Organic Pollutants in the Water Cycle

Properties, Occurrence, Analysis and Environmental Relevance of Polar Compounds

Edited by
Thorsten Reemtsma and Martin Jekel
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Preface

The perspective on contamination of aqueous environment by anthropogenic trace pollutants has experienced a remarkable change in the past ten to fifteen years. Traditionally hydrophobic persistent organic pollutants (POP) that may accumulate in sediments and enrich along food chains were studied extensively. Meanwhile the awareness developed that also polar contaminants may pose a significant problem to water quality, especially if they are not well degradable.

This growing awareness of polar pollutants has several reasons, of which only a few may be mentioned here.

• studying the occurrence of polar pollutants requires that these contaminants are analytically accessible. It was only in the second half of the 1990s that the effective coupling of liquid chromatography to mass spectrometry by electrospray ionization offered a highly sensitive approach to determine polar pollutants from water (see Chapter 1). This progress in analytical chemistry was a prerequisite to direct more attention towards such polar pollutants and to study them in more detail.

• Also in the 1990s it was shown, that trace organic pollutants present in municipal wastewater effluents may have severe sub-lethal effects to aquatic biota. It was shown that xeno-estrogens may interfere with the hormone cycle of wildlife at trace level.

• Globally an increasing water demand calls for an increasing portion of indirect potable reuse of treated municipal wastewater. However, such a partial closure of water cycles at local and regional scale urges to consider new criteria for contaminant evaluation. Especially polar and persistent pollutants can be problematic as they may travel along a water cycle from wastewater to raw waters used for drinking water production. The past ten years have seen increasing evidence that such compounds are present.

The Partially Closed Water Cycle

One example of a partially closed water cycle is displayed in Figure 1. In such a cycle a polar and persistent component that is neither removed by sorption nor by
biodegradation could pass all barriers such as wastewater treatment or underground passage and would, then, appear in raw waters used for drinking water production. Polar pollutants may originate from consumer products used in household, pesticides applied in agriculture or chemicals used in industry. Surface runoff may also contribute. The occurrence of trace pollutants in raw waters requires an ever increasing technical effort in drinking water production.

Of the various components of such a water cycle (Fig. 1) the municipal wastewater treatment plants are, certainly, best investigated. Meanwhile, an impressive body of literature is available concerning the occurrence and removal of polar trace pollutants from municipal wastewater by biological treatment. Other processes such as the transport of pesticides applied in agriculture to groundwater are also comparatively well studied. The occurrence of polar pollutants in other compartments of this cycle, however, and their removal in or passage through other barriers than wastewater treatment or soil are less thoroughly investigated. Even less so has the occurrence and behaviour of polar pollutants in all components of a partially closed water cycle been studied systematically.

Therefore this book aims at bringing together results obtained in various studies concerning all compartments and barriers of a (hypothetic) partially closed water cycle.

The Polar Pollutants

As this book focuses on the water cycle the selection of contaminant classes that are covered is, among others, based on polarity. The authors agreed to select an upper limit of the octanol/water partition coefficient (log $K_{ow}$) of 3 for inclusion into this book. Therefore, the reader may miss certain contaminant classes that he became familiar with in the past years, like endocrine disruptors. Certainly, these compounds would be an issue in a more general book on ‘contaminants in water’ but, due to the comparatively high log $K_{ow}$ values of many of these compounds, they are not relevant as ‘contaminants in the water cycle’.

The production volume is another relevant criterion as a high production volume chemical, even with an almost complete removal in wastewater treatment, could still lead to significant amounts being discharged into surface water. For this rea-
son a number of high production volume chemicals are included in this book. The first to mention are surfactants which are used almost everywhere (Chapter 9). The occurrence of poorly degradable surfactants in surface waters and groundwaters made this class of compounds the first, for which a minimum extent of biodegradability was required by regulations in Western Europe and the United States in the early 1960s. Other important groups of polar high production volume chemicals that are covered in this book are herbicides (Chapter 6), complexing agents (Chapter 7) and amines (Chapter 8).

Also compounds used and released in substantially less amount can be problematic, if their use profile requires a certain level of stability. Pharmaceuticals are an example for this and the occurrence of such compounds in wastewater discharges and surface waters has received significant attention within the last years. Several chapters of this book deal with this ‘dark side’ of the so beneficial development in pharmaceuticals (Chapters 2–5).

Finally, polar pollutants may even be generated in wastewater treatment or drinking water production as it is the case for disinfection byproducts (Chapter 10).

With improved analytical capabilities (Chapter 1) that allow to detect nanogram per litre concentrations of trace pollutants positive findings in virtually all aquatic compartments are almost inevitable. Thus, the need for proper knowledge how the occurrence of low concentrations of polar pollutants has to be evaluated is becoming more urgent. Chapter 11 deals with such aspects of ecotoxicology. A combined evaluation of physico-chemical and ecotoxicological properties of high production volume chemicals is necessary to avoid contamination and to reduce the risk related with the use of chemicals. This is the basis of the chemicals management (REACH) in the European Union (Chapter 12).

Also in the European Union the Water Framework Directive (WFD) has bundled many different regulations concerning the protection of freshwater resources. While the WFD has strengthened biological quality criteria for waters and water bodies, there is growing concern with respect to chemical quality criteria. Inter alia chemicals that may not be harmful to human health or the quality of aquatic ecosystems are not considered pollutants. Thus, the WFD may hamper rather than foster the protection of the water cycle from anthropogenic compounds that are polar and persistent and that may spread in aquatic environment.

We would be pleased if this book contributes to increasing the knowledge on and the awareness of the relevancy of polar pollutants for the quality of waters, not at least those being used as drinking waters.

We are grateful to all the authors that shared this view on polar pollutants and contributed with their expertise, time and effort in preparing the different chapters of this book.

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1
Analytical Methods for Polar Pollutants

Thorsten Reemtsma and José Benito Quintana

1.1
Introduction

The last few decades have shown that analytical chemistry and environmental chemistry are “conjoined twins”. Neither can move significantly forward without the contribution and support of the other discipline. But in their conjoined development both disciplines have contributed much to our knowledge of environmental pollution, to the understanding of environmental processes, and to the development of measures and strategies to reduce contamination.

Complementary to the following book chapters that focus on the occurrence and behavior of different classes of polar pollutants in the water cycle, this chapter provides an overview of the recent status of the other half of the “conjoined twins”, the analytical methods to determine these polar pollutants. This subject could easily be the topic of an independent book. Condensing it to one chapter requires considerable selectivity. Therefore, analytical strategies and approaches to the trace analysis of polar pollutants from environmental samples are outlined rather than described in detail.

1.2
The Analytical Process

A scheme of the analytical process for the determination of polar pollutants in water and particulate samples (sludge, sediment and soil) is presented in Fig. 1.1. This scheme excludes sampling, which is outside of the scope of this overview. Obviously not all the steps presented in this scheme are always necessary, and in many cases, for example, clean-up or derivatization prior to GC determination and sometimes even the enrichment step can be skipped.

The most common and important steps will be considered in separate sections, paying special attention to the most relevant techniques and to expected future developments, according to current trends in analytical chemistry: e.g., miniaturization, automation, reduction in solvent consumption, and sample manipulation.
Examples will be presented from different compound classes that are covered in this book and that exhibit different physicochemical properties. The analytical methods for some of these compound classes, namely surfactants \([1, 2]\), herbicides and other pesticides \([3–9]\), pharmaceuticals \([10–13]\), disinfection byproducts \([14]\), and complexing agents \([15, 16]\), have been the subject of specific reviews, which can provide the reader with more detailed information.

1.3 Sample Pretreatment and Analyte Extraction

1.3.1 Sample Pretreatment

Several steps may be required after sampling and before analyte extraction and final determination. These steps include sample preservation, filtration, pH adjustment of aqueous samples, drying and homogenization of solid samples, etc. They

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are very straightforward, but if they are not performed properly the original sample composition may be seriously altered by these steps.

Even sample storage and shipping can be a critical step in sample preparation. For instance, significant losses of salicylic acid, acetaminophen, and fenofibrate were observed from a mixture of 12 acidic pharmaceuticals spiked to a treated wastewater that was stored in the dark at 4 ºC [17]. It may be advisable to analyze samples as soon as possible or to store samples in the dark at –20 ºC if they cannot be analyzed immediately. Sample storage may also influence the relative importance of adducts like sulfates and glucoronides as compared to the parent compound [18].

Another common step for sample preservation is acidification, but analytes may not be stable at certain pH values. For example, some fibrate drugs hydrolyze to clofibric acid and fenofibric acid at pH 2 [19], and tetracyclines may undergo epimerization [11]. Furthermore, pH adjustment should be carried out after filtration in order to avoid possible losses during filtration due to the increase in the analyte hydrophobicity.

1.3.2 Solid Samples

To date, the analysis of polar organic contaminants in the water cycle has focused on the aqueous phase, whereas particulate material has not been much considered. Therefore, analytical methods for the determination of polar compounds from solid samples, mainly sediment and sludge, are less developed [20]. Although sorption may not be considered a relevant process for many polar organic compounds, its importance gradually increases with decreasing polarity and increasing solids concentration. Moreover, complexation of ionic and ionizable polar pollutants may occur through inorganic constituents of the matrix, especially in the case of sediments and soils [8, 12]. Thus, in the development of extraction methods for sorbed compounds, one needs to consider their properties, hydrophobicity, and acid-base properties, as well as those of the particulate phase. To develop appropriate extraction conditions that are able to overcome the matrix-analyte interactions, one needs to know whether these interactions are primarily hydrophobic or electrostatic.

In contrast, methods for the determination of pesticides from soil samples are comparatively well developed [8]. Additionally, reviews have appeared recently on the determination of pharmaceuticals [11, 12], surfactants, and their metabolites [1, 2] in environmental solid samples.

The classical extraction method, both for polar and non-polar analytes, was Soxhlet extraction, which consumes large amounts of solvent as well as of the sample, and which is relatively time consuming. Therefore, current methods tend to minimize the consumption of solvents, sample amount, and extraction time by providing additional energy and/or pressure to the mixture of sample and solvent. This supports desorption and diffusion of the analytes from the sample to the solution and enhances their solubility in the extraction media. The different methods are distinguished by the way the energy is supplied to the system and the kind of ex-
tracting fluid employed, namely: microwave assisted extraction (MAE), supercritical fluid extraction (SFE), pressurized liquid extraction (PLE), and ultrasound assisted extraction (USE) [21, 22]. Most of them have been fully automated, which is another major advantage over Soxhlet extraction. For example antibiotics were extracted from agricultural soils by PLE [23] at room temperature and 1000 kPa to avoid tetracycline degradation at high temperatures, but allowing the process to be automated.

A first class of compounds that may be considered is phosphoric acid triesters. They are non-ionic and do not have ionizable groups, so they somewhat resemble classical hydrophobic organic pollutants. However, these compounds cover a broad polarity group, from relatively polar short-chain alkyl phosphates (e.g., triethylphosphate and trichloroethylphosphate; log $K_{ow}$ 0.09 and 1.43 respectively) to quite hydrophobic long-chain alkyl phosphates and aryl phosphates (e.g., triphenylphosphate; log $K_{ow}$ 4.76) [24]. Thus, a typical method designed for extracting PAHs or PCBs based on Soxhlet extraction with hexane or toluene works very well for the non-polar analytes but not for the most polar ones, while choosing an intermediate polarity solvent or a solvent mixture provides acceptable recoveries for the whole group of analytes. In one of the pioneering works on MAE, this was compared to Soxhlet extraction and the shake-flask system using a mixture of ethyl acetate and dichloromethane [25]. Microwave extraction yielded better recoveries except for the very polar trimethylphosphate.

More hydrophobic ionizable compounds can also be extracted by an appropriate solvent. The biocides triclosan and triclocarban have been extracted with dichloromethane [26] or acetone/methanol mixtures [27, 28]. Several pharmaceuticals can be extracted also by acetone and methanol from sediment [29], sludge [30], and suspended particulate material [31]. The clean-up by reextraction from water was achieved by using different SPE sorbents and pH values for the different pharmaceutical classes [29, 30].

In the case of more polar and ionizable analytes, however, pure organic solvents are not adequate extractants. Fluoroquinolones are amphoteric species, and their charge state depends on the pH value. Even when their net charge is zero, they are present in the zwitterionic form. For that reason, best recoveries for PLE of fluoroquinolone antibiotics from sludge and soil were obtained by a mixture of acetonitrile and water (1/1) [32]. Moreover, acidification (pH 2) further improved the extraction efficiency, and this was attributed not only to the enhanced solubility of fluoroquinolones at acidic pH but also to the protonation of the acidic sites of the matrix constituents. Finally, the clean-up of the extracts was accomplished by SPE, employing a mixed-phase cation-exchange disk cartridge, like the method for the extraction of fluoroquinolones from water samples [33]. In a similar way, Crescenzi et al. [34] extracted triazine herbicides from soil by hot water containing a phosphate buffer at pH 7.5 in a fully automated process.

The use of hot (subcritical) water extraction is an innovative way of extracting analytes of different polarity from solid matrices. Though water is a rather polar solvent at 20 °C, its dielectric constant decreases markedly as the temperature is raised to 200 °C, and it is then able to efficiently extract hydrophobic compounds,
e.g., PAHs [35, 36]. Hence, the polarity of water may be matched to the analyte polarity by selecting an optimized extraction temperature. A good example of this is the extraction of surfactants from sludge. Surfactants comprise a broad group of compounds with different chemical properties, including basic, acidic, and neutral compounds. As a result, most analytical methods are dedicated to one or two compound classes [1]. However, the use of subcritical water at pH 9.4 allows the efficient extraction of more than 10 different acidic and neutral chemical groups of surfactants, providing better recoveries than Soxhlet extraction for the nonylphenol ethoxy carboxylates [37]. A clear advantage of using water as a solvent is the ecological aspect and its straightforward application to reverse-phase SPE or SPME clean-up without need for solvent evaporation.

As mentioned previously, the kind of interaction (hydrophilic or hydrophobic) between the analyte and the matrix constituents is another critical point in the extraction. In the case of ionic interactions, the pH of the extraction solution may be shifted or chemicals may be added that can compete with the analytes for the matrix constituents. This technique is used in the case of phenoxyacid herbicide extraction from soils and sediments, where the addition of EDTA to the extracting solvent has been proven to improve recoveries [38–40]. The proposed mechanisms of the simultaneous extraction and derivatization of 2,4-D from soil by PLE are represented in Fig. 1.2 [39]. The same is true for the extraction of tetracycline antibiotics, where a buffer containing EDTA or an acid with chelating properties (e.g., citric acid) is employed to overcome the complexation of these analytes with sample cations [12, 23].

![Fig. 1.2 Suggested mechanisms of the PLE-PFBBBr derivatization of the herbicide 2, 4-D from soil (F atoms not represented): (a) 2,4-D is released while being derivatized with PFBBBr, then EDTA occupies its position at the soil surface (b) EDTA replaces 2,4-D from the active surface site, then the freely dissolved EDTA is derivatized by PFBBBr. Reprinted from [39], with permission from Elsevier.](image-url)
After extraction, the resulting extracts from solid samples, particularly in the case of sludge, normally need to be purified before analysis. This has been done in most cases by SPE of the extracts, either employing normal-phase materials (silica, florisil, etc.) if the analytes are relatively non-polar [26, 31, 41, 42] or by reverse and ion exchange phase sorbents if the analytes are relatively polar or possess ionic groups [23, 27, 29, 30, 32]. In many cases a method developed for the SPE of water samples was employed for this purpose after reconstituting or diluting the extract with water.

1.3.3

**Aqueous Samples**

The determination of polar contaminants in water samples is normally preceded by an extraction step in order to enrich the analytes of interest. This extraction should be as selective as possible in order to minimize the coextraction of matrix that may interfere with analyte detection.

Several extraction techniques for aqueous samples are available, with SPE being the standard procedure. LLE has remained important for only a few applications, e.g., the determination of haloacetic acids [14]. In fact, the US-EPA has two methods available for their determination: one based on SPE [43] and the other based on LLE [44], where, however, the volume of extracting solvent has been minimized to 4 mL of MTBE. The alternatives to SPE are microextraction techniques, namely SPME and, more recently, LPME, as they consume less organic solvent or sample volume (or virtually none in the case of SPME) [45]. Both SPE and microextractions are discussed in more detail.

Other techniques used for the analysis of volatile compounds, like headspace (HS) and purge and trap (PT), are applicable to very few of the polar target analytes considered here (e.g., some haloacetic acids [46]) because of the often ionic character and high water solubility of many polar compounds.

1.3.3.1 **Solid Phase Extraction**

As already mentioned, SPE is nowadays the most widely used extraction technique for polar organic analytes in water samples. SPE is very convenient; it can be automated and adapted to various analytes by a proper selection from the wide range of sorbent materials available. In the case of polar analytes, the breaking point has been the development of new polystyrene-divinylbenzene (PS/DVB) polymeric sorbent materials [47]. A scheme of the SPE sorbents and retention mechanism as a function of the analyte’s properties is presented in Fig. 1.3. Obviously, some analytes can be extracted using different approaches, and selection of the most suitable extraction must take into account many factors, like experience with the specific SPE technique, simplicity of the procedure, possibilities of extending the method toward other analyte classes, and, of course, cost.

Regarding this last aspect, cost, classical silica-bonded reverse phase (RP) materials (C-18, C-8, etc.) are clearly advantageous. Nevertheless, its application towards
polar species is restricted to weakly acidic or basic compounds, which can be brought into the neutral species by adjusting the sample pH. Thus, C-18 cartridges and disks have been successfully employed for the extraction of acidic drugs [10, 13, 48] and pesticides [3] by adjusting the sample pH to 2–3. However, recoveries of the most polar drugs and their metabolites (e.g., salicylic acid, hydroxy-ibuprofen…) are often incomplete [10, 13, 48]. Furthermore, pH adjustment of samples is limited by the stability of the silica. Therefore, this strategy cannot be applied to strongly acidic or basic analytes or to permanently charged species (e.g., amphoteric or quaternary ammonium compounds). Other problems encountered with silica-based RP materials are the residual silanol groups, which can interact with these analytes even when end-capped cartridges are used, and traces of metals in the silica if compounds with complexing properties (e.g., tetracyclines) are to be determined. In the case of tetracyclines, the problem is solved by adding EDTA to the sample [49].

The first approach to extracting strongly acidic or basic compounds by SPE was the use of ion exchange (IE) SPE [50]. Thus, as mentioned, one of the US-EPA methods for the determination of haloacetic acids is based on anion exchange SPE [43], where the sample pH is adjusted to 5. The extraction of these compounds by an RP SPE employing silica-based materials would not be possible as the sample would need to be acidified to pH 0.5 [44], where the silica bonds would be hydrolyzed. Another official method that relies on IE-SPE is the determination of complexing agents in water samples [51]. Here the International Standards Organization offers two possibilities: either evaporation of the water sample to dryness or IP-SPE before their derivatization and GC determination. Obviously, water evaporation requires a high temperature and is a time-consuming process, while IE-SPE can provide not just preconcentration but also a clean-up that evaporation cannot.

Other applications include quaternary ammonium and acidic herbicides [3, 4]. Yet, IE-SPE has some drawbacks, the major one being that recoveries are strongly affected by the ionic strength of the sample [4]. Therefore, strong matrix effects
may occur in IE-SPE of environmental samples, where this parameter may change from sample to sample. For example, it was observed that the recoveries of the complexing agents NTA and EDTA decreased by 20 and 45%, respectively, when 60 mg L\(^{-1}\) of sulfate was added to the sample [52].

The other way to extract very polar analytes on silica-bonded phases is to use ion-pair (IP) reagents with RP materials (e.g., C-18), avoiding in this way the use of IE materials, facilitating the adaptation of conventional RP methods and allowing the combined extraction of a wide range of polarities. The retention of analytes can be tuned by selecting the chain length of the IP reagent, as a wide range of these are available (Table 1.1) for both basic/cationic and acidic/anionic compounds. Some of these ion-pairing agents are volatile enough to be compatible with LC-MS. Furthermore, the ion-pairing agent can suppress interactions with silanol groups of the sorbent [3]. Applications of IP-SPE in water analyses include the determination of acidic and quaternary ammonium herbicides [3, 4], acidic phosphoric acid mono- and diesters [53], and acidic pharmaceuticals and their microbial metabolites [54]. IP-SPE is the US-EPA official method for the determination of diquat and paraquat in drinking water [55] by using a C-8 disk and sodium 1-hexanesulfonate as IP reagent for retention; the analytes are then eluted by an HCl acidified solution, which breaks the IP. The technique of IP-SPE was reviewed by Carson in 2000 [56], who nevertheless recognized that this approach was seldom used for the SPE of polar compounds, in spite of the common use of IP formation for improvement of HPLC retention of polar compounds. A reason for this may be the fact that polymeric materials have had more success for SPE than for LC and a much wider chemistry is also available for SPE. In any case, IP-SPE can also be combined with polymeric materials, and it proved useful for the reduction of phenol breakthrough.

<table>
<thead>
<tr>
<th>For basic/cationic analytes</th>
<th>For acidic/anionic analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trifluoroacetic acid(^{[a]})</td>
<td>Ammonia(^{[a]})</td>
</tr>
<tr>
<td>Pentafluoroproponic acid(^{[a]})</td>
<td>Triethylamine(^{[a]})</td>
</tr>
<tr>
<td>Heptafluorobutyric acid(^{[a]})</td>
<td>Dimethylbutylamine(^{[a]})</td>
</tr>
<tr>
<td>Propanesulfonic acid salts</td>
<td>Tributylamine(^{[a]})</td>
</tr>
<tr>
<td>Butanesulfonic acid salts</td>
<td>Tetramethylammonium salts</td>
</tr>
<tr>
<td>1-Pentanesulfonic acid salts</td>
<td>Tetraethylammonium salts</td>
</tr>
<tr>
<td>1-Hexanesulfonic acid salts</td>
<td>Tetrapropylammonium salts</td>
</tr>
<tr>
<td>1-Heptanesulfonic acid salts</td>
<td>Tetrabutylammonium salts</td>
</tr>
<tr>
<td>1-Octanesulfonic acid salts</td>
<td>Tetrapentylammonium salts</td>
</tr>
<tr>
<td>1-Nonanesulfonic acid salts</td>
<td>Tetrahexylammonium salts</td>
</tr>
<tr>
<td>1-Decanesulfonic acid salts</td>
<td>Tetraheptylammonium salts</td>
</tr>
<tr>
<td>1-Dodecanesulfonic acid salts</td>
<td>Tetraoctylammonium salts</td>
</tr>
<tr>
<td>Dodecylsulfate, sodium salt</td>
<td>Hexadecyltrimethylammonium salt</td>
</tr>
<tr>
<td>Dioctylsulfosuccinate, sodium salt</td>
<td>Decamethylenbis(trimethylammonium bromide)</td>
</tr>
<tr>
<td>Bis-2-ethylhexylphosphate</td>
<td></td>
</tr>
</tbody>
</table>

\(^{[a]}\) LC-MS compatible