



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 polarity. 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 $\geq 50\%$ of the samples at estimated concentrations in the low ng L⁻¹ up to $\mu\text{g L}^{-1}$ 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.

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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-Martínavarro et al., 2013), saccharine, acesulfame (Buerge et al., 2009), and sulfanilic acid (Holm et al., 1995). PMOCs are particularly critical if they also exhibit toxic 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

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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 the 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 4–5 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 4–5). 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 methods of utmost sensitivity were required. 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 logD 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 6 weeks at $+4^\circ\text{C}$ 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 $\mu\text{g L}^{-1}$ 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 $0.45 \mu\text{m}$ 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 ultrapure 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 ultrapure water:acetonitrile (90:10). Finally, the extract was filtered through

a 0.22 μm PP filter. For more details see [Montes et al. \(submitted\)](#).

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 ultrapure water. Elution of the analytes was performed with 10 mL of 2% formic acid in methanol ([Montes et al., submitted](#)).

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. \(2018\)](#).

Enrichment IV. An aliquot of 10 mL of the unfiltered sample was evaporated to dryness at 45 °C and 9 mbar. The residues were reconstituted in 500 μL of acetonitrile:water (95:5) and the extract was filtered through a 0.2 μm cellulose syringe filter ([Köke et al., 2018](#)).

Enrichment V. The water sample was filtered through a glass fiber filter. An aliquot of 50 mL was adjusted to pH 2 (with 0.02 M Glycin/HCl buffer) and submitted automatically to a WAX SPE cartridge. The cartridge was previously conditioned with 3 mL methanol and 3 mL ultrapure water. After sample loading the cartridge was washed with 4 mL 2% formic acid in ultrapure water (discarded) and the analytes were eluted with 4 mL methanol and 4 mL 5% ammonia in methanol. The combined extracts were evaporated to dryness and the residues were reconstituted in 1 mL ultrapure water for *Chromatography C₁/C₂* or in 1 mL acetonitrile:ultrapure water (90:10) for *Chromatography D₁/D₂* (see section 2.4). Finally, the extract was filtered through glass wool in the tip of a Pasteur pipette.

Enrichment VI. Identical to *Enrichment V* but employing a strong mixed-mode cation exchange (MCX) SPE cartridge.

Enrichment VII. Identical to *Enrichment V* with the following modifications. An aliquot of 50 mL was adjusted to pH 7 (with 0.02 M phosphate buffer) and submitted automatically to a highly retentive non-polar SPE phase (ENV+) previously conditioned with 3 mL methanol and 3 mL ultrapure water. After sample loading the cartridge was washed with 2 mL methanol:ultrapure water (5:95, discarded) and the analytes were eluted with 4 mL methanol.

Enrichment VIII. Identical to *Enrichment V* with the following modifications. An aliquot of 50 mL was adjusted to pH 12 (with 0.02 M Glycin/NaOH buffer) and submitted automatically to a graphitized non-porous carbon SPE phase (ENVI-Carb) previously conditioned with 5 mL methanol:dichloromethane (20:80), 2 mL methanol, and 5 mL ultrapure water. After sample loading the cartridge was washed with 5 mL ultrapure water (discarded) and the analytes were eluted with 4 mL methanol, 2 mL methanol:dichloromethane (20:80), and 4 mL 2% formic 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 C₁/C₂* and *Chromatography D₁/D₂*, 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 $\mu\text{L min}^{-1}$ 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 $\mu\text{L min}^{-1}$ 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 C₁/C₂ was used with extracts from *Enrichments V-VIII*. *Chromatography C₁* consisted of C₁₈-based liquid chromatography (Waters Acquity UPLC HSS T3 column) and *Chromatography C₂* 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 C₁* was performed at 60 °C at a flow rate of 500 $\mu\text{L min}^{-1}$ using a water-methanol gradient containing 5 mM ammonium formate ([Figure S2](#)). Separation for *Chromatography C₂* was performed at 50 °C at a flow rate of 250 $\mu\text{L min}^{-1}$ 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 D₁/D₂ was used with extracts from *Enrichments V-VIII*. *Chromatography D₁/D₂* consisted of supercritical fluid chromatography (SFC, Waters Acquity UPC² BEH (*D₁*) or Waters Torus Diol (*D₂*) 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 $\mu\text{L min}^{-1}$ 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 $\mu\text{L min}^{-1}$ 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-dimethylaminoethyl)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-hydroxyethyl)-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 *N*-isopropyl-*N*-4-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. *Enrichment 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 (0.02–2000 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 (Fig. 1). Fig. 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. Fig. 2 shows boxplots of estimated concentrations of selected PMOCs in the water samples. The selection of PMOCs for Fig. 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 Fig. 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 (Fig. 2 and Figure S6). Of the PMOCs shown in Fig. 2, these were notably ID-13 (acesulfame), ID-25 (sulfanilic acid), ID-26 (melamine), ID-33 (trifluoromethanesulfonic acid), ID-37 (cyano-guanidine), ID-39 (*p*-toluenesulfonic acid), ID-40 (saccharine), ID-44 (dimethylbenzenesulfonic acid), and ID-45 (benzylidimethylamine). 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 (Fig. 2).

3.4. Discussion of detected PMOCs

All of the 43 detected PMOCs were industrial chemicals registered under REACH with calculated logD 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

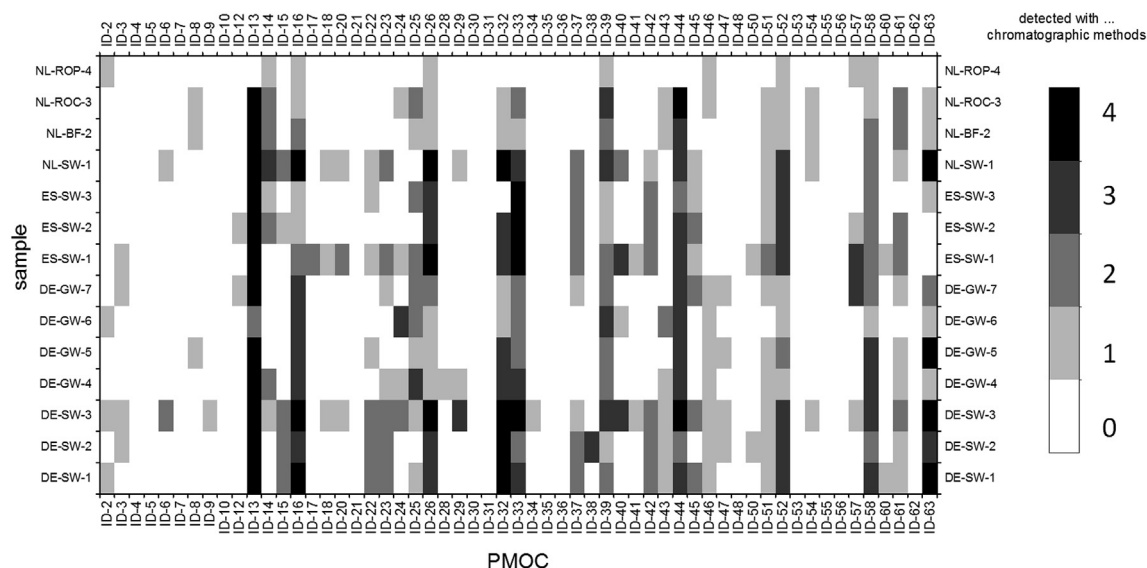


Fig. 1. Detection frequencies of the target PMOCs in the 14 water samples. The gray shading shows the number of principally different separation methods (Chromatography A–D) with which the PMOCs were detected.

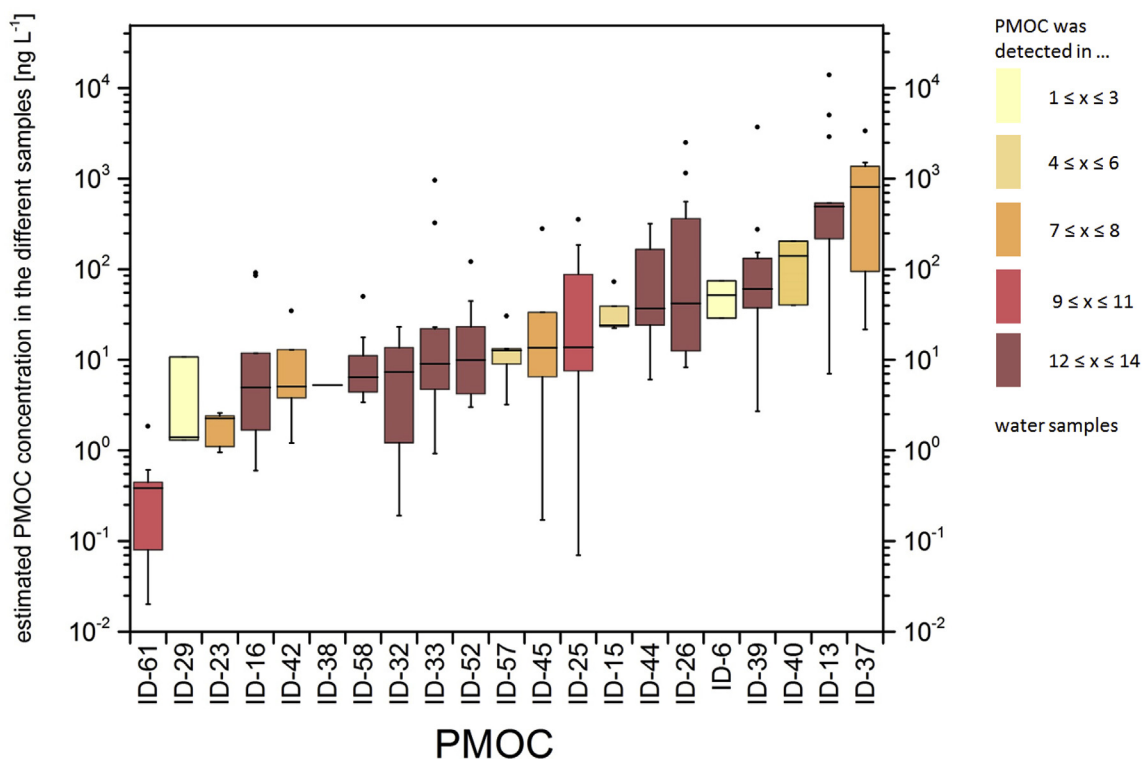


Fig. 2. Estimated concentrations of selected PMOCs in the water samples. The color shading indicates the detection frequency in the 14 samples. The horizontal line marks the median value, the box comprises the interquartile range (IQR), and the whiskers reach to the outmost measuring points that are 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. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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 (Fig. 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 Fig. 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 Fig. 3 and are 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 $1\text{--}10\text{ ng L}^{-1}$, 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 $\mu\text{g L}^{-1}$ range (Fig. 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

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

Index	Substance name	logD*	CAS no.	Use**	Tonnage/ yr**	Literature
<i>Priority 1: Novel and high frequency of detection</i>						
ID-14	Methyl sulfate	−2.84	512-42-5	<ul style="list-style-type: none"> • Surface active agent • Laboratory chemical 	10–100	
ID-16	2-Acrylamino-2-methylpropane sulfonate	−2.71	5165-97-9	<ul style="list-style-type: none"> • Monomer for polymerization and in hydrogels 	10000 –100000	
ID-23	Benzyltrimethylammonium	−2.24	56-93-9	<ul style="list-style-type: none"> • Process regulator, surface active agent • Used in vulcanization or polymerization processes • Removal of charged micropollutants from water by ion exchange polymers 	100 - 1000	
ID-33	Trifluoromethanesulfonic acid	−1.23	1493-13-6	<ul style="list-style-type: none"> • Processing aid, process regulator, laboratory chemical • Used in vulcanization or polymerization processes • Ingredient of ionic liquids 	100 - 1000	Zahn (2016) Montes (2017)
ID-42	6-Methyl-1,3,5-triazine-diamine	−0.39	542-02-9	<ul style="list-style-type: none"> • 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	Benzyltrimethylamine	0.02	103-83-3	<ul style="list-style-type: none"> • Process regulator • Used in vulcanization or polymerization processes • Used in binding agents, fixing agents, polymers, adhesives and sealants, and coating products 	100 - 1000	
ID-58	1,3-Di-o-tolylguanidine	2.25	97-39-2	<ul style="list-style-type: none"> • Process regulator • Used in vulcanization or polymerization processes and in rubber products 	100 - 1000	Montes (2017)
<i>Priority 2: Scarcely investigated and high frequency of detection</i>						
ID-32	Adamantan-1-amine	−1.49	768-94-5	<ul style="list-style-type: none"> • Intermediate • Antiviral and antiparkinsonian pharmaceutical 	Intermediate	Möhle and Metzger (2001)
ID-37	Cyanoguanidine	−1.03	461-58-5	<ul style="list-style-type: none"> • Modifying agent for melamine resins • Processing aid • Used in fertilizers, textile treatment products, and dyes • Used for the manufacture of textile, leather and fur 	10000 –100000	Scheurer et al. (2016) Smith and Schallenberg (2013)
ID-39	p-Toluenesulfonic acid	−0.71	104-15-4	<ul style="list-style-type: none"> • Processing aid, process regulator, pH-regulating agent • Used in vulcanization or polymerization processes and in water treatment products 	10000 –100000	Crathorne et al. (1984)
ID-44	Dimethylbenzenesulfonic acid	−0.20	1300-72-7 25321-41-9	<ul style="list-style-type: none"> • Process regulator • Used in vulcanization or polymerization processes • pH-regulating agent • Laboratory chemical 	1000–10000	Betwoski et al. (1996)
ID-51	Toluenesulfonamide	1.09	70-55-3 88-19-7	<ul style="list-style-type: none"> • Processing aid, laboratory chemical • Used in polymers 	10–100	Richter et al. (2007)
ID-52	1,3-Diphenylguanidine	1.23	102-06-7	<ul style="list-style-type: none"> • Process regulator • Used in vulcanization or polymerization processes • In rubber products, polymers, tires, treated wooden products, bridges a.o. 	1000–10000	Tang et al. (2015)
<i>Priority 3: Novel and low frequency of detection</i>						
ID-2	2-Piperazin-1-ylethylamine	−5.61	140-31-8	<ul style="list-style-type: none"> • Used in adhesives and sealants • Coating products, fillers, putties, plasters, modelling clay, finger paints and polymers 	1000–10000	
ID-3	Isophoronediamine	−4.59	2855-13-2	<ul style="list-style-type: none"> • Adhesives and sealants • Coating products, fillers, putties, plasters, modelling clay • Laboratory chemical 	10000 –100000	
ID-6	Methacrylamido propyl trimethyl ammonium	−3.74	51410-72-1	<ul style="list-style-type: none"> • Intermediate • Industrial use of monomers for manufacture of thermoplastics 	100 - 1000	
ID-9	2-[4-(2-Hydroxyethyl)-1-piperazinyl]ethanesulfonic acid	−3.25	7365-45-9	<ul style="list-style-type: none"> • 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 - 1000	
ID-12	3-Allyloxy-2-hydroxy-1-propanesulfonic acid	−3.13	52556-42-0	<ul style="list-style-type: none"> • Processing aids at industrial sites • Corrosion inhibitor • Anti-scaling agent 	1000–10000	
ID-15	1,4-Diazabicyclo-[2.2.2]octane	−2.83	280-57-9	<ul style="list-style-type: none"> • Process regulator • Used in vulcanization or polymerization processes 	1000–10000	
ID-17	4-Hydroxy-1-(2-hydroxyethyl)-2,2,6,6-tetramethylpiperidine	−2.62	52722-86-8	<ul style="list-style-type: none"> • Used for the manufacture of chemicals and plastic products 	1000–10000	
ID-18	Vinylsulfonate	−2.60	3039-83-6	<ul style="list-style-type: none"> • Plating agents and metal surface treating agents • Surface active agent • Used in metal working fluids 	100 - 1000	
ID-24	2-Methyl-2-propene-1-sulfonic acid	−2.21	1561-92-8	<ul style="list-style-type: none"> • Process regulator • Used in vulcanization or polymerization processes • Used for the manufacture of textile, leather, and fur (water repellent) 	1000–10000	
ID-28	Carbodihydrazide	−1.96	497-18-7	<ul style="list-style-type: none"> • Corrosion inhibitor and anti-scaling agent • Used in water treatment chemicals and polymers 	100 - 1000	

Table 1 (continued)

Index	Substance name	logD*	CAS no.	Use**	Tonnage/ yr**	Literature
ID-29	N-(3-(Dimethylamino)-propyl)methacrylamide	−1.85	5205-93-6	• Used in adhesives and sealants	1000–10000	
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 - 1000	
ID-47	Dicyclohexyl sulfosuccinate	0.42	23386-52-9	• Used in adhesives and sealants, coating products and fillers, putties, plasters, modelling clay	100 - 1000	
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	10–100	
ID-60	4,4-Diaminodiphenylmethane	2.40	101-77-9	• Used in inks and toners, electrical batteries and accumulators • Used in lubricants and lubricant additives, polymers, greases	10000 –100000	
<i>Priority 4: Well-known and high frequency of detection</i>						
ID-13	Acesulfame	−3.06	55589-62-3	• Sweetener	1000–10000	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	10000 –100000	Reemtsma et al. (2013)
ID-25	Sulfanilic acid	−2.04	121-47-1 121-57-3	• pH regulator • Water treatment product • Laboratory chemical	1000–10000	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	100000 – 1000000	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 dyestuffs	no information available	Alonso and Barcelo (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 000000 – 10000000	Wang et al. (2003)
ID-61	Ametryn	2.57	834-12-8	• Plant protection active substance	1000–10000	Lanchote et al. (2000)
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)
<i>Priority 5: Scarcely investigated and low frequency of detection</i>						
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	1000–10000	Scheurer et al. (2016)
<i>Priority 6: Well-known and low frequency of detection</i>						
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 - 1000	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	10000 –100000	Yamazaki et al. (2015)

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

** ECHA 2018.

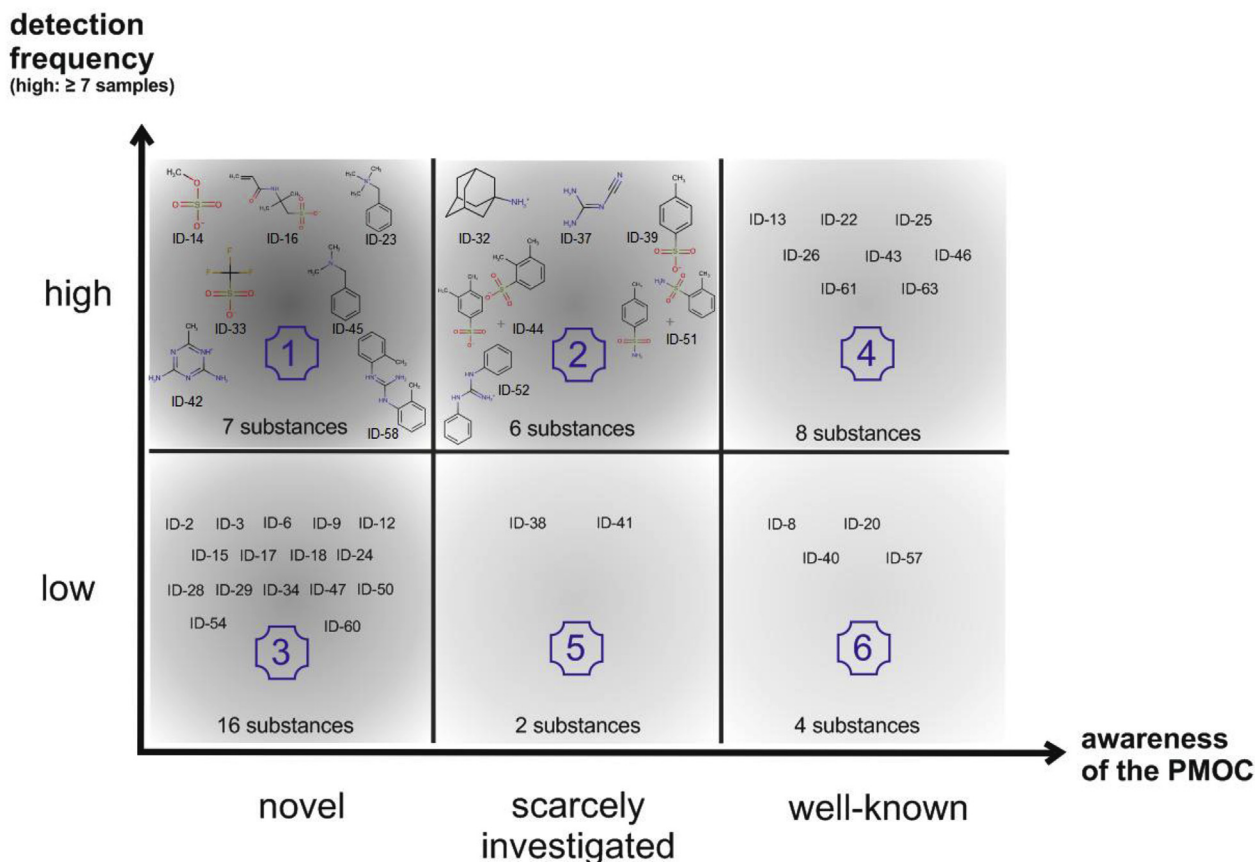


Fig. 3. Classification of PMOCs in priority classes (1–6) according to their frequency of detection and level of awareness as environmental water pollutants.

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} (Fig. 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, Fig. 1) at estimated concentrations typically around 10 ng L^{-1} (Fig. 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 (Fig. 1)

at concentrations exceeding 3000 ng L^{-1} (Fig. 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-dimethylbenzenesulfonic acid, were both detected in 13 samples (Fig. 1). Only the reverse osmosis permeate from the Netherlands showed levels $< \text{MDL}$. Betowski and co-workers have earlier reported on the presence of xylene-sulfonic 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 toluenesulfonamide was found at concentrations up to $50 \mu\text{g L}^{-1}$ in wastewater and $0.27 \mu\text{g L}^{-1}$ 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} (Fig. 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 to this article can be found online at <https://doi.org/10.1016/j.watres.2019.01.008>.

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