Supporting Information

Desorption Electrospray Ionization – Mass Spectrometry for the Detection of Analytes Extracted by Thin-Film 2,4-Dichlorophenoxyacetic Acid Molecularly Imprinted Polymers

Geert Van Biesen, Justin M. Wiseman and Christina S. Bottaro*

This supporting information gives a detailed description of the derivatization of the glass slides, the preparation of the MIPs, the experimental conditions for DESI-MS, a mass spectrum of a MIP before and after removal of the template, a MS/MS spectrum of 2,4-D, and DESI-MS spectra of a TLC plate, NIP and MIP used for extraction from river water containing 1.0 mg/L 2,4-D and analogs.

Derivatization of glass slides

Microscope glass slides (Fisherbrand) were cut in half and cleaned by immersion in an HCl/methanol (1:1 v/v) solution for 30 minutes. They were rinsed with deionized water, followed by ethanol (95%), and were then dried at 60 ºC for about an hour. The cleaned, dry glass slides were derivatized overnight with a 2% (v/v) solution of 3-(trimethoxysilyl) propylmethacrylate in toluene, rinsed with ethanol (95%) and blown dry with a stream of nitrogen gas.

Preparation of MIPs

All reagents were from Sigma-Aldrich and were used as received. The ingredients (Table S1) were weighed or pipetted into a 2-mL vial, and vortex mixed until complete dissolution. The clear solution was sonicated for a few minutes to remove dissolved air, and 8 μL was then pipetted onto a derivatized glass slide. The drop was allowed to spread out for a few seconds, and a glass cover slide was placed on top. Polymerization was initiated with a UV lamp (254 nm – 6 W) positioned approximately 0.5 cm above the slides, for 30 minutes. The cover slide was then removed, and the glass slide with MIP was placed in a methanol/acetic acid solution (90:10 v/v) under stirring for 3 hours to remove the template and any unreacted reagents. This was repeated with fresh methanol/acetic acid solution for another 3 hours, methanol for 3 hours, and finally methanol overnight. The MIPs were dried with a stream of nitrogen gas, and stored under ambient conditions until use. As a control, non-imprinted polymers (NIPs), which did not contain the 2,4-D template, were prepared using the same methodology.

Table S1: Composition of MIPs and NIPs

	MIP	NIP
2,4-D	8.84 mg (0.04 mmol)	-
4-Vinylpyridine	17 μL (0.16 mmol)	17 μL (0.16 mmol)
Ethyleneglycol dimethacrylate	151 μL (0.80 mmol)	151 μL (0.80 mmol)
2,2-dimethoxy-2-phenylacetophenone	3.1 mg (0.012 mmol)	3.1 mg (0.012 mmol)
MeOH/H_2O 4/1	200 μL	200 μL

DESI source settings and diagnostic ions

Table S2: DESI source settings

Parameter	Settings
ES voltage	3 kV
Solvent flow rate	5 μL/min
Gas pressure	150 psi
Distance from tip to surface	1 mm
MS inlet temperature	350 ºC
Spray impact angle (α)	55º
Collect angle (β)	~ 10º
Solvent	MeOH/HOAc 90:10
Surface scan rate	200 μm/s

Table S3: Precursor and product ions for identifying analytes

Analyte	Precursor (*m/z*)	Product ion (*m/z*)
PAA	151	107
2,4-DCAA	203	159
4-CPA	185	127
2,4-D	219	161
2,4,5-T	253	195

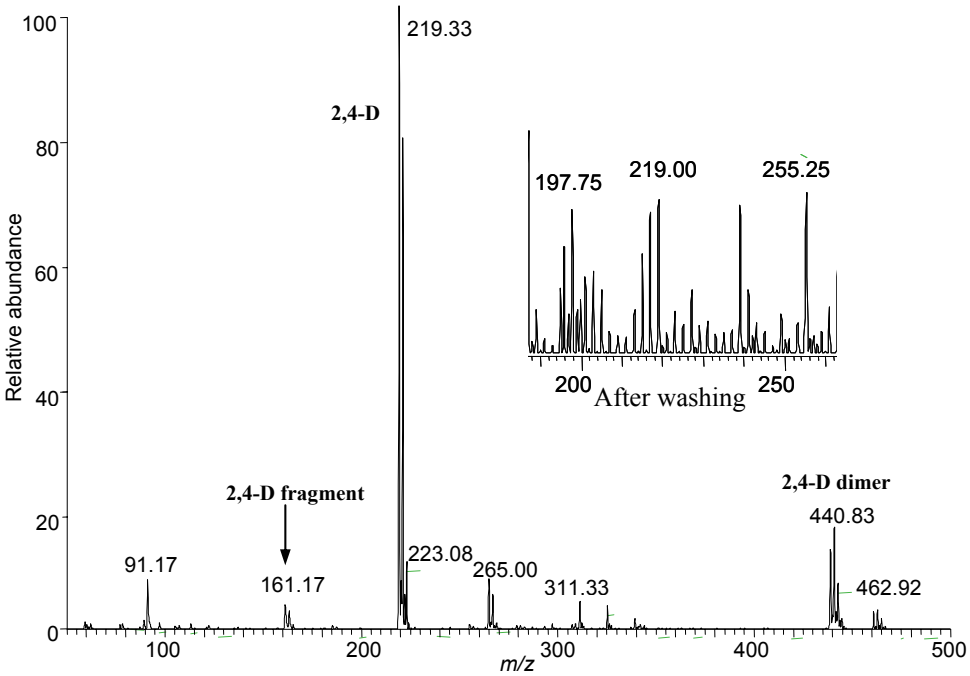

Fig S1: Full scan DESI-MS spectra of MIP after preparation (before washing). The absolute intensity of the base peak is ~ 3200.
The inset shows the spectrum of an MIP after washing to remove the 2,4-D template. There is a small peak at *m/z* 219 (absolute intensity = 5), but it is unlikely that this is 2,4-D since there is no accompanying isotope peak of the right intensity at *m/z* 221, and MS/MS did not find the characteristic fragment at *m/z* 161.

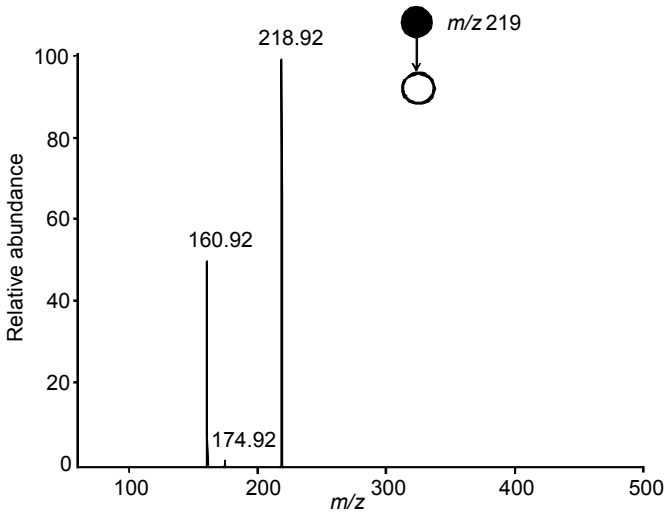

Fig. S2: DESI-MS/MS of 2,4-D using the Thermo Scientific LTQ mass spectrometer. CE (collision energy, arb units): 15; isolation width: ±1 *m/z*; activation time: 30 ms.

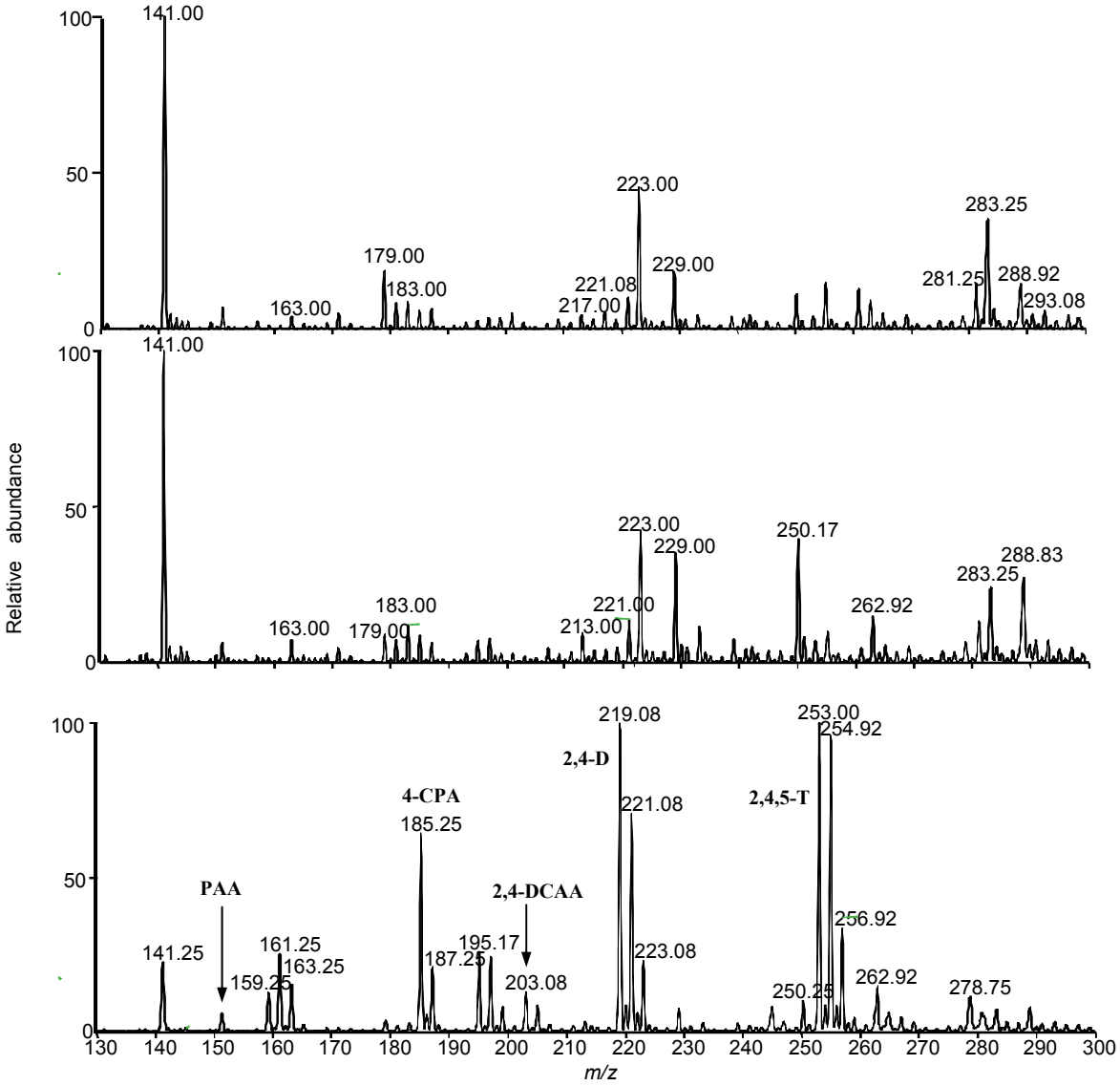

Fig. S3: DESI-MS negative ion mass spectra of 1.0 ppm spiked river water samples extracted with (a) TLC plate (b) NIP and (c) MIP.