

Supporting Information for:

**Are Neutral Chloroacetamide Herbicide Degradates of Potential
Environmental Concern? Analysis and Occurrence in the Upper Chesapeake
Bay**

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Environmental Science and Technology

Supporting Information describes methods used to synthesize neutral chloroacetamide degradates, including their ^1H NMR spectral data and electron ionization mass spectra (Figures S1-S17); summarizes recoveries, MDL and MRL values for ionic degradates; and provides a tabular listing of all measurements of herbicides, degradates, dissolved oxygen and chloride in samples obtained from the Chesapeake Bay on July 17, 2003.

Synthesis

The following describes methods used to synthesize the chloroacetamide degradates sought in the present investigation. All ^1H NMR (proton nuclear magnetic resonance) spectra were obtained using a Varian Unity 400 MHz FT-NMR after dissolving compounds in CDCl_3 containing tetramethylsilane (TMS). Concentrations were ~ 500 mg/L for NMR samples. Chemical shifts are reported as ppm referenced to TMS. All mass spectra were obtained using a ThermoQuest Trace 2000 gas chromatograph with a programmed temperature vaporization injector (PTV) coupled to a quadrupole mass spectrometer (GC/MS). Concentrated stock solutions of each compound were initially prepared by dissolving analytes in acetone, and subsequently diluting the acetone stock solutions into toluene to yield analyte concentrations of approximately 10 mg/L. Aliquots (1 μL) were analyzed via GC/MS using a splitless injector, and mass spectra were obtained in full scan (m/z 50-450) electron ionization (EI) mode. The column used to effect separations was an Equity-5 (30 m length \times 0.25 mm ID \times 0.25 μm phase thickness; Supelco). The GC temperature program was 90 $^\circ\text{C}$ for 1 min, 10 $^\circ\text{C}/\text{min}$ to 290 $^\circ\text{C}$, with a final hold for 5 minutes at 290 $^\circ\text{C}$. The mass spectrometer temperature was set to 250 $^\circ\text{C}$, with an energy of 70 eV, and the transfer line was maintained at 285 $^\circ\text{C}$.

II. Hydroxyalachlor [2-hydroxy-2',6'-diethyl-N-(methoxymethyl)acetanilide]. Alachlor (as much as would dissolve in 100 mL water, no co-solvent used) was allowed to sit at room temperature in 2 N aqueous NaOH in the dark for several months, until the reaction was complete (as determined by loss of the parent compound in gas chromatographic analyses of hexane extracts). At this point, the product was extracted with dichloromethane (50 mL) and the solvent phase was dried at ambient temperature under a stream of nitrogen gas. The product is a colorless oily liquid with purity >95% (as determined by GC/MS analysis). Structure and mass spectrum are shown in Figure S1. MS m/z (relative intensity): 251 $[M]^+$ (0), 219 $[M-OCH_3-H]^+$ (19.7), 188 $[M-OCH_3, CH_2OH-H]^+$ (100), 160 $[M-OCH_3, COCH_2OH-H]^+$ (94.3). 1H NMR ($CDCl_3$) δ 7.34 (t, 1H, CHCHCH), 7.18 (d, 2H, CHCHCH), 4.95 (d, 2H, CH_2OCH_3), 3.61 (d, 2H, $COCH_2OH$), 3.49 (s, 3H, CH_2OCH_3), 3.28 (t, 1H, OH), 2.50 (m, 4H, 2- CH_3CH_2), 1.17 (t, 6H, 2- CH_3CH_2).

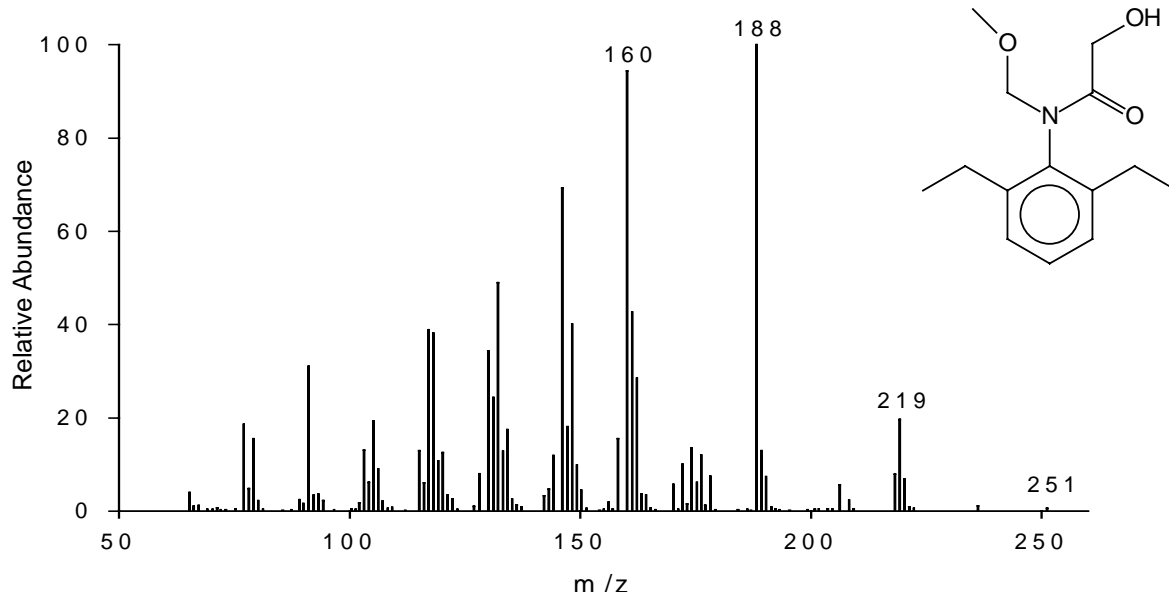


Figure S1. Structure and mass spectrum of hydroxyalachlor.

III. Deschloroalachlor [2',6'-diethyl-N-(methoxymethyl)acetanilide]. Procedure was based on one reported by Eykholt and Davenport, *Environ. Sci. Technol.*, **1998**, 32, 1482-1487. A small amount (100 mg) of alachlor was added to 100 mL of a 1:1 (v/v) water:acetone solution containing 2 g Fe(0) powder. The reductive dehalogenation occurred via a surface mediated reaction that (after several weeks of incubation at room temperature) results in replacement of chlorine by hydrogen. Once the reaction was complete, the product was extracted with hexane (50 mL). The final product (obtained on evaporation of the hexane) was a white powder with >95% purity (determined by GC/MS). Structure and mass spectrum are shown in Figure S2. MS m/z (relative intensity): 235 $[M]^+$ (26.7), 203 $[M-OCH_3-H]^+$ (42.4), 178 $[M-COCH_3, CH_3+H]^+$ (60.4), 161 $[M-COCH_3, OCH_3]^+$ (100). 1H NMR ($CDCl_3$) δ 7.26 (t, 1H, CHCHCH), 7.17 (d, 2H, CHCHCH), 4.89 (s, 2H, CH_2OCH_3), 3.43 (s, 3H, CH_2OCH_3), 2.54 (m, 4H-, 2- CH_3CH_2), 1.72 (s, 3H, $COCH_3$), 1.22 (t, 6H, 2- CH_3CH_2).

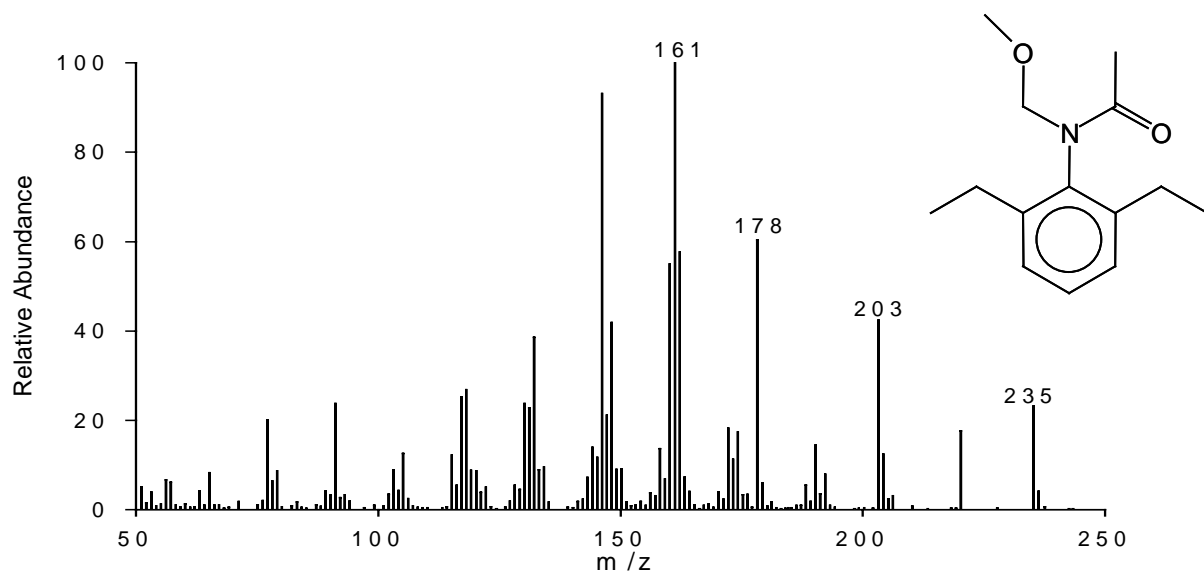


Figure S2. Structure and mass spectrum of deschloroalachlor.

IV. 2-Chloro-2'-6'-diethylacetanilide. Procedure was based on that given by Potter and Carpenter, *Environ. Sci. Technol.*, **1995**, 29, 1557-1563. A 200-mg sample of alachlor was dissolved in 250 mL of a 1:1 (v/v) solution of acetone/ 3 N aqueous HCl. This solution was heated at reflux for 24 hours. The resulting acid-catalyzed hydrolysis effects the loss of the *N*-alkoxymethyl group. Once the product was formed (as verified by gas chromatographic analysis of solvent extracts), the solution was cooled, NaCl was added to saturate the solution, and the product was extracted with dichloromethane (100 mL). The final product (obtained on evaporation of the dichloromethane) was a colorless crystal with >95% purity (determined by GC/MS). Structure and mass spectrum are shown in Figure S3. MS m/z (relative intensity): 225 $[M]^+$ (13.3), 176 $[M-CH_2Cl]^+$ (100), 148 $[M-COCH_2Cl]^+$ (19.6). 1H NMR ($CDCl_3$) δ 7.85 (s, 1H, NH), 7.28-7.10 (m, 3H, phenyl), 4.25 (s, 2H, $COCH_2Cl$), 2.60 (q, 4H, 2- CH_3CH_2), 1.22 (t, 6H, 2- CH_3CH_2).

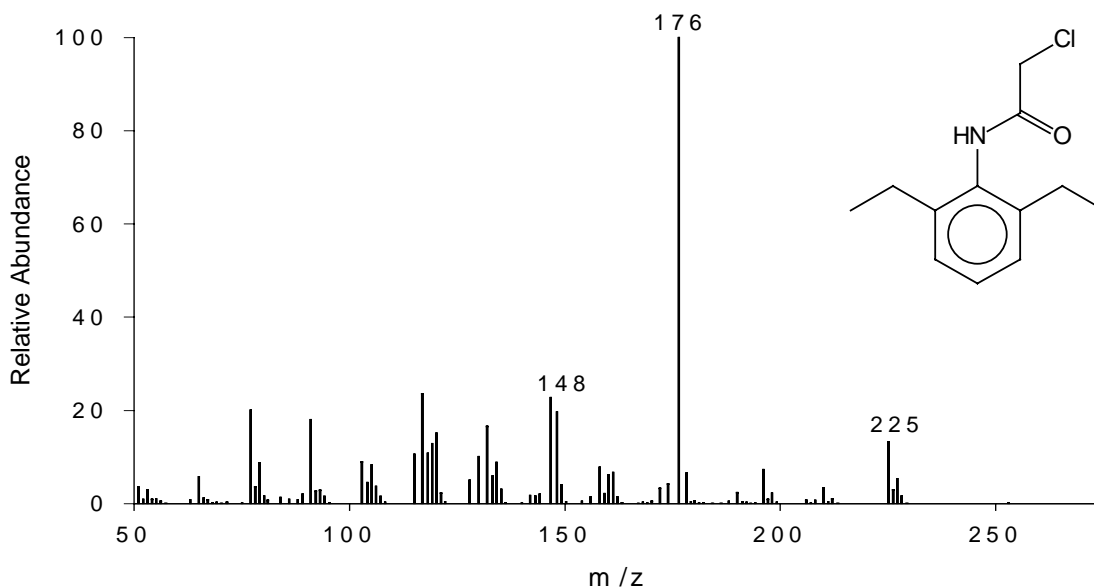


Figure S3. Structure and mass spectrum of 2-chloro-2'-6'-diethylacetanilide.

V. 2-Hydroxy-2'-6'-diethylacetanilide. Procedure was based upon that given by Potter and Carpenter, *Environ. Sci. Technol.*, **1995**, 29, 1557-1563. A 100-mg sample of 2-chloro-2'-6'-diethylacetanilide was dissolved in 100 mL of a 35:65 (v/v) solution of acetone/ 0.7 N aqueous NaOH. This solution was heated at reflux for 8 hours. The solution was cooled, was saturated with NaCl, and the product was then extracted with dichloromethane (50 mL). The white powder (obtained on evaporation of the dichloromethane) had a final purity of >95% (determined by GC/MS). Structure and mass spectrum are shown in Figure S4. MS m/z (relative intensity): 207 $[M]^+$ (7), 176 $[M-CH_2OH]^+$ (100), 148 $[M-COCH_2OH]^+$ (15.1). 1H NMR ($CDCl_3$) δ 7.85 (s, 1H, NH), 7.25-7.10 (m, 3H, phenyl), 4.35 (d, 2H, $COCH_2OH$), 3.48 (s, 1H, OH), 2.60 (q, 4H, $2-CH_3CH_2$), 1.22 (t, 6H, $2-CH_3CH_2$).

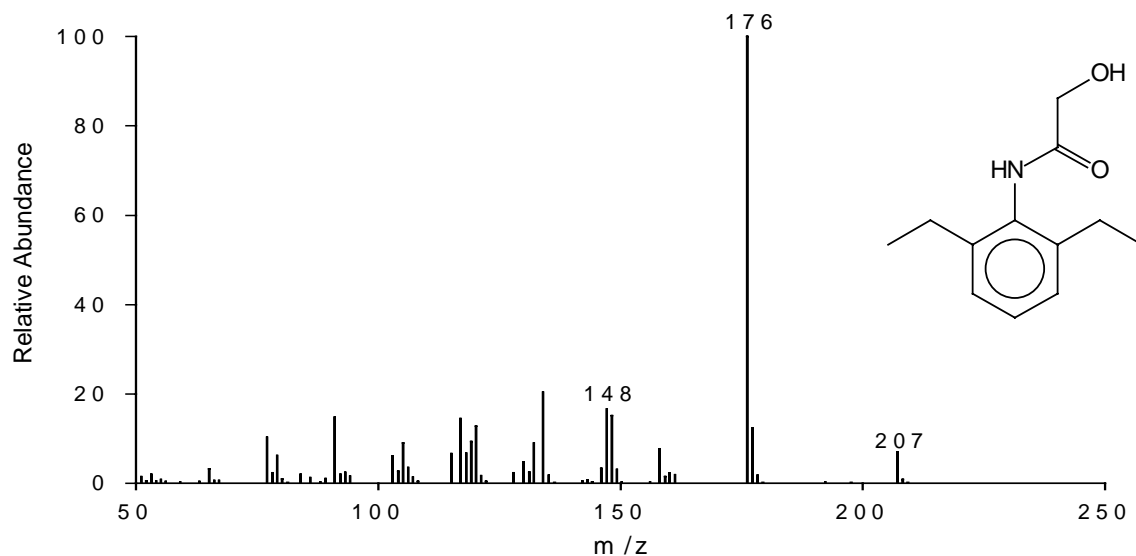


Figure S4. Structure and mass spectrum of 2-hydroxy-2'-6'-diethylacetanilide.

VI. 2-Hydroxy-2'-6'-diethyl-N-methylacetanilide. Procedure was based on that of Chiron *et al.*, *Environ. Toxicol. and Chem.*, **1995**, *14*, 1287-1298. In 50 mL of dichloromethane (DCM), a 1.4-mL aliquot of triethylamine, a 0.55-mL aliquot of 2,6-diethylaniline, and 0.67 mL of acetoxyacetylchloride were added in succession. Reaction was allowed to proceed at room temperature for 21 hours. The reaction mixture was then washed with 25 mL water and was dried over MgSO₄. The remaining DCM solution was evaporated. To 0.10 g of the above product in 20 mL anhydrous tetrahydrofuran (THF), 0.15 g of NaH in 3 mL anhydrous THF was added. The reaction was allowed to proceed for 1 hour at room temperature before adding 0.20 mL of CH₃I in 10 mL of THF, at which point the reaction was allowed to continue for an additional 2 hours. The remaining solution was blown dry with nitrogen gas. To this product in 12 mL of THF, 25 mL of 1% aqueous NaOH was added and reacted for 15 min. Work-up yielded the product, a brownish oily liquid, at >90% purity (determined by GC/MS). Structure and mass spectrum are shown in Figure S5. MS *m/z* (relative intensity): 221 [M]⁺· (2.9), 190 [M-CH₂OH]⁺· (100), 162 [M-COCH₂OH]⁺· (19.4). ¹H NMR (CDCl₃) δ 7.38-7.10 (m, 3H, phenyl), 3.59 (d, 2H, COCH₂OH), 3.39 (s, 1H, OH), 3.24 (s, 3H, NCH₃), 2.51 (m, 4H, 2-CH₃CH₂), 1.24 (t, 6H, 2-CH₃CH₂).

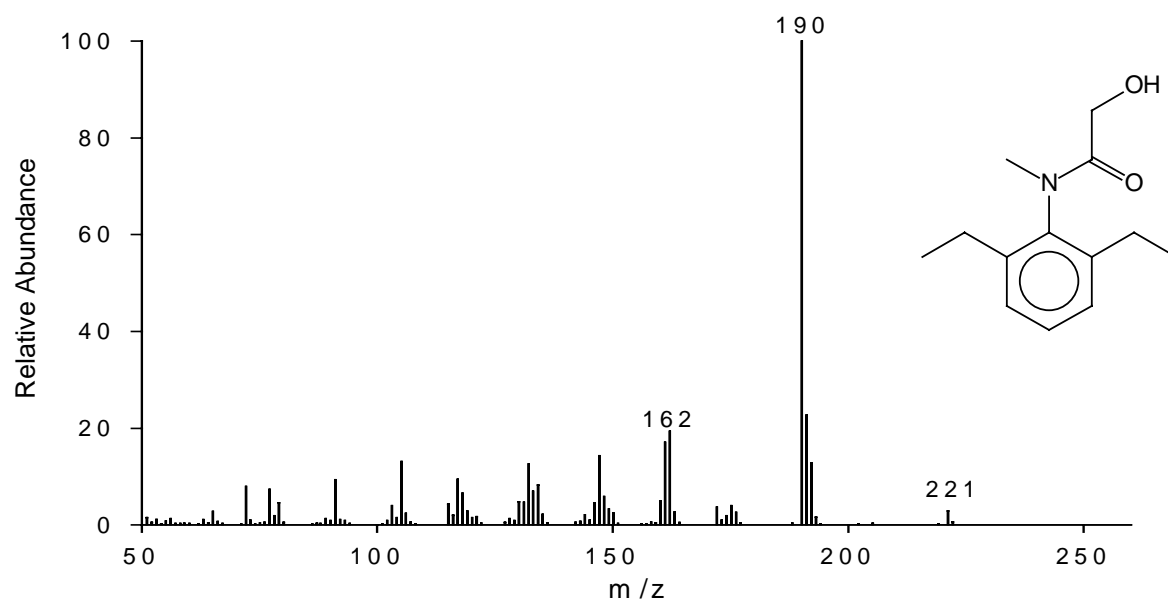


Figure S5. Structure and mass spectrum of 2-hydroxy-2'-6'-diethyl-N-methylacetanilide.

VII. 2'-6'-Diethylacetanilide. Procedure was based on that given by Nesnow *et al.*, *Chem Res. Toxicol.*, **1995**, 8, 209-217. To a 125 mL sample of anhydrous ethyl acetate, 17 g of 2,6-diethylaniline was added under nitrogen. To this mixture, 25 mL of acetylchloride was added dropwise, and the solution was heated at reflux for 2 hours under nitrogen. After the reaction was complete, the ethyl acetate was distilled off, and 100 mL ice-cold water was added to the oily residue. This solution was extracted with dichloromethane (150 mL). The organic layer was washed with water (3×125 mL), dried over MgSO_4 , filtered and then concentrated by evaporation. The final product was isolated by extracting the resulting solid with dichloromethane (50 mL). The product (obtained on evaporation of the dichloromethane) was a white powder with a purity >95% (determined by GC/MS). Structure and mass spectrum are shown in Figure S6. MS m/z (relative intensity): 191 $[\text{M}]^+$ (54.1), 148 $[\text{M}-\text{COCH}_3]^+$ (100), 134 $[\text{M}-\text{COCH}_3, \text{N}]^+$ (91.9). ^1H NMR (CDCl_3) δ 7.25-7.09 (m, 3H, phenyl), 6.65 (s, 1H, NH), 2.71 (dq, 4H, 2- CH_3CH_2), 2.22 (s, 3H, COCH_3), 1.20 (t, 6H, 2- CH_3CH_2).

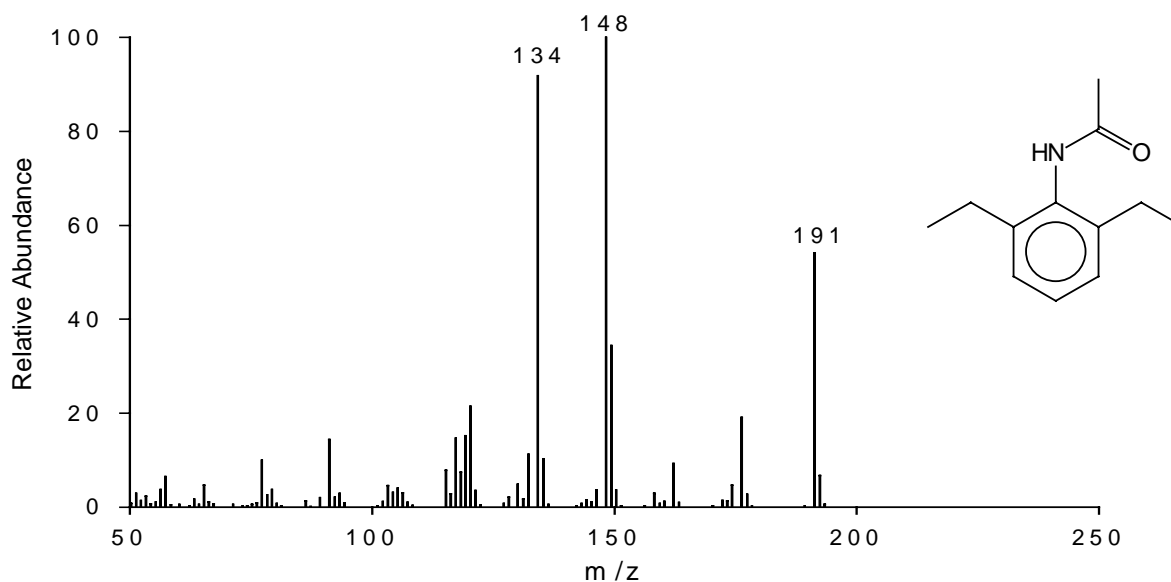


Figure S6. Structure and mass spectrum of 2'-6'-diethylacetanilide.

XII. Hydroxymetolachlor [2-hydroxy-2'-ethyl-6'-methyl-N-(2-methoxy-1-methyl-ethyl)acetanilide]. To 30 mL of glycol dimethyl ether, 1.6 g of sodium acetate and 0.1 g NaI were added in succession, followed by 200 mg of metolachlor. The solution was refluxed at 95 °C with stirring for 5-7 hours. The liquid was decanted and the solvent evaporated. A 5-mL aliquot of 1 N aqueous NaOH was added immediately, and the reaction was left to stand overnight at room temperature. The final product, a yellowish oily residue, was extracted with dichloromethane. Purity >95% (determined by GC/MS). Structure and mass spectrum are shown in Figure S7. MS m/z (relative intensity): 265 $[M]^+$ (0), 220 $[M-CH_2OCH_3]^+$ (40.7), 193 $[M-CH(CH_3)CH_2OCH_3+H]^+$ (13.1), 162 $[M-CH(CH_3)CH_2OCH_3, CH_2OH+H]^+$ (100). 1H NMR ($CDCl_3$) δ 7.25-7.07 (m, 3H, phenyl), 4.35 (m, 1H, $CH(CH_3)CH_2$), 3.80 (m, 2H, $CH(CH_3)CH_2$), 3.57 (d, 2H, $COCH_2OH$), 3.41 (s, H, OH), 3.27 (s, 3H, OCH_3), 2.55 (m, 2H, CH_3CH_2), 2.23 (s, 3H, CH_3), 1.25 (t, 3H, CH_3CH_2), 1.10 (d, 3H, $CH(CH_3)CH_2$).

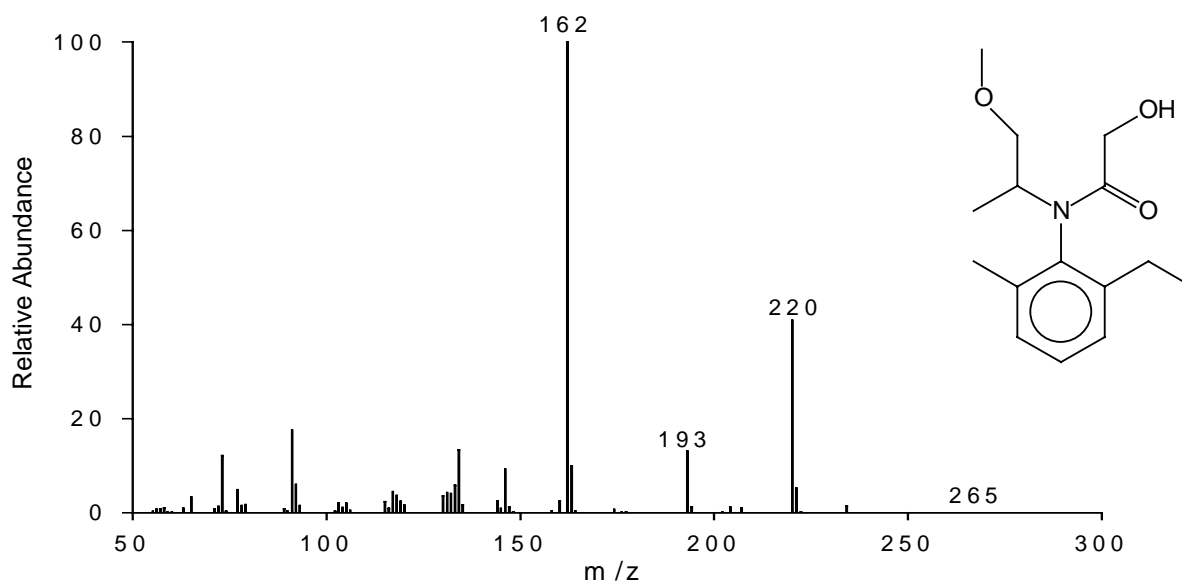


Figure S7. Structure and mass spectrum of hydroxymetolachlor.

XIII. Deschlorometolachlor [2'-ethyl-6'-methyl-N-(2-methoxy-1-methylethyl)

acetanilide]. Procedure was based on one reported by Eykholt and Davenport, *Environ. Sci. Technol.*, **1998**, 32, 1482-1487. To 100 mL of a 1:1 (v/v) mixture of water and methanol, 2 g of Fe(0) powder was added, followed by 100 mg of metolachlor. The reductive dehalogenation occurred via a surface-mediated reaction that results in replacement of chlorine by hydrogen. Once the reaction was complete, the product was extracted with hexane (50 mL). The final product (on evaporation of the hexane) was a white powder with >95% purity (determined by GC/MS). Structure and mass spectrum are shown in Figure S8. MS m/z (relative intensity): 249 $[M]^+$ (0), 204 $[M-CH_2OCH_3]^+$ (28.1), 177 $[M-CH(CH_3)CH_2OCH_3+H]^+$ (7.2), 162 $[M-CH(CH_3)CH_2OCH_3, CH_3+H]^+$ (100), 133 $[M-CH(CH_3)CH_2OCH_3, COCH_3]^+$ (6.3). 1H NMR ($CDCl_3$) δ 7.21-7.10 (m, 3H, phenyl), 4.24 (m, 1H, $CH(CH_3)CH_2$), 3.72-3.42 (2m, 2H, $CH(CH_3)CH_2$), 3.21 (2s, 3H, CH_2OCH_3), 2.55 (m, 2H, CH_3CH_2), 2.23 (2s, 3H, CH_3), 1.67 (2s, 3H, $COCH_3$), 1.21 (t, 3H, CH_3CH_2), 1.10 (2d, 3H, $CH(CH_3)CH_2$).

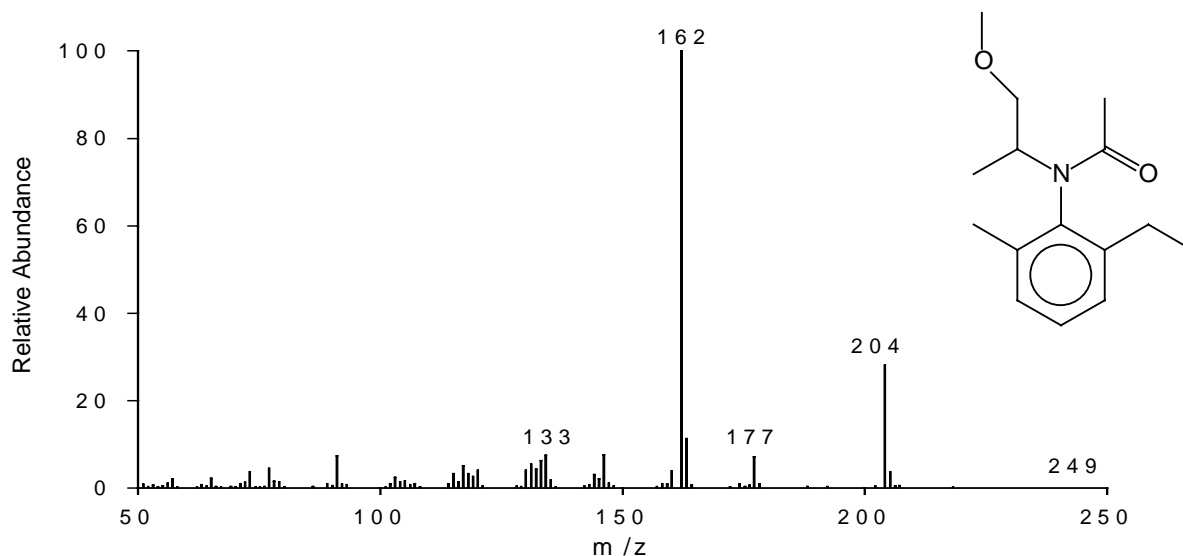


Figure S8. Structure and mass spectrum of deschlorometolachlor.

XIV. Metolachlor morpholinone [4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholinone].

To 100 mL of an aqueous solution of HCL (6 N), 56 mg of metolachlor (dissolved in 1 mL of methanol) was added and was incubated at 85 °C for 120 min. After cooling and extracting any unreacted metolachlor with hexane (100 mL), the aqueous solution was basified with 350 mL of 2 N aqueous NaOH. The aqueous solution was extracted with 200 mL of dichloromethane. The solvent was blown down to give the product, a white powder, with >95% purity (determined by GC/MS). Structure and mass spectrum are shown in Figure S9. MS m/z (relative intensity): 233 $[M]^+$ (50.3), 188 $[M-CH_2OCH_2-H]^+$ (48.8), 161 $[M-CH_2OCH_2CH(CH_3)]^+$ (83.0), 146 $[M-CH_2OCH_2CH(CH_3), O+H]^+$ (100). 1H NMR ($CDCl_3$) δ 7.25-7.09 (m, 3H, phenyl), 4.39 (q, 2H, $NCOCH_2$), 4.05 (m, 1H, $NCH(CH_3)CH_2$), 3.75 (m, 2H, $NCH(CH_3)CH_2$), 2.57 (2q, 2H, CH_3CH_2), 2.25 (2s, 3H, CH_3), 1.26 (2t, 3H, CH_3CH_2), 1.13 (2d, 3H, $NCH(CH_3)CH_2$).

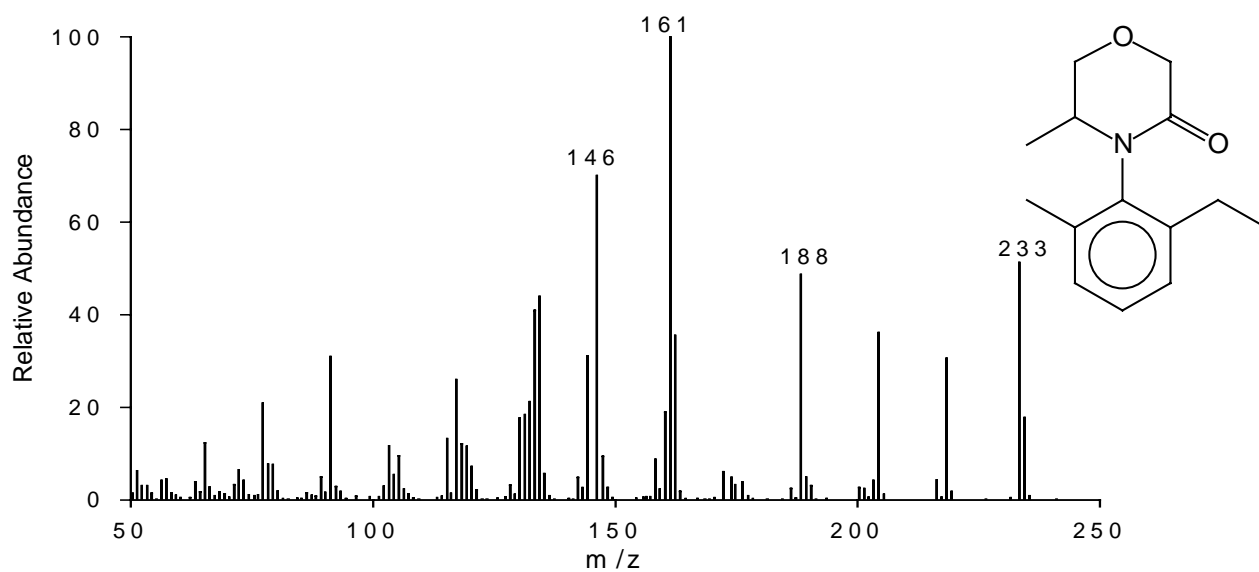


Figure S9. Structure and mass spectrum of metolachlor morpholinone.

XV. Metolachlor propanol [2-chloro-2'-ethyl-6'-methyl-N-(2-hydroxy-1-methyl-ethyl)acetanilide]. To 100 mL of 6 N HCl, 54 mg of metolachlor (dissolved in 1 mL methanol) was added and was incubated at 85 °C for 120 min. After cooling and extracting the remaining metolachlor with hexane (100 mL), the aqueous solution was neutralized with 51.5 g of NaCO₃. After neutralization, the product was extracted from the aqueous solution with 50 mL dichloromethane. The solvent was evaporated to give the product, a white powder, with >83% purity (determined by GC/MS). The structure and mass spectrum are shown in Figure S10. MS *m/z* (relative intensity): 269 [M]⁺ (1.4), 238 [M-CH₂OH]⁺ (49.4), 162 [M-CH₂OH, -COCH₂Cl + H]⁺ (100), 146 [M-CH₂OH, CH₃, COCH₂Cl]⁺ (56.3). ¹H NMR (CDCl₃) δ 7.26-7.10 (m, 3H, phenyl), 4.05 (m, H, CH(CH₃)CH₂), 3.87 (m, 2H, CH(CH₃)CH₂), 3.66 (2q, 2H, COCH₂Cl), 3.45 (s, 1H, OH), 2.60 (2q, 2H, CH₃CH₂), 2.25 (2s, 3H, CH₃), 1.25 (2t, 3H, CH₃CH₂), 1.18 (2d, 3H, CH(CH₃)CH₂).

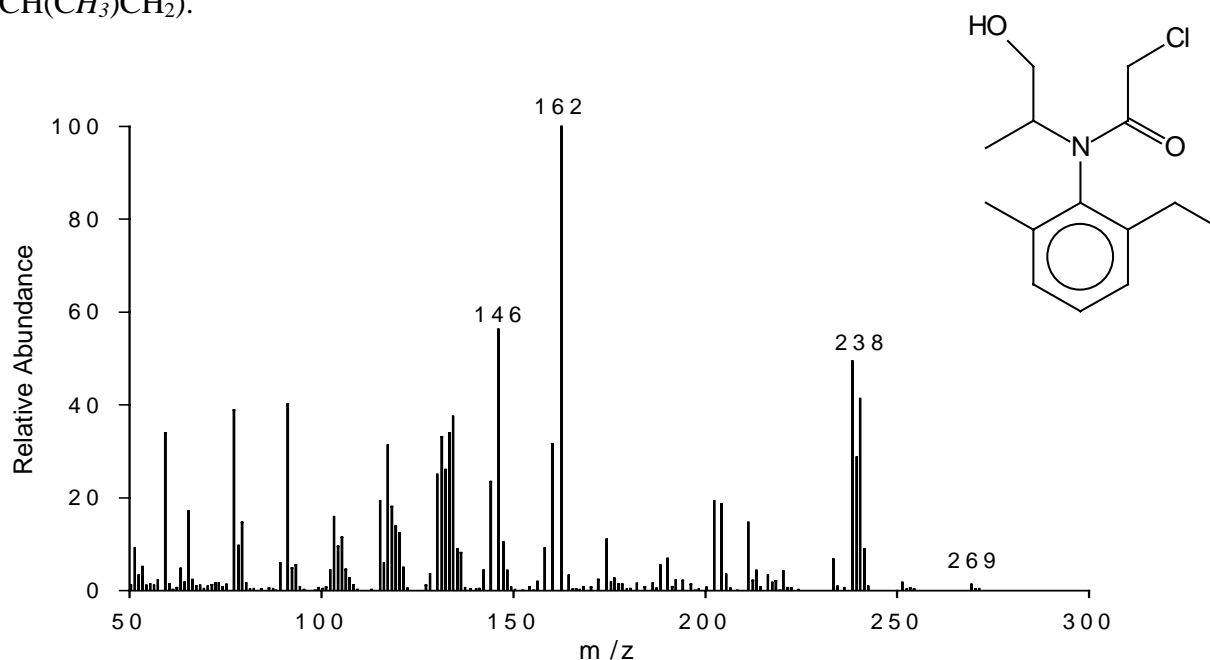


Figure S10. Structure and mass spectrum of metolachlor propanol.

XVI. Deschloroacetylmetolachlor [2'-ethyl-6'-methyl-N-(2-methoxy-1-methylethyl)aniline].

A 53 mg sample of tosyl chloride was dissolved in 127 mL of pyridine. To this mixture, 28 mL of 1-methoxy-2-propanol was added dropwise while maintaining the solution in an ice bath. The ice bath was removed and the solution was stirred overnight at room temperature. After stirring, the solution was extracted with 250 mL of deionized water. A 200-mL portion of the aqueous extract was then extracted with ether 3 times (30 mL: 30 mL: 15 mL). The ether extracts were combined and were washed with 2 N aqueous H₂SO₄ until the wash came through acidic. The ether solution was dried with sodium sulfate and was left to evaporate, leaving 1-methoxy-2-tosylpropane. To 12 mL of the 1-methoxy-2-tosylpropane, 3 mL of 2-ethyl-6-methyl aniline was added, along with 2 mL of pyridine. The reaction was heated at 100 °C overnight to yield deschloroacetylmetolachlor. The product, a yellowish liquid, was further purified using a silica gel column. Final purity was >95% (determined by GC/MS). Structure and mass spectrum are shown in Figure S11. MS *m/z* (relative intensity): 207 [M]⁺ (6.8), 162 [M-CH₂OCH₃]⁺ (100), 133 [M-CH(CH₃)CH₂OCH₃-H]⁺ (17.5). ¹H NMR (CDCl₃) δ 7.03-6.83 (m, 3H, phenyl), 3.35 (m, 1H, CH(CH₃)CH₂), 3.34 (m, 2H, CH₂OCH₃), 3.32 (s, 3H, CH₂OCH₃), 2.60 (m, 2H, CH₃CH₂), 2.25 (s, 3H, CH₃), 1.20 (t, 3H, CH₃CH₂), 1.10 (m, 3H, CH(CH₃)CH₂).

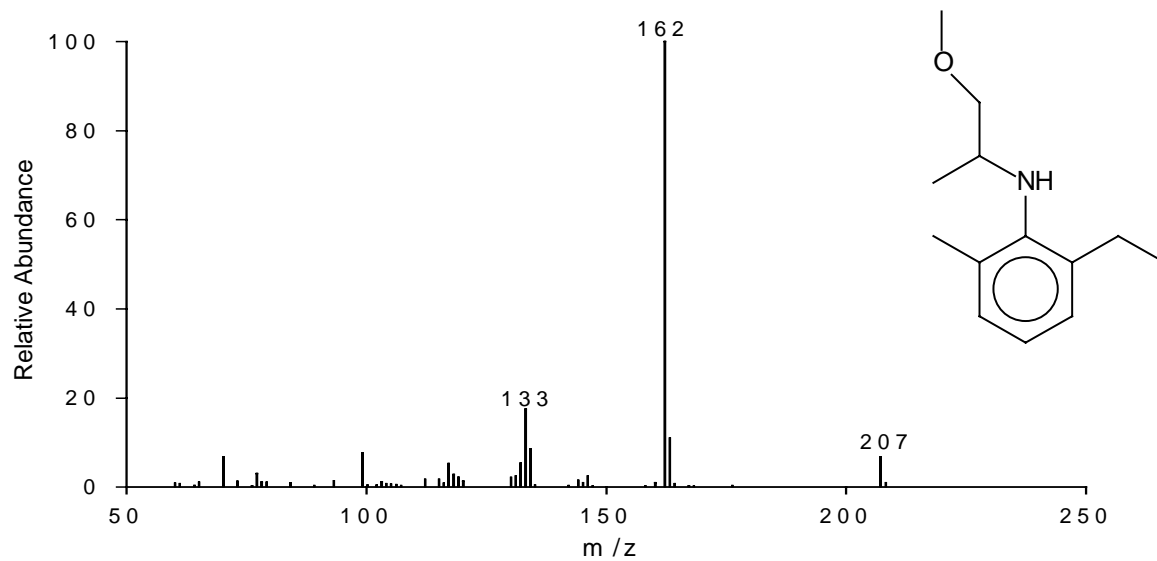


Figure S11. Structure and mass spectrum of deschloroacetylmetolachlor.

XXI. Hydroxyacetochlor [2-hydroxy-2'-ethyl-6'-methyl-N-(ethoxymethyl)

acetanilide]. Procedure was based on that of Feng, *Pestic. Biochem. Physiol.*, **1991**, *40*, 136-142. To 30 mL of glycol dimethyl ether, 1.6 g of sodium acetate and 0.1 g NaI were added in succession, followed by 200 mg of acetochlor. The solution was refluxed at 95 °C with stirring for 5-7 hours. The liquid was decanted and the solvent evaporated. A 5-mL aliquot of 1 N aqueous NaOH was immediately added, and the solution was left overnight to react. The final product, a yellow liquid, was extracted with dichloromethane (50 mL). Final purity was >95% (determined by GC/MS). Structure and mass spectrum are shown in Figure S12. MS m/z (relative intensity): 251 $[M]^+$ (4.5), 205 $[M-OCH_2CH_3-H]^+$ (66.8), 174 $[M-OCH_2CH_3, CH_2OH-H]^+$ (100), 146 $[M-OCH_2CH_3, COCH_2OH-H]^+$ (98.6). 1H NMR ($CDCl_3$) δ 7.25-7.12 (m, 3H, phenyl), 5.03 (dd, 2H, $CH_2OCH_2CH_3$), 4.26 (d, 2H, $COCH_2OH$), 3.61 (s, H, OH), 3.50 (q, 2H, $CH_2OCH_2CH_3$), 2.54 (m, 2H, CH_3CH_2), 2.22 (s, 3H, CH_3), 1.23 (t, 3H, CH_3CH_2), 1.16 (q, 3H, $CH_2OCH_2CH_3$).

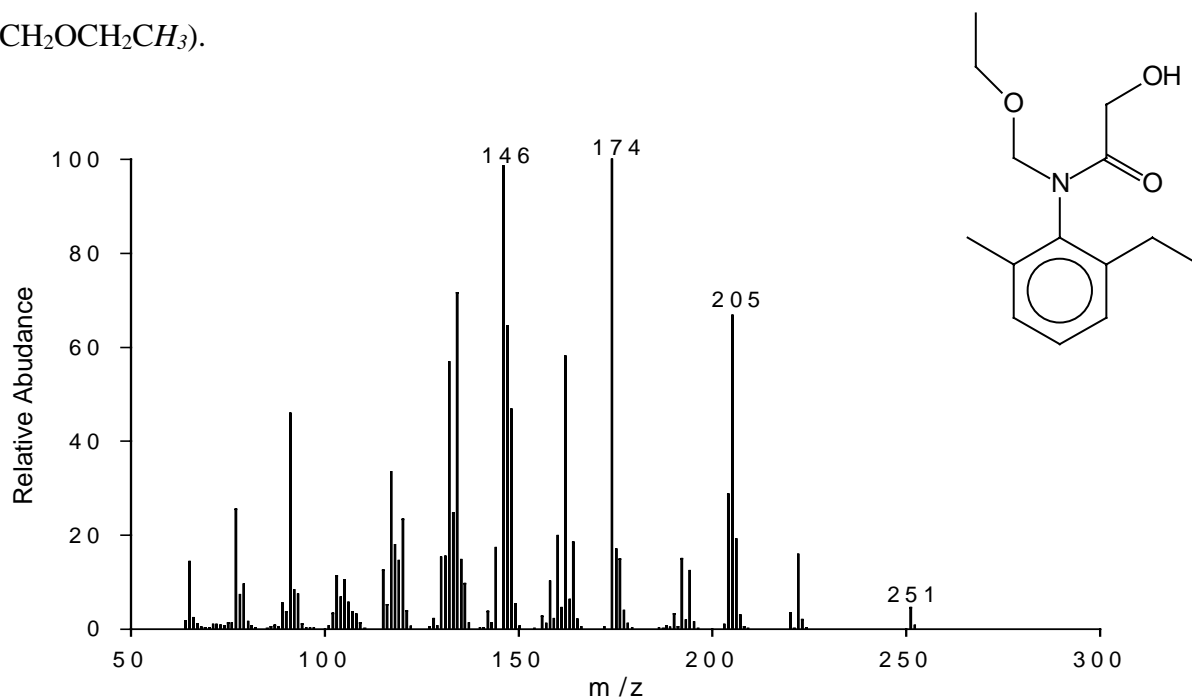


Figure S12. Structure and mass spectrum of hydroxyacetochlor.

XXII. Deschloroacetochlor [2'-ethyl-6'-methyl-N-(ethoxymethyl)acetanilide]. To 100 mL of a 1:1 (v/v) mixture of water and methanol, 2 g of Fe(0) powder was added, followed by 100 mg of acetochlor. The reductive dehalogenation occurred via a surface-mediated reaction that resulted in replacement of chlorine by hydrogen. Once the reaction was complete, the product was extracted with hexane (50 mL). The final product (obtained on evaporation of the hexane) was a white powder, >95% pure (determined by GC/MS). Structure and mass spectrum are shown in Figure S13. MS m/z (relative intensity): 235 $[M]^+$ (10.8), 206 $[M-CH_2CH_3]^+$ (65.6), 189 $[M-CH_3, OCH_3]^+$ (26.6), 164 $[M-CH_2CH_3, COCH_3+H]^+$ (100). 1H NMR ($CDCl_3$) δ 7.25-7.12 (m, 3H, phenyl), 4.98 (dd, 2H, $CH_2OCH_2CH_3$), 3.71 (q, 2H, $CH_2OCH_2CH_3$), 2.57 (m, 2H, CH_3CH_2), 2.16 (s, 3H, CH_3), 1.75 (s, 3H, $COCH_3$), 1.24 (t, 3H, CH_3CH_2), 1.18 (t, 3H, $CH_2OCH_2CH_3$).

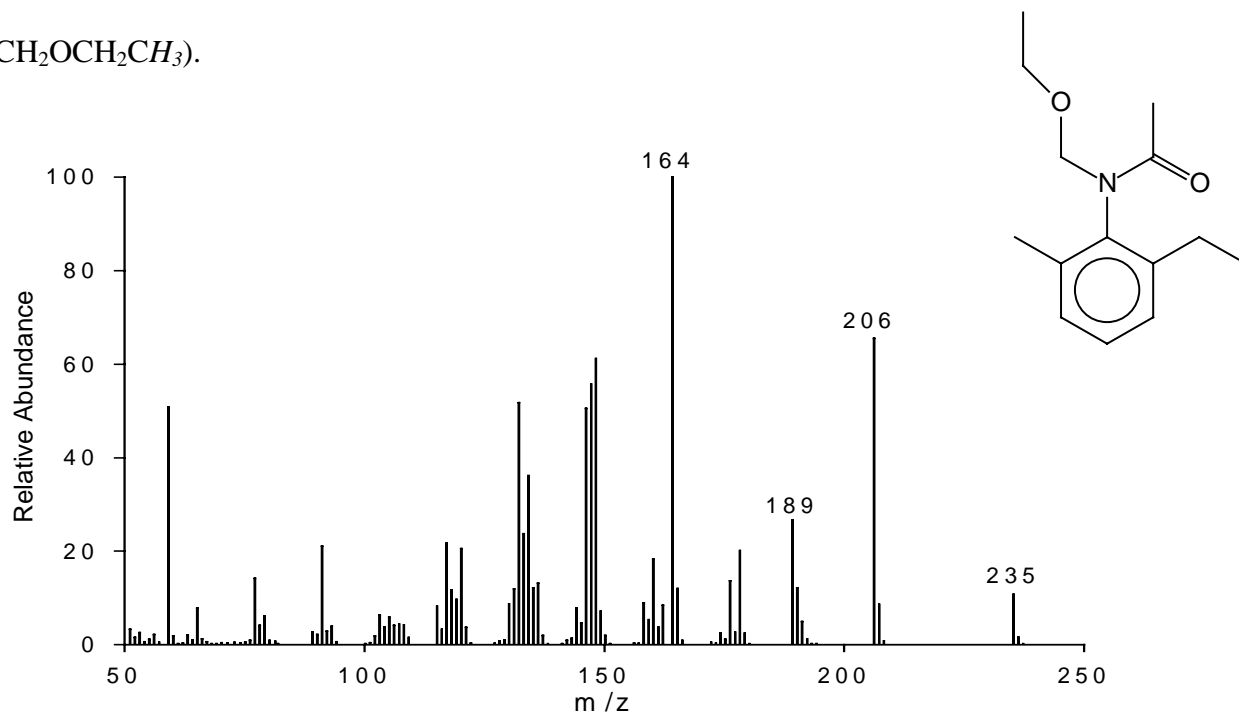


Figure S13. Structure and mass spectrum of deschloroacetochlor.

XXV. 2-Chloro-2'-ethyl-6'-methylacetanilide. To 250 mL of anhydrous ethyl acetate, 30 g of 2-ethyl-6-methyl aniline was added under nitrogen. To this mixture, 44 g of chloroacetyl-chloride was added dropwise, and the solution was heated at reflux for 2 hours under nitrogen. After the reaction was complete, the ethyl acetate was distilled off, and 200 mL ice-cold water was added to the oily residue. The resulting solution was extracted with 300 mL of dichloromethane (DCM). The organic layer was washed with water (3×250 mL), was dried over MgSO_4 , was filtered and was then concentrated by evaporation. The desired product was isolated from its di-chloroacetylated side-product by adding 5 mL of an aqueous solution of NaOH (2 N), and conducting a subsequent extraction using 100 mL of DCM. The final product (obtained by evaporating the DCM) was a white powder, >95% pure (determined by GC/MS). Structure and mass spectrum are shown in Figure S14. MS m/z (relative intensity): 211 $[\text{M}]^+$ (19.1), 162 $[\text{M}-\text{CH}_2\text{Cl}]^+$ (100), 134 $[\text{M}-\text{COCH}_2\text{Cl}]^+$ (26.5). ^1H NMR (CDCl_3) δ 7.85 (s, 1H, NH), 7.88-7.24 (m, 3H, phenyl), 4.25 (s, 2H, COCH_2Cl), 2.60 (q, 2H, CH_3CH_2), 2.20 (s, 3H, CH_3) 1.20 (t, 3H, CH_3CH_2).

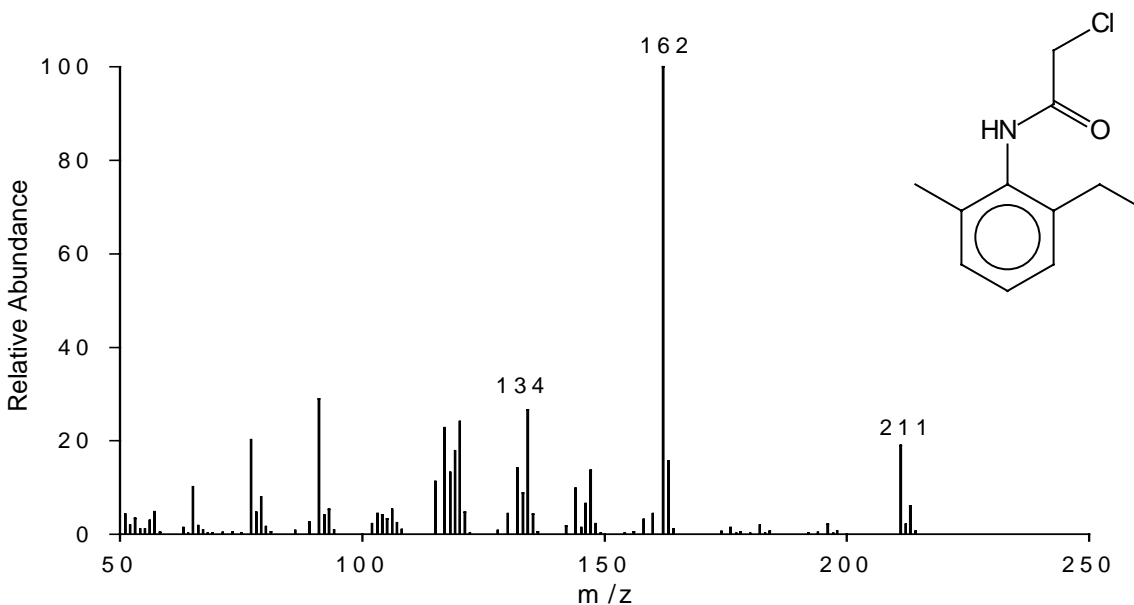


Figure S14. Structure and mass spectrum of 2-chloro-2'-ethyl-6'-methylacetanilide.

XXVI. 2-Hydroxy-2'-ethyl-6'-methylacetanilide. To 100 mL of a 35:65 (v/v) mixture of acetone/ 0.7 N aqueous NaOH, 100 mg of 2-chloro -2'-ethyl-6'-methyl acetanilide was added, and the solution was heated at reflux for 8 hours. The solution was cooled, saturated with NaCl, and the product was then extracted with dichloromethane (50 mL). The final product, a white powder, was >95% pure (determined by GC/MS). Structure and mass spectrum are shown in Figure S15. MS m/z (relative intensity): 193 $[M]^+$ (14.5), 162 $[M-CH_2OH]^+$ (100), 134 $[M-COCH_2OH]^+$ (41.4). 1H NMR ($CDCl_3$) δ 7.75 (s, 1H, NH), 7.23-7.04 (m, 3H, phenyl), 4.34 (d, 2H, $COCH_2OH$), 3.70 (s, 1H, OH), 2.60 (q, 2H, CH_3CH_2), 2.23 (s, 3H, CH_3), 1.15 (t, 3H, CH_3CH_2).

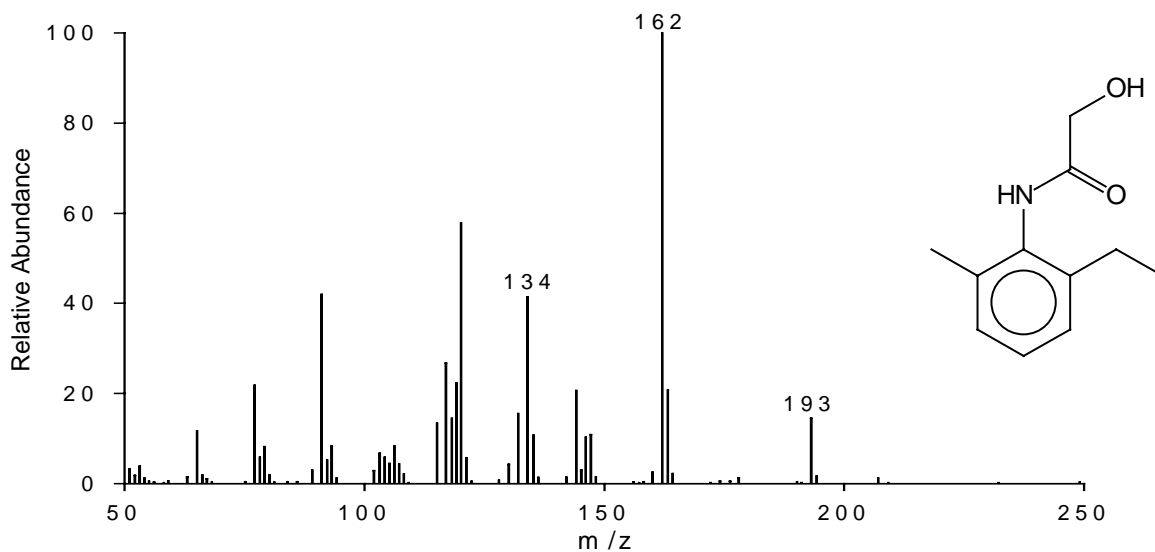


Figure S15. Structure and mass spectrum of 2-hydroxy-2'-ethyl-6'-methylacetanilide.

XXVII. 2'-Ethyl-6'-methylacetanilide. In 125 mL anhydrous ethyl acetate, 15 g of 2-ethyl-6-methyl aniline was dissolved under nitrogen. To this mixture, 25 mL of acetylchloride was added dropwise, and the solution was heated at reflux for 2 hours under nitrogen. After the reaction was complete the ethyl acetate was distilled off and 100 mL ice-cold water was added to the oily residue. The resulting solution was extracted with dichloromethane (150 mL). The organic layer was washed with water (3×125 mL), was dried over MgSO_4 , was filtered, and then was concentrated by evaporation of the dichloromethane. The final product was isolated by extracting the resulting solid with dichloromethane. The product (obtained on evaporation of the dichloromethane) is a white powder with a purity >95% (determined by GC/MS). Structure and mass spectrum are shown in Figure S16. MS m/z (relative intensity): 177 $[\text{M}]^+$ (38.4), 134 $[\text{M}-\text{COCH}_3]^+$ (77.0), 120 $[\text{M}-\text{COCH}_3, \text{N}]^+$ (100). ^1H NMR (CDCl_3) δ 7.25-7.06 (m, 3H, phenyl), 6.76 (s, 1H, NH), 2.62 (m, 2H, CH_3CH_2), 2.27 (m, 3H, CH_3), 2.23 (1.75) (2s, 3H, COCH_3), 1.10 (s, 3H, CH_3CH_2).

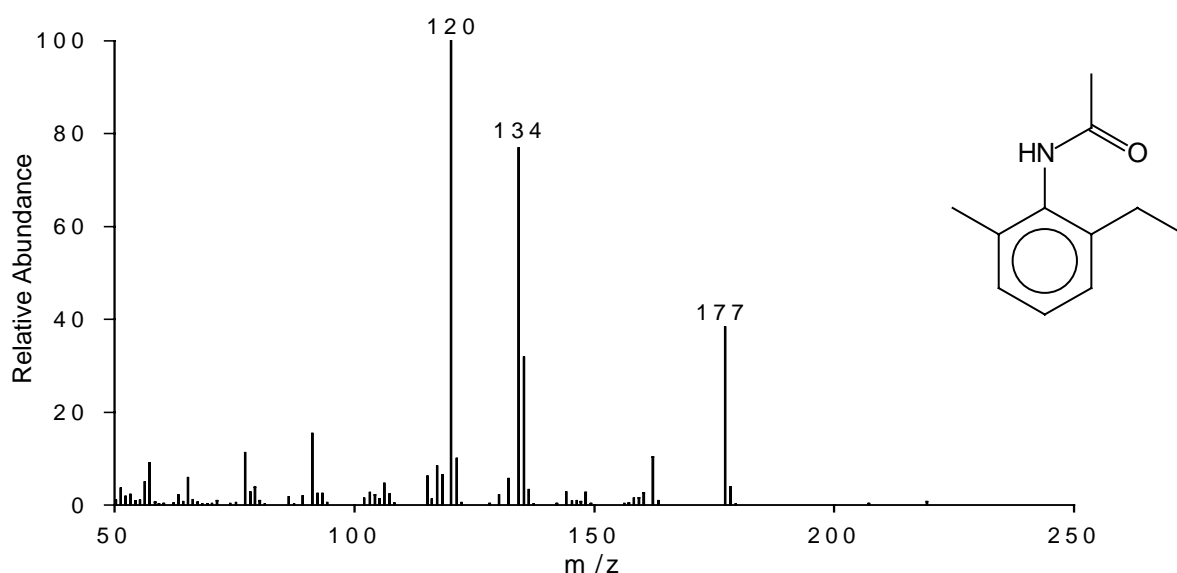


Figure S16. Structure and mass spectrum of 2'-ethyl-6'-methylacetanilide.

XXX. Deschlorodimethenamid [*N*-(2,4-dimethyl-3-thienyl)-*N*-(2-methoxy-1-methylethyl)acetamide]. To a 100-mL aliquot of a 1:1 (v/v) mixture of water and methanol, 2 g of Fe (0) powder was added, followed by 100 mg of dimethenamid. The reductive dehalogenation occurred via a surface-mediated reaction that results in replacement of chlorine by hydrogen. Once the reaction was complete, the product was extracted with hexane (50 mL). The final product (on evaporation of the hexane) was a white powder with >95% purity (determined by GC/MS). Structure and mass spectrum are shown in Figure S17. MS m/z (relative intensity): 241 $[M]^+$ (1.9), 196 $[M-CH_2OCH_3]^+$ (58.2), 169 $[M-CH(CH_3)CH_2OCH_3+H]^+$ (51.0), 154 $[M-CH(CH_3)CH_2OCH_3, CH_3+H]^+$ (100). 1H NMR ($CDCl_3$) δ 6.77 (s, 1H, SCHC), 4.68 (4.58) (m, 1H, $CH(CH_3)CH_2$), 3.54 (3.31) (m, 2H, CH_2OCH_3), 3.21 (3.23) (s, 3H, CH_2OCH_3), 2.06 (2.31) (d, 6H, 2- CH_3), 1.72 (s, 3H, $COCH_3$), 1.19 (1.06) (d, 3H, $CH(CH_3)CH_2$).

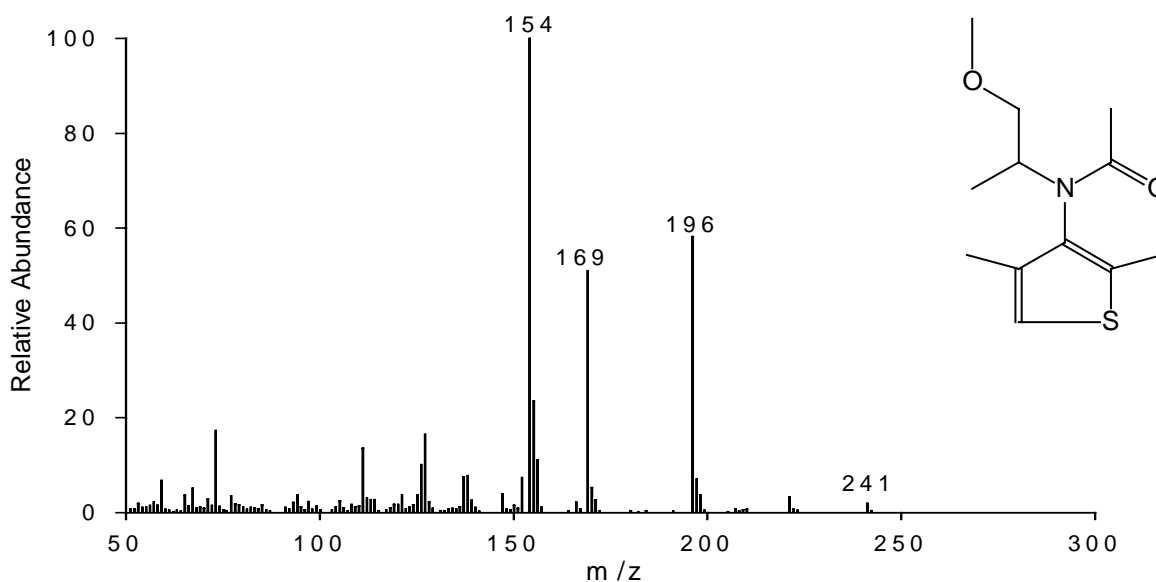


Figure S17. Structure and mass spectrum of deschlorodimethenamid.

Table S1. Mean SPE recoveries of ionic chloroacetamide degradates obtained from triplicate analyses of 500 mL water samples fortified at 3 µg/L, along with method detection limits (MDLs) and minimum reporting limits (MRLs). Note that preservatives were not used, as these were found to adversely affect recovery of ionic analytes.

Analyte #	Identity	DI Water		Loch Raven Water		MDL (ng/L)	MRL (ng/L)
		Mean Recovery (%)	RSD* (%)	Mean Recovery (%)	RSD (%)		
IX	alachlor oxanilic acid	76	4	78	5	7	20
X	alachlor ethane sulfonic acid	93	5	94	4	100	320
XVIII	metolachlor oxanilic acid	85	3	87	5	7	20
XIX	metolachlor ethane sulfonic acid	94	3	91	7	90	280
XXIII	acetochlor oxanilic acid	81	4	80	4	7	20
XXIV	acetochlor ethane sulfonic acid	96	5	98	4	100	320
	2-benzoylbenzoic acid (surrogate standard)	76	4	Nt†		Nt	

*RSD = relative standard deviation

†Nt = Not tested

Table S2. Concentrations of herbicide and herbicide degradates (in ng/L) along with dissolved oxygen (mg/L) and chloride (g/L) measured in the upper Chesapeake Bay on July 17, 2003. Standard deviations are based on triplicate analyses for the neutral herbicide degradates and parent herbicides, and standard deviations for the OAs are based on duplicate analyses.

#	Identity	Depth (m)											20	21
		2	5	8	10.5	11	11.5	13.5	18	19				
I	alachlor	9.7(0.3)	8.9(1.9)	9.7(0.3)	9.5(0.9)	10(1)	8.5(1.5)	8.4(0.2)	6.8(0.5)	6.4(1.3)	6.4(0.9)	4.3(1.0)		
II	hydroxyalachlor	14(2)	12(1)	12(2)	12(1)	10(1)	12(1)	12(2)	11(1)	9.1(0.7)	10(1)	8.0(2.4)*		
III	deschloroalachlor	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd		
IV	2-chloro-2'-6'-diethylacetanilide	94(5)	64(4)	58(3)	41(3)	46(2)	47(6)	46(2)	27(1)	25(1)	23(2)	12(2)		
V	2-hydroxy-2'-6'-diethylacetanilide	50(2)	41(1)	36(2)	19(1)	21(2)	16(1)	22(2)	18(3)	14(2)	14(2)	9.1(1.9)		
VI	2-hydroxy-2'-6'-diethyl-N-methylacetanilide	33(4)	31(2)	30(2)	29(1)	25(2)	28(4)	23(3)	22(5)	16(2)	16(1)	9.2(0.7)*		
VII	2'-6'-diethylacetanilide	110(5)	93(5)	70(4)	52(1)	70(6)	71(1)	67(3)	33(2)	29(1)	27(2)	25(4)		
VIII	2,6-diethylaniline	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33		
IX	alachlor oxanilic acid	Nm	Nm	25(4)	Nm	10(1)*	Nm	Nd	Nd	Nd	Nm	Nd		
X	alachlor ethane sulfonic acid	Nm	Nm	Nd	Nm	Nd	Nm	Nd	Nd	Nd	Nm	Nd		
XI	metolachlor	19(1)	16(1)	16(1)	12(1)	13(1)	14(1)	11(1)	7.4(0.6)	6.5(0.5)	5.3(0.2)	4.1(0.4)		
XII	hydroxymetolachlor	53(3)	47(3)	46(2)	35(1)	29(1)	33(2)	26(1)	24(2)	24(4)	23(2)	21(3)		
XIII	deschlorometolachlor	18(1)	16(1)	16(1)	12(1)	15(1)	13(2)	14(1)	11(1)	12(1)	9.9(0.1)	9.0(0.7)		
XIV	metolachlor morpholinone	26(4)	21(3)	22(2)	16(1)	13(1)	17(2)	20(1)	9.8(6.8)	8.1(1.8)	9.8(2.9)	6.3(1.0)		
XV	metolachlor propanol	23(4)	32(2)	23(1)	20(1)	19(4)	20(1)	16(1)	12(1)	11(4)	11(2)	11(3)		
XVI	deschloroacetyl-metolachlor	26(7)	18(3)	14(2)	12(1)	12(2)	12(2)	10(1)	13(2)	14(1)	15(1)	15(1)		
XVII	deschloroacetyl-metolachlor propanol	14(5)	12(1)	10(1)	7.6(0.7)	7.0(3.0)	7.1(0.7)	5.7(0.4)	5.4(1.0)	3.4(0.8)	3.5(0.1)	2.6(0.5)		
XVIII	metolachlor oxanilic acid	Nm	Nm	148(2)	Nm	38(2)	Nm	40(3)	36(1)	34(1)	Nm	30(2)		

Table S2 (cont'd)

#	Identity	Depth (m)										20	21
		2	5	8	10.5	11	11.5	13.5	18	19	Nd	Nm	Nd
XIX	metolachlor ethane sulfonic acid	Nm	Nm	Nd	Nm	Nd	Nm	Nd	Nd	Nd	Nd	Nm	Nd
XX	acetochlor	7.9(1.1)	2.7(0.4)	2.3(0.1)	1.8(0.1)	1.4(0.3)	1.3(0.2)	1.0(0.4)	Nd	Nd	Nd	Nd	Nd
XXI	hydroxyacetochlor	24(2)	23(2)	24(1)	21(1)	20(1)	20(20)	19(1)	16(6)	11(2)*	13(2)	13(2)	7.9(0.2)*
XXII	deschloroacetochlor	10(3)	14(3)	15(3)	17(1)	16(2)	16(4)	16(2)	12(3)	8.1(2.5)	7.8(1.8)	3.7(0.4)	
XXIII	acetochlor oxanilic acid	Nm	Nm	45(3)	Nm	12(2)*	Nm	17(1)*	17(1)*	12(1)*	Nm	11(1)*	
XXIV	acetochlor ethane sulfonic acid	Nm	Nm	Nd	Nm	Nd	Nm	Nd	Nd	Nd	Nm	Nd	Nd
XXV	2-chloro-2'-ethyl-6'-methylacetanilide	220(5)	189(18)	173(2)	148(4)	138(5)	136(5)	136(3)	108(4)	101(9)	100(8)	52(5)	
XXVI	2-hydroxy-2'-ethyl-6'-methylacetanilide	49(1)	45(3)	30(2)	17(3)	17(1)	15(1)	17(1)	15(3)	14(1)	14(1)	8.7(1.0)	
XXVII	2'-ethyl-6'-methylacetanilide	129(2)	78(5)	77(3)	61(4)	82(2)	87(2)	88(2)	47(1)	52(3)	37(2)	34(2)	
XXVIII	2-ethyl-6-methylaniline	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
XXIX	dimethenamid	5.1(0.5)	7.7(0.6)	6.1(0.7)	5.8(1.0)	4.0(0.2)	5.3(0.8)	5.7(0.2)	3.9(0.7)	2.7(1.1)	2.2(0.6)	1.1(0.5)	
XXX	deschloro-dimethenamid	23(1)	21(1)	19(1)	17(1)	19(2)	22(2)	21(2)	21(4)	20(1)	21(4)	29(1)	
XXXI	atrazine	168(7)	137(10)	125(2)	85(1)	109(3)	105(3)	70(7)	57(2)	55(3)	50(3)	47(1)	
XXXII	desethyl atrazine	67(1)	63(5)	61(1)	40(2)	39(4)	38(5)	28(3)	23(2)	22(1)	18(1)	15(2)	
XXXIII	desisopropyl atrazine	40(1)	38(2)	28(1)	20(2)	22(3)	20(10)	17(2)	11(3)	11(1)	8.4(1.0)	8.3(2.7)	
XXXIV	simazine	59(2)	47(3)	45(1)	32(5)	44(3)	40(5)	31(3)	24(2)	24(1)	23(1)	21(1)	
XXXV	cyanazine	22(2)	33(2)	35(2)	28(3)	25(4)	21(7)	30(1)	29(14)	17(5)	18(5)	15(8)	
	dissolved oxygen	5.3	3.4	2.5	0.96	0.97	1.0	0.9	0.68	0.53	0.25	0.22	
	chloride	9.0	10.9	11.4	15.1	15.1	15.3	18.8	20.3	20.4	20.5	20.6	

Nd = not detected

Nm = not measured

*Measurement below the MRL but above the MDL