

S3 Table. Optimized UHPLC-(ESI-)-MS/MS parameters. The precursor and product ions of the studied compounds (MRM transition) and optimized cone/collision energies are listed for each analyte. The retention time stability, limits of detection, dynamic linear range, method linearity (correlation coefficients, R^2) are shown for UHPLC-ESI(-)-MS/MS analysis. The settings of the mass spectrometer in negative electrospray (ESI-) mode were as follows: Capillary Coltage, 3.0 kV; Cone Voltage, 21-30 V; Collision Energy, 10-22 eV; Low/High Resolutions, 3.0/15.0; Desolvation/Source Temperatures, 120/550°C. The gas flows were set to 0.21 ml/min of collision gas (Argon), 1000 l/h of desolvation gas and 70 l/h of cone gas (Nitrogen).

Compound	MRM transition	Cone Voltage [V]	Collision Energy [eV]	Retention time ^a [min]	LOD ^b [fmol]	Linear range [pmol]	R^2
2,4-D	219 > 161	21	10	4.742 ± 0.009	23	0.05–250	0.9995
[²H₅]-2,4-D	224 > 164						
2,4-D-Asp	334 > 161	30	22	3.551 ± 0.011	20	0.05–250	0.9991
[¹³C₂, ¹⁵N]-2,4-D-Asp	337 > 161						
2,4-D-Glu	348 > 161	25	22	4.014 ± 0.006	19	0.05–250	0.9989
[¹³C₂, ¹⁵N]-2,4-D-Glu	351 > 161						
2,4-DB	247 > 161	17	9	6.801 ± 0.008	19	0.05–250	0.9986
MCPA	199 > 141	15	12	4.932 ± 0.004	14	0.05–250	0.9991
MCPB	227 > 141	18	9	6.941 ± 0.005	15	0.05–250	0.9975
MCPP	213 > 141	20	11	6.134 ± 0.008	10	0.05–250	0.9992
2,4,5-T	253 > 195	20	10	6.251 ± 0.006	150	0.5–250	0.9987

^a Values are means ± SD (n = 10); ^b Lower Limit of Detection (LOD) defined as a signal-to-noise ratio of 3:1.