Central California.
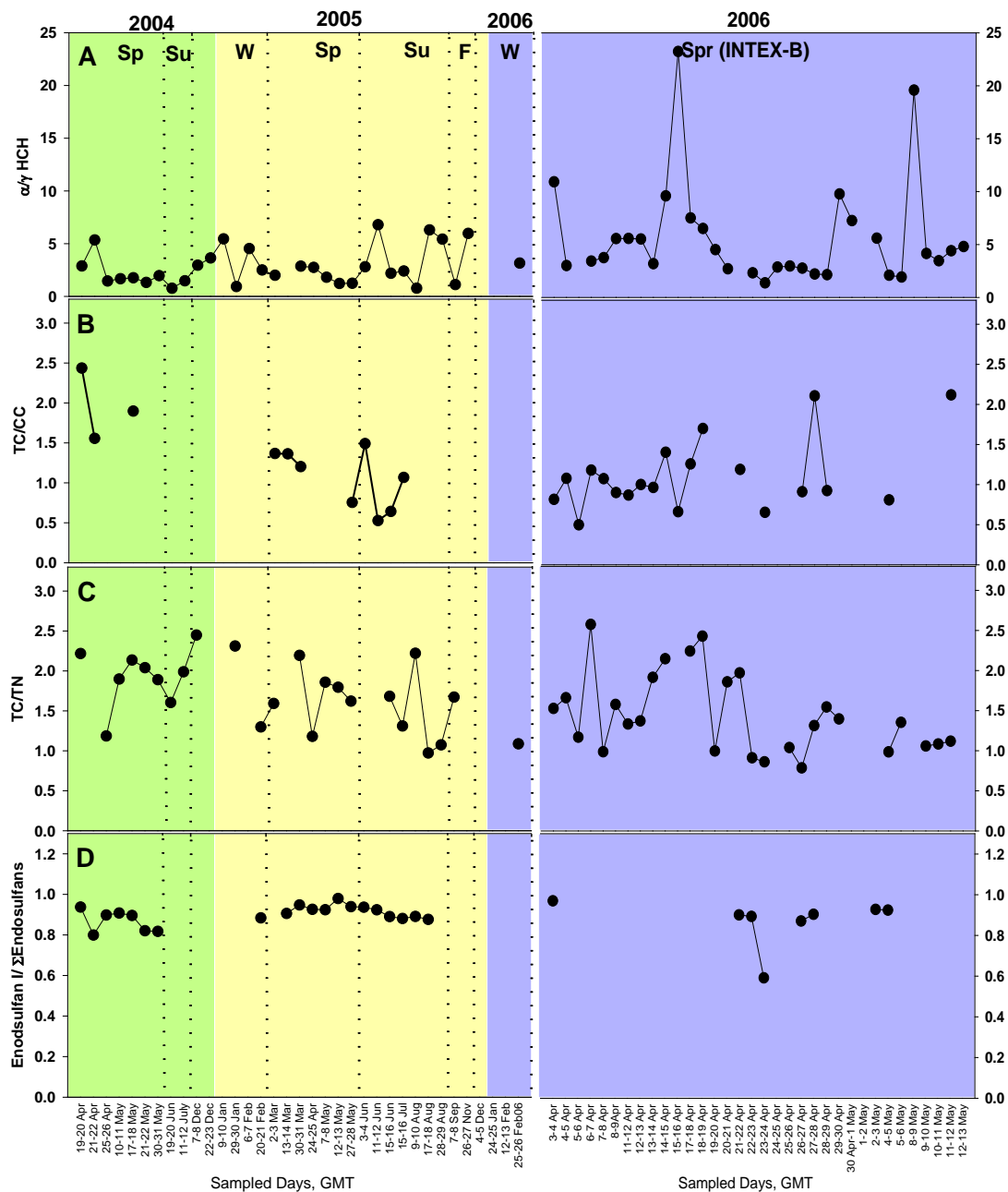
Figure S4: Pesticide ratios **(A)** α/γ HCH, **(B)** trans-chlordane/cis-chlordane (TC/CC), **(C)** trans-chlordane/ trans-nonachlor TC/TN, and **(D)** endosulfan I/ Σendosulfans. Winter (W) (Dec. Jan., Feb.), Spring (Sp) (Mar., Apr., May), Summer (Su) (June, July, Aug.), Fall (F) (Sept., Oct., Nov.) are separated by dashed lines. Background colors designate different years. Only consecutive points, where a ratio could be calculated, are connected by a line to show general patterns.