## Supporting Information for

## Comparing herbicide behavior and exports in urban, rural and mixed-use watersheds

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a) November 2014 rainfall event



**Figure S1**. Discharge (colored lines) and sampling times ("X") for rainfall (a,c) and snowmelt (b) events at sites in Little Rouge Creek (RHW: headwater, RMD: about halfway downstream, ROL: outlet) and Mimico Creek (MHW: headwater, MMD: about halfway downstream, MOL: outlet). MWP is a reference site in Mimico Creek watershed 5 km downstream from MHW. Reprinted with permission from Parajulee et al. (2017). Copyright 2017 American Chemical Society.



Figure S2. Snowpack depth [cm] measured at Pearson International Airport (M, purple) in Mimico Creek watershed and Buttonville Airport (R, orange) west of the Little Rouge Creek watershed. Mean (solid lines), minimum and maximum (dashed lines) air temperatures measured in Mimico (purple) and Little Rouge Creek (orange) watersheds. Grey arrows denote sampling dates. Reprinted (adapted) with permission from Parajulee et al. (2017). Copyright 2017 American Chemical Society.

Text S1. GC-MS/MS instrument program

Sample extracts were analyzed for atrazine and metolachlor using an Agilent 7890A gas chromatograph coupled to an Agilent 7000A triple quadrupole mass spectrometer in electron impact ionization mode. 2.0 µL of each sample was injected via autosampler (Agilent 7683 series) in pulsed splitless mode. Chromatographic separation was performed with a DB-5 column (J&W Scientific: 30 m x 0.25 mm i.d., 0.25 µm film thickness) using helium as a carrier gas. The inlet temperature was set to 250 °C, and the GC oven temperature program was as follows: hold at 70°C for 1 min, ramp to 150 °C in 1.6 min, ramp to 200 °C in 8.3 min, hold for 3 min, ramp to 300°C in 10 min. The GC-MS interface, ion source, and quadrupole temperatures were set to 250 °C, 230 °C and 150 °C, respectively. MS parameters, in addition to method detection limits (MDLs) are listed in Table S1. MDLs were defined as the average plus three times the standard deviation in field blank samples. Table S1 on the following page contains the average MDLs across the three events.

	Quantifier (m/z),	Qualifier (m/z),	MDI [ng I -1]
	Collision Energy (eV)	Collision Energy (eV)	MDL [lig·L ]
Metolachlor	162.1→133.1, 15	162.1→132.1, 25	2.2
Atrazine	200.1→122.1, 10	200.1→104.0, 20	2.2

Table S1. GC-MS/MS transitions and method detection lim
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Surrogate Standard:

	7	
A frozi	$n \circ d_{-}$	
Auazi	$110-a_5$	
	5	

205→127, 10

*Internal Standard (instrument performance):* Mirex 271.9→236.9, 15 271.9→116.9, 40

#### Text S2. LC-MS/MS instrument details

Sample extracts were analyzed for 2,4-D and mecoprop with an Acquity ultra performance liquid chromatograph (UPLC) coupled to a Xevo TQ-S MS/MS (Waters Corporation) operating with an electrospray interface in negative ionization mode. 4 uL of each sample extract was injected into the instrument. Chromatographic separation was performed on an Acquity CSH Fluoro Phenyl column (CSH-FP, 1.7um, 130Å, 2.1 x 50 mm, Waters, Milford, MA) at 40°C. The mobile phases were 0.1% formic acid in MilliQ water (A) and acentonitrile (B). The LC gradient, MS paramters and transitions are described in Table S2. Because concentrations in field blanks were less than the limit of quantification (i.e.  $0.50 \text{ ng} \cdot \text{mL}^{-1}$  for both herbicides), MDLs were calculated as the LOQ multiplied by the extract volume (1.0 mL), then divided by the average sample volume (0.7 L).

#### Table S2. LC-MS/MS instrument parameters

Time (min)	Flow rate (mL/min)	%A	%B
0	0.4	90	10
0.50	0.4	70	30
4.00	0.4	40	60
4.50	0.4	10	90
5.00	0.4	10	90
5.50	0.4	90	10
5.60	0.4	90	10

a. LC gradient, total run time 7 minutes

#### b. MS parameters

Capillary (kV)	0.5
Source Temperature (°C)	150
Desolvation Temperature (°C)	400
Cone gas flow (L/hr)	150
Desolvation gas flow (L/hr)	800
Collision gas flow (mL/min)	0.15
Nebuliser gas flow (Bar)	5.20

c. Transitions and method detection limits

	Quantifier (m/z), Collision Energy (eV)	Qualifier (m/z), Collision Energy (eV)	MDL $[ng \cdot L^{-1}]$
2,4 <b>-</b> D	219→161, 14	219→125, 24	0.7
Mecoprop	213→141, 16	213→71, 8	0.7
Surrogate Standa 2,4-D-d <sub>3</sub> Mecoprop-d <sub>3</sub>	ards: 222→164, 14 216→144, 16		

Text S3. Quality assurance and quality control

Three and ten field blanks were analysed for the two rainfall events and snowmelt event, respectively. Field blanks were the filtrate resulting from filtration of deionized water samples that had been transported in pre-cleaned bottles to the field, uncapped for one minute, then recapped and transported back to the lab in the same manner as all other samples. A lab blank (deionized water) was extracted during each day of sample extraction. Duplicate extractions were performed for 6, 5 and 8 samples for the November 2014, March 2015 and October 2015 sampling campaigns, respectively. Data were recovery and matrix-corrected using relative responses of the mass-labelled compounds, which were added to every sample. Data were also blank corrected by subtracting the average of all field blanks for a particular sampling event (in  $ng \cdot L^{-1}$ : atrazine:  $\leq 0.70$ , metolachlor:  $\leq 1.44$ , 2,4-D: n.d., mecoprop: n.d.). Average recoveries for each sampling event are in Table S3. Note that the wide spread in recoveries for the acidic herbicides is due to recoveries in lab and field blanks that were up to 30% higher, on average, compared to recoveries in the environmental samples. A native spike recovery test was performed using baseflow water obtained from site MMD. A large aliquot was split into 6 aliquots of 500 mL each. Three aliquots (samples 1, 2, and 3) were spiked with 100 ng of 2,4-D and mecoprop, while three aliquots remained unspiked (samples 4-6) to correct sample recoveries of 1, 2, and 3. A lab blank consisting of 500 mLs of deionized water was also included. Recoveries of mecoprop and 2,4-D in samples 1 to 3 were: 101%, 105%, and 102%; and 97%, 100%, and 97%, respectively.

**Table S3**. Deuterated herbicide recoveries (average  $[\%] \pm 1$  S.D.) for water samples and the three passive air sampler deployments (Air: D1=May to Nov. 2014; D2=Nov. to Jul. 2015; D3=Jul. to Dec. 2015). n/a = not applicable

	Nov. 2014	Mar. 2015	Oct. 2015	Air D1	Air D2	Air D3
ATR-d <sub>5</sub>	$116 \pm 11$	$104 \pm 11$	$99 \pm 23$	$167 \pm 21$	$144 \pm 19$	$143 \pm 18$
<b>2,4-D-</b> $d_3$	$96 \pm 25$	$84 \pm 20$	$76 \pm 16$	n/a	n/a	n/a
MCPP-d <sub>3</sub>	$97 \pm 26$	$85 \pm 12$	$80 \pm 14$	n/a	n/a	n/a

Sample	Atrazine	Metolachlor	Mecoprop	2,4-D
		November 20	14	
RMD3a	21	13	8.1	17
RMD3b	16	8.8	7.6	18
RMD6a	23	23	7.3	9.0
RMD6b	19	17	7.5	6.6
ROL4a	20	10	8.0	12
ROL4b	18	10	13	14
ROL5a	17	11	27	32
ROL5b	26	13	27	38
ROL6a	32	44	4.5	2.1
ROL6b	29	44	5.8	3.6
MHW5a	6.9	2.7	3.0	1.0
MHW5b	5.3	3.4	1.4	n.d.
		March 2015		
RHW6a	33	69	1.4	2.5
RHW6b	38	68	1.4	1.8
RHW8a	8.8	19	6.4	0.59
RHW8b	16	28	6.4	0.82
MHW1a	17	4.0	2.8	5.2
MHW1b	26	4.1	n.d.	5.3
MMD1a	21	6.8	3.8	n.d.
MMD1b	29	6.1	3.7	n.d.
MOL1a	21	6.5	n.d.	n.d.
MOL1b	35	14	n.d.	n.d.
		October 201.	5	
RHW7a	12	52	17	6.6
RHW7b	11	50	18	6.4
RHW8a	17	21	13	5.5
RHW8b	20	32	11	2.8
ROL7a	32	59	26	21
ROL7b	33	55	24	18
ROL8a	30	42	21	10
ROL8b	27	39	24	11
MMD5a	6.0	5.7	9.5	7.4
MMD5b	7.1	6.8	11	8.0
MMD6a	7.5	9.0	9.6	5.5
MMD6b	6.7	13	11	7.9
MMD7a	7.1	17	11	7.6
MMD7b	9.3	12	9.6	6.1
MMD8a	11	15	11	7.2
MMD8b	14	12	12	6.0

**Table S4**. Duplicate sample concentrations  $[ng \cdot L^{-1}]$ . Air sampler duplicate agreements can be seen in Figure S3.

**Table S5**. Stream water concentrations of each herbicide  $[ng \cdot L^{-1}]$ . "n.d.": non-detect; "n.s": no sample. Note that RHW1 for the November 2014 rainfall event is a composite of samples 1 and 2, and MHW3-8 for the October 2015 rainfall event is a composite of samples 3 to 8.

1v0vember 2014				
Sample	Atrazine	Metolachlor	Mecoprop	2,4-D
MHW1	13	5.9	2.6	3.4
MHW2	13	6.6	3.4	3.3
MHW3	16	7.6	4.6	3.8
MHW4	10	6.4	n.d.	n.d.
MHW5	6.1	3.0	2.2	0.76
MHW6	5.3	3.4	8.9	11
MHW7	8.4	5.4	6.3	7.6
MHW8	8.3	6.0	22	33
MHW9	8.3	4.2	7.6	14
MMD1	18	7.6	5.6	1.8
MMD2	19	7.8	4.5	0.92
MMD3	20	9.2	6.5	2.0
MMD4	16	8.6	n.d.	n.d.
MMD5	n.s.	n.s.	n.s.	n.s.
MMD6	16	9.6	n.d.	n.d.
MMD7	12	11	n.d.	n.d.
MMD8	12	11	4.0	n.d.
MMD9	13	10	12	1.1
MOL1	20	12	8.2	4.0
MOL2	21	8.9	8.8	2.7
MOL3	21	7.9	7.7	2.8
MOL4	16	11	12	1.9
MOL5	17	6.7	n.d.	n.d.
MOL6	14	10	n.d.	n.d.
MOL7	12	9.7	0.14	n.d.
MOL8	13	7.4	2.1	n.d.
MOL9	20	11	0.38	n.d.
RHW1+2	13	18	17	1.2
RHW3	7.8	14	13	0.16
RHW4	13	19	21	0.97
RHW5	34	79	4.6	2.4
RHW6	29	55	1.5	1.2
RHW7	26	64	3.5	1.2
RHW8	19	43	9.6	1.3
RHW9	11	19	16	0.59
RHW10	8.5	14	20	n.d.
RMD1	13	6.4	9.4	22
RMD2	13	6.4	7.3	13
RMD3	18	11	7.9	18
RMD4	15	12	8.5	17
RMD5	14	13	6.4	11
RMD6	21	20	7.4	7.8
RMD7	18	26	5.7	7.8

November 2014

Sample	Atrazine	Metolachlor	Mecoprop	2,4-D
RMD8	26	37	3.8	4.2
RMD9	24	90	5.3	8.1
RMD10	24	23	9.0	11
ROL1	23	35	4.1	3.4
ROL2	19	16	3.4	3.3
ROL3	16	9.3	4.1	3.4
ROL4	19	10	10	13
ROL5	21	12	27	35
ROL6	31	44	5.2	2.9
ROL7	25	28	11	18
ROL8	22	33	6.6	9.1
ROL9	n.d.	n.d.	5.5	7.3
ROL10	23	27	7.6	10

## March 2015

Sample	Atrazine	Metolachlor	Mecoprop	2,4-D
MHW1	21	4.1	1.7	5.3
MHW2	11	2.5	11	5.5
MHW3	13	0.36	19	12
MHW4	12	1.4	17	2.3
MHW5	12	0.44	21	5.4
MHW6	n.s.	n.s.	n.s.	n.s.
MHW7	n.s.	n.s.	n.s.	n.s.
MHW8	20	1.8	5.4	3.1
MHW9	20	2.6	4.1	2.9
MMD1	25	6.5	3.8	n.d.
MMD2	19	10	9.0	2.3
MMD3	15	4.5	14	5.3
MMD4	13	3.6	4.6	n.d.
MMD5	13	1.1	19	n.d.
MMD6	n.s.	n.s.	n.s.	n.s.
MMD7	n.s.	n.s.	n.s.	n.s.
MMD8	18	9.9	33	25
MMD9	19	11	40	11
MOL1	28	10	n.d.	n.d.
MOL2	17	6.3	n.d.	n.d.
MOL3	15	4.3	15	4.7
MOL4	16	3.0	7.6	0.93
MOL5	20	5.5	14	0.97
MOL6	n.s.	n.s.	n.s.	n.s.
MOL7	n.s.	n.s.	n.s.	n.s.
MOL8	36	11	28	11
MOL9	31	8.0	27	10
RHW1	3.5	1.4	n.d.	n.d.
RHW2	3.0	2.4	n.d.	n.d.
RHW3	14	36	n.d.	2.7
RHW4	15	23	0.55	2.1
RHW5	16	27	1.6	0.66

Sample	Atrazine	Metolachlor	Mecoprop	2,4-D
RHW6	35	68	1.4	2.1
RHW7	14	31	4.0	1.0
RHW8	12	23	6.4	0.70
RHW9	6.8	7.7	77	n.d.
RMD1	6.0	n.d.	4.5	5.4
RMD2	3.4	n.d.	2.3	3.9
RMD3	13	17	3.9	11
RMD4	13	15	2.7	4.7
RMD5	16	40	3.8	7.4
RMD6	26	58	3.8	2.9
RMD7	24	50	4.0	11
RMD8	14	19	3.3	5.7
RMD9	14	12	4.7	6.2
ROL1	6.5	0.84	4.3	2.0
ROL2	23	6.6	5.0	3.6
ROL3	11	23	12	9.1
ROL4	16	25	9.2	7.0
ROL5	16	27	4.2	1.8
ROL6	22	55	6.0	4.5
ROL7	23	38	3.7	2.9
ROL8	12	11	3.3	6.2
ROL9	16	17	4.8	5.1

# October 2015

Sample	Atrazine	Metolachlor	Mecoprop	2,4-D
MHW1	22	3.7	3.7	7.4
MHW2	18	6.9	3.2	9.0
MHW3-8	20	0.48	3.7	7.9
MHW9	11	3.2	100	93
MHW10	14	4.5	10	14
MMD1	21	6.2	21	20
MMD2	23	9.5	34	25
MMD3	13	17	17	15
MMD4	7.8	7.9	8.1	7.8
MMD5	6.5	6.2	10	7.7
MMD6	7.1	11	10	6.7
MMD7	8.2	14	10	6.8
MMD8	12	13	12	6.6
MMD9	14	8.6	22	15
MMD10	19	11	24	16
MOL1	26	12	27	27
MOL2	25	28	18	18
MOL3	23	13	12	19
MOL4	10	14	35	25
MOL5	7.8	14	16	13
MOL6	6.1	14	13	9.0
MOL7	8.7	10	14	9.6
MOL8	7.6	15	13	10

Sample	Atrazine	Metolachlor	Mecoprop	2,4-D
MOL9	11	13	18	10
MOL10	14	11	22	16
RHW1	15	8.9	20	1.0
RHW2	14	5.1	23	1.3
RHW3	15	8.6	22	1.9
RHW4	18	11	15	3.1
RHW5	28	14	17	2.1
RHW6	19	11	25	2.8
RHW7	12	51	17	6.5
RHW8	18	26	12	4.2
RHW9	27	36	24	1.4
RHW10	20	21	29	0.75
RHW11	9.5	32	35	0.52
RMD1	28	12	8.9	14
RMD2	19	9.9	8.8	13
RMD3	22	9.7	6.9	13
RMD4	18	14	8.4	12
RMD5	21	10	7.1	11
RMD6	20	17	5.6	8.7
RMD7	24	14	4.9	9.0
RMD8	26	12	12	21
RMD9	31	43	19	29
RMD10	34	21	18	21
RMD11	31	4.9	17	19
ROL1	24	9.7	7.7	14
ROL2	23	7.2	7.2	12
ROL3	22	9.7	6.7	13
ROL4	23	10	6.7	11
ROL5	15	5.7	9.0	19
ROL6	14	4.5	12	18
ROL7	33	57	25	20
ROL8	28	41	23	11
ROL9	27	9.5	22	31
ROL10	24	12	21	23
ROL11	20	16	18	17



**Figure S3**. Gas-phase air concentrations  $[pg \cdot sampler^{-1} \cdot d^{-1}]$  of atrazine and metolachlor measured by passive air samplers in Mimico (purple bars) and Rouge (orange bars) in three consecutive deployments: DEPL.1 (May 8 to Nov 7 2014), DEPL. 2 (Nov 7 2014 to Jul 9 2015), and DEPL. 3 (Jul 9 to Dec 11 2015). Error bars represent range of duplicate samples. Most measurements for the third deployment were below method detection limits.

### REFERENCES

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