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Emerging Contaminants in Waste Waters: Sources and Occurrence

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Abstract There is a growing concern about possible ecotoxicological importance of various classes of emerging contaminants in the environment. Numerous field studies designed to provide basic scientific information related to the occurrence and potential transport of specific classes of emerging contaminants in the environment are being conducted with the aim to identify the sources and points of entry of these contaminants into the environment, and to determine their concentrations in both input streams (i.e., urban and industrial wastewaters) and receiving environment. This chapter summarizes the data regarding the occurrence of emerging contaminants in urban and industrial wastewaters, including some prominent classes such as pharmaceuticals, hormones, illicit drugs, surfactants and their degradation products, plasticizers, and perfluorinated compounds.

Keywords Emerging contaminants · Municipal waste waters · Occurrence · Sources

Abbreviations

AP	Alkylphenol
APEC	Alkylphenoxy carboxylates

APEO	Alkylphenol ethoxylate
BBP	Butylbenzyl phthalate
BE	Benzoylecgonine
BPA	Bisphenol A
CAFO	Concentrated animal feeding operation
CE	Cocaethylene
DA	Drug of abuse
DBP	Dibutyl phthalate
DEHP	Di(2-ethylhexyl) phthalate
DEP	Diethyl phthalate
DMP	Dimethyl phthalate
DnOP	Di-*n*-octyl phthalate
E1	Estrone
E2	Estradiol
E3	Estriol
EDC	Endocrine disrupting compound
EDDP	2-ethylidine-1,5-dimethyl-3,3-diphenylpyrrolidine perchlorate
EE2	Ethinylestradiol
FTOH	Fluorotelomer alcohol
LC-MS/MS	Liquid chromatography and tandem mass spectrometry
LSD	Lysergic acid diethylamide
MDE or MDEA	Methylenedioxyethylamphetamine
MDMA	3,4-Methylenedioxymetamphetamine hydrochloride
NP	Nonylphenol
NSAID	Non-steroidal anti-inflammatory drug
O-H-LSD	2-Oxo-3-hydroxy-LSD
OPEO	Octylphenol ethoxylate
OTC	Over-the-counter (drug)
PAEs	Phthalate acid ester
PEC	Predicted environmental concentration
PFBS	Perfluorobutane sulfonate
PFCA	Perfluoro carboxylic acid
PFCs	Perfluorinated compound
PFNA	Perfluorononanoic acid
PFOS	Perfluorooctane sulphonate
PhAC	Pharmaceutically active compound
POP	Persistent organic pollutant
THC	Δ^9-Tetrahydrocannabinol
WWTP	Wastewater treatment plant

1 Introduction

Until the beginning of the 1990s, non-polar hazardous compounds, i.e., persistent organic pollutants (POP) and heavy metals, were the focus of interest and awareness as priority pollutants and consequently were part of intensive monitoring programs. Today, these compounds are less relevant for the in-

dustrialized countries since a drastic reduction of emission has been achieved due to the adoption of appropriate measures and elimination of the dominant pollution sources.

However, the emission of so-called "emerging" or "new" unregulated contaminants has emerged as an environmental problem and there is a widespread consensus that this kind of contamination may require legislative intervention.

A wide range of man-made chemicals, designed for use in industry, agriculture, and as consumer goods and chemicals unintentionally formed or produced as by-products of industrial processes or combustion, are potentially of environmental concern. The term "emerging contaminants" does not necessarily correspond to "new substances", i.e., newly introduced chemicals and their degradation products/metabolites or by-products, but also refers to compounds with previously unrecognized adverse effects on the ecosystems, including naturally occurring compounds. Therefore, "emerging contaminants" can be defined as contaminants that are currently not included in routine monitoring programmes and which may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects, public perception and on monitoring data regarding their occurrence in the various environmental compartments [1].

Today, there are several groups of compounds that emerged as particularly relevant:

- Algal and cyanobacterial toxins
- Brominated flame retardants
- Disinfection by-products
- Gasoline additives
- Hormones and other endocrine disrupting compounds
- Organometallics
- Organophosphate flame retardants and plasticisers
- Perfluorinated compounds
- Pharmaceuticals and personal care products
- Polar pesticides and their degradation/transformation products
- Surfactants and their metabolites

For most emerging contaminants, occurrence, risk assessment, and ecotoxicological data are not available, and therefore it is difficult to predict what health effects they may have on humans and aquatic organisms. Numerous field studies designed to provide basic scientific information related to the occurrence and potential transport of specific classes of emerging contaminants in the environment are being conducted with the aim to identify the sources and points of entry of these contaminants into the environment, and to determine their concentrations in both input streams (i.e., urban and industrial wastewaters) and receiving environment.

The objective of this chapter is to give an overview of recent monitoring data, focusing on urban and industrial wastewaters. It reports the levels detected for some prominent classes such as pharmaceuticals, hormones, illicit drugs, surfactants and their degradation products, plasticizers and perfluorinated compounds. Possible sources and routes of entry of selected emerging contaminants into the environment are also discussed.

2 Pharmaceutical Residues

2.1 Sources

Pharmaceutically active compounds (PhACs) are an important group of emerging environmental contaminants that has been an issue of increasing interest in the international scientific community. In the European Union (EU), around 3000 different PhACs are used in human medicine (i.e., analgesics and anti-inflammatory drugs, β-blockers, lipid regulators, antibiotics, etc), thus their main route into the aquatic environment is ingestion following excretion and disposal via wastewater. After administration, pharmaceutical can be excreted as an unchanged parent compound, in the form of metabolites or as conjugates of glucuronic and sulphuric acid, primarily via urine and faeces. By analyzing the excretion pathways of 212 PhAC, equaling 1409 products, Lienert et al. [2] concluded that on average, 64% ($\pm$27%) of each PhAC was excreted via urine, and 35% ($\pm$26%) via faeces. In urine, 42% ($\pm$28%) of each PhAC was excreted as metabolites. Figure 1 shows the average total fraction excreted via urine and the fraction of the non-metabolized parent compound for selected therapeutic groups.

Metabolites of drugs can be expected to be bioactive and even more persistent, due to their increased polarity. Also, conjugates of parent compounds can be cleaved back into the original drug during the sewage treatment in wastewater treatment plants (WWTPs) [3]. Besides these WWTP discharges that are usually a consequence of their incomplete removal, other environmental exposure pathways of PhACs are manufacturing and hospital effluents, land applications (e.g., biosolids and water reuse), concentrated animal feeding operations (CAFOs), and direct disposal/introduction into the environment. For example, a survey conducted in the USA reported that the vast majority of people were disposing of expired medications via municipal garbage or domestic sewage [4].

In comparison to conventional priority pollutants, PhACs are designed to have specific pharmacologic and physiologic effects at low doses and thus are inherently potent, often with unintended outcomes in wildlife. They can undergo different chemical, photolytic, and biological reactions that mod-

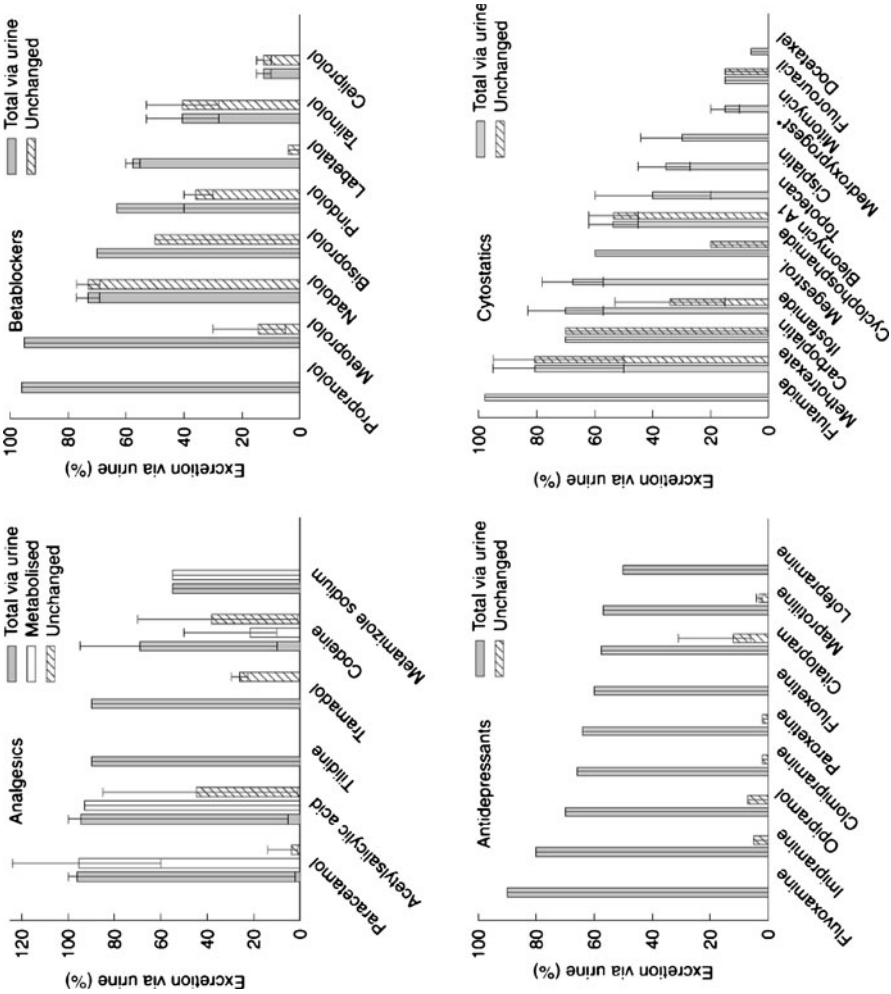


Fig. 1 Excretion via urine of selected therapeutic groups. The average for each PhAC is shown. *Error bars* denote the minimal and maximal value detected for each PhAC. The total fraction excreted via urine and the fraction of the non-metabolised parent compound (unchanged) is shown. For clarity, excretion via feces is not included. If bars are missing, then respective data were missing (e.g., no data on metabolism for the analgesic tilidine). For antidepressants, β-blockers, and cytostatics, metabolism data were missing for most PhAC. Cytostatics: cyclophosphamide includes cyclophosphane; *p*, medroxyprogesteronacetate. Reprinted with permission from [2]. © IWA Publishing 2007

ify the structure and physical transport of a compound in the environmental media. Furthermore, many PhACs do not exhibit acute toxicity but have a significant cumulative effect on the metabolism of non-target organisms [5] and ecosystem as a whole [6]. Some pharmaceuticals such as antidepressants, β-blockers or lipid regulators, can be prone to biococentra-

tion/bioaccumulation in aquatic organisms [7–9]. These results have led to concerns about the ongoing exposure to PhACs, as a result of constant patient use. Also, little is known about their fate and transport in the natural aquatic environment [5, 10], especially when soil/sediment media is in question. There are only a few studies that have dealt with distribution of pharmaceuticals in a natural porous system [11–13]. Therefore, the occurrence of these emerging contaminants in different environmental compartments (e.g., natural waters, waste waters, soil, sludge, sediment) has become a serious issue for the scientific community.

2.2 Occurrence in Wastewaters

Due to their continuous input into the aquatic media through wastewater as a main point-source, PhACs are considered to be "pseudo-persistent". In a proper evaluation of persistency of a certain compound, both transformation of a compound in the environment and its supply rate should be taken into consideration [6]. Factors of environmental concern are production volume, ecotoxicity, and persistence. To the extent of feasibility, predicted environmental concentration (*PEC*) can be calculated, based on the excretion rates and portions of pharmaceutical production. Bendz et al. [14] estimated loads of several pharmaceuticals in the influent of a WWTP in Sweden, based on a per-capita consumption rate, number of inhabitants, and the percentage of excretion of drugs as parent compounds. In this attempt they used the following formula published by Alder et al. [15]:

$$PEC_{\mathrm{STPin}} = \frac{F_{\mathrm{API}} E}{PopAWW} \times \frac{10^{12}}{365},$$

where PEC_{WWTPin} is predicted concentration in the WWTP influent ($\mathrm{ng\,L^{-1}}$), F_{API} consumption of β-blockers per year ($\mathrm{kg\,yr^{-1}}$), E fraction excreted as active substance without metabolization in urine and/or not absorbed (dimensionless), *Pop* population of Switzerland: 7.3 million inhabitants (cap) and *AWW* is amount of wastewater per capita and day ($400\,\mathrm{L\,cap^{-1}\,d^{-1}}$). The measured concentrations of some of them were of the same order of magnitude as the predicted ones (i.e., diclofenac, naproxen, and metoprolol). However, significantly lower concentrations of gemfibrozil, trimethoprim and atenolol, and significantly higher concentrations of carbamazepine were measured compared to the theoretical values. These discrepancies may be explained with seasonal variations in consumption rates and differences in excretion rates for humans depending on their age, sex, thyroid function, nutrition, etc [14]. In another study [16], predictions made out of excretion rates of atenolol (90%), sotalol (70%), metoprolol (5%) and propranolol (10%) and the data on their consumption in Switzerland gave PEC_{WWTPin} very similar to their measured concentrations in the influents of two Swiss WWTPs.

Estimations of pharmaceutical concentration in sewage have been usually performed by back-calculating the total prescribed mass from prescription rate data (number of defined daily doses) and excretion rates, partitioning, biodegradation, and the potential hydrolysis of conjugates [17, 18]. However, predictions based on annual sales of drugs are likely to be underestimating the loads of PhACs in the influents of WWTPs. This is because sales figures refer only to prescription drugs, and do not include over-the-counter drugs and Internet sales. Nevertheless, although these predictions have a high degree of uncertainty, they can focus attention on drugs that are candidates for further analytical studies.

The data on measured environmental loads of pharmaceutical residues is still scarce. The inputs of PhACs are generally considered to be constant and widely distributed. However, for some of them (e.g., antibiotics), differences between winter and summer influent loads were noted, probably because of higher attenuation in summer, and also less use of pharmaceuticals [19, 20]. On the other side, for other drugs (e.g., β-blockers, diuretics and anti-ulcer drugs) this seasonal variability was absent, which was consistent with the data on their occurrence [19].

Over the last 10 years, scattered data all over the world has demonstrated an increasing frequency of appearance in wastewater. The most ubiquitous drugs in WWTP influents are summarized in Table 1, together with their concentration ranges reported in literature.

The ubiquity of drugs is related to specific sales and practices in each country. For example, antihistamines, analgesics, and antidepressants are the families of drugs with major consumption in Spain, according to the National Health System. Indeed, in a study by Gros et al. [21] of the Ebro river basin, the highest influent loads from seven WWTPs were found for non-steroidal anti-inflammatory drugs (NSAIDs), lipid regulators, β-blockers and histamine H_1- and H_2-receptor antagonists. The total load of 29 monitored pharmaceuticals ranged from 1 to 5 g/day/1000 inhabitants for influent wastewater (Fig. 2). The results of a study in six WWTPs conducted in Italy [19] indicated high inputs of antibiotics sulfamethoxazole, ofloxacin, and ciprofloxacin, β-blocker atenolol, anti-histaminic ranitidine, diuretics furosemide and hydrochlorothiazide, and NSAID ibuprofen. A recent comprehensive reconnaissance of more than 70 individual wastewater contaminants in the region of Western Balkan (Bosnia and Herzegovina, Croatia, and Serbia) revealed the presence of 31 out of 44 analyzed pharmaceutical compounds at a concentration above the detection limit (typically $1–10\ \mathrm{ng\,L^{-1}}$) [22]. The most abundant drug groups included analgesics and antiinflammatories, antimicrobials, β-blockers and lipid regulators, as shown in Fig. 3.

Generally, the most abundant loads are commonly reported for NSAIDs, which could be attributed to their wide consumption because they can be purchased without medical prescription (i.e., over-the counter (OTC) drugs).

Table 1 Occurrence of pharmaceutical residues in WWTP influents

Compound	Influent concentration ($\mu g\,L^{-1}$)	Refs.
Analgesics and anti-inflammatory drugs		
Ibuprofen	53.48–373.11; 150.73 [a]	[23]
	0.381–1.13; 0.672 [b]	[25]
	2.6–5.7	[134]
	8.45 [a]; 16.5 [c]	[38]
	23.4 [a]	[39]
	34–168; 84 [a]	[37]
Ketoprofen	0.108–0.369; 0.208 [b]	[25]
	0.146 [a]; 0.289 [c]	[38]
	2.9 [a]	[39]
	0.57 [c]	[40]
	0.16–0.97; 0.451 [a]	[28]
Naproxen	0.038–0.23; 0.1 [b]	[25]
	1.8–4.6	[134]
	8.6 [a]	[39]
	5.58 [a]; 17.1 [c]	[38]
Diclofenac	0.204 [a]; 1.01 [c]	[38]
	0.46 [a]	[39]
	3.25 [a]; 4.114 [a]; 3.19 [a]; 1.4 [a]; 0.905 [a]	[33]
	0.05–0.54; 0.25 [a]	[28]
	2.94 [c]	[40]
Indomethacin	0.23 [a]; 0.64 [c]	[38]
	nd	[28]
Acetyl-salicylic acid	0.47–19.4; 5.49 [b]	[25]
Salicylic acid	13.7 [a]; 27.8 [c]	[38]
Acetaminophen	0.13–26.09; 10.194 [a]	[28]
	29–246; 134 [a]	[37]
Lipid regulator and cholesterol lowering statin drugs		
Gemfibrozil	0.453 [a]; 0.965 [c]	[38]
	nd–0.36; 0.155 [a]	[28]
Bezafibrate	2.2 [a]	[39]
	1.96 [a]; 2.014 [a]; 6.84 [a]; 7.6 [a]; 1.55 [a]	[33]
	nd–0.05; 0.023 [a]	[28]
Clofibric acid	nd–0.11; 0.072 [a]	[28]
	0.36 [c]	[40]
Psychiatric drugs		
Carbamazepine	0.015–0.27; 0.054 [b]	[25]
	1.85 [a]; 1.2 [a]; 0.704 [a]; 0.67 [a]; 0.325 [a]	[33]
	nd–0.95; 0.42 [a]	[28]
	0.12–0.31; 0.15 [a]	[37]
Caffeine	52–192; 118 [a]	[37]

Table 1 (continued)

Compound	Influent concentration ($\mu g\,L^{-1}$)	Refs.
Antibiotics		
Sulfamethoxazole	nd–0.87; 0.59 [a]	[28]
Ofloxacin	nd	[28]
Ciprofloxacin	3.8 [b]; 4.6 [c]	[32]
Norfloxacin	0.17 [b]; 0.21 [c]	[32]
Trimethoprim	0.34 [b]; 0.93 [c]	[32]
	nd–4.22; 1.172 [a]	[28]
Antihistamines		
Ranitidine	nd–0.29; 0.188 [a]	[28]
β-blockers		
Atenolol	nd–0.74; 0.395 [a]	[28]
	(0.971 ± 0.03) [a]	[135]
Metoprolol	(0.411 ± 0.015) [a]	[135]
Sotalol	0.12–0.2; 0.167 [a]	[28]
	(0.529 ± 0.01) [a]	[135]
Propranolol	0.08–0.29; 0.168 [a]	[28]
	(0.01 ± 0.001) [a]	[135]
X-ray contrast media		
Iopromide	6.0–7.0	[134]
	(7.5 ± 1.5) [a]	[136]
Diatrizoate	(3.3 ± 0.7) [a]	[136]
Iopamidol	(4.3 ± 0.9) [a]	[136]

[a] mean,
[b] median,
[c] maximum concentrations.

For example, ibuprofen is usually detected at very high concentrations (in $\mu g\,L^{-1}$) [23–25]. Although the percentage of elimination of this drug is very high [21], it is still detected in rivers downstream WWTPs due to a very high usage in human medicine. Other very popular pain killers are acetaminophen (paracetamol) and aspirin (acetyl-salicylic acid). Acetyl-scalycilic acid is deacetylated in human organism into its more active form, salicylic acid, and two other metabolites, ortho-hydroxyhippuric acid and gentisic acid [26]. Ternes et al. [27] detected all three metabolites in sewage influent samples at very high $\mu g\,L^{-1}$ concentrations. Gros et al. [28] encountered an average concentration of 10.2 $\mu g\,L^{-1}$ in WWTP influents. The environmental loads of these drugs are expected to be substantially higher than the values predicted from their sales figures, as their use is often abused.

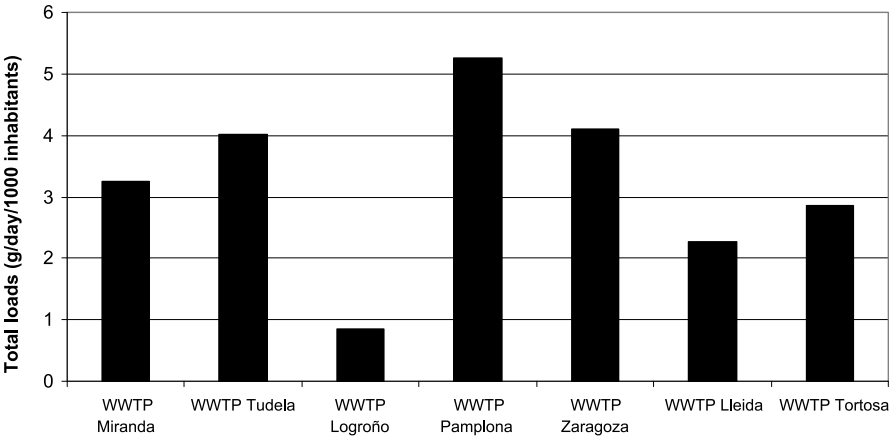
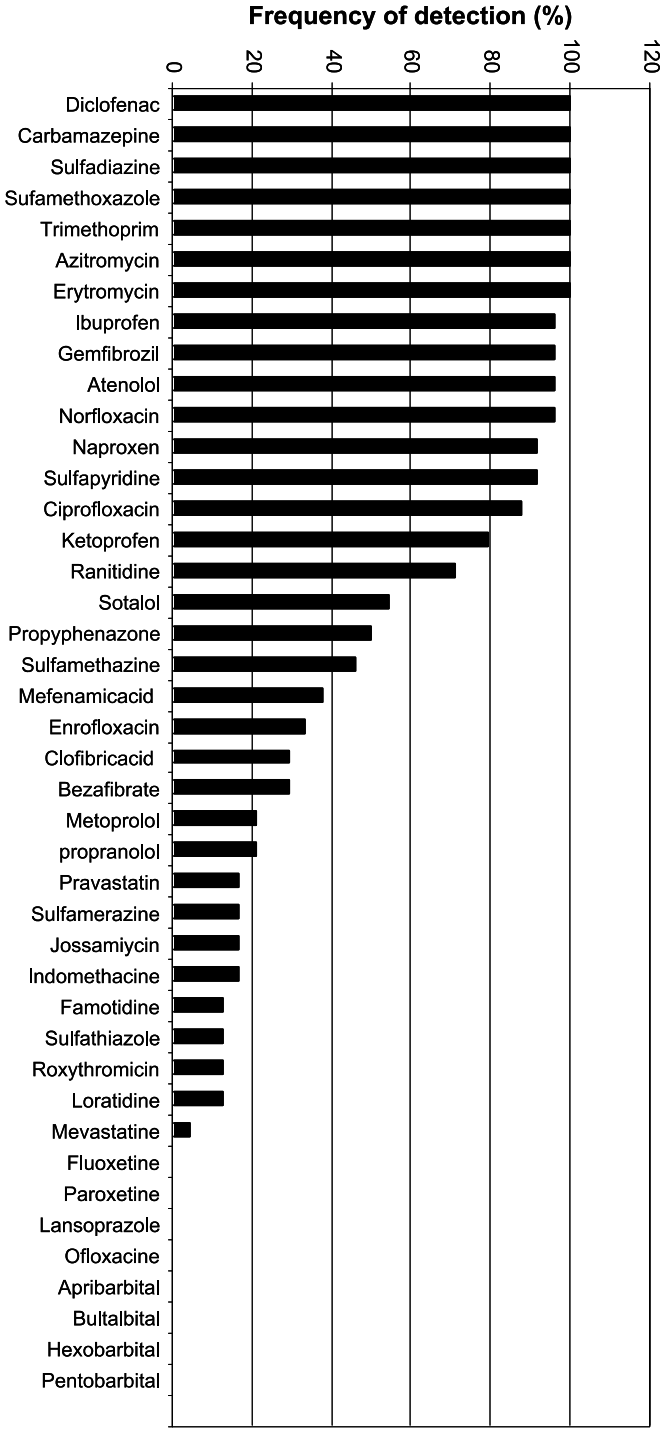


Fig. 2 Total loads of 29 multi-class pharmaceuticals, expressed as g/day/1000 inhabitants, measured in the raw wastewater entering seven major WWTP in the Ebro River basin. Modified from [21]

Besides these OTC drugs, pharmaceuticals ubiquitous in raw sewage are also prescription drugs β-blockers [21, 24, 29]. Atenolol seems to be the most frequently found β-blocker worldwide in WWTP influents [19, 30]. Atenolol, metoprolol, and propranolol were detected at high influent concentrations in a study by Nikolai et al. [30] (i.e., 110–1200, 170–520 and 20–92 ng L^{-1}, respectively). As far as their toxicity is concerned, it is suspected that mixtures of β-blockers are concentration-additive, since they all have the same mode of toxic action in the aquatic environment [31]. These drugs are also used in high quantities and are not efficiently eliminated in WWTPs, thus they are frequently encountered in surface waters [21].

Antibiotic losses to the environment are considered to be substantial due to their widespread consumption in human and veterinary medicine. Sulfamethoxazole, trimethoprim, ciprofloxacin, norfloxacin, and cephalexin had the highest median influent concentrations in a WWTP in Brisbane, Australia (360, 340, 3800, 170, and 4600 ng L^{-1}, respectively) [32]. Other studies confirmed high ubiquity of several antibiotics (i.e., ofloxacin, trimethoprim, roxyhtromycin and sulfamethoxazole) in sewage influent, though at low ng L^{-1} level [28, 33]. However, even at very low concentrations they can have significant ecotoxicological effects in the aquatic and terrestrial compartment [34, 35]. Indiscriminate or excessive use of antibiotics has been widely blamed for the appearance of so-called "super-bugs" that are antibiotic resistant. It is of crucial importance to control their emissions into the

Fig. 3 Frequency of detection for individual pharmaceuticals (%) in the Croatian wastewaters (modified from [22]) ►


Frequency of detection (%)
0
20
40
60
80
100
120
Diclofenac
Carbamazepine
Sulfadiazine
Sufamethoxazole
Trimethoprim
Azitromycin
Erytromycin
Ibuprofen
Gemfibrozil
Atenolol
Norfloxacin
Naproxen
Sulfapyridine
Ciprofloxacin
Ketoprofen
Ranitidine
Sotalol
Propyphenazone
Sulfamethazine
Mefenamicacid
Enrofloxacin
Clofibricacid
Bezafibrate
Metoprolol
propranolol
Pravastatin
Sulfamerazine
Jossamiycin
Indomethacine
Famotidine
Sulfathiazole
Roxythromicin
Loratidine
Mevastatine
Fluoxetine
Paroxetine
Lansoprazole
Ofloxacine
Apribarbital
Bultalbital
Hexobarbital
Pentobarbital

environment through more cautious utilization and monitoring of outbreaks of drug-resistant infections.

The anti-epileptic drug carbamazepine is one of the most prominent drugs with a long history of clinical usage and it is frequently found in the environment [21, 24, 29, 36]. This drug has proven to be very recalcitrant since it by-passes sewage treatment [24, 36]. Common WWTP influent concentrations are in the order of magnitude of several hundreds ng L^{-1} [25, 28, 33, 37].

Lipid regulators are ordinarily applied drugs in clinical practice used to lower the level of cholesterol and regulate the metabolism of lipids. Clara et al. [33] detected a lipid regulator bezafibrate at concentrations up to 7.6 μg L^{-1}, although normally they are found at lower ng L^{-1} range [28, 33, 38–40].

In all countries with developed medical care, X-ray contrast media can be expected to be present at appreciable quantities in sewage water. Clara et al. [33] detected iopromide at a mean concentration of 3.84 μg L^{-1} in the influent of a WWTP receiving hospital wastewater, while in WWTPs without a hospital within their drainage area this contrast media was not present. Iodinated X-ray contrast media are proved to contribute significantly total absorbable organic iodine in clinical wastewaters; up to 130 μg L^{-1} of iodine in the influent of municipal WWTP in Berlin, and 10 mg L^{-1} in hospital sewage was detected [41].

We could assume that a drug that is highly metabolized in humans will be subjected to extensive degradations in the environment, however, a high metabolic rate in humans does not necessarily mean that the lifetime of the pharmaceutical in the environment will be short. For some compounds, this assumption is correct (e.g., ibuprofen, diclofenac, propranolol, metoprolol, and carbamazepine), and they were found to be easily dissipated in the environment [42]. On the other side, atenolol, trimethoprim, and naproxen are substances with a low metabolic rate in humans, and they are excreted mainly unchanged or as acyl-glucuronide (naproxen), whereas their half-lives range from 10 days to 1 year [43]. Furthermore, monitoring of metabolic products should be included in risk-assessment analysis. Commonly, glucuronide and sulphate conjugates are the major Phase II metabolites that leave the biologically active group of the parent drug intact [44]. Some evidence suggests that these metabolites can be cleaved back into the original compound [45, 46]. Moreover, Bendz et al. [14] reported very high influent concentrations of metabolites of ibuprofen, carboxy-ibuprofen and hydroxyl-ibuprofen (10.75 and 0.99 μg L^{-1}, respectively). Although more polar metabolites are presumed to be less hazardous to aquatic organisms, the European Medicines Agency (EMEA) guideline suggests environmental risk assessment of all human metabolites that constitute more than 10% of the total excretion of drug [47].

Due to their beneficial health effects and economic importance, the reduction of drug inputs into the environment through restricting or banning

their use is not possible. Moreover, the use of pharmaceutical compounds is expected to grow with the increasing age of the population. The only possible way is to regulate their environmental pathways, perhaps on the source through labelling of medicinal products and/or developing disposal and awareness campaigns. Another option is to add sewage-treatment facilities in hospitals, and to enhance current wastewater-treatment techniques in order to eliminate more efficiently such polar pollutants.

3
Natural and Synthetic Estrogens

Estrogens are female steroid sex hormones based on a cholesterol structure. They are produced naturally in vertebrates in the gonads and adrenal cortex of both sexes and are responsible for the development of secondary sexual characteristics in the body. Their presence in the environment can cause negative effects to the endocrine functions of wildlife (e.g., aquatic organisms), posing an environmental risk. Estrogens reach the aquatic environment mainly due to incomplete removal in WWTP [48]. Other sources, such as livestock wastes will not be discussed in this section since these residues follow other pathways and do not end up in WWTPs.

3.1
Metabolism and Sources of Estrogens

In terms of binding to the human estrogen receptor, estradiol is the principal endogenous phenolic steroid estrogen. Estradiol is both metabolized reversibly and irreversibly. In the reversible metabolism, estradiol is transformed to estrone and estrone sulphate, meanwhile in the irreversible metabolism, estradiol is transformed to cathecol estrogens or estriol. These metabolites are mostly conjugated with glucuronides and, to a smaller extent, sulfates and excreted in the urine. A minor amount of the estrogens are excreted via feces as un-conjugated metabolites [49, 50].

Blocking the oxidation to estrone by, for instance, introducing an ethinyl group in position 17α or 17β of estradiol leads to much more stable products, which remain longer in the body. The consequence of this increased stability is that the so-formed synthetic steroid ethinylestradiol is excreted up to 80% unchanged in its conjugated form [51].

The human daily excretion of estradiol, estrone, and estriol vary from men (1.6, 3.9, 1.5 μg) to women (3.5, 8, 4.8 μg) maintaining similar proportions with estrone being the most abundant estrogen [5]. Pregnant women show a different profile with higher levels of estradiol and estrone by a factor of ten, and estriol daily excretion at 6000 μg. Women taking contraceptives based on ethinylestradiol excrete 35 μg of this synthetic estrogen daily [52].

In addition to the natural endogenous estrogens discussed above, other estrogens have to be taken into account, such as natural and/or synthetic estrogens administered as medicine. One of the main applications of estrogens is in contraceptives. The estrogen content in birth control pills is usually in the range of 20 to 50 μg daily [53]. Besides contraception, the uses of estrogens can largely be put into three main groups: the management of the menopausal and postmenopausal syndrome (its widest use); physiological replacement therapy in deficiency states; and the treatment of prostatic cancer in men and of breast cancer in postmenopausal women.

The main sources of estrogens to WWTPs are therefore from the natural production of estrogens by humans, from hormone and estrogen replacement therapies and the intake of hormone contraceptives containing ethinylestradiol.

3.2 Occurrence in Wastewater

The occurrence and environmental fate of estrogens have been reviewed in several articles [52, 54, 55]. The analysis of estrogens in wastewater has been discussed by Lopez de Alda et al. [56].

Estrogens are mainly excreted as their less active sulfate, glucuronide and sulfo-glucuronide conjugates [57]. However, in raw sewage and sewage-treatment plants (WWTPs), as well as in the environment, these conjugates may suffer deconjugation and act as precursors of the corresponding free steroids [58–61]. Thus, an appropriate evaluation of their occurrence and impact requires the analysis of both free and conjugated estrogens.

Most of the studies dealing with the investigation of estrogens in wastewaters have been performed in WWTPs receiving urban/domestic discharges and concentrations reported have been most usually in the ng/L range. Estradiol (E2) and estrone (E1) have been the free estrogens most frequently found, whereas estriol (E3) has been studied and detected only sporadically. However, E3 concentrations, when detected, have been usually higher than those of E2 and E1. In general, estrogens concentrations decrease in the order E3 > E1 > E2 (see Table 2 for examples). Thorough revision of all data available situates mean and median concentrations in the range of 9 to 20 ng/L for E2, 20 to 55 ng/L for E1 and 45 to 75 ng/L for E3 [58, 62–79].

The most studied synthetic estrogen, ethinylestradiol (EE2), has been either not detected [65, 67, 68] or detected at concentrations in general much lower than the other estrogens [58, 66, 77] (see Table 2). Levels higher than 100 ng/L have been only occasionally reported (e.g., 155 ng/L [63] and 138 ng/L [75]).

High levels of E1, E2, and E3 have also been reported by a few authors, e.g., 2100 ng/L of E2 [62], 200, 400, and 670 ng/L of E1 [62, 70, 79, 80] and 250 and 660 ng/L of E3 [79, 80].

Table 2 Levels of free estrogens in wastewater reported in some selected studies. Values are given as minimum–maximum (average or median) concentrations in ng L^{-1}

Estradiol	Estrone	Estriol	Ethinylestradiol	Refs.
3–22 (9)	8–52 (16)	n.a.	n.a.	[69]
10–31 (25)	16–60 (35)	23–48 (31)	n.d.	[68]
4.7–25 (12)	25–132 (52)	24–188 (80)	0.4–13 (3)	[58]
n.d.–21 (5.7)	10–57 (24)	27–220 (110)	n.d.	[67]
n.d.–234 (89)	9.4–232 (108)	n.d.–108 (23)	2.4–138 (57)	[75]

n.d. not detected;
n.a. not analysed

In general, it appears that the concentration of the un-conjugated estrogens in wastewater reflects roughly their excretion by the human body, where the high levels of estriol originate from pregnant women. This relation, however, is not found in influent wastewaters from WWTPs receiving industrial, or mainly industrial, wastes. In these cases, either estrone is the only estrogen detected [65] or the estrone concentration is significantly higher than that of estradiol and estriol [75].

The concentration of estrogens in wastewater entering WWTPs, together with other relevant data form the WWTP, such as influent flow-rate and the population served, has been used by some authors to calculate the loads of compounds (g/day) entering WWTPs. In a study dealing with the removal of pharmaceuticals, the calculated loads (mg/day/100 inhabitants) of estradiol (from not detected to 4), estrone (from not detected to 28) and ethinylestradiol (not detected) in six WWTPs were far below those of most of the other pharmaceuticals investigated [81]. Small loads of estrogens were also calculated by Ternes et al. [82] in a study performed in Germany (1 g/day E1, 0.5 g/day E2), and Brazil (5 g/day E1, 2.5 g/day E2).

In contrast to free estrogens, conjugated estrogen derivatives have been included only in a few studies [64, 65, 67, 74]. Mostly sulphates and glucuronides of E1, E2, and E3 have been included as target analytes and detected at similar levels as the free estrogens (see Table 3). Derivatives from the chemically more stable synthetic estrogen EE2 were studied by Gomes et al. [65], but no positive samples were found. Komori et al. [67] studied the presence of di-conjugated E2 derivatives and found high levels of the disulfate and moderately high levels of the sulfate-glucuronide derivative (see Table 3).

Although most estrogens are excreted as glucuronides the concentrations found at the entrance of WWTPs do not reflect this fact. Glucuronides levels are usually low; sulfates dominate the load of estrogens [74]. D'Azcenzo et al. [64] compared the amount of glucuronides and sulfates detected in female urine, a septic tank from a condominium and the entrance of a WWTP and found a higher percentage of sulfates (60%) at the entrance of the WWTP

Table 3 Levels (ng L^{-1}) of conjugated estrogen derivatives detected in waste water

Refs.	E1-3S	E2-S	E3-S	EE2-S	E1-G	E2-G	E2-2G	E3-G	EE2-G	E2-SG	E2-SS
[65]	10–14	n.a.	n.a.	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.a.	n.a.
[74]	34	3.2	n.a.	n.a.	0.4	0.3	n.a.	n.a.	n.a.	n.a.	n.a.
[64]	27	9	47	n.a.	10	n.d.	9	39	n.a.	n.a.	n.a.
[67]	42	110	22	n.a.	11	18	n.a.	22	n.a.	5.5	77

S, sulphate;
G, glucuronide;
n.a., not analysed;
n.d., not detected

than in the septic tank (55%) and the female urine (22%), suggesting that glucuronides might be de-conjugated in the sewer moiety and reach the WWTP at lower levels. In contrast, sulfates appear to be more stable than glucuronides, probably because bacterial sulfatases are present at lower concentrations than glucuronidases and/or because they have low affinity towards steroid sulfates. One example presented by Huang et al. [83] showed that sulfatases enzymes convert only 30% of E2 sulfate into E2.

In conclusion, the levels of estrogens in wastewater are occasionally very high (>100 ng/L), although in average values are usually below 100 ng/L. The calculated loads of estrogens entering the WWTPs are relatively low compared to those of pharmaceutical residues. However, there is no sufficient data on the concentration of the conjugated derivatives and their loads. Their de-conjugation can pose a problem if elimination is not complete.

4 Drugs of Abuse

According to the World Drug Report 2007, about 200 million people use illicit drugs each year globally. Drugs of abuse (DAs) consumption seems now to be stabilized after the increasing trends observed over a decade [84, 85]. Similar to PhACs, these substances are considered to be "pseudo-persistent" in the environment, thus they have become a group of emerging environmental contaminants of interest. DAs reach aquatic systems mainly through sewage water. After drug ingestion, diverse proportions of the parent compound, conjugated forms and metabolites are excreted via urine and flushed towards municipal WWTPs. Some of them may not be efficiently or completely removed at WWTPs and therefore they will be released into the environment via WWTP effluents. In addition to WWTPs discharges, direct disposal into the environment is to a lesser extent another pathway to the aquatic media.

The toxicological or cumulative effect of these substances on the ecosystem has not yet been studied. These compounds have specific physiologic and psychological effects in humans at low-concentration doses (mg or even μg in the case of lysergic acid diethylamide), thus the evaluation of the exposure of the wildlife to the bioactive molecules may be of interest, according to their occurrence in the environment. Fate and transport in aquatic environments is also not known. Most of them are polar compounds that will be concentrated in aqueous environmental matrices; however, some of them, such as cannabinoids, are likely to bioaccumulate in organisms or concentrate in sediments due to their physico-chemical properties (octanol–water partition coefficient, solubility...). A study of the distribution of these compounds in the different environmental compartments may also be a matter of scientific interest.

Since 2004, several authors have developed analytical methodologies based on liquid chromatography and tandem mass spectrometry (LC-MS/MS) detection to evaluate the occurrence of drugs of abuse in sewage and natural waters [86–92]. The target drugs of abuse and metabolites studied so far belong to five different classes: cocainics, amphetamine-like compounds, opiates, cannabinoids, and lysergics. Although a lack of data on drugs of abuse residues in environmental waters is still remarkable, mean values of these substances reported so far in the peer-reviewed literature are summarized in Table 1. The table gathers levels of common drugs of abuse and their metabolites detected in influent waters collected at different European WWTPs located in Spain [86, 92], Ireland [88], Italy [87, 89], Switzerland [87] and Germany [90].

The ubiquity of the different target compounds is directly related to local patterns of drug abuse. The highest loads, thus the highest consumption, are usually reported for two cocainic compounds, namely, cocaine and its main metabolite benzoylecgonine (BE), that are commonly detected at the high $ng\,L^{-1}$ or even the $\mu g\,L^{-1}$ level. The highest concentrations have been found in influent waters collected at a WWTP located in Barcelona, where BE, an inactive metabolite of cocaine with a relatively long half-life, was present at a mean concentration of $4226\,ng\,L^{-1}$ [92]. Cocaethylene (CE), which is a transesterification product of cocaine formed when cocaine is consumed together with ethanol, has not been detected at high levels; thus either this practice is rather limited or, what is more likely, CE transforms rapidly into metabolites not studied yet in WWTPs, such as norcocaethylene and ecgonine ethyl ester. Other cocaine metabolites, norcocaine and norbenzoylecgonine, have been studied at two WWTPs in Italy but their levels did not surpass $40\,ng\,L^{-1}$.

From the studied opiates, only morphine has been found in some WWTPs at high $ng\,L^{-1}$ levels, resulting probably from its medical applications. Although morphine is excreted in urine mainly as glucuronide metabolites, cleavage of the conjugated molecules in wastewater is likely to occur in the

light of the low levels found for morphine-3β-d-glucuronide (the only conjugated compound studied) in comparison with those usually detected for morphine [87]. Heroine has been either not detected or detected at very low concentrations due to its low consumption and its also rapid hydrolysis to morphine and 6-acetylmorphine (heroine is quite unstable in blood serum) [93]. The results of the study done in WWTPs located in Italy and Switzerland [87] indicate that methadone, that is a long-acting opioid agonist used for treating acute and chronic pain and for preventing opiate withdrawal, is commonly present at lower levels than its pharmacologic inactive metabolite 2-ethylidine-1,5-dimethyl-3,3-diphenylpyrrolidine perchlorate (EDDP); both compounds were found in both areas at ng L^{-1}.

Concerning lysergic acid diethylamide (LSD) and its metabolites nor-LSD and nor-iso LSD (nor-LSD) and 2-oxo-3-hydroxy-LSD (O-H-LSD), absence or very low concentrations have been reported in influent samples. These results are in line with the very low doses of LSD needed to produce an effect compared to those needed in the case of other drugs (μg vs. mg), as LSD is the most potent psychoactive drug known so far [93].

The most abundant amphetamine-like compound detected in influent sewage waters is the phenylethylamine ephedrine. Besides a recreational and illicit use, this drug presents medical applications as topical decongestant and bronchodilator in the treatment of asthma and in the reversal of hypotension states. The so-called "designer drugs" 3,4-methylenedioxymetamphetamine hydrochloride (MDMA or "ecstasy"), methylenedioxyethylamphetamine (MDE, MDEA or "Eve") and 3,4-methylenedioxyamphetamine (MDA or "Love pills", and metabolite of both MDE and MDMA), have been detected frequently at the ng L^{-1} level in the different studied WWTPs. As shown in Table 4, amphetamine and methamphetamine are usually present in this type of matrix at lower concentrations than MDMA.

The presence of Δ^9-tetrahydrocannabinol (THC), which is the most psychologically active constituent of Cannabis (the most widely used illicit drug), in influent sewage waters has been observed insignificant as compared to that of its metabolites since THC is extensively metabolized before excretion. 11-nor-9 carboxy THC (nor-THC) is the major THC urinary metabolite and 11-hydroxy-THC (OH-THC) is the main psychoactive metabolite in the body. Thus, monitoring of these metabolites seems to be more appropriate to study the occurrence of cannabinoids in waters.

Measured values of DAs in sewage waters provide real-time data to estimate drug abuse at the community level. This strategy was first proposed by Daughton in 2001 [94] and implemented 4 years later by Zucatto et al. [89] to estimate cocaine abuse in the north of Italy. Such estimations, obtained in a fairly cheap and anonymous way (avoiding potential privacy conflicts), allow the immediate adoption of appropriate measures by the responsible authorities to fight drug abuse by the population. Efficiency of removal of DAs in WWTPs is largely unknown and should be addressed in order to control their

Table 4 Occurrence of drugs of abuse residues in WWTPs influents

Compound	Concentration (ng L^{-1})	Refs.
Cocainics		
Cocaine	225[a], 79[b]	[86]
	(421.4±83.3)[b], (218.4±58.4)[b]	[87]
	(489±117)[b]	[88]
	42–120; 80.25[b]	[89]
	(860.9±213.6)[b]; 502.3[b]	[92]
Norcocaine	(13.7±5.3)[b]; (4.3±0.9)[b]	[87]
Benzoylecgonine	2307[a], 810[b]	[86]
	(1132.1±197.2)[b], (547.4±169.4)[b]	[87]
	(290±11)[b]	[88]
	390–750; 550[b]	[89]
	78	[90]
	(4225.7±1142.8)[b]; 1456.7[b]	[92]
Norbenzoylecgonine	(36.6±7.8)[b], (18.8±5.6)[b]	[87]
Cocaethylene	(11.5±5.1)[b], (5.9±2.6)[b]	[87]
	(77.5±33.2)[b], (78.5)[b]	[92]
	n.d.	[88]
Opiates		
Heroine	n.d., 2.4[b]	[92]
Morphine	(83.3±11.8)[b], (204.4±49.9)[b]	[87]
	n.d	[88]
	820[a]; 310[c]	[90]
	(162.9±20.0)[b], 68.1[b]	[92]
6 Acetyl morphine	(11.8±8.5)[b], (10.4±4.8)[b]	[87]
	(12.8±3.1)[b], 8.4[b]	[92]
Morphine-3β-d-glucuronide	(2.5±7.1)[b], (18.1±30)[b]	[87]
Methadone	(11.6±1.7)[b], (49.7±9.6)[b]	[87]
	n.d.	[88]
EDDP	(19.8±3.1)[b], (91.3±19.2)[b]	[87]
	n.d.	[88]
Amphetamine-like compounds		
Amphetamine	15[a]; 15[b]	[86]
	(14.7±10.6)[b]; < LOQ	[87]
	(41.1±9.1)[b]; 20.8[b]	[92]
Methamphetamine	(16.2±7.1)[b]; < LOQ	[87]
	(18.2±5.8)[b]; 4.8[b]	[92]
	n.d.	[86]
MDMA	91[a]; 49[b]	[86]
	(14.2±14.5)[b], (13.6±12.6)[b]	[87]
	(133.6±29.8)[b], (135.13)[b]	[92]
	n.d.	[88]

Table 4 (continued)

Compound	Concentration (ng L^{-1})	Refs.
MDEA	27[a]; 28[b]	[86]
	(1.5 ± 3.8)[b], < LOQ	[87]
MDA	(4.6 ± 7.3)[b], < LOQ	[87]
Ephedrine	(591.9 ± 124.5)[b], 399.3[b]	[92]
LSD and its metabolites		
LSD	(2.8 ± 1.2)[b], 2.9[b]	[92]
	n.d.	[86]
	n.d.	[88]
2-oxo-3-hydroxy-LSD	(5.6 ± 12.1)[b], 3.4[b]	[92]
Nor-LSD & nor-iso LSD	(4.3 ± 1.8)[b], 13.5[b]	[92]
Cannabinoids		
THC	nd; 14.24[b]	[92]
11-nor-9-carboxy-THC	(62.7 ± 5)[b]; (91.2 ± 24.7)[b]	[87]
	(4.3 ± 7.8)[b]; 21.03[b]	[92]
11-hydroxy-THC	(8.4 ± 2.1)[b]; 46.3[b]	[92]

[a] maximum concentration,
[b] mean,
[c] median

release to the environment and avoid potential adverse effects in the aquatic ecosystem.

5 Surfactants (Alkylphenol Ethoxylates and Related Compounds)

Surfactants are produced in huge amounts and used in households as well as in industrial cleansing processes and as such they make up one of the most relevant organic pollutants of anthropogenic origin with the high potential to enter the environment. After use, detergents are usually discarded down the drain into sewer systems and afterwards treated in WWTP where they are completely or partially removed by a combination of sorption and biodegradation.

Among various classes of non-ionic, anionic, and cationic surfactants, alkylphenol ethoxylates (APEOs) are the group that raised the most concern. APEOs are effective nonionic surfactants, widely used as industrial cleaning agents and wherever their interfacial effects of detergency, (de)foaming, (de)emulsification, dispersion or solubilization can enhance products or process performance. Although parent APEOs are not classified as highly toxic

substances (EC_{50}, 48 h, *Daphnia magna* 1.5 mg L^{-1}) their environmental acceptability is strongly disputed because of estrogenic metabolic products (alkylphenols (APs) and carboxylic derivatives (APECs)) generated during wastewater treatment. Because of these findings, APEOs are banned or restricted in Europe. Throughout northern Europe (Scandinavia, UK, and Germany) a voluntary ban on APEO use in household cleaning products began in 1995 and restrictions on industrial cleaning applications in 2000 [95]. This resulted in a significant reduction of APEO concentrations found. For example, in five Norwegian WWTP nonylphenol (NP) was found in the range of 0.2–7 $\mu g\,L^{-1}$ in the effluent samples in 2002, while concentrations below the detection limit (2 ng L^{-1}) were found in the 2004 samples [96], which is attributed to new restrictions implemented in 2002. Similarly, the NP concentrations in digested sewage sludge in Switzerland were around 1.3 g/kg dry sludge before the ban of NP surfactants in laundry detergents in 1986. In the 1990s, the NP concentrations in sludge ranged from 0.1 to 0.2 mg/kg dry sludge [97]. In Catalonia (Spain), typical levels of NP measured in WWTPs in 1998 and 1999 ranged from 100 to 200 $\mu g\,L^{-1}$ in influents, while 2002–2003 data show almost a 10-fold decrease (Fig. 4), which suggests a gradual withdraw and replacement of NPEOs by Spanish tanneries and textile industry [98].

However, mainly because of lower production costs, APEOs are still being used in substantial amounts in institutional and industrial applications. Hence information about the total concentrations of APEOs and their degradation products in environmental matrices is essential in assessing the environmental impact of these compounds.

Several extensive monitoring programs were conducted with the objective of determining the concentrations of APEO and their degradation products in raw and treated wastewaters. The concentrations of NPEOs (Table 5) in WWTP influents varies from less than 30 to 1035 $\mu g\,L^{-1}$. In industrial wastewaters (especially from tannery, textile, pulp, and paper industry) much higher values, up to 22 500 $\mu g\,L^{-1}$, are detected. Octylphenol ethoxylates (OPEOs) typically comprised 5–15% of total APEOs in WWTP influents, which is congruent with their lower commercial use. Concentrations found in WWTP effluents rarely exceeded 100 $\mu g\,L^{-1}$, corresponding to an elimination of the parent compound ranging from 80–98%.

However, their removal led to the formation of transformation products that are much more resistant to further microbial degradation. Acidic and neutral degradation products of NPEOs have been found to be rather resistant to further degradation, being NP the most recalcitrant intermediate. NPEO metabolites, NP and NPECs are already detected in WWTP influents, due to in-sewer degradation, in concentrations up to 40 $\mu g\,L^{-1}$. Recently, a comprehensive study in the region of Western Balkan (Bosnia and Herzegovina, Croatia, and Serbia) [22] showed widespread occurrence of surfactant-derived alkylphenolic compounds, although the concentration levels were

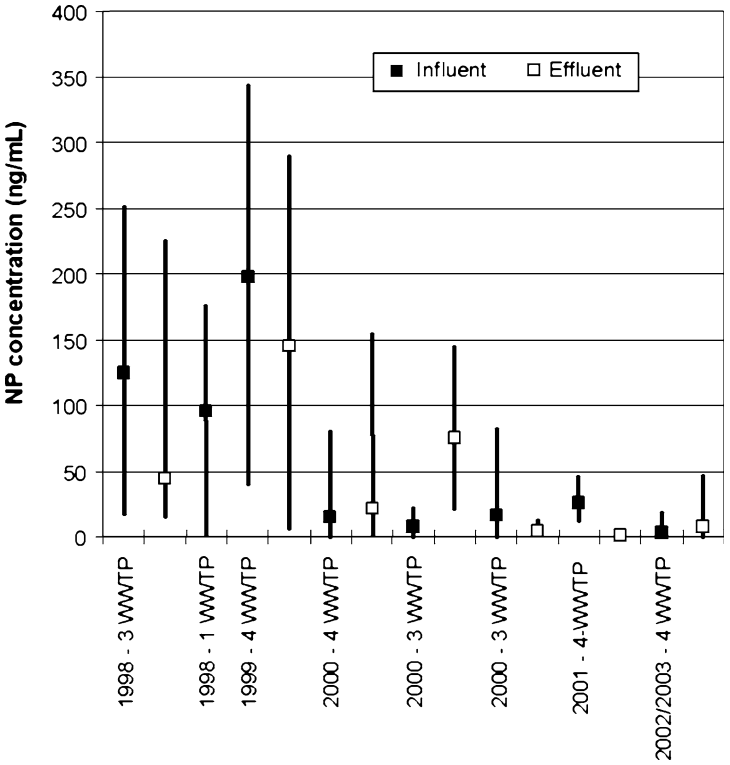


Fig. 4 Concentration of NP in influents and effluents of WWTP in Catalonia (NE Spain) in the period from 1998 to 2003 (Adapted from [98])

relatively low and suggest a decreasing trend in comparison to some previous campaigns conducted in early 1990s [99]. The concentration of NP, as the most toxic and most potent estrogen disrupting compound derived from NPEO surfactants [100], was present in concentrations up to 4.4 $\mu g\,L^{-1}$ with an average value of 1.7 $\mu g\,L^{-1}$. It is interesting to mention that Croatia was one of the first countries that introduced water-quality criteria for NP with a maximum permissible concentration in ambient water of 1 $\mu g\,L^{-1}$ [101], 15 years before it was accepted as a priority pollutant in the EU Water Framework Directive. Besides NP, all municipal wastewaters contained measurable levels of other metabolites derived from NPEO surfactants, in particular NPEC. The composition of alkylphenolic compounds was highly variable and revealed a strong impact of various biotransformation and physico-chemical processes on the distribution of individual alkylphenolic compounds in various types of wastewater samples. The most abundant alkylphenolic species in non-treated wastewaters was NP, while NPEC were the dominant species in biologically treated effluents, which is in agreement with earlier reports on this subject [102].

Table 5 Concentration ranges of alkylphenolic surfactants and their metabolites in raw wastewater entering WWTP

Compounds	Country	Concentration ($\mu g\,L^{-1}$)	Refs.
NPEO	Germany	120–270	[137]
	Austria	2.6–35 (NP_1EO)	[138]
		1.2–5.8 (NP_2EO)	
	Italy	29–145	[139]
		127–221	[140]
	Spain	27–880 (2120)[a]	[141–143]
	Switzerland	96–430	[144, 145]
	The Netherlands	< 0.1–125	[146]
		50–22500[a]	
	Croatia	5–392	[22]
NPEC	Spain	< 0.2–14[a]	[147]
		< 0.4–219	[141, 143]
	Croatia	< 0.001–3.20 (NPE_1C)	[22]
		< 0.001–4.37 (NPE_2C)	
NP	Belgium	< 0.4–219[b]	[148]
	Italy	2–40	[149]
	Spain	< 0.5–22	[141, 147]
		17–251[a]	[143]
	The Netherlands	< lod-19 (40)[a]	[146]
	Croatia	0.460–4.40	[22]
	Norway	< 0.002–5.2	[96]
	Austria	1.05–8.6	[138]

[a] WWTP receiving high percentage of industrial wastewater
[b] effluent of a textile plant

Octylphenolic analogues of NPEOs and their metabolites represented only a small percentage of the total alkylphenolic compounds in all analyzed samples, typically less than 10%. This is important for the assessment of the endocrine disrupting potential associated with APEO surfactants and their metabolites, because OP is an endocrine disrupting compound (EDC) four times more potent than NP [100].

6 Perfluorinated Compounds

Perfluorinated compounds (PFCs) have been manufactured for more than 50 years, and released into the environment following production and use. As a result, PFCs are now acknowledged to be widespread environmental contaminants. PFCs repel both water and oil and these compounds are therefore

ideal chemicals for surface treatments. These compounds have been used for many industrial applications such as stain repellents (such as Teflon), textile, paints, waxes, polishes, electronics, adhesives, and food packaging.

PFCs are both hydrophobic and lipophobic, and are highly stable in the environment. Many of the degradation products of PFCs have been found in the environment throughout the world, because of the strong carbon–fluorine (C–F) bond associated with FASs. In addition, the most important PFC: perfluorooctane sulphonate (PFOS) and perfluoro carboxylic acids (PFCAs) are also stable degradation products/metabolites of neutral PFC. These precursor compounds are more volatile and therefore more likely to undergo long-range atmospheric transport, with sufficient atmospheric lifetimes to reach remote locations, where they can break down.

Possible precursor compounds for PFCAs and PFOS are fluorotelomer alcohols (FTOHs). Fluorotelomeralcohols are manufactured as a raw material used in the synthesis of fluorotelomer-based surfactants and polymeric products. The manufacture of FTOHs usually results in a mixture containing six to 12 fluorinated carbon congeners, the 8 : 2 FTOH being the dominant one. Release of the volatile FTOH may occur all along the supply chain from production application.

PFOS and PFOA are environmentally persistent substances that have been detected worldwide in human blood, water, soils, sediments, air, and biota samples [103].

PFCs are currently receiving great attention because of their persistence [104, 105]], bioaccumulation [106], and potential health concerns including toxicity [107] and cancer promotion [108], and they are now included in different health programs in EEUU to provide a better assessment of the distribution, toxicity, and persistence of these compounds in humans [109]. Research questions include understanding the sources of perfluorinated compounds and their environmental fate and transport.

In the EU, there is currently no legislation on the use of PFCs associated with their (potential) environmental and/or human health effects. It should, however, be noted that some legislation which generally applies to the release of substances to the environment may be relevant to the release of PFOS. This is the case with the IPPC Directive 96/61/EC concerning integrated pollution prevention and control, which includes fluorine and its compounds in the "indicative list of the main polluting substances to be taken into account if they are relevant for fixing emission limit values" (Annex III to the Directive) [110].

Recent studies have attempted to explain the occurrence of PFOA in the Arctic environment by oceanic transport as a result of the manufacture and use of PFOA [104, 111, 112]. Armitage et al. assumed emissions via waste water treatment plants effluents and their predictions have indicated PFOA concentrations in the Northern Polar Zone (equivalent to the Arctic Ocean) would increase until about 2030 and then gradually decline as ocean concentrations adjust to lower emission rates.

Table 6 Concentrations ($ng\,L^{-1}$) of perfluorinated compounds found in wastewaters and different environmental waters

Type of water	Country and site	PFOS	PFOA	PFHpA	PFNA	PFDA	Refs.
Wastewater							
Effluent	Austria	4.5–20	10–21	2.5–4.6	0–2	0–2	[150]
Effluent	EEUU (New York)	3–68	58–1050		0–376	0–47	[114]
Effluent	EEUU (Kentucky)	8–993	8.3–334	–	0–15.7	0–201	[115]
Effluent	EEUU (Georgia)	0–70	7–227	–	0–54	0–86	[115]
River							
Dalälven	Sweden	–	< 0.97	0.36	< 0.14	–	[151]
Vindelälven	Sweden	–	< 0.65	0.2	0.22	–	[151]
Elbe	Germany	–	7.6	2.7	0.27	–	[151]
Oder	Poland	–	3.8	0.73	0.73	–	[151]
Vistula	Poland	–	3.0	0.48	0.36	–	[151]
Po	Italy	–	200	6.6	1.46	–	[151]
Danuve	Romania/ Ucrania	–	16.4	0.95	0.27	–	[151]
Daugava	Letonia	–	< 2.2	0.86	0.36	–	[151]
Seine	France	–	8.9	3.7	1.26	–	[151]
Loire	France	–	3.4	0.90	0.43	–	[151]
Thames	UK	–	23	4.1	0.79	–	[151]
Rhine	Germany	–	12.3	3.3	1.50	–	[151]
Guadalquivir	Spain	–	4.6	1.58	1.02	–	[151]
Rhine	Germany (Breisach)	26	2	–	–	–	[120]
Rhine	Germany (Mainz)	12	3	–	–	–	[120]
Rhine	Germany (Ludwigshafen)	5	2	–	–	–	[120]
Ruhr	Germany (Duisburg)	5	48	–	–	–	[120]
Ruhr	Germany (Schwerte)	14	177	–	–	–	[120]
Elpe	Germany (Bestwig)	–	1168	–	–	–	[120]
Moehne	Germany (Heidelberg)	193	3640	148	–	–	[120]
Tenjin	Japan	4.7	39	–	–	–	[152]
Katsura	Japan	< 5.2	7.9	–	–	–	[152]
Lake							
Shihwa	Korea	89.11	19.22	2.50	3.26	1.98	[153]
Maggiore	Italy	7.8	2.4	2.4	0.6	3.7	[153]

Table 6 (continued)

Type of water	Country and site	PFOS	PFOA	PFHpA	PFNA	PFDA	Refs.
Huron	Canada	4.2	3.6	–	3.6	3.7	[154]
Ontario	Canada	3.9	2.6	–	3.1	–	[154]
Michigan	Canada	3.8	3.4	–	–	–	[154]
Sea							
Harbor	Norway	71–749		3–30	Nd	3–30	[155]
Harbor	Iceland	26–67		6–14	Nd	6–14	[155]
Harbor	Denmark	129–650		5–36	Nd	5–36	[155]
Baltic Sea		232–1149		18–59	Nd	18–59	[155]
North Sea		12–395			Nd	Nd	[156]
Black sea		33–1790		1.0–19	1.4–7.2	1.9–19	[157]

PFCs reach the aquatic environment either through their release into rivers or via wastewater discharge into receiving waters. In Table 6 are summarized occurrence of PFCs reported in different aquatic environments reported in Europe during recent years. Different studies on EEUU reported high concentrations in wastewater, in a recent study by Logannathan et al. [113], PFCs including perfluoroalkyl sulfonates (PFASs; PFOS, PFOSA, PFHxS) and perfluoroalkyl carboxylates (PFACs; PFOA, PFNA, PFDA, PFDoDA, PFUnDA) were investigated in two wastewater treatment plats (WWTPs). The first plant was located in Kentucky and it was representative of a rural area. The second plant was located in Georgia and it was representative of an urban area. PFOS was a major contaminant in samples from Kentucky (8.2–990 ng g^{-1} dry wt. in solid samples and 7.0–149 ng L^{-1} in aqueous samples), followed by PFOA (8.3–219 ng g^{-1} dry wt. in solid samples and 22–334 ng L^{-1} in aqueous samples). PFOA was the predominant contaminant in samples from the urban WWTP (7.0–130 ng g^{-1} dry wt. in solid samples and 1–227 ng L^{-1} in aqueous samples), followed by PFOS (<2.5–77 ng g^{-1} dry wt. in solid samples and 1.8–22 ng L^{-1} in aqueous samples). PFHxS, PFNA, PFDA, and PFOSA were detected in most of the samples, whereas PFUnDA and PFDoDA were detected in very few samples. Concentrations of some PFCs, particularly PFOA, were slightly higher in effluent than in influent, suggesting that biodegradation of some precursors contributes to the increase in PFOA concentrations in wastewater treatment processes. These mass loading values were similar to the values reported by Sinclair and Kannan [114] for New York plants and slightly higher than values reported for a Pacific Northwestern WWTP [115].

In Europe these quantities were even higher. Fifteen effluents from representative industry sectors (printing, electronics, leather, metals, paper, photographic and textiles) from Austria were analysed for PFOS. The PFOS

levels ranged from 0–2.5 μg/L (2.5 μg L^{-1} for leather, 0.120 μg L^{-1} for metal, 0.140–1.2 μg L^{-1} at four paper sites, 1.2 μg L^{-1} for photographic, not found in textiles or electronics) [116]. Concentrations from 0.05 to 8.2 μg L^{-1} were quantifies in the effluents of urban wastewater in Spain [117]. Predominantly, however, they are adsorbed to sewage sludge [118]. The use of sludge for land treatment or its disposal on dump sites leads to a remobilization of these recalcitrant compounds. Also, their polarity and mobility in water and soil allow them to reach the sea or groundwater unaffected.

Several studies have reported the presence of PFCs in surface waters. The occurrence of PFOA and PFOS in several surface waters in Germany was described in 2004 [119]. In summer 2006, the discovery of perfluorinated compounds in waters of the Arnsberg district in the North Rhein Westfalian Sauerland region caused a stir [120]. In this study, 12 different perfluorinated surfactants in German rivers (the Rhine River and its main tributaries, as well as the Moehne River), canals and drinking waters of the Ruhr catchments area are presented. Furthermore, the main contamination source was identified as an agricultural area on the upper reaches of the Moehne River, which is an important tributary of the Ruhr River. PFOA was the compound quantified in higher concentrations, it was found at 519 ng L^{-1} in drinking water and at 4385 ng L^{-1} in surface waters. In this case, the concentrations were higher than the highly polluted Tokyo Bay. In addition, the Möhne Reservoir is a source of drinking water.

In a survey study of contamination of surface and drinking waters around Lake Maggiore in northern Italy, PFCs were investigated in conjunction with other polar anthropogenic environmental pollutants [121].

PFOS and PFOA were identified as major PFCs being PFOS the most abundant one. PFOS was detected in two river water samples (Creek Vevera and River Strona) at concentrations >20 ng L^{-1}, and in the Lake Maggiore at concentrations around 8 ng L^{-1}. In addition, detection of some compounds such as PFOS and PFOA at high concentrations in rain water suggested that atmospheric deposition contributes to the contamination of the lake by these substances.

In this sense, different studies are examining precipitation (rainwater) to test for the atmospheric transformation of FTOHs as a source of PFOA and other perfluorocarboxylic acids (PFCAs) [122, 123].

A number of studies have been carried out in recent years in order to measure the occurrence of PFCs in marine environments. Sea water is a particularly challenging matrix because of the lower levels (pg L^{-1}, part-per-quadrillion) of PFCs in sea water. Yamashita used LC/ESI-MS/MS to carry out a global survey of PFOS, PFOA, PFHS, perfluorobutane sulfonate(PFBS), perfluorononanoic acid (PFNA), and perfluoro octane sulphonamide in sea water samples [124]. This paper also provides a nice summary of PFOS and PFOA measurements in the livers of various marine animals.

7
Industrial Chemicals (Corrosion Inhibitors and Plasticizers)

2-substituted benzothiazoles are a class of high-production-volume chemicals used as anticorrosion additives and biocides as well as vulcanization accelerators and antifungal agents in the paper and tanning industry. Owing to the wide application, they are regularly detected in the municipal wastewaters, being benzothiazole-2-sulfonate, benzothiazole and 2-hydroxybenzothiazole the most abundant, as shown by Kloepfer et al. [125, 126] (Fig. 5). The total concentration of six benzothiazoles in the wastewater of Berlin summed up to 3.4 $\mu g\,L^{-1}$ with the range of the temporal variability of 2–40% within 3 months.

Benzotriazoles are a class of corrosion inhibitors mainly used in deicing fluids and dishwashing agents. The main representatives 1H-benzotriazole and tolyltriazole are frequently found in wastewater of Swiss WWTP (10 and 1.6 $\mu g\,L^{-1}$ on average) [127] and in untreated municipal wastewater in the Berlin region with mean dissolved concentrations of 12 $\mu g\,L^{-1}$ for 1H-benzotriazole and 2.1 $\mu g\,L^{-1}$ and 1.3 $\mu g\,L^{-1}$ for 4- and 5-tolyltriazole, respectively [128].

Phthalate acid esters (PAEs) are a class of chemical compounds widely used in different industrial applications, mainly as plasticizers for polyvinyl chloride (PVC) resins, adhesives and cellulose film coatings and with minor applications in cosmetics, medical products, and insecticide carriers. They comprise a large group of compounds, several of them considered as

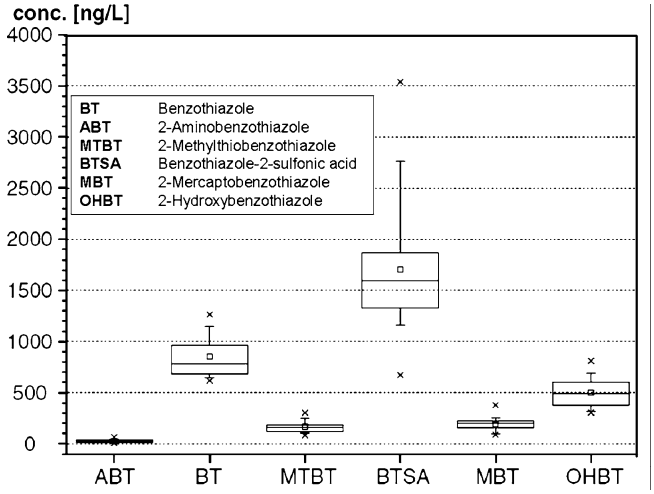


Fig. 5 Concentrations (ng/L) of the benzothiazoles in the municipal wastewater (influent to Berlin-Puhleben WWTP), summary of 20 composite samples (24 h) collected over 3 months. Adapted from [125]

priority pollutants: dimethyl (DMP), diethyl (DEP), dibutyl (DBP), butylbenzyl (BBP), di(2-ethylhexyl) (DEHP) and di-n-octyl phthalate(DnOP). The worldwide production of PAEs approximates 2.7 million metric tons a year [129] and considerable direct (production of plastic materials) and indirect emission via leaching and volatilization from plastic products after their usage, disposal and incineration, explains their ubiquity in the environment.

In all reported studies, DEHP was found to be a predominant PAE due to its high production (nearly 90% of European plasticizer use) and its physico-chemical properties (low solubility and relatively high K_{ow}). Marttineen et al. [130] reported DEHP concentrations of 98–122 $\mu g\,L^{-1}$ in WWTP inlet samples in Finland. Somewhat lower levels were reported by Fauser et al. [131] for inlets to WWTP in Denmark. In five Norwegian WWTP, phthalates (DEHP, BBP, DEP, DMP, and DnOP) were found in raw influent water in concentrations up to 23 $\mu g\,L^{-1}$ with an average of $8.0 \pm 6.4\ \mu g\,L^{-1}$ [96]. However, contrary to other studies, DEHP was the dominant compound in only four out of 10 influent samples, while DEP was the dominating congener in the other six influent samples. The most systematic study on the occurrence of PAEs in the aquatic environment was conducted by Fromme et al. [132]. The levels of DEHP and dibutyl phthalate (DBP) were reported for 116 surface-water samples, 35 sediments from rivers, lakes and channels, 39 sewage effluents and 38 sewage sludges collected in Germany. The phthalate burden was mainly from DEHP, whilst DBP was found in minor concentrations and BBP at concentrations near the detection limit. The concentrations found ranged from 0.3–98 $\mu g\,L^{-1}$ (surface water), 1.7–182 $\mu g\,L^{-1}$ (sewage effluent), 28–154 mg/kg dw (sewage sludge) and 0.2–8.4 mg/kg (sediment). The highest concentrations found were closely related to the input of industrial wastewaters from plastic production and were limited to a few kilometers downstream of the source of contamination.

Bisphenol A (BPA) is used extensively in the production of polycarbonate, epoxy resins, flame-retardants, and many other products. Its global production is more than 1 million tons per year and a significant portion is released into surface waters [133]. In the same study, a high concentration of BPA was confirmed in waste dump water and compost water samples as well as in the liquid manure samples (61–1112 $\mu g\,L^{-1}$). In sewage effluents, concentrations ranged from 18 to 702 $ng\,L^{-1}$ and in surface waters concentrations from 0.5 to 410 $ng\,L^{-1}$.

8 Conclusions

The issue of emerging contaminants is closely tied to analytical capabilities. Increased sensitivity in mass spectrometry, as a result of more efficient ion-

ization techniques and better detectors, has allowed detection of virtually any new and potentially harmful contaminant at a very low level. Consequently, a number of new or previously ignored and/or unrecognized contaminants have bean brought under scrutiny and have been detected in different environmental compartments.

Numerous papers reported on the occurrence of a wide range of emerging contaminants in the aquatic environment, being wastewater and treated wastewater (WWTP effluents) the principle source and route of their entry into the environment. However, additional monitoring studies are needed not only to confirm the presence of emerging substances in the aquatic environment but also to allow the refinement of risk assessments in combination with relevant ecotoxicological test data. In relation to the emergence of new pollutants in the environment, the integration of physical/chemical techniques, effect monitoring techniques (e.g., bioassays, functional monitoring, etc.) and ecological monitoring/assessment (community surveys) techniques play a crucial role. The main drawback of the conventional approach is target-compound monitoring, which is often insufficient to assess the environmental relevance of emerging contaminants. An integrated approach combining analytical chemistry and toxicity identification evaluation (TIE) seems to be a more appropriate way to tackle the complex problems of environmental contamination.

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