Appendix H:

Potential Chlorpyrifos-oxon Generation Sub-Study

Documents:

Study of Potential Oxon Formation during Chlorpyrifos Air Sampling. Study Plan February 20,2009. [laboratory study]Table H1. Transformation of Chlorpyrifos to Chlorpyrifos Oxon on XAD-2 Resin during Air Sampling

Quality Control Study of Potential Oxon Formation during Chlorpyrifos Air Sampling. Study Summary June 22, 2009. [Field Study] Table H2. Potential Generation of CPF-oxon Field Study

ORGANOPHOSPHORUS PESTICIDE AIR MONITORING PROJECT

Study of Potential Oxon Formation During Chlorpyrifos Air Sampling

As a part of the quality control component of this study, the University of Washington will conduct a study to determine whether chlorpyrifos-oxon is formed from chlorpyrifos in OVS tubes during air sampling. These are the same sample tubes that were used for field sampling in the air monitoring project. This quality control study will be conducted in DEOHS laboratories at the University of Washington.

Study Plan

OVS sample tubes will be spiked with known amounts of chlorpyrifos. The tubes will then be attached to calibrated air sampling pumps, and air will be drawn through the tubes at several different flow rates, in each case for 24 hours. The spiking levels and flow rates will be representative of field conditions and findings from the air monitoring project.

Spiking levels and flow rates. Three sets of samples will be prepared for this experiment:

- 1. Three tubes will be spiked with 50 nanograms of chlorpyrifos. This loading represents approximately the 50th percentile value of what was measured in the air monitoring project receptor samples. The flow rate for these samples will be 2 liters per minute, the same flow rate used for receptor sampling in the field. Duration will be 24 hours
- 2. Three tubes will be spiked with 200 nanograms of chlorpyrifos. This loading represents approximately the 90th percentile value of what was measured in the air monitoring project receptor samples. The flow rate for these samples will be 2 liters per minute, the same flow rate used for receptor sampling in the field. Duration will be 24 hours
- 3. Three tubes will be spiked with 2,000 nanograms of chlorpyrifos. This loading represents approximately the 90th percentile value of what was measured in the air monitoring project perimeter samples. The flow rate for these samples will be 6 liters per minute, the same flow rate used for perimeter sampling in the field. Duration will be 24 hours.

Quality control OVS tubes. Three tubes will be spiked with chlorpyrifos (one at each of the levels indicated above), but will not be attached to air sampling pumps. One unspiked tube will be attached to an air sampling pump with a flow rate of 2 liters per minute. A second unspiked tube will be attached to an air sampling pump with a flow rate of 6 liters per minute. Duration will be 24 hours in each case.

Analytical Method. The UW Environmental Health Laboratory has developed an LC-MS-MS method for analysis of chlorpyrifos and chlorpyrifos-oxon, and reports a limit of quantification of 2 nanograms per sample for each analyte. The front and back section of each tube will analyzed for both compounds for a total of 28 analyses.

Sample Type	Number	Spike Level (ng)	Flow Rate (24 hours)
Receptor: median loading	3	50	2 liters per minute
Receptor: high loading	3	200	2 liters per minute
Perimeter: high loading	3	2000	6 liters per minute
QC: spiked OVS tube	1	50	none (control)
QC: spiked OVS tube	1	200	none (control)
QC: spiked OVS tube	1	2000	none (control)
QC: blank OVS tube	1	0 (control)	2 liters per minute
QC: blank OVS tube	1	0 (control)	6 liters per minute
Total for analysis	14		

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^a Oxon Equiv = CPF-oxon mass expressed as the molar equivalent of CPF. CPF-oxon equiv (ng) = [CPF-oxon ng] * Molecular Weight CPF/molecular weight CPF-oxon]	Footnotes																			
^b QC samples tubes (without air) were left on the lab counter next to the pumps during sampling period. Room temperature = 20C. Otherwise they were stored at -20C.	^a Oxon Equiv = CPF-oxo	on mass exp	ressed	as the molar eq	uivalent of CPF	. CPF-oxo	n equiv (ng) = [CPF-0>	(on ng) '	* Molecu	lar Weig	ht CPF	/molecular	weight CPF	-oxon]					
	^b QC samples tubes (with	thout air) wei	re left o	n the lab counte	er next to the pu	mps during	g sampling	period. Roo	om temp	oerature	= 20C. C	Otherwis	se they we	re stored at	-20C.					

Table H1. Transformation of Chlorpyrifos to Chlorpyrifos-oxon on XAD-2 Resin during Air Sampling

ORGANOPHOSPHORUS PESTICIDE AIR MONITORING PROJECT

Quality Control Study of Potential Oxon Formation during Chlorpyrifos Air Sampling

In addition to the laboratory based quality control study conducted in February 2009, the University of Washington conducted a field-based study to determine the amount of chlorpyrifos-oxon generation during field air sampling methods using OVS XAD-2 resin tubes. The outdoor field methods are representative of the 2008 Organophosphate Pesticide Air Monitoring Project. Flow rates and sample generations were run for a continuous, 24 hour sample time period. Unlike previous laboratory and field tests, this experiment is unique because the sampling is conducted in the field using spiked sampling tubes containing different known amounts of chlorpyrifos as experimental controls.

Study Plan

OVS sample tubes were spiked with different known amount of chlorpyrifos. The tubes were attached to calibrated air sampling pumps. Volumes were collected for two sample conditions for 24 hours: at 2 LPM to receptor sampling conditions and at 6 LPM to represent perimeter sampling conditions. The spiked levels were determined relative to the amount of Total Chlorpyrifos found in the 2008 Air Monitoring study and corrected for an approximate 75% recovery rate fund in the 2009 laboratory based oxon study.

Spiking levels and flowrates. Eight sets of samples were prepared for this sub study.

- 1. Three tubes were spiked with 15 nanograms of chlorpyrifos. This loading represents approximately the 25th percentile of what was measured in the Air Monitoring project receptor samples. The flowrates for these samples were 2 liters per minute, the same flowrate used for receptor sampling in the field. Duration was 24 hours.
- 2. Three tubes were spiked with 30 nanograms of chlorpyrifos. This loading represents approximately the 50th percentile of what was measured in the Air Monitoring project receptor samples. The flowrates for these samples were 2 liters per minute, the same flowrate used for receptor sampling in the field. Duration was 24 hours.
- 3. Three tubes were spiked with 60 nanograms of chlorpyrifos. This loading represents approximately the 75th percentile of what was measured in the Air Monitoring project receptor samples. The flowrates for these samples were 2 liters per minute, the same flowrate used for receptor sampling in the field. Duration was 24 hours.
- 4. Three tubes were spiked with 200 nanograms of chlorpyrifos. This loading represents approximately the 90th percentile of what was measured in the Air Monitoring project receptor samples. The flowrates for these samples were 2 liters per minute, the same flowrate used for receptor sampling in the field. Duration was 24 hours.
- 5. Three tubes were spiked with 200 nanograms of chlorpyrifos. This loading represents approximately the 10th percentile of what was measured in the Air Monitoring project

perimeter samples. The flowrates for these samples were 6 liters per minute, the same flowrate used for receptor sampling in the field. Duration was 24 hours.

- 6. Three tubes were spiked with 592 nanograms of chlorpyrifos. This loading represents approximately the 50th percentile of what was measured in the Air Monitoring project perimeter samples. The flowrates for these samples were 6 liters per minute, the same flowrate used for receptor sampling in the field. Duration was 24 hours.
- 7. Three tubes were spiked with 2628 nanograms of chlorpyrifos. This loading represents approximately the 90th percentile of what was measured in the Air Monitoring project perimeter samples. The flowrates for these samples were 6 liters per minute, the same flowrate used for receptor sampling in the field. Duration was 24 hours.
- 8. Three tubes were not spiked with chlorpyrifos but were attached to air sampling pumps. There samples were used to determine the background level of chlorpyrifos. The flowrates for these samples were 2 liters per minute, the same flowrate used for receptor sampling in the field. Duration was 24 hours.

Quality control OVS tubes. Three sets of tubes were trip blanks. One set of the trip blanks were unspiked, second set were spiked with 30 nanograms of chlorpyrifos, and the last set were spiked with 592 nanograms of chlorpyrifos. All three sets of trip blanks were closed tubes and not attached to air sampling pumps. Another three sets of tubes were field blanks. These samples contained one set that were unspiked, a second set spiked with 30 nanograms of chlorpyrifos, and the third set spiked with 592 nanograms of chlorpyrifos. All three sets of tubes were field blanks. These samples contained one set that were unspiked, a second set spiked with 30 nanograms of chlorpyrifos, and the third set spiked with 592 nanograms of chlorpyrifos. All three sets of field blanks were uncapped and hung for 24 hours on the sampling masts.

Analytical Method. The UW Environmental Health Laboratory developed an LC-MS-MS method for analysis of chlorpyrifos and chlorpyrifos-oxon, and reports a limit of quantification of 2 nanograms per sample for each analyte. The front and back section for each tube were analyzed for both compounds.

Sample Type	Number of Tubes	Spiked amount CPF (ng)	Flowrate (24 hours)
Receptor: 25 th Percentile	3	15	2 liters per minute
Receptor: 50 th Percentile	3	30	2 liters per minute
Receptor: 75 th Percentile	3	60	2 liters per minute
Receptor: 90 th Percentile	3	200	2 liters per minute
Perimeter: 10 th Percentile	3	200	6 liters per minutes
Perimeter: 50 th Percentile	3	592	6 liters per minutes
Perimeter: 90 th Percentile	3	2628	6 liters per minutes
Background	3	0	2 liters per minute
Trip blank, Closed Tube (control)	3	0	None
Trip blank, Closed Tube	3	30	None

Sample Type	Number of Tubes	Spiked amount CPF (ng)	Flowrate (24 hours)
Trip blank, Closed Tube	3	592	None
Field Blank, Uncapped Open Tube (control)	3	0	None
Field Blank, Uncapped Open Tube	3	30	None
Field Blank ,Uncapped Open Tube	3	592	None

Results. Samples were analyzed for chlorpyrifos and its oxon. Refer to Table H2 for full results table. Percent (%) recoveries were generated for spike samples and ranged from 92% to >100% for spiked receptors, 84 to >100% for spiked perimeters, and 73% to 91% for spiked quality control samples. Recovery percentage increased at lower chlorpyrifos spiking levels. No trip blanks, unspiked, or 30 ng spiked tubes converted to oxon in the tubes without air drawn through them. Only a small portion (< 1%) was converted into oxon at the highest spiking level (592 ng). Instead, it was assumed that most oxon-conversion created in this experiment was a direct result of pulling air through the tubes.

The studies demonstrate that the oxygen analog could be produced by the air sampling process, with an inverse relationship between percent oxon produced and spiking level. For example, at a two liter per minute flow rate the oxon fraction averaged 25% +/-8% at the lowest spike level (15 ng), but was only 12% +/-3% at the highest level (200 ng). At the 6 liter per minute flow rate the oxon fraction averaged 19% +/-2% at the lowest spiked level (200ng) and only 7% +/-2% at the highest spiked level (2628 ng).

The results from the field-based quality control study suggest that there is still a portion of oxygen analog in the samples that was not an artifact of sampling or generated in the tubes. These findings call for additional research to be able to fully characterize the exposures of organophosphorus pesticide air contaminants and oxon analogs in these regions.

Table H2: Potentia	Generation	of CPF-oxon	Field Study
	Generation		i loid Olday

					,	·····	,	<i>,</i>										
				Sampling F	Parameters	<u> </u>	L			Reco	overv Mass	5	<u> </u>			Air Conc	entration	(na/m ³)
ID Number	Spike Mass ng		Start Date & Time	Stop Date & Time	TWA Flow rate Ipm	Duration min	Volume m ³	CPF ng	CPF- oxon ng	Oxon ^a Equiv ng	CPF Total ng	CPF- Oxon fraction (%)	Recovery (%)	CPF	CPF- oxon	Oxon Equiv ^a	CPF Total	CPF- oxon fraction (%)
Receptor	r - 2.0 lp	m																
9101	0	Į	4/16/09 11:59	4/17/09 11:59	1.93	1440	2.77	21	6	6.29	27.29	23.04		7.57	2.16	2.27	9.84	23.04
9102 ²	0	Į	4/16/09 11:54	4/17/09 11:55	1.98	1441	2.85	na	na	na	na	na		na	na	na	na	na
9103	0	Į	4/16/09 12:01	4/17/09 12:02	1.94	1441	2.80	12	7	7.34	19.34	37.94		4.29	2.50	2.62	6.92	37.94
		ļ			Į	ļ	ļ			Mean	23.31	30.49			Mean	2.45	8.38	30.49
		ļ			ļ	Į	ļ	.	ļ	Std Dev	5.62	10.53			Std Dev	0.13	1.03	5.27
		ļ			Į	ļ			ļļ	CV	0.24	0.35			CV	0.05	0.12	0.17
		ļ			ļ	ļ						ļ						
9104	15	ļ	4/16/09 11:19	4/17/09 11:20	1.90	1441	2.74	21	10	10.48	31.48	33.29	209.87	7.65	3.64	3.82	11.47	33.29
9105	15	ļ	4/16/09 11:22	4/17/09 11:22	1.22	1440	1.75	31	7	7.34	38.34	19.14	255.57	17.68	3.99	4.18	21.86	19.14
9106	15	ļ	4/16/09 11:24	4/17/09 11:24	2.30	1440	3.32	27	7	7.34	34.34	21.37	228.91	8.13	2.11	2.21	10.35	21.37
		ļ			ļ					Mean	34.72	24.60	231.45		Mean	3.40	14.56	24.60
		ļ			ļ					Std Dev	3.44	7.61	22.96		Std Dev	1.05	6.35	7.61
		ļ			Į	ļ				CV	0.10	0.31	0.10		CV	0.31	0.44	0.31
	~ ~ ~	<u> </u>					~ ~ ~ ~					ļ						
91072	30		4/16/09 11:43	4/17/09 11:43	1.99	1440	2.87	na	na	na	na	na	na	na	na	na	na	na
9108	30		4/16/09 11:49	4/17/09 11:49	2.14	1440	3.08	34	10	10.48	44.48	23.56	148.27	11.03	3.25	3.40	14.43	23.56
9109	30	 	4/16/09 11:46	4/17/09 11:50	2.01	1444	2.90	36	1	7.34	43.34	16.93	144.45	12.42	2.42	2.53	14.95	16.93
										Mean	43.91	20.25	146.36		Mean	2.97	14.69	20.25
										Std Dev	0.81	4.69	2.70		Std Dev	0.61	0.37	4.69
								.		CV	0.02	0.23	0.02		υ	0.21	0.03	0.23
0110	60		4/46/00 44:07	4/47/00 44:07	2.02	1440	2.02	60	10	10.40	70.40	10.10	100.47	22 50	2 40	2 50	07 47	12.10
9110	60		4/16/09 11:27	4/17/09 11:27	2.03	1440	2.92	69	10	10.40	79.40	13.19	132.47	23.59	3.42	3.38	27.17	13.19
9111	60		4/10/09 11:30	4/17/09 11:30	1.97	1440	2.04	69	10	11.55	70.00	14.00	130.00	23.01	3.00	4.00	27.00	14.00
9112	60		4/10/09 11.32	4/17/09 11.32	1.95	1440	2.00	00	10	10.40 Moan	70.40	13.30	130.00	24.21	3.57 Moan	2 00	20.01	13.33
										Std Dov	10.03	13.74	131.30		Std Dov	0.24	27.02	13.74
											0.00	0.02	0.94			0.24	0.42	0.02
		<u></u>			<u>.</u>	}		+			0.01	0.00	0.01			0.00	0.02	0.00
9113	200	<u> </u>	4/16/09 11:36	4/17/09 11:36	2 32	1440	3.35	184	18	18.86	202.86	9,30	101.43	54.97	5.38	5.64	60.60	9.30
9114	200	ł	4/16/09 11:38	4/17/09 11:38	1.97	1440	2.84	156	.0 26	27.25	183.25	14.87	91.62	55.01	9.17	9.61	64.62	14 87
9115	200	<u> </u>	4/16/09 11:40	4/17/09 11:40	2 25	1440	3.25	172	20	20.96	192.96	10.86	96.48	53.00	6.16	6.46	59.46	10.86
0.10	_50	1	.,,					<u> · · -</u>		Mean	193.02	11.68	96.51		Mean	7.23	61.56	11.68
		1			<u></u>	<u> </u>	<u>.</u>	1		Std Dev	9,81	2.87	4.90		Std Dev	2.10	2.71	2.87
		1				1		1		CV	0.05	0.25	0.05		CV	0.29	0.04	0.25

	1					ş		·												
				<u>I</u>	Sampling F	' arameters				l	Reco	overy Mass		L			Air Conc	centration (ng/m ³)		
ID Number	Spike Mass ng			Start Date & Time	Stop Date & Time	TWA Flow rate Ipm	Duration min	Volume m ³	CPF ng	CPF- oxon ng	Oxon ^a Equiv ng	CPF Total ng	CPF- Oxon fraction (%)	Recovery (%)	CPF	CPF- oxon	Oxon Equiv ^a	CPF Total	CPF- oxon fraction (%)	
Perimete	r - 6.0 lı	pm				il			<u>}</u>											
9117	0		1	4/16/09 12:39	4/17/09 12:39	5.87	1440	8.45	46	18	18.86	64.86	29.08		5.44	2.13	2.23	7.67	29.08	
9116	0			4/16/09 12:46	4/17/09 12:46	6.95	1440	10.01	53	21	22.01	75.01	29.34		5.29	2.10	2.20	7.49	29.34	
9118	. 0			4/16/09 12:46	4/17/09 12:46	6.18	1440	8.90	51	21	22.01	73.01	30.15		5.73	2.36	2.47	8.20	30.15	
							1			· • • •	Mean	70.96	29.52			Mean	2.30	7.79	29.52	
	ş		Ī			1	1	/	ſ		Std Dev	5.37	0.55		·····	Std Dev	0.15	0.37	0.55	
	·····					1	(The second sec	1		1	CV	0.08	0.02			CV	0.07	0.05	0.02	
						1	1			1										
9119	200			4/16/09 12:33	4/17/09 12:34	6.64	1441	9.57	205	44	46.11	251.11	18.36	125.56	21.43	4.60	4.82	26.25	18.36	
9120	200		Ī	4/16/09 12:33	4/17/09 12:34	6.09	1441	8.78	207	41	42.97	249.97	17.19	124.98	23.58	4.67	4.89	28.47	17.19	
9121	200	1	Ī	4/16/09 12:39	4/17/09 12:39	7.68	1440	11.05	193	49	51.35	244.35	21.02	122.18	17.46	4.43	4.65	22.11	21.02	
Î		(T	Ī		······	1	1				Mean	248.48	18.86	124.24		Mean	4.79	25.61	18.86	
Î	·····		Ī			1 1	(The second sec	 		:	Std Dev	3.62	1.96	1.81		Std Dev	0.13	3.23	1.96	
ĺ			I		7	1	1			1	C۷	0.01	0.10	0.01		C۷	0.03	0.13	0.10	
	·····				******	1	1	 	1	1								-		
9123	592		Ī	4/16/09 12:23	4/17/09 12:23	5.94	1440	8.55	556	46	48.21	604.21	7.98	102.06	65.01	5.38	5.64	70.64	7.98	
9122	592		Ī	4/16/09 12:28	4/17/09 12:28	6.07	1440	8.74	467	84	88.03	555.03	15.86	93.76	53.45	9.61	10.08	63.53	15.86	
9124	592		Ī	4/16/09 12:28	4/17/09 12:28	7.07	1440	10.18	505	82	85.94	590.94	14.54	99.82	49.63	8.06	8.45	58.08	14.54	
		(T	Ī			1	1	i			Mean	583.39	12.79	98.55		Mean	8.05	64.08	12.79	
1	······		l l			1			1	· · · · · · · · · · · · · · · · · · ·	Std Dev	25.44	4.22	4.30		Std Dev	2.25	6.30	4.22	
	······		I			1	1		1	i T	CV	0.04	0.33	0.04		CV	0.28	0.10	0.33	
	·\$					1		!	t	:					·····					
9125	2628		1	4/16/09 12:17	4/17/09 12:17	6.41	1440	9.24	2208	149	156.16	2364.16	6.61	89.96	239.03	16.13	16.90	255.94	6.61	
9126	2628		1	4/16/09 12:17	4/17/09 12:17	5.84	1440	8.41	1974	222	232.66	2206.66	10.54	83.97	234.73	26.40	27.67	262.40	10.54	
8127	2628		I	4/16/09 12:23	4/17/09 12:23	6.90	1440	9.93	2124	192	201.22	2325.22	8.65	88.48	213.92	19.34	20.27	234.19	8.65	
		(l				Mean	2298.68	8.60	87.47		Mean	21.61	250.84	8.60	
Ì						()	j		ţt	· · · · · · · · · · · · · · · · · · ·	Std Dev	82.03	1.97	3.12	,	Std Dev	5.51	14.78	1.97	
	······	1			••••••	1	1			;	CV	0.04	0.23	0.04	·····	C۷	0.25	0.06	0.23	

Table H2. Potential Generation of CPF-oxon Field Study (cont.)

Sampling Parameters Recovery Mass Air Concentration (ng/m³) CPF-CPF-CPF CPF Spike TWA CPF-Oxon^a CPF ID Start Date Stop Date Volume CPF-Oxon Duration Oxon oxon CPF Mass Flow rate oxon Total Recovery Total Equiv Number m³ & Time & Time min ng fraction oxon Equiv^a fraction ng lpm ng ng (%) ng (%) (%) Quality Control Trip Blanks closed Tube 9141 0 4/16/09 13:00 4/16/09 13:00 <1 <1 <1 9142 0 4/16/09 13:00 4/16/09 13:00 <1 <1 <1 4/16/09 13:00 9143 0 4/16/09 13:00 <1 <1 <1 4/16/09 12:58 4/16/09 12:58 22 9137 30 22 <1 73.33 9138 30 4/16/09 12:59 4/16/09 12:59 22 <1 22 73.33 Mean 22.00 73.33 Std Dev 0.00 0.00 C۷ 0.00 0.00 9139 592 4/16/09 12:56 4/16/09 12:56 519 <1 519 87.67 4/16/09 12:56 4/16/09 12:56 9140 592 528 <1 528 89.19 523.50 Mean 88.43 Std Dev 6.36 1.07 CV 0.01 0.01 Uncapped, Open Tube (Hanging) Blanks Receptor 9128 4/16/09 12:09 4/17/09 12:09 0 <1 <1 <1 9129 0 4/16/09 12:10 4/17/09 12:08 <1 <1 <1 9130 4/16/09 12:13 4/17/09 12:08 0 <1 <1 <1 9131 30 4/16/09 12:05 4/17/09 12:12 25 <1 25 83.33 9132 30 4/16/09 12:04 4/17/09 12:11 22 <1 22 73.33 9133 30 4/16/09 12:06 4/17/09 12:05 23 <1 23 76.67 Mean 23.33 77.78 Std Dev 1.53 5.09 C۷ 0.07 0.07 Perimeter 4/16/09 12:51 4/17/09 12:49 5.24 534.24 90.24 9134 592 529 5 0.98 9135 592 4/16/09 12:52 4/17/09 12:48 531 4 4.19 535.19 0.78 90.40 4/16/09 12:49 4/17/09 12:49 90.54 9136 592 536 <1 536 535.14 0.88 90.40 Mean Std Dev 0.15 0.88 0.14 C۷ 0.00 0.16 0.00 Footnotes ² Tubes disconnected from sampling device during sampling. No lab da ³Oxon Equiv = CPF-oxon mass expressed as the molar equivalent of CPF. CPF-oxon equiv (ng) = [CPF-oxon ng] * Molecular Weight CPF/molecular weight CPF-oxon]

Table H2. Potential Generation of CPF-oxon Field Study (cont.)