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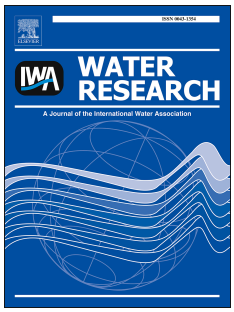

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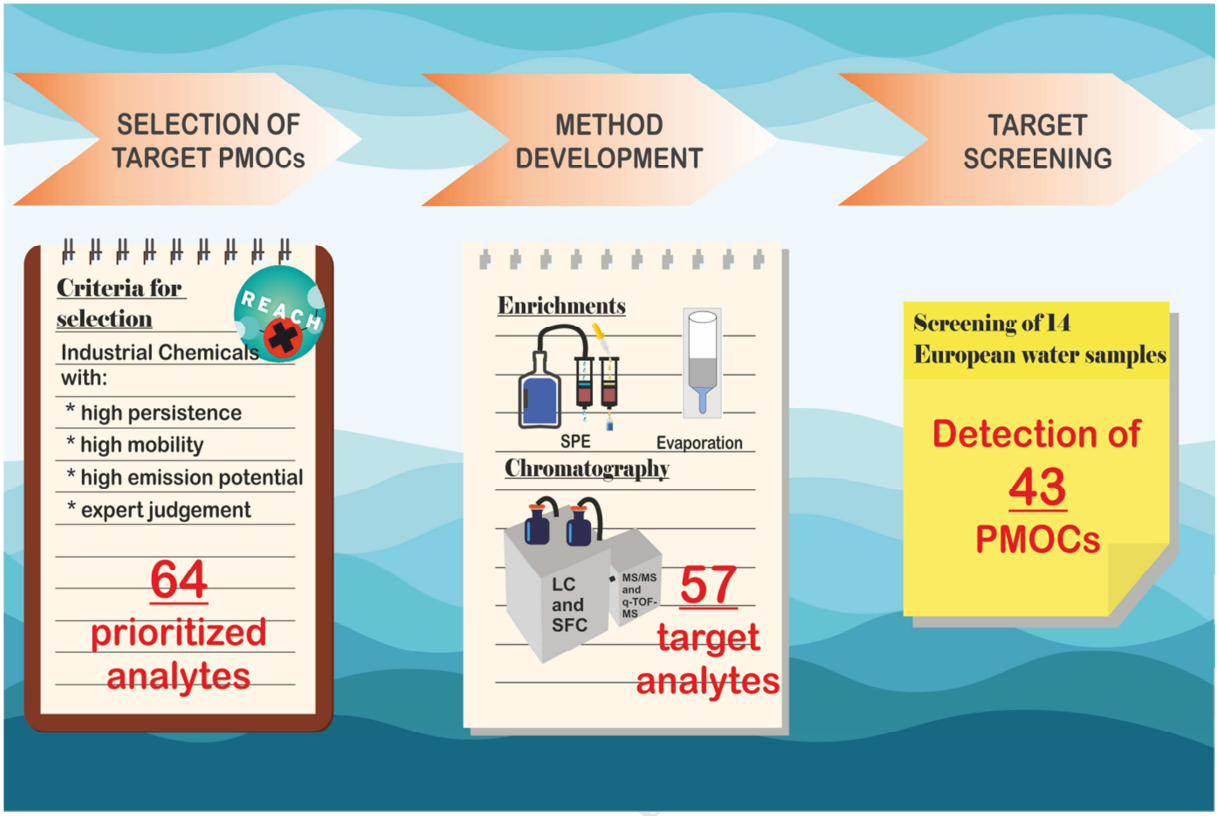
Graphical Abstract



Occurrence of emerging persistent and mobile organic contaminants in European water samples

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Abstract

The release of persistent and mobile organic chemicals (PMOCs) into the aquatic environment puts the quality of water resources at risk. PMOCs are challenging to analyze in water samples, due to their high mobility. The aim of this study was to develop novel analytical methods for PMOCs and to investigate their occurrence in surface and groundwater samples. The target compounds were culled from a prioritized list of industrial chemicals that were modeled to be persistent, mobile, and emitted into the environment. Analytical screening methods based on mixed-mode liquid chromatography (LC), hydrophilic interaction LC, reversed phase LC, or supercritical fluid chromatography in combination with mass spectrometric detection were successfully developed for 57 target PMOCs and applied to 14 water samples from three European countries. A total of 43 PMOCs were detected in at least one sample, among them 23 PMOCs that have not been reported before to occur in environmental waters. The most prevalent of these novel PMOCs were methyl sulfate, 2-acrylamino-2-methylpropane sulfonate, benzyltrimethylammonium, benzyldimethylamine, trifluoromethanesulfonic acid, 6-methyl-1,3,5-triazine-diamine, and 1,3-di-*o*-tolylguanidine occurring in ≥50 % of the samples at estimated concentrations in the low ng L^{-1} up to µg L^{-1} range. The approach of focused prioritization combined with sensitive target chemical analysis proved to be highly efficient in revealing a large suite of novel as well as scarcely investigated PMOCs in surface and groundwater.

Keywords: Persistent and mobile organic chemicals, PMOC, water, occurrence, chromatography

1. Introduction

Persistent and mobile organic compounds (PMOCs, also referred to as PM substances) are man-made, highly polar organic chemicals that only degrade very slowly (if at all) in the environment and that show a low tendency to sorb to surfaces or to organic matter in soil and sediments (Reemtsma et al. 2016). PMOCs can enrich in (semi-)closed water cycles, as the only relevant process leading to decreasing concentrations in the aquatic environment is dilution. Consequently, if PMOCs are emitted in significant quantities, they may threaten the quality of surface water bodies, groundwater aquifers, and ultimately also our drinking water resources (Reemtsma et al. 2016). Known examples of such PMOCs are melamine (Beltrán-Martinavarro et al. 2013), saccharine, acesulfame (Buerge et al. 2009), and sulfanilic acid (Holm et al. 1995). PMOCs are particularly critical if they also exhibit toxicological effects. Such compounds are then denoted as PMT (persistent, mobile, and toxic) substances (Neumann 2017). In Europe there is a currently ongoing discussion whether or not PMT substances should be regulated under the European Union chemical regulation REACH (European Parliament 2006) in a similar way as is the case for PBT (persistent, bioaccumulative, and toxic) substances (Neumann and Schliebner 2017).

Whereas chemical analytical methods to detect and quantify PBT substances are well established, PMOCs are much more challenging to analyze in environmental water samples. This is due to their intrinsic property of high mobility, which makes PMOCs extremely difficult to extract and enrich from water samples or to separate (retain) using routine liquid chromatography techniques (Reemtsma et al. 2016). The most commonly applied separation method for polar environmental contaminants is undoubtedly reversed phase liquid chromatography (RPLC). However, in RPLC, PMOCs tend to elute with or close to the void volume, together with most of the waterborne matrix constituents. Furthermore, they often exhibit poor peak shape. This severely hampers unambiguous identification, sensitive detection, and reliable quantification of PMOCs. Recently, alternative liquid chromatographic

methods for separation of highly polar compounds such as PMOCs have been developed, based on either hydrophilic interaction liquid chromatography (HILIC) (Mazzarino et al. 2011; Christophoridis et al. 2016; Zahn et al. 2016) or tri-functional mixed-mode liquid chromatography (MMLC) separation columns (Montes et al. 2017). Furthermore, also supercritical fluid chromatography (SFC) with hybrid or normal phase columns and a polar modifier/co-solvent can be used as an orthogonal technique to RPLC (Parr et al. 2016; Bieber et al. 2017).

A recent modeling study identified potential PMOCs as well as precursors to PMOCs among the high production volume substances registered under REACH (Arp et al. 2017). Arp and co-workers came up with a list of 2167 unique substance identities, whereof 1811 have been modeled to be persistent and mobile in the aquatic environment (PMOC score of 4 to 5 in Arp et al. 2017) and 356 have been modeled to be PMOC precursors (i.e. to have the potential to be hydrolyzed to PMOCs with a PMOC score of 4 to 5). Building on this work, we estimated the environmental emission potential of the 2167 substances (Schulze et al. 2018). This study resulted in two consolidated lists, one for PMOCs that are expected to be emitted into the environment (936 substances) and a corresponding list for PMOC precursors (174 substances) (supplementary data in Schulze et al. 2018). Both lists are ranked according to the environmental emission potential, i.e. the magnitude of expected emissions. However, the ultimate proof that a substance is released into the environment in significant quantities and possesses PMOC properties is its presence in environmental water samples far from potential points of emissions.

The aim of the present study was thus to screen for PMOCs of concern in selected water samples from three European countries. The target analytes were primarily chosen from the list of 936 PMOCs prioritized with regard to expected emissions (Schulze et al. 2018). Enrichment methods based on solid phase extraction or evaporation as well as instrumental methods based on MMLC (Montes et al. 2017), HILIC (Zahn et al. submitted), or SFC were

employed, as well as two RPLC-based separation methods. Target chemical analytical methods were used (rather than HRMS-based suspect screening) for two reasons. 1) PMOCs are not expected to be sufficiently retained on a generic RPLC-based separation column (Reemtsma et al. 2016). 2) We intended to screen for the PMOCs in surface and groundwater, rather than in WWTP effluent, to verify their persistence and mobility (i.e. their occurrence far from primary environmental emission points), and thus we needed methods of utmost sensitivity. The results of the present study should be used to validate the PMOC and emission modeling (Arp et al. 2017; Schulze et al. 2018) and to obtain a first picture of the potential magnitude of the problem of PMOCs in European water cycles.

2. Materials and methods

2.1 Target analytes

A total of 64 target analytes were selected for the present study. Table S1 in the supplementary data shows the structures and CAS registry numbers of all analytes and lists the suppliers and purities of the commercial standards. The majority of these analytes (54 substances) originated from the top 300 substances on the list of modeled PMOCs ranked according to their expected emission potential (Table S1 in the supplementary data in Schulze et al. 2018). The selection of the 54 target analytes was based on the prerequisites of availability of chemical standards and amenability to at least one of the employed instrumental methods (see section 2.4). Additionally, substances were excluded if they were assessed to be non-persistent or volatile by expert judgement. The remaining ten target analytes were ID-2, -22, -32, -37, -38, -41, -43, -49, -52, and -59 (Table S1). They were chosen based on knowledge or suspicion of their occurrence in environmental water samples (e.g. Stüber and Reemtsma 2004; Landesamt für Natur, Umwelt und Verbraucherschutz NRW 2015; Scheurer et al. 2016; Montes et al. 2017).

ChemAxon (JChem for Office, JChem for Excel) was used to estimate substance properties, as the studied chemicals are within its application domain (personal communication with D. Szisz, ChemAxon). The majority of the selected analytes (44) are highly hydrophilic compounds with a negative log*D* value at pH 7 (Table S1). Among the analytes there were 26 compounds possessing acidic properties, with either a carboxylic, sulfonic, sulfuric or phosphonic acid moiety (strongest acidic pK_a between -4.6 and 5.5) and 35 compounds possessing basic properties (strongest basic pK_a between 2.4 and 10.7) (ChemAxon). Stock standard solutions of analytes were prepared in acetonitrile, acetonitrile:water (50:50) or water (depending on solubility) at 1 mg mL^{-1} and stored at -20 °C. Aliquots of the stock standard solutions were combined to obtain standard mixture solutions, which were subsequently diluted with acetonitrile or water depending on the chromatographic system to be used (see section 2.4).

2.2 Samples

The 14 water samples analyzed in the present study were grab samples obtained from different locations in Germany (DE, country code used in sample names), Spain (ES), and The Netherlands (NL). They consisted of surface water (SW, 7 samples), groundwater (GW, 4), bank filtrate (BF, 1), as well as reverse osmosis concentrate (ROC, 1) and permeate (ROP, 1) from a full-scale pilot plant for drinking water production. The samples were taken in 2016 and stored for up to six weeks at +4 °C in the dark until analysis. Details on all samples are given in Table S2 and Figure S1 in the supplementary data.

2.3 Sample preparation

Chemical analysis of all samples was performed in parallel in three different labs with complementary instrumental techniques. A number of sample preparation methods were used in each lab, which are briefly described individually hereafter. In total 8 different sample preparation techniques (denoted as *Enrichment I-VIII*) were developed, using spike and recovery experiments at PMOC concentrations in the ng L^{-1} to µg L^{-1} range in surface and

drinking water. Materials, chemicals, and instrumentation used in the different enrichments are listed in Table S3 in the supplementary data.

Enrichment I. The water sample was filtered through a 0.45 µm cellulose filter and an aliquot of 100 mL was submitted to a mixed-mode weak anion exchange (WAX) solid phase extraction (SPE) cartridge. The cartridge was previously conditioned with 5 mL of 2 % formic acid in methanol and 5 mL of Milli-Q water. After sample loading the cartridge was dried and analytes were eluted with 10 mL of 5 % ammonia in methanol. The extract was evaporated to dryness and the residues were reconstituted in 200 µL of Milli-Q water:acetonitrile (90:10). Finally, the extract was filtered through a 0.22 µm PP filter. For more details see Montes et al. (manuscript).

Enrichment II. Identical to *Enrichment I* but employing a mixed-mode weak cation exchange (WCX) SPE cartridge previously conditioned with 5 mL of 5 % ammonia in methanol and 5 mL of Milli-Q water. Elution of the analytes was performed with 10 mL of 2 % formic acid in methanol (Montes et al., manuscript).

Enrichment III. A multi-layer SPE cartridge (3 mL) was prepared by filling in (from bottom to top) 60 mg (±5 mg) of graphitized carbon black (GCB), 60 mg (±5 mg) of WCX bulk material, and 60 mg (±5 mg) of WAX bulk material, separated by polyethylene frits. The cartridge was conditioned with 1 mL 5 % ammonia in methanol, 1 mL 2 % formic acid in methanol, 1 mL methanol, and 3 mL deionized water. The water sample was filtered through a glass fiber filter and the pH was adjusted to 5.5 ± 0.1 with formic acid or ammonium hydroxide. An aliquot of 100 mL was passed through the cartridge. The cartridge was dried and elution was performed with 3 mL 5 % ammonia in methanol, 3 mL 2 % formic acid in methanol, and 1.5 mL methanol:dichloromethane (80:20). The combined extracts were evaporated to dryness and the residues were reconstituted in 500 µL of acetonitrile:water (95:5). Finally, the extract was filtered through a 0.2 µm cellulose syringe filter. For more details see Köke et al. (2018).

169 *Enrichment IV.* An aliquot of 10 mL of the unfiltered sample was evaporated to dryness at
170 45°C and 9 mbar. The residues were reconstituted in 500 µL of acetonitrile:water (95:5) and
171 the extract was filtered through a 0.2 µm cellulose syringe filter (Köke et al. 2018).
172 *Enrichment V.* The water sample was filtered through a glass fiber filter. An aliquot of 50 mL
173 was adjusted to pH 2 (with 0.02 M Glycin/HCl buffer) and submitted automatically to a WAX
174 SPE cartridge. The cartridge was previously conditioned with 3 mL methanol and 3 mL
175 ultrapure water. After sample loading the cartridge was washed with 4 mL 2 % formic acid in
176 ultrapure water (discarded) and the analytes were eluted with 4 mL methanol and 4 mL 5 %
177 ammonia in methanol. The combined extracts were evaporated to dryness and the residues
178 were reconstituted in 1 mL ultrapure water for *Chromatography* C_1/C_2 or in 1 mL
179 acetonitrile:ultrapure water (90:10) for *Chromatography* D_1/D_2 (see section 2.4). Finally, the
180 extract was filtered through glass wool in the tip of a Pasteur pipette.
181 *Enrichment VI.* Identical to *Enrichment V* but employing a strong mixed-mode cation
182 exchange (MCX) SPE cartridge.
183 *Enrichment VII.* Identical to *Enrichment V* with the following modifications. An aliquot of 50
184 mL was adjusted to pH 7 (with 0.02 M phosphate buffer) and submitted automatically to a
185 highly retentive non-polar SPE phase (ENV+) previously conditioned with 3 mL methanol
186 and 3 mL ultrapure water. After sample loading the cartridge was washed with 2 mL
187 methanol:ultrapure water (5:95, discarded) and the analytes were eluted with 4 mL methanol.
188 *Enrichment VIII.* Identical to *Enrichment V* with the following modifications. An aliquot of 50
189 mL was adjusted to pH 12 (with 0.02 M Glycin/NaOH buffer) and submitted automatically to
190 a graphitized non-porous carbon SPE phase (ENVI-Carb) previously conditioned with 5 mL
191 methanol:dichloromethane (20:80), 2 mL methanol, and 5 mL ultrapure water. After sample
192 loading the cartridge was washed with 5 mL ultrapure water (discarded) and the analytes were
193 eluted with 4 mL methanol, 2 mL methanol:dichloromethane (20:80), and 4 mL 2 % formic
194 acid in methanol:dichloromethane (20:80).

2.4 Instrumental analyses

In total 4 different, complementary instrumental analytical techniques (denoted as *Chromatography A-D*) were used. *Chromatography C* and *D* were performed with two different separation columns each (*Chromatography* C_1/C_2 and *Chromatography* D_1/D_2, respectively). Chemicals and instrumentation used in the different instrumental analytical techniques are listed in Table S4, the gradient profiles for all separation methods are shown in Figure S2, and mass spectrometric parameters are listed in Tables S5A-D (for *Chromatography A-D*, respectively) in the supplementary data.

Chromatography A was used with extracts from *Enrichments I and II*. *Chromatography A* consisted of mixed-mode liquid chromatography (MMLC, Thermo Acclaim Trinity P1 column) coupled to triple quadrupole tandem mass spectrometry (MS/MS) (Table S4). Aliquots of 10 µL of the sample extracts were injected. MMLC separation was performed at a flow rate of 200 µL min^{-1} using a water-acetonitrile gradient buffered with ammonium acetate at pH 5.5 (Figure S2). The mass spectrometer was operated in positive and negative electrospray ionization (ESI) and in the multiple reaction monitoring (MRM) mode, acquiring two transitions for each analyte (Table S5A).

Chromatography B was used with extracts from *Enrichments III and IV*. *Chromatography B* consisted of hydrophilic interaction liquid chromatography (HILIC, Waters Acquity BEH Amide column) coupled to MS/MS (Table S4). Aliquots of 5 µL of the sample extracts were injected. HILIC separation was performed at a flow rate of 500 µL min^{-1} using an acetonitrile-water gradient buffered with ammonium formate (Figure S2). The mass spectrometer was operated in positive and negative ESI and in the scheduled MRM mode, acquiring two to three transitions for each analyte (Table S5B).

Chromatography C_1/C_2 was used with extracts from *Enrichments V-VIII*. *Chromatography* C_1 consisted of C_{18}-based liquid chromatography (Waters Acquity UPLC HSS T3 column) and *Chromatography* C_2 consisted of porous graphitic carbon-based liquid chromatography

(Thermo Hypercarb column). Both these RPLC-techniques were coupled to MS/MS (Table S4). Aliquots of 10 µL of the sample extracts were injected. Separation for *Chromatography C_1* was performed at 60 °C at a flow rate of 500 µL min^{-1} using a water-methanol gradient containing 5 mM ammonium formate (Figure S2). Separation for *Chromatography C_2* was performed at 50 °C at a flow rate of 250 µL min^{-1} using a water-acetonitrile gradient containing 0.1 % diethylamine (Figure S2). The mass spectrometer was operated in positive/negative ESI switching and in the scheduled MRM mode, typically acquiring two transitions for each analyte (Table S5C).

Chromatography D_1/D_2 was used with extracts from *Enrichments V-VIII*. *Chromatography D_1/D_2* consisted of supercritical fluid chromatography (SFC, Waters Acquity UPC^2 BEH (D_1) or Waters Torus Diol (D_2) column) coupled to high resolution quadrupole time-of-flight MS (HRMS) (Table S4). Aliquots of 5 µL of the sample extracts were injected. Separation was performed at 55 °C at a flow rate of 1500 µL min^{-1} using a carbon dioxide-methanol/water gradient containing 0.2 % ammonium hydroxide in the methanol/water co-solvent (Figure S2). A methanol/water make-up flow at 300 µL min^{-1} containing 0.1 % formic acid was used for transferring the column effluent into the mass spectrometer. The HRMS instrument was operated in positive and negative ESI and full scan mode (*m/z* 50 to 600). A mass tolerance of 5 ppm was used when extracting high resolution mass chromatograms of the analytes (Table S5D).

2.5 Method performance evaluation and concentration estimations

Method performance evaluation had the main purpose to prevent false positive results and to allow for semi-quantitative concentration estimations. It consisted of the determination of instrumental blanks, instrumental detection limits (IDLs), retention time repeatability, procedural blanks, and estimation of method detection limits (MDLs). A full method validation was not envisaged, as highly variable compound-specific and sample-specific apparent recoveries (i.e. combination of extraction recovery and matrix effect) hampered

proper quantification in this multi-chemical screening approach. It is thus important to keep in mind that all concentrations given in the present study are semi-quantitative estimates. Details on how method evaluation (including procedural blank experiments and determination of MDLs) and semi-quantitative concentration estimation were performed are given in the supplementary data (page S24).

3. Results and discussion

3.1 Performance of the different enrichment and instrumental methods

The method development targeted at analytical methods encompassing a maximum number of PMOCs, rather than optimization of parameters for certain analytes. Since the 64 targeted PMOCs widely varied in their properties (functional groups, molecular weight, log*D*, pK_a), a number of complementary analytical methods were required to cover the large range of analytes.

3.1.1 Separation methods, instrumental blanks, and instrumental detection limits

Four principally different instrumental separation methods (section 2.4) were developed and compared for the analysis of the 64 selected PMOCs. The separation methods comprised MMLC, HILIC, RPLC, and SFC. In contrast to MMLC and HILIC, which were used with one separation column each, two different column types were tested for both RPLC and SFC (see 2.4). A total of 57 compounds were amenable to at least two separation methods, i.e. leading to a distinct chromatographic signal in two MRM transitions (Tables S5A-C) or, in case of HRMS data, in two extracted high resolution mass chromatograms (usually the quasi-molecular ion and a fragment at higher collision energy, Table S5D). The remaining 7 compounds could only be analyzed by one separation method each, i.e. 3 by HILIC (bis(2-dimethylminoethyl)ether (ID-7), pyrazole (ID-49), 5-chloro-2-methylaniline (ID-59)), 3 by RPLC (gluconate (ID-1), 1,5-naphthalenedisulfonic acid (ID-8), phenylphosphonic acid (ID-27)), and 1 by SFC (1,3,5-triallyl-1,3,5-triazinane-2,4,6-trione (ID-55)). Retention time

repeatability was excellent (max. +/- 0.1 min) for all PMOCs in all separation methods (Table S6).

The instrumental detection limits (IDLs) for all PMOCs with the different instrumental methods are listed in Table S7. Almost all PMOCs (60 out of 64) could be sensitively detected (single digit pg to sub pg injected) with at least one of the tested instrumental methods. The good sensitivity is facilitated by the high polarity of PMOCs, which consequently tend to readily ionize in the ESI-source. Exceptions were bis(2-dimethylaminoethyl)ether (ID-7, with an IDL of 0.13 ng injected), pyrazole (ID-49, IDL 0.5 ng), 1,3,5-triallyl-1,3,5-triazinane-2,4,6-trione (ID-55, IDL 0.013 ng), and 2,6-dimethylaniline (ID-56, IDL 0.012 ng), for which higher IDLs were found. These four PMOCs were all substances that were detected in positive ESI mode based on amine groups. Reasons for their relatively high IDLs were poor ionization efficiency and/or poor fragmentation (in MRM). Furthermore, the following analytes suffered from elevated IDLs due to instrumental blank contamination: Methyl sulfate (ID-14), 4-hydroxy-1-(2-hydroxyehtyl)-2,2,6,6,-tetramethylpiperidine (ID-17), *N*-(3-(dimethylamino)-propyl)methacrylamide (ID-29), dicyclohexyl sulfosuccinate (ID-47), 1,3-diphenylguanidine (ID-52), 3,5-di-*tert*-butylsalicylic acid (ID-54), 1,3-di-*o*-tolylguanidine (ID-58), and tri-(2-chloroisopropyl)phosphate (ID-63).

3.1.2 Retention of PMOCs in the different separation systems

One challenge with highly mobile substances is to retain (and separate) them in a chromatographic system (Reemtsma et al. 2016). Certain retention is, however, mandatory in order to minimize matrix effects in ionization and to facilitate quantification. Table S8 and Figure S3 show the retention factors k' of the PMOCs (i.e. their retention relative to the dead time of the system) for the different methods. HILIC and RPLC show a clear trend of low retention, i.e. early elution for many PMOCs. However, while RPLC shows early elution especially for PMOCs with a very low log*D* value, HILIC shows an opposite trend (Figure

S4). In MMLC the retention factors of the PMOCs cover a wide range including very late elution (k'>30, predominantly for sulfonic acids), despite a steep gradient profile (though ending at 80 % organic mobile phase, Figure S2). The SFC methods (*Chromatography D_1 and D_2*) show moderate retention for most PMOCs, which is a favorable compromise in terms of separation from matrix components and time efficient chromatography. A strong positive relationship of k' values and calculated log*D* values of the substances was observed in RPLC-HSST3 (*Chromatography C_1*), whereas this relationship was weaker (and partly negative) for the other separation techniques (Figure S4). In conclusion, RPLC is generally only applicable to PMOCs with moderate polarity (log*D*>0, Reemtsma et al. 2016). PMOCs with log*D*<0 should be analyzed with alternative methods such as HILIC, MMLC, or SFC (Figure S4), whereby the MMLC method used in the present study was inefficient for many sulfonic acids (long retention times). SFC showed moderate retention and very narrow signals for most of the investigated PMOCs but has the drawback that it cannot be performed on a conventional LC system.

3.1.3 Evaluation of the analytical methods

Enrichment of mobile substances from water samples is another challenge in PMOC analysis (Reemtsma et al. 2016). A total of 8 different enrichment methods (section 2.3) were tested in specific combinations with the instrumental methods (section 2.4). Table S9 lists the method combinations that were successfully applied for analysis of the different target PMOCs. For seven of the 64 PMOCs (gluconate (ID-1), 1,1,4,7,7-pentamethyl-diethylenetriamine (ID-11), 3-mercapto-1-propanesulfonic acid (ID-19), phenylphosphonic acid (ID-27), pyrazole (ID-49), 5-chloro-2-methylaniline (ID-59), and N1-isopropyl-N4-phenylbenzene-1,4-diamine (ID-64)) none of the tested method combinations worked. These seven PMOCs could thus not be analyzed in the present study and are not discussed further. All in all 20 different combinations of enrichment and instrumental methods were tested and used for environmental water analysis (Table S9 and Figure S5). None of the method combinations was applicable to

more than 24 of the investigated PMOCs (Figure S5), which demonstrates the complementarity of the methods. Nevertheless, there were distinct differences in the broadness of applicability. *Enrichments III* and *IV* (multi-layer SPE and evaporation, both in combination with HILIC) and *Enrichment VII* (ENV+ SPE, in combination with RPLC or SFC) were the enrichment methods capturing most PMOCs. Multi-layer SPE methods have also earlier been used successfully in environmental water analysis for a variety of polar micropollutants (Huntscha et al. 2012). On the other hand, *Enrichment VI* (MCX) was only successful for few PMOCs in the present study. MCX is a strong reversed-phase mixed-mode cation-exchange polymer. Some cationic analytes may have sorbed too strongly on this polymer to be eluted with the chosen elution method. In terms of separation methods, *Chromatography* C_2 (RPLC with Hypercarb column) showed a comparatively poor performance. It worked well for standard chemicals, but many signals broadened significantly in the presence of sample matrix, preventing this method from a broad applicability range among the selected target PMOCs (Figure S5).

3.1.4 Procedural blanks and method detection limits

The estimated method detection limits (MDLs) for all PMOCs applying the developed methods (i.e. combinations of enrichment and instrumental methods) are listed in Table S9. They were generally in the low to sub ng L^{-1} range, but covered overall five orders of magnitude (0.02 to 2000 ng L^{-1}) for the different PMOCs and methods. Also for some individual PMOCs the MDLs of different methods varied considerably. It is important to note that the MDLs were not only dependent on the enrichment and separation methods, but also on the employed MS instrument and on the presence (or absence) of procedural blank contamination. A total of 29 investigated PMOCs seem to be widely dispersed water pollutants or contaminants in lab consumables and equipment, as they were detected repeatedly in procedural blank experiments, leading to correspondingly elevated MDLs. These compounds were ID-2, -10, -14, -16, -17, -20, -21, -22, -23, -24, -25, -26, -32, -33, -34,

-36, -37, -39, -40, -43, -44, -46, -47, -51, -52, -54, -58, -61, and -63. No effort was made in the present study to elucidate or eliminate the source(s) of the procedural blank contaminations.

3.2 Detection frequencies in target screening of environmental water samples

All developed method combinations were applied to 14 water samples (section 2.2 and Table S2) to screen for the 57 PMOCs amenable to at least one of the methods (see 3.1.3). The samples comprised surface water, groundwater, and bank filtrate as well as reverse osmosis concentrate and permeate. In total 43 PMOCs (75 % of the investigated substances) were detected above their MDL in at least one sample with at least one of the applied methods (Figure 1). Figure 1 shows the detection frequency for the individual PMOCs in the 14 samples including information on the number of underlying principally different separation methods (*Chromatography A-D*). Of the 43 detected PMOCs, 21 were found in at least 50 % of the samples and often at relatively high concentrations (Figure S6 and section 3.3 below). Chromatography method-specific detection frequencies are listed in Table S10, underpinning the complementarity of the employed separation methods in analysis of the target PMOCs. The most important detected PMOCs are discussed in section 3.4 below.

3.3 Concentration estimates

Concentrations of the detected PMOCs in the water samples were estimated according to section 2.5. They need to be considered as semi-quantitative estimates. Since extraction recoveries and matrix effects (suppression more common than enhancement) were not taken into account, it can be assumed that the estimated concentrations are mostly underestimations. Figure 2 shows boxplots of estimated concentrations of selected PMOCs in the water samples. The selection of PMOCs for Figure 2 was based on the quality criteria that the substance was detected by more than one method and that the estimated concentrations by the different methods for a given sample were consistent (i.e. typically within one order of magnitude, then averaged over all methods in Figure 2). Furthermore, Figure S6 depicts the maximum

estimated concentration (gray shade) for all detected PMOCs together with the frequency of detection.

Some PMOCs were detected in the high ng L^{-1} up to µg L^{-1} range (Figure 2 and Figure S6). Of the PMOCs shown in Figure 2, these were notably ID-13 (acesulfame), ID-25 (sulfanilic acid), ID-26 (melamine), ID-33 (trifluoromethanesulfonic acid), ID-37 (cyanoguanidine), ID-39 (*p*-toluenesulfonic acid), ID-40 (saccharine), ID-44 (dimethylbenzenesulfonic acid), and ID-45(benzyldimethylamine). It is noteworthy that a high frequency of detection did not necessarily go along with high concentrations. An example is ametryn (ID-61), which was detected in 11 samples, but at a low maximum concentration (Figure 2).

3.4 Discussion of detected PMOCs

All of the 43 detected PMOCs were industrial chemicals registered under REACH with calculated log*D* values at pH 7 ranging between -5.6 and 3.4 (average -1.9, ChemAxon). Their uses cover many different fields of application, including coating products, inks and paints, adhesives and sealants, water treatment products, leather and textile treatment products, cosmetics and personal care products, vulcanization or polymerization processes, and processing aids in other applications (Table 1). Also the tonnages manufactured in and/or imported into the European Union vary widely. They range from single digit up to hundred thousands of tons (Table 1, ECHA 2018).

The detected PMOCs were categorized according to two criteria: Frequency of detection and level of awareness as environmental water pollutants (Figure 3 and Table 1). PMOCs that were detected in at least half of the samples (≥7 samples) were placed in the category “high frequency of detection”, other detected PMOCs were placed in the category “low frequency of detection”. For the awareness criterion, three categories were made based on a literature search using Google Scholar including the substance name (IUPAC or trivial name) and the search terms ‘environment’, ‘surface water’, ‘groundwater’, or ‘drinking water’. The three categories were “novel” PMOCs, i.e. substances that have not been reported as environmental

water pollutants so far, "scarcely investigated" PMOCs, i.e. substances for which very few reports on environmental occurrence exist (often only from industrial sites or waste water treatment effluents), and "well-known" PMOCs, for which ample literature data exist. This categorization allows a prioritization of the detected PMOCs for future investigations as indicated in Figure 3, with PMOCs in the top left corner having the highest priority (priority 1), followed by PMOCs in the top middle (priority 2), PMOCs in the bottom left corner (priority 3), and so forth. The PMOCs in the two top priority categories are shown with their structures in Figure 3 and shortly discussed individually in the following sub-sections, while all detected PMOCs are presented in Table 1.

3.4.1 Priority 1 PMOCs

Methyl sulfate (ID-14) as a relatively small surfactant was detected in surface and groundwater samples primarily from The Netherlands at levels up to the high ng L^{-1} range. The present study is the first report on the occurrence of methyl sulfate in the environment.

2-Acrylamino-2-methylpropane sulfonate (ID-16) was one of several sulfonic acids/sulfonates frequently detected in the present study. This compound was typically found in the range of 1-10 ng L^{-1}, but occasionally also exceeding 100 ng L^{-1}. ID-16 was detected in every analyzed sample type. The occurrence of ID-16 in environmental waters is reported here for the first time.

Benzyltrimethylammonium (ID-23), a permanently charged quaternary ammonium cation, and **benzyldimethylamine** (ID-45) are two PMOCs with similar basic structures that were frequently detected here for the first time. They were both primarily found in surface water, but in single cases also in groundwater samples. ID-23 was detected in single digit ng L^{-1} concentrations while ID-45 occurred in up to several hundreds of ng L^{-1}.

Trifluoromethanesulfonic acid (TFMSA, ID-33) was found in all analyzed samples with the exception of the reverse osmosis permeate and at levels up to the µg L^{-1} range (Figure 2). TFMSA could be analyzed by all of the separation methods (Table S9), even though the

retention in HILIC and RPLC was poor (Table S8). We have chosen to categorize TFMSA as "novel" since we are the only ones so far who have reported on the occurrence of TFMSA in environmental water samples (Zahn et al. 2016; Montes et al. 2017, in another context and in other samples from the same larger collaborative study). TFMSA belongs to the group of short-chain perfluoroalkane sulfonic acids. Other short-chain perfluoroalkyl acids, such as trifluoroacetic acid, have already been found in drinking water (Mak et al. 2009; Janda et al. 2018).

6-Methyl-1,3,5-triazine-diamine (acetoguanamine, ID-42) was detected in all of the 7 surface water samples at concentrations typically around or below 10 ng L^{-1} (Figure 2). To the best of our knowledge the presence of acetoguanamine in environmental water samples is reported here for the first time.

1,3-Di-*o*-tolylguanidine (DTG, ID-58) was detected in all 14 analyzed samples (in 11 samples with at least two methods, Figure 1) at estimated concentrations typically around 10 ng L^{-1} (Figure 2). Likewise TFMSA (ID-33), so far only our reports exist on the presence of DTG in surface water, groundwater, and drinking water (present study and Montes et al. 2017 with a different sample set).

3.4.2 Priority 2 PMOCs

Adamantan-1-amine (amantadine, ID-32) is a pharmaceutical used as antiviral (against influenza A virus) and antiparkinsonian medication. Moreover, amantadine is also a chemical registered under REACH because of its use as an intermediate in industrial processes (ECHA 2018). Also this PMOC was identified in every sample with the exception of the reverse osmosis permeate. It has earlier been identified in German municipal effluent water (Möhle and Metzger 2001).

All of the three guanidine derivatives that were analyzed (including DTG discussed above and DPG discussed below) were detected in the majority of samples. **Cyanoguanidine** (CG, ID-37) was detected in 8 of the analyzed water samples, i.e. in all 7 surface water samples and in

one German groundwater sample (Figure 1) at concentrations exceeding 3000 ng L^{-1} (Figure 2). Few studies have previously reported the environmental occurrence of CG. Scheurer and co-workers detected CG in German surface water in the mg L^{-1} range, with an industrial site as a point source (Scheurer et al. 2016). In surface water samples in a coastal agricultural catchment from New Zealand CG was quantified with a maximum concentration close to 1 mg L^{-1} (Smith and Schallenberg 2013).

***p*-Toluenesulfonic acid** (ID-39) was detected in all 14 samples and at concentrations exceeding 1000 ng L^{-1}. It has earlier been detected in drinking water in the United Kingdom (Crathorne et al. 1984).

The two isomers of **dimethylbenzenesulfonic acid** (ID-44), i.e. xylenesulfonic acid and 2,3-dimethylbenenzenesulfonic acid, were both detected in 13 samples (Figure 1). Only the reverse osmosis permeate from the Netherlands showed levels <MDL. Betowski and co-workers have earlier reported on the presence of xylenesulfonic acid in groundwater (Betowski et al. 1996).

Two isomers of the compound **toluenesulfonamide** (ID-51) were detected in 12 out of 14 samples, with the exception of one groundwater sample and the reverse osmosis permeate. In a study by Richter et al. (2017) with different types of water from Berlin ID-51 was found at concentrations up to 50 µg L^{-1} in wastewater and 0.27 µg L^{-1} in drinking water.

Likewise DTG, **1,3-diphenylguanidine** (DPG, ID-52) was detected in all 14 analyzed samples, but at higher estimated concentrations up to 100 ng L^{-1} (Figure 2). In an earlier study on drinking water in China DPG was found at levels up to 0.74 mg L^{-1} due to migration from high density polyethylene pipes (Tang et al. 2015).

3.5 Evaluation of the prioritization and analytical strategy

While a number of prioritization approaches for chemicals (based on regulatory databases or other available datasets) with respect to environmental and/or human exposure and risk have been published (as reviewed in e.g. Muir and Howard 2006; Bu et al. 2013; Mitchell et al.

2013), relatively few chemical analytical studies have been conducted taking direct advantage of such prioritization exercises (McLachlan et al. 2014; Singer et al. 2016; Sjerps et al. 2016; Montes et al. 2017; Gago-Ferrero et al. 2018). Nevertheless, monitoring is necessary to validate the prioritization approaches.

The present chemical analytical study builds on a prioritized list of industrial chemicals that have been modeled to be persistent, mobile, and to possess a high environmental emission potential (Schulze et al. 2018). Additionally, we used targeted analytical methods with generally very high sensitivity. Still, several target analytes were not detected in the analyzed samples. This could be due to one or several of the following uncertainties of our overall prioritization and analytical strategy. I) The modeling of especially persistence, but also mobility and emission potential, is tainted with considerable uncertainties, as discussed in detail in Arp et al. 2017 and in Schulze et al. 2018. II) For some of the target analytes enrichment from water, chromatographic retention and/or peak shape, or ionization in ESI was poor, hampering sensitive detection. III) The analyzed water samples were not representative for all European countries or regions. Some PMOCs may have well defined points of emission that were not covered by the sampling design.

Despite these uncertainties, our overall strategy was highly successful. Among the 54 target PMOCs selected from the prioritized list in the supplementary data in Schulze et al. 2018 (section 2.1), 49 were amenable to at least one of the developed methods. Out of these 49 substances 35 PMOCs were found in surface and/or groundwater, among them 23 PMOCs that have not been reported before to occur in environmental waters. The high detection rate of 71 % (35/49) validates the good accuracy of the modeling and corroborates the strength of the chosen approach, i.e. a focused prioritization combined with sensitive target analysis.

4 Conclusions

The present study has validated and proven the strength of the chosen modeling and analytical approach consisting of a focused prioritization combined with sensitive target chemical analysis. The developed enrichment and chromatographic methods proved to be useful and complementary for analysis of PMOCs in water samples. They can be used individually or in combination with each other to further investigate the occurrence and fate of PMOCs in water cycles. In the present study 75 % of the analyzed PMOCs were detected in selected water samples from Germany, Spain and The Netherlands. This high rate of detection together with the fact that more than 1000 PMOC candidates with an environmental emission potential were identified only among the substances registered under REACH (Schulze et al. 2018) leads to the conclusion that there are likely hundreds of so far undiscovered PMOCs present in environmental waters, threatening the quality of drinking water resources. An important follow-up study would thus be to use the list published by Schulze et al. (2018) in order to better characterize the number and identity of PMOCs occurring in environmental waters. Furthermore, the development of quantitative analytical methods for PMOCs would enable more detailed fate studies of PMOCs, e.g. investigating the removal in different steps of drinking water production. Finally, the toxicity of the most abundant of the identified PMOCs (e.g. TFMSA, CG, and *p*-toluenesulfonic acid occurring in high ng L^{-1} up to µg L^{-1} concentrations) needs to be investigated as another important step in PMOC risk assessment. In this respect, activities are ongoing by national and European authorities to classify substances according to their persistence, mobility, and toxicity (PMT) properties (Neumann and Schliebner 2017). The results of the present study inform such activities.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at …

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Table 1. PMOCs detected in at least one water sample classified according to their frequency of detection and level of awareness (Figure 3). The underlying analytical methods are listed in Table S9.

Index	Substance name	log*D**	CAS no.	Use**	Tonnage/yr**	Literature
Priority 1: Novel and high frequency of detection						
ID-14	Methyl sulfate	-2.84	512-42-5	• Surface active agent • Laboratory chemical	10 - 100	
ID-16	2-Acrylamino-2-methylpropane sulfonate	-2.71	5165-97-9	• Monomer for polymerization and in hydrogels	10 000 - 100 000	
ID-23	Benzyltrimethylammonium	-2.24	56-93-9	• Process regulator, surface active agent • Used in vulcanization or polymerization processes • Removal of charged micropollutants from water by ion exchange polymers	100 - 1 000	
ID-33	Trifluoromethanesulfonic acid	-1.23	1493-13-6	• Processing aid, process regulator, laboratory chemical • Used in vulcanization or polymerization processes • Ingredient of ionic liquids	100 - 1 000	Zahn (2016) Montes (2017)
ID-42	6-Methyl-1,3,5-triazine-diamine	-0.39	542-02-9	• Stabilizer for formaldehyde solutions • Used in the manufacturing of melamine resins, in adhesives and sealants, in the decorative layer of high-pressure laminates	0 - 10	
ID-45	Benzyldimethylamine	0.02	103-83-3	• Process regulator • Used in vulcanization or polymerization processes • Used in binding agents, fixing agents, polymers, adhesives and sealants, and coating products	100 - 1 000	
ID-58	1,3-Di-*o*-tolylguanidine	2.25	97-39-2	• Process regulator • Used in vulcanization or polymerization processes and in rubber products	100 - 1 000	Montes (2017)
Priority 2: Scarcely investigated and high frequency of detection						
ID-32	Adamantan-1-amine	-1.49	768-94-5	• Intermediate • Antiviral and antiparkinsonian pharmaceutical	Intermediate	Möhle and Metzger (2001)
ID-37	Cyanoguanidine	-1.03	461-58-5	• Modifying agent for melamine resins • Processing aid • Used in fertilizers, textile treatment products, and dyes • Used for the manufacture of textile, leather and fur	10 000 - 100 000	Scheurer et al. (2016) Smith and Schallenberg (2013)
ID-39	*p*-Toluenesulfonic acid	-0.71	104-15-4	• Processing aid, process regulator, pH-regulating agent • Used in vulcanization or polymerization processes and in water treatment products	10 000 - 100 000	Crathorne et al. (1984)

ID-44	Dimethylbenzenesulfonic acid	-0.20	1300-72-7 25321-41-9	• Process regulator • Used in vulcanization or polymerization processes • pH-regulating agent • Laboratory chemical	1 000 - 10 000	Betwoski et al. (1996)
ID-51	Toluenesulfonamide	1.09	70-55-3 88-19-7	• Processing aid, laboratory chemical • Used in polymers	10 - 100	Richter et al. (2007)
ID-52	1,3-Diphenylguanidine	1.23	102-06-7	• Process regulator • Used in vulcanization or polymerization processes • In rubber products, polymers, tires, treated wooden products, bridges a.o.	1 000 - 10 000	Tang et al. (2015)
Priority 3: Novel and low frequency of detection						
ID-2	2-Piperazin-1-ylethylamine	-5.61	140-31-8	• Used in adhesives and sealants • Coating products, fillers, putties, plasters, modelling clay, finger paints and polymers	1 000 - 10 000	
ID-3	Isophoronediamine	-4.59	2855-13-2	• Adhesives and sealants • Coating products, fillers, putties, plasters, modelling clay • Laboratory chemical	10 000 - 100 000	
ID-6	Methacrylamido propyl trimethyl ammonium	-3.74	51410-72-1	• Intermediate • Industrial use of monomers for manufacture of thermoplastics	100 - 1 000	
ID-9	2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid	-3.25	7365-45-9	• Used in water treatment products, adhesives and sealants, coatings, fillers, putties, plasters, modelling clay, inks, toners, leather and textile treatment products, lubricants, greases, perfumes, fragrances, polishes, waxes, dyes, cosmetics, and personal care products	100 - 1 000	
ID-12	3-Allyloxy-2-hydroxy-1-propanesulfonic acid	-3.13	52556-42-0	• Processing aids at industrial sites • Corrosion inhibitor • Anti-scaling agent	1 000 - 10 000	
ID-15	1,4-Diazabicyclo-[2.2.2]octane	-2.83	280-57-9	• Process regulator • Used in vulcanization or polymerization processes	1 000 - 10 000	
ID-17	4-Hydroxy-1-(2-hydroxyehtyl)-2,2,6,6,-tetramethylpiperidine	-2.62	52722-86-8	• Used for the manufacture of chemicals and plastic products	1 000 - 10 000	
ID-18	Vinylsulfonate	-2.60	3039-83-6	• Plating agents and metal surface treating agents • Surface active agent • Used in metal working fluids	100 - 1 000	
ID-24	2-Methyl-2-propene-1-sulfonic acid	-2.21	1561-92-8	• Process regulator • Used in vulcanization or polymerization processes	1 000 - 10 000	

				• Used for the manufacture of textile, leather, and fur (water repellent)		
ID-28	Carbodihydrazide	-1.96	497-18-7	• Corrosion inhibitor and anti-scaling agent • Used in water treatment chemicals and polymers	100 - 1 000	
ID-29	*N*-(3-(Dimethylamino)-propyl)methacrylamide	-1.85	5205-93-6	• Used in adhesives and sealants	1 000 - 10 000	
ID-34	Dimethyl-5-sulfoisophthalate	-1.22	3965-55-7	• Processing aid • Used for the manufacture of plastic products and chemicals • Used in textile and leather treatment products and dyes, polymers, and non-metal-surface treatment products	100 - 1 000	
ID-47	Dicyclohexyl sulfosuccinate	0.42	23386-52-9	• Used in adhesives and sealants, coating products and fillers, putties, plasters, modelling clay	100 - 1 000	
ID-50	4-((4-Aminophenyl)diazenyl)benzene-sulfonic acid	0.36	104-23-4	• Intermediate • Laboratory chemical	Intermediate	
ID-54	3,5-Di-*tert*-butylsalicylic acid	1.62	19715-19-6	• Surface active agent • Used in inks and toners, electrical batteries and accumulators	10 - 100	
ID-60	4,4-Diaminodiphenylmethane	2.40	101-77-9	• Used in lubricants and lubricant additives, polymers, greases	10 000 - 100 000	
Priority 4: Well-known and high frequency of detection						
ID-13	Acesulfame	-3.06	55589-62-3	• Sweetener	1 000 - 10 000	Buerge et al. (2009)
ID-22	Cyanuric acid	-2.39	108-80-5	• Water treatment chemical • Used in health services and municipal supply (e.g. electricity, steam, gas, water), in sewage treatment, and in swimming pools for pH control • Used for the manufacture of plastic products	10 000 - 100 000	Reemtsma et al. (2013)
ID-25	Sulfanilic acid	-2.04	121-47-1 121-57-3	• pH regulator • Water treatment product • Laboratory chemical	1 000 - 10 000	Holm et al. (1995)
ID-26	Melamine	-2.02	108-78-1	• Production of melamine resins • Used flame retardants, laboratory chemicals, anti-set off and adhesive agents, impregnation agents, coloring agents, dyes, textile treatment products, non-metal-surface treatment products, paper chemicals, pH regulators, water and leather treatment products, and finger paints	100 000 – 1 000 000	Ruff et al. (2015) Jiang et al. (2015)
ID-43	Naphthalene-1-sulfonic acid	-0.23	85-47-2	• Used in rubbers, pharmaceuticals, pesticides, varnishes and	no information	Alonso and Barcelo

				dyestuffs	available	(1999)
ID-46	ε-Caprolactam	0.31	105-60-2	• Processing aid • Used in tanning agents, solvents, impregnation agents, reprographic agents (roners), bleaching agents, inks and toners, plastic products, textile, leather, and fur • Laboratory chemical	1 000 000 – 10 000 000	Wang et al. (2003)
ID-61	Ametryn	2.57	834-12-8	• Plant protection active substance	1 000 - 10 000	Lanchote et al. (1999)
ID-63	Tri-(2-chloroisopropyl)phosphate	3.36	13674-84-5	• Flame retardant • Used in adhesives and sealants, coating products, laboratory chemicals, leather treatment products, plastic and rubber products	0 - 10	Reemtsma et al. (2008) Li et al. (2014)
Priority 5: Scarcely investigated and low frequency of detection						
ID-38	2-Amino-4,5-dichlorobenzenesulfonic acid	-0.84	6331-96-0	• Intermediate (for paints)	10 - 100	Landesamt für Umwelt, Wasserwirtschaft und Gewerbeaufsicht Rheinland-Pfalz (2011)
ID-41	1,2,4-Triazole	-0.41	288-88-0	• Semiconductors and photovoltaic agents • In fertilizers, forestry, fishing	1 000 - 10 000	Scheurer et al. (2016)
Priority 6: Well-known and low frequency of detection						
ID-8	1,5-Naphthalenedisulfonic acid	-3.43	81-04-9	• Intermediate	Intermediate	Knepper et al. (1999)
ID-20	Ethyl sulfate	-2.48	342573-75-5	• Anti-static agent	Pre-registration process	Mastroianni et al. (2014)
ID-40	Saccharine	-0.49	81-07-2	• Food/feedstuff additive (sweetener) • Used in cosmetics and personal care products, textile treatment products, fur, leather • Pharmaceutical substance	100 - 1 000	Buerge et al. (2009) Scheurer et al. (2009)
ID-57	Bisphenol S	2.17	80-09-1	• Homologue to BPA • Used in leather treatment products, polymers, coating products, pH regulators, water and textile treatment products, paper chemicals and dyes	10 000 - 100 000	Yamazaki et al. (2015)

* Calculated at pH 7.0 using ChemAxon (https://www.chemaxon.com/download/jchem-for-office/#jc4x)
** ECHA 2018

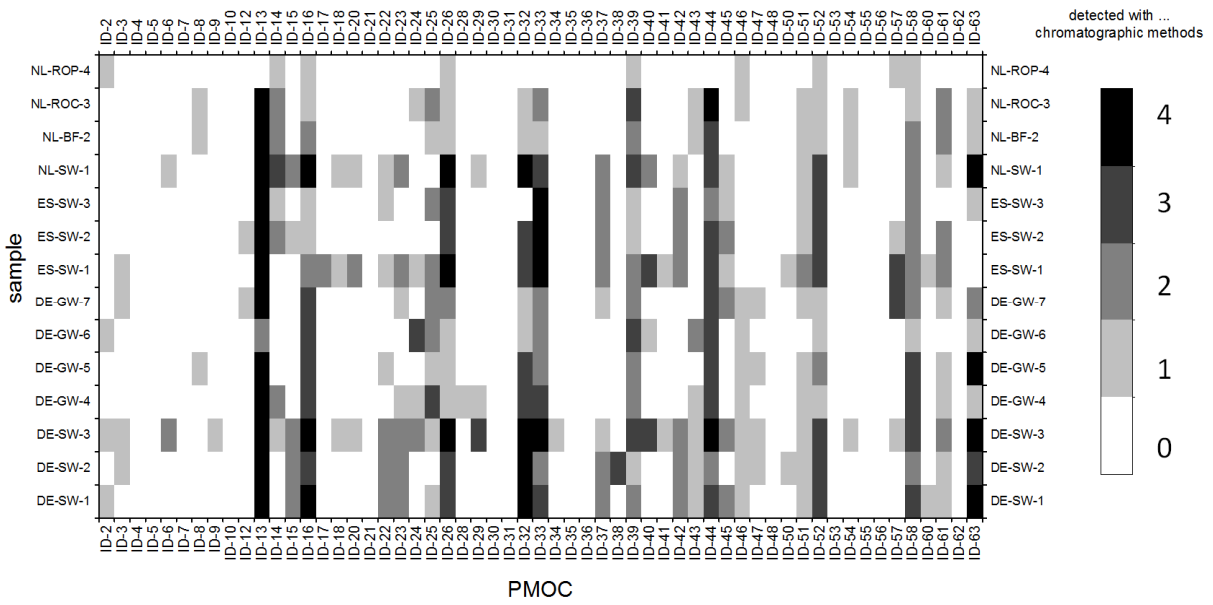

Figure 1. Detection frequencies of the target PMOCs in the 14 water samples. The gray shading shows the number of principally different separation methods (*Chromatography A-D*) with which the PMOCs were detected.

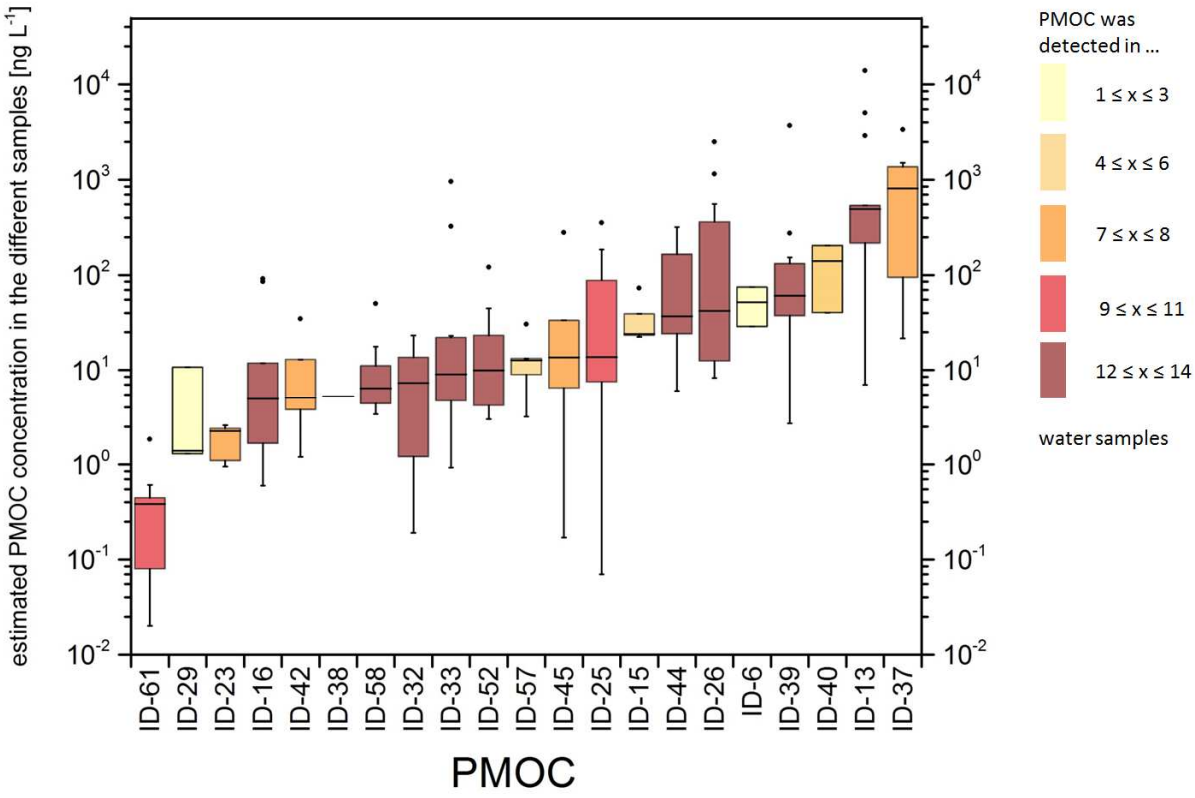

Figure 2. Estimated concentrations of selected PMOCs in the water samples. The color shading indicates the detection frequency in the 14 samples. The horizontal line marks the median value, the box comprises the interquartile range (IQR), and the whiskers reach to the outmost measuring points that are within 1.5 times the IQR. Dots represent single high concentrations. ID-6: methacrylamido propyl trimethyl ammonium, ID-13: acesulfame, ID-15: 1,4-diazabicyclo-[2.2.2]octane, ID-16: 2-acrylamino-2-methylpropane sulfonate, ID-23: benzyltrimethylammonium, ID-25: sulfanilic acid, ID-26: melamine, ID-29: N-(3-(dimethylamino)-propyl)methacrylamide, ID-32: adamantan-1-amine, ID-33: trifluoromethanesulfonic acid, ID-37: cyanoguanidine. ID-38: 2-amino-4,5-dichlorobenzenesulfonic acid, ID-39: *p*-toluenesulfonic acid, ID-40: saccharine, ID-42: 6-methyl-1,3,5,-triazine-diamine, ID-44: dimethylbenzenesulfonic acid, ID-45: benzyldimethylamine, ID-52: 1,3-diphenylguanidine, ID-57: bisphenol S, ID-58: 1,3-di-*o*-tolylguanidine, ID-61: ametryn.

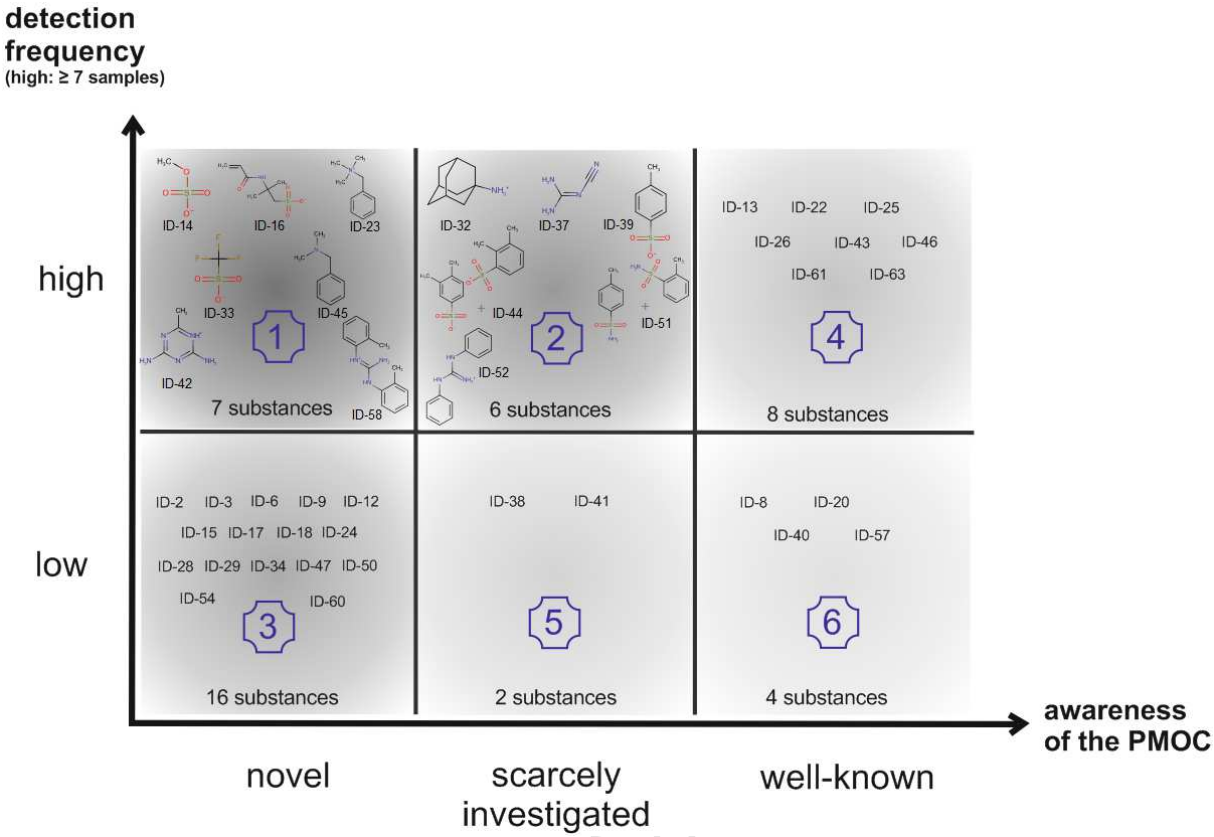

Figure 3. Classification of PMOCs in priority classes (1-6) according to their frequency of detection and level of awareness as environmental water pollutants.

Highlights

- Persistent and mobile organic chemicals (PMOCs) occur in drinking water resources
- Innovative methods for analysis of PMOCs in water samples are presented
- 57 PMOCs are selected and analyzed in 14 European water samples
- 43 PMOCs (75 %) are detected, among them 23 for the first time
- PMOC concentrations range up to µg L^{-1} in surface and groundwater

Supplementary Data

Occurrence of emerging persistent and mobile organic contaminants in European water samples

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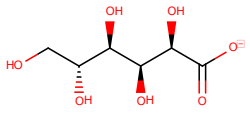
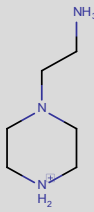
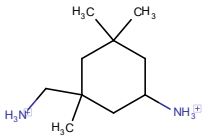
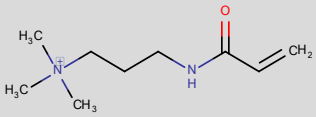
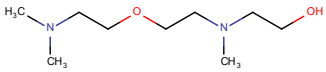
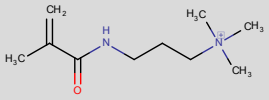
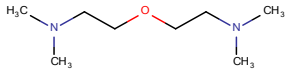
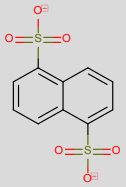
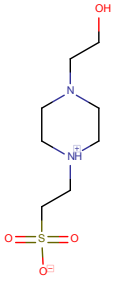
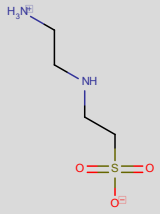
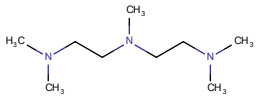
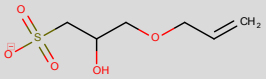
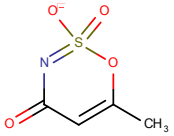
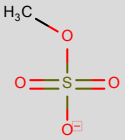
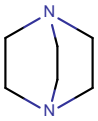
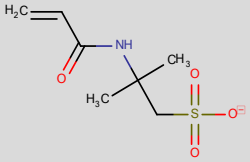
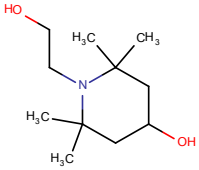
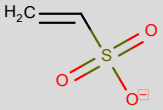
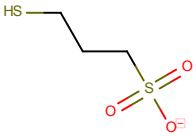
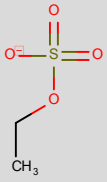
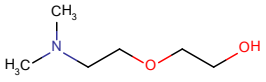
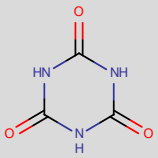
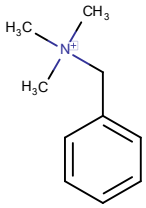
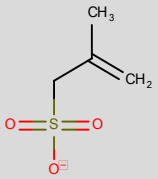
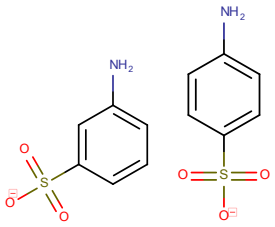
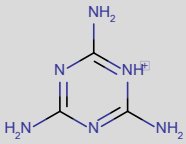
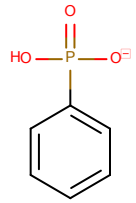
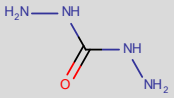
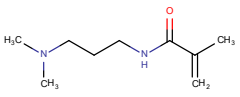
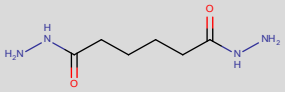
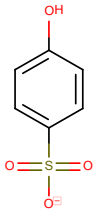
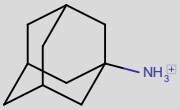
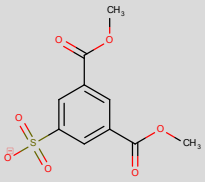
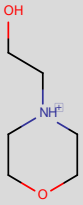
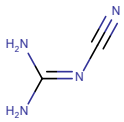
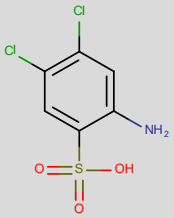
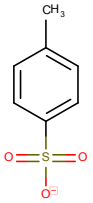
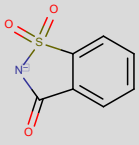
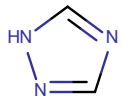
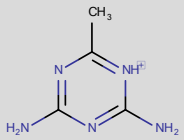
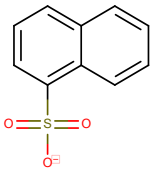
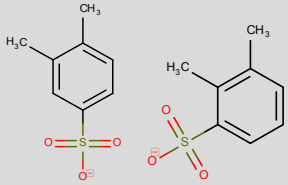
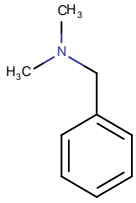
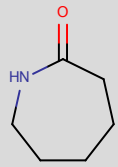
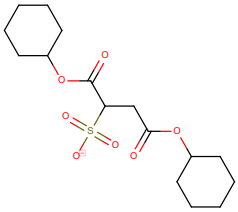
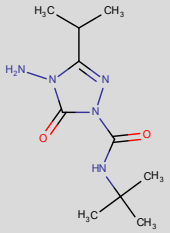
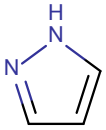
Table S1. List of target PMOCs sorted by log*D* (pH 7.0)[1]

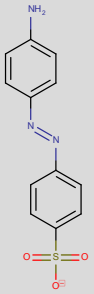
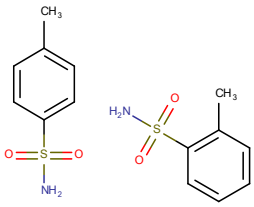
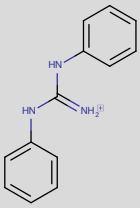
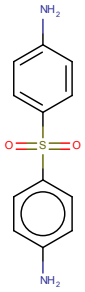
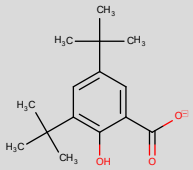
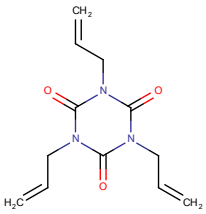
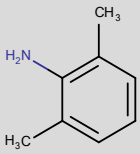
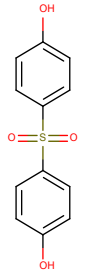
Index	CAS registry number	Substance name	log*D* (pH 7.0)[1]	Structure (main structure at pH 7.0)[1]	Supplier	Chemical standard grade
ID-1	299-27-4	(Potassium) gluconate	-6.68		Sigma Aldrich	Pharmaceutical secondary standard
ID-2	140-31-8	2-Piperazin-1-ylethylamine	-5.61		Fluorochem	
ID-3	2855-13-2	Isophoronediamine	-4.59		abcr GmbH	99%
ID-4	45021-77-0	(3-Acrylamidopropyl)-trimethylammonium (chloride)	-4.13		Sigma Aldrich	75%
ID-5	83016-70-0	N,N,N'-Trimethyl-N'-(2-hydroxyethyl)-bis(2-aminoethyl)ether	-3.99		abcr GmbH	98%
ID-6	51410-72-1	Methacrylamido propyl trimethyl ammonium (chloride)	-3.74		abcr GmbH	50%
ID-7	3033-62-3	Bis(2-dimethylaminoethyl)ether	-3.57		Alfa Aesar	98%
ID-8	81-04-9	1,5-Naphthalenedisulfonic acid	-3.43		abcr GmbH	
ID-9	7365-45-9	2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid	-3.25		Sigma Aldrich	≥ 99,5 %

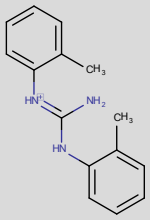
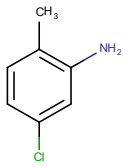
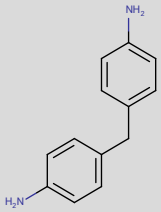
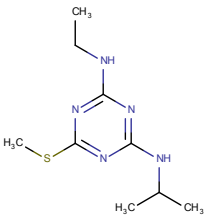
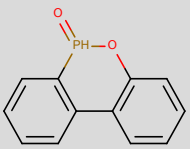
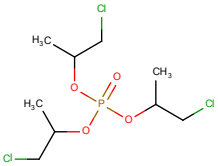
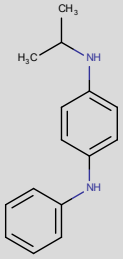
ID-10	34730-59-1	(Sodium) 2-(2-aminoethylamino)ethanesulfonate	-3.25		Ark Pharm Fine Chemicals	40%
ID-11	3030-47-5	1,1,4,7,7-Pentamethyl-diethylenetriamine	-3.20		Acros Organics	≥ 99,5 %
ID-12	52556-42-0	3-Allyloxy-2-hydroxy-1-propanesulfonic acid (sodium salt)	-3.13		Sigma Aldrich	
ID-13	55589-62-3	Acesulfame (K)	-3.06		Sigma Aldrich	≥ 99 %
ID-14	512-42-5	(Sodium) methyl sulfate	-2.84		Sigma Aldrich	
ID-15	280-57-9	1,4-diazabicyclo-[2.2.2]octane	-2.83		Sigma Aldrich	≥ 99 %
ID-16	5165-97-9	(Sodium) 2-acrylamino-2-methylpropane sulfonate	-2.71		abcr GmbH	
ID-17	52722-86-8	4-Hydroxy-1-(2-hydroxyethyl)-2,2,6,6,-tetramethylpiperidine	-2.62		abcr GmbH	98%
ID-18	3039-83-6	(Sodium) vinylsulfonate	-2.60		abcr GmbH	25%
ID-19	17636-10-1	3-Mercapto-1-propanesulfonic acid (sodium salt)	-2.56		Sigma Aldrich	90 % (technical grade)
ID-20	342573-75-5	(1-Ethyl-3-methylimidazolium) ethyl sulfate	-2.48		Fluka Analytical	≥ 98,5 %

ID-21	1704-62-7	2-(2-(Dimethylamino)ethoxy)ethanol	-2.41		Sigma Aldrich	98%
ID-22	108-80-5	Cyanuric acid	-2.39		Sigma Aldrich	analytical standard
ID-23	56-93-9	Benzyltrimethylammonium (chloride)	-2.24		Sigma Aldrich	97%
ID-24	1561-92-8	2-Methyl-2-propene-1-sulfonic acid (sodium salt)	-2.21		Sigma Aldrich	98%
ID-25	121-47-1 121-57-3	Sulfanilic acid	-2.04		Sigma Aldrich	99%
ID-26	108-78-1	Melamine	-2.02		Sigma Aldrich	analytical standard
ID-27	1571-33-1	Phenylphosphonic acid	-1.98		Sigma Aldrich	98%
ID-28	497-18-7	Carbodihydrazide	-1.96		Sigma Aldrich	98%
ID-29	5205-93-6	N-(3-(dimethylamino)-propyl)methacrylamide	-1.85		Fluorochem	
ID-30	1071-93-8	Adipic acid dihydrazide	-1.72		Fluorochem	

ID-31	98-67-9	p-Phenolsulfonic acid hydrate	-1.53		abcr GmbH	85%
ID-32	768-94-5	Adamantan-1-amine	-1.49		Fluorochem	
ID-33	1493-13-6	Trifluoromethanesulfonic acid	-1.23		Sigma Aldrich	≥ 99 %
ID-34	3965-55-7	Dimethyl 5-sulfoisophthalate (sodium salt)	-1.22		Alfa Aesar	98%
ID-35	7529-22-8	N-methylmorpholin-N-oxid	-1.15		Sigma Aldrich	97%
ID-36	622-40-2	2-(4-Morpholinyl)ethanol	-1.13		Sigma Aldrich	99%
ID-37	461-58-5	Cyanoguanidine	-1.03		Acros Organics	99.50%
ID-38	6331-96-0	2-Amino-4,5-Dichlorobenzenesulfonic acid	-0.84		Fluorochem	
ID-39	104-15-4	p-Toluenesulfonic acid	-0.71		MP Biomedicals	≥ 99 %
ID-40	81-07-2	Saccharine	-0.49		Sigma Aldrich	≥ 99%

ID-41	288-88-0	1,2,4-Triazole	-0.41		Fluorochem	
ID-42	542-02-9	6-Methyl-1,3,5-triazine-diamine	-0.39		Sigma Aldrich	98%
ID-43	85-47-2	Naphtalene-1-sulfonic acid	-0.23		Fluorochem	
ID-44	1300-72-7 25321-41-9	Dimethylbenzenesulfonic acid	-0.20		Sigma Aldrich	
ID-45	103-83-3	Benzyldimethylamine	0.02		Serva	research grade
ID-46	105-60-2	ε-Caprolactam	0.31		Sigma Aldrich	analytical standard
ID-47	23386-52-9	Dicyclohexyl sulfosuccinate (sodium salt)	0.42		Sigma Aldrich	≥ 98 %
ID-48	129909-90-6	Amicarbazone	0.96		Sigma Aldrich	99.90%
ID-49	288-13-1	Pyrazole	0.28		Sigma Aldrich	98%

ID-50	104-23-4	4-((4-Aminophenyl)diazenyl) benzene sulfonic acid	0.36		Fluorochem	
ID-51	70-55-3 88-19-7	Toluenesulfonamide	1.09		Sigma Aldrich	99%
ID-52	102-06-7	1,3-Diphenylguanidine	1.23		Sigma Aldrich	97%
ID-53	80-08-0	Dapsone	1.27		Sigma Aldrich	99.50%
ID-54	19715-19-6	3,5-Di-tert-butylsalicylic acid	1.62		Sigma Aldrich	97%
ID-55	1025-15-6	1,3,5-Triallyl-1,3,5-triazinane-2,4,6-trione	1.83		Fluorochem	
ID-56	87-62-7	2,6-Dimethylaniline	2.17		Sigma Aldrich	Analytical standard
ID-57	80-09-1	Bisphenol S	2.17		Sigma Aldrich	≥ 98 %

ID-58	97-39-2	1,3-Di-o-tolylguanidine	2.25		Sigma Aldrich	99%
ID-59	95-79-4	5-Chloro-2-methylaniline	2.26		Alfa Aesar	99%
ID-60	101-77-9	4,4-Diaminodiphenylmethane	2.40		Sigma Aldrich	analytical standard
ID-61	834-12-8	Ametryn	2.57		Sigma Aldrich	98.50%
ID-62	35948-25-5	9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide	2.74		abcr GmbH	97%
ID-63	13674-84-5	Tri-(2-chloroisopropyl)phosphate	3.36		Sigma Aldrich	analytical standard
ID-64	101-72-4	N1-isopropyl-N4-phenylbenzene-1,4-diamine	3.56		Fluorochem	

[1] Calculated using ChemAxon (https://www.chemaxon.com/download/jchem-for-office/#jc4x)

Table S2. Sample description

Name	Collection date	Sample type	Depth	Location	Connections between the samples
DE-SW-1	19.10.2016	surface water from a river with expected sources from urban/industrial wastewater	-	South Hessia (Germany)	-
DE-SW-2	19.10.2016	surface water from a river with expected sources from urban/industrial wastewater	-	South Hessia (Germany)	-
DE-SW-3	24.10.2016	surface water from a river with expected sources from industrial wastewater	-	South Hessia (Germany)	DE-SW-3 and DE-GW-4 are hydrologically connected
DE-GW-4	26.10.2016	groundwater with expected sources from industrial wastewater	10.5 m	South Hessia (Germany)	DE-GW-4 and DE-SW-3 are hydrologically connected
DE-GW-5	20.10.2016	groundwater with expected sources from industrial wastewater	93 m	South Hessia (Germany)	-
DE-GW-6	25.10.2016	groundwater with expected sources from urban/industrial wastewater	75 m	South Hessia (Germany)	-
DE-GW-7	01.11.2016	groundwater from an active drinking water fountain with infiltration of municipial wastewater	32.3 m	South Hessia (Germany)	-
ES-SW-1	20.10.2016	surface water from a river near a landfill with expected sources from urban/industrial landfill	-	West Galicia (Spain)	ES-SW-1 is connected with ES-SW-2; large dilution between the sampling points (~10 km) (see also comment to ES-SW-2)
ES-SW-2	20.10.2016	surface water from a river with expected sources from urban/industrial landfill	-	West Galicia (Spain)	ES-SW-2 is connected with ES-SW-1, the river from which sample ES-SW-1 was collected runs into the river where sample ES-SW-2 was collected, with a large dilution in between the two sampling points; ES-SW-2 is connected with ES-SW-3, there is a large dam between both locations
ES-SW-3	20.10.2016	surface water from a river with expected sources from urban/industrial landfill	-	West Galicia (Spain)	ES-SW-3 is connected with ES-SW-2 with a large dam between ES-SW-2 and ES-SW-3

Samples from full-scale Reverse Osmosis installation operated at drinking water treatment plant for research purposes

NL-SW-1	03.11.2016	surface water from a canal connected to Oude Rijn river	-	Zuid Holland (Netherlands)	all Dutch samples are connected among each other; the surface water was infiltrated to the water of the bank filtrate; the bank filtrate was used for the reverse osmosis; the permeate is the filtrated water and the concentrate is the residue (brine) of the reverse osmosis process
NL-BF-2	03.11.2016	river bank filtrate from sample NL-SW-1	15-40 m	Zuid Holland (Netherlands)	
NL-ROC-3	03.11.2016	reverse osmosis concentrate produced from river bank filtrate NL-BF-2	-	Zuid Holland (Netherlands)	
NL-ROP-4	03.11.2016	reverse osmosis permeate produced from river bank filtrate NL-BF-2	-	Zuid Holland (Netherlands)	

SW – surface water; GW – groundwater; BF – bank filtrate; ROC – reverse osmosis concentrate; ROP – reverse osmosis permeate

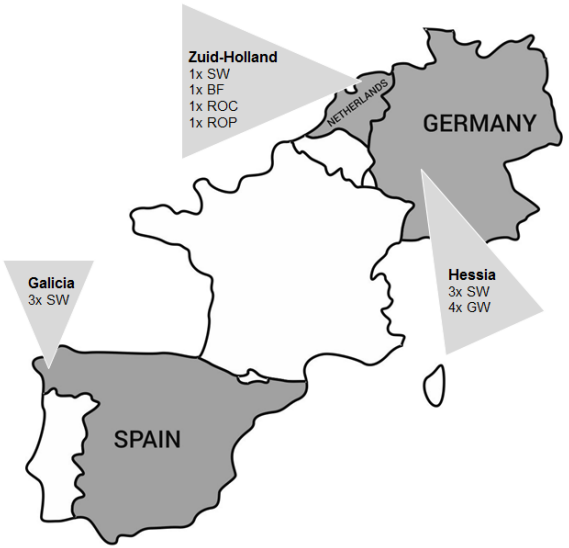


Figure S 1. Sampling regions

Table S3. Materials, chemicals and instrumentation for *Enrichment I-VIII*

Enrichment method	Materials, chemicals and instrumentation
I	*Materials:* Weak anion exchanger (WAX), OASIS, 150 mg, 6 mL (Waters, Milford, United States of America) Cellulose 0.45 um filters (Millipore, Bedford, MA, United States of America) PP 0.22 um filters (Millipore, Bedford, MA, United States of America) *Chemicals:* Formic acid, ammonia methanolic solution 7N (Sigma Aldrich, Milwaukee, United States of America)
II	*Materials:* Weak cation exchanger (WCX), OASIS, 150 mg, 6 mL (Waters, Milford, United States of America) Cellulose 0.45 um filters (Millipore, Bedford, MA, United States of America) PP 0.22 um filters (Millipore, Bedford, MA, United States of America) *Chemicals:* Formic acid, ammonia methanolic solution 7N (Sigma Aldrich, Milwaukee, United States of America)
III	*Materials:* *Multi-layer SPE:* Chromabond polypropylene cartridges (3 mL), polyethylene filters (Macherey Nagel, Düren, Germany) Weak anion exchanger (60 mg WAX) and weak cation exchanger (60 mg WCX) (Waters, Eschborn, Germany) ENVI-Carb bulk material, 120-400 mesh, 60 mg (Supelco, Bellfonte, United States of America) Glass fiber filters, GF6 (GE Helathcare, Little Chalfont, UK) Cellulose syringe 0.2 um filters (GE Helathcare, Little Chalfont, UK) *Chemicals:* Formic acid (98-100%, Merck, Darmstadt, Germany), methanol (LC-MS Ultra Grade), ammonium hydroxide (30% in water), dichloromethane, acetonitrile (Carl Roth GmbH, Karlsruhe, Germany), ultrapure water (18 MΩcm, supplied by Simplicity UV water purification system, Merck, Darmstadt, Germany)
IV	*Instrumentation:* Genevac EZ-2 evaporation unit (Genevac, Ipswich, UK) Cellulose syringe 0.2 um filters (GE Helathcare, Little Chalfont, UK) *Chemicals:* Acetonitrile (Carl Roth GmbH, Karslruhe, Germany)

V	*Materials and instrumentation:* Weak anion exchanger (WAX), OASIS, 150 mg, 6 mL (Waters, Eschborn, Germany) Freestyle SPE unit (LCTech GmbH, Obertaufkirchen, Germany) Glas Fibre Filters Whatman (GE Healthcare, Freiburg, Germany) *Chemicals:* Methanol (Biosolve, Valkenswaard, Netherlands) Hydrochloric acid (Chemsolute, Th. Geyer, Berlin, Germany) Glycine, formic acid (Sigma Aldrich, Taufkirchen, Germany) Ammonium hydroxide (Fisher Scientific, Schwerte, Germany)
VI	*Materials and instrumentation:* Moderate cation exchanger (MCX), OASIS, 150 mg, 6 mL (Waters, Eschborn, Germany) Freestyle SPE unit (LCTech GmbH, Obertaufkirchen, Germany) *Chemicals:* Methanol (Biosolve, Valkenswaard, Netherlands) Hydrochloric acid (Chemsolute, Th. Geyer, Berlin, Germany) Glycine, formic acid (Sigma Aldrich, Taufkirchen, Germany) Ammonium hydroxide (Fisher Scientific, Schwerte, Germany)
VII	*Materials and instrumentation:* Hydroxylated polystyrene divenylbenzene (ENV+), Isolute, 150 mg, 6 mL (Biotage, Uppsala, Sweden) Freestyle SPE unit (LCTech GmbH, Obertaufkirchen, Germany) *Chemicals:* Methanol (Biosolve, Valkenswaard, Netherlands) Disodium hydrogen phosphate, potassium dihydrogen phosphate (abcr GmbH, Karlsruhe, Germany)
VIII	*Materials and instrumentation:* Graphitized carbon black (ENVI-Carb), Supelclean, 150 mg, 6 mL (Sigma Aldrich, Steinheim, Germany) Freestyle SPE unit (LCTech GmbH, Obertaufkirchen, Germany) *Chemicals:* Methanol (Biosolve, Valkenswaard, Netherlands) Dichloromethane (Fisher Scientific GmbH, Schwerte, Germany) Glycine, formic acid, sodium hydroxide (Sigma Aldrich, Taufkirchen, Germany)

Table S4. Chemicals and instrumentation for the instrumental methods *Chromatography A-D.*

Method	Material
A	*Instrumentation:* *HPLC:* Varian 212LC *Column:* Thermo Acclaim Trinity P1 2.1x50mm, 3 um *Mass Spectrometer*: Varian 320 MS *Software*: MS Workstation (Varian) *Chemicals:* Acetonitrile (Merck, Darmstadt, Germany) Ammonia, Acetic acid (Sigma Aldrich, St. Louis, United States of America)
B	*Instrumentation:* *UHPLC:* Nexera X2 (Shimadzu) *Column:* Waters Acquity BEH Amide 2.1x100mm, 1.7 um *Mass Spectrometer:* Qtrap 5500 (AB Sciex) *Software:* Analyst 1.6.2 (Build 8489) (AB Sciex) *Chemicals:* Acetonitrile (Carl Roth GmbH, Karslruhe, Germany) Ammonium formate (Sigma Aldrich, Schnelldorf, Germany)
C_1/C_2	*Instrumentation:* *UHPLC:* Acquity i-Class (Waters) *Column:* Waters Acquity UPLC HSS T3, 2.1x50mm, 1.8 um (C_1) Thermo ScientificTM Hypercarb, 2.1x100mm, 3.0 um (C_2) *Mass Spectrometer*: Xevo TQ-S (Waters) *Software*: MassLynx (Waters) *Chemicals:* Acetonitrile, methanol, ammonium formate (Biosolve, Valkenswaard, Netherlands) Diethylamine (Sigma Aldrich, Taufkirchen, Germany)
D_1/D_2	*Instrumentation:* *SFC:* Acquity UPC2 (Waters) *Column:* Waters Acquity UPC2 BEH 3.0x100mm, 1.7 um (D_1) Waters Acquity UPC2Torus Diol 3.0x100mm, 1.7 um (D_2) *Mass Spectrometer:* Synapt G2S (Waters) *Software:* MassLynx (Waters) *Chemicals:* Carbon dioxide (Air Products, Pennsylvania, USA) Methanol, ammonium hydroxide (Biosolve, Valkenswaard, Netherlands) Formic acid (Sigma Aldrich, Taufkirchen, Germany)

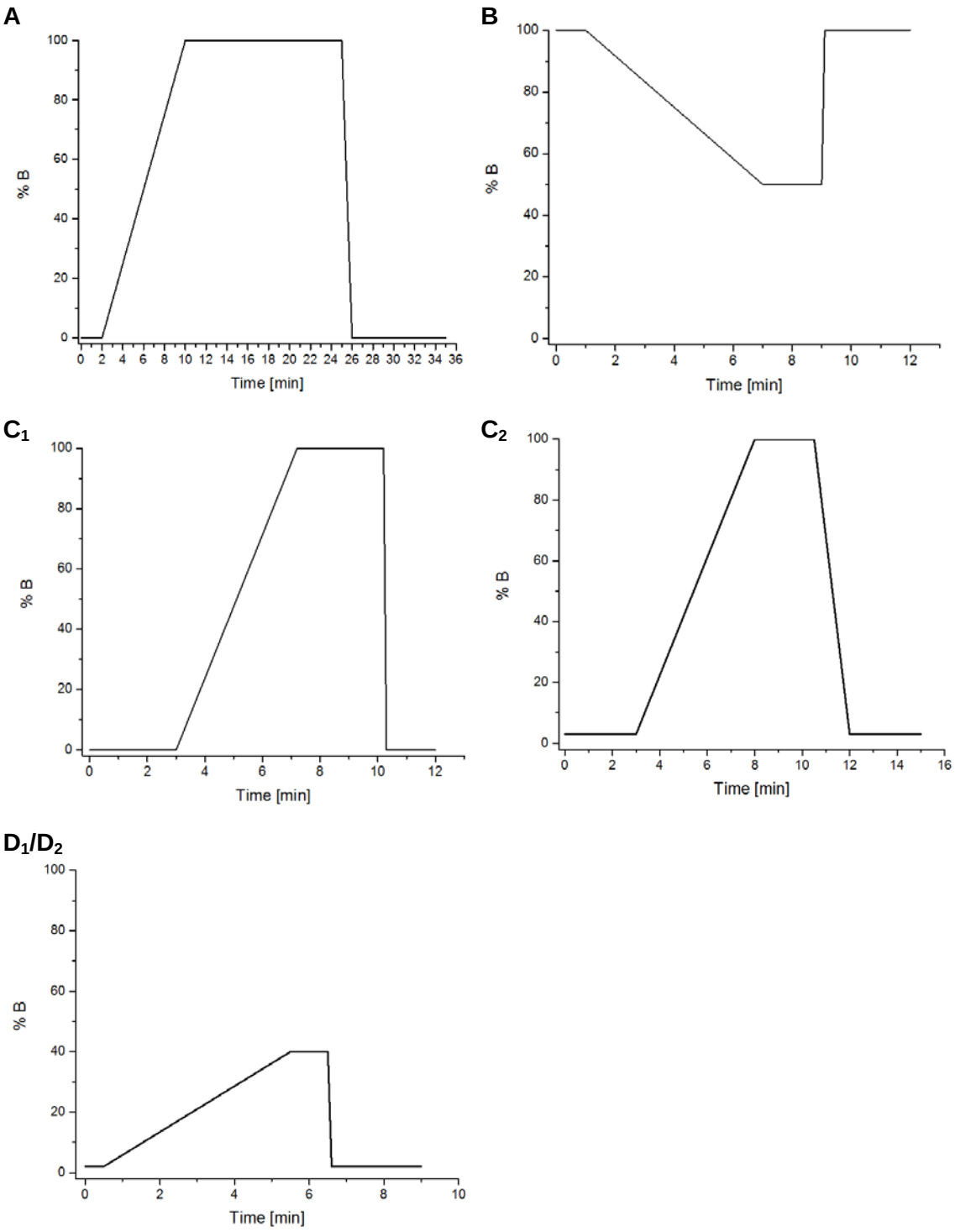


Figure S2. Gradient profiles of the mobile phases as a function of time for A) MMLC on a Acclaim Trinity P1 column; solvent A: H2O/ACN 98/2, 5 mM NH4COO, pH 5.5; solvent B: H2O/ACN 20/80, 20 mM NH4COO, pH 5.5; B) HILIC on an Acquity BEH Amide column; solvent A: H2O/ACN 95/5, 5 mM NH4COO, pH 3; solvent B: H2O/ACN 5/95, 5 mM NH4COO, pH 3; C1) RPLC on an Acquity UPLC HSS T3; solvent A: H2O, 5 mM COOH; solvent B: MeOH, 5 mM COOH; C2) RPLC on a porous graphitic carbon Hypercarb column; solvent A: H2O, 0.1 % diethylamine; solvent B: ACN, 0.1 % diethylamine; D1/D2) SFC on an Acquity UPC2 BEH and Torus Diol column, respectively; solvent A: CO2; solvent B: MeOH/H2O 95/5, 0.2 % NH4OH; make-up: 0.3 mL min-1 MeOH/H2O 90/10, 0.1 % COOH, pH 6.

Table S5A. *Chromatography A* (MMLC-MS/MS) mass spectrometric parameters (see also footnote).

Index	ESI mode	Q1 *m/z*	Q2 *m/z*	Capillary [V]	Collision energy [eV]
ID-4	pos	171	112	52	8
ID-4	pos	171	84	52	16
ID-6	pos	185	126	44	8.5
ID-6	pos	185	69	44	21
ID-15	pos	113	84	80	14.5
ID-15	pos	113	70	80	17
ID-17	pos	202	102	64	13
ID-17	pos	202	84	64	23.5
ID-21	pos	134	72	36	9
ID-21	pos	134	57	36	22
ID-23	pos	150	91	48	15.5
ID-23	pos	150	65	48	32
ID-26	pos	127	85	64	13.5
ID-26	pos	127	68	64	21
ID-29	pos	171	126	32	9.5
ID-29	pos	171	69	32	19.5
ID-30	pos	175	143	44	6.5
ID-30	pos	175	115	44	14
ID-32	pos	152	135	52	14.5
ID-32	pos	152	93	52	24.5
ID-35	pos	118	101	60	9.5
ID-35	pos	118	71	60	16
ID-36	pos	132	114	48	10.5
ID-36	pos	132	70	48	14
ID-41	pos	70	43	60	16.5
ID-45	pos	136	91	36	13
ID-45	pos	136	65	36	31
ID-46	pos	114	79	72	11
ID-46	pos	114	96	72	9.5
ID-48	pos	242	143	30	6.5
ID-48	pos	242	113	30	26
ID-52	pos	212	119	64	15.5
ID-52	pos	212	94	64	13.5
ID-53	pos	249	156	72	10
ID-53	pos	249	92	72	19.5
ID-56	pos	122	105	56	12
ID-56	pos	122	77	56	23.5
ID-58	pos	240	133	60	16.5
ID-58	pos	240	108	60	17
ID-60	pos	199	106	76	18.5
ID-60	pos	199	77	76	40
ID-61	pos	228	186	56	15
ID-61	pos	228	96	56	21
ID-62	pos	217	199	88	16
ID-62	pos	217	152	88	35.5
ID-63	pos	327	99	44	20
ID-63	pos	327	251	44	7.5
ID-64	pos	227	184	40	13.5
ID-64	pos	227	107	40	36
ID-9	neg	237	80	-96	-27
ID-9	neg	237	206	-96	-19.5
ID-12	neg	195	80	-56	-25.5
ID-12	neg	195	95	-56	-17
ID-13	neg	162	82	-40	-12.5
ID-13	neg	162	40	-40	-15.5
ID-14	neg	111	80	-52	-20
ID-14	neg	111	96	-52	-19.5

ID-16	neg	206	80	-64	-28
ID-16	neg	206	135	-64	-15
ID-18	neg	107	80	-44	-19
ID-18	neg	107	45	-44	-30
ID-19	neg	155	80	-88	-29.5
ID-19	neg	155	121	-88	-13.5
ID-20	neg	125	97	-52	-13.5
ID-20	neg	125	80	-52	-28.5
ID-22	neg	128	85	-40	-9
ID-22	neg	128	42	-40	-13
ID-24	neg	135	80	-48	-15
ID-24	neg	135	64	-48	-45
ID-25	neg	172	80	-72	-24.5
ID-25	neg	172	108	-72	-17.5
ID-33	neg	149	99	-60	-22
ID-33	neg	149	80	-60	-38.5
ID-34	neg	273	150	-76	-27.5
ID-34	neg	273	209	-76	-21.5
ID-37	neg	83	41	-56	-9
ID-37	neg	83	66	-56	-23
ID-39	neg	171	80	-90	-25.5
ID-39	neg	171	107	-90	-20
ID-40	neg	182	106	-56	-17.5
ID-40	neg	182	62	-56	-16.5
ID-43	neg	207	143	-68	-21
ID-43	neg	207	80	-68	-29
ID-44	neg	185	80	-72	-26
ID-44	neg	185	121	-72	-19
ID-47	neg	361	81	-72	-21
ID-47	neg	361	133	-72	-31.5
ID-47	neg	361	81	-72	-21
ID-47	neg	361	133	-72	-31.5
ID-51	neg	170	79	-128	-25
ID-51	neg	170	62	-128	-29
ID-54	neg	249	205	-84	-21.5
ID-54	neg	249	189	-84	-28.5
ID-57	neg	249	108	-92	-29
ID-57	neg	249	156	-92	-20.5

ESI-MS/MS parameters: ESI needle voltage 4000 V; ionization source temperature 50°C; drying gas temperature (N_2) 200 °C; nebulizer gas pressure (N_2) 55 psi; drying gas pressure (N_2) 18 psi; CID gas pressure (Ar) 2 mTorr; resolution of Q1 and Q2 1 u; centroid mode for acquisition

Table S5B. *Chromatography B* (HILIC-MS/MS) mass spectrometric parameters (see also footnote).

Index	ESI mode	Q1 *m/z*	Q2 *m/z*	DP [V]	EP [V]	CE [V]	CXP [V]
ID-2	pos	113	84	140	10	20	10
ID-2	pos	113	70	140	10	23	10
ID-2	pos	113	56	140	10	23	10
ID-3	pos	171	154	76	10	19	14
ID-3	pos	171	81	76	10	31	10
ID-3	pos	171	95	76	10	29	10
ID-4	pos	171	112	61	10	17	10
ID-4	pos	171	55	61	10	37	8
ID-4	pos	171	84	61	10	27	10
ID-5	pos	191	102	66	10	23	12
ID-5	pos	191	72	66	10	23	12
ID-5	pos	191	116	66	10	19	12
ID-6	pos	185	126	46	10	17	12
ID-6	pos	185	69	46	10	33	10
ID-6	pos	185	41	46	10	55	8
ID-7	pos	161	72	66	10	23	10
ID-7	pos	161	116	66	10	17	12
ID-7	pos	161	42	66	10	59	8
ID-9	pos	239	131	141	10	29	10
ID-9	pos	239	70	141	10	41	8
ID-9	pos	239	56	141	10	67	8
ID-11	pos	174	72	66	10	25	14
ID-11	pos	174	129	66	10	17	12
ID-11	pos	174	42	66	10	69	10
ID-15	pos	113	84	236	10	29	10
ID-15	pos	113	56	236	10	31	8
ID-15	pos	113	70	236	10	29	10
ID-17	pos	202	102	61	10	25	10
ID-17	pos	202	62	61	10	25	8
ID-17	pos	202	44	61	10	49	8
ID-21	pos	134	72	61	10	19	10
ID-21	pos	134	42	61	10	49	8
ID-21	pos	134	44	61	10	33	8
ID-23	pos	150	91	61	10	25	8
ID-23	pos	150	65	61	10	51	10
ID-23	pos	150	58	61	10	19	8
ID-26	pos	127	85	101	10	25	10
ID-26	pos	127	43	101	10	45	8
ID-26	pos	127	68	101	10	39	10
ID-28	pos	91	65	171	10	25	10
ID-28	pos	91	39	171	10	43	8
ID-28	pos	91	50	171	10	59	8
ID-29	pos	171	126	71	10	19	12
ID-29	pos	171	69	71	10	31	12
ID-29	pos	171	41	71	10	53	8
ID-32	pos	152	135	96	10	23	12
ID-32	pos	152	77	96	10	55	10
ID-32	pos	152	79	96	10	41	10
ID-35	pos	118	101	81	10	21	12
ID-35	pos	118	71	81	10	27	12
ID-35	pos	118	42	81	10	51	6
ID-36	pos	132	114	86	10	21	12
ID-36	pos	132	70	86	10	27	10
ID-36	pos	132	45	86	10	37	8
ID-37	pos	85	68	76	10	25	10
ID-37	pos	85	43	76	10	21	6
ID-37	pos	85	41	76	10	43	6
ID-41	pos	70	43	120	10	30	7

ID-41	pos	70	28	120	10	45	7
ID-41	pos	70	42	120	10	55	7
ID-42	pos	126	43	106	10	49	8
ID-42	pos	126	85	106	10	21	10
ID-42	pos	126	84	106	10	23	10
ID-45	pos	136	91	131	10	23	12
ID-45	pos	136	65	131	10	45	10
ID-45	pos	136	39	131	10	71	8
ID-46	pos	114	44	121	10	43	8
ID-46	pos	114	79	121	10	21	10
ID-46	pos	114	69	121	10	23	10
ID-48	pos	242	143	66	10	19	14
ID-48	pos	242	85	66	10	41	10
ID-48	pos	242	43	66	10	59	8
ID-49	pos	69	42	120	10	25	7
ID-49	pos	69	29	120	10	45	7
ID-49	pos	69	41	120	10	40	7
ID-50	pos	278	92	106	10	35	10
ID-50	pos	278	65	106	10	65	8
ID-50	pos	278	109	106	10	33	10
ID-52	pos	212	77	96	10	53	10
ID-52	pos	212	119	96	10	29	12
ID-52	pos	212	94	96	10	27	12
ID-53	pos	249	156	151	10	19	14
ID-53	pos	249	92	151	10	33	12
ID-53	pos	249	108	151	10	29	10
ID-56	pos	122	105	56	10	23	12
ID-56	pos	122	77	56	10	37	12
ID-56	pos	122	79	56	10	29	10
ID-58	pos	240	133	81	10	29	12
ID-58	pos	240	108	81	10	29	10
ID-58	pos	240	106	81	10	39	12
ID-59	pos	142	89	100	10	40	10
ID-59	pos	142	125	100	10	30	15
ID-59	pos	142	106	100	10	37	15
ID-60	pos	199	106	131	10	33	12
ID-60	pos	199	77	131	10	67	10
ID-60	pos	199	79	131	10	57	10
ID-61	pos	228	186	71	10	25	16
ID-61	pos	228	68	71	10	53	10
ID-61	pos	228	43	71	10	61	8
ID-63	pos	327	99	100	10	35	12
ID-63	pos	327	81	100	10	85	10
ID-63	pos	327	175	100	10	17	17
ID-64	pos	227	184	81	10	29	16
ID-64	pos	227	212	81	10	27	6
ID-64	pos	227	107	81	10	55	10
ID-9	neg	237	80	-160	-10	-55	-10
ID-9	neg	237	107	-160	-10	-32	-15
ID-9	neg	239	82	-160	-10	-55	-10
ID-10	neg	167	80	-105	-10	-32	-9
ID-10	neg	167	107	-105	-10	-24	-11
ID-10	neg	167	81	-105	-10	-26	-9
ID-12	neg	195	80	-85	-10	-44	-9
ID-12	neg	195	95	-85	-10	-26	-11
ID-12	neg	195	79	-85	-10	-26	-9
ID-13	neg	162	82	-65	-10	-20	-9
ID-13	neg	162	78	-65	-10	-44	-9
ID-13	neg	162	40	-65	-10	-36	-5
ID-14	neg	111	80	-95	-10	-30	-9
ID-14	neg	111	96	-95	-10	-30	-11
ID-14	neg	111	81	-95	-10	-24	-9
ID-16	neg	206	80	-100	-10	-42	-9

ID-16	neg	206	135	-100	-10	-26	-13
ID-16	neg	206	42	-100	-10	-60	-7
ID-18	neg	107	80	-35	-10	-28	-9
ID-18	neg	107	45	-35	-10	-20	-7
ID-18	neg	107	81	-35	-10	-24	-9
ID-19	neg	155	80	-80	-10	-42	-9
ID-19	neg	155	33	-80	-10	-34	-15
ID-19	neg	155	137	-80	-10	-28	-13
ID-20	neg	125	97	-70	-10	-25	-10
ID-20	neg	125	80	-70	-10	-45	-10
ID-20	neg	127	82	-70	-10	-45	-10
ID-22	neg	128	42	-75	-10	-36	-7
ID-22	neg	128	85	-75	-10	-14	-7
ID-22	neg	128	26	-75	-10	-110	-5
ID-24	neg	135	80	-60	-10	-25	-16
ID-24	neg	135	64	-60	-10	-75	-16
ID-24	neg	137	82	-60	-10	-25	-16
ID-25	neg	172	80	-155	-10	-38	-9
ID-25	neg	172	108	-155	-10	-28	-11
ID-25	neg	172	66	-155	-10	-36	-9
ID-33	neg	149	80	-80	-10	-30	-9
ID-33	neg	149	99	-80	-10	-34	-11
ID-33	neg	149	83	-80	-10	-26	-9
ID-34	neg	273	80	-170	-10	-68	-9
ID-34	neg	273	150	-170	-10	-38	-13
ID-34	neg	273	209	-170	-10	-34	-19
ID-38	neg	240	80	-130	-10	-56	-9
ID-38	neg	240	176	-130	-10	-32	-15
ID-38	neg	240	35	-130	-10	-64	-15
ID-39	neg	171	80	-125	-10	-38	-9
ID-39	neg	171	107	-125	-10	-28	-11
ID-39	neg	171	107	-125	-10	-36	-11
ID-40	neg	182	42	-105	-10	-60	-7
ID-40	neg	182	106	-105	-10	-26	-11
ID-40	neg	182	62	-105	-10	-26	-7
ID-43	neg	207	80	-80	-10	-50	-9
ID-43	neg	207	143	-80	-10	-32	-13
ID-43	neg	207	163	-80	-10	-18	-15
ID-44	neg	185	80	-145	-10	-40	-9
ID-44	neg	185	121	-145	-10	-30	-11
ID-44	neg	185	170	-145	-10	-32	-15
ID-47	neg	361	81	-120	-10	-60	-10
ID-47	neg	361	197	-120	-10	-30	-10
ID-47	neg	363	83	-120	-10	-60	-10
ID-54	neg	249	205	-100	-10	-32	-15
ID-54	neg	249	189	-100	-10	-45	-11
ID-54	neg	249	93	-100	-10	-35	-7
ID-57	neg	249	108	-65	-10	-36	-11
ID-57	neg	249	113	-65	-10	-14	-9
ID-57	neg	249	92	-65	-10	-48	-11

ESI-MS/MS parameters: Ion spray voltage: 5500 V (pos), -4500 V (neg); Curtain gas: 45 psi; Temperature: 550 °C; Ion Source gas 1 (nebulizer gas): 55 psi; Ion Source gas 2 (heater gas): 65 psi

Table S5C. *Chromatography C_1/C_2* (RPLC-MS/MS) mass spectrometric parameters (see also footnote).

Index	ESI mode	Q1 *m/z*	Q2 *m/z*	Cone [V]	Collision energy [eV]
ID-2	pos	130	84	2	18
ID-2	pos	130	113	2	12
ID-4	pos	171	84	20	20
ID-4	pos	171	112	20	14
ID-5	pos	191	58	4	24
ID-5	pos	191	102	4	14
ID-6	pos	185	69	2	24
ID-6	pos	185	126	2	12
ID-9	pos	239	88	6	24
ID-9	pos	239	131	6	18
ID-15	pos	113	56	12	20
ID-15	pos	113	84	12	18
ID-17	pos	202	62	16	16
ID-17	pos	202	102	16	16
ID-21	pos	134	72	24	14
ID-21	pos	134	85	24	10
ID-23	pos	150	58	2	14
ID-23	pos	150	91	2	20
ID-26	pos	127	43	2	20
ID-26	pos	127	85	2	16
ID-28	pos	91	47	24	8
ID-28	pos	91	74	24	8
ID-29	pos	171	69	2	22
ID-29	pos	171	126	2	12
ID-30	pos	175	115	2	16
ID-30	pos	175	143	2	8
ID-32	pos	152	93	38	24
ID-32	pos	152	135	38	16
ID-35	pos	118	71	12	16
ID-35	pos	118	101	12	14
ID-36	pos	132	69	40	14
ID-36	pos	132	114	40	14
ID-37	pos	85	41	60	14
ID-37	pos	85	68	60	12
ID-41	pos	70	43	42	14
ID-42	pos	126	43	50	18
ID-42	pos	126	85	50	14
ID-46	pos	114	69	12	16
ID-46	pos	114	79	12	14
ID-48	pos	264	165	44	16
ID-48	pos	264	202	44	12
ID-52	pos	212	77	28	32
ID-52	pos	212	119	28	20
ID-53	pos	249	65	2	40
ID-53	pos	249	156	2	14
ID-55	pos	250	41	18	22
ID-55	pos	250	81	18	22
ID-57	pos	251	93	50	22
ID-57	pos	251	157	50	18
ID-58	pos	240	108	2	20
ID-58	pos	240	133	2	20
ID-60	pos	199	106	54	26
ID-60	pos	199	167	54	4
ID-61	pos	228	96	30	28
ID-61	pos	228	186	30	18
ID-63	pos	327	99	10	26
ID-63	pos	327	175	10	12

ID-1	neg	195	59	2	18
ID-1	neg	195	75	2	20
ID-8	neg	287	143	4	36
ID-8	neg	287	207	4	22
ID-10	neg	167	80	10	22
ID-10	neg	167	137	10	16
ID-12	neg	195	80	2	28
ID-12	neg	195	95	2	20
ID-13	neg	162	78	4	22
ID-13	neg	162	82	4	14
ID-14	neg	111	80	8	16
ID-14	neg	111	96	8	14
ID-16	neg	206	80	48	24
ID-16	neg	206	135	48	18
ID-18	neg	107	43	8	10
ID-18	neg	107	80	8	18
ID-20	neg	125	45	32	16
ID-20	neg	125	97	32	12
ID-22	neg	128	42	10	10
ID-22	neg	128	85	10	14
ID-24	neg	135	80	58	14
ID-24	neg	135	91	58	8
ID-25	neg	172	80	2	22
ID-25	neg	172	108	2	20
ID-27	neg	157	79	2	18
ID-31	neg	173	80	30	24
ID-31	neg	173	109	30	18
ID-33	neg	149	80	4	18
ID-33	neg	149	99	4	18
ID-34	neg	273	150	26	26
ID-34	neg	273	209	26	22
ID-38	neg	240	80	64	26
ID-38	neg	240	176	64	20
ID-39	neg	171	80	2	26
ID-39	neg	171	107	2	20
ID-40	neg	182	42	4	18
ID-40	neg	182	106	4	18
ID-43	neg	207	80	42	30
ID-43	neg	207	143	42	26
ID-44	neg	185	80	6	24
ID-44	neg	185	121	6	22
ID-47	neg	361	81	6	22
ID-47	neg	361	197	6	24
ID-50	neg	276	80	58	40
ID-50	neg	276	156	58	26
ID-51	neg	170	79	14	30
ID-51	neg	170	106	14	16
ID-51	neg	170	79	2	24
ID-51	neg	170	106	2	16
ID-54	neg	249	189	2	32
ID-54	neg	249	205	2	24

ESI-MS/MS parameters: Capillary Voltage 1000 – 1420 V (+/-); Source Temperature 150 °C; Desolvation Temperature 600 °C; Cone Gas Flow 150 L h^{-1}; Collision Gas Flow 0.15 mL min^{-1}; Nebuliser Gas Flow 100 psi

Table S5D. *Chromatography D_1/D_2* (SFC-HRMS) mass spectrometric parameters (see also footnote).

Index	ESI mode	Quantifyer *m/z*	Qualifyer *m/z*
ID-3	pos	171.19	154.16
ID-4	pos	171.15	112.08
ID-5	pos	191.18	72.08
ID-6	pos	185.17	126.09
ID-9	pos	239.11	131.12
ID-11	pos	174.20	129.14
ID-15	pos	113.11	
ID-17	pos	202.18	102.09
ID-21	pos	134.12	72.08
ID-23	pos	150.13	91.06
ID-26	pos	127.07	85.05
ID-29	pos	171.15	126.09
ID-32	pos	152.14	134.11
ID-35	pos	118.09	101.09
ID-36	pos	132.10	114.09
ID-37	pos	85.05	
ID-42	pos	126.08	85.05
ID-45	pos	136.11	
ID-46	pos	114.09	96.08
ID-48	pos	143.09	264.14
ID-52	pos	212.12	195.09
ID-53	pos	249.07	156.01
ID-55	pos	250.12	
ID-56	pos	122.10	107.07
ID-58	pos	240.15	133.08
ID-60	pos	199.13	106.07
ID-61	pos	228.13	186.08
ID-63	pos	327.01	251.00
ID-64	pos	225.14	184.10
ID-1	neg	195.05	
ID-12	neg	195.03	94.98
ID-13	neg	161.99	82.03
ID-14	neg	110.98	
ID-16	neg	206.05	135.01
ID-18	neg	106.98	79.96
ID-19	neg	154.99	176.97
ID-20	neg	124.99	96.96
ID-24	neg	135.01	
ID-25	neg	172.01	108.05
ID-31	neg	172.99	108.02
ID-33	neg	148.95	79.96
ID-34	neg	273.01	209.05
ID-38	neg	239.93	203.95
ID-39	neg	171.01	107.05
ID-40	neg	181.99	105.96
ID-43	neg	207.01	143.05
ID-44	neg	185.03	121.07
ID-47	neg	361.13	80.97
ID-51	neg	170.03	205.16
ID-54	neg	249.15	205.16
ID-57	neg	249.02	108.02
ID-62	neg	169.07	215.03

ESI-HRMS parameters: Full Scan recording *m/z* 50 to 600; Analyser Mode Resolution; Scan time 0.08 sec; Cone Voltage 20000 V; Capillary 700 V (+) / 2000 V (-); Source Temperature 140 °C; Desolvation Temperature 550 °C; Function 1: Trap Collision Energy 4 eV, Transfer Collision Energy 2 eV; Function 2: Trap Collision Energy 15 eV, Transfer Collision Energy 40 eV; Function 3 (Lock Spray Configuration): Reference Cone Voltage 30 V, Reference Trap Collision Energy 4 eV, Lock Mass (leucine enkephaline) 556.2771 (+) / 554.2615 (-)

Method performance evaluation and semi-quantitative concentration estimates

Instrumental blanks were determined by 10 solvent injections and IDLs were defined as the amount of chemical standard injected producing a signal with a signal-to-noise ratio of 3 or, in case of instrumental blank contamination, the amount of chemical injected leading to a signal area exceeding the mean signal area + 3 times standard deviation of the blank injections.

Retention time repeatability was investigated within one analytical sequence. The approaches for retention time repeatability testing for the different chromatographic methods *Chromatography A-D* are listed in Table S6 below.

Procedural blank experiments for the different methods were performed as follows, applying the full sample preparation procedure. For *Enrichments I-II* triplicates of procedural blank extractions were performed starting from 5 mL ultrapure water, for *Enrichments III-IV* triplicates were performed with 100 mL ultrapure water, and for *Enrichments V-VIII* a single procedural blank experiment was performed per method starting from 1 mL ultrapure water. For compounds that did not show procedural blank contamination, estimation of the MDL was based on quantification of the signal area in a sample chromatogram close to the MDL and extrapolation to a signal to noise ratio of 3. In case of procedural blank contamination, the MDL was calculated as mean + 3 times standard deviation of 3 quantified procedural blank signals for *Chromatography A*, as 2x(mean + 3 times standard deviation) of 3 quantified procedural blanks for *Chromatography B*, or as 3 times the quantified procedural blank signal for *Chromatography C* and *D*.

Semi-quantitative concentration estimates were based on solvent-based external one-point calibration without correction for apparent recoveries. However, for analytes showing signals in the procedural blank chromatograms, the average blank signal area was subtracted from the signal area in the sample before concentration estimation.

Table S6. Retention time repeatability for the different chromatographic methods over a relevant sample batch bracketed between standards.

Method	Approach	Retention time variabiltiy
A	5 injections of the same standard in solvent	max. +/- 0.1 min
B	3 injections evenly distributed over a 10 hour sequence	max. +/- 0.05 min
C_1	3 injections of the same standard in solvent/matrix with 10 other samples in between	max. +/- 0.05 min
C_2	3 injections of the same standard in solvent/matrix with 10 other samples in between	max. +/- 0.1 min
D_1	3 injections of the same standard in solvent/matrix with 8 other samples in between	max. +/- 0.03 min
D_2	3 injections of the same standard in solvent/matrix with 8 other samples in between	max. +/- 0.03 min

Method abbreviations: A) MMLC-MS/MS; B) HILIC-MS/MS; C_1/C_2) RPLC-MS/MS; D_1/D_2) SFC-HRMS

Table S7. Instrumental detection limits for the target PMOCs given as injected quantities [ng] with the different instrumental methods.

Index	A	B	C_1	C_2	D_1	D_2
ID-1	-	-	0.031	0.0018	-	-
ID-2	-	0.005	0.0064	0.0045	-	-
ID-3	-	0.005	-	-	0.002	0.0125
ID-4	0.006	-	0.00008	0.00065	-	0.005
ID-5	-	0.00025	-	-	-	0.00125
ID-6	0.003	0.00025	0.000033	0.000082	0.01	0.0017
ID-7	-	0.125	-	-	-	-
ID-8	-	-	-	0.00073	-	-
ID-9	0.18	-	0.00006	0.00048	-	0.003
ID-10	-	-	0.0014	-	-	-
ID-11	-	-	-	-	-	0.0015
ID-12	0.015	0.0005	-	0.0068	0.005	0.0009
ID-13	0.0018	0.00025	0.0005	0.00005	0.0006	0.0005
ID-14	0.06	0.0005	-	0.00153	0.003	0.0008
ID-15	0.03	0.005	0.004	0.0052	0.005	0.002
ID-16	0.09	0.00025	0.00023	0.00021	0.00021	0.00003
ID-17	0.02	0.00025	0.00003	0.0002	0.00004	0.00009
ID-18	0.03	0.0005	0.0038		0.0023	0.00038
ID-19	0.072	0.3	-	-	-	0.005
ID-20	0.009	0.025	-	0.00023	0.0015	0.0003
ID-21	0.009	0.00005	0.00025	0.00021	0.00034	0.0023
ID-22	1.5	0.005	0.0034	-	-	-
ID-23	0.0006	0.00005	0.00256	-	0.0003	0.0003
ID-24	0.015	0.0005	0.0005	0.00043	0.003	0.00039
ID-25	0.03	0.00025	-	0.003	0.0017	0.0075
ID-26	0.006	0.001	0.0035	-	0.00027	0.0038
ID-27	-	-	0.0054	0.002	-	-
ID-28	-	0.0025	0.0033	-	-	-
ID-29	0.003	0.000125	0.00031	0.000071	0.00027	0.00062
ID-30	0.21	-	0.00042	-	-	-
ID-31	-	-	0.0042	0.00062	0.0017	0.025
ID-32	0.006	0.00025	0.00041	-	0.0002	0.0038
ID-33	0.006	0.0005	0.00075	0.000134	0.00012	0.00005
ID-34	0.003	0.0005	0.0001	0.00008	0.00013	0.0001
ID-35	0.001	0.5	0.000078	0.000079	0.0013	0.017
ID-36	0.15	0.00025	0.00152	-	0.0011	0.00036
ID-37	0.3	0.0025	0.0027	-	0.005	0.0107
ID-38	-	0.0005	0.00033	-	0.00015	0.00009
ID-39	0.22	0.0005	0.029	0.00018	0.0005	0.0002
ID-40	0.015	0.0025	0.00072	0.019	0.0008	0.0008
ID-41	0.62	0.0025	0.0053	-	-	-
ID-42	-	0.00025	0.00019	-	0.00008	0.00028
ID-43	0.0039	0.0005	0.001	0.00042	0.0004	0.,0005
ID-44	0.0015	0.00025	-	0.0007	0.00066	0.00017
ID-45	0.015	0.0005	0.014	-	0.0005	0.0002
ID-46	0.03	0.005	-	-	0.0011	0.0015

ID-47	0.018	0.00025	0.0001	0.00025	0.0003	0.00008
ID-48	0.009	0.025	0.000147	-	0.00011	0.00025
ID-49	-	0.5	-	-	-	-
ID-50	-	0.0025	0.000253	-	-	-
ID-51	0.15	-	0.0005	0.0007	0.013	0.0125
ID-52	0.003	0.00025	0.0004	-	0.00003	0.00003
ID-53	0.003	-	0.000015	-	0.0003	0.0025
ID-54	0.009	0.00025	0.0016	0.000047	0.0005	0.00054
ID-55	-	-	-	-	0.013	-
ID-56	0.45	0.25	-	-	-	0.012
ID-57	0.0033	0.00025	0.00071	-	0.00008	0.00023
ID-58	0.0015	0.00025	0.0002	-	0.0003	0.001
ID-59	-	0.005	-	-	-	-
ID-60	0.01	0.005	0.00006	-	0.00009	0.0022
ID-61	0.008	0.00005	0.00002	0.0011	0.00008	0.00004
ID-62	0.0045	-	0.00357	-	0.001	0.0015
ID-63	0.33	0.015	0.08	-	0.0013	0.0003
ID-64	0.3	0.25	-	-	0.0014	0.00049

Method abbreviations: A) MMLC-MS/MS; B) HILIC-MS/MS; C_1/C_2) RPLC-MS/MS; D_1/D_2) SFC-HRMS

Table S8. Retention factor k' of the target chemicals for the different chromatographic methods.[1]

Index	A	B	C_1	C_2	D_1	D_2
ID-1	n.p.[2]	n.p.	0.1	0.1	n.p.	n.p.
ID-2	n.p.	11.9	0.3	1.4	n.p.	n.p.
ID-3	n.p.	13.1	n.p.	n.p.	17.5	15.0
ID-4	16.8	9.2	1.3	3.1	n.p.	14.2
ID-5	n.p.	13. 5	n.p.	n.p.	n.p.	13.4
ID-6	16.7	8.3	3.4	4.2	19.2	13.7
ID-7	n.p.	13.1	n.p.	n.p.	n.p.	n.p.
ID-8	n.p.	n.p.	n.p.	4.1	n.p.	n.p.
ID-9	33.9	12.8	0.3	2	n.p.	17.1
ID-10	n.p.	14.7	0.2	n.p.	n.p.	n.p.
ID-11	n.p.	12.8	n.p.	n.p.	n.p.	13.1
ID-12	32.4	3.2	n.p.	2.5	13.1	13.9
ID-13	24.2	0.6	1.8	3.9	12.6	14.0
ID-14	25.2	1.5	n.p.	0.1	13.0	14.4
ID-15	21.3	11.9	0.4	0.5	20.0	11.1
ID-16	24.9	3.2	4.6	3.9	13.7	14.1
ID-17	17.5	9.1	3.4	4.7	12.6	10.0
ID-18	24.2	3.3	0.3	0.1	13.1	14.2
ID-19	26.7	3.5	n.p.	n.p.	n.p.	14.3
ID-20	19.4	1.2	n.p.	0.2	12.6	13.7
ID-21	15.4	9.3	0.7	3.7	15.1	9.3
ID-22	2.7	3.8	0.7	n.p.	n.p.	n.p.
ID-23	20.9	3.4	9.4	n.p.	12.8	13.7
ID-24	27.0	3.1	1.4	1	12.4	13.1
ID-25	26.4	4.7	n.p.	3	15.7	18.0
ID-26	14.6	8.8	0.6	n.p.	12.5	14.0
ID-27	n.p.	n.p.	0.8	0.2	n.p.	n.p.
ID-28	n.p.	4.0	0.3	n.p.	n.p.	n.p.
ID-29	17.5	7.84	5.4	4.9	14.2	9.6
ID-30	2.9	n.p.	1.0	n.p.	n.p.	n.p.
ID-31	n.p.	n.p.	0.3	0.2	14.9	17.3
ID-32	24.5	8.1	19.0	n.p.	12.3	11.2
ID-33	27.7	0.2	0.8	0.4	12.1	13.1
ID-34	40.5	0.7	18	5.8	12.7	13.7
ID-35	4.6	10.3	0.5	0.2	14.9	9.5
ID-36	17.3	8.5	1.9	n.p.	7.7	4.2
ID-37	1.9	1.7	0.4	n.p.	10.4	9.6
ID-38	n.p.	0.8	17.3	n.p.	13.8	16.5
ID-39	23.0	2.6	7.3	4.2	12.8	14.1
ID-40	27.6	1.0	1.0	4.4	13.0	14.8
ID-41	2.17	1.4	0.6	n.p.	n.p.	n.p.
ID-42	n.p.	4.2	2.3	n.p.	9.7	9.6
ID-43	32.4	1.1	17.0	5	13.3	15.4
ID-44	29.2	1.3	n.p.	4.52	12.5	13.6
ID-45	21.8	4.0	16.1	n.p.	6.6	11.2
ID-46	3.1	1.0	n.p.	n.p.	6.5	5.3

ID-47	28.7	0.6	23.5	5.4	11.7	12.2
ID-48	13.7	0.5	21.7	n.p.	6.2	5.8
ID-49	n.p.	0.8	n.p.	n.p.	n.p.	n.p.
ID-50	n.p.	1.4	17.5	n.p.	n.p.	n.p.
ID-51	12.8	n.p.	18.0	11	6.7	7.7
ID-52	22.2	4.9	19.2	n.p.	12.1	11.6
ID-53	15.3	0.6	17.3	n.p.	11.9	12.9
ID-54	21.0	0.5	25	5.5	8.2	8.4
ID-55	n.p.	n.p.	n.p.	n.p.	1.2	n.p.
ID-56	15.2	0.5	n.p.	n.p.	n.p.	1.2
ID-57	33.9	0.7	19.0	n.p.	10.1	11.1
ID-58	21.2	2.5	19.9	n.p.	11.7	11.2
ID-59	n.p.	0.4	n.p.	n.p.	n.p.	n.p.
ID-60	19.7	0.5	20.6	n.p.	8.6	8.8
ID-61	17.9	0.5	24.1	8.9	4.2	3.9
ID-62	16.2	n.p.	19.3	n.p.	14.8	14.6
ID-63	17.9	0.4	24.4	n.p.	3.5	1.7
ID-64	21.7	0.7	n.p.	n.p.	3.2	3.0

Method abbreviations: A) MMLC-MS/MS; B) HILIC-MS/MS; C_1/C_2) RPLC-MS/MS; D_1/D_2) SFC-HRMS

[1] k' = $(t_R-t_0)/t_0$, t_R – retention time of the substance, t_0 – void time

[2] n.p. means that it was not possible to analyze the chemical (no peak) with the chromatographic method in combination with ESI-MS

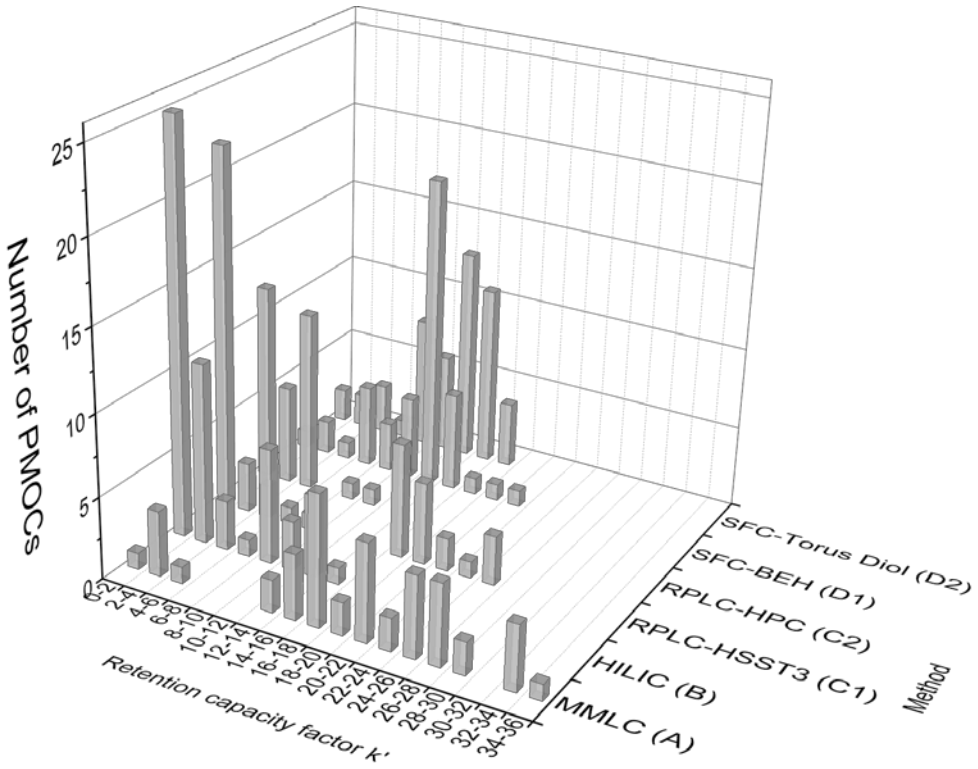


Figure S3. Retention factors k' of all PMOCs for the different chromatographic method.

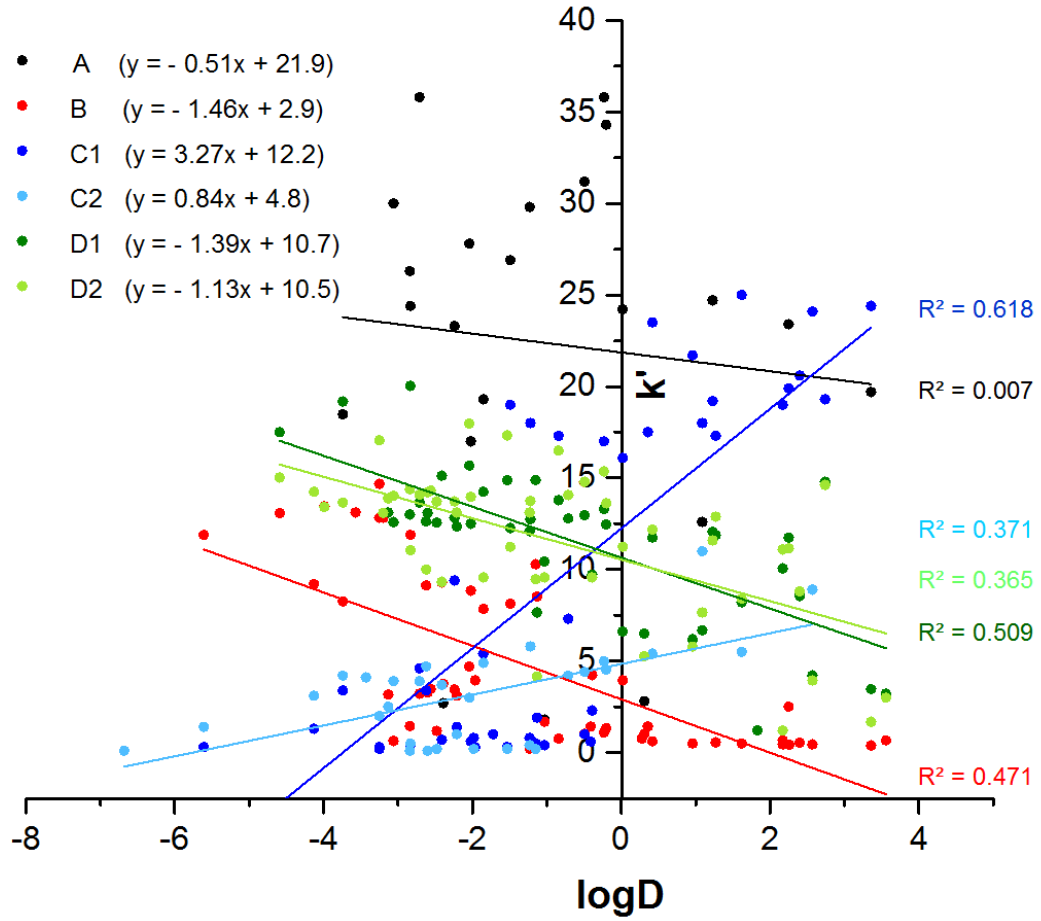


Figure S4. Retention factors k' versus log*D* for all PMOCs and all chromatographic methods. Method abbreviations: A) MMLC-MS/MS; B) HILIC-MS/MS; C_1/C_2) RPLC-MS/MS; D_1/D_2) SFC-HRMS

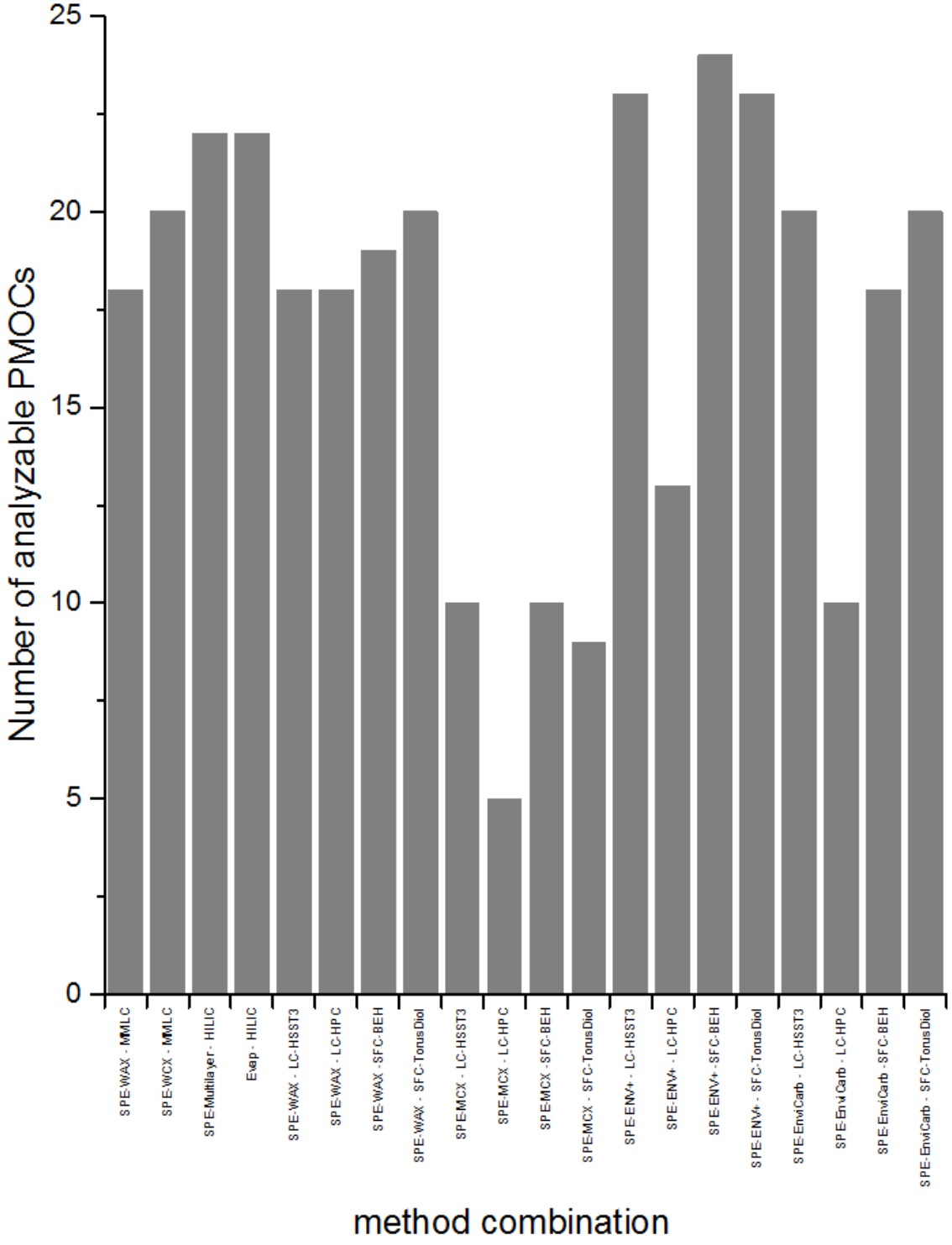


Figure S5. Number of PMOCs that were amenable to the different combinations of enrichment and instrumental methods.

Table S9. Enrichment and instrumental methods that were successfully applied for analysis of the different PMOCs (indicated with +). Combinations of enrichment and instrumental methods that were used in the target screening of water samples are listed in the last column with their individual estimated method detection limits (MDLs).

Index	Applicability of enrichment methods								Applicability of instrumental methods						Method combinations applied in the target screening of water samples In gray: methods that led to only not-detects **In blue: methods that led to at least one detect** **In parentheses: estimated MDL [ng L^{-1}]**
	I	II	III	IV	V	VI	VII	VIII	A	B	C_1	C_2	D_1	D_2	
ID-1	n.t.	n.t.	n.t.	n.t.	-	-	-	-	-	-	+	+	-	-	
ID-2	n.t.	n.t.	-	+	+	-	+	-	-	+	+	+	-	-	**B-IV (37), C_1-V (335)**
ID-3	n.t.	n.t.	+	-	-	-	-	-	-	+	-	-	+	+	**B-III (0.4)**
ID-4	-	+	-	-	-	-	-	+	+	+	+	+	-	+	A-II (0.5), C_2-VIII (60), D_2-VIII (2000)
ID-5	n.t.	n.t.	+	-	-	-	-	-	-	+	-	-	-	+	B-III (0.06)
ID-6	-	+	-	+	-	-	-	+	+	+	+	+	+	+	**A-II (5.5)**, B-IV (5), **C_2-VIII (0.5)**
ID-7	n.t.	n.t.	-	+	n.t.	n.t.	n.t.	n.t.	-	+	-	-	-	-	B-VI (1250)
ID-8	n.t.	n.t.	n.t.	n.t.	+	-	-	-	-	-	-	+	-	-	**C_2-V (1.2)**
ID-9	-	-	-	-	-	-	-	+	+	+	+	+	-	+	**C_2-VIII (3)**, D2-VIII (5)
ID-10	n.t.	n.t.	-	-	+	-	-	-	-	+	+	-	-	-	C1-V (600)
ID-11	n.t.	n.t.	-	-	-	-	-	-	-	+	-	-	-	+	
ID-12	+	-	+	-	+	-	-	-	+	+	-	+	+	+	**A-I (189), B-III (3.9)**, C_2-V (600)
ID-13	+	-	-	+	+	-	-	-	+	+	+	+	+	+	**A-I (16.8), B-IV (11), C_2-V (0.5), D_2-V (10)**
ID-14	+	-	+	-	-	-	-	+	+	+	-	+	+	+	**A-I (367), B-III (375), C_2-VIII (39)**
ID-15	-	+	-	+	-	+	-	-	+	+	+	+	+	+	**A-II (15.4), B-IV (19)**, C_1-VI (600), D_1-VI (10), D_2-VI (15)
ID-16	+	-	+	-	+	-	-	-	+	+	+	+	+	+	**A-I (182), B-III (0.6), C_2-V (0.2), D_2-V (4)**
ID-17	-	+	-	+	-	+	+	+	+	+	+	+	+	+	A-II (46), B-IV (3), **C_2-VII (42), D_1-VII (30)**
ID-18	-	-	-	+	+	-	-	-	+	+	+	+	+	+	**B-IV (12)**, C_1-V (60)
ID-19	-	-	-	-	-	-	-	-	+	+	-	-	-	+	
ID-20	+	-	+	-	+	-	-	-	+	+	-	+	+	+	A-I (219), B-III (20), **C_2-V (10), D_2-V (40)**

ID-21	-	+	-	+	-	+	+	+	+	+	+	+	+	+	A-II (30), B-IV (0.9), C_2-VI (600)
ID-22	+	-	-	+	-	-	-	+	+	+	+	-	-	-	A-I (500), **B-IV (38), C_1-VIII (2.5)**
ID-23	-	+	+	-	-	-	+	+	+	+	+	-	+	+	**A-II (0.3)**, B-III (0.75), **C_1-VIII (0.2), D_2-VIII (2.5)**
ID-24	+	-	-	+	+	-	-	-	+	+	+	+	+	+	A-I (15.6), **B-IV (140), C_1-V (10), D_2-V (55)**
ID-25	+	-	+	-	+	-	+	-	+	+	-	+	+	+	A-I (167), **B-III (0.04), C_2-V (6), D_2-V (140)**
ID-26	-	+	-	+	-	+	+	+	+	+	+	-	+	+	**A-II (176), B-IV (23), C_1-VIII (10), D_1-VIII (1.4)**
ID-27	n.t.	n.t.	n.t.	n.t.	-	-	-	-	-	-	+	+	-	-	
ID-28	n.t.	n.t.	+	-	-	-	-	-	-	+	+	-	-	-	**B-III (0.3)**
ID-29	-	+	-	+	-	-	-	+	+	+	+	+	+	+	**A-II (3.1)**, B-IV (1.4), **C_2-VIII (0.7), D_1-VIII (0.6)**
ID-30	-	-	n.t.	n.t.	-	-	+	-	+	-	+	-	-	-	C_1-VII (100)
ID-31	n.t.	n.t.	n.t.	n.t.	-	-	-	-	-	-	+	+	+	+	C_2-V (60)
ID-32	-	+	+	-	-	-	-	+	+	+	+	-	+	+	**A-II (11.4), B-III (0.12), C_1-VIII (1.2), D_1-VIII (0.9)**
ID-33	+	-	+	-	+	-	-	-	+	+	+	+	+	+	**A-I (55.1), B-III (0.21), C_1-V (3), D_2-V (0.7)**
ID-34	+	-	+	-	+	-	+	-	+	+	+	+	+	+	A-I (4.0), B-III (0.2), **C_1-V (0.6)**
ID-35	-	-	-	-	-	+	+	-	+	+	+	+	+	+	C_1-VII (0.1)
ID-36	-	+	-	+	-	+	+	-	+	+	+	-	+	+	A-II (50.9), B-IV (1), C_1-VI (600)
ID-37	+	-	-	+	-	-	-	+	+	+	+	-	+	+	A-I (372), **B-IV (70), D_1-VIII (20)**
ID-38	n.t.	n.t.	+	-	-	-	+	-	-	+	+	-	+	+	**B-III (0.2), C_1-VII (1), D_2-VII (8)**
ID-39	-	-	+	-	+	-	+	-	+	+	+	+	+	+	**B-III (0.6), C_2-V (18), D_2-V (2.5)**
ID-40	+	-	-	+	+	+	+	-	+	+	+	+	+	+	**B-IV (50), C_1-V (2), D_2-V (32)**
ID-41	-	-	-	+	-	-	-	-	+	+	+	-	-	-	**B-IV (7.6)**
ID-42	n.t.	n.t.	-	+	-	+	+	+	-	+	+	-	+	+	B-IV (1.2), **C_1-VII (0.8), D_1-VII (0.6)**
ID-43	+	-	+	+	+	-	+	-	+	+	+	+	+	+	**A-I (10), B-III (15), C_1-VII (10), D_2-VII (10)**
ID-44	+	-	+	-	+	-	+	-	+	+	-	+	+	+	**A-I (26.6), B-III (2.6), C_2-V (9), D_2-V (3)**
ID-45	-	+	+	-	-	-	-	+	+	+	+	-	+	+	**A-II (9.6), B-III (0.07)**
ID-46	-	+	-	+	-	-	+	-	+	+	-	-	+	+	**A-II (14.6)**, B-IV (1400), C_1-VII (600)
ID-47	+	-	-	-	+	-	+	-	+	+	+	+	+	+	A-I (0.6), **C_1-V (1.5)**
ID-48	-	+	-	-	-	-	+	-	+	+	+	-	+	+	A-II (15.7), C1-VII (6)
ID-49	n.t.	n.t.	-	-	-	-	-	-	-	+	-	-	-	-	

ID-50	n.t.	n.t.	+	-	-	-	+	-	-	+	+	-	-	-	B-III (4), **C1-VII (0.01)**
ID-51	+	-	n.t.	n.t.	-	-	+	+	+	-	+	+	+	+	A-I (105), **C_2-VIII (1.6), D_2-VII (100)**
ID-52	-	+	-	+	+	-	-	+	+	+	+	-	+	+	**A-II (3.2)**, B-IV (0.5), **C_1-VIII (1), D_1-VIII (0.6)**
ID-53	-	+	n.t.	n.t.	-	-	+	-	+	-	+	-	+	+	A-II (3.9), C_1-VII (60)
ID-54	+	-	-	+	+	-	+	+	+	+	+	+	+	+	A-I (20.6), **B-IV (2.9)**, C1-VII (91)
ID-55	n.t.	n.t.	n.t.	n.t.	-	-	+	-	-	-	-	-	+	-	D1-VII (2000)
ID-56	-	+	-	-	-	-	-	-	+	+	-	-	-	+	A-II (85)
ID-57	+	-	+	-	+	-	+	+	+	+	+	-	+	+	**A-I (5.7)**, B-III (20), **C_1-V (1.7), D_2-V (3.2)**
ID-58	-	+	+	-	+	+	-	+	+	+	+	-	+	+	**A-II (4.3)**, B-III (0.28), **C_1-VIII (1.5), D_1-VIII (1.5)**
ID-59	n.t.	n.t.	-	-	-	-	-	-	-	+	-	-	-	-	
ID-60	-	-	+	-	-	+	-	-	+	+	+	-	+	+	B-III (0.02), C_1-VI (60), **D_1-VI (9)**
ID-61	-	+	-	+	+	-	-	+	+	+	+	+	+	+	A-II (7.5), **B-IV (0.5), C_1-VIII (0.02), D_2-VIII (0.7)**
ID-62	-	+	n.t.	n.t.	-	-	+	-	+	-	+	-	+	+	A-II (71.1), D_1-VII (15), D2-VII ()
ID-63	-	+	+	-	-	-	+	+	+	+	+	-	+	+	**A-II (72.1), B-III (0.5), C_1-VIII (100), D_1-VIII (120)**
ID-64	-	-	-	-	-	-	-	-	+	+	-	-	+	+	

Method abbreviations – Enrichment methods: I) SPE-WAX; II) SPE-WCX; III) SPE-Multilayer; IV) Evaporation; V) SPE-WAX; VI) SPE-MSX; VII) SPE-ENV+; VIII) SPE-EnviCarb
Instrumental methods: A) MMLC-MS/MS; B) HILIC-MS/MS; C_1/C_2) UHPLC-MS/MS; D_1/D_2) SFC-HRMS
+ enrichment or chromatographic method applicable
- enrichment or chromatographic method not applicable
n.t. not tested

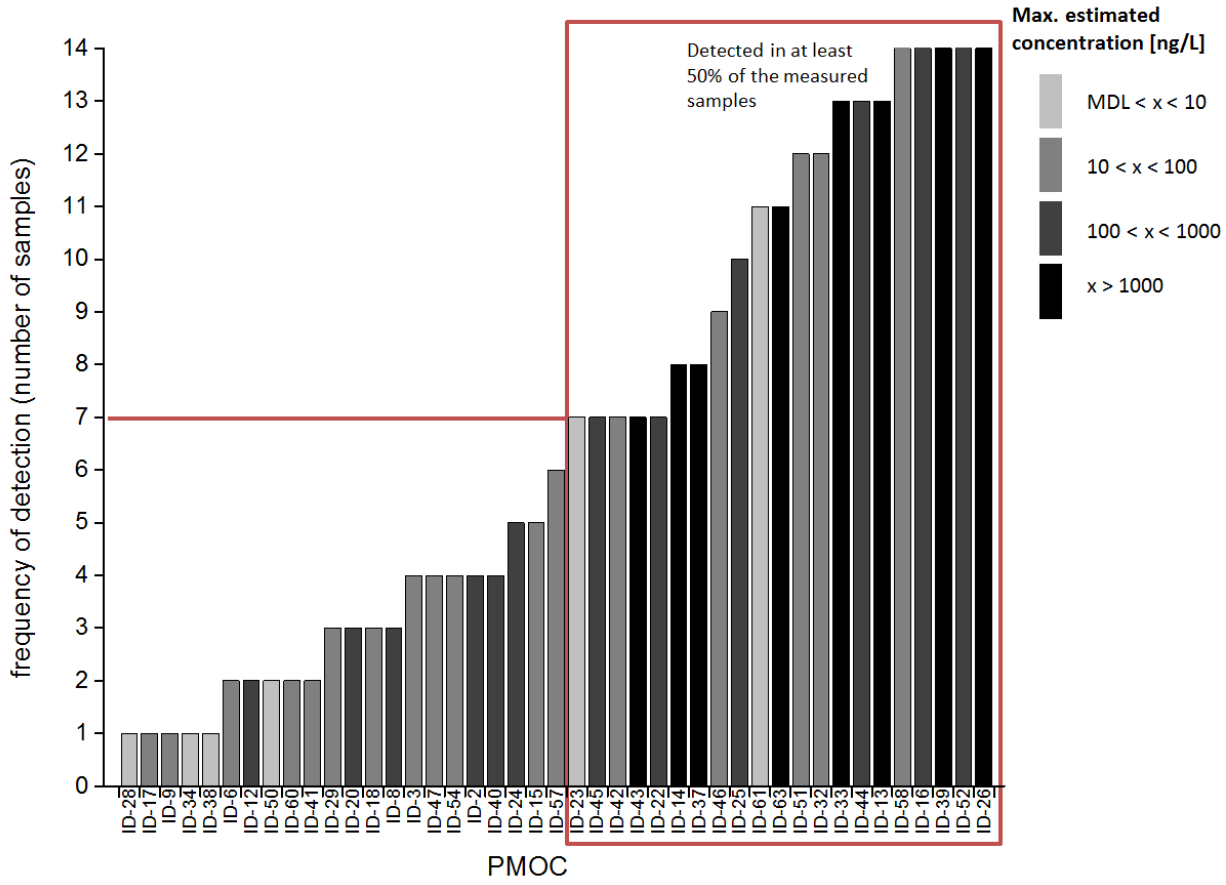


Figure S6. Frequency of detection (including all methdos) and maximum estimated concentration of the detected PMOCs in the 14 water samples.

Table S10. Chromatography method-specific detection frequencies (number of samples) of the detected PMOCs in the 14 water samples.

Index	Detection frequency *Chromatography A* (with *Enrichment I/II*)	Detection frequency *Chromatography B* (with *Enrichment III/IV*)	Detection frequency *Chromatography C_1/C_2* (with *Enrichment V-VIII*)	Detection frequency *Chromatography D_1/D_2* (with *Enrichment V-VIII*)
ID-2	-	2	2	-
ID-3	-	4	-	-
ID-6	2	-	1	-
ID-8	-	-	3	-
ID-9	-	-	1	-
ID-12	1	1	-	-
ID-13	12	13	13	12
ID-14	8	2	4	-
ID-15	5	4	-	-
ID-16	13	7	10	5
ID-17	-	-	1	1
ID-18	-	3	-	-
ID-20	-	-	1	3
ID-22	-	5	5	-
ID-23	6	-	5	1
ID-24	-	1	5	2
ID-25	-	9	6	2
ID-26	3	7	8	14
ID-28	-	1	-	-
ID-29	1	-	3	1
ID-32	6	10	8	8
ID-33	5	8	10	13
ID-34	-	-	1	-
ID-37	-	6	-	8
ID-38	-	1	1	1
ID-39	-	4	10	14
ID-40	2	1	3	3
ID-41	-	2	-	-
ID-42	-	-	6	7
ID-43	3	-	1	4
ID-44	3	10	13	13
ID-45	6	5	-	-
ID-46	9	-	1	-
ID-47	-	-	4	-
ID-50	-	-	2	-
ID-51	-	-	12	1
ID-52	14	-	8	7
ID-54	-	4	-	-
ID-57	3	-	2	4
ID-58	4	-	14	11
ID-60	-	-	-	2
ID-61	-	5	10	1
ID-63	7	10	4	5