Electronic Supplementary Material (ESI) for Environmental Science: Advances.

Supporting information

Pesticides and transformation products in surface waters of western Montérégie, Canada: Occurrence, spatial distribution and ecotoxicological risks

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Section S1 Classification of pesticides

Table S1 Details on pesticide types, treatment methods, and modes of action.

Compounds	Types	Treatment	Modes of action
2,4-dichlorophenoxyacetic acid (2,4-D)	Herbicide	Foliage	Growth regulator, auxin mimic
4-chloro-2-methylphenoxyacetic acid (MCPA)	Herbicide	Foliage, soil	Growth regulator, auxin mimic
Acetamiprid	Insecticide	Foliage, seed, soil	Systemic, nicotinic agonist
Alachlor	Herbicide	Soil, foliage	Growth regulator, biosynthetic inhibition
Atrazine	Herbicide	Soil, foliage	Systemic, photosystem inhibition
Azoxystrobin	Fungicide	Foliage, seed	Systemic, respiratory inhibition
Bentazon	Herbicide	Foliage	Contact, photosystem inhibition
Bromoxynil	Herbicide	Foliage	Both contact and systemic, photosystem inhibition
Carbaryl	Insecticide	Foliage	Contact, acetylcholinesterase inhibition
Carbendazim	Fungicide	Foliage, seed	Systemic, cell division inhibition
Chlorantraniliprole	Insecticide	Foliage, soil	Systemic, ryanodine receptor activation
Chlorothalonil	Fungicide	Foliage	Non-systemic, metabolic inhibition
Chlorpyrifos	Insecticide	Foliage	Contact, acetylcholinesterase inhibition
Clothianidin	Insecticide	Seed, soil, foliage	Systemic, nicotinic agonist
Cyanazine	Herbicide	Soil, foliage	Systemic, photosystem inhibition
Dicamba	Herbicide	Foliage	Systemic, auxin mimic
Dimethenamid	Herbicide	Soil	Contact, cell division inhibition
Dinotefuran	Insecticide	Foliage, soil	Systemic, nicotinic agonist
Fipronil	Insecticide	Soil, seed	Both contact and ingestion, GABAA-gated chloride channel blocker
Flonicamid	Insecticide	Foliage	Both contact and ingestion, feeding behaviour inhibition
Fluazinam	Fungicide	Foliage, soil	Protectant, energy production disruption
Flumetsulam	Herbicide	Soil	Systemic, acetolactate synthase inhibition
Fluxapyroxad	Fungicide	Foliage, seed	Systemic, succinate dehydrogenase inhibition
Fomesafen	Herbicide	Soil	Contact, protoporphyrinogen oxidase inhibition
Glufosinate	Herbicide	Foliage	Contact, glutamine synthetase inhibition
Glyphosate	Herbicide	Foliage, soil	Systemic, EPSP synthase inhibition
Hexazinone	Herbicide	Soil, foliage	Systemic, photosynthesis inhibition
Imazethapyr	Herbicide	Foliage, soil, seed	Systemic, acetolactate synthase inhibition
Imidacloprid	Insecticide	Soil, seed	Systemic, neurotransmission blocker
Linuron	Herbicide	Foliage, soil	Systemic, photosystem II inhibition
Mecoprop	Herbicide	Foliage, soil	Systemic, auxin mimic
Mesotrione	Herbicide	Foliage, seed	Systemic, 4-hydroxyphenylpyruvate dioxygenase (HPPD) inhibition
Metconazole	Fungicide	Foliage, seed	Systemic, ergosterol biosynthesis inhibition
Metribuzin	Herbicide	Foliage, soil	Systemic, photosystem II inhibition
Nicosulfuron	Herbicide	Foliage, soil	Systemic, acetolactate synthase inhibition
Nitenpyram	Insecticide	Foliage, seed	Systemic, neurotransmission blocker
Pendimethalin	Herbicide	Soil	Systemic, cell division inhibition
Prometryn	Herbicide	Foliage, soil	Systemic, photosystem II inhibition
Propiconazole	Fungicide	Foliage, seed	Systemic, 14-α-sterol demethylase inhibition
Pyrimethanil	Fungicide	Foliage, fruit	Systemic, biosynthesis of methionine inhibition
Simazine	Herbicide	Foliage, soil	Systemic, photosystem II inhibition

(S)-Metolachlor	Herbicide	Soil, seed	Systemic, synthesis of long chain fatty acids inhibition
Tebuconazole	Fungicide	Foliage, seed	Systemic, demethylation inhibition
Thiacloprid	Insecticide	Foliage, soil, seed	Systemic, nicotinic acetylcholine receptor agonist
Thiamethoxam	Insecticide	Foliage, seed	Systemic, nicotinic acetylcholine receptor agonist
Topramezone	Herbicide	Foliage, soil	Systemic, HPPD (4-hydroxyphenylpyruvate dioxygenase) inhibition
Triclopyr	Herbicide	Foliage, stem	Systemic, auxin mimic
Triclopyr 2-butoxyethylester	Herbicide	Foliage, stem	Systemic, auxin mimic

Section S2 Chemical standards and other materials

Table S2 Details on chemical standards and other materials used in the present study.

Chemicals/materials	Purity	Supplier
2,4-dichlorophenoxyacetic acid	≥ 98%	
3,5,6-trichloro-2-pyridinol	≥ 98%	
4-chloro-2-methylphenoxyacetic acid	≥ 99.8%	
Acetamiprid	≥ 99.9%	
Alachlor	≥98%	
Aminomethylphosphonic acid	≥ 99%	
Atrazine	≥ 98.8%	
Atrazine-2-hydroxy	≥ 99%	
Azoxystrobin	≥ 98%	
Bentazon	≥ 99.9%	
Bromoxynil	≥ 98%	
Chlorantraniliprole	≥ 98%	
Carbaryl	≥ 98%	
Carbendazim	≥ 98%	
Chlorothalonil	≥ 98%	
Chlorpyrifos	≥ 98%	
Clothianidin	≥ 98%	
Cyanazine	≥ 99.8%	
Desethylatrazine	≥ 97%	
Desisopropylatrazine	≥ 96.3%	
Dicamba	≥ 98%	
Dimethenamid	≥98%	
Dinotefuran	≥ 98%	
Desnitro-imidacloprid	≥ 99%	
Fipronil	≥ 95%	
Flonicamid	≥ 95%	
Fluazinam	≥ 98%	
Fluxapyroxad	≥ 99.9%	Sigma Aldrich (St. Louis, MO, USA)
Glufosinate	≥ 98%	
Glyphosate	≥ 99.7%	
Hexazinone	≥ 99%	
Imidacloprid	≥ 99.9%	
Linuron	≥ 99.7%	
Mecoprop	≥ 98%	
Mesotrione	≥ 98%	
Metconazole	≥ 98.9%	
(S)-metolachlor	≥ 98.4%	
Metolachlor ethanesulfonic acid	≥ 98%	
Metolachlor oxanilic acid	≥ 98%	
Metribuzin	≥ 99.7%	
Nitenpyram	≥ 98%	
Pendimethalin	≥ 98%	
Prometryn	≥ 99.4%	
Propiconazole	≥ 99%	
Pyrimethanil	≥ 99.2%	
Simazine	≥ 99.9%	
Triclopyr	≥ 98%	
Triclopyr 2-butoxyethylester	≥ 95%	
Tebuconazole	≥ 98%	
Thiacloprid	≥ 98%	
Thiamethoxam	≥ 98%	
Topramezone	≥ 98%	
Acetamiprid-d_3	≥ 98%	
Aminomethylphosphonic acid-$^{13}C^{15}Nd_2$	≥ 98%	
Clothianidin-d_3	≥ 97%	

Dicamba-d_3 Glyphosate-$^{13}C_2{}^{15}N$ Imidacloprid-d_4 Nicosulfuron-d_6 Tebuconazole-d_9 Thiamethoxam-d_3	≥ 98% ≥ 98% ≥ 99% ≥ 98% ≥ 98% ≥ 98%	
Flumetsulam Fomesafen Imazethapyr Nicosulfuron 2,4-dichlorophenoxyacetic acid-$^{13}C_6$ Atrazine-2-hydroxy-d_5 Chlorantraniliprole-d_6 Dimethenamid-d_3 Metolachlor-d_6 Carbanyl-d_7 Metolachlor ethanesulfonic acid-d_6 Propiconazole-d_7 Pyrimethanil-d_5	≥ 98% ≥ 98% ≥ 98% ≥ 98% ≥ 98% ≥ 98% ≥ 98% ≥ 98% ≥ 98% ≥ 98% ≥ 98% ≥ 98% ≥ 98%	Toronto Research Chemicals Inc. (North York, ON, Canada)
Atrazine-$^{13}C_3$ Deethylatrazine-$^{13}C_3$	≥ 99% ≥ 99%	Cambridge Isotope Laboratories, Inc. (Andover, MA, U.S.A.)
Fipronil-$^{13}C_2{}^{15}N_2$ Linuron-d_6	≥ 98% ≥ 98%	Santa Cruz Biotechnology (Dallas, TX, USA)
LC-MS grade HPLC-water Methanol (MeOH) Acetonitrile (ACN)	- - -	Fisher Scientific (Whitby, ON, Canada)
Ammonium acetate Ammonium fluoride Formic acid Hydrochloric acid Sodium citrate dibasic sesquihydrate Sodium tetraborate decahydrate	≥ 97% ≥ 98% ≥ 95% ≥ 37% ≥ 99% ≥ 99.5%	Sigma Aldrich (St. Louis, MO, U.S.A.)
9-fluorenylmethyl chloroformate	≥ 98%	Fisher Scientific
Nitrogen (N_2)	99.998%	MEGS Inc. (St-Laurent, Quebec, Canada)
Strata^{tm}-X Polymeric Reversed Phase SPE cartridges (200 mg/6 ml)	-	Phenomenex (Torrance, CA, U.S.A.)
Regenerated cellulose filters (0.45μm, 47 mm diameter) Regenerated cellulose syringe filters (0.2 μm, 15 mm diameter)		Sartorius Stedim Biotech (Göttingen, Germany)
Regenerated cellulose syringe filters (0.2 μm, 4 mm diameter)		Thermo Fisher Scientific (Rockwood, TN, USA)

Table S3 Details on surrogate isotope-labelled internal standards (ILIS).

Internal standards	Abbreviation	Theoretical *m/z*
2,4-D-$^{13}C_6$	24D-$^{13}C_6$	224.97985
Acetamiprid-d_3	Aceta-d_3	226.09333
Aminomethylphosphonic acid-$^{13}C^{15}Nd_2$	AMPA-$^{13}C^{15}Nd_2$	338.09574
Atrazine-$^{13}C_3$	ATZ-$^{13}C_3$	219.10948
Atrazine-2-hydroxy-d_5	ATZ-OH-d_5	203.16632
Chlorantraniliprole-d_6	CAP-d_6	488.01572
Carbanyl-d_7	Carba-d_7	209.13019
Clothianidin-d_3	Clothia-d_3	251.01917
Deethylatrazine-$^{13}C_3$	DEA-$^{13}C_3$	191.07818
Dicamba-d_3	Dicam-d_3	221.97986
Dimethenamid-d_3	Dime-d_3	279.10078
Fipronil-$^{13}C_2{}^{15}N_2$	Fipro-$^{13}C_2{}^{15}N_2$	438.92892
Glyphosate-$^{13}C_2{}^{15}N$	Gly-$^{13}C_2{}^{15}N$	395.09147
Imidacloprid-d_4	Imida-d_4	260.08468
Linuron-d_6	Linu-d_6	255.05687
Metolachlor-d_6	Meto-d_6	290.17884
Metolachlor ESA-d_6	Meto ESA-d_6	334.15898
Nicosulfuron-d_6	Nico-d_6	417.14579
Propiconazole-d_7	Propico-d_7	349.12099
Pyrimethanil-d_5	Pyrime-d_5	205.14960
Tebuconazole-d_9	Tebuco-d_9	317.20890
Thiamethoxam-d_3	Thiame-d_3	295.04539

Table S4 Details on target pesticide names, abbreviation, analyzed ion formula, theoretical *m/z*, and associated ILIS.

Compounds	Abbreviation	Ion formula	Theoretical *m/z*	Associated ILIS
2,4-Dichlorophenoxyacetic acid	2,4-D	$[C8H5Cl2O3]^-$	218.96103	2,4-D-$^{13}C_6$
3,5,6-Trichloro-2-pyridinol	TCP	$[C5HCl3NO]^-$	195.91182	2,4-D-$^{13}C_6$
4-chloro-2-methylphenoxyacetic acid	MCPA	$[C9H8ClO3]^-$	199.01565	2,4-D-$^{13}C_6$
Acetamiprid	Aceta	$[C10H12ClN4]^+$	223.07450	Acetamiprid-d_3
Alachlor	Alacl	$[C14H21ClNO2]^+$	270.12553	Metolachlor-d_6
Aminomethylphosphonic acid	AMPA	$[CH7NO3P\text{-}FMOC]^+$	334.08389	AMPA-$^{13}C^{15}Nd_2$
Atrazine	ATZ	$[C8H15ClN5]^+$	216.10105	Atrazine-$^{13}C_3$
Atrazine-2-hydroxy	ATZ-OH	$[C8H16N5O]^+$	198.13494	Atrazine-2-hydroxy-d_5
Azoxystrobin	Azoxy	$[C22H18N3O5]^+$	404.12409	Pyrimethanyl-d_5
Bentazon	Benta	$[C10H11N2O3S]^-$	239.04849	2,4-D-$^{13}C_6$
Bromoxynil	Bromo	$[C7H2Br2NO]^-$	275.84772	2,4-D-$^{13}C_6$
Chlorantraniliprole	CAP	$[C18H15BrCl2N5O2]^+$	481.97807	Chlorantraniliprole-d_6
Carbaryl	Carba	$[C12H12NO2]^+$	202.08625	Carbanyl-d_7
Carbendazim	Carben	$[C9H10N3O2]^+$	192.07675	Acetamiprid-d_3
Chlorothalonil	Chloro	$[C8Cl3N2O]^-$	244.90707	Fipronil-$^{13}C_2{}^{15}N_2$
Chlorpyrifos	Chlorpy	$[C9H12Cl3NO3PS]^+$	349.93356	Propiconazole-d_7
Clothianidin	Clothia	$[C6H7ClN5O2S]^-$	248.00035	Clothianidin-d_3
Cyanazine	Cyana	$[C9H14ClN6]^+$	241.09630	Atrazine-$^{13}C_3$
Desethylatrazine	DEA	$[C6H11ClN5]^+$	188.06975	Desethylatrazine-$^{13}C_3$
Desisopropylatrazine	DIA	$[C5H9ClN5]^+$	174.05410	Desethylatrazine-$^{13}C_3$
Dicamba	Dicam	$[C8H5Cl2O3]^-$	218.96103	Dicamba-D3
Dimethenamid	Dimet	$[C12H19ClNO2S]^+$	276.08195	Dimethenamid-d_3
Dinotefuran	Dinote	$[C7H13N4O3]^-$	201.09821	Clothianidin-d_3
Desnitro-imidacloprid	DN-Imi	$[C9H12ClN4]^+$	211.07450	Thiamethoxam-d_3
Fipronil	Fipro	$[C12H3Cl2F6N4OS]^-$	434.93033	Fipronil-$^{13}C_2{}^{15}N_2$
Flonicamid	Flonica	$[C9H5F3N3O]^-$	228.03792	2,4-D-$^{13}C_6$
Fluazinam	Fluaz	$[C13H3Cl2F6N4O4]^-$	462.94300	Fipronil-$^{13}C_2{}^{15}N_2$
Flumetsulam	Flume	$[C12H10F2N5O2S]^+$	326.05178	Imidacloprid-d_4
Fluxapyroxad	Fluxa	$[C18H13F5N3O]^+$	382.09733	Pyrimethanyl-d_5

Fomesafen	Fomesa	$[C15H9ClF3N2O6S]^-$	436.98165	Fipronil-$^{13}C_2{}^{15}N_2$
Glufosinate	Gly	$[C5H13NO4P\text{-}FMOC]^+$	404.12575	Glyphosate-$^{13}C_2{}^{15}N$
Glyphosate	Glu	$[C3H9PNO5\text{-}FMOC]^+$	392.08936	Glyphosate-$^{13}C_2{}^{15}N$
Hexazinone	HXZ	$[C12H21N4O2]^+$	253.16590	Atrazine-$^{13}C_3$
Imazethapyr	Imaze	$[C15H20N3O3]^+$	290.14992	Acetamiprid-d_3
Imidacloprid	Imida	$[C9H11ClN5O2]^+$	256.05958	Imidacloprid-d_4
Linuron	Linu	$[C9H11Cl2N2O2]^+$	249.01921	Linuron-d_6
Mecoprop	Mecop	$[\ C10H10ClO3]^-$	213.03130	2,4-D-$^{13}C_6$
Mesotrione	Meso	$[C14H14NO7S]^+$	340.04855	Thiamethoxam-d_3
Metconazole	Metco	$[C17H23ClN3O]^+$	320.15242	Propiconazole-d_7
Metolachlor ethanesulfonic acid	Meto-ESA	$[C15H22NO5S]^-$	328.12132	Metolachlor ESA-d_6
Metolachlor oxanilic acid	Meto-OA	$[C15H20NO4]^-$	278.13868	Metolachlor ESA-d_6
Metribuzin	Metri	$[C8H14N4OS]^+$	215.09611	Atrazine-$^{13}C_3$
Nicosulfuron	Nico	$[C15H19N6O6S]^+$	411.10813	Nicosulfuron-d_6
Nitenpyram	Niten	$[C11H16ClN4O2]^+$	271.09563	Thiamethoxam-d_3
Pendimethalin	Pendi	$[C13H20N3O4]^+$	282.14483	Propiconazole-d_7
Prometryn	Prome	$[C10H20N5S]^+$	242.14339	Atrazine-$^{13}C_3$
Propiconazole	Propico	$[C15H18Cl2N3O2]^+$	342.07706	Propiconazole-d_7
Pyrimethanil	Pyrime	$[C12H14N3]^+$	200.11822	Pyrimethanyl-d_5
Simazine	SMZ	$[C7H13ClN5]^+$	202.08540	Atrazine-$^{13}C_3$
(S)-Metolachlor	Meto	$[C15H23ClNO2]^+$	284.14118	Metolachlor-d_6
Tebuconazole	Tebuco	$[C16H23ClN3O]^+$	308.15242	Tebuconazole-d_9
Thiacloprid	Thiacl	$[C10H10ClN4S]^+$	253.03092	Acetamiprid-d_3
Thiamethoxam	Thiam	$[C8H11ClN5O3S]^+$	292.02656	Thiamethoxam-d_3
Topramezone	Topra	$[C16H18N3O5S]^+$	364.09617	Thiamethoxam-d_3
Triclopyr	TA	$[C7H3Cl3NO3]^-$	253.91730	2,4-D-$^{13}C_6$
Triclopyr 2-butoxyethylester	TE	$[C13H17Cl3NO4]^+$	356.02177	Propiconazole-d_7

Section S3 Study area and sampling coordinates

Table S5 The surface area, cropland occupation, and crop proportion of each watershed in western Montérégie.

	Châteauguay	Saint-Louis	Saint-Jacques	Tortue	Saint-Régis
Surface area (km^2)	1503	187	171	159	100
Cropland occupation (%)	37	>50*	43	0.4	59
Crop proportion (%)					
- Corn	40	47	45	7	29
- Soybean	28	30	47	7	31
- Multiple cropping	10	8	4	7	24
- Hay	9	5	0.3	4	7
- Wheat	3	3	3	16	2
- Others (beans, cereals, vegetables, fruits, nuts etc.)	9	7	0.8	60	8

* The cropland occupancy of the Saint-Louis watershed was estimated using data from the Fiducie Agricole (Quebec) 2019 (1).

Table S6 Sampling point coordinates and sampling dates.

River name	Date		Latitude	Longitude	Direction	Sample depth (m)
Saint-Pierre	2019-07-17	2021-07-13	45°20'42.3"	73°35'08.4"	Downstream	Subsurface between 1-2m
Châteauguay	2019-07-17		45°11'53.8"	73°51'48.6"	Upstream	Subsurface between 1-2m
	2019-07-17		45°15'10.5"	73°47'59.0"	Upstream	Subsurface between 1-2m
	2019-07-17		45°16'50.3"	73°48'06.9"	Upstream	Subsurface between 1-2m
	2019-07-17	2021-07-13	45°22'52.5"	73°45'02.4"	Downstream	Subsurface between 1-2m
Saint Louis	2019-07-17		45°16'15.6"	73°53'44.3"	Upstream	Subsurface between 1-2m
	2019-07-17		45°17'16.9"	73°53'14.5"	Upstream	Subsurface between 1-2m
	2019-07-17		45°18'51.4"	73°52'47.2"	Downstream	Subsurface between 1-2m
Anglais	2019-07-17		45°10'59.2"	73°50'41.9"	Upstream	Subsurface between 1-2m
	2019-07-17	2021-07-13	45°12'45.1"	73°49'39.8"	Downstream	Subsurface between 1-2m
Noire	2019-07-17	2021-07-13	45°05'10.9"	73°46'58.7"	Downstream	Subsurface between 1-2m
Norton	2019-07-17	2021-07-13	45°08'55.4"	73°47'13.0"	Downstream	Subsurface between 1-2m
Fèves	2019-07-17	2021-07-13	45°13'48.8"	73°48'47.5"	Downstream	Subsurface between 1-2m
Saint-Jaques	2019-07-17	2021-07-13	45°22'50.0"	73°28'44.5"	Downstream	Subsurface between 1-2m
Tortue	2019-07-17		45°19'40.0"	73°31'31.5"	Upstream	Subsurface between 1-2m
	2019-07-17	2021-07-13	45°23'32.7"	73°32'16.7"	Downstream	Subsurface between 1-2m
Saint-Régis	2019-07-17		45°19'48.5"	73°39'55.7"	Upstream	Subsurface between 1-2m
	2019-07-17	2021-07-13	45°23'57.5"	73°33'50.1"	Downstream	Subsurface between 1-2m
Esturgeon	2019-07-17	2021-07-13	45°15'37.2"	73°47'24.1"	Downstream	Subsurface between 1-2m

Section S4 Filter selection

Table S7 The mean ± SD filtration recovery (%) (n=3) of target pesticides during filtration of surface water (spiked at 500 ng L^{-1}) onto glass fiber filter (GFF), nitrocellulose filter (NC), polyester filter (PETE), and regenerated cellulose filter (RC).

	GFF			NC			PTFE			RC		
2,4-D	96	±	2	102	±	4	101	±	3	100	±	5
3,5,6-Trichloro-2-pyridinol	93	±	6	92	±	3	99	±	8	94	±	6
4-chloro-2-methylphenoxyacetic acid (MCPA)	101	±	2	105	±	7	104	±	3	105	±	5
Acetamiprid	95	±	2	88	±	8	100	±	3	101	±	5
Alachlor	95	±	6	76	±	12	95	±	2	100	±	8
Atrazine	97	±	2	101	±	6	100	±	3	102	±	5
Atrazine-2-hydroxy	96	±	3	100	±	5	99	±	3	102	±	6
Azoxystrobin	87	±	4	3	±	4	91	±	3	92	±	7
Bentazon	82	±	5	92	±	6	97	±	5	91	±	6
Bromoxynil	80	±	5	88	±	4	93	±	8	85	±	4
Carbaryl	90	±	4	92	±	4	98	±	5	99	±	5
Carbendazim	96	±	2	99	±	12	99	±	2	100	±	3
Chlorantraniliprole	91	±	6	92	±	10	95	±	5	100	±	5
Chlorothalonil	123	±	16	56	±	13	102	±	11	110	±	6
Chlorpyrifos	82	±	4		ND		76	±	5	76	±	7
Clothianidin	97	±	2	101	±	4	103	±	4	104	±	5
Cyanazine	79	±	6	93	±	9	97	±	1	99	±	9
Deethylatrazine	96	±	5	100	±	6	99	±	3	100	±	5
Deisopropylatrazine	100	±	4	107	±	6	104	±	6	104	±	8
Dicamba	85	±	12	92	±	14	84	±	1	87	±	10
Dimethenamid	95	±	6	89	±	7	100	±	3	100	±	3
Dinotefuran	84	±	7	89	±	7	105	±	12	93	±	14
Desnitro-imidacloprid	60	±	4	96	±	13	114	±	11	98	±	19
Fipronil	89	±	1	69	±	12	85	±	5	93	±	4
Flonicamid	88	±	6	98	±	10	103	±	14	100	±	17
Fluazinam	69	±	8		ND		12	±	7	64	±	6
Flumetsulam	93	±	6	99	±	3	100	±	4	100	±	8
Fluxapyroxad	98	±	3	41	±	15	94	±	7	103	±	11
Fomesafen	100	±	1	105	±	9	106	±	7	105	±	1
Hexazinone	94	±	4	97	±	8	100	±	1	101	±	6
Imazethapyr	93	±	4	100	±	9	95	±	2	96	±	3
Imidacloprid	96	±	3	89	±	8	99	±	3	102	±	4
Linuron	93	±	3	66	±	10	100	±	3	102	±	4
Mecoprop	102	±	4	93	±	1	99	±	7	96	±	9
Mesotrione	94	±	6	99	±	8	100	±	4	98	±	7
Metconazole	88	±	4	49	±	14	91	±	4	95	±	6
Metolachlor ESA	101	±	2	114	±	10	104	±	5	110	±	6

Metolachlor OA	115	±	3	117	±	7	100	±	6	120	±	8
Metribuzin	100	±	1	102	±	7	105	±	6	103	±	6
Nicosulfuron	95	±	3	99	±	6	99	±	5	100	±	6
Nitenpyram	93	±	5	98	±	8	100	±	4	98	±	8
Pendimethalin	86	±	7		ND		71	±	9	83	±	9
Prometryn	96	±	7	93	±	8	99	±	5	103	±	10
Propiconazole	92	±	4	29	±	16	95	±	5	100	±	7
Pyrimethanil	94	±	3	76	±	7	99	±	4	101	±	7
Simazine	94	±	6	95	±	6	98	±	2	100	±	6
(S)-Metolachlor	99	±	5	78	±	11	98	±	3	103	±	7
Tebuconazole	89	±	4	59	±	11	95	±	4	98	±	9
Thiacloprid	95	±	1	67	±	15	100	±	5	100	±	3
Thiamethoxam	98	±	5	97	±	7	100	±	4	103	±	5
Topramezone	103	±	6	113	±	7	109	±	8	115	±	7
Triclopyr	106	±	4	100	±	3	101	±	8	104	±	1
Triclopyr 2-butoxyethylester	88	±	6	1	±	1	94	±	9	95	±	6

Section S5 Instrument parameters

Table S8 LC-HRMS method summary for the analysis of dicamba.

Instrument	Thermo Q-Exactive Orbitrap mass spectrometer Dionex Ultimate 3000 UHPLC chain
Ionization	Heated electrospray ionization source, operated in negative ionization mode
Acquisition mode	Full Scan MS mode
Analytical column	Thermo Hypersil Gold C18 column (100 × 2.1 mm; 1.9 µm)
Column Temperature	50°C
Analytical Mobile Phases	A: 0.1 mM ammonium fluoride in HPLC-water B: 0.1 mM ammonium fluoride in HPLC-methanol Flow rate (mL/min) 0.45
Gradient Profile (analytical column)	Time (min) % B 0.0 40 3.5 40 4.5 55 5.5 75 7.5 100 8.8 100 8.9 40 9.0 40
Injection Volume	5 mL (on-line SPE)
On-line SPE column	Thermo Hypersil Gold aQ C18 column (20 mm × 2.1 mm, 12 µm)
On-line SPE Mobile Phases	A: 0.1% formic acid in HPLC-water B: 0.1% formic acid in HPLC-methanol Flow rate (mL/min) 2
Gradient Profile (on-line SPE)	Time (min) % B 0.0 0 3.5 0 3.6 100 6.6 100 6.7 0 9 0
Source/gas	Sheath gas flow rate 70 Aux gas flow rate 10 Sweep gas flow rate 0 Spray voltage (|V|) 3500 Capillary temperature (°C) 350 Vaporizer temperature (°C) 400 S-lens RF level 60
Orbitrap	Resolution 70,000 at *m/z* 200

parameters	AGC target 3e6 Maximum Inject Time (ms) 100 Scan range (*m/z*) 150-450

Table S9 LC-HRMS method summary for the analysis of glyphosate, glufosinate and AMPA (analyzed as the FMOC-grafted compounds after derivation).

Instrument	Thermo Q-Exactive Orbitrap mass spectrometer Dionex Ultimate 3000 UHPLC chain
Ionization	Heated electrospray ionization source, operated in positive ionization mode
Acquisition mode	Full Scan MS mode
Analytical column	Thermo Hypersil Gold C18 column (50 × 2.1 mm; 1.9 μm)
Column Temperature	40°C
Analytical Mobile Phases	A: 5 mM ammonium acetate in HPLC-water B: HPLC-acetonitrile Flow rate (mL/min) 0.45
Gradient Profile (analytical column)	Time (min) — % B 0.0 — 25 2.0 — 25 8.0 — 95 9.4 — 95 9.5 — 25 10.0 — 25
Injection Volume	1 mL (on-line SPE)
On-line SPE column	Thermo Hypersep Retain PEP column (20 mm × 2.1 mm, 40–60 μm)
On-line SPE Mobile Phases	A: 0.1% formic acid in HPLC-water B: 0.1% formic acid in HPLC-methanol Flow rate (mL/min) 1.5
Gradient Profile (on-line SPE)	Time (min) — % B 0.0 — 0 2.0 — 0 2.1 — 100 6.9 — 100 7.0 — 0 10.0 — 0
Source/gas	Sheath gas flow rate 50 Aux gas flow rate 10 Sweep gas flow rate 0 Spray voltage (|V|) 3500 Capillary temperature (°C) 320 Vaporizer temperature (°C) 350 S-lens RF level 60
Orbitrap parameters	Resolution 70,000 at *m/z* 200 AGC target 3e6 Maximum Inject Time (ms) 100

	Scan range (*m/z*) 200-450

Table S10 LC-HRMS method summary for the analysis of 52 target pesticides.

Instrument	Thermo Q-Exactive Orbitrap mass spectrometer Dionex Ultimate 3000 UHPLC chain
Ionization	Heated electrospray ionization source, operated in fast polarity-switching mode
Acquisition mode	Full Scan MS
Analytical column	Thermo Hypersil Gold C18 column (100 mm × 2.1 mm; 1.9 µm particle size)
Column Temperature	50°C
Mobile Phases	A: 0.1 mM ammonium fluoride in HPLC-water B: 0.1 mM ammonium fluoride in HPLC-methanol Flow rate (mL/min) 0.45
Gradient Profile	Time (min) % B 0.0 10 7.0 100 9.0 100 9.1 10 11.0 10
Injection Volume	50 µL
Source/gas	Sheath gas flow rate 45 a.u. (arbitrary units) Aux gas flow rate 15 a.u. Sweep gas flow rate 0 a.u. Positive spray voltage (|V|) 4500 Negative spray voltage (|V|) 3600 Capillary temperature (°C) 320 Vaporizer temperature (°C) 350 S-lens RF level 55
Orbitrap parameters	Resolution 70,000 at *m/z* 200 AGC target 3e6 Maximum Inject Time (ms) 50 Scan range (*m/z*) 100-600

Section S6 Method validation

Matrix-matched calibration curves and quality control spikes were established by spiking a clean surface water matrix (with nondetectable levels of pesticides) according to a previous survey (2). Blank surface water was collected from the Saint-Maurice River at Grande Mère, a tract of the river located upstream from agricultural and urban areas.

For analytes that required pre-concentration by offline SPE, this blank surface water matrix was spiked with certified standards with 9 increasing levels from 0.01 to 100 ng L^{-1}. Quality control samples were spiked at 75 ng L^{-1}. Calibration curves of glyphosate, AMPA and glufosinate were set between 1 ng L^{-1} and 1000 ng L^{-1}, with quality controls spiked at 100 ng L^{-1}. For dicamba, an 8-level calibration curve was established with concentrations between 0.5 and 1000 ng L^{-1} and the quality control was set at 100 ng L^{-1}. Calibration curves were generated using linear regressions (performance criterion on determination coefficients: R^2 >0.9900).

After the initial calibration had been run, continued calibration verification (CCV) standards were run during the LC-MS batch sequence to control accuracy performance (performance criterion: 70-130%). The matrix-matched quality control spikes were used to derive the method accuracy, intra-day precision, and inter-day precision. If analytes surpassed the upper calibration level in specific field samples, these were reanalyzed by applying a dilution factor to remain within the linear range.

Table S11 Method validation in matrix-matched surface water, including the coefficient of determination (R^2) of the calibration curve, whole-method accuracy (%) of matrix spikes, intra-day precision (%RSD), inter-day precision (%RSD), and the accuracy of continued calibration verification standards (%).

	Matrix-matched calibration	**Matrix-spikes**			
	R^2	**Accuracy (%) (n=5)**	**Intra-day precision (%RSD) (n=5)**	**Inter-day precision (%RSD) (n=15)**	**Continued calibration verification (%) (n=3)**
2,4-Dichlorophenoxyacetic acid	0.9979	93	10	13	74
3,5,6-Trichloro-2-pyridinol	0.9969	98	9	12	81
4-chloro-2-methylphenoxyacetic acid (MCPA)	0.9988	94	7	10	84
Acetamiprid	0.9995	106	2	2	98
Alachlor	0.9980	103	4	4	96
Aminomethylphosphonic acid	1.0000	103	2	NA	103
Atrazine	0.9997	105	2	2	94
Atrazine-2-hydroxy	0.9997	107	2	2	100
Azoxystrobin	0.9997	105	1	3	99
Bentazon	0.9997	100	9	12	78
Bromoxynil	0.9986	94	6	11	77
Carbaryl	0.9999	102	5	6	95
Carbendazim	0.9996	110	4	4	100
Chlorantraniliprole	0.9994	102	4	7	95
Chlorothalonil	0.9956	95	9	13	77
Chlorpyrifos	0.9962	108	8	15	92
Clothianidin	0.9995	100	2	5	96
Cyanazine	0.9969	107	3	4	102
Desethylatrazine	0.9998	98	4	5	86
Desisopropylatrazine	0.9995	96	5	6	82
Desnitro-imidacloprid	0.9952	97	5	6	105
Dicamba	0.9980	94	2	NA	94
Dimethenamid	0.9997	104	3	3	99
Dinotefuran	0.9989	110	4	5	105
Fipronil	0.9991	101	8	11	77
Flonicamid	0.9971	90	8	11	82
Fluazinam	0.9977	105	12	16	92
Flumetsulam	0.9997	111	4	7	97
Fluxapyroxad	0.9998	120	2	5	116
Fomesafen	0.9998	100	9	12	83
Glufosinate	0.9999	100	2	NA	100

Glyphosate	0.9974	103	6	NA	105
Hexazinone	0.9986	101	2	3	92
Imazethapyr	0.9998	116	4	4	103
Imidacloprid	0.9990	110	4	4	96
Linuron	0.9998	105	1	3	100
Mecoprop	0.9993	97	7	12	79
Mesotrione	1.0000	109	5	6	107
Metconazole	0.9992	101	2	3	95
Metolachlor ethanesulfonic acid	0.9974	99	4	6	91
Metolachlor oxanilic acid	0.9959	99	4	6	91
Metribuzin	0.9986	105	2	3	93
Nicosulfuron	0.9997	101	8	9	99
Nitenpyram	0.9987	113	3	3	102
Pendimethalin	0.9955	113	7	18	90
Prometryn	0.9997	107	5	6	94
Propiconazole	0.9995	103	2	3	99
Pyrimethanil	0.9997	108	2	3	101
Simazine	0.9997	107	3	4	98
(S)-Metolachlor	0.9999	104	3	3	98
Tebuconazole	0.9965	115	3	4	111
Thiacloprid	0.9996	106	2	4	101
Thiamethoxam	0.9996	108	3	3	104
Topramezone	0.9995	108	3	4	103
Triclopyr	0.9973	90	10	13	80
Triclopyr 2-butoxyethylester	0.9980	89	4	12	92

Section S7 Absolute extraction efficiency evaluation

The preparation procedure involved a surface water matrix from the Saint-Maurice River spiked with certified standards prior to the extraction step (n=3) versus the same matrix spiked before the LC-MS analysis (3).

The absolute extraction efficiency was calculated as follows:

$$Absolute\ extraction\ efficiency = 100 * \frac{Before - Blank}{After - Blank}$$

Where ***before*** and ***after*** refer to the chromatogram responses of certified analyte spiked before and after sample extraction, respectively, and ***blank*** refers to the analyte response in non-spiked matrix sample.

Table S12 Absolute extraction efficiencies (%) (mean ± SD, n=3) of selected pesticides on Strata^{TM}-X Polymeric Reversed Phase SPE cartridge (X) versus Strata^{TM} X-AW weak-anion exchange cartridge (X-AW).

	X			X-AW		
2,4-Dichlorophenoxyacetic acid	82	±	21	102	±	16
3,5,6-Trichloro-2-pyridinol	107	±	0	96	±	19
4-chloro-2-methylphenoxyacetic acid (MCPA)	82	±	12	105	±	12
Acetamiprid	102	±	3	88	±	1
Alachlor	103	±	8	94	±	4
Atrazine	94	±	3	86	±	8
Atrazine-2-hydroxy	100	±	7	94	±	7
Azoxystrobin	97	±	5	92	±	9
Bentazon	81	±	16	100	±	11
Bromoxynil	114	±	4	94	±	14
Carbaryl	80	±	15	81	±	16
Carbendazim	97	±	3	87	±	5
Chlorantraniliprole	92	±	13	79	±	5
Chlorothalonil	97	±	14	11	±	19
Chlorpyrifos	131	±	32	87	±	2
Clothianidin	103	±	7	109	±	2
Cyanazine	100	±	19	97	±	4
Desethylatrazine	103	±	3	105	±	5
Desisopropylatrazine	95	±	15	82	±	4
Desnitro-imidacloprid	95	±	1	-2	±	2
Dimethenamid	99	±	2	96	±	1
Dinotefuran	51	±	7	51	±	8
Fipronil	100	±	9	93	±	3
Flonicamid	94	±	6		ND	
Fluazinam	111	±	26	52	±	15
Flumetsulam	104	±	12	113	±	6
Fluxapyroxad	83	±	6	93	±	10
Fomesafen	111	±	3	110	±	12
Hexazinone	100	±	5	96	±	5
Imazethapyr	98	±	5	67	±	8
Imidacloprid	92	±	12	127	±	14
Linuron	100	±	2	97	±	8
Mecoprop	97	±	4	92	±	16
Mesotrione	61	±	5	79	±	5
Metconazole	102	±	2	94	±	2
Metolachlor ethanesulfonic acid	88	±	17	98	±	13
Metolachlor oxanilic acid	103	±	8	104	±	13
Metribuzin	103	±	11	131	±	15
Nicosulfuron	83	±	4	99	±	15
Nitenpyram	112	±	6	95	±	7

Pendimethalin	118	±	13	94	±	25
Prometryn	99	±	2	88	±	3
Propiconazole	95	±	5	99	±	8
Pyrimethanil	96	±	2	88	±	5
Simazine	92	±	9	103	±	3
(S)-Metolachlor	101	±	4	93	±	8
Tebuconazole	85	±	10	70	±	7
Thiacloprid	96	±	5	95	±	0
Thiamethoxam	106	±	5	100	±	7
Topramezone	90	±	14	98	±	11
Triclopyr	114	±	19	108	±	32
Triclopyr 2-butoxyethylester	115	±	1	84	±	2

Section S8 Determination of method limit of detection

The limit of detection (LOD) for each analyte was evaluated using one of the following approaches. 1) When method blanks contain detectable analytes, the LOD was primarily derived from the standard deviation of the calculated concentrations of the blank samples (n), multiplied by the t-distributions value with (n-1) degrees of freedom at a 99% percentile (4); 2) the LOD was determined based on the signal/noise height ratio of a lower calibration level (3); 3) For analytes not applicable to the above LOD determination methods, the calibration curve method was used, i.e., derived from the ratio of the standard error of y-intercept and the slope of the regression curve (5). A fourth approach consisted in assigning the LOD to the first acceptable concentration level of the calibration curve. The LODs for all the analytes are presented below in Table S13.

Table S13 Limit of detection (LOD, ng L^{-1}) for the targeted compounds in surface water and corresponding estimation methods.

	LOD (ng L^{-1})	Estimation methods
2,4-D	0.1	The first detectable level of calibration curve
3,5,6-Trichloro-2-pyridinol	0.2	Standard error/slope ratio method
4-chloro-2-methylphenoxyacetic acid (MCPA)	0.05	The first detectable level of calibration curve
Acetamiprid	0.01	The first detectable level of calibration curve
Alachlor	0.249	Standard error/slope ratio method
Aminomethylphosphonic acid	2	The first detectable level of calibration curve
Atrazine	0.001	Signal/noise ratio method
Atrazine-2-hydroxy	0.02	Blank variation method
Azoxystrobin	0.02	Standard error/slope ratio method
Bentazon	0.3	Signal/noise ratio method
Bromoxynil	0.026	Standard error/slope ratio method
Carbaryl	0.025	Signal/noise ratio method
Carbendazim	0.015	Signal/noise ratio method
Chlorantraniliprole	0.1	The first detectable level of calibration curve
Chlorothalonil	0.5	The first detectable level of calibration curve
Chlorpyrifos	1.2	Standard error/slope ratio method
Clothianidin	0.1	The first detectable level of calibration curve
Cyanazine	4.5	Signal/noise ratio method
Desethylatrazine	0.13	Blank variation method
Desisopropylatrazine	0.058	Blank variation method
Desnitro-imidacloprid	0.024	Standard error/slope ratio method
Dicamba	5	The first detectable level of calibration curve
Dimethenamid	0.034	Standard error/slope ratio method
Dinotefuran	0.018	Standard error/slope ratio method
Fipronil	0.05	The first detectable level of calibration curve

Flonicamid	0.31	Standard error/slope ratio method
Fluazinam	0.1	The first detectable level of calibration curve
Flumetsulam	0.032	Standard error/slope ratio method
Fluxapyroxad	0.01	The first detectable level of calibration curve
Fomesafen	0.05	The first detectable level of calibration curve
Glufosinate	0.6	Blank variation method
Glyphosate	2	Blank variation method
Hexazinone	0.07	Standard error/slope ratio method
Imazethapyr	0.01	The first detectable level of calibration curve
Imidacloprid	0.015	Signal/noise ratio method
Linuron	0.01	The first detectable level of calibration curve
Mecoprop	0.05	The first detectable level of calibration curve
Mesotrione	0.328	Standard error/slope ratio method
Metconazole	0.05	The first detectable level of calibration curve
Metolachlor ESA	0.007	Signal/noise ratio method
Metolachlor OA	0.008	Signal/noise ratio method
Metribuzin	0.37	Standard error/slope ratio method
Nicosulfuron	0.05	The first detectable level of calibration curve
Nitenpyram	0.046	Signal/noise ratio method
Pendimethalin	0.5	The first detectable level of calibration curve
Prometryn	0.05	The first detectable level of calibration curve
Propiconazole	0.19	Blank variation method
Pyrimethanil	0.01	The first detectable level of calibration curve
Simazine	0.02	Blank variation method
(S)-Metolachlor	0.08	Blank variation method
Tebuconazole	0.018	Blank variation method
Thiacloprid	0.05	The first detectable level of calibration curve
Thiamethoxam	0.01	The first detectable level of calibration curve
Topramezone	0.5	The first detectable level of calibration curve
Triclopyr	2.15	Standard error/slope ratio method
Triclopyr 2-butoxyethylester	0.1	The first detectable level of calibration curve

Section S9 Quebec's water quality criteria for the protection of aquatic life

Table S14 Quebec's water quality criteria[1] for the protection of aquatic life (ng L^{-1}).

	CALC	AALC		CALC	AALC
2,4-Dichlorophenoxyacetic acid	220000	1400000	Fomesafen		
3,5,6-Trichloro-2-pyridinol			Glufosinate		
4-chloro-2-methylphenoxyacetic acid (MCPA)	2600[2]				
Acetamiprid	8.3[3]	200[3]	Glyphosate	800000	
Alachlor	11000	150000	Hexazinone	330[2]	1000000[2]
Aminomethylphosphonic acid (AMPA)			Imazethapyr	8100[2]	34000000[2]
Atrazine	1800[4]	50000	Imidacloprid	8.3[3]	200[3]
Atrazine-2-hydroxy	1800[4]		Linuron	7000[2]	
Azoxystrobin	1240[5]		Mecoprop	13000[2]	10000000[2]
Bentazon	510000[2]	11000000[2]	Mesotrione		
Bromoxynil	5000		Metconazole		
Carbaryl	200		Metolachlor ESA		
Carbendazim			Metolachlor OA		
Chlorantraniliprole	100[2]	560[2]	Metribuzin	1000[2]	
Chlorothalonil	180[2]		Nicosulfuron		
Chlorpyrifos	2	20	Nitenpyram	8.3[3]	200[3]
Clothianidin	8.3[3]	200[3]	Pendimethalin		
Cyanazine	2000[2]	1000000	Prometryn		
Deethylatrazine	1800[4]		Propiconazole	3700	
Deisopropylatrazine	1800[4]		Pyrimethanyl		
Desnitro-imidacloprid			Simazine	10000	160000
Dicamba	10000[2]		(S)-metolachlor	7800[2]	110000
Dimethenamide	5600[2]	260000[2]	Tebuconazole		
Dinotefuran	8.3[3]	200[3]	Thiacloprid	8.3[3]	200[3]
Fipronil			Thiamethoxam	8.3[3]	200[3]
Flonicamid			Topramezone		
Fluazinam			Triclopyr		
Flumetsulame	3100[2]	25000000[2]	Triclopyr 2-butoxyethylester		
Fluxapyroxad					

[1] MELCC (2023) https://www.environnement.gouv.qc.ca/eau/criteres_eau/index.asp

[2] Provisional criterion

[3] CALC and AALC were developed for one or the sum of neonicotinoids

[4] CALC of 1800 ng/L for the sum of atrazine and its transformation products

[5] Giroux I. Présence de pesticides dans l'eau au Québec : Portrait et tendances dans les zones de maïs et de soya – 2018 à 2020, Québec. Ministère de l'Environnement et de la Lutte contre les changements climatiques, Direction de la qualité des milieux aquatiques; 2022

Section S10 Occurrence of pesticides in the surface water of western Montérégie

Table S15 Detection frequencies (DF), concentrations (min, max, median, mean), and method detection limits (MDL) for the detected pesticides and transformation products in the surface waters (n=8 for upstream and n=11 for downstream) of western Montérégie in the summer of 2019.

	MDL	Summer 2019 upstream					Summer 2019 downstream				
		DF	Min	Max	Median	Mean	DF	Min	Max	Median	Mean
	(ng L^{-1})	(%)	(ng L^{-1})				(%)	(ng L^{-1})			
Herbicides											
Glyphosate	2	100	30	915	127	259	100	87	4095	681	1137
(*S*)-Metolachlor	0.08	100	158	2788	345	761	100	36	2519	858	906
2,4-D	0.1	100	6	229	74	86	100	6	189	53	69
Metribuzin	0.37	100	12	123	40	52	100	28	203	92	96
Atrazine	0.001	100	40	158	54	73	100	12	426	74	132
Bentazon	0.3	100	11	45	22	23	100	3	574	46	139
MCPA	0.05	100	5	172	25	63	100	3	530	24	85
Dimethenamid	0.034	100	1	44	8	13	100	3	174	15	40
Simazine	0.02	100	0.5	50	2	10	100	0.4	19	2	4
Flumetsulam	0.032	100	0.1	17	2	4	100	0.2	21	3	5
Mesotrione	0.328	88	6	366	21	81	100	6	256	23	63
Cyanazine	4.5	100	12	20	17	16	91	9	44	17	21
Fomesafen	0.05	100	0.3	25	6	7	91	2.6	45	7	12
Prometryn	0.05	75	0.1	22	6	8	100	0.1	178	26	47
Pendimethalin	0.5	100	1	6	3	4	73	4	18	7	9
Linuron	0.01	75	0.04	5	2	2	91	0.02	553	4	71
Mecoprop	0.05	63	0.3	5	1	2	91	0.1	7	1	2
Topramezone	0.5	63	2	4	3	3	91	2	4	2	3
Bromoxynil	0.026	50	0.08	0.2	0.1	0.1	73	0.1	3	0.3	1
Imazethapyr	0.01	38	43	43	43	43	64	43	43	43	43
Dicamba	5	38	31	234	33	99	45	7	67	27	33
Hexazinone	0.07	13	0.1	0.1	0.1	0.1	18	0.2	3	2	2
Nicosulfuron	0.05	-	-	-	-	-	9	21	21	21	21
Insecticides											
Chlorantraniliprole	0.1	100	1	10	4	5	100	2	45	6	10
Clothianidin	0.1	88	7	73	17	27	100	11	265	32	65
Thiamethoxam	0.01	88	1	34	10	12	91	2	514	22	123
Imidacloprid	0.015	63	3	28	8	10	100	1	161	23	57
Acetamiprid	0.01	38	0.02	0.03	0.02	0.02	64	0.07	5	0.1	1
Chlorpyrifos	1.2	25	3	20	11	11	64	3	6	3	4
Flonicamid	0.31	38	1	1	1	1	27	1	19	5	8
Nitenpyram	0.046	25	0.1	0.2	0.1	0.1	27	0.1	0.2	0.1	0.1
Thiacloprid	0.05	-	-	-	-	-	27	0.1	1	0.2	0.4
Carbaryl	0.025	13	1	1	1	1	-	-	-	-	-
Fungicides											
Propiconazole	0.19	100	1	5	1	2	100	1	11	2	3
Azoxystrobin	0.02	100	0.1	6	1	1	100	0.1	25	5	7
Fluxapyroxad	0.01	100	1	2	1	1	100	1	4	1	2
Tebuconazole	0.018	100	0.6	16	1	3	100	0.5	7	1	2
Carbendazim	0.015	100	0.1	4	0.1	1	100	0.1	8	0.7	2
Metconazole	0.05	38	0.05	0.2	0.1	0.1	73	0.1	1	0.2	0.3
Pyrimethanil	0.01	25	0.01	0.01	0.01	0.01	82	0.01	1	0.03	0.2
Fluazinam	0.1	13	0.1	0.1	0.1	0.1	9	0.2	0.2	0.2	0.2
Chlorothalonil	0.5	-	-	-	-	-	9	1	1	1	1
Transformation Products											
Metolachlor	0.007	100	321	1405	681	745	100	447	2489	1248	1287

ethanesulfonic acid											
AMPA	2	100	57	781	196	303	100	153	5836	934	1564
Metolachlor oxanilic acid	0.008	100	138	910	246	363	100	143	944	447	500
Desethylatrazine	0.13	100	16	63	39	40	100	16	60	35	35
Atrazine-2-hydroxy	0.02	100	8	32	19	19	100	9	52	28	31
Desisopropylatrazine	0.058	100	7	35	17	19	100	5	23	12	13
Desnitro-imidacloprid	0.024	13	0.8	0.8	0.8	0.8	-	-	-	-	-
3,5,6-Trichloro-2-pyridinol	0.2	13	0.9	0.9	0.9	0.9	-	-	-	-	-

Section S11 Pesticide sales in Quebec

Table S16 The sales of pesticide in Quebec for 2018 (6), 2019 (7), and 2020 (8)

Active ingredient (a.i.)	Type	Sales volume (kg a.i.) *		
		2018	2019	2020
2,4-D	Herbicide	C	C	C
Acetamiprid	Insecticide	B	B	B
Alachlor	Herbicide	A	A	A
Atrazine	Herbicide	D	D	C
Azoxystrobin	Fungicide	C	C	C
Bentazon	Herbicide	D	D	D
Bromoxynil	Herbicide	C	C	C
Carbaryl	Insecticide	C	C	C
Carbendazim	Fungicide	A	A	A
Chlorantraniliprole	Insecticide	C	C	C
Chlorothalonil	Fungicide	D	D	D
Chlorpyrifos	Insecticide	D	D	C
Clothianidin	Insecticide	C	B	C
Cyanazine	Herbicide	A	A	A
Dicamba	Herbicide	D	D	D
Dimethenamid	Herbicide	C	C	C
Dinotefuran	Insecticide	A	A	B
Fipronil	Insecticide	A	A	A
Flonicamid	Insecticide	B	B	B
Fluazinam	Fungicide	C	C	C
Flumetsulam	Herbicide	B	C	B
Fluxapyroxad	Fungicide	C	C	C
Fomesafen	Herbicide	C	D	C
Glufosinate	Herbicide	C	C	D
Glyphosate	**Herbicide**	**E**	**E**	**E**
Hexazinone	Herbicide	D	D	D
Imazethapyr	Herbicide	C	C	C
Imidacloprid	Insecticide	C	B	D
Linuron	Herbicide	D	D	D
MCPA	Herbicide	D	D	D
Mecoprop	Herbicide	C	C	C
Mesotrione	Herbicide	D	D	D
Metconazole	Fungicide	C	C	C
Metribuzin	Herbicide	D	D	D
Nicosulfuron	Herbicide	A	B	B
Nitenpyram	Insecticide	A	A	A
Pendimethalin	Herbicide	D	D	D
Prometryn	Herbicide	C	C	C
Propiconazole	Fungicide	C	C	C
Pyrimethanil	Fungicide	C	C	C

Simazine	Herbicide	C	C	C
(S)-Metolachlor	**Herbicide**	**E**	**E**	**E**
Tebuconazole	Fungicide	C	C	C
Thiacloprid	Insecticide	B	B	C
Thiamethoxam	Insecticide	C	C	C
Topramezone	Herbicide	B	A	A
Triclopyr	Herbicide	A	A	A
Triclopyr 2-butoxyethylester	Herbicide	C	C	D

*Sales scale (kg a.i.)

A: Not sold

B: 0-1000

C: 1000-10,000

D: 10,000-100,000.

E: 100,000-1,000,000

Section S12 Flowrate estimation for the watersheds in western Montérégie

For the Châteauguay River, we adopted the daily flowrate ($m^3\ s^{-1}$) of July 2019 and July 2021 monitored by a hydrometric station (9) to calculate the monthly range of pesticide loads transported into the St. Lawrence River. However, for the Saint-Régis River, Tortue River, and Saint-Jacques River, no hydrometric stations were available, so we used simulated daily flowrate ($m^3\ s^{-1}$) at 50^{th} percentile (10). Finally, for the Saint-Louis River, we used the historical daily flowrate ($m^3\ s^{-1}$) from July 1987, 1988, and 1989 to estimate the mass loads of pesticides (11).

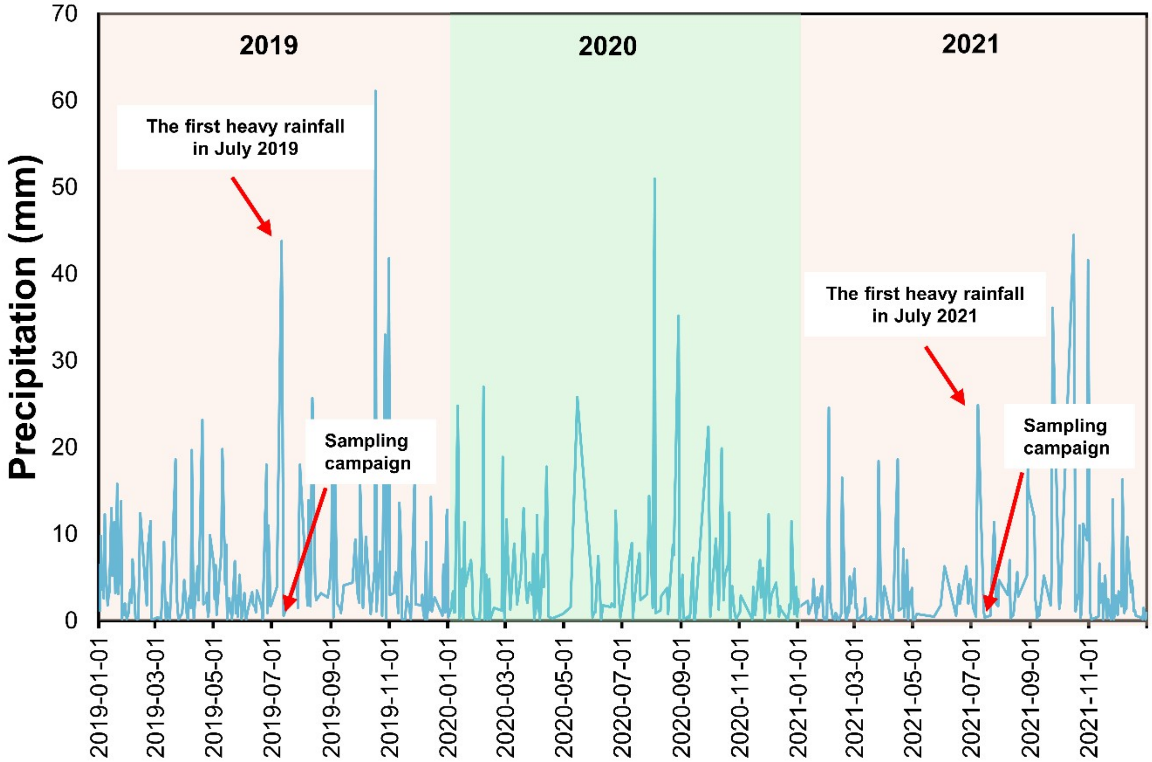

Figure S1 Precipitation in western Montérégie from 2019 to 2021. Precipitation data were taken from Saint-Rémi, a city in western Montérégie (12).

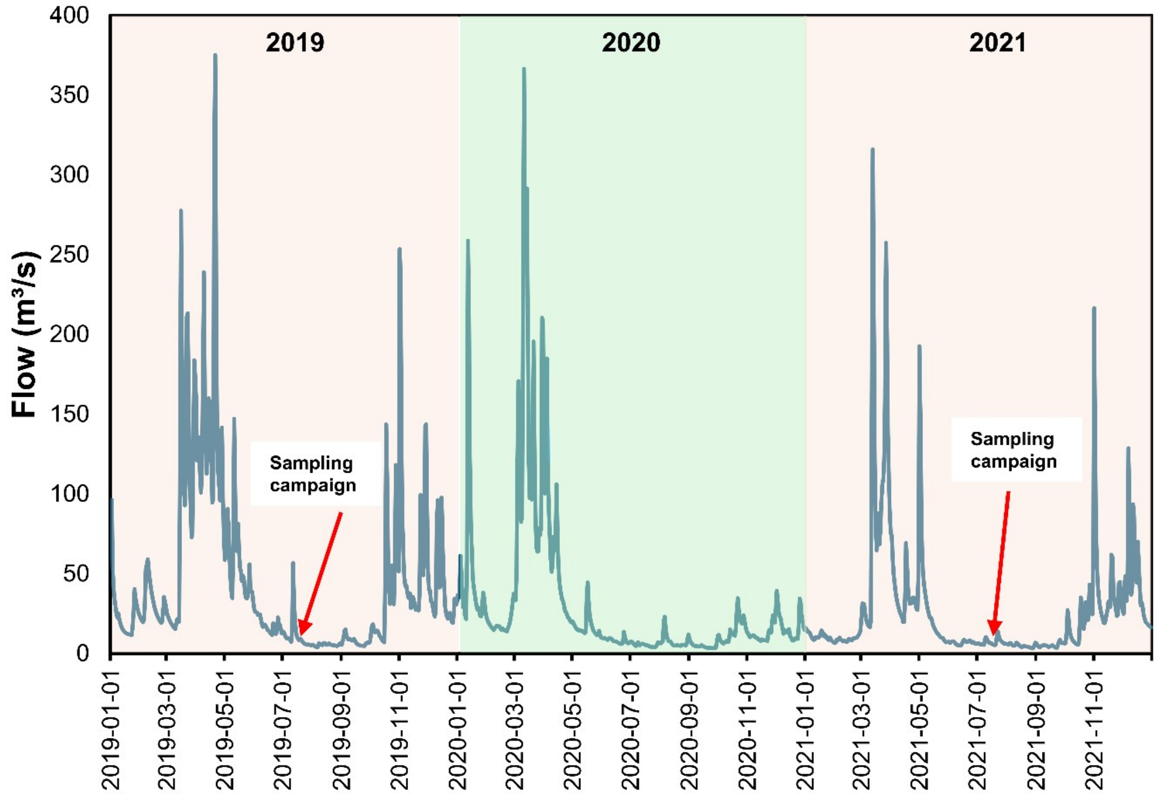

Figure S2 Flowrates for the River Châteauguay from 2019 to 2021 (9).

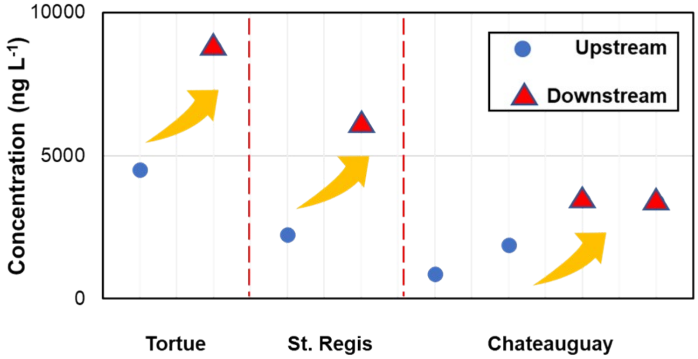

Figure S3 Total pesticide concentrations in upstream and downstream sampling points of the Tortue River, St. Régis River, and the Châteauguay River in the summer of 2019.

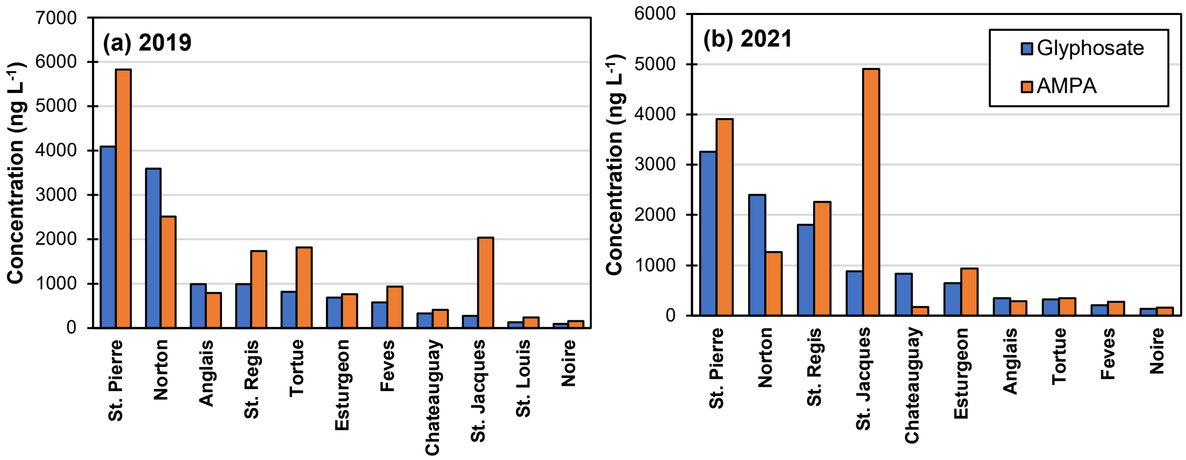

Figure S4 Concentration of glyphosate and AMPA for all the investigated rivers in western Montérégie for 2019 (a) and 2021 (b). Only downstream data were used for analysis.

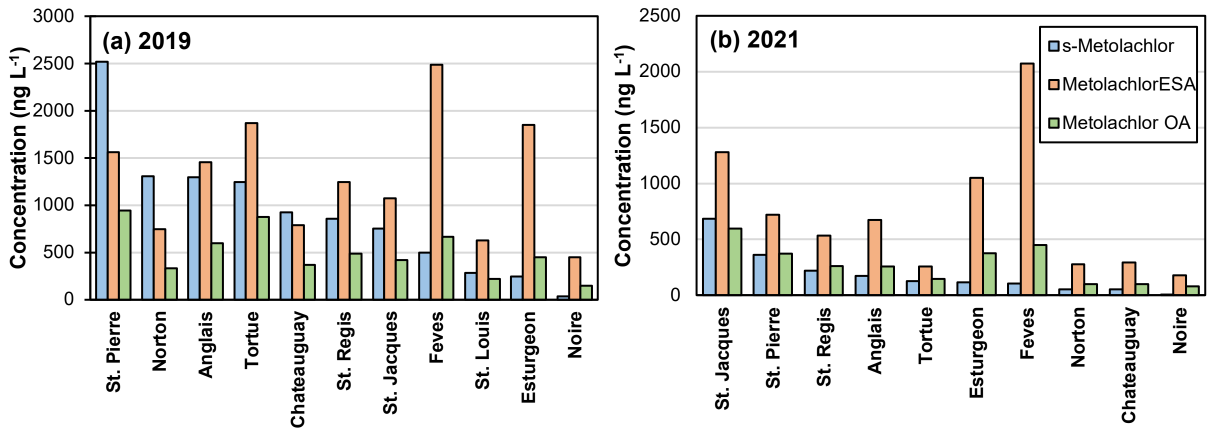

Figure S5 Concentration of *S*-metolachlor, metolachlor ESA and metolachlor OA for all the investigated rivers in western Montérégie for 2019 (a) and 2021 (b). Only downstream data were used for analysis.

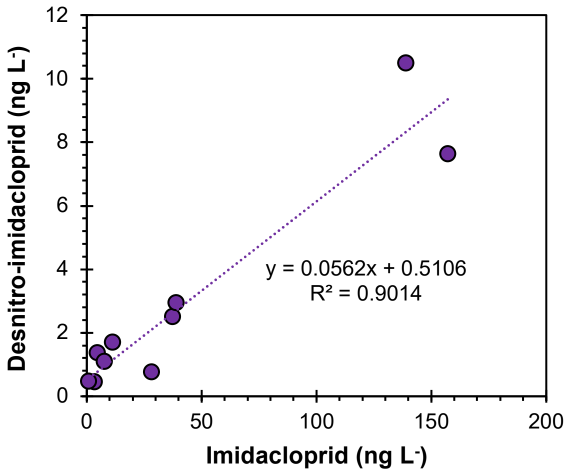

Figure S6 The concentration of desnitro-imidacloprid versus the concentration of imidacloprid at all sampling points. Only the data that are higher than the limit of detection are presented.

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