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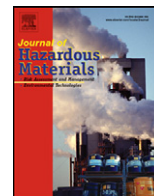
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## Occurrence of organic microcontaminants in the wastewater treatment process. A mini review

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### HIGHLIGHTS

- ▶ Ten-fold increase in the number of papers on PPCPs in WWTPs in ten years.
- ▶ Wastewater analysis can help tackle societal problems.
- ▶ PFCs in WWTPs present negative removal rates.

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### ABSTRACT

A wastewater treatment plant may receive various types of wastewater namely, urban, industrial, agricultural, washout from the streets, wet or/and dry atmospheric deposition. As such, scientists have detected in wastewaters all major categories of pollutants like persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs) and pesticides, but also substances that are widely used as pharmaceuticals and cosmetics, classified as “PPCPs” (pharmaceuticals and personal care products). Finally, the latest categories of compounds to be looked upon in these types of matrices are illicit drugs (drugs of abuse, like cocaine, etc.) and doping substances.

This review article summarises major categories of organic microcontaminants that have been detected in wastewaters and studies their fate during the wastewater treatment process. Occurrence of these compounds in the influents and effluents are reported, as well as percents of removal, mass balances and phase distributions.

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### 1. Introduction

Wastewater treatment plants (WWTPs) were initially designed to remove/decrease conventional pollution parameters (BOD<sub>5</sub>, COD, total suspended solids, etc.) from the wastewater stream, so that the final effluent did not constitute a new source of pollution for the water body receiving it. However, it was soon found out that the wastewater organic load included high levels of a variety of hazardous organic pollutants and thus additional treatment steps and control measures became necessary. The quality of wastewater varies according to what types of influents the WWTP may receive, such as domestic wastewater, dry and wet atmospheric deposition, urban runoff containing traffic related pollution or agri-

cultural runoff and the range of contaminants is even broader when industrial effluents are also included in the input wastewater [1–4].

WWTPs are also called “biological treatments” due to the secondary treatment step, during which the wastewater comes in contact with “activated sludge” and conventional contaminants are removed by means of biological degradation. Whilst this is the case for most of the organic load, for modern organic contaminants such as persistent organic pollutants (POPs), brominated flame retardants (BFRs), fluorinated compounds (PFCs) or pharmaceuticals among others, it has been shown that the biological treatment is not so efficient in their removal. These chemicals are not completely degraded and are either removed by sorption and deposition to the final sludge, by volatilisation, or by discharge onto a surface water body, if they remain in the wastewater effluent stream [7]. This last fraction is the most concerning, since it has been shown to be of relevant toxicity, readily bioavailable to living organisms, able to enter the food chain and hence ultimately exposing humans [5,6]. One of the most important factors that tend to keep organic microcontaminants in the wastewater stream is the dissolved organic carbon

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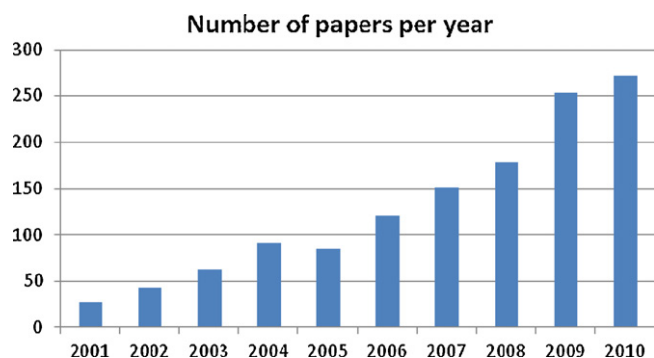


Fig. 1. Number of publications per year studying PPCPs in WWTPs.

Source: SCOPUS™ Database.

(DOC) [7]. In particular, and due to its affinity with organic microcontaminants, DOC acts as an antagonist to sorption on particles and that way keeps organic microcontaminants in the wastewater stream.

In recent years, scientists have been considering as microcontaminants some compounds (or classes of compounds) that until some years ago were deemed safe or broadly supposed to be totally biodegradable, such as personal care products, pharmaceuticals or chemicals like caffeine, benzotriazole, etc. [8–13]. As a result of their broad usage, these microcontaminants have been detected in concentrations up to several  $\mu\text{g/L}$  in WWTP effluents and in surface waters.

Bearing in mind the aforementioned information, the scope of this paper is to present concentration levels, to describe the fate and trends and to discuss the respective implications of new categories of microcontaminants detected in wastewaters/WWTPs. These classes of chemicals include (a) pharmaceuticals and personal care products (b) illicit drugs (c) prohibited doping substances (d) persistent organic pollutants (e) perfluorinated compounds.

## 2. Methodology

Given the large number of studies present in literature, this study goes over some of the most important characteristics that govern the fate of OPs during the wastewater treatment process and presents interesting scientific aspects that derive from the chemical analysis of wastewaters for the aforementioned compounds.

## 3. Discussion

### 3.1. Pharmaceuticals and personal care products (PPCPs)

It has been known for over 20 years that pharmaceuticals and personal care products (PPCPs) enter into the environment through individual human activity and as residues from manufacturing, agribusiness, veterinary use, and hospitals and community use. Individuals may add PPCPs to the environment through waste excretion or bathing, as well as by directly disposing of unused medications into septic tanks, sewers, or trash containers. Their presence has been identified and quantified in WWTP effluents [14], surface waters [15], drinking water [150], groundwater [151], biosolids [152], agricultural manures [153] and biota [154]. With hundreds of different PPCPs in the market (see Table 1), WWTPs represent a key potential point source to the aquatic environment, but at the same time a major opportunity for centralised removal processes. This justifies the increasing number of studies dealing with pharmaceuticals in WWTPs in the last decade (Fig. 1). Summarizing research results in this area is not a simple task, given the large number of PPCPs found in WWTPs. The most common belong to the categories of antibiotics, analgesic

and anti-inflammatory. However, other groups include diuretics, antibiotics, antidiabetics, anticoagulants, psychiatric drugs, lipid regulators, histamine H2 antagonists [14,15], anti-epileptic drugs [15,16], antifungics, antineoplasics, disinfectants, antidepressants, antiseptics, hormones, vasodilators [15], antifungics, vasodilators, barbiturates, anticancers, anticonvulsants [17], anti-hypersensitives and antilipidemics [18]. Recently, a review by Miega et al. [15] presented the concentrations of PPCPs in WWTP influents and effluents, their removal efficiency and their loads to the aquatic environment. Their database covered 184 PPCPs from 117 scientific publications until 2008.

It is difficult to discuss typical concentration levels (Table 1) of PPCPs as these can range from hundreds of  $\text{pg/L}$  up to hundreds of  $\mu\text{g/L}$  [13,15,19–25], depending on the target PPCP and the type of wastewater. Other important factors that play a role in the occurring levels are the types of products that can be found in the pharmaceutical market in each country, or the possibility in some countries to purchase medicines without a medical prescription [15]. As a matter of fact, reported average influent concentrations ranging between 0.1  $\text{ng/L}$  for hormones and 34  $\mu\text{g/L}$  for naproxen, whilst naproxen in a study by Nakada et al. [26] occurred in concentrations of only a few  $\text{ng/L}$ . If specific circumstances occur, the concentration levels of PPCPs in WWTPs can increase even further, to tens of  $\text{mg/L}$ . Such a case was the outbreak of the avian influenza, which led to concentrations of 20  $\text{mg/L}$  for oseltamivir carboxylate in WWTPs with low flow and high population equivalents [20]. In the same study, it is stated that under normal conditions, the majority of PPCPs do not exhibit seasonality, but for some like antibiotics, temporal variation is observed due to increased winter usage.

Individual PPCPs have also distinct chemical and physical properties that suggest potentially different mechanisms and locations for removal/reduction in a WWTP. PPCPs can have octanol–water partition coefficients ( $K_{ow}$ ) or water solubility (WS) values that vary up to 7–8 orders of magnitude. As an example,  $\log K_{ow}$  of iopromide:  $-2.05$  and  $\log K_{ow}$  of mefenamin acid:  $5.12$  [23,27], or WS of roxithromycin:  $0.0189 \text{ mg/mL}$  and WS of diclofenac:  $50 \text{ mg/mL}$ . Many of the PPCPs are ionisable chemicals and it may not be appropriate to assess their lipophilicity based only on the  $K_{ow}$  value. Wells [171,172] addressed the latter issue underlining the value of using a different physical–chemical property which takes into account both hydrophobicity and ionogenicity (especially for the cases where  $\text{p}K_a < \text{pH}$ ). Thus, Wells [171,172] suggested that the pH-dependent *n*-octanol–water partition coefficient  $D_{ow}$  should be used. High  $K_{ow}$  (or  $D_{ow}$ ) values mean that PPCPs tend to sorb onto suspended particles and end up in the sewage sludge, whereas compounds with low  $K_{ow}$  and high WS are expected to remain in the wastewater stream and, if resistant against microbial degradation, to be discharged with the final effluents. Removal rates can also vary largely between various contaminants. For example diclofenac showed low removal rates ( $21.8 \pm 28.5\%$ ), whereas ibuprofen showed a removal of  $99.1 \pm 1.8\%$  [16]. Interestingly, in many cases PPCP loads increase during the wastewater treatment. Thus, diclofenac showed a raise of 105% in a sewage treatment plant of Sweden [28], and up to 300% in a WWTP in Korea [24]. In the latter study, other PPCPs showing a negative removal rate were acetylsalicylic acid, naproxen, ketoprofen and clofibrac acid. A possible explanation for negative removal rates is the influent–effluent mismatching, or the formation of “conjugated compounds” throughout the treatment steps, like for example happens with glucuronic acid [172]. A review by Onesios et al. [17] reported removal rates for a very large number of PPCPs. Authors evidenced that removal rates may vary considerably even for the same PPCP, and inter-comparisons are most of the times problematic, due to different definitions of removal, decrease or elimination rates, but also to different sampling strategies applied (integrated versus grab samples). In addition, the different treatment approaches described in



Table 1 (Continued)

	MW	log <i>K</i> <sub>ow</sub>	p <i>K</i> <sub>a</sub>	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Reference
				900	170		[24]
				315	103		[24]
				21 (11–36)	<10		[27]
Chloramphenicol	323.13	0.92	13.59	14 (<4–319)	<6		[157]
Tetracyclin	444.43	–1.33	3.3	457 (240–790)	282 (50–850)		[15]
Hormones							
Estrone	270.4	3.13	10.34	47 (32–70)	6 (0–24)	87.1	[18]
				67.2 (2.4–670)	20.9 (0.6–95)		[15]
				32.0 ± 6.0			[28]
				150 ± 16			[28]
Estriol	288.4	2.8	10.38	415 (125–802)	0	100	[18]
				115 (14.6–660)	13.1 (0.4–275)		[15]
Estradiol	272.4	4.01	10.46	4 (0–4)	0	100	[18]
				26.5 ± 6.0			[28]
				17.0 ± 5.0			[28]
17a-estradiol				7.4 (1.5–17.2)	0.8 (0.1–3.1)		[15]
17b-estradiol				22.2 (2.5–125)	2.8 (0.3–30)		[15]
Analgesics/ antiinflammatories							
Acetaminophen/ paracetamol	151.17	0.46	9.04	7460 (3540–10,234)	10 (0–27)	99.9	[18]
				13,200 (1340–51,900)	652		[23]
				23,600 (804–85,200)	ND		[23]
				25,500 (271–63,100)	ND		[23]
				29,100 (40–104,000)	431		[23]
				3410	ND		[24]
				9610	ND		[24]
				10,100	ND		[24]
				62,600	ND		[24]
				48,100	ND		[24]
				9500	ND		[24]
				5950	ND		[24]
				7010	ND		[24]
				3130	ND		[24]
				8270	ND		[24]
				4190	6760		[24]
					293		[156]
				211,380 (68,107–482,687)	11,733 (1826–24,525)		[157]
				80,000 (5530–292,000)			[15]
				80,000 (37,000–130,000)	<50		[27]
Diclofenac	296.15	0.7	4.2	131 (59–243)	24 (13–49)	81.4	[18]
				69 (26–257)	98 (33–142)		[157]
				1340 (105–4110)	680 (350–1950)		[15]
				237 (94–523)	191 (52–1760)		[23]
				ND	186		[23]
				1920 (28–6880)	161 (46–221)		[23]
				181,000 (160,000–203,000)	7560 (457–19,200)		[23]
				107–981	37–176		[158]
				42	33		[24]
				5	17		[24]
				39	29		[24]
				16	29		[24]
				14	18		[24]
				12	46		[24]
				20	29		[24]
				11	25		[24]
				14	2		[24]
				2	5		[24]
				ND	ND		[24]
					1090		[156]
				859 (50–4200)			[25]
				220 (140–280)	<10		[27]
				700 ± 120			[28]
				380 ± 10			[28]
				210 ± 100			[28]
Ibuprofen	206.23	3.97	4.9	2265 (1599–2853)	40 (15–75)	98.2	[18]
				1681 (968–2986)	263 (131–424)		[157]
				14,600 (170–83,500)	1960 (20–24,600)		[15]
				69,700 (3730–353,000)	4130 (<LOD–26,500)	87	[159]
				84,400 (<LOD–294,000)	6690 (<LOD–40,200)	84	[159]
				105,000 (<LOD–319,000)	1160 (<LOD–55,000)	80	[159]
				115,000 (<LOD–603,000)	76,200 (<LOD–48,200)	87	[159]

Table 1 (Continued)

MW	log $K_{ow}$	pK <sub>a</sub>	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Reference	
			1100	ND		[24]	
			1170	ND		[24]	
			982	ND		[24]	
			852	ND		[24]	
			612	ND		[24]	
			73	ND		[24]	
			1120	ND		[24]	
			1040	ND		[24]	
			1020	ND		[24]	
			ND	ND		[24]	
			213	238		[24]	
				2400		[156]	
			3200 (<LOD–11,900)			[25]	
			11,000 (3900–15,000)	<10		[27]	
			14,300 ± 130			[28]	
			8800 ± 100			[28]	
			10,800 ± 100			[28]	
Ketoprofen	254.29	3.12	4.5	202 (81–286)	12 (0–37)	94.2	[18]
				28 (<4–119)	–		[157]
				1030 (800–5700)	325 (400–1620)		[15]
				1580 (<LOD–5520)	860 (<LOD–2270)	52	[159]
				1740 (<LOD–6470)	800 (<LOD–1950)	56	[159]
				1910 (<LOD–8560)	820 (<LOD–3920)	72	[159]
				2070 (<LOD–5700)	880 (<LOD–2030)	58	[159]
				114	ND		[24]
				83	ND		[24]
				226	35		[24]
				49	41		[24]
				44	ND		[24]
				81	ND		[24]
				50	ND		[24]
				18	ND		[24]
					2980		[156]
				561 (<LOD–1520)			[25]
Naproxen	230.27	3.18	4.2	2584 (1360–5033)	111 (37–166)	95.7	[18]
				838 (400–1457)	370 (234–703)		[157]
				25,400 (1790–611,000)	1890 (170–33,900)		[15]
				3810 (480–12,500)	250 (21–740)		[23]
				3170 (306–6040)	309 (248–370)		[23]
				59,700 (410–206,000)	13,300 (361–39,300)		[23]
				4830 (2020–8500)	2740 (540–5090)	43	[159]
				8070 (2030–52,900)	1640 (220–3520)	71	[159]
				4690 (1630–27,400)	2180 (830–3640)	48	[159]
				4280 (1140–9100)	1670 (290–4280)	60	[159]
				1210	254		[24]
				827	104		[24]
				962	114		[24]
				823	57		[24]
				487	48		[24]
				524	138		[24]
				532	ND		[24]
				451	183		[24]
				565	ND		[24]
				761	ND		[24]
				278	77		[24]
					1740		[156]
				335 (<LOD–1550)			[25]
				20,200 ± 210			[28]
				9300 ± 100			[28]
				6600 ± 110			[28]
Mefenamic acid	241.3	5.12	4.2	121 (55–328)	153 (44–392)	–26.30	[18]
				205 (<20–1269)	61 (<5–222)		[157]
				1730 (136–3200)	1140 (900–2400)		[15]
				1900 (232–8810)	385 (68–1360)		[23]
				ND	167		[23]
				14,200 (329–36,400)	ND		[23]
				119	32		[24]
				52	43		[24]
				192	68		[24]
				42	53		[24]
				127	83		[24]
				121	11		[24]
				92	21		[24]
				55	25		[24]

Table 1 (Continued)

	MW	log $K_{ow}$	pK <sub>a</sub>	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Reference
				61	3		[24]
				23	6		[24]
				53 (<LOD–120)			[25]
Aspirin	180.15	1.19	3.49	664 (485–2042)	27 (<3–85)		[157]
Acetyl salicylic acid	180.15	1.29		5866 (1479–18,479)	164 (<1–497)		[157]
				212,000 (16,000–606,000)	2500 (300–4800)		[15]
				176,000 (3090–1,407,000)	7240 (2340–12,100)		[23]
				313,000 (41,800–1,030,000)	89,500 (1000–193,000)		[23]
				126,000 (1540–384,000)	507 (396–618)		[23]
				551,000 (3850–1,731,000)	25,200 (2830–47,600)		[23]
				2040	ND		[24]
				11,100	9		[24]
				7640	10		[24]
				3160	ND		[24]
				2610	27		[24]
				7600	6		[24]
				3910	10		[24]
				3970	ND		[24]
				11,100	32		[24]
				9780	30		[24]
				2670	78		[24]
Codeine	299.36	1.28	8.21	10,321 (1732–32,295)	5271 (2940–15,593)		[157]
Tramadol	263.37	2.51	9.41	36,750 (8505–89,026)	43,813 (24,132–97,616)		[157]
Dextropropoxyphene		4.18		27.3 (22–33)	52.3 (37–64)		[15]
Antiepileptic Carbamazepine	263.27	2.45	3.19	72 (43–127)	55 (40–74)	23.1	[18]
				1694 (709–2930)	437 ± 117		[160]
				968 (100–1900)	2499 (644–4596)		[157]
				1920 (95–21,600)	674 (150–2300)		[15]
				167 (40–399)	1750 (208–21,000)		[23]
				827 (18–6080)	2430 (128–10,200)		[23]
				10,100 (35–19,100)	3560 (241–14,400)		[23]
				530 (<LOD–3780)	51,700 (61–150,000)		[23]
				470 (<LOD–2100)	580 (<LOD–1180)	11	[159]
				410 (<LOD–1310)	610 (150–1290)	7	[159]
				490 (<LOD–2150)	490 (<LOD–840)	7	[159]
					560 (150–1550)	8	[159]
					(233–1061)		[158]
				258	180		[24]
				327	188		[24]
				481	175		[24]
				214	140		[24]
				290	183		[24]
				450	170		[24]
				311	243		[24]
				338	235		[24]
				105	173		[24]
				103	96		[24]
				207	36		[24]
				419 (120–1550)			[25]
				230 (130–440)	1 (<10–12)		[27]
Gabapentin	171.24	–1.10		15,034 (2059–37,426)	15,747 (3001–42,611)		[157]
Antilipidemic Clofibrac acid	214.5	2.57	3.2	28 (0–65)	2 (0–6)	93.6	[18]
				19 (<1–57)	15 (<1–75)		[157]
				294 (15–651)	150 (42–230)		[15]
				33	8		[24]
				ND	6		[24]
				ND	35		[24]
				55	35		[24]
				ND	4		[24]
					30		[156]
				25.0 ± 3.0			[28]
				12.5 ± 7.0			[28]
				17.0 ± 6.5			[28]
Gemfibrozil	250.34	4.77	4.7	222 (101–318)	17 (9–26)	92.3	[18]
				1630 (700–3000)	564 (60–1340)		[15]
				21	ND		[24]
				14	ND		[24]
					520		[24]
				377 (<LOD–1700)			[25]

Table 1 (Continued)

	MW	log $K_{ow}$	pK <sub>a</sub>	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Reference
Bezafibrate	361.82		14.75	420 (209–1391) 2440 (100–7600) 65 (<LOD–260)	231 (<85–667) 816 (20–4800)	92	[157] [15] [25]
Simvastatin	418.57			115 (<7–798)	5 (<3–20)	38	[157]
Stimulant Caffeine	194.19	−0.07	10.4	2349 (3217–1608) 2400 6170 7310 4860 3270 1950 1920 2500 1160 2190 56,100 80,000 (54,000–120,000)	18 (0–60) 24 ND ND ND ND ND ND ND ND ND ND 17 (<10–50)	98.2	[18] [24] [24] [24] [24] [24] [24] [24] [24] [24] [24] [24] [27]
Nicotine	162.23		3.1		373 (72–1706) 235 (93–755) 430 (76–3857) 213 (75–253) 538 (101–3249)		[161] [161] [161] [161] [161]
Antihypersensitive Atenolol	266.3	0.16	9.6	7801 (5113–11,239) 12,913 (3090–33,106) 30 1880 (<LOD–7560)	2772 (261–5911) 271 ± 91 2870 (1260–7602) 154 (10–380) 1094	64.5	[18] [160] [157] [15] [156] [25]
Metoprolol	267.3	2.15	9.6	4 (2–6) 75 (39–117) 160 953 (<LOD–4680)	3 (3) 274 ± 192 69 (35–130) 338 (10–688) 13	23	[18] [160] [157] [15] [156] [25]
Solatol				221 (<LOD–1080)	274 ± 192		[160] [25]
Acebutolol	336.43				2 ± 2		[160]
Propranolol	259.34			557 (125–1962) 74.7 (50–119)	265 (121–405) 341 (10–615) (16–135)		[157] [15] [158]
Antiseptic (dinfectant) Triclosan	289.6	4.76	7.8	547 (247–785) 380	112 (79–149) 150 (70–430)	99.6	[18] [15]
Diuretics Furosemide	330.74			1476 (836–5111)	1161 (583–1956)		[157]
Antidepressant Amitriptyline	277.40			1249 (341–5143)	197 (53–357)		[157]
Personal care products Galaxolide	258.4	5.9		2510 (790–4443) 1941 9710 (+5090) 16,600 (+10700)	642 (451–1080) 695 32–3750 10–25,947		[15] [162] [163] [161]
Tonalide	258.4	5.7		990 (210–1690) 583 5970 (+3880) 12,500 (+7350)	162 (144–200) 212 24–2670 2.1–2151		[15] [161] [163] [161]
Celestoide	244.4				ND-92		[161]
Benzophenone-1	182.2	3.15		258 (51–700)	12 (<2–38)		[157]
Benzophenone-2				194 (61–403)	4 (<13–13)		[157]
Benzophenone-3				1195 (<104–3975)	22 (<80–223)		[157]
Benzophenone-4				4152 (2218–6084)	3370 (<10–6325)		[157]
Methylparaben	152.2	2.0		11,601 (4550–30 688)	<3–36 (9)		[157]



Table 1 (Continued)

	MW	log $K_{ow}$	pK <sub>a</sub>	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Reference
Ethylparaben	166.2	2.5		2002 (715–3312)	4 (<0.6–43)		[157]
Propylparaben	180.2	2.9		3090 (820–8286)	26 (<1–84)		[157]
Butylparaben	194.2	3.5		723 (274–1595)			[157]
Vasodilator							
Pentoxifyllin	278.31				533 (500–600)		[15]

each study render these comparisons less useful. As a matter of fact, Onesios et al. [17] reported removal rates for diclofenac between 1 and 94%, for a variety of treatment systems, whereas in many studies it was not reported.

The elimination efficiency of PPCPs in WWTPs can be further complicated by biological transformations, mixture effects, hydraulic and temperature variations and the combination of treatment processes. It is however known that this efficiency increases with higher hydraulic retention times (HRT) [155]. In the last few years, the application of more advanced treatment processes such as ozonation, activated carbon, and tight membrane filtration are receiving considerable attention, although studies addressed to a better understanding of removal in conventional treatments (primary, secondary and tertiary) remain active. The use of advanced oxidation technologies increases the formation of intermediate degradation products that may be more toxic than the parental ones. Further analytical and toxicological research studies are needed to increase the knowledge in this area. Lin et al. [29] reported that the combined ozone systems ( $O_3/H_2O_2$ ) contribute to an enhancement in the removal of sulphonamide and macrolides antibiotics. Four antibiotics (sulfamethoxazole, sulfamethoxine, sulfamethazine and trimethoprim) and four non-steroidal anti-inflammatory drugs (acetaminophen, ibuprofen, retoprofen and naproxen) were also successfully removed using extended sludge age biological system [30]. However, the same study showed that the removal efficiency is strongly related to the initial influent concentration of each target compound. The combination of a UV/TiO<sub>2</sub> system was reported to be highly efficient to the complete elimination of naproxen, clofibrac acid and carbamazepine [31] in addition to ofloxacin [32], and a removal efficiency ranging from 12 to 80% was reported for iomeprol [33,34]. Moreover, the use of UV/H<sub>2</sub>O<sub>2</sub> systems in the presence of humic acids resulted in very effective removal of carbamazepine and diclofenac [35] and clofibrac acid [36]. The capacity of granular activated carbon (GAC) in comparison with other adsorbents was tested to remove estrone and 17  $\alpha$ -estradiol [37], showing that the elimination rate increased at pH above 8 and adsorption capacity of GAC decreased by the presence of surfactants or humic acids. Maniero et al. [38] investigated the degradation of natural (17 $\beta$ -estradiol) and synthetic (17 $\alpha$ -ethinylestradiol) estrogens (pure or in the mixture) and the cease of estrogenic activity by the ozonation and  $O_3/H_2O_2$  process at three different pH levels (3, 7 and 11). Both these processes were effective in eradicating the estrogens from aqueous solutions, for all ozone doses and pH values in question. Senta et al. [39] evaluated membrane bioreactors (MBRs), nanofiltration, reverse osmosis and ozonation, as well as their combinations, for the removal of antimicrobials including sulfonamides, fluoroquinolones, macrolides and trimethoprim from a synthetic wastewater which simulated highly contaminated industrial effluents. MBR system was only efficient for the elimination of sulfonamides whereas nanofiltration and reverse osmosis achieved high elimination rates, yet producing a highly contaminated concentrate.

Many studies have also reported the occurrence of PPCPs in sewage sludge. A review by Diaz-Cruz et al. [40] summed up the

occurrence of 12 PPCPs (only 8 at detectable levels), yet with considerably variable concentrations. According to their summary, limits of detection for PPCPs under different techniques can be at the sub- $\mu$ g/kg level, and concentrations of up to 1500  $\mu$ g/kg have been reported (triclosan from a WWTP in Galicia, Spain, [40,41]). Triclosan occurred at even higher levels in the sludge from the major WWTP of Athens, Greece, reaching 1790  $\mu$ g/kg [42]. This compound has a log  $K_{ow}$  of 4.8 and a pK<sub>a</sub> of 7.9, which at wastewater conditions (pH around 7) can be considered a hydrophobic compound prone to sorption onto the sludge. The concentrations of PPCPs detected in sewage sludge reflect their use in the society [40], although the influent wastewater is a better indicator, especially for hydrophilic and water soluble PPCPs that are not likely to be detected in sludge. According to Horsing et al. [43], who studied the sorption of 75 common PPCPs, only 14 were found to have strong affinity with particles/sludge, whereas for 37 of them, more than 80% of their predicted occurrence would be in the liquid phase. In that study, pH was also identified as an important factor for the partition to the sludge. Other parameters affecting the sewage concentration of PPCPs can be the sludge retention time or the biosolids acclimatisation [44,45].

### 3.2. Illicit drugs (IDs)

In the last few years, the scientific community started paying more attention to the occurrence of drugs of abuse or illicit drugs (IDs) in various environmental compartments. The number of studies dealing with IDs in WWTPs is not as large as for PPCPs, but is increasing continuously. Compounds of interest in this category belong to the groups of stimulants, hallucinogens, opioids, dissociative anaesthetics, etc. [46], whilst key target chemicals are cocaine (COC), heroin, nicotine, amphetamine, methamphetamine, opiates or cannabis, among others, and their metabolites, e.g. benzoylecgonine (BE), ecgonine methyl ester, norbenzoylecgonine, norcocaine and cocaethylene [13,46–52]. For compounds like nicotine and caffeine, a study in Spain has shown that average concentrations of 13 and 23  $\mu$ g/L are detected in influent wastewaters, respectively, and that the mean values for effluent wastewaters can be as high 2.7 and 4.4  $\mu$ g/L, respectively. Instead, for the stronger narcotic (COC), the highest concentration observed to date was in the influent of a WWTP in Barcelona (4.7  $\mu$ g/L) [51]. The concentrations of IDs in the influents of WWTPs can reflect both societal habits and the financial situation. As a matter of fact, their levels have been found to increase during weekends [50,53,54], or after the “Street Parade” event in Zurich [55]. MDMA (an amphetamine-type drug) was found to be more abundant on Sundays and Tuesdays, in WWTPs from Paris [50]. Regarding the temporal trends of IDs, the existing dataset is still insufficient for such an assessment. [56]. According to the latter study that took place in Italy, there is a decreasing trend in the consumption of expensive IDs and a simultaneous increase in the less expensive ones.

The important implication of the analysis of IDs in WWTPs is the back estimation of equivalent drug users and consumption. This has been applied by many scientific groups and, recently, a review has been published on this topic [48].

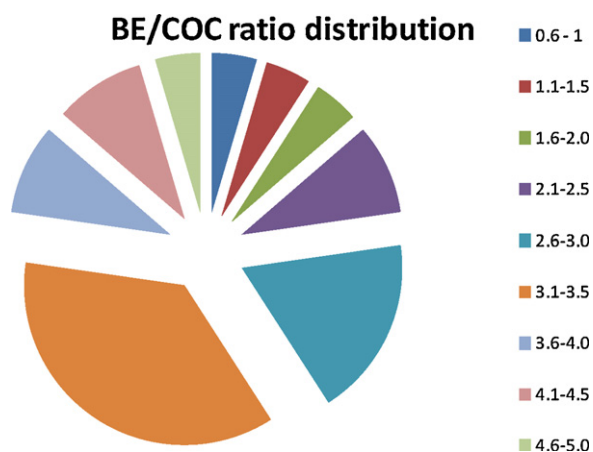
**Table 2**  
Cocaine and benzoylecgonine concentrations in wastewaters (ng/L).

	Cocaine		Benzoylecgonine		Reference
	Influent	Effluent	Influent	Effluent	
WWTPs in UK (7)	70.9	29.2	243.1	115.9	[46]
WWTP Paris 1	4.8–52.6	ND-7	64.0–175.6	15.9–25.4	[50]
WWTP Paris 2	67.2–282	ND-20.7	147.2–849.2	82.0–149.0	
WWTP Paris 3	12.0–53.7	1.2–5.3	136.1–218.0	14.5–36.3	
WWTP Paris 4	32.7–99.2	ND-3.2	129.4–303.1	7.9–18.2	
WWTP Oslo	86 (35–166)		273 (121–669)		[60]
WWTP Geneva	NQ-1928		101–1788		[103]
WWTP Luzern	NQ-297		244–1040		
WWTP Basel	177–262		872–1299		
WWTP Berne	159–336		522–1132		
WWTP Zurich	406–1109		802–2400		
WWTP Back River	2.66 ± 0.005		9.31 ± 0.17		[104]
WWTP, Prison in Catalonia	128 ± 94 (max. 462)		556 ± 291 (max. 1760)		[105]
WWTP Milan	255		712		[54]
WWTP Como	98		380		
WWTP Cagliari	138		316		
WWTP Olbia	131		337		
WWTP Sassari	48		149		
WWTP Nuoro	55		153		
WWTP Chicago	868		1553		
WWTP Villaseca	160–2486	NQ-9	1169–3336	1–42	[53]
WWTP Canada 1	209–823		287–1488		[52]
WWTP Canada 2	475–776		658–2624		
WWTP Canada 3	487–656		588–722		

One of these approaches is the “sewage epidemiology”, which uses wastewater concentrations for the abovementioned purpose. The concept of this tool is to combine the concentrations of COC and its major metabolites with its breakdown pattern. For example, only 1–9% of a COC dose is excreted in urine unchanged, whilst 35–54% and 32–49% is excreted as BE and ecgonine methyl ester, respectively. Norbenzoylecgonine, norcocaine and cocaethylene are minor metabolites and only account for traces of the urinary excretion pattern. In the back-calculations, a mean excretion rate of 45% for BE and of 10% for COC is taken into account, values in very good agreement with the distributions of BE/COC ratios of Fig. 2. The broad ranges for the excretion values of BE (15–55%) and COC (1–15%) can lead to uncertainties in the calculations. Table 2 summarises concentrations of BE and COC in various WWTPs, published the last 3 years. It can be seen that BE is coherently higher than COC with BE/COC ratios ranging from 0.9 to 5.0. However, 36.4% of the

samples exhibits a BE/COC ratio in the range of 3.1–3.5 and a further 18.2% between 3.6 and 4.0 (Fig. 2). According to Karolak et al. [50], BE/COC ratios lower than 5.0 suggest that COC has been discharged in WWTPs without being consumed, thus not metabolised to BE. The first formula, proposed by Zuccato et al. [57], was based on concentrations of BE, the major metabolite of COC, and which is present in wastewater at relatively high levels. From the concentrations of BE (ng/L) and the flow rate (L/day) of the wastewater stream, BE loads (g/day) can be calculated. These loads are then subsequently transformed into consumed COC (g/day) taking into account the molecular mass ratio of COC to BE (1.05) and the mid-range excretion percentage of 45% as BE [58]. This leads to the following equation:

$$\text{COC (g/day)} = \text{concentration BE (ng/L)} \times \text{flow rate (L/day)} \times 2.33$$



**Fig. 2.** Distribution of the BE/COC ratios in influents from WWTPs.

The result is the grams of COC used per day. Then, dividing the grams by the average dose (~100 mg [59]), we can have the number of doses per day and per number of equivalent inhabitants (by the in-flow rate of the WWTP). Most studies that report use of COC through wastewater analysis report consumption in the range of 31–2800 mg/day/1000 inhabitants [50,59–61]. Metcalfe et al. [52] also stated the use of other drugs through similar approaches and found that methamphetamine in Canada can be up to ~60 doses/day/1000 inhabitants.

IDs similarly to PPCPs are not efficiently removed during the wastewater treatment process. Karolak et al. [50] reported removal rates of COC ranging from 89.6 to 97.8% and BE removal rates from 69 to 93%, but MDMA removal rates were much lower and varied between 48.6 and 80.1%. Hummel et al. [62], Bones et al. [49] and Pedrouzo et al. [53] also reported that IDs are only partially removed through the sewage treatment and that further enhancements of the treatment technology are deemed necessary.

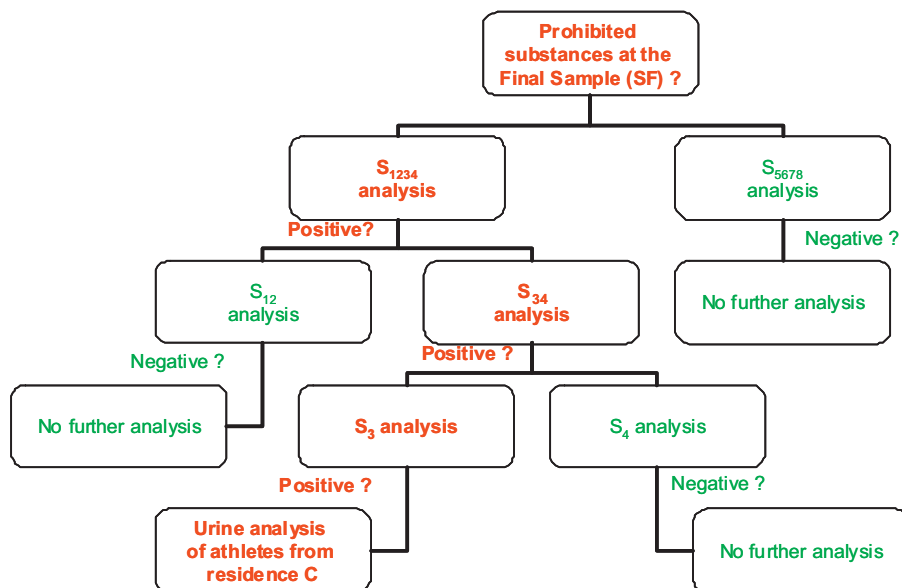


Fig. 3. Analysis strategy proposed by Katsoyiannis and Jones [64].

### 3.3. Prohibited doping substances

In 2010, Schroder et al. [21] published a study which for the first time presented concentrations of prohibited doping substances (steroids,  $\beta$ 2-agonists, stimulants, diuretic agents, and PDE V inhibitors) in the effluents of a sports centre, but also in large municipal WWTPs. Chemicals like testosterone, boldenone, ephedrine or stanozol were studied, and for some of these, the levels in the municipal WWTPs had reached values even in the levels of  $\mu\text{g/L}$  (i.e. salbutamol's maximum concentration was  $5.008 \mu\text{g/L}$ ).

Important implications from this study came from the view point by Katsoyiannis and Jones [63,64], according to which this kind of environmental analysis would be feasible during major athletic events (e.g. the Olympic Games). This way, anti-doping authorities could enhance their targeted testing and be more effective in identifying doped athletes. In light of this strategy, it should be possible to enhance targeted sampling to catch athletes using prohibited substances in main sport events through the analysis of wastewaters from all individual residences. It was suggested that the extensive number of collected samples should be used only as an "archive", leaving the routine analyses for the more centralised samples. Then, in cases of positive results, the archived samples should be analysed in order to backtrack where the breaching of regulations took place, as shown in Fig. 3. Furthermore, Katsoyiannis and Jones [64] suggested that epidemiology approaches similar to those for IDs should be applied to allow sports authorities to understand and tackle the consumption levels of doping substances. These compounds were found by Schroder et al. [21] to be removed at levels up to  $\sim 100\%$  during conventional activated sludge treatment.

### 3.4. Persistent organic pollutants

Persistent organic pollutants (POPs), especially the legacy ones (polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins/furans and organochlorine pesticides) have been studied in detail since the early 1980s [65–71]. It is widely known that legacy POPs in wastewaters originate from a variety of sources and, once in the WWTP, tend to partition mainly on the particulate phase and end up that way in the final sludge. Their fate is essentially governed by the physical–chemical properties, with  $K_{ow}$  playing the most important role [2,3,72–75]. The DOC has also been

shown to be of critical importance, enhancing the percent of POPs subject to advection, rather than sorption on particles [7,76]. For these compounds, modelling studies can be found in literature that have tried to estimate the final effluent, or sludge concentrations of POPs based on the respective influent concentrations [75,77,78], or works where the wastewater toxicity is correlated with POPs concentrations [79].

In the current study, the occurrence and fate of some of the newly introduced POPs to the Stockholm Convention is presented. In particular, flame retardants (FRs) (brominated and organophosphate, Table 3) and fluorinated organic chemicals (Table 4) are discussed.

As far as brominated FRs are concerned, polybrominated diphenyl ethers (PBDEs) are the most studied class and concentrations for  $\Sigma$ PBDEs in wastewaters can vary from few  $\text{ng/L}$  up to tens of  $\mu\text{g/L}$  ( $33 \mu\text{g/L}$  in influents from a WWTP in China [80]). In almost all studies, the range of  $\Sigma$ PBDE concentrations is too large, showing the impact that non-ordinary wastes can have on the load of WWTPs. PBDEs are hydrophobic compounds so they are expected to be removed mainly by sorption on particles and subsequent sedimentation. As can be seen in Table 3, in all studies reporting removal, the rates are higher than  $\sim 70\%$  [80,81]. This results in very high concentrations of BDEs in sewage sludge. The profile and total BDE levels in wastewater or sludge depends highly on whether the deca-BDE (BDE-209) is analysed and taken into account or not. BDE-209 occurs in higher concentrations than the other BDEs, reflecting its widespread usage. As a matter of fact, in Europe, the deca-bromodiphenyl ether mixture (in which the main ingredient is BDE-209) accounted for 75% of the total usage. In a work by De la Torre et al. [82], a typical profile of PBDEs in sludges is characterised by BDE-209, which represents  $77 \pm 11\%$  of the total BDE burden. Based on this and in the fact that BDE-209 comprised 75% of the European market, this result could be a strong evidence that under activated sludge treatment process, there is no substantial debromination of deca-BDE. This is further supported by the results of Peng et al. [80] and Fabrellas et al. (cited in Gevaio et al. [83]), where BDE-209 is up to 100 times higher than the sum of the other BDEs.

Daso et al. [84] reported that the occurrence of BDE-209 in influents of a WWTP in South Africa exhibits seasonality, with particularly low concentrations in warmer periods (April and June) than in cold ones. On the contrary, the levels of BDEs-47 and -99

**Table 3**  
Flame retardants in WWTPs.

Compounds	Country	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Sludge (ng/g dw)	References
PBDEs BB 153	South Africa	369 < $\Sigma$ BDEs < 4370; BBE 153: mean 15.8	90.4 < $\Sigma$ BDEs < 15,100; nd < BB 153 < 18.4	–	13.1 < $\Sigma$ BDEs < 652; nd < BB 153 < 9.97	[84]
PBDEs	USA	Not specified	$\Sigma$ BDEs: 0.004–29.1	–	$\Sigma$ BDEs: 61–1440	[106]
PBDEs	Canada	$\Sigma$ BDEs: 265 $\pm$ 210	$\Sigma$ BDEs: 36 $\pm$ 10	BDEs: 86%	PS: 1626 $\pm$ 576; AS: 2698 $\pm$ 1141	[107]
PBDEs	China	3–7-BDEs: 1545–32,939 deca-BDE: 11.6–2412.6 $\Sigma$ BDEs: 1557–35,350	3–7-BDEs: 0.267–0.689; 10-BDE: 0.6–3.4 $\Sigma$ BDEs: 0.867–4.09	3–7-BDEs: >99%; 10-BDE: >70%	Tri-hepta BDEs: 8.5–96 Deca BDE: 150–22,894 Total BDEs: 158.5–23,856	[80]
PBDEs; BB 153	Australia	$\Sigma$ BDEs: 70	$\Sigma$ BDEs: 0.34	$\Sigma$ BDEs: 99.5%	$\Sigma$ BDEs: 220–460	[108]
PBDEs	Norway	$\Sigma$ BDEs: nd-9.3	$\Sigma$ BDEs nd-0.6	90–99%;	–	[109]
deBDethane, BDE 209	Sweden	deBDethane: 21.5 BDE-209: 200	deBDethane: 0.066; BDE 209: 0.405	deBDethane: 99.7%; BDE 209: 99.8%	deBDethane: 81; BDE 209: 800	[110]
PBDEs	USA	$\Sigma$ BDEs: 4200–4300	$\Sigma$ BDEs: 310–900	$\Sigma$ BDEs: >78.6%	$\Sigma$ BDEs: 1320–3800 ng/L	[111]
OPFRs	Sweden	–	Total FRs: <500–36,000	–	–	[112]
OPFRs	USA	Total FRs: 475–700	Total FRs: 450–700	Residual	Not applicable	[113]
OPFRs	Bosnia-Herzeg, Croatia, Serbia	TCEP: nd-500 TCPP: nd-2500	–	–	–	[114]
OPFRs	Germany	FRs: 81–4000	FRs: 20–3000	FRs: 0–89%	–	[115]
TCPP	Germany	240–1000 (520 $\pm$ 300)	230–610 (380 $\pm$ 170)	0–41%	TCPP: 5100	[87]
TCEP, TCPP	Austria, Belgium, Germany, Spain	FRs: 600	FRs: 200	66.7%	–	[116]
OPFRs	Sweden	Total FRs: 17,000–69,000	Total FRs: 7900–17,000	Total FRs: 23.5–79.7%	Total FRs: 620–6900	[86]
OPFRs	Germany	FRs: 180–61,000	FRs: 27–4700	FRs: 72.2–98.3%	–	[117]
BDEs, PBBs, TBBPA, 2,4,6-Tribromophenol	Sweden	–	–	–	Total BDEs nd-450 Individual BFRs: <0.3–390 TBBPA nd-220 2,4,6-Tribromophenol: nd-0.9 PBBs: nd	[118]
13 BDEs	China	–	$\Sigma$ BDEs: 0.84	–	–	[119]
11 BDEs	Spain	–	–	–	BDEs: nd-1082 $\Sigma$ BDEs: 197–1185	[120]
Tetra-, penta-, hexa-BDEs	UK	$\Sigma$ BDEs: 180	–	–	–	[121]
13 BDEs, HBCD	Switzerland	–	–	–	BDEs: 0.2–617; HBCD: 39–597	[122]
PBDEs	Kuwait	–	–	–	$\Sigma$ BDEs: 5.7–1599	[83]
PBDEs	Canada	–	–	–	BDEs: Raw: 20–650 PS: 10–320 Digested: 10–800	[123]
BDEs 47, 99, 153, 209	Holland	–	–	–	$\Sigma$ BDEs: Influent: 31.5	[124]

Table 3 (Continued)

Compounds	Country	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Sludge (ng/g dw)	References
PBDEs	Holland	BDEs: <0.02–330 ng/g ΣBDEs: <9.8–365 ng/g	BDEs: <0.3–920 ng/g ΣBDEs: 348–997 ng/g	-	Effluent: 372 BDEs: <0.4–330 ΣBDEs: 96–219	[124]
PBDEs	Germany	-	-	-	BDEs: 0.3–2217 ΣBDEs: 142–2491	[124]
20 BDEs	USA	-	-	-	BDEs: nd-58,800 ΣBDEs: 97,400	[125]
16 BDEs, OPFRs	USA	-	-	-	BDEs: nd-51,000 ΣBDEs: 185,000–627,000 Total FRs: 300,000–1,860,000	[126]
HBOD	Sweden	-	-	-	Primary sludge: 30–33 Digested sludge: nd	[127]
TBBPA	Canada	-	-	-	310 ± 90–330 ± 70	[128]
HBOD, TBBPA	Holland, UK, Ireland	HBOD: <0.4–3800 ng/g (dw); TBBPA: <3.9–21.7 ng/g (dw)	HBOD: <1–18 ng/g (dw); TBBPA: 3.1–63 ng/g (dw)	-	HBOD: <0.6–9120 TBBPA: 2–600	[129]
PBDEs	Italy	-	-	-	ΣPBDEs: 2763 (158–9427)	[130]

(the most important congeners of the penta-bromodiphenyl ether mixtures [85]) were much higher in the winter.

Table 3 also displays the occurrence of organophosphate FRs (OPFRs), which are less hydrophobic than PBDEs, having poor WS. They tend to occur in concentrations of hundreds to thousands of ng/L. In general, OPFRs are not efficiently removed during the wastewater treatment process. Marklund et al. [86] reported removal rates for individual OPFRs that ranged between –20% (tris-chloropropyl-phosphate, TCPP) and 85% (tributylphosphate, TBP), whereas for the total OPFRs, the average elimination was 50%. Even lower removals were reported by Bester [87] (0–41% for TCPP).

Chlorinated OPFRs are more stable against degradation processes than alkyl-, or aryl- OPFRs, and whether OPFRs will partition onto particles or remain in the water stream will be affected by the occurrence of DOC and other detergents, shifting the partition towards the aqueous phase [86].

### 3.5. Perfluorinated compounds

Contrarily to most BFRs, PFCs are not efficiently eliminated along a WWTP process. In fact, in some cases it is often common to observe a phenomenon of negative removal or in-plant production [88]. Pan et al. [89] suggested the same fate when confronted with overall higher levels of PFCs in the effluents comparing to the influent flows. According to Heidler and Halden [88], several mass balances performed for fluorochemicals also reflect a net mass flow increase at the WWTP effluents. However, this family of compounds have dissimilar behaviour among them, depending on the functional groups [90]. For instance, some authors reported that perfluorooctanesulfonic acid or perfluorooctane sulfonate (PFOS) levels have a decreasing tendency after treatment in most WWTPs, whilst perfluorooctanoic acid or perfluorooctanoate (PFOA) showed an inverse pattern [89–91]. According to Guo et al. [90], this could be due to the higher organic carbon-normalised distribution coefficient of perfluoroalkylsulfonate (PFASs) in comparison with the carboxylate analog, a sign of preferential uptake of PFASs by the sludge, which seems to be a key mechanism in the process. Although Zhou et al. [92] state that, in terms of electrostatic interaction, PFOS and PFOA would suffer repulsion, making their adsorption impossible on activated sludge, they also consider that some cations present in the sludge (e.g. Ca<sup>2+</sup> and Mg<sup>2+</sup>) could provide the necessary ion bridges to allow the sorption of the negatively charged PFCs. Indeed, a review by Rayne and Forest [93] indicates that PFCs removal happens mainly through sorption on sludge. In a study to assess the sorption abilities of seven PFCs (heptafluorobutyric acid (PFBA), potassium perfluorobutanesulfonate (PFBS), undecafluorohexanoic acid (PFHxA), perfluorohexanesulfonic acid potassium salt (PFHxS), PFOA, PFOS, and perfluorododecanoic acid (PFDOA) on aerobic activated sludge, Zhou et al. [92] found out that the sorption of PFOS was highest when considering each compound individually. The same authors refer that the overall sorption capacities increased with the enlargement of the chain length for both the carboxylic and sulfonate compounds and, for the same number of carbons, were higher for the latter than for the former. Perfluorinated sulfonates possess one more tail carbon (longer CAF chain) than perfluorinated carboxylates, which enhances their hydrophobicity and reflects the significance of hydrophobic interaction in the sorption activity. Using a mixture of the seven PFCs, the same authors reported a significant decrease on the sorption capacities. For instance, PFOS sorption in the mixed solution was much higher than that of PFOA (as suggested by the respective isotherms), whose sorption decreased more than that of PFOS comparing to the single compound samples. The equilibrium of both compounds was obtained after about 11 h, enough time for them to be adsorbed on activated sludge on a WWTP normal process. Furthermore, their removal was lowered by the pH increase.

**Table 4**  
PFCs in WWTPs.

Compounds	Country	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Sludge (ng/g dw)	References
21 PFCs	Germany	–	PFCs: <0.004–82.2 ± 6.5; ΣPFCs: 30.5 ± 3.7–266.3 ± 17.2	–	–	[131]
9 PFCs	Japan	PFCs: <0.5–336; ΣPFCs: 56.7–449	PFCs: <0.1–635; ΣPFCs: 95.8–874.1	–	–	[97]
PFOS, PFOA	Japan	PFOS: 3.4–33 PFOA: 49–250	PFOS: 14–67 PFOA: 62–550	–	–	Nozoe et al. (2008), in [97]
PFHxS, PFOS, PFOA, PFNA, PFDA, PFUDA, 8:2 FTCA, 8:2 FTUCA	USA	PFCs: 0.12–8.9 g/day (1.8–117.0 ng/L); ΣPFCs: 4.6–15.5 g/day (68.2–203.7 ng/L)	PFCs: 0.13–21 g/day (1.8–276.0 ng/L); ΣPFCs: 8.0–43.7 g/day (118.7–574.2 ng/L); (6 WWTPs) PFCs: <2.5–398 ng/L; ΣPFCs: 86.5–1095.5 ng/L	–	(5 PFCs) PFCs: <10–241; ΣPFCs: 88–530	[98]
PFOS, PFOSA, PFHxS, PFOA, PFNA, PFDA, PFUnA	Denmark	PFCs: <0.2–32.8; ΣPFCs: 11.3–76.6	PFCs: <0.2–24.4; ΣPFCs: 6.3–39.9 PFCs: <0.16–1115; ΣPFCs: 17.8–1225.6	–	PFCs: 0.4–74.1; ΣPFCs: 8.5–152.5	[100]
10 PFCs	Norway, Finland, Sweden, Denmark, Iceland, Faroe Islands	–	PFOS: 1.2–62.6; PFOSA: nd-0.48; ΣPFAS: 5–105.4	–	PFOS: 55–2644; PFOSA: nd-94	[132]
10 PFCs	USA	PFCs: <2–190 ΣPFCs: 90–470	PFCs: <2–85 Total PFCs: 100–170	–	–	[133]
PFC <sub>8</sub> A, PFC <sub>10</sub> A	Spain	–	PFC <sub>8</sub> A: <100–4300; PFC <sub>10</sub> A: 50–8170	–	–	[134]
PFOA, PFOS, PFBS, PFHxS, 6:2 FIS, PFHxA, PFNA, PFDA, FOSA	USA	PFCs: nd-400 ± 29; ΣPFCs: 60.4–509.2	PFCs: nd-370 ± 19 ΣPFCs: 3.6–569.5	–	–	[135]
15 PFCs	USA	PFCs: nd-33 ΣPFCs: 74.3	PFCs: nd-34 ΣPFCs: 70.9	–	–	[91]
11 PFCs	Japan, Thailand	Individual PFCs: nd-908.3; ΣPFCs: 20–1862.4	PFCs: nd-1529.8; ΣPFCs: 21.5–3051.3	PFOS: –53% PFDS: –30% PFOA: 27% PFNA: –209% FDA: 59% Not specified	PFCs: nd-160 ΣPFCs: 459.4	[136]
PFOS, PFOA	Singapore	PFOS: 7.9 ± 1.9–374.5 ± 61.6; PFOA: 14.1 ± 4.0–638.2 ± 135.9	PFOS: 7.3 ± 2.2–461.7 ± 82.0; PFOA: 15.8 ± 2.8–1057.1 ± 205.8	Not specified	ΣPFCs: 187.4–4222.6 ng/L PFOS: 30.7 ± 6.8–702.2 ± 173.2; PFOA: 17.4 ± 5.4–69.0 ± 12.2	[137]
PFOS, PFOA	Singapore	–	PFOS: 5.8–532; PFOA: 7.9–1060	–	–	[138]

Table 4 (Continued)

Compounds	Country	Influent (ng/L)	Effluent (ng/L)	Removal (%)	Sludge (ng/g dw)	References
PFHxS, PFHpA, PFOA, PFOS, PFNA, PFDA, PFUnDA	China	ΣPFCs: 2.88–176	ΣPFCs: 5.48–498	Not specified	ΣPFCs: 1.21–326	[89]
PFOS, N-EFOSE, N-EFOSAA, PFOSAA, N-EFOSA, FOSA, PFOSulfinate, PFOA	USA	PFCs: nd->400; ΣPFCs: >409.1	PFCs: nd-26±2.0; ΣPFCs: 51.6	Not specified	-	[95]
PFOA, PFNA, PFDA, PFUnA, PFOS	Canada	-	-	-	PFCs: nd-460; ΣPFCs: 47.4	[102]
[1,0]12 PFCs USA	Switzerland	-	-	-	PFCs: nd-2610; ΣPFCs: 5–3390	[139]
12 PFCs	Switzerland	-	-	-	PFCs: nd-750±20; ΣPFCs: 26–780	[140]
PFOS, PFOA	Germany	PFOS: <1–85; PFOA: 1.8–40	PFOS: <1–85; PFOA: 12–140	PFOS: 64% to –3000% PFOA: –25% to –511%	PFOS: 80–120 PFOA: 11–18	[141]
17 PFCs	Switzerland	-	-	-	PFCs: 1.1–670; ΣPFCs: 129–734	[142]
19 PFCs	China	PFCs: nd-49.9; ΣPFCs: 41.9–58.3	PFCs: nd-28.8; ΣPFCs: 25.8–31.4	PFBuS: –36.4 and 53.6%; PFOS: 2.0 and 61.9%; PFHxA: –20% and 30%	PFCs: nd-157.9; ΣPFCs: 19.9–224.3	[143]
13 PFCs	USA	-	ΣPFCs: 62.3–418	-	-	[144]
10 PFCs	Thailand	PFCs: 0.1–465.4; ΣPFCs: 673.3–847.1	PFCs: nd-552.8; ΣPFCs: 661.8–1143.4	PFOA: –5.4 and –156%; PFOS: 59 and –54%	PFCs: nd-552.6; ΣPFCs: 1200.4–1534.5	[94]
PFOS, PFOA, PFBS, PFHxS, PFNA	Spain	-	PFCs: <0.03–72.1; ΣPFCs: 3.47–132	-	-	[145]
11 PFCs	Taiwan	PFCs: <0.1–348.3±66.2; ΣPFCs: 335.2–686.3	PFCs: <0.1–264.7±34; ΣPFCs: 379.2–481.4 PFCs: 2.8±0.3–5663.3±427.4; Mean ΣPFCs: 9456.5	PFOA: –7.6 and –9.6%; PFOS: 7 and –22.2%	-	[146]
PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS	Australia	PFCs: nd-38.6±1; ΣPFCs: 24.2–137.7	-	-	-	[147]
13 PFCs	South Korea	PFCs: nd-615; Total PFCs: nd-628.6	PFCs: nd-591; ΣPFCs: nd-598.7	Not specified	PFCs: nd-54.1; ΣPFCs: nd-59.3	[90]
PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS, PFOS	China	PFCs: nd-71.1; ΣPFCs: 71.8–120.5	PFCs: nd-41.1; ΣPFCs: 44.5–60.1	PFOA: –22 to 42%; PFOS: 41–70%	-	[148]
PFHxS, PFNA, PFOA, PFOS, PFOSA, PFDA, PFUnDA, PFDoDA	USA	PFCs: 0.17–184; ΣPFCs: 7.73–203.3	PFCs: <0.5–183; ΣPFCs: 12.2–205.9	PFOA: –577 to 0.5%; PFOS: –300 to 28%	PFCs: <2.5–993; ΣPFCs: 151–1616.5	[99]
18 PFCs	Greece	PFCs: <0.09–453.0 ΣPFCs: 12.6–856.3	PFCs: <0.09–209.4 ΣPFCs: 4.3–533.0	PFHxS: 73% PFOS: –408 to 64%	ΣPFCs: 0.58–233.3	[149]

Rayne and Forest [93] mentioned filtration and sorption methodologies as the most promising existing removal approaches for PFCs in wastewaters, together with the possibility of some sonochemical advances. Evaporative, extractive, thermal, advanced oxidative, direct and catalysed photochemical, reductive, and biodegradation techniques are yet short of validation for these systems. Slow kinetics impedes the direct use of most PFCs treatment methods in low residence time systems. In addition, the authors state that in concentrated solutions the polyfluorinated acid counterion is bound to influence the degradation and/or partitioning processes, but the extent of such influence is so far undetermined. In more dilute media (such as most wastewaters), the substrate reactivity and partitioning would potentially be independent of the input counterion.

On the other hand, Kunacheva et al. [94] found that two WWTPs with activated sludge processes failed to remove PFCs efficiently, which was a consequence of the non-biodegradability of those microcontaminants. Still, the authors agree that bio-accumulation in sludge could be the major removal mechanism of PFCs and that their increase in the effluents could be attributed to the existence and subsequent chemical and/or biological degradation of PFCs precursors such as perfluoroalkyl telomers or sulfonamides. This was confirmed by Boulanger et al. [95] and Schultz et al. [91].

Martin et al. [96] studied the importance of the precursors on the exposure of PFOS, whose concentrations in WWTPs exceed those of its precursors by one or more orders of magnitude. PFOSA, the most frequently analysed precursor, was often found below LODs. But even if they seldom appear in quantifiable limits, some studies advocate that precursors do play an important role in the levels of PFOS found in WWTP effluents and increases in its mass flow were found after activated sludge treatment in facilities from all over the world [97–100]. Rhoads et al. [101] found three potential precursors (perfluorooctanesulfonamide (PFOSA), methyl perfluorobutane sulfonamide (MeFBSA) and methyl perfluorobutane sulfonamidoethanol (MeFBSE)) in WWTPs and D'Eon et al. [102] stated the possibility of 4-carbon-chain (C4) compounds like MeFBSA and MeFBSE degrading into the C4 homologues of perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSA). Some researchers reported that laboratory experiments supported the field studies and concluded that aerobic microbial biodegradation of precursors can yield important loads of PFCs [101], but the actual understanding of these processes is still weak. In addition, it is also suggested that the percentage of industrial, commercial or domestic loads in the influents of WWTPs will affect the PFCs levels and profiles [98].

The physicochemical properties of fluorinated chemicals are not well known as for other microcontaminants (like PBCs for example). For PFOS, it is said that octanol/water partition coefficient cannot be calculated because PFOS forms multiple layers in octanol/water determination. According to US-EPA, PFOA, PFOS and other related microcontaminants have  $\log K_{ow}$  that range between  $-1$  and  $7$ . PFOS is almost totally water soluble and its  $pK_a$  is  $-3.3$ . The latter value for PFOA is said to range between  $2$  and  $3$  [164–170].

Hence, the current knowledge on the behaviour of PFCs in WWTPs is influenced by all these intertwining and sometimes confounding factors, by the inexistence of a strong dataset reporting evidences on a significant number of facilities and treatment options and by a scarce experimental expertise on the physicochemical properties of almost all straight chain PFAs [93]. According to Heidler and Halden [88], future work to enhance the removal responses of WWTP systems should include an environmental impact assessment for chemicals accumulating in digested sludge and with high persistence throughout aerobic and anaerobic sewage treatment. Should degradation be limited or inexistent, more biodegradable and sustainable alternatives could ultimately prevent environmental and human health hazards.

#### 4. Conclusions

The present review gave brief information about the occurrence of five categories of organic microcontaminants in WWTPs. PPCPs, IDs, doping substances, BFRs or PFCs are compounds that were probably present in wastewaters for decades. However, the scientific community only started dealing with them during the last years, either because the methodologies used in the past were not powerful enough to achieve low enough LODs, or simply because there was always the impression that these chemicals were easily biodegradable, making no sense to try to analyse them in WWTPs.

But since then, the analysis of these compounds has proved to have an outstanding impact and also important implications that go as far as the intersection between science and the society. For example, the epidemiological approach used to assess the consumption of cocaine in a city, based on the concentrations in WWTPs or the understanding of the use of doping substances, based on well designed sampling and analysis of effluents from Olympic villages.

Equally important is the recognition that many processes are yet poorly described and even unknown. This urges the continuous pursue of better analytical methodologies and optimised sampling strategies, in order to build an extensive dataset to help the enlightenment of such processes.

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