

Supplemental information

Supplementary Information S1. Materials:

Pharmaceutical standards, carbamazepine, diclofenac, ibuprofen, ketoprofen, naproxen and triclosan were supplied by Sigma-Aldrich (Schnelldorf, Germany).

Different isotopically labelled internal standards (ILIS) were used: carbamazepine- D_{10} solution $100\text{ }\mu\text{g mL}^{-1}$ in methanol, ibuprofen- d_3 , from Sigma-Aldrich, (Schnelldorf, Germany), diclofenac-(acetophenyl ring $-^{13}\text{C}_6$) sodium salt 4.5-hydrate and ketoprofen D_3 from VETRANAL from Fluka with purity degree $>98\%$, were purchased from Sigma-Aldrich, (Schnelldorf, Germany). Triclosan D_3 (2,4-dichlorophenoxy D_3) 100 ng mL^{-1} in cyclohexane was supplied by Dr Ehenstorfer (Augsburg, Germany). Pharmaceutical standards of carbamazepine (CBZ), diclofenac (DCF), ibuprofen (IBP) and Ketoprofen (KTP) were provided by Sigma Aldrich, while naproxen (NPX) and triclosan (TCS) were provided by Fluka. Ultrapure water (gradient HPLC) from Scharlau (Sachalab, Barcelona, Spain) was used for the blanks and ongoing precision and recovery standard samples. Methanol and acetone multisolvent (HPLC grade), ter-butyl methyl ether (HPLC grade) were obtained from Sacharlau (Barcelona, Spain). Formic acid ($<95\%$) was obtained from Sigma-Aldrich (Spain). Oasis HLB (60 mg, 3 mL) extraction cartridges, from Waters Corporation (Dublin, Ireland), were used for solid phase extractions (SPE). Nylon filters (45 μm pore size, 25 mm diameter) were acquired from Análisis vinílicos S.A. (Tomelloso, Spain).

Supplementary Information S2. Instrumental analysis and quality control

The liquid chromatography analysis was achieved using a binary gradient consisting of 0.1% formic acid (v/v) in water (A) and 100% methanol (B) at a flow rate of $700\text{ }\mu\text{L min}^{-1}$. The gradient employed was as follows: 5% B held for 3.5 min, increased linearly to 80% by 10 min and held for 3 min, and stepped to 100% and held for 8 min. A 9 min equilibration step at 5% B was used at the beginning of each run to bring the total run time per sample to 30 min. An injection volume of $10\text{ }\mu\text{L}$ was used for all analyses. All the analysis were performed in an UPLC Acquity I-Class System and HR-QTOF-MS maXis Series (Daltonik GmbH, German, Bruker), using an ACQUITY UPLCBEH C18 column ($50 \times 2.1\text{ mm}$) with $1.7\text{ }\mu\text{m}$ particle size (Milford, MA, USA, Waters) to separate the target compounds.

Four types of quality controls were included: untreated controls wetted without PPCPs were used to detect any PPCPs contamination emanating from other sources during the experiment; and PPCPs-spiked controls without plant were used to assess the possible degradation of PPCPs in the soils.

Extraction recoveries for target compounds were determined for different matrices (water, plant and soil) by spiking samples with 2500 ng mL^{-1} of ILIS ([D_{10}]-carbamazepine, [$^{13}\text{C}_6$]-diclofenac, [D_3]-ibuprofen, [D_3]-ketoprofen and [D_3]-triclosan). The first of the three replicates samples were spiked in the first step of the extraction process in order to have a final concentration of 100 ng mL^{-1} . Afterwards, samples were successively extracted until the last step when the second the three replicates samples were spiked with 2500 ng mL^{-1} of surrogate standards ([D_{10}]-carbamazepine, [$^{13}\text{C}_6$]-diclofenac, [D_3]-ibuprofen, [D_3]-ketoprofen and [D_3]-triclosan). Then, the recovery of the PPCP deuterated concentration (differences between the PPCP in the first sample and the second one) was evaluated and this value was employed to correct the PPCP concentrations obtained in the samples.

In addition, to checking the recovery efficiency in the extraction processes of the PPCP of the different matrices (mentioned above), quality controls of the analysis procedure were carried out. To this end, analytical targets were used, ie. clean water samples in order to detect any contamination problem during the treatment of the samples in the laboratory and test samples were also used with distilled water but adding a known concentration of unlabelled drug with deuterium (OPR samples) were used continuously to reveal that the analytical system was robust and reproducible. The precision of the

method was determined by calculating the relative standard deviation (% RSD) of the triplicate spiked samples. Quantification of target analytes, based on peak area, was achieved using the internal standard approach, and results were corrected for recovery of analytes. The recovery of Calibration curves were produced using the linear regression method.

In the following tables (Table S.I.1-S.I.3) the detection (DL) and quantification (QL) limits obtained by the analysis equipment can be observed.

Table S1. Detection and quantification limits, extraction efficiency and linearity in soils obtained with the method used by the UPLC Acquity I-Class System (DW).

Compound	DL (ng g ⁻¹)	QL (ng g ⁻¹)	Extraction efficiency (%)	Linearity (ng mL ⁻¹)
CBZ	0.01	0.03	82.8	1.9-1000
DCF	0.23	0.46	78.3	1.9-100
IBP	0.26	0.97	75.8	4-1000
KTP	0.02	0.26	75.1	0.91-1000
NPX	0.28	0.63	-	2-1000
TCS	0.28	0.98	43.3	6-1000

Table S2. Detection and quantification limits, extraction efficiency and linearity in water obtained with the method used by the UPLC Acquity I-Class System.

Compound	DL (ng mL ⁻¹)	QL (ng mL ⁻¹)	Extraction efficiency (%)	Linearity (ng mL ⁻¹)
CBZ	0.03	0.07	95.2	0.01-2000
DCF	0.71	0.91	83.8	0.9-2000
IBP	0.56	1.89	70.5	1.94-2000
KTP	0.05	0.61	68.6	0.18-2000
NPX	0.08	1.21	-	1-2000
TCS	0.55	2.11	89.4	2.1-2000

Table S3. Detection and quantification limits, extraction efficiency and linearity in vegetables obtained with the method used by the UPLC Acquity I-Class System (DW).

Compound	DL (ng g ⁻¹)	QL (ng g ⁻¹)	Extraction efficiency (%)	Linearity (ng mL ⁻¹)
CBZ	0.35	1.50	98.9	0.08-1000
DCF	3.90	7.50	94.5	1.1-2000
IBP	3.55	10.0	69.8	1.89-2000
KTP	0.45	4.40	77.3	0.5-1000
NPX	3.00	6.00	-	1.25-200
TCS	2.75	10.5	86.7	5-1000