Supplemental Information

Leaching of Three Imidazolinone Herbicides during Sprinkler Irrigation
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Chemicals and Reagents
Analytical grade imazamethabenz-methyl (mixture of para- and meta-isomers), imazethapyr and imazamox (99.5%) were obtained from ChemService (West Chester, PA, USA). Imazamethabenz acid (mixture of para- and meta-isomers) was obtained from NuFarm Agriculture Inc., Calgary, AB, Canada and from Huntingdon Life Sciences (Suffolk, UK). HPLC grade acetonitrile and methanol were obtained from Fisher Scientific (Edmonton, AB, Canada). Deionized water (18 MΩ) containing less than 4 µg L⁻¹ total organic carbon was obtained using a Millipore Milli-Q Gradient A10 (with TOC detector) purification system (Millipore Corp., Billerica, MA, USA). Certified A.C.S grade formic acid and 20-30 mesh Ottawa sand were purchased from Fisher Scientific.

Tile-Drain and Piezometer Water Extraction
Fortification experiments showed that higher recoveries of imazamethabenz-methyl and imazamethabenz were obtained when the water samples were acidified to pH ≈ 2 by the addition of 10% sulfuric acid solution prior to solid-phase extraction. In contrast, recoveries of imazethapyr and imazamox were higher when the tile-drain and piezometer water samples, which were slightly alkaline (pH = 7.77 ± 0.24; N = 161 and pH = 7.44 ± 0.08; N = 56, respectively) were not acidified. Consequently, all water samples were analyzed with and without acidification.

A water subsample (250 mL) was passed (~10 mL min⁻¹) under vacuum (400 mm of Hg)
through an Oasis hydrophilic-lipophilic balance (HLB) cartridge (225 mg; Waters Corporation, Milford, MA) that had been conditioned sequentially with methanol (10 mL) and then de-ionized water (10 mL). After sample loading, the cartridges were washed with de-ionized water (10 mL) and then eluted with methanol (10 mL) and the eluate evaporated to dryness using a stream of dry nitrogen gas (water bath at 50°C). The eluate residue was dissolved in de-ionized water (1 mL) and transferred to a 2-mL amber HPLC vial for analysis by LC-MS-MS.

**Soil Extraction**

The soil cores from each sampling depth were freeze-dried individually using a Labconco freeze-drying system (Kansas City, KA). The freeze-dried samples were then passed through a 1-mm screen and the screened soil (approximately 100 g) was ground and mixed using a mortar and pestle to create a homogenous sample for herbicide residue analysis.

The soil samples were extracted by pressurized liquid extraction (PLE) (ASE 200; Dionex, Sunnyvale, CA). Two GF/X filter papers were placed at the exit end of a 33-mL stainless steel extraction cell followed by 7 – 8 mL of Ottawa sand followed by a third filter paper. Freeze-dried soil (5 g) mixed with Ottawa sand (40 g) was added to the cell followed by sufficient Ottawa sand to fill the cell and a fourth filter paper placed at the inlet end of the cell. The sample was then extracted by PLE with an aqueous solution of 2 mM sodium hydroxide containing 5% acetonitrile (v/v) using the following operating conditions: temperature, 70°C; static mode time, 5 min at 1500 psi; one static cycle; 90% flush volume; and 90 s purge time with UHP nitrogen at the end of each run. The total extraction volume was approximately 1.5 times the cell volume (approximately 50 mL).
The PLE extracts were then subjected to cleanup using solid-phase extraction cartridges (Oasis HLB cartridges; Waters, Manchester, UK). Using a 12-position vacuum manifold (Supelco, Gland, Switzerland), the cartridges were conditioned with 10 mL methanol followed by 10 mL of deionized water. Sample extracts were diluted with 200 mL of deionized water and, after the addition of 0.5 mL of 10% sulfuric acid solution, passed through the SPE cartridges at a flow rate of approximately 0.5 mL min\(^{-1}\) under a slight vacuum (600 mm of Hg) and rinsed with 10 mL of deionized water. The cartridges were eluted with 10 mL of methanol and the eluates evaporated and concentrated to near dryness under a gentle stream of nitrogen gas. The eluate residues were dissolved in deionized water (1 mL) and transferred to 2-mL amber glass HPLC vials for LC/MS/MS analysis.

**LC/MS/MS Analysis**

An Alliance 2695 Separations Module interfaced with a Micromass Quattro Ultima mass spectrometer (Waters, Milford, MA, USA) equipped with an electrospray ionization interface set to positive ion mode was used to analyze all sample extracts. Ionization and MS/MS conditions were optimized by infusing a 0.5 mg L\(^{-1}\) solution of each compound into the ion source in a 50:50 acetonitrile:water solution with a syringe pump. The (M+H)\(^{+}\) ion for each analyte was selected for fragmentation using the first quadrupole. The second quadrupole, into which argon gas was introduced, functioned as a collision cell and the third quadrupole was used to monitor the resulting major fragment ions.

Three MRM transitions were chosen for each compound from the corresponding product ion scans for confirmation purposes (mazamethabenz-methyl: m/z 289 to 86, 289 to 144 and 289 to 215; imazamethabenz: m/z 275 to 86, 275 to 144 and 275 to 161; imazethapyr: m/z 290 to 77,
290 to 86 and 290 to 202; and imazamox: m/z 306 to 193, 306 to 218 and 306 to 246) and the most intense transitions (in bold font) were used for quantification purposes. The instrument and operating conditions were as follows: source temperature, 90°C; cone voltage, 68 V; collision energy, 68 V; capillary voltage, 2.88 kV; hex 1 voltage, 6.9 V; hex 2 and aperture voltage, 0V; desolvation temperature, 220°C; nitrogen desolvation gas flow rate, 488 L h⁻¹; nitrogen cone gas flow rate, 154 L h⁻¹; nitrogen nebulizer gas flow rate was at maximum flow; multiplier voltage, 700 V; and the interchannel delay was 0.10 s while dwell time was 0.10 s for all MRM channels. Argon was used as the collision gas at a pressure which increased the Pirani gauge reading to 1.53 x 10⁻⁴ torr. Resolution was set to achieve unit mass resolution for quadrupole 1 and approximately 2 amu resolution for quadrupole 3.

Liquid chromatographic separation was achieved with a Xterra Mass C₁₈ column (100-mm x 2.1-mm inside diameter, 3.5 μm particle size; Waters Corporation, Milford, MA, USA) maintained at 30°C and an acetonitrile/water [15:85 (v/v)] mobile phase containing 0.1% formic acid. A flow rate of 200 μL min⁻¹ resulted in retention times of 2.71, 3.53, 5.15 and 6.08 min for imazamethabenz, imazamox, imazamethabenz-methyl and imazethapyr, respectively, with baseline separation of all four compounds. The injection volume was 20 μL.

**Fortification Experiments**

**Water**

Fortification experiments were carried out to determine the recovery of the three imidazolinone herbicides plus imazamethabenz from South Saskatchewan River water (pH = 7.8) which was used as a surrogate for tile-drain effluent and for ground water. Water (250 mL) was fortified with 25 ng of each compound dissolved in 100 μL of acetonitrile, resulting in a concentration
100 ng L\(^{-1}\). The water samples were extracted immediately after fortification and mean recoveries (± standard deviation; N = 9) of imazamethabenz-methyl, imazamethabenz, imazethapyr and imazamox from the river water were 104 ± 4%, 102 ± 9%, 94 ± 7% and 117 ± 10%, respectively. The higher recoveries for imazamox may indicate enhancement of ionization in the source of the mass spectrometer due to dissolved organic matter in river water. The similar recoveries for imazamethabenz-methyl and imazamethabenz indicate that little hydrolysis of imazamethabenz-methyl occurred during the fortification experiments. Based on a signal to noise ratio of 3:1 for a 100 ng L\(^{-1}\) solution of each compound, the method detection limits (limits of quantification) were as follows: imazamethabenz-methyl (9 ng L\(^{-1}\)), imazamethabenz (20 ng L\(^{-1}\)), imazethapyr (13 ng L\(^{-1}\)) and imazamox (17 ng L\(^{-1}\)). Corresponding instrument detection limits were 18, 16, 24 and 17 ng, respectively.

**Soil**

Freeze-dried control soil (5 g) from soil cores collected prior to herbicide application was fortified by adding 50 ng each of imazamethabenz-methyl, amazethapyr and imazamox in 50 μL of water which resulted in a fortification level of 10 μg kg\(^{-1}\). Pressurized liquid extraction of the fortified soil showed that some hydrolysis of imazamethabenz-methyl occurred during the fortification experiment. Consequently, the recovery of imazamethabenz-methyl was determined as the sum of imazamethabenz-methyl and imazamethabenz. Recoveries (mean ± standard deviation; N = 3) of imazamethabenz-methyl, amazethapyr and imazamox were 58 ± 2.4%, 118 ± 11% and 29 ± 8%, respectively.