Supporting Information for

Precipitation-induced transport and phase partitioning of organophosphate esters (OPEs) in urban and rural watersheds

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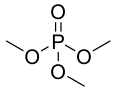
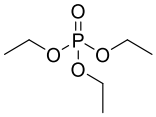
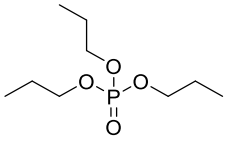
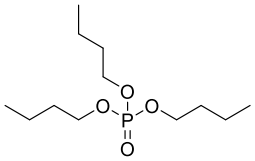
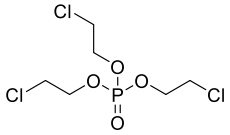
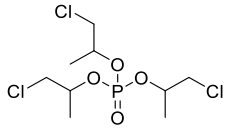
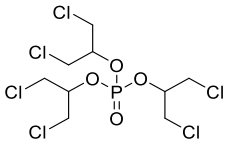
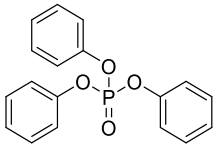
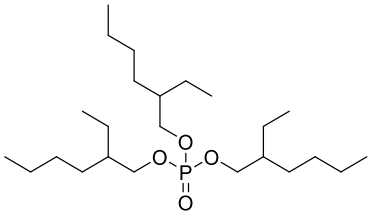
Table S1. List of target OPEs

Acronym	Name	CAS Number	Structure
TMP	Trimethyl phosphate	512-56-1	
TEP	Triethyl phosphate	78-40-0	
TPrP	Tripropyl phosphate	513-08-6	
TNBP	Tri(n-butyl) phosphate	126-73-8	
TCEP	Tris(2-chloroethyl) phosphate	115-96-8	
TCIPP	Tris(1-chloro-2-propyl) phosphate	13674-84-5	
TDCPP	Tris(1,3-dichloro-2-propyl) phosphate	13674-87-8	
TPP	Triphenyl phosphate	115-86-6	
TEHP	Tris(2-ethylhexyl) phosphate	78-42-2	

Text S1. GC-MS/MS program

Quantification was done using an Agilent 7890A gas chromatograph coupled to an Agilent 7000A triple quadrupole mass spectrometer in electron impact ionization mode. Samples were injected using an autosampler (Agilent 7683 series) in pulsed splitless mode. A DB-5 column (Restek: 30 m x 0.25 mm i.d., 0.25 μm film thickness) was used for separation, with helium as the carrier gas at a flow rate of 1.2 mL/min. The inlet temperature was set to 250 ºC and 1.0 μL of each sample was injected. The GC oven temperature program was set to start at 50 ºC, hold for 1 minute, ramp to 135 ºC at 10 ºC/min, ramp to 145 ºC at 2 ºC/min, ramp to 250 ºC at 10 ºC/min, and finally, ramp to 300 ºC at 5 ºC/min and hold for 3 minutes. GC-MS/MS transitions and method detection limits (MDLs) for all target compounds are listed in Table S2. MDLs were calculated from calibration curves and are defined as three times the standard error divided by the slope. Values shown are the average of 6 MDL calculations.

Table S2 Target native and surrogate analytes, compound specific recoveries, GC-MS/MS transitions, method detection limits and blank concentrations. The MDLs are reported as averages, because they were calculated from multiple calibration curves. Blank concentrations in brackets indicate values less than the MDL. These were not used in correction calculations.

Native Compounds	Quantifier (m/z), Collision Energy (eV)	Qualifier (m/z), Collision Energy (eV)	MDL (average [ng/sample] ± 1 S.D.)
TMP	110.1 -> 79, 15	110.1 -> 95, 10	2.05 ± 0.67
TEP	155.1 -> 99, 15	155.1 -> 127.1, 5	2.73 ± 0.48
TPrP	141.1 -> 99, 5	141.1 -> 81.1, 35	2.56 ± 0.71
TNBP	99 -> 81, 25	155.1 -> 99, 5	1.37 ± 0.75
TCEP	249 -> 187.1, 5	249 -> 125.1, 10	2.51 ± 1.88
TCIPP	201 -> 125, 5	201 -> 99, 25	2.34 ± 1.46
TDCPP	381 -> 159.1, 15	381 -> 271, 5	2.58 ± 0.97
TPP	326.1 -> 325.2, 10	326.1 -> 169.2, 35	0.24 ± 0.11
TEHP	99 -> 81, 25	113 -> 95, 20	0.82 ± 0.71

Surrogate Compounds	Quantifier (m/z), Collision Energy (eV)	Surrogate recoveries (average (%) ± 1 S.D.) Dissolved phase	Particle phase
TEP-d_{15}	167 -> 103, 15	76 ± 16	75 ± 25
TNBP-d_{27}	231 -> 103, 15	88 ± 14	79 ± 15
TCEP-d_{12}	261 -> 67.2, 25	98 ± 7	91 ± 22
TPP-d_{15}	341 -> 243, 15	86 ± 16	99 ± 20
Injection Standard			
Mirex	274 -> 238.9, 30		

Native Compounds	SPE		ASE	
	Average [ng/sample] ± 1 S.D.			
	Lab Blanks	Field Blanks	Lab Blanks	Field Blanks
TMP	(0.7) ± 0.6	(0.4) ± 0.5	(0.1) ± 0.1	(0.2) ± 0.2
TEP	(0.5) ± 0.7	(0.2) ± 0.2	(0.4) ± 0.6	(0.1) ± 0.1
TPrP	(0.7) ± 1.5	(0.04) ± 0.05	(0.04) ± 0.1	(0.04) ± 0.03
TNBP	2.9 ± 1.8	3.6 ± 2.8	(0.6) ± 0.6	(0.6) ± 0.1
TCEP	(2.2) ± 0.9	3.9 ± 1.5	(1.5) ± 1.8	(0.2) ± 0.3
TCIPP	3.1 ± 1.7	5.9 ± 1.8	(1.2) ± 1.2	(1.0) ± 0.5
TDCPP	(1.5) ± 1.4	3.0 ± 1.7	(0.8) ± 1.9	(0.2) ± 0.2
TPP	3.8 ± 1.3	5.8 ± 2.7	1.8 ± 1.4	1.1 ± 0.4
TEHP	(0.5) ± 0.6	(0.4) ± 0.8	(0.1) ± 0.1	(0.2) ± 0.2

Table S3 Logarithm of predicted and field-derived organic carbon-water partitioning coefficients (log K_{oc})

	TNBP	TCEP	TCIPP	TDCPP	TPP
COSMOtherm					
Model Organic Matter					
ARHA2	4.9	2.5	3.1	4.0	5.3
ARHA3	4.6	2.1	2.8	3.6	4.7
Leonardite	4.4	2.4	3.1	4.5	5.5
Buffle	4.8	2.9	3.2	3.8	4.9
SRFA1	5.8	3.0	3.6	4.1	5.5
SRFAa	3.4	2.3	2.8	4.4	4.9
SRFAc	4.6	2.6	3.2	4.2	5.1
ppLFERs					
Sorbent					
Organic carbon/water [1]	2.2	1.3	2.3	3.2	4.2
Organic carbon/water[2]	2.3	1.8	2.5	3.4	4.1
OPERA					
	2.4	1.2	2.2	2.5	4.3
EPISuite					
	3.2	1.8	2.5	3.0	3.2
Field-derived values					
MHW	3.3	3.6	3.2	3.6	4.1
MMD	4.9	4.1	5.2	5.6	
MOL	3.7	4.2	5.6	4.5	5.0
RHW	3.7	4.3	4.4	4.7	3.6
RMD	3.6	3.6	3.6	3.9	4.6
ROL	4.7	4.0	3.2	3.7	5.5

Table S4 OPE concentrations in the dissolved phase (ng/L). Blank spaces indicate non-detects. Samples with 'a' and 'b' indicate duplicates. TEHP was not detected in any sample.

	TMP	TEP	TPrP	TNBP	TCEP	TCIPP	TDCPP	TPP
MHW1		18		6	39	90	26	8
MHW2	4	34		27	222	197	58	27
MHW3		25		31	130	150	43	6
MHW4		38		9	99	111	14	
MHW5		66		47	124	212	45	7
MHW6		48		48	157	256	31	12
MHW7		39		40	126	244	46	4
MHW8		30		29	66	121	19	11
MHW9	11	35		33	62	106	14	
MHW10		16		13	28	60	19	4
MHW11		9		15	27	58	19	13
MMD1		52		8	11	60		
MMD2		37		4	71	5		
MMD3		27		7		12	5	
MMD4		45		7	18	5		
MMD5		39		9	14	7		16
MMD6		52		4		2		
MMD7		108		4				
MMD8		61		6	310	33		
MMD9		97		9	95	19		
MMD10		58		12	187	46	3	
MMD11		55		2	34	10		15
MMD12	2	142		2	16	74	2	
MOL1		134		9	130	50	3	
MOL2		93		36	11	27	3	9
MOL3		52		10	39	11		
MOL4	2	23		21	38	25	11	54
MOL5		42		60	28	14	4	49
MOL6		32		22	18	9		11
MOL7	4	15		43	7			9
MOL8		54		13	65	5		5
MOL9		27			39		3	
MOL10		97		14	47	4		17
MOL11		36			8	26	5	12
RHW1a		27			72	23	2	
RHW1b	20	11			6	3	3	
RHW2a		15			57	11		
RHW2b	19	10			4	12	3	
RHW3a		20		11	17	20		
RHW3b	8	7			11	18	2	
RHW4a		15		2	30	34		
RHW4b	6	8		3	32	23		
RHW5a		24			19	13	2	11
RHW5b	12	9			29	12		16
RHW6a		27		21	10	10		
RHW6b	14	14			14	41	5	

	TMP	TEP	TPrP	TNBP	TCEP	TCIPP	TDCPP	TPP
RHW7a		26			6	9		
RHW7b	14	10		4				
RHW8a		16			5	39	3	
RHW8b	4	22			8	26	2	
RHW9		6			3	20	4	
RHW10	2	6		2	10	28	3	3
RHW11		4			6	17		
RHW12		5			7	26	4	
RMD1		12			24	96	18	21
RMD2a		20			20	25	23	12
RMD2b		15			2		23	3
RMD3a		29		3	212	179	88	15
RMD3b		23			128	74	25	13
RMD4a		18			60	86	15	12
RMD4b		25		4	69	42	12	
RMD5a		14		5	62	82	19	15
RMD5b		16		2	19	13	9	1
RMD6a		26			9	2	7	3
RMD6b		24		2	61	51	17	2
RMD7a		19			25	40	16	19
RMD7b		23		6	126	87	22	13
RMD8a		18			18	6	8	11
RMD8b		17		8	81	64	18	27
RMD9a		15			31	46	14	13
RMD9b		37			10	5	14	
RMD10		14			8	21	11	5
RMD11		11		4	10	7	8	4
RMD12		5			13	21	6	3
RMD13		9			8	10	11	7
ROL1		29				2	15	5
ROL2		27		1			4	
ROL3		27					3	
ROL4		27		6		22	13	
ROL5		20			8	64	12	
ROL6		24		2	15	99	32	
ROL7		15		3	40	151	30	
ROL8		18		3	31	165	21	
ROL9		16		1		59	6	
ROL10		14					3	
ROL11		15		3		48	8	3
ROL12		15		1	3	74	12	
ROL13		13		5		57	20	1
ROL14		15					2	1
ROL15		19		1			5	3
ROL16		13				5	7	8

Table S5 OPE concentrations in the particle phase (ng/L), SS concentrations (mg/L), and particulate organic carbon (POC). Blank spaces for OPEs indicate n.d. while those for SS and POC indicate not quantified.

	TMP	TEP	TPrP	TNBP	TCEP	TCIPP	TDCPP	TPP	TEHP	SS	POC (%)
MHW1									1	19	**9**
MHW2					5	13	2	1	11	63	11
MHW3								1	6	65	9
MHW4								1	3	20	
MHW5								2	40	26	
MHW6								1	28	17	
MHW7									9	14	
MHW8									4	14	
MHW9									10	8	
MHW10									1	9	
MHW11								1	1	24	
MMD1		8		7	10	24	7	10	205		
MMD2										7116	5
MMD3										12344	**4**
MMD4										12367	4
MMD5										12520	4
MMD6		7		6	8	19	3	16	46	729	3
MMD7				8	16	21	7	12	52	2878	3
MMD8		2		5	25	5	4	9	19	68	5
MMD9				5	7	44	3	3	27	690	3
MMD10				3	5	5		4	26	23	
MMD11				5					10	28	
MMD12				6	6	3	3		7	10	
MOL1								2	3	9	
MOL2		5				20		11	60	103	13
MOL3		3		3		175	8	31	99	408	**7**
MOL4				3		57	3	18	34	494	5
MOL5				2	17	38	3	20	25	335	5
MOL6				2		113	4	34	54	290	6
MOL7		2		1		24		8	27	139	5
MOL8		4				5		5	29	73	6
MOL9									16	23	
MOL10							2		3	11	
MOL11									2	12	
RHW1a									1	32	
RHW1b						4			1	15	
RHW2a								3	1	19	
RHW2b				1		5			1	16	
RHW3a				1		7		2	4	256	8
RHW3b				3		14	2	2	2	250	8
RHW4a						7			4	189	9
RHW4b				2		9			1	200	8
RHW5a						2		1	2	114	8

	TMP	TEP	TPrP	TNBP	TCEP	TCIPP	TDCPP	TPP	TEHP	SS	POC (%)
RHW5b						6			1	101	9
RHW6a								1	2	120	7
RHW6b						7			1	101	8
RHW7a								1	2	79	7
RHW7b						7			1	79	9
RHW8a									1	57	7
RHW8b				1		4			1	59	9
RHW9								1	1	27	
RHW10										7	
RHW11										3	
RHW12										9	
RMD1										5	
RMD2a										25	
RMD2b								1		40	3
RMD3					4			1	2	232	4
RMD4a						3		12	3	255	5
RMD4b							2		3	177	5
RMD5a					4			2	2	239	3
RMD5b					2		2		4	201	7
RMD6a						2		3	3	350	4
RMD6b							2	2	2	163	4
RMD7a								6	3	247	4
RMD7b									2	112	7
RMD8a								3	2	128	5
RMD8b					4				2	97	5
RMD9a								1	2	90	3
RMD9b							6		3		
RMD10								1		18	
RMD11										2	
RMD12										2	
RMD13										1	
ROL1								18		14	
ROL2								38		63	5
ROL3								2	1	39	
ROL4								8	1	90	6
ROL5				1				3	1	155	6
ROL6				1		6	3	4	2	826	5
ROL7				1		2			1	798	5
ROL8				1		3			1	639	4
ROL9				1	3	3			1	397	4
ROL10				2					1	253	5
ROL11				1	3			5	1	233	3
ROL12				1	2			6		143	4
ROL13										52	6
ROL14								5		25	
ROL15										6	
ROL16											

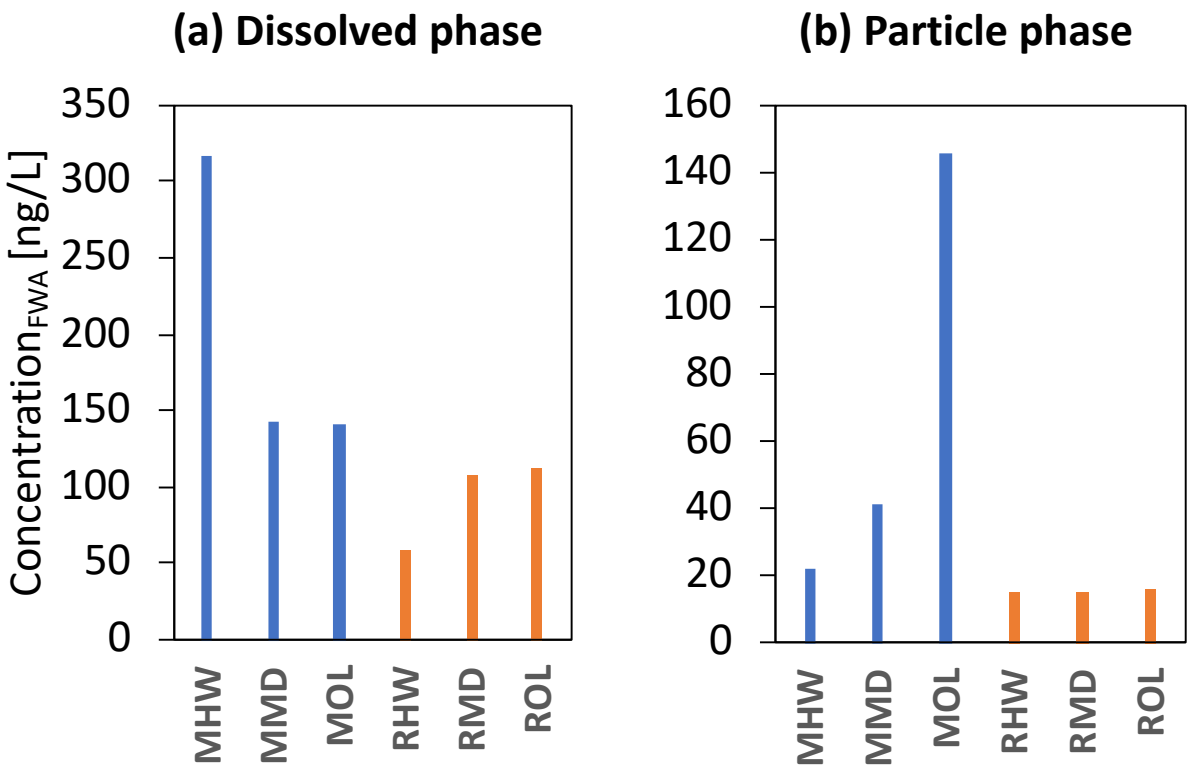


Figure S1. Flow-weighted event average concentrations of (a) dissolved and (b) particle bound OPEs.