Supporting Information

Electrochemistry-Coupled to Liquid Chromatography-Mass Spectrometry-Density Functional Theory as New Tool to Mimic the Environmental Degradation of Selected Phenylurea Herbicides

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LC-HRMS^2 (Liquid Chromatography High Resolution Tandem Mass Spectrometry) analyses

LC-HRMS^2 experiments were performed with a collision energy ramping from 10 to 40 V. Mass traces were extracted for each targeted molecule with an absolute window of 0.01 Da, and data were processed using *MassLynx* 4.1 software (Waters).

The fitting of the theoretical isotopic distribution with experimental data was particularly helpful to structural elucidation, because of the presence of chlorine in some parent molecules and some of the degradation products.

The analysis of thio-adducts demonstrates losses of neutral molecules such as γ-glu-ala-gly (-274), glycine (-75), glutamine (-145) as well as pyroglutamic acid (-130), which are characteristics of MSMS fragmentation of a glutathione adduct in positive ionization mode.

1- HRMS^2 fragmentation of *m/z* 181.09, 179.08, 197.09 and 486.17 ions $[M+H]^+$ attributed to the oxidation products of **FENU** and for the GSH adduct of quinone imine (QI).

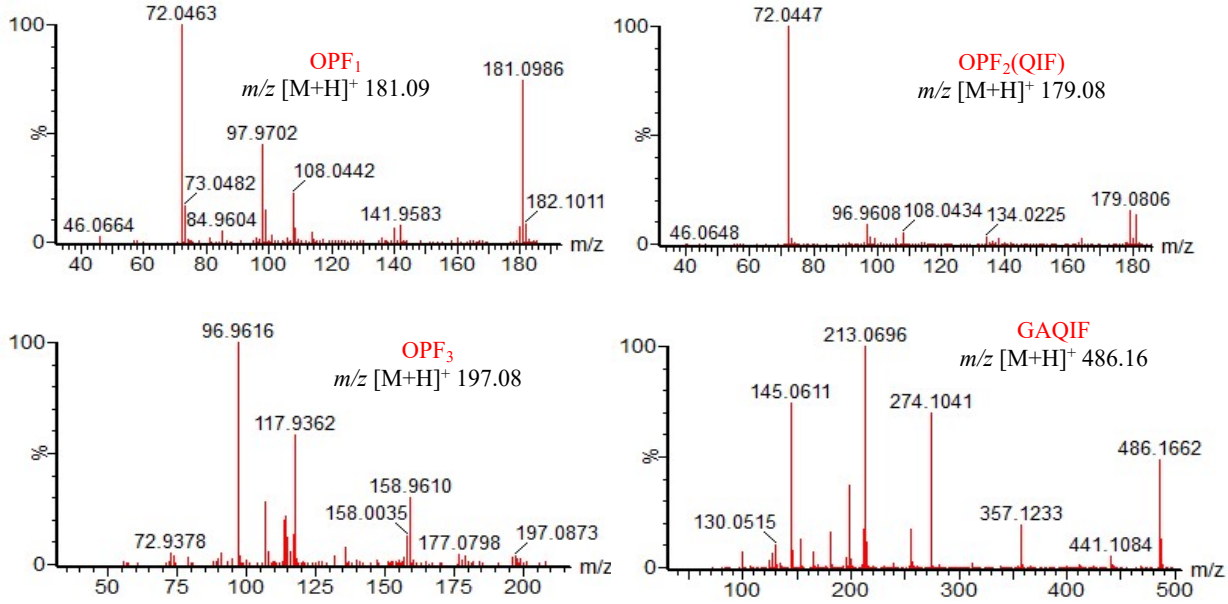

Figure S1. HRMS^2 spectrum of OPF_1, OPF_2, OPF_3 and GAQIF

2- HRMS^2 fragmentation of *m/z* 181.09, 179.08, 215.05 and 520.12 ions $[M+H]^+$ attributed to the oxidation products of **MONU** and for the GSH adduct of quinone imine (QI).

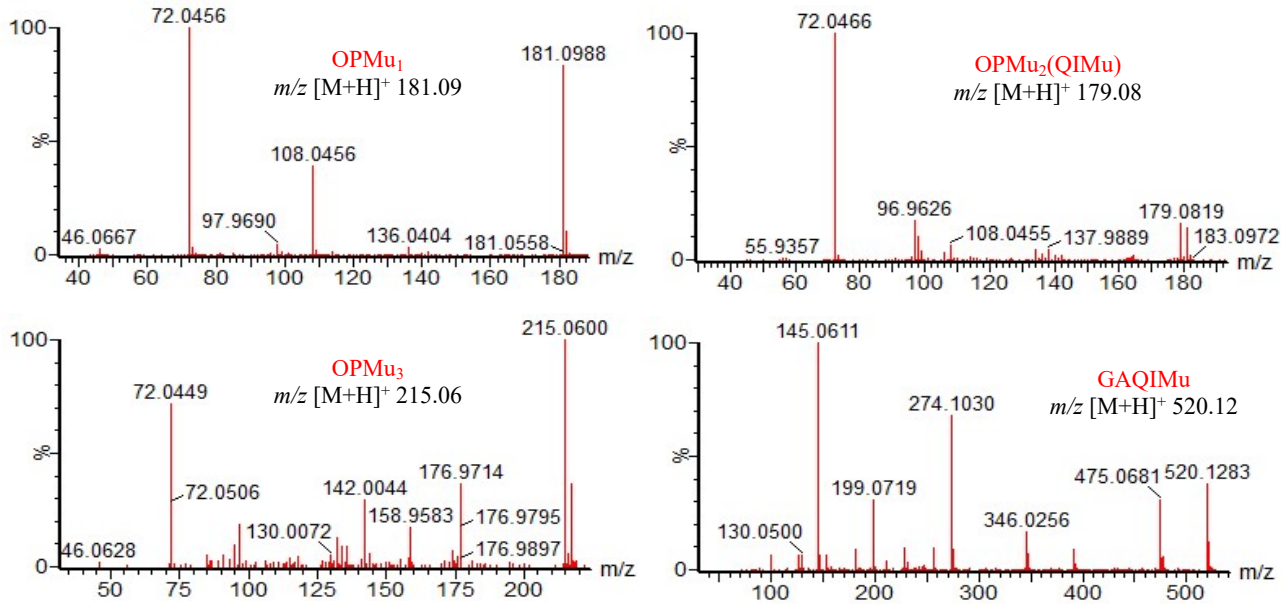

Figure S2. HRMS^2 spectrum of $OPMu_1$, $OPMu_2$, $OPMu_3$ and GAQIMu

3- HRMS^2 fragmentation of *m/z* 181.09, 223.14, 221.12, 205.13 and 528.21 ions $[M+H]^+$ attributed to the oxidation products of **ISO** and for the GSH adduct of quinone imine (QI).

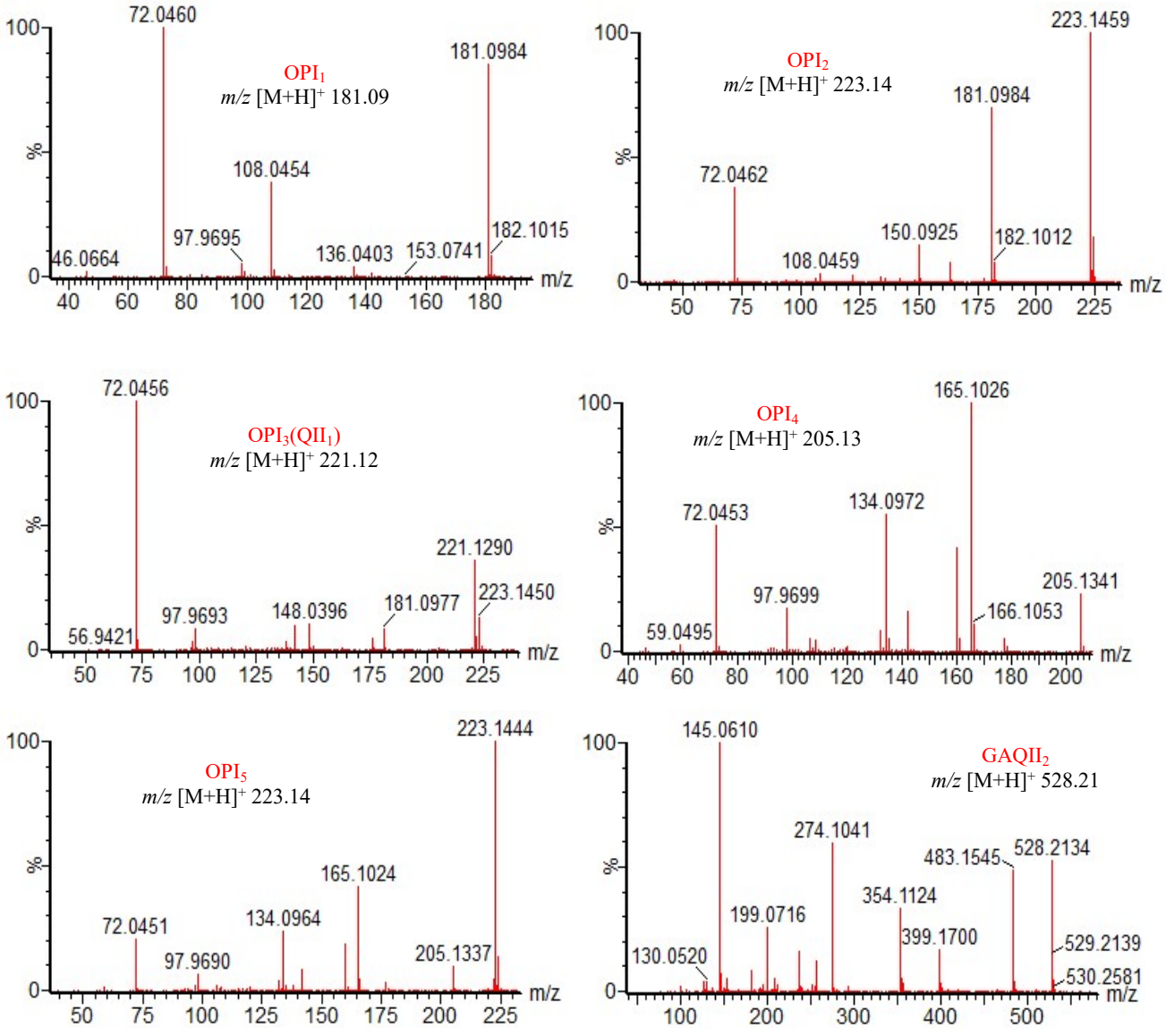

Figure S3. HRMS^2 spectrum of OPI_1, OPI_2, OPI_3, OPI_4, OPI_5 and $GAQII_2$

4- HRMS^2 fragmentation of *m/z* 215.06, 229.07, 211.06 and 534.14 ions $[M+H]^+$ attributed to the oxidation products of **CHLORTO** and for the GSH adduct of quinone imine (QI).

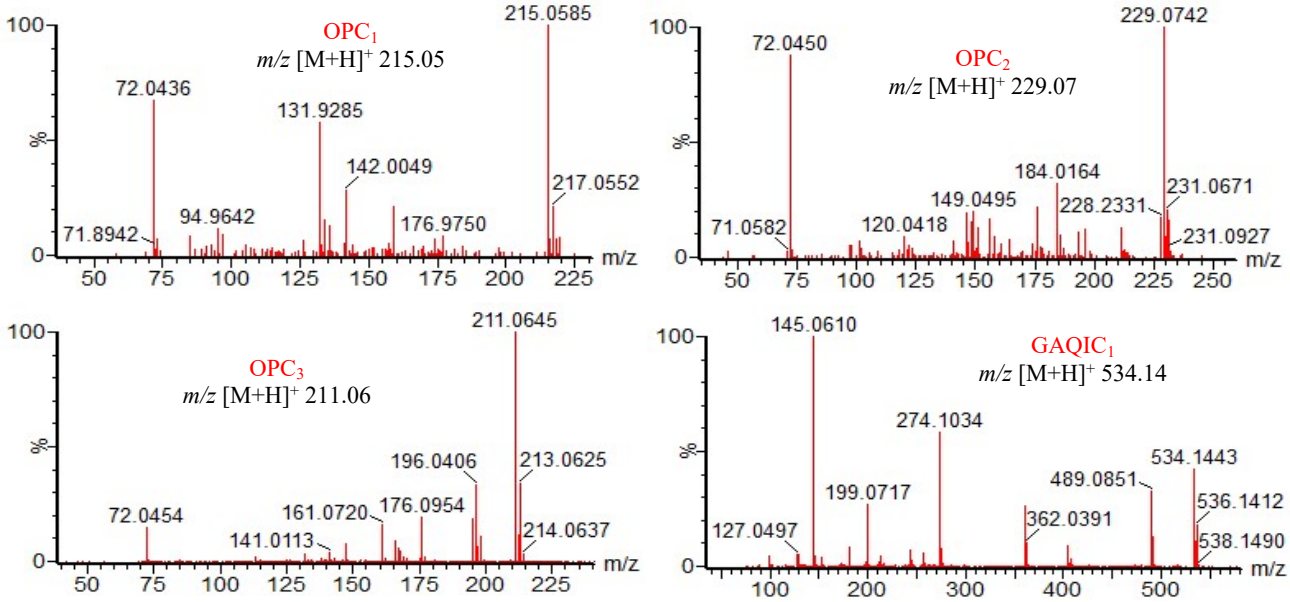

Figure S4. HRMS^2 spectrum of OPC_1, OPC_2, OPC_3 and $GAQIC_1$

5- HRMS^2 fragmentation of *m/z* 215.05, 213.04, 520.12 and 550.13 ions $[M+H]^+$ attributed to the oxidation products of **METOX** and for the GSH adduct of quinone imine (QI).

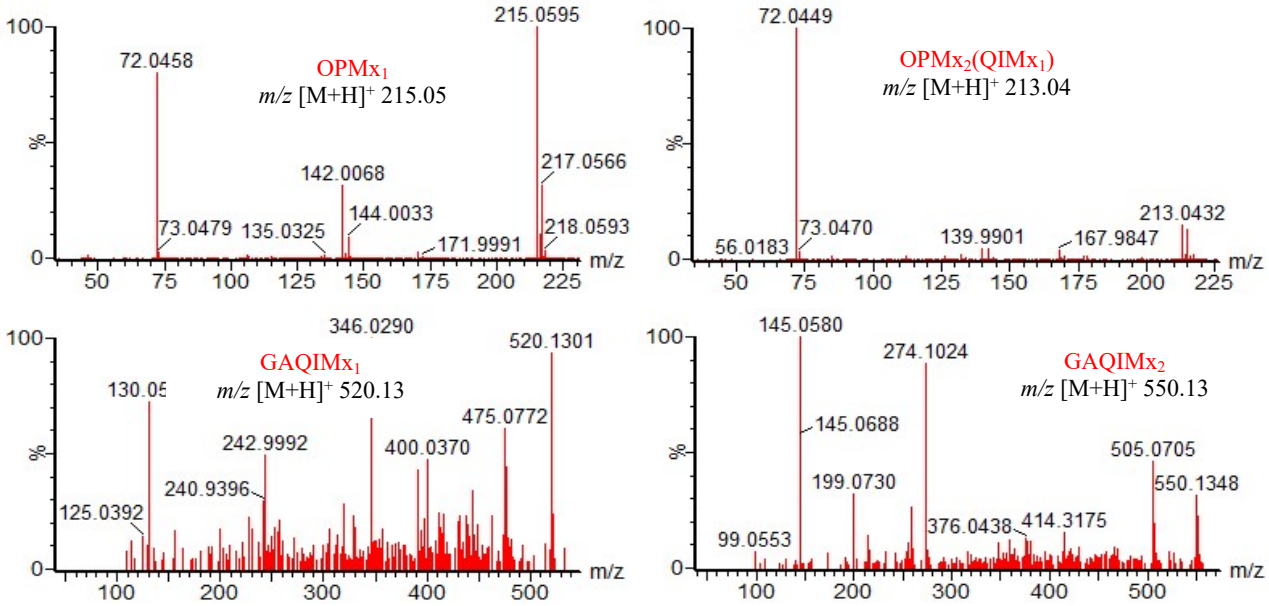

Figure S5. HRMS^2 spectrum of $OPMx_1$, $OPMx_2$, $GAQIMx_1$ and $GAQIMx_2$

6- HRMS^2 fragmentation of *m/z* 197.09, 502.16, 231.05 and 536.12 ions $[M+H]^+$ attributed to the oxidation products of **MONO** and for the GSH adduct of quinone imine (QI).

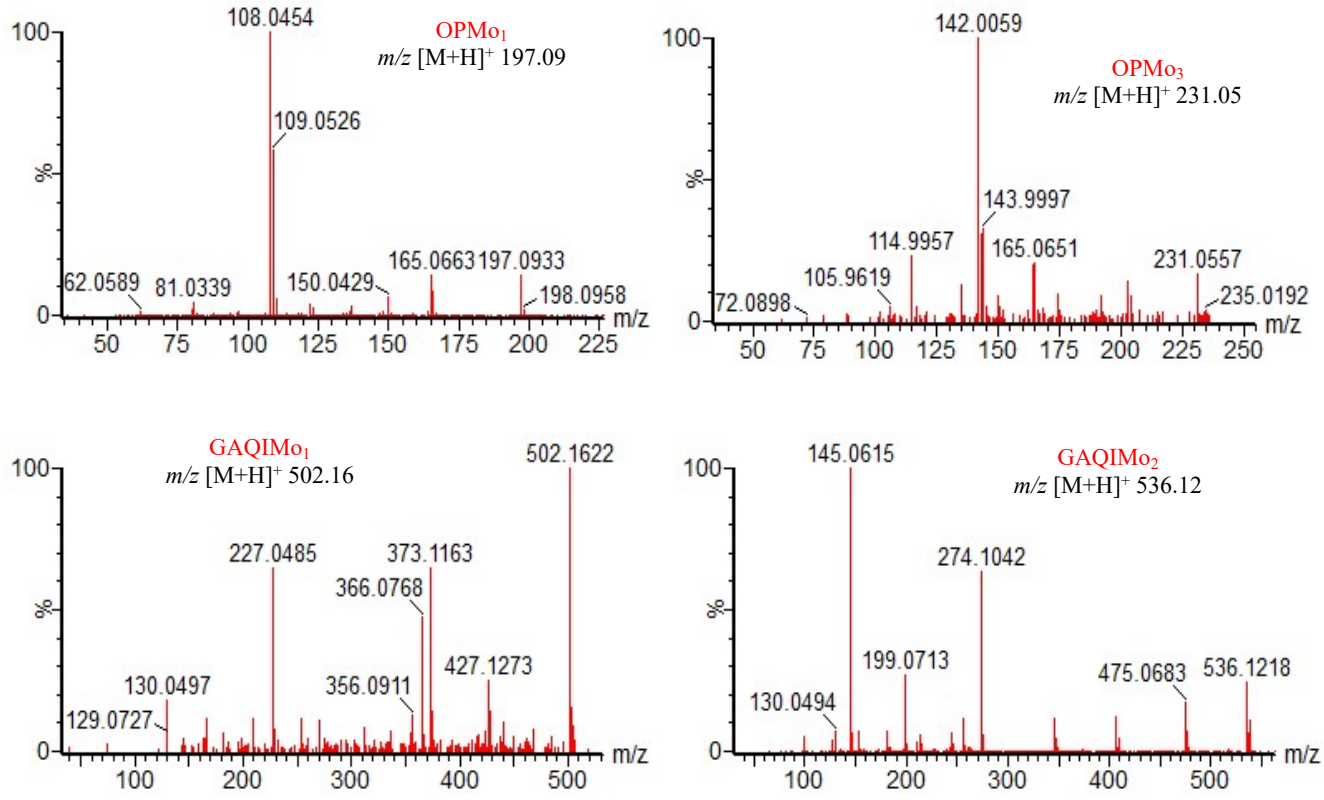

Figure S6. HRMS^2 spectrum of $OPMo_1$, $OPMo_3$, $GAQIMo_1$ and $GAQIMo_2$

7- HRMS^2 fragmentation of *m/z* 231.05 and 570.08 ions $[M+H]^+$ attributed to the oxidation products of **LINU** and for the GSH adduct of quinone imine (QI).

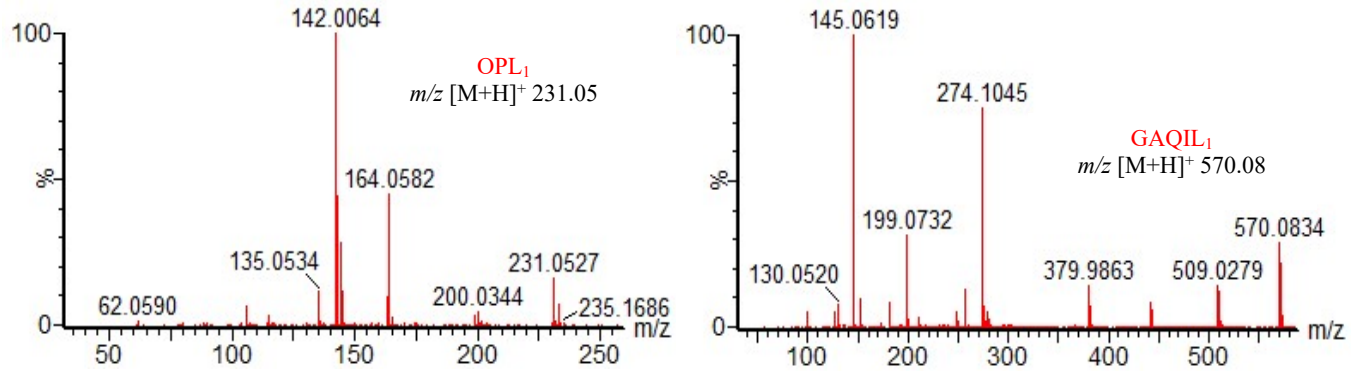

Figure S7. HRMS^2 spectrum of OPL_1 and $GAQIL_1$