Supplementary Material (ESI) for Journal of Environmental Monitoring

## Optimisation of PLE and SPE methods

Initial PLE conditions were as follows (for soil samples): temperature, 100 $^oC$; pressure, 1500 p.s.i.; solvent, 50:50 v/v MeOH:$H_2O$; cycles, 1; preheat time, 5 min; heat time, 5 min; static time, 5 min; flush volume, 50 % of cell volume; purge time, 100 sec. Temperatures investigated during optimisation ranged from 40-120 $^oC$ ($n$=5), heat time from 5-15 min ($n$=3), cycles from 1-3 (5 min segments), flush volumes from 50-100 % ($n$=3) and preheat times from 0-2 min ($n$=2). Pressure was maintained at 1500 p.s.i. throughout, as was $N_2$ purge time at 100 sec. Extraction solvents investigated were 50 % aqueous solutions of methanol, acetonitrile, acetone and isopropyl alcohol as well as one solution of 50:50 v/v ethylacetate:acetone. Soil sample size was increased from 1-5 g ($n$=5) to observe any loss of analyte recovery due to matrix effects. All optima were chosen based upon conditions resulting in the highest number of analyte recoveries above 70 % when compared to standards in ultra pure water.

The above PLE conditions were optimised using an adapted working SPE procedure of Bones *et al.*[43] This SPE step was itself subsequently optimised with respect to sorbent type and extraction pH. Phenomenex Strata X - 200 mg, 3 mL and 6 mL barrels; Waters Oasis HLB - 200 mg, 6 mL barrel; Merck LiChrolut EN - 50 mg, 3 mL barrel (Merck Darmstadt, Germany); and Varian Focus - 50 mg, 6 mL barrel, were all investigated, together with one weak cation exchange cartridge (Phenomenex Strata X-CW). All extractions for this study were from the same batch of soil sample and were each spiked with 1 $\mu g.g^{-1}$ of analyte and compared to a 10 $\mu g.g^{-1}$ standard in ultra pure water (% relative recoveries).

An Agilent HP1100 liquid chromatograph was used throughout this work. An Agilent diode array UV detector G1315B module set to 225 and 270 nm was initially used to develop standard separations before switching to a Bruker Daltonics Esquire~LC electrospray ionization octopole ion trap mass spectrometer (Bruker Daltonics Coventry, UK) for neat and spiked soil or sludge samples in both positive and negative electrospray ionization modes. All separations were performed on a Waters Sunfire 150 x 2.1 mm octadecylsilica analytical column with a particle size of 3.5 µm. The flow rate was set to 0.2 $mL.min^{-1}$ throughout and injection volumes were 10 µL. All instrument control was carried out using a Hewlett Packard (Palo Alto, CA, USA) personal computer with Agilent Chemstation version A.06.01 and Bruker Daltonics Esquire Control version 6.08 installed. Two mobile phase reservoirs contained 100 % 10 mM ammonium acetate in water (A) and 100 % acetonitrile (B) and separations were carried out under gradient conditions. Mobile phase composition was maintained at 10 % B for the first five mins after injection and then linearly ramped to 45 % B at 28 mins. Over the range 28-35 mins, mobile phase composition was linearly ramped to 80 % B and maintained for a further 10 mins. Re-equilibration time was 15 mins.

Optimisation of electrospray tandem mass spectrometric conditions was carried out by direct infusion using a Cole Parmer 74900 Series syringe pump set to deliver 300 $\mu L.hr^{-1}$. Solutions of approximately 10 $mg.L^{-1}$ of each analyte in the approximate mobile phase composition at elution were infused separately and conditions systematically optimised for all analytes in both positive and negative modes ($MS^1$). Base peak ions were noted for each analyte and fragmented to the 2nd degree with tandem MS ($MS^2$) in both electrospray ionization polarities. Of the peaks observed, the most abundant was chosen for monitoring of the $MS^2$ signal. When used in conjunction with LC, all extracted ion chromatograms (EICs) were smoothed using a 3.8 point (soil) or 4.8 point (sludge) Gaussian averaging algorithm to allow for enhanced sensitivity with minimal peak distortion.