Supplementary material

The occurrence, spatial and seasonal variations, and gas-particle partitioning of atmospheric current use pesticides (CUPs) in the Great Lakes basin

Shaorui Wang[a,b], Amina Salamova[a], and Marta Venier[a]

a. O'Neill School of Public and Environmental Affairs, Indiana University, Bloomington, Indiana 47405, United States

b. National-Regional Joint Engineering Research Center for Soil Pollution Control and Remediation in South China, Guangdong Key Laboratory of Integrated Agro-environmental Pollution Control and Management, Institute of Eco-environmental and Soil Sciences, Guangdong Academy of Sciences, Guangzhou 510650, China

* Corresponding author: Marta Venier. Email: mvenier@indiana.edu; Phone: +1-(812) 855-1005

Table S1. Full name, abbreviation, category (catg), CAS number, physico-chemical properties, instrument used for analyses of the targeted chemicals. F, H, P, OI, I, and C represent fungicides, herbicides, pyrethroids, organophosphate insecticides, insecticides, and carbamates, respectively. Physico-chemical properties calculated at 25 degree were obtained from EPI suite.

Full name (abbreviation)	Catg	CAS	MW	log K_{oa}	log K_{ow}	log K_{aw}	Vapor pressure (pascals)	Solubility (mg/L)	Instruments
Chlorothalonil	F	1897-45-6	265.91	7.14	3.05	-4.09	1.28E-02	2.60E+01	GC-MS
Boscalid	F	188425-85-6	343.21	12.72	2.96	-9.76	1.17E-06	2.02E+01	LC-MS-MS
Azoxystrobin	F	131860-33-8	403.40	14.03	2.50	-11.53	8.73E-10	1.16E+01	LC-MS-MS
Dacthal	H	1861-32-1	331.97	8.33	4.28	-4.05	6.44E-03	1.76E+00	GC-MS
Trifluralin	H	1582-09-8	335.29	7.72	5.34	-2.38	1.05E-02	2.09E-01	GC-MS
Oxyfluorfen	H	42874-03-3	361.71	9.21	4.73	-4.48	1.02E-04	1.96E-01	GC-MS
Ametryn	H	834-12-8	227.33	9.98	2.98	-7.00	1.53E-03	8.97E+01	LC-MS-MS
Atrazine	H	1912-24-9	215.69	9.63	2.61	-7.02	1.12E-03	2.14E+02	LC-MS-MS
Bromacil	H	314-40-9	261.12	10.32	2.11	-8.28	8.47E-04	3.24E+02	LC-MS-MS
Desethylatrazine (CIAT)	H	6190-65-4	187.63	8.71	1.51	-7.20	1.51E-01	2.59E+03	LC-MS-MS
Diuron	H	330-54-1	233.10	10.37	2.68	-7.69	1.91E-04	1.51E+02	LC-MS-MS
Metolachlor	H	51218-45-2	283.80	9.33	3.13	-6.43	4.19E-03	5.09E+01	LC-MS-MS
Prometon	H	1610-18-0	225.30	10.42	2.99	-7.43	1.40E-03	9.02E+01	LC-MS-MS
Pendimethalin	H	40487-42-1	281.31	9.64	5.18	-4.46	8.11E-03	5.94E-01	GC-MS
Pronamide	H	23950-58-5	256.13	9.83	3.43	-6.40	2.68E-03	2.57E+01	LC-MS-MS
Bifenthrin	P	82657-04-3	422.88	12.54	8.15	-4.39	6.53E-05	2.41E-04	GC-MS
λ-cyhalothrin	P	91465-08-6	449.86	11.22	6.80	-4.22	3.47E-07	8.50E-04	GC-MS
Cis-permethrin	P	61949-76-6	391.30	10.62	6.50	-4.12	3.57E-06	9.75E-03	GC-MS
Trans-permethrin	P	61949-76-6	391.30	10.62	6.50	-4.12	3.57E-06	9.75E-03	GC-MS
Cyfluthrin	P	68359-37-5	434.30	11.88	5.95	-5.93	4.44E-08	8.43E-03	GC-MS
Cypermethrin	P	52315-07-8	416.31	11.71	6.60	-4.77	6.64E-01	1.56E-03	GC-MS
Deltamethrin	P	52918-63-5	505.21	9.89	6.20	-3.69	1.10E-05	1.83E-03	GC-MS
Esfenvalerate	P	66230-04-4	419.91	12.07	6.20	-5.85	4.39E-07	6.10E-03	GC-MS
Fenpropathrin	P	39515-41-8	349.43	9.51	5.70	-3.51	1.21E-03	2.55E-02	GC-MS
3-Phenoxybenzoic acid (3-PBA)	P	3739-38-6	214.22	10.92	3.91	-7.01	7.68E-03	1.69E+01	LC-MS-MS
4-Fluoro-3-Phenoxybenzoic acid (4-F-3-BA)	P	77279-89-1	232.21	10.24	3.29	-6.95	8.89E-03	4.58E+01	LC-MS-MS
3-(2,2-dichlorovinyl)-2,2-dimethyl-1-cyclopropane carboxylic acid (Cis-DCCA)	P	55701-05-8	209.07	8.06	3.38	-4.68	7.36E-01	1.28E+02	LC-MS-MS
3-(2,2-dichlorovinyl)-2,2-dimethyl-1-cyclopropane carboxylic acid (Trans-DCCA)	P	55701-05-8	209.07	8.06	3.38	-4.68	7.36E-01	1.28E+02	LC-MS-MS
Chlorpyrifos	OI	2921-88-2	350.59	8.88	4.96	-3.92	3.99E-03	3.57E-01	GC-MS
Chlorpyrifos-oxon	OI	5598-15-2	334.52	9.54	2.89	-6.65	3.21E-03	2.60E+01	GC-MS
3,5,6-trichloro-2-pyridinol (TCPy)	OI	6515-38-4	198.44	9.32	3.01	-6.11	4.87E-01	8.09E+01	LC-MS-MS
Carbaryl	I	63-25-2	201.23	9.23	2.35	-6.87	2.79E-03	4.16E+02	LC-MS-MS
Diazinon	C	333-41-5	304.35	9.15	3.81	-5.34	1.20E-02	6.46E+00	LC-MS-MS
Ethoprophos	OI	13194-48-4	242.33	8.77	3.59	-5.18	5.07E-02	2.24E+01	LC-MS-MS
Desulfinyl Fipronil	I	205650-65-3	389.08	----	----	----			LC-MS-MS
Fipronil	I	120068-37-3	437.15	11.46	4.00	-7.46	2.01E-05	3.74E-01	LC-MS-MS

19 **Table S2**. Recoveries (in %) of surrogates in the gas and particle samples.

	Gas-phase				Particle-phase			
	Median	**Average**	**St.Dev**	**St.E**	**Median**	**Average**	**St.Dev**	**St.E**
% d_{10}-Chlorpyrifos	93	94	25	1.7	112	112	23	1.7
% d_{14}-Trifluralin	64	67	18	1.2	80	83	25	1.8

20

21 **Table S3**. Recoveries of spiked samples to determine the efficiency of this processing method.

	Filter 1	Filter 2	XAD 1	XAD 2
Chlorothalonil	89	56	51	59
Boscalid	59	107	105	117
Azoxystrobin	61	72	63	66
Dacthal	54	59	62	52
Trifluralin	93	92	79	72
Oxyfluorfen	121	131	133	136
Ametryn	62	84	123	136
Atrazine	93	108	128	134
Bromacil	67	69	115	120
CIAT	72	80	127	122
Diuron	89	95	123	123
Metolachlor	70	78	89	92
Prometon	77	69	127	128
Pendimethalin	107	114	113	100
Pronamide	103	102	107	105
Bifenthrin	93	103	100	101
λ-cyhalothrin	91	94	103	81
Cis-permethrin	98	104	101	106
Trans-permethrin	97	110	106	106
Cyfluthrin	79	62	89	66
Cypermethrin	102	84	95	76
Deltamethrin	102	99	112	103
Esfenvalerate	137	138	148	135
Fenpropathrin	79	74	77	92
3-Phenoxybenzoic acid (3-PBA)	54	53	53	57
4-F-3-BA	45	56	60	62
Cis-DCCA	76	87	67	68
Trans-DCCA	78	83	64	69

Chlorpyrifos	86	86	87	85
Chlorpyrifos-oxon	51	43	52	59
TCPy	56	65	65	54
Carbaryl	66	97	100	133
Diazinon	81	79	83	79
Ethoprophos	89	93	101	109
Desulfiny Fipronil	84	113	113	110
Fipronil	72	88	100	102

Table S4. Recoveries (in %) of the most abundant CUPs in vapor and particle matrix spike samples.

	Gas-phase (n = 9)				**Particle-phase (n = 10)**			
	Average	**Median**	**St Dev**	**St E**	**Average**	**Median**	**St Dev**	**St E**
Chlorothalonil	70	64	27	8.9	88	86	13	4.2
Chlorpyrifos	80	83	18	5.9	88	82	14	4.5
Trifluralin	69	62	17	5.8	84	79	14	4.4
Bifenthrin	73	71	9	3.1	91	86	22	7.0
λ-cyhalothrin	103	99	28	9.3	100	99	29	9.1
Cis-permethrin	97	84	37	12	87	80	21	6.5
Trans-permethrin	83	82	12	4.0	95	85	28	8.7
Cyfluthrin	79	69	21	7.1	74	69	16	5.2
Cypermethrin	67	67	24	8.1	83	94	24	7.5
Deltamethrin	100	75	59	20	96	101	31	9.8
Esfenvalerate	63	59	12	3.9	75	72	13	4.1
Fenpropathrin	61	60	6	1.9	68	69	10	3.1
Atrazine	90	90	20	6.6	79	79	15	4.8
Metolachlor	77	76	16	5.5	83	80	20	6.2

Table S5. The geomean levels (ng) of measured CUPs in field blanks. nd: not detected.

	Gas-phase (n = 8)						**Particle-phase (n = 13)**					
	CH	**LH**	**EH**	**PH**	**SH**	**TH**	**CH**	**LH**	**EH**	**PH**	**SH**	**TH**
Chlorothalonil	nd	nd	nd	nd	nd	nd	3.44	3.47	0.15	0.49	0.06	4.06
Boscalid	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Azoxystrobin	nd	nd	nd	nd	nd	nd	nd	0.09	0.01	0.01	nd	0.05
Dacthal	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.73	0.04
Trifluralin	0.06	0.09	0.07	0.02	0.06	0.09	0.46	1.14	0.13	0.16	0.03	0.22
Oxyfluorfen	nd	nd	nd	nd	nd	nd	nd	0.15	nd	nd	nd	nd
Ametryn	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Atrazine	nd	nd	nd	nd	nd	nd	0.72	0.13	0.05	0.06	0.06	0.27
Bromacil	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CIAT	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Diuron	0.44	nd	nd	nd	nd	nd	0.27	0.07	0.03	0.07	0.78	0.27

Metolachlor	nd	nd	nd	nd	nd	1.66	0.17	0.11	0.02	0.06	0.03	0.33
Prometon	nd	nd	nd	0.01	nd	nd	0.17	0.04	nd	0.02	nd	0.02
Pendimethalin	0.07	nd	nd	0.85	nd	nd	0.14	2.15	0.29	0.94	nd	0.16
Bifenthrin	nd	nd	nd	nd	nd	nd	nd	nd	0.17	nd	nd	nd
λ-cyhalothrin	nd	nd	nd	nd	nd	nd	nd	nd	0.11	0.09	nd	nd
Cis-permethrin	nd	nd	nd	nd	nd	nd	nd	2.29	nd	nd	0.44	nd
Trans-permethrin	nd	nd	nd	nd	nd	nd	nd	2.21	nd	0.87	nd	nd
Cyfluthrin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Cypermethrin	nd	nd	nd	nd	nd	nd	nd	1.81	nd	nd	nd	nd
Deltamethrin	nd	nd	nd	nd	0.15	nd	nd	nd	0.44	0.23	3.49	0.31
Esfenvalerate	nd	nd	nd	nd	nd	nd	nd	0.00	nd	nd	nd	nd
Fenpropathrin	nd	nd	nd	nd	nd	nd	nd	0.06	nd	0.09	nd	nd
3-Phenoxybenzoic acid (3-PBA)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4-F-3-BA	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Cis-DCCA	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Trans-DCCA	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chlorpyrifos	nd	nd	nd	nd	nd	nd	nd	0.13	0.03	0.12	0.03	0.24
Chlorpyrifos-oxon	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
TCPy	nd	0.23	nd	nd	nd	1.95	nd	nd	nd	nd	nd	nd
Carbaryl	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Diazinon	nd	nd	nd	nd	nd	nd	nd	0.03	nd	0.04	nd	nd
Ethoprophos	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Desulfinyl Fipronil	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fipronil	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Pronamide	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table S6. Median (Med) and detection frequency (DF) of atmospheric gas-phase concentration (in pg/m^3) in samples collected at the six IADN sites during January 1 – December 31, 2017. The total concentrations of each CUPs categories, fungicides, herbicides, pyrethroids insecticides, and other insecticides, were also provided.

	Chicago			Cleveland			Sturgeon point			Point petre			Sleeping bear dunes			Eagle Harbor		
	Med	**SE**	**DF**	**Med**	**SE**	**DF**	**Med**	**SE**	**DF**	**Med**	**SE**	**DF**	**Med**	**SE**	**DF**	**Med**	**SE**	**DF**
Chlorothalonil	12	5.8	6.1	6.2	1.4	6.7	2.4	0.39	18	4.2	1.5	20	6.0	2.8	18	0.86	0.46	9.1
Azoxystrobin	0.15	0.057	6.1	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
ΣFungicide	**3.0**	**4.1**	**12**	**6.2**	**1.4**	**6.7**	**2.4**	**0.39**	**18**	**4.2**	**1.5**	**20**	**6.0**	**2.8**	**18**	**0.86**	**0.46**	**9.1**
Trifluralin	51	33	55	87	26	70	21	4.9	76	1.1	4.3	60	1.5	0.84	52	2.1	1.5	12
Atrazine	0.51	0.19	9.1	2.2	0.25	13	--	--	--	1.1	0.75	20	1.9	5.5	12	--	--	--
Metolachlor	0.42	0.94	45	1.1	0.24	27	--	--	--	1.4	1.3	20	0.51	1.0	33	0.14	--	3.0
Pendimethalin	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Oxyfluorfen	--	--	--	5.3	0.015	6.7	--	--	--	--	--	--	--	--	--	--	--	--
Diuron	--	--	--	--	--	--	--	--	--	--	--	--	0.54	--	3.0	--	--	--
Prometon	0.18	0.31	12	0.21	--	3.3	--	--	--	--	--	--	--	--	--	--	--	--
ΣHerbicide	**49**	**27**	**67**	**87**	**27**	**70**	**21**	**4.9**	**76**	**0.47**	**3.8**	**70**	**1.7**	**2.0**	**61**	**1.1**	**1.4**	**15**
Bifenthrin	44	--	3.0	50	--	3.3	7.2	--	3.0	--	--	--	9.7	--	3.0	--	--	--
λ-cyhalothrin	0.46	0.08	9.1	69	--	3.3	9.9	--	3.0	--	--	--	0.32	0.33	18	--	--	--
Cis-permethrin	43	--	3.0	53	--	3.3	2.2	--	3.0	--	--	--	9.1	--	3.0	--	--	--
Trans-permethrin	52	--	3.0	64	--	3.3	8.9	--	3.0	--	--	--	13	--	3.0	--	--	--
Cyfluthrin	7.3	--	3.0	11	--	3.3	1.8	--	3.0	--	--	--	2.4	--	3.0	--	--	--
Cypermethrin	2.4	0.80	9.1	37	--	3.3	6.7	--	3.0	--	--	--	7.0	--	3.0	--	--	--
Deltamethrin	58	--	3.0	72	33	10	19	9.2	9.1	0.34	--	10	19	--	3.0	--	--	--
Esfenvalerate	18	--	3.0	30	--	3.3	5.4	--	3.0	--	--	--	0.12	0.030	15	3.7	--	3.0
Fenpropathrin	9.8	--	3.0	15	--	3.3	2.9	--	3.0	--	--	--	2.4	--	3.0	1.9	--	3.0
ΣPyrethroid Insecticides	**1.8**	**0.58**	**12**	**72**	**33**	**10**	**19**	**9.2**	**9.1**	**0.34**	**--**	**10**	**0.40**	**0.28**	**21**	**5.6**	**5.0**	**3.0**
Chlorpyrifos	2.5	7.0	24	4.4	4.0	33	0.90	2.6	45	3.3	2.1	30	2.1	6.6	39	--	2.2	--
TCPy	5.1	2.3	48	5.8	2.2	33	--	--	--	1.3	0.59	80	2.5	2.6	58	1.4	1.0	30
Diazinon	--	--	--	--	--	--	--	--	--	0.22	--	10	--	--	--	--	--	--
ΣOther insecticides	**7.4**	**3.1**	**61**	**5.0**	**4.3**	**50**	**0.90**	**2.6**	**45**	**1.4**	**1.2**	**80**	**4.6**	**5.3**	**70**	**1.4**	**1.0**	**30**
Total CUPs	**30**	**26**	**76**	**90**	**30**	**73**	**21**	**5.4**	**79**	**3.0**	**4.5**	**90**	**5.6**	**6.7**	**79**	**1.7**	**1.3**	**48**

Total Fungicides: sum of chlorothalonil, boscalid, and azoxystrobin; Total Herbicides: sum of dacthal, trifluralin, oxyfluorfen, ametryn, atrazine, bromacil, CIAT, diuron, metolachlor, prometon, pronamide, and pendimethalin; Total Pyrethroid insecticides: sum of bifenthrin, λ-cyhalothrin, cis-permethrin, trans-permethrin,

cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, 3-phenoxybenzoic acid, 4-F-3-BA, cis-DCCA, and trans-DCCA; Total Other insecticides: sum of chlorpyrifos, chlorpyrifos-oxon, TCPy, carbaryl, diazinon, ethoprophos, desulfiny fipronil, and fipronil.

.

Table S6. Median (Med) and detection frequency (DF) of atmospheric particle-phase concentration (in pg/m^3) in samples collected at the six IADN sites during January 1 – December 31, 2017. The total concentrations of each CUPs categories, fungicides, herbicides, pyrethroids insecticides, and other insecticides, were also provided.

	Chicago			**Cleveland**			**Sturgeon point**			**Point petre**			**Sleeping bear dunes**			**Eagle Harbor**		
	Med	**SE**	**DF**	**Med**	**SE**	**DF**	**Med**	**SE**	**DF**	**Med**	**SE**	**DF**	**Med**	**SE**	**DF**	**Med**	**SE**	**DF**
Chlorothalonil	115	32	79	114	34	77	72	33	61	25	95	90	20	43	85	11	12	55
Azoxystrobin	0.24	3.3	42	1.8	1.4	20	0.85	0.23	36	0.24	0.10	50	0.29	0.44	33	0.35	1.2	18
ΣFungicide	**115**	**31**	**82**	**114**	**34**	**77**	**65**	**30**	**70**	**25**	**95**	**90**	**18**	**40**	**91**	**9.8**	**11**	**61**
Trifluralin	8.3	8.9	67	7.7	5.0	37	2.2	3.4	33	1.5	0.67	40	0.26	0.09	48	0.91	1.8	12
Atrazine	24	76	18	1.2	27	63	1.8	52	15	0.46	1.2	70	0.61	1.9	36	0.84	0.5	33
Metolachlor	3.1	44	64	3.4	25	53	6.5	22	21	1.9	2.2	80	0.23	2.3	52	0.11	0.08	45
Pendimethalin	0.84	0.42	9.1	14	3.3	27	0.78	0.19	18	--	--	--	7.8	1.1	82	1.2	0.17	12
Oxyfluorfen	0.97	0.28	58	1.4	2.8	40	0.33	0.3	9.1	0.49	--	10	0.11	0.03	12	0.03	0.02	6.1
Diuron	1.7	0.9	6.1	0.43	2.1	40	--	--	--	0.68	0.23	20	4.6	1.9	33	0.17	0.01	6.1
Prometon	4.63	58	45	2.1	2.3	73	0.33	0.20	33	1.1	1.0	20	0.07	0.03	27	0.02	0.015	15
ΣHerbicide	**15**	**55**	**91**	**21**	**37**	**87**	**3.4**	**24**	**58**	**3.0**	**3.8**	**80**	**11**	**2.7**	**85**	**0.59**	**0.46**	**73**
Bifenthrin	44	31	55	17	7.6	57	7.6	2.0	42	7.4	6.3	20	11	3.0	21	2.2	3.2	15
λ-cyhalothrin	2.3	2.1	82	1.5	1.4	77	1.5	0	64	1.0	1.4	40	0.38	2.6	67	0.56	1.4	15
Cis-permethrin	27	15	55	23	42	40	7.2	2.3	21	1.2	--	10	3.7	2.7	21	2.6	0.73	15
Trans-permethrin	30	19	48	20	36	43	11	2.4	24	--	--	--	4.3	2.9	21	2.3	1.4	15
Cyfluthrin	2.4	2.4	45	2.2	0.83	43	1.1	0.82	42	1.0	0.86	20	1.5	0.83	18	0.82	0.78	12
Cypermethrin	6.1	4.2	85	12	3.1	53	1.0	0.35	67	0.62	0.28	70	0.82	4.8	27	0.24	0.21	24
Deltamethrin	3.2	0.48	36	4.3	1.8	67	3.3	3.2	21	1.1	0.10	40	12	4.0	12	2.9	3.4	24
Esfenvalerate	0.24	0.20	58	0.27	0.05	73	0.08	0.03	42	0.07	0.04	30	0.07	1.1	39	0.01	0.02	18
Fenpropathrin	0.12	0.03	27	0.61	0.28	20	0.22	0.19	24	0.84	--	10	0.23	1.2	33	0.05	--	3.0
ΣPyrethroid Insecticides	**34**	**32**	**94**	**28**	**41**	**93**	**6.2**	**4.5**	**79**	**2.1**	**2.1**	**80**	**4.1**	**6.6**	**76**	**2.9**	**3.5**	**42**
Chlorpyrifos	1.3	0.38	64	0.71	0.75	63	1.6	4.3	15	1.1	0.16	30	0.22	1.3	55	0.10	0.18	9.1
TCPy	0.51	--	3.03	1.1	0.65	6.7	0.53	--	3.0	--	--	--	1.7	1.7	9.1	1.1	--	3.0
Diazinon	0.40	--	3.03	--	--	--	--	--	--	0.12	--	10	--	--	--	--	--	--

ΣOther insecticides	**1.1**	**0.37**	**67**	**0.74**	**0.87**	**63**	**1.6**	**3.6**	**18**	**1.2**	**0.17**	**30**	**0.22**	**1.6**	**55**	**0.37**	**0.21**	**18**
Total CUPs	**209**	**77**	**97**	**151**	**73**	**100**	**56**	**31**	**91**	**30**	**96**	**90**	**53**	**41**	**94**	**5.7**	**10**	**82**

Total Fungicides: sum of chlorothalonil, boscalid, and azoxystrobin; Total Herbicides: sum of dacthal, trifluralin, oxyfluorfen, ametryn, atrazine, bromacil, CIAT, diuron, metolachlor, prometon, pronamide, and pendimethalin; Total Pyrethroid insecticides: sum of bifenthrin, λ-cyhalothrin, cis-permethrin, trans-permethrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, 3-phenoxybenzoic acid, 4-F-3-BA, cis-DCCA, and trans-DCCA; Total Other insecticides: sum of chlorpyrifos, chlorpyrifos-oxon, TCPy, carbaryl, diazinon, ethoprophos, desulfiny fipronil, and fipronil.

Table S8. Percentages (in %) of land use categories around five sampling sites within a 25 km radius. Land cover data was obtained from USDA CropScape-Cropland data layer, 2017. No data were available for Point Petre, since the CropScape database covers only the United States and not Canada.

	Agriculture	**Non-agriculture**	**Developed**
Chicago	0.06	6.9	93
Cleveland	0.24	22	78
Sturgeon Point	21	61	18
Sleeping Bear Dunes	7.6	85	7.2
Eagle Harbor	0.31	96	3.4

Table S9. Results of the Pearson correlation analysis between the logarithmically transformed average concentrations and the land use percentages shown in Table 2. *P*-values and coefficients (Coef.) that are significant at a 5% level are marked in bold.

		Herbicides	**Pyrethroid Insecticides**	**Other Insecticides**	**Agriculture**	**Non-agriculture**	**Developed**
Fungicides	Coef.	**.903**	**.884**	0.47	0.054	**-.938**	0.853
	p-value	***0.036***	***0.047***	*0.425*	*0.932*	***0.019***	*0.066*
Herbicides	Coef.		0.807	0.639	0.116	-0.789	0.703
	p-value		*0.099*	*0.246*	*0.853*	*0.112*	*0.185*
Pyrethroid Insecticides	Coef.			0.75	-0.381	**-.975**	**.980**
	p-value			*0.145*	*0.527*	***0.005***	***0.003***

Other Insecticides	Coef.	-0.459	-0.592	0.643
	p-value	*0.437*	*0.293*	*0.242*
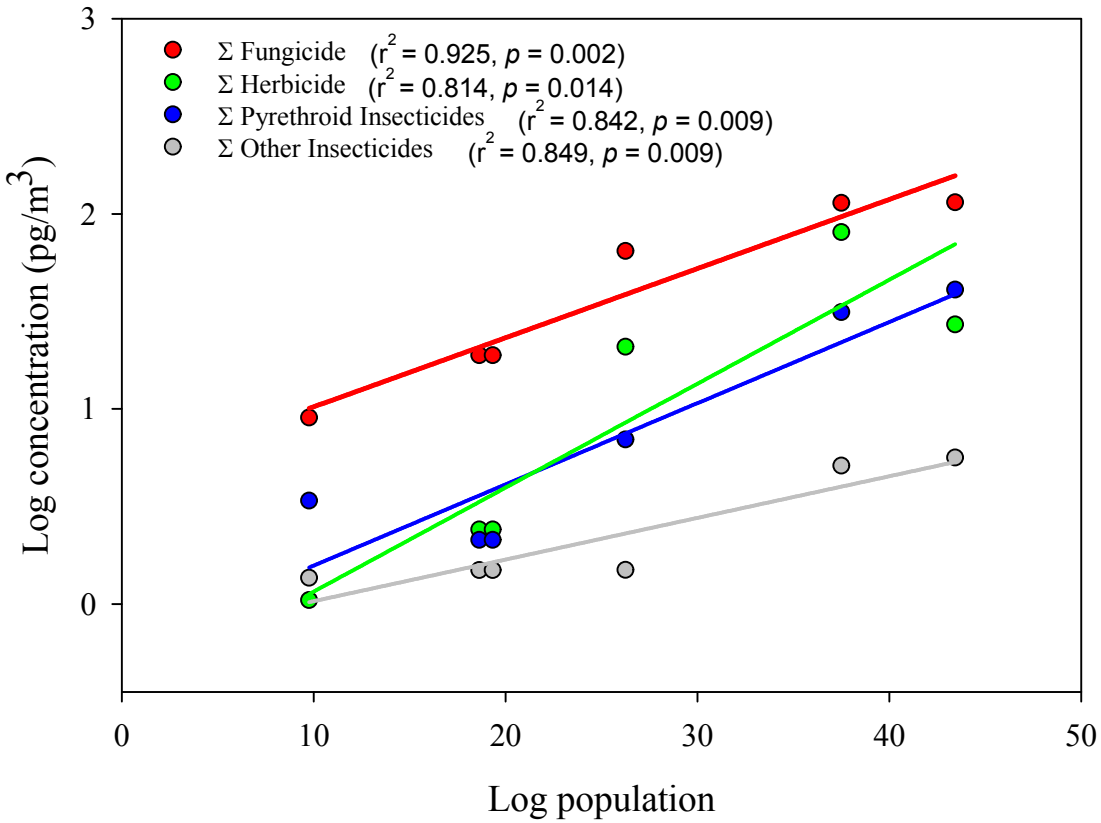
Figure S1. Regression of the logarithmically transformed median concentration vs. local population for fungicides, herbicides, pyrethroids insecticides, and other insecticides.