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The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters

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ABSTRACT

A 5-month monitoring program was undertaken in South Wales in the UK to determine the fate of 55 pharmaceuticals, personal care products, endocrine disruptors and illicit drugs (PPCPs) in two contrasting wastewater plants utilising two different wastewater treatment technologies: activated sludge and trickling filter beds. The impact of treated wastewater effluent on the quality of receiving waters was also assessed.

PPCPs were found to be present at high loads reaching 10 kg day^{-1} in the raw sewage. Concentrations of PPCPs in raw sewage were found to correlate with their usage/consumption patterns in Wales and their metabolism. The efficiency of the removal of PPCPs was found to be strongly dependent on the technology implemented in the wastewater treatment plant (WWTP). In general, the WWTP utilising trickling filter beds resulted in, on average, less than 70% removal of all 55 PPCPs studied, while the WWTP utilising activated sludge treatment gave a much higher removal efficiency of over 85%. The monitoring programme revealed that treated wastewater effluents were the main contributors to PPCPs concentrations (up to 3 kg of PPCPs day^{-1}) in the rivers studied. Bearing in mind that in the cases examined here the WWTP effluents were also major contributors to rivers' flows (dilution factor for the studied rivers did not exceed 23 times) the effect of WWTP effluent on the quality of river water is significant and cannot be underestimated.

1. Introduction

Pharmaceuticals, personal care products, endocrine disruptors and illicit drugs (PPCPs) are regarded as emerging environmental contaminants as many PPCPs are ubiquitous, persistent and biologically active compounds with recognised endocrine disruption functions (Daughton and Ternes, 1999; Fent et al., 2006). Pharmaceuticals such as antibiotics or analgesics have frequently been found in surface waters at concentrations reaching μg L^{-1} (Ashton et al., 2004; Bendz et al., 2005; Calamari et al., 2003; Glassmeyer et al., 2005; Gross et al., 2006; Kolpin et al., 2002, 2004; Moldovan, 2006; Roberts and Thomas, 2006; Vanderford et al., 2003; Vieno et al., 2005, 2006). In contrast personal care products and illicit drugs have

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hardly been studied in environmental matrices and limited evidence of their presence in the environment exists to date (Boleda et al., 2007; Hummel et al., 2006; Zuccato et al., 2008).

There are several direct and indirect pathways through which PPCPs can be introduced into the aqueous environment. Insufficiently treated municipal wastewater discharge is identified as the major route responsible for surface water contamination with PPCPs (Bendz et al., 2005; Bernhard et al., 2006; Carballa et al., 2004; Castiglioni et al., 2006a; Göbel et al., 2007; Gómez et al., 2007; Jones et al., 2007; Joss et al., 2005; Lindqvist et al., 2005; Lishman et al., 2006; Nakada et al., 2006; Palmer et al., 2008; Santos et al., 2007; Spongberg and Witter, 2008; Tauxe-Wuersch et al., 2005; Terzić et al., 2008; Vieno et al., 2006; Yu et al., 2006). The likelihood of water contamination with PPCPs as a result of discharge of WWTP effluent depends on several factors. Among the most important are: physico-chemical properties of pollutants, the type of wastewater treatment technology implemented and climatic conditions (e.g. dilution of wastewater effluent, rainfall, temperature and level of sunlight).

The main objective of the research presented in this paper was to verify the occurrence and fate of different classes of 55 PPCPs during wastewater treatment. These were: pharmaceuticals (analgesic/anti-inflammatory drugs, antibiotics, antiepileptics, beta-adrenoceptor blocking drugs, lipid regulating agents, etc.), personal care products (sunscreen agents, preservatives and disinfectant/antiseptics), endocrine disruptors (bisphenol A and 4-*tert*-octylphenol) and illicit drugs (amphetamine, cocaine and benzoylecgonine). Studies previously presented have tended to concentrate on small subsets of these pollutants, whereas in reality treatment works will have to treat wastewaters containing a large variety of these potential pollutants and successfully remove them simultaneously with many other compounds. Therefore it is important to assess plants' effectiveness in the context of the substantial number of PPCPs treated simultaneously. In order to evaluate it the 5-month long monitoring program was undertaken in South Wales in the UK. The two contrasting WWTPs (utilising two different wastewater treatment processes: activated sludge and trickling filter beds) discharging treated wastewater in the two contrasting rivers (the River Taff – major river flowing through urbanised area and the River Ely – small river flowing through rural areas) were chosen for the research in order to better understand factors affecting the occurrence and fate of PPCPs in the environment. An assessment of the efficiency of PPCPs removal using two contrasting wastewater treatment technologies was undertaken. The impact of treated wastewater effluent on the quality of receiving waters was also investigated.

2. Experimental

2.1. Chemicals and materials

Reference standards were obtained from Sigma–Aldrich (Gillingham, UK) and Sequoia Products Research Limited (Pangbourne, UK). Surrogate/internal standards (IS): phenacetin-ethoxy-1-^{13}C (CAS no. 72156-72-0), caffeine-d9 (1,3,7-trimethyl-d9, CAS no. 72238-85-8), clofibric-d4 acid (4-chlorophenyl-d4, CAS no. 882-09-7), 3,4-dichlorobenzoic (2,5,6-d3) acid (CAS no. 350818-53-0), bisphenol A-d16 (CAS no. 96210-87-6) and 4-chlorophenol (2,3,5,6-d4, CAS no. 344298-84-6) were purchased from QMX Laboratories Limited (UK) and Sigma–Aldrich (UK). All glassware was deactivated with dimethylchlorosilane (5% DMDCS in toluene, Sigma–Aldrich) (Kasprzyk-Hordern et al., 2007).

2.2. Sampling

Two contrasting rivers (rivers Taff and Ely) and two contrasting wastewater plants (WWTP Cilfynydd and Coslech) were the subject of the study (Table 1).

WWTP Cilfynydd discharges treated wastewater into the River Taff, which is one of 10 major rivers in the United Kingdom (Fig. 1). It rises in the Brecon Beacons National Park and subsequently it flows through the urbanised areas of Merthyr Tydfil (population, 55 000), Pontypridd (population, 33 000), and Cardiff (population, 320 000) where it flows into the Severn Estuary and Bristol Channel. Sewage is collected in extensive trunk sewer systems and is treated for discharge into the River Taff at Cilfynydd WWTP and the Cynon Valley WWTP on the opposite bank from Cilfynydd. This large sewage effluent discharge receives relatively little dilution in

Table 1 – General information on the studied WWTPs and rivers.

Parameter	River Taff	River Ely
Flows [$m^3 s^{-1}$][a]	AC: 0.7–2.9; PD: 4.4–14.3	TG: 0.2–2.5; SF[c]: 0.8–7.1
Catchment area [km^3][b]	526	169
Population[b]	~500 000	~230 000
	WWTP Cilfynydd	WWTP Coslech
Population served	111 000	30 000
Flows [$L s^{-1}$][a]	247–590	150–307
Type of wastewater treated	Mainly communal	Communal/industrial
Technology	Biological, trickling filter beds	Biological, activated sludge

a Measured over the course of the study.
b Data is obtained from Environment Agency (2000a,b).
c St. Fagans point (see Fig. 1).

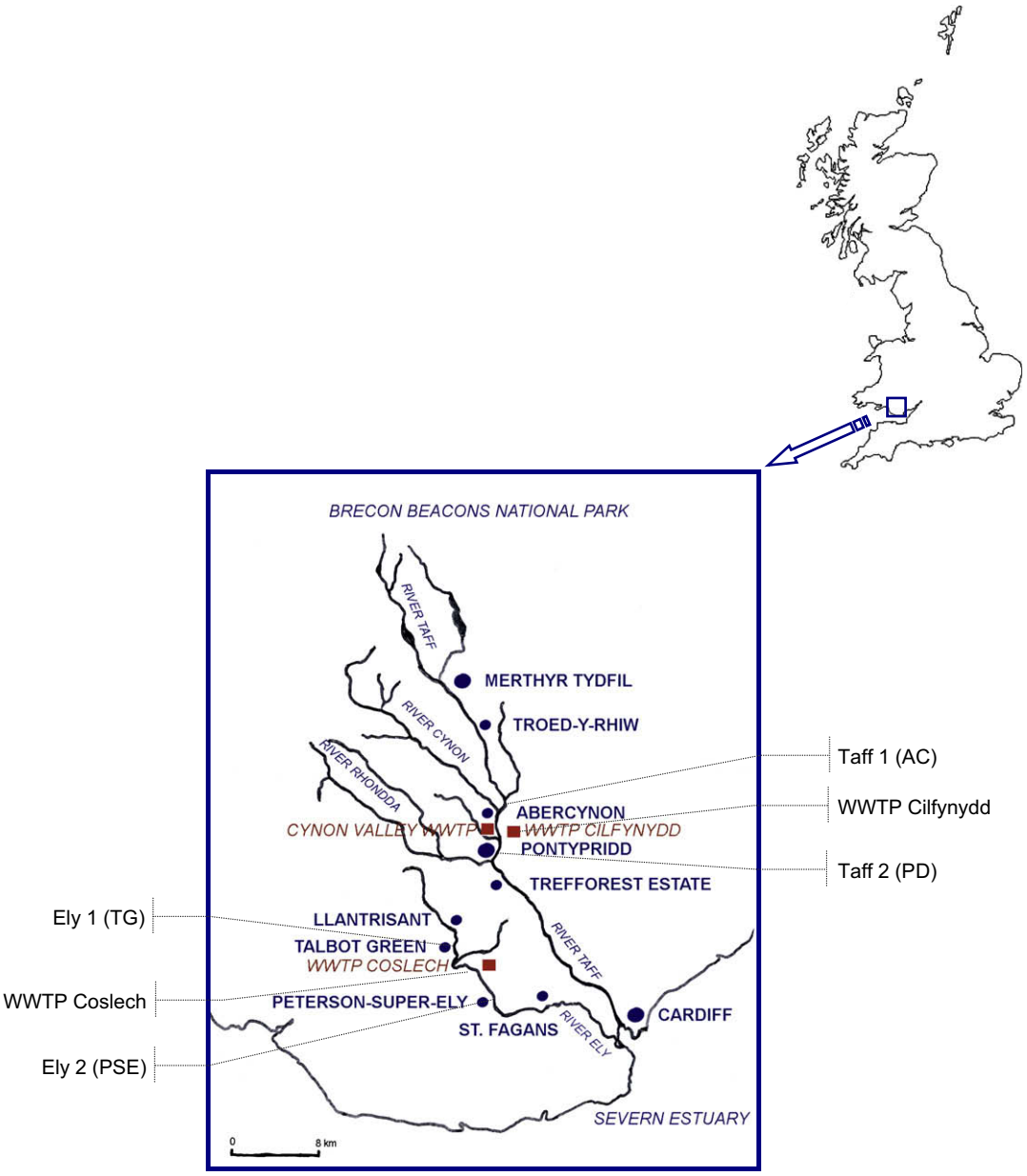

Fig. 1 – Location of sampling points (AC – Abercynon, PD – Pontypridd, TG – Talbot Green, PSE – Peterson-super-Ely).

the middle reaches of the Taff system, and it is an important addition to the water resource (Environment Agency, 2000a). WWTP Cilfynydd treats mainly communal wastewater. It serves 111 000 people. The technology utilised in WWTP Cilfynydd is biological process, using trickling filter beds. This is a simple technology combining initial solids removal, biological secondary treatment and final clarification.

WWTP Coslech discharges treated wastewater into the River Ely, which is a small and shallow river that flows through rural lowlands and villages such as: Talbot Green, Peterson-super-Ely and St. Fagans. Finally it arrives in Cardiff where it flows into the Severn Estuary and Bristol Channel (Fig. 1). Treated effluent enters the River Ely from several sewage treatment works and is an important contributor to flows. The largest works discharging treated wastewater is Coslech WWTP. There are numerous industrial discharges into the foul sewers within this area and these discharges give rise to an unusually high percentage of the dry weather flow to this works (Environment Agency, 2000b). WWTP Coslech, as opposed to WWTP Cilfynydd, also treats industrial wastewater. The population served approximates to 30 000 people. The treatment process utilised here is a biological activated sludge process, deployed as an extended aeration oxidation ditch for BOD/COD removal and nitrification.

In the case of the River Taff and WWTP Cilfynydd discharging treated wastewater into the River Taff, four sampling points were chosen (Fig. 1):

1. AC: Abercynon – 1 km upstream of WWTP Cilfynydd.
2. WWTP Cilfynydd – wastewater influent.

Table 2 – Chosen PPCPs, their properties (RxList; Prescription Cost Analysis; US National Library of Medicine; Drug Bank; Household Products Database) and methods used to quantify PPCPs in surface water and wastewater.

Compound	CAS no.	Prescription in Wales, 2006 [kg]	Excretion	Method
			Unchanged [%]	
Pharmaceuticals				
Trimethoprim	738-70-5	722	80	a
Sulfamethoxazole	723-46-6	115	30	a
Chloramphenicol	56-75-7	–	8–12	b, c
Erythromycin-H_2O	114-07-8	~3024	5	a
Metronidazole	443-48-1	~700	20	a
Paracetamol	103-90-2	140 680	80 as conjugates	a
Ibuprofen	15687-27-1	~11 000	1	b, c
Diclofenac	15307-86-5	~2200	5–10	b, c
Ketoprofen	22071-15-4	~70		b, c
Naproxen	22204-53-1	2198	<1	b, c
Aspirin	50-78-2	6308	Little	b, c
Salicylic acid (aspirin metabolite)	69-72-7	–	–	b, c
Mefenamic acid	61-68-7	884	5–11	b, c
Codeine	76-57-3	3145	70 free or as conjugates	a
Tramadol	27203-92-5	2145	15–35	a
Carbamazepine	298-46-4	2515	3	a
Gabapentin	60142-96-3	2808	100	a
Propranolol	525-66-6	463	<0.5	a
Metoprolol	37350-58-6	126	10–30	a
Atenolol	29122-68-7	2328	50	a
Clofibric acid	882-09-7	–	–	b, c
Bezafibrate	41859-67-0	504	50	b, c
Simvastatin	79902-63-9	1643		a
Pravastatin	81093-37-0	146		b
Ranitidine	66357-35-5	2357	30	a
Cimetidine	51481-61-9	660	48–75	a
Sulfasalazine	599-79-1	3146	–	b, c
Sulfapyridine (sulfasalazine metabolite)	144-83-2	1	–	a
5-Aminosalicylic acid (sulfasalazine metabolite)	89-57-6	–	<12	a
Furosemide	54-31-9	1296	Little	b, c
Bendroflumethiazide	73-48-3	133	–	b, c
Digoxin	20830-75-5	1	50–70	b
Digoxigenin (metabolite of digoxin)	1672-46-4	–	–	c
Valsartan	137862-53-4	654	80	b, c
Diltiazem	42399-41-7	1862	2–4	a
Salbutamol	18559-94-9	~15	30	a
Amitriptyline	50-48-6	418	Little	a
Illicit drugs				
Amphetamine	300-62-9	–	30	a
Cocaine	50-36-2	–	1–9	a
Benzoylecgonine (cocaine metabolite)	519-09-5	–	–	a
Personal care products				
Benzophenone-1	131-56-6	–	–	b, c
Benzophenone-2	131-55-5	–	–	b, c
Benzophenone-3	131-57-7	–	–	b, c
Benzophenone-4	4065-45-6	–	–	b, c
Methylparaben	99-76-3	–	–	b, c
Ethylparaben	120-47-8	–	–	b, c
Propylparaben	94-13-3	–	–	b, c
Butylparaben	94-26-8	–	–	b, c
Triclosan	3380-34-5	–	–	b, c
4-Chloroxylenol	88-04-0	–	–	b, c
Chlorophene	120-32-1	–	–	b, c
3,4,5,6-Tetrabromo-o-cresol	576-55-6	–	–	b, c
p-Benzylphenol	101-53-1	–	–	b, c

Table 2 (continued)

Compound	CAS no.	Prescription in Wales, 2006 [kg]	Excretion	Method
			Unchanged [%]	
Endocrine disruptors				
Bisphenol A	80-05-7	–	–	b, c
4-*tert*-Octylphenol	140-66-9	–	–	b, c

a Kasprzyk-Hordern et al., 2007.
b Kasprzyk-Hordern et al., 2008a.
c Kasprzyk-Hordern et al., 2008b.

3. WWTP Cilfynydd – treated wastewater effluent.
4. PD: Pontypridd – 2 km downstream of WWTP Cilfynydd, just before Pontypridd.

In the case of the River Ely and WWTP Cilfynydd discharging treated wastewater into the River Ely, four additional sampling points were chosen (Fig. 1):

1. TG: Talbot Green – 7 km upstream of WWTP Coslech.
2. WWTP Coslech – wastewater influent.
3. WWTP Coslech – treated wastewater effluent.
4. PSE: Peterson-super-Ely – 3.5 km after WWTP Coslech.

The choice of sampling points was to verify the efficiency of wastewater treatment and to identify the influence of treated wastewater effluent on the quality of receiving waters. Samples were collected at least twice a month over the period of 5 months (April 2007–August 2007).

Two replicate grab and in the case of WWTP Coslech also 24 h-composite wastewater samples were collected in 1 L silanized bottles with Teflon faced phenolic caps, acidified with 31% HCl to pH 2.0 and vacuum filtered through GF/D 2.7 μm and GF/F 0.7 μm glass fibre filters (Whatman, UK). Surface grab water samples were collected in 2.5 L silanized amber bottles with Teflon faced phenolic caps, acidified with 31% HCl to pH 2.0 and vacuum filtered through 0.7 μm glass fibre filter GF/F (Whatman, UK). Because similar results were obtained for both grab and 24 h-composite samples, no additional discussion will be carried out here.

2.3. *Sample preparation and analysis*

PPCPs were extracted from 1 L surface water or 0.25 L wastewater (both influent and effluent) using SPE Gilson ASPEC XL4 (Anachem, UK). Oasis MCX sorbent (Waters, UK) was chosen for the extraction of all PPCPs. Before extraction the samples were spiked with 200 ng of surrogate/internal standards. PPCPs were eluted with MeOH and 5% NH_4OH in MeOH. The extracts were subsequently evaporated to dryness and reconstituted in 0.5 mL of mobile phase. The detailed SPE procedure is discussed elsewhere (Kasprzyk-Hordern et al., 2007, 2008a,b).

Separation of analytes was undertaken with Waters ACQUITY UPLC™ system (Waters, Manchester, UK) using ACQUITY UPLC BEH C18 column (1.7 μm; 1 mm × 100 mm). Identification and quantification of separated analytes were carried out with a Quatro Micro triple–quadrupole mass spectrometer (Micromass, Manchester, UK), equipped with an electrospray ionisation (ESI) source.

PPCPs were identified and quantified in environmental samples using three analytical methods (Table 2). Basic/neutral analytes were separated using a gradient method and the following mobile phase composition: water, methanol and acetic acid (0.5%). The MS analyses were performed in positive ESI mode (Kasprzyk-Hordern et al., 2007, 2008b). Acidic/neutral analytes were separated using the mobile phase with the following composition: water, methanol, 0.5% acetic acid and 5 mM NH_4OH or 10 mM TrBA. The MS analyses were performed in negative ESI mode (Kasprzyk-Hordern et al., 2008a,b). Quantification of PPCPs was carried out by means of MRM. All instrumental and methods validation parameters such as: linearity and range, accuracy, precision, detection and quantification limits and calibration curve were determined. A detailed discussion of the methods and their validation is presented elsewhere (Kasprzyk-Hordern et al., 2007, 2008a,b).

3. Results and discussion

Fifty-five PPCPs were studied and are presented in Table 2. In the selection process of pharmaceuticals, the number of prescriptions dispensed in the community in Wales (NHS (National Health Service), Prescription Cost Analysis, Wales, 2004) and the metabolism routes of pharmaceuticals were taken into consideration. The choice of personal care products was based on their high annual usage in a wide range of household products and concern over their possible effect on human and aquatic organisms (Household Products Database). Illicit drugs were chosen due to their high estimated illegal usage. Only some PPCPs studied in this research have been investigated by others. These are mainly antibiotics, anti-inflammatory/analgesics, beta-blockers and antiepileptics. The other groups of PPCPs have hardly been investigated and limited evidence on their fate during wastewater treatment and presence in the environment exists to date.

3.1. *PPCPs during wastewater treatment*

3.1.1. *Pharmaceuticals*

3.1.1.1. Antibacterial drugs. Trimethoprim and erythromycin-H_2O were found at the highest levels exceeding 4 $\mu g\,L^{-1}$ in raw sewage in both WWTP Coslech and Cilfynydd (Tables 3 and 4). All the studied antibacterial drugs were found in all

Table 3 – Concentrations of pharmaceuticals in WWTP Cilfynydd and receiving waters (the River Taff) calculated for samples collected over the period of the 5-month monitoring programme (April 2007–August 2007).

Compounds	Concentration [ng L^{-1}]							
	River Taff				WWTP Cilfynydd			
	AC		PD		Influent		Effluent	
	L–H (M)	%	L–H (M)	%	L–H (M)	%	L–H (M)	%
Antibacterial drugs								
Trimethoprim	<0.5*–7 (1)	29	30–120 (89)	100	464–6796 (2192)	100	625–3052 (1152)	100
Sulfamethoxazole	<0.5–1 (0)	29	<0.5–8 (2)	86	<3–150 (29)	67	<3–23 (10)	82
Chloramphenicol	<2	0	<2	0	<4–319 (14)	33	<6 (<6)	0
Erythromycin-H_2O	<0.5–20 (4)	43	11–121 (52)	100	242–6755 (1609)	100	292–2841 (1385)	100
Metronidazole	<1.5–10 (1)	14	2–11 (5)	100	158–1583 (643)	100	60–421 (265)	100
Anti-inflammatory/analgesics								
Paracetamol	305–1534 (706)	100	185–1530 (615)	100	68 107–482 687 (211 380)	100	1826–24 525 (11 733)	100
Ibuprofen	5–48 (22)	100	12–62 (29)	100	968–2986 (1681)	100	131–424 (263)	100
Diclofenac	<0.5–85 (12)	92	9–40 (24)	100	26–257 (69)	100	33–142 (98)	100
Ketoprofen	<0.5–4 (1)	58	0–7 (2)	67	<4–119 (28)	62	<3–33 (16)	69
Naproxen	<0.3–28 (11)	92	17–146 (59)	100	400–1457 (838)	100	234–703 (370)	100
Aspirin	<0.5–13 (3)	50	0–10 (3)	50	485–2042 (664)	100	<3–85 (27)	92
Salicylic acid	<0.3–67 (25)	75	0–34 (15)	75	1479–18 479 (5866)	100	<1–497 (164)	92
Mefenamic acid	<0.3–20 (3)	67	1–31 (13)	100	<20–1269 (205)	92	<5–222 (61)	92
Codeine	14–98 (40)	100	170–529 (347)	100	1732–32 295 (10 321)	100	2940–15 593 (5271)	100
Tramadol	<30–435 (227)	71	1302–5970 (3522)	100	8505–89 026 (36 750)	100	24 132–97 616 (43 813)	100
Antiepileptic drugs								
Carbamazepine	1–27 (11)	100	71–327 (199)	100	709–2930 (1694)	100	644–4596 (2499)	100
Gabapentin	52–210 (105)	100	606–1879 (1224)	100	2059–37 426 (15 034)	100	3001–42 611 (15 747)	100
Beta-adrenoceptor blocking drugs								
Propranolol	<0.5–9 (6)	86	9–40 (24)	100	125–1962 (557)	100	121–405 (265)	100
Metoprolol	7 (7)	100	8–11 (9)	100	39–117 (75)	100	35–130 (69)	100
Atenolol	5–258 (63)	100	190–560 (388)	100	3090–33 106 (12 913)	100	1260–7602 (2870)	100
Lipid regulating agents								
Clofibric acid	<0.3–8 (1)	17	<0.3–3 (1)	42	<1–57 (19)	62	<1–75 (15)	62
Bezafibrate	<10–49 (12)	25	<10–64 (34)	83	209–1391 (420)	100	<85–667 (231)	92
Simvastatin	<50	0	<50	0	<7–798 (115)	29	<3–20 (5)	38
Pravastatin	<60	0	<60	0	<60	0	<60	0
H2-receptor antagonists								
Ranitidine	<3	0	<3–70 (25)	86	<10–11 664 (1733)	60	<9–455 (224)	75
Cimetidine	<0.5–13 (5)	86	32–217 (105)	100	733–13 057 (3452)	100	828–9395 (2605)	100
Sulfasalazine	<1.5–16 (8)	83	37–168 (66)	100	<80–447 (116)	92	100–2185 (484)	100
Sulfapyridine	<2	0	17–34 (28)	100	26–5763 (914)	100	127–378 (277)	100
5-Aminosalicylic acid	<15–22 (4)	29	<15–123 (65)	86	841–2828 (1667)	100	1417–3072 (2111)	100
Diuretics								
Furosemide	<6–44 (11)	58	35–197 (86)	100	836–5111 (1476)	100	583–1956 (1161)	100
Triazides								
Bendroflumethiazide	<0.5	0	<0.5	0	<8–66 (17)	38	<8–58 (11)	38
Cardiac glicozides								
Digoxin	<30	0	<30	0	<538	0	<268	0
Digoxigenin	<30	0	<30	0	<538	0	<268	0
Angiotensin II antagonists								
Valsartan	2–24 (10)	100	6–69 (25)	100	132–1660 (342)	100	<5–71 (192)	92
Calcium channel blockers								
Diltiazem	<1–2 (0)	14	3–20 (11)	100	228–3207 (770)	100	95–642 (267)	100
Bronchodilators								
Salbutamol	<1	0	<1–3 (1)	43	<2–321 (0.1)	100	<1–234 (63)	88
Antidepressants								
Amitriptyline	<0.5–17 (3)	43	<0.5–9 (4)	86	341– 5143 (1249)	100	53–357 (197)	100

L – the lowest recorded concentration; H – the highest recorded concentration; M – mean concentration; % – frequency of detection; <0.5* – below method quantification limit.

Table 4 – Concentrations of pharmaceuticals in WWTP Coslech and receiving waters (the River Ely) calculated for samples collected over the period of the 5-month monitoring programme (April 2007–August 2007).

Compounds	Concentration [ng L^{-1}]							
	River Ely				WWTP Coslech			
	TG		PSE		Influent		Effluent	
	L–H (M)	%	L–H (M)	%	L–H (M)	%	L–H (M)	%
Antibacterial drugs								
Trimethoprim	<50*–90 (19)	40	10–183 (62)	100	1514–4673 (2925)	100	385–1218 (876)	100
Sulfamethoxazole	<0.5–1 (0)	40	<0.5–4 (1)	40	20–274 (115)	100	4–44 (19)	100
Chloramphenicol	<2	0	<2–40 (5)	20	150–452 (248)	100	<6–69 (21)	50
Erythromycin-H_2O	<0.5–2 (0)	20	<0.5–72 (15)	40	144–10 025 (2530)	100	23–2772 (696)	100
Metronidazole	<1.5	0	<1.5–24 (12)	80	347–962 (569)	100	129–561 (353)	100
Anti-inflammatory/analgesics								
Paracetamol	<1.5–716 (312)	80	<1.5–662 (299)	60	108 383–246 641 (178 116)	100	<80–1575 (353)	86
Ibuprofen	<0.3–56 (17)	70	4–74 (28)	100	984–6328 (2294)	100	65–491 (143)	100
Diclofenac	<0.5–261 (49)	90	9–119 (32)	100	57–1161 (260)	100	6–496 (179)	100
Ketoprofen	<0.5–3 (1)	40	<0.5–12 (4)	30	31–346 (123)	100	7–37 (18)	75
Naproxen	1–55 (12)	100	7–113 (44)	100	620–3504 (1173)	100	<2–269 (170)	92
Aspirin	<0.5–36 (6)	40	<0.5–14 (4)	60	1321–5448 (2490)	100	<3–65 (20)	50
Salicylic acid	<0.3–44 (16)	60	<0.3–140 (37)	90	5644–32 082 (12 647)	100	<1–391 (75)	83
Mefenamic acid	<0.3–12 (4)	80	3–33 (11)	100	<17–32 (8)	83	<5–103 (39)	83
Codeine	<1.5–205 (51)	80	81–511 (294)	100	2496–12 599 (6954)	100	1457–4178 (2716)	100
Tramadol	46–3468 (956)	100	731–1898 (1292)	100	23 037–85 843 (48 488)	100	12 779–56 810 (28 147)	100
Antiepileptic drugs								
Carbamazepine	<0.5–495 (137)	80	9–647 (186)	100	104–3110 (950)	100	152–2324 (826)	100
Gabapentin	27–565 (182)	100	184–1269 (517)	100	10 674–25 079 (17 925)	100	1786–3514 (2592)	100
Beta-adrenoceptor blocking drugs								
Propranolol	<0.5–27 (12)	60	7–74 (25)	100	110–1946 (638)	100	130–523 (264)	100
Metoprolol	<0.5–8 (6)	80	7–12 (8)	100	56–146 (94)	100	34–57 (41)	100
Atenolol	<1–152 (53)	80	103–510 (276)	100	8102–25 146 (14 223)	100	1292–3168 (2123)	100
Lipid regulating agents								
Clofibric acid	<0.3–6 (1)	20	<0.3–5 (1)	20	<1–12 (1)	8	<1–48 (6)	25
Bezafibrate	<10–66 (13)	30	<10–90 (33)	70	135–1285 (600)	100	<94–393 (177)	92
Simvastatin	<50	0	<50	0	<7	0	<3	0
Pravastatin	<60	0	<60	0	<60	0	<60	0
H2-receptor antagonists								
Ranitidine	<3	0	<3	0	2005–11 153 (5060)	100	15–783 (425)	100
Cimetidine	<0.5–14 (4)	40	21–138 (48)	100	680–6509 (2219)	100	253–781 (462)	100
Sulfasalazine	<1.5–37 (17)	80	14–106 (42)	100	0.05–0.4 (0.2)	100	0.5–1.5 (0.3)	100
Sulfapyridine	<2–60 (19)	40	<2–59 (16)	80	2164–12 397 (4971)	100	94–1112 (455)	100
5-Aminosalicylic acid	<15	0	<15–52 (28)	80	3160–27 490 (10 691)	100	<172–1218 (630)	86
Diuretics								
Furosemide	<6–56 (14)	40	34–630 (129)	100	1580–6022 (2789)	100	<43–1823 (629)	92
Triazides								
Bendroflumethiazide	<0.5	0	<0.5	0	<8–101 (44)	64	<8	0
Cardiac glicozides								
Digoxin	<30	0	<30	0	<538	0	<268	0
Digoxigenin	<30	0	<30	0	<538	0	<268	0
Angiotensin II antagonists								
Valsartan	<0.5–56 (15)	90	7–144 (55)	100	354–5388 (1734)	100	6–711 (275)	100
Calcium channel blockers								
Diltiazem	<1–16 (4)	60	<1–40 (13)	60	405–5258 (1559)	100	108–1156 (357)	100
Bronchodilators								
Salbutamol	<0.5	0	<0.5–5 (1)	20	50–150 (89)	100	<1–22 (10)	86
Antidepressants								
Amitriptyline	<0.5–3 (1)	40	<0.5–7 (3)	40	504–6711 (2092)	100	<2–335 (85)	71

L – the lowest recorded concentration; H – the highest recorded concentration; M – mean concentration; % – frequency of detection; <50* – below method quantification limit.

wastewater samples collected over the monitoring period, which indicates their high usage. Only in the case of WWTP Cilfynydd both sulfamethoxazole and chloramphenicol were quantified in collected samples with a frequency lower than 70%. A similar pattern to wastewater results was observed in receiving waters where both trimethoprim and erythromycin-H_2O were found at the highest concentrations exceeding on average 50 ng L^{-1} (Tables 3 and 4). All antibacterial drugs were found with similar frequency and at similar levels in the two rivers studied (the rivers Taff and Ely). Detailed discussion on the presence and fate of the studied pharmaceuticals in the rivers Taff and Ely is presented elsewhere (Kasprzyk-Hordern et al., 2008c).

Out of all studied antibiotics, only chloramphenicol was removed in 100% during wastewater treatment in WWTP Cilfynydd. Ninety percent removal of this pharmaceutical was observed in the case of WWTP Coslech. As a result chloramphenicol was detected only in receiving waters in the River Ely, and therefore in this case wastewater treatment was not sufficient. In contrast, no chloramphenicol was detected in the River Taff over the period of 10 months (Kasprzyk-Hordern et al., 2008c). Apart from chloramphenicol, WWTP Cilfynydd was found to remove antibiotics less efficiently than WWTP Coslech (Fig. 2). For example over 50% of erythromycin-H_2O and 70% of sulfamethoxazole were removed during wastewater treatment in WWTP Coslech with no removal of these antibiotics observed in WWTP Cilfynydd. This pattern was also observed in the case of the other studied PPCPs. This is because two different biological processes are used in the two wastewater plants: trickling filter beds in WWTP Cilfynydd and activated sludge in WWTP Coslech.

The removal of some of the studied antibiotics during wastewater treatment has been investigated by several research groups. Bendz et al. (2005) reported that activated sludge treatment resulted in <50% removal efficiency of trimethoprim and sulfamethoxazole, which is lower than the one observed in the discussed research (>60%). Göbel et al. (2007) reported the following percentage removal of three antibiotics during conventional activated sludge treatment: sulfamethoxazole, −138 to 60%; trimethoprim, −40 to 20% and erythromycin-H_2O, −22 to 6%. These results are in agreement with the literature data (Spongberg and Witter, 2008; Terzić et al., 2008; Castiglioni et al., 2006a; Carballa et al., 2004) and the current research, although the activated sludge technology studied here gave on average higher efficiencies. No reports on the performance of trickling filter beds for the removal of the studied PPCPs were identified by the authors.

All antibiotics, with the exception of only chloramphenicol, were detected at often high concentrations (Tables 3 and 4) in treated effluent and finally, in receiving waters. Due to a low dilution factor of wastewater effluent in the studied rivers (average dilution over the course of the study: 23 times in the River Taff and 13 times in the River Ely), the impact of wastewater effluent on the quality of river water is particularly significant and noticeable. Erythromycin-H_2O is a good example. Only a 26 times lower average concentration of this compound was observed in the River Taff 2 km downstream of WWTP Cilfynydd than in the treated effluent.

3.1.1.2. *Anti-inflammatory/analgesics*. High concentrations of several anti-inflammatory and analgesic pharmaceuticals were detected with 100% frequency in raw sewage in both

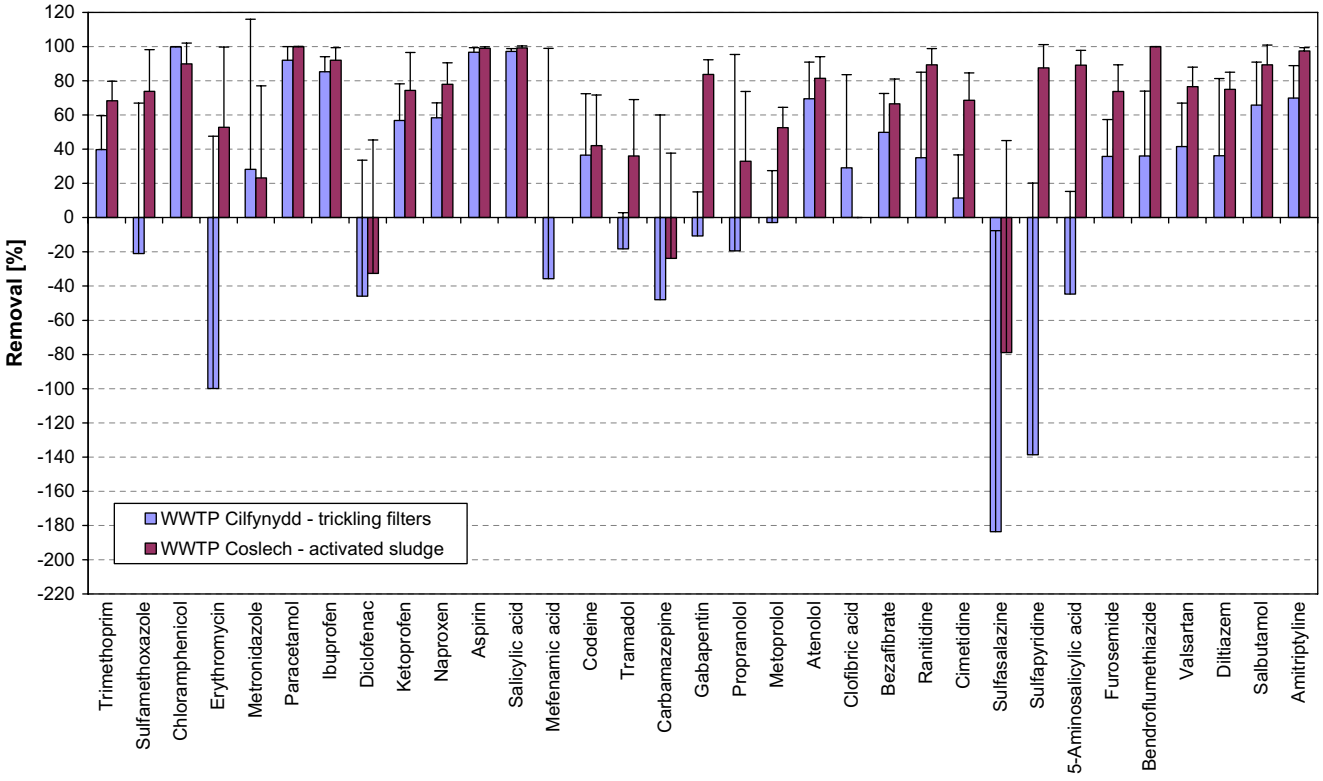

Fig. 2 – Efficiency of pharmaceuticals removal during wastewater treatment calculated for samples collected over the period of the 5-month monitoring programme (April 2007–August 2007) in raw and treated wastewater.

WWTPs (Tables 3 and 4). These are: paracetamol (average >180 $\mu g L^{-1}$), tramadol (average >30 $\mu g L^{-1}$) and codeine (average >7 $\mu g L^{-1}$). High concentrations of paracetamol and codeine can be explained by the high number of these pharmaceuticals dispensed in Wales. According to NHS data paracetamol was prescribed in 2006 in Wales at levels exceeding 140 tonnes and no data exists concerning non-prescription consumption. Codeine was dispensed in Wales at over 3 tonnes in 2006. Both paracetamol and codeine are excreted mainly as conjugates which can undergo hydrolysis during wastewater treatment resulting in the release of the parent compound. Very high concentrations of tramadol cannot be rationally explained at the moment and will be investigated further. High concentrations of these pharmaceuticals were also observed in the river water due to both the already discussed relatively low dilution of final wastewater effluent as well as insufficient wastewater treatment. Paracetamol and tramadol have been quantified in receiving waters at concentrations exceeding single $\mu g L^{-1}$ and codeine was found at concentrations reaching 0.5 $\mu g L^{-1}$. Despite the lower dilution factor of treated wastewater in the case of the River Ely, concentrations of paracetamol were much higher in the River Taff. This is because of the less effective wastewater treatment in WWTP Cilfynydd (92% removal in WWTP Cilfynydd and almost 100% removal of paracetamol in WWTP Coslech). Codeine was found to be removed from wastewater in only <50%. No removal of tramadol was observed in WWTP Cilfynydd (Fig. 2). However, treatment of wastewater at WWTP Coslech resulted in the removal of <40% of this compound.

The other anti-inflammatory/analgesics such as: ibuprofen, diclofenac, ketoprofen, naproxen, mefenamic acid, aspirin and its metabolite salicylic acid were quantified at lower levels due to their lower usage in the community (Tables 3 and 4). However, due to very often insufficient wastewater treatment, they were also quantified in the studied rivers at concentrations ranging from a few to few hundred $ng L^{-1}$. Generally, WWTP Coslech was characterised by higher efficiency of anti-inflammatory/analgesics removal. For example ketoprofen and naproxen were removed in <58% in the case of WWTP Cilfynydd and in >74% in the case of WWTP Coslech (Fig. 2). Aspirin and salicylic acid were characterised by very high (>98%) removal in both WWTPs and therefore were present in the receiving waters at relatively low concentrations. It was reported that analgesics such as ibuprofen and naproxen are removed from wastewater mainly due to their bio-degradability. As a result of low partition coefficient their removal through adsorption onto solid particles during primary treatment in sedimentation tanks or to the activated sludge is low (Bernhard et al., 2006; Carballa et al., 2004). Diclofenac, as opposed to other anti-inflammatory/analgesics, was not removed during either activated sludge or trickling filter beds treatment. Additionally, its concentrations were found to increase in treated wastewater when compared to raw wastewater. This phenomenon was also observed in the case of a few other studied pharmaceuticals (e.g. erythromycin, carbamazepine and sulfasalazine) and can result from several factors including hydrolysis of pharmaceuticals' conjugates.

The group of anti-inflammatory/analgesics is the most frequently studied in environmental matrices. Here again activated sludge treatment was frequently investigated. No reports on trickling beds efficiency in the removal of anti-inflammatory/analgesics were identified by the authors. Out of four anti-inflammatory/analgesics studied (ibuprofen, ketoprofen, naproxen and diclofenac) by Bendz et al. (2005), ibuprofen was removed from wastewater treated using activated sludge technology with the highest efficiency (96%), while only 22% removal was observed for diclofenac. Similarly, Lindqvist et al. (2005) reported 78–100%, 60–98%, 51–100%, 9–60% and 11–100% removal efficiency of ibuprofen, naproxen, ketoprofen, diclofenac and bezafibrate, respectively, at different WWTPs utilising activated sludge treatment. Yu et al. (2006) obtained similar results: 87, >99, 88, 77 and only 18% removal of ibuprofen, acetaminophen, naproxen, ketoprofen and diclofenac, respectively. No or negligible removal of diclofenac was observed by Lishman et al. (2006) and Spongberg and Witter (2008). Very high degradation of aspirin and ibuprofen was also observed by Nakada et al. (2006). The same research group revealed lower degradation efficiency of naproxen and ketoprofen. Jones et al. (2007) reported very high removal of paracetamol. These results are in agreement with data obtained in the discussed research and presented in other reports (Bernhard et al., 2006; Castiglioni et al., 2006a; Gómez et al., 2007; Jones et al., 2007; Joss et al., 2005; Lishman et al., 2006; Santos et al., 2007; Tauxe-Wuersch et al., 2005; Terzić et al., 2008). In contrast, Carballa et al. (2004) reported lower removal efficiencies of ibuprofen (60–70%) and naproxen (40–55%) than those discussed here. Boleda et al. (2007) studied the removal of codeine in several WWTPs utilising activated sludge treatment. The results varied for different WWTPs from −231 to 83%. Sixty-one percent removal of codeine was observed by Hummel et al. (2006).

3.1.1.3. Antiepileptic drugs. Neither carbamazepine nor gabapentin were removed during wastewater treatment in WWTP Cilfynydd. Carbamazepine, due to its poor bio-degradability, was also not removed in WWTP Coslech (Fig. 2). Furthermore, an increase of carbamazepine concentration was observed in some cases in WWTP effluent, which can be attributed to the hydrolysis of carbamazepine glucuronide conjugate and cleavage of free parent compound (Radjenović et al., 2007). The efficiency of gabapentin removal was on average 84% during activated sludge treatment in WWTP Coslech, which again proved the superiority of activated sludge treatment over trickling filter beds.

Bendz et al. (2005) and Nakada et al. (2006) revealed a much higher efficiency of carbamazepine removal (30% and >80%, respectively) during activated sludge treatment than the one observed in the discussed research and presented by others (Castiglioni et al., 2006a; Joss et al., 2005; Lindqvist et al., 2005; Santos et al., 2007; Spongberg and Witter, 2008). Gabapentin was hardly studied. Yu et al. (2006) observed >99% removal of this compound after activated sludge treatment, which is in agreement with the discussed results.

Because of limited degradation during wastewater treatment and high dispension rates in Wales (almost 3 tonnes a year) both compounds were found at very high concentrations in the receiving waters (Tables 3 and 4). Similar to the other groups of pharmaceuticals, discharge of treated

Table 5 – Concentrations of illicit drugs in the River Taff and WWTP Cilfynydd calculated for samples collected over the period of the 5-month monitoring programme (April 2007–August 2007).

Compounds	Concentration [ng L^{-1}]							
	River Taff				WWTP Cilfynydd			
	AC		PD		Influent		Effluent	
	L–H (M)	%	L–H (M)	%	L–H (M)	%	L–H (M)	%
Illicit drugs								
Amphetamine	<1*–11 (3)	57	2–13 (7)	100	292–12 020 (4310)	100	19–739 (201)	100
Benzoylecgonine	<1	0	3–92 (55)	100	126–2114 (992)	100	202–3275 (1091)	100
Cocaine	<0.3	0	<0.3–4 (2)	57	21–1837 (521)	100	48–324 (128)	100

L – the lowest recorded concentration; H – the highest recorded concentration; M – mean concentration; % – frequency of detection; <1* – below method quantification limit.

wastewater effluent into river water is the main reason for its contamination with antiepileptics. Low wastewater dilution factor in the studied rivers additionally increases the extent of contamination.

It is worth emphasising here that despite similar quantities of the two antiepileptic drugs dispensed in the Welsh community in 2006, their concentrations in raw wastewater were found to differ significantly (WWTP Cilfynydd: carbamazepine, ~1.7 μg L^{-1}; gabapentin, ~15 μg L^{-1}). Similar pattern was observed in surface water (Kasprzyk-Hordern et al., 2008c). This is because of different metabolism pathways of carbamazepine and gabapentin. While carbamazepine is almost entirely metabolised, gabapentin is excreted entirely as an unchanged drug and therefore it is found in raw wastewater at much higher concentrations.

3.1.1.4. *Beta-adrenoceptor blocking agents*. All three beta-adrenoceptor blocking drugs studied were found to be ubiquitous as they were quantified in all analysed samples including both wastewater and receiving waters (Tables 3 and 4). Concentrations of the three pharmaceuticals in wastewater and receiving waters decreased in the following order: atenolol > propranolol > metoprolol, and are strongly correlated with the amount of the active compound dispensed in the community (Table 2). Due to the low dilution factor of treated wastewater, concentrations of beta-blockers were high in receiving waters, reaching 500 μg L^{-1} in the case of atenolol. Wastewater treatment processes were found not to be effective enough to remove beta-blockers from treated wastewater (Fig. 2). Here again WWTP Cilfynydd resulted in no or only limited (with the exception of atenolol) reduction of beta-blockers in wastewater. WWTP Coslech, on the other hand, gave much better removal efficiency (33–81%), but unfortunately still not high enough to meet acceptable levels of contamination of receiving waters with beta-blockers. Lower beta-blockers degradation efficiency of activated sludge technology than the one reported in the discussed research was observed by others (Bendz et al., 2005; Terzić et al., 2008; Vieno et al., 2006). Mainly atenolol has been studied as a representative of beta-blockers. The efficiency of its removal during activated sludge treatment was assessed to be 10–55% (Castiglioni et al., 2006a).

3.1.1.5. *Lipid regulating agents*. Lipid regulating agents were detected in raw wastewater at much lower concentrations than other studied pharmaceuticals (Tables 3 and 4). Therefore, they were also only sporadically detected in river water at concentrations not exceeding 100 ng L^{-1}. Pravastatin and simvastatin, due to low distribution in the community, were found at very low concentrations in wastewater influent. Consequently, they were not detected at concentrations exceeding method quantification limits in any of the collected samples in both Taff and Ely rivers. Bezafibrate was the only studied lipid regulating agent that

Table 6 – Concentrations of illicit drugs in the River Ely and WWTP Coslech calculated for samples collected over the period of the 5-month monitoring programme (April 2007–August 2007).

Compounds	Concentration [ng L^{-1}]							
	River Ely				WWTP Coslech			
	TG		PSE		Influent		Effluent	
	L–H (M)	%	L–H (M)	%	L–H (M)	%	L–H (M)	%
Illicit drugs								
Amphetamine	<1*	0	<1–3 (1)	20	255–3225 (1196)	100	<3–11 (2)	14
Benzoylecgonine	<1	0	<1–54 (12)	60	187–3715 (1082)	100	<1–29 (13)	86
Cocaine	<0.3	0	<0.3	0	54–471 (207)	100	<1	0

L – the lowest recorded concentration; H – the highest recorded concentration; M – mean concentration; % – frequency of detection; <1* – below method quantification limit.

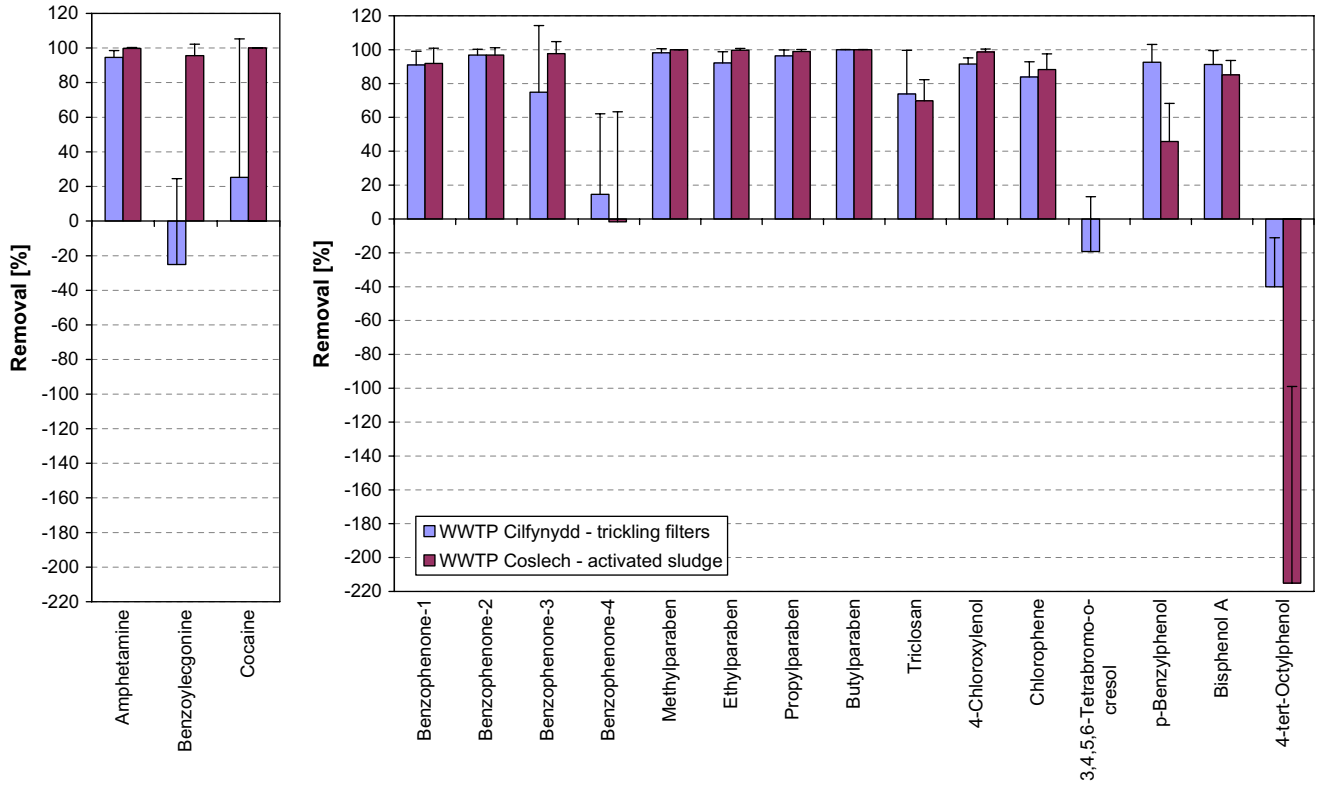

Fig. 3 – Efficiency of illicit drugs and personal care products removal during wastewater treatment calculated for samples collected over the period of the 5-month monitoring programme (April 2007–August 2007) in raw and treated wastewater.

Table 7 – Concentrations of personal care products and endocrine disruptors in the River Taff and WWTP Cilfynydd calculated for samples collected over the period of the 5-month monitoring programme (April 2007–August 2007).

Compounds	Concentration [$\mu g\,L^{-1}$]							
	River Taff				WWTP Cilfynydd			
	AC		PD		Influent		Effluent	
	L–H (M)	%	L–H (M)	%	L–H (M)	%	L–H (M)	%
Sunscreen agents								
Benzophenone-1	<0.3*–17 (4)	50	<0.3–9 (4)	50	46–400 (134)	100	<2–41 (18)	69
Benzophenone-2	<0.5–1 (0)	25	<0.5	0	9–247 (53)	100	<13–17 (4)	62
Benzophenone-3	<15–43 (9)	23	<15–44 (10)	25	<104–1068 (638)	58	<80–2196 (231)	38
Benzophenone-4	<3–45 (16)	92	53–302 (161)	100	1425–13 248 (3597)	100	818–4309 (2701)	100
Preservatives								
Methylparaben	<0.3–150 (29)	67	<0.3–144 (24)	58	661–15 646 (2819)	100	<3–155 (50)	69
Ethylparaben	<0.5–12 (5)	67	<0.5–11 (4)	58	192–1918 (589)	100	<0.6–69 (38)	92
Propylparaben	<0.2–11 (4)	50	<0.2–9 (4)	58	<2–1703 (598)	92	<1–95 (35)	77
Butylparaben	<0.3	0	<0.3	0	<2–114 (50)	58	<1	0
Disinfectants/antiseptics								
Triclosan	<5–11 (5)	57	<5–20 (6)	43	<97–240 (87)	86	<72–52 (25)	86
4-Chloroxylenol	<30–254 (57)	43	<30–225 (112)	86	4069–33 974 (15 792)	100	441–3010 (1565)	100
Chlorophene	<3	0	<3–16 (5)	71	27–258 (80)	100	<26–39 (16)	88
3,4,5,6-Tetrabromo-*o*-cresol	<1–44 (9)	29	<1–140 (20)	14	51–1362 (287)	100	288–1312 (419)	100
p-Benzylphenol	<15	0	<15–58 (25)	43	<94–517 (143)	29	<86–73 (9)	13
Other – endocrine disruptors								
Bisphenol A	<6–20 (4)	29	16–68 (31)	100	222–727 (416)	100	<105–237 (86)	75
4-*tert*-Octylphenol	<15	0	<15–536 (182)	57	16–558 (225)	100	418–1459 (724)	100

L – the lowest recorded concentration; H – the highest recorded concentration; M – mean concentration; % – frequency of detection; <0.3* – below method quantification limit.

Table 8 – Concentrations of personal care products and endocrine disruptors in the River Ely and WWTP Coslech calculated for samples collected over the period of the 5-month monitoring programme (April 2007–August 2007).

Compounds	Concentration [μg L^{-1}]							
	River Ely				WWTP Coslech			
	TG		PSE		Influent		Effluent	
	L–H (M)	%	L–H (M)	%	L–H (M)	%	L–H (M)	%
Sunscreen agents								
Benzophenone-1	<0.3–9 (3)	40	<0.3–13 (5)	30	51–700 (258)	100	<2–38 (12)	58
Benzophenone-2	<0.5	0	<0.5–26 (5)	40	61–403 (194)	100	<13–13 (4)	42
Benzophenone-3	<15	0	<15	0	<104–3975 (1195)	64	<80–223 (22)	8
Benzophenone-4	<3–144 (24)	40	32–323 (106)	100	2218–6084 (4152)	100	<10–6325 (3370)	75
Preservatives								
Methylparaben	<0.3–68 (17)	70	<0.3–305 (46)	70	4550–30 688 (11 601)	100	<3–36 (9)	50
Ethylparaben	<0.5–15 (3)	20	<0.5–12 (4)	40	715–3312 (2002)	100	<0.6–43 (4)	8
Propylparaben	<0.2–22 (7)	70	<0.2–10 (4)	70	820–8286 (3090)	100	<1–84 (26)	67
Butylparaben	<0.3	0	<0.3–16 (2)	10	274–1595 (723)	100	<1–2 (0)	8
Disinfectants/antiseptics								
Triclosan	<5–12 (5)	60	<5–24 (13)	80	33–463 (228)	100	13–82 (57)	100
4-Chloroxylenol	<30–99 (20)	20	<30–358 (157)	80	7811–65 381 (27 832)	100	<84–888 (318)	83
Chlorophene	<3	0	<3–3 (1)	20	37–141 (67)	100	<26–16 (8)	83
3,4,5,6-Tetrabromo-o-cresol	<1	0	<1	–	–	–	–	–
p-Benzylphenol	<15	0	<15–52 (10)	20	<94–1111 (349)	67	<86–214 (51)	33
Other – endocrine disruptors								
Bisphenol A	<6–17 (5)	40	<6–22 (12)	80	322–1163 (557)	100	31–99 (71)	100
4-*tert*-Octylphenol	<15–156 (31)	20	233–1293 (641)	100	<20–1151 (332)	50	2023–3949 (3216)	100

L – the lowest recorded concentration; H – the highest recorded concentration; M – mean concentration; % – frequency of detection; <0.3* – below method quantification limit.

was detected in all matrices with high frequency and relatively high concentrations. It was removed from treated wastewater with average 67% efficiency at WWTP Coslech. Only limited degradation of bezafibrate was observed during treatment at WWTP Cilfynydd. Castiglioni et al. (2006a) reported variable efficiency of bezafibrate removal during activated sludge treatment, which depended on the season and denoted 15% in winter and 87% in summer.

3.1.1.6. H2-receptor antagonists. Among H2-receptor antagonists, ranitidine, cimetidine and 5-aminosalicylic acid were found in raw wastewater at high concentrations exceeding on average 1.5 μg L^{-1} (Tables 3 and 4). Due to insufficient treatment in WWTP Cilfynydd and despite a higher dilution factor than in the case of WWTP Coslech, concentrations of H2-receptor antagonists in the River Taff were found to be higher than in the River Ely.

The efficiency of the removal of H2-receptor antagonists during activated sludge treatment has hardly been studied. Castiglioni et al. (2006a) studied ranitidine removal during activated sludge treatment. The efficiency of its removal from wastewater varied depending on season and denoted 39–84%, which was lower than the efficiency of the same technology in the discussed research (average 89%).

3.1.1.7. Other pharmaceuticals. Digoxin and its metabolite digoxigenin were the only pharmaceuticals not identified in any of the rivers studied, which is a result of the very low quantities of these pharmaceutical dispensed in the Welsh community (Table 2). Also, due to low usage and as a result low concentration in raw wastewater, bendroflumethiazide was not identified in WWTP effluent and receiving waters. On the other hand furosemide as well as valsartan and diltiazem were commonly present in wastewater and found in both the studied rivers at levels reaching 100 ng L^{-1} (Tables 3 and 4). Activated sludge treatment was again found to be superior to trickling filter beds for the removal of pharmaceuticals from sewage (Fig. 2). This group of compounds has hardly been investigated by other research groups. Both furosemide and salbutamol were studied by Castiglioni et al. (2006a) during activated sludge treatment. In contrast to the current research (salbutamol, 89%; furosemide, 74%), no removal of salbutamol and on average 8–54% removal of furosemide was observed (Castiglioni et al., 2006a).

The results obtained for all groups of pharmaceuticals studied clearly indicate that the activated sludge treatment is a much more efficient process than trickling filter beds for the removal of organic micropollutants although it still does not cause the removal of all micropollutants from wastewater. In general, out of all the pharmaceuticals studied only a few were characterised by low removal efficiency (<50%) during activated sludge treatment. These were: metronidazole (23%), diclofenac (−33%), codeine (42%), tramadol (36%), carbamazepine (−24%), propranolol (33%) and sulfasalazine (−79%). As opposed to activated sludge, the trickling filter beds technology utilised in WWTP Cilfynydd is characterised by rather poor efficiency as more than a half of the studied pharmaceuticals were not removed from wastewater with an

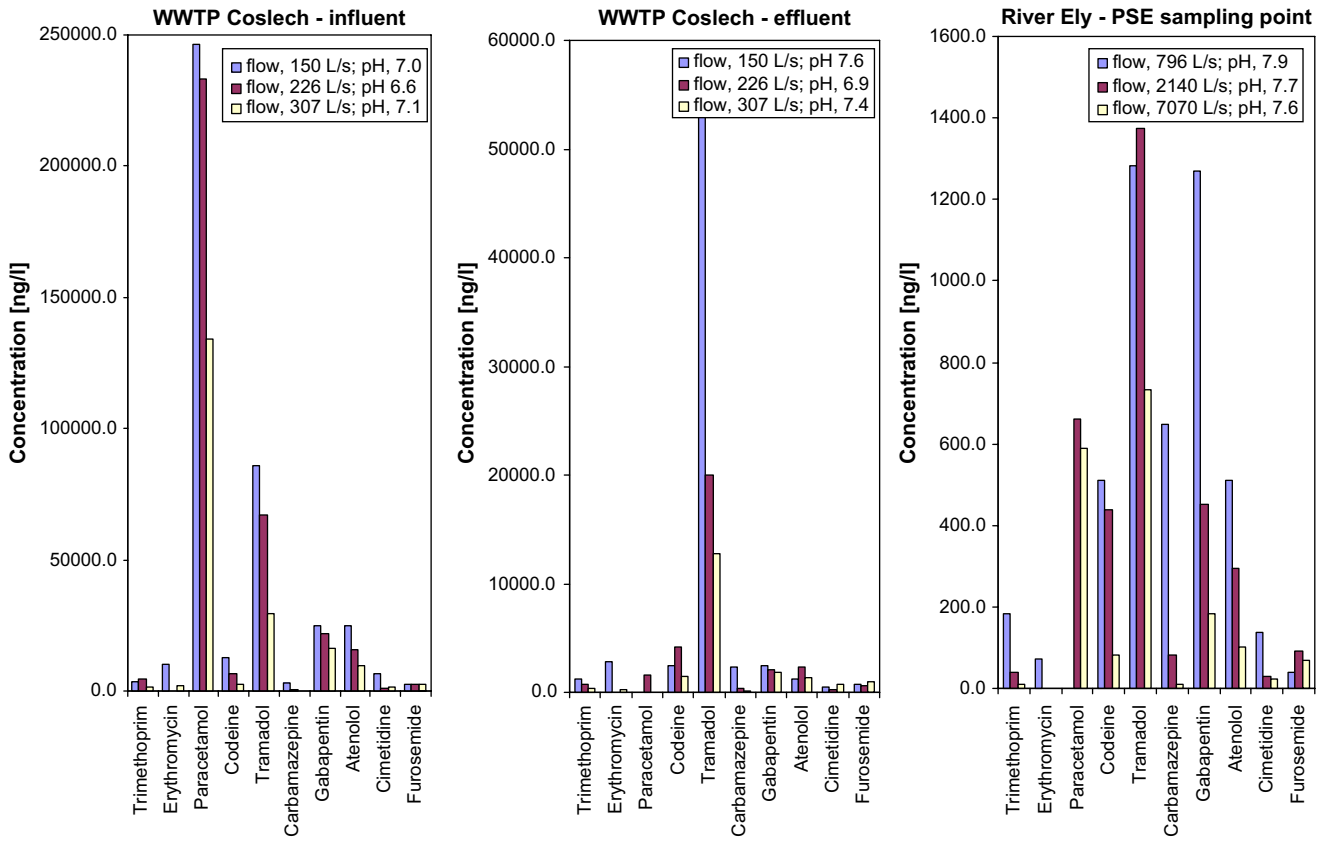

Fig. 4 – Concentrations of pharmaceuticals in WWTP Coslech (influent and effluent) and receiving waters at variable flow conditions (samples collected during four consecutive weeks: 12 June, 26 June, 03 July 2007).

efficiency exceeding 50%. These are for example: antibiotics (with an exception of chloramphenicol), several analgesics: diclofenac (−46%), tramadol (−18%), codeine (37%), antiepileptics, beta-blockers, H2-receptor antagonists and several other pharmaceuticals. It has to be, however, remembered that the activated sludge process results in the production of significant quantities of surplus activated sludge which is removed regularly from the process. This waste activated sludge is likely to adsorb significant quantities of non-biodegradable compounds of low polarity which are co-removed from the process with the waste activated sludge. In trickling filters the generation of waste activated sludge is significantly lower; hence fewer micropollutants are removed via the process of non-sludge removal.

3.1.2. *Illicit drugs*

Two illicit drugs were chosen for the research: amphetamine, cocaine and its main metabolite benzoylecgonine. There is interest in their presence in wastewater from both a forensic and an environmental perspective. First, illicit drugs are considered to be emerging environmental pollutants. Second, the knowledge of their concentration in raw sewage might be invaluable in estimation of the usage of illicit drugs in local communities (Zuccato et al., 2005).

Both cocaine and amphetamine were found with very high frequency in the River Taff at low levels of single ng L^{-1} (Kasprzyk-Hordern et al., 2008c). Their presence in the River Taff is again strongly associated with the discharge of treated wastewater effluent as is indicated in Tables 5 and 6. Benzoylecgonine was also often found in the River Taff but at levels 10 times higher than the parent compound. In the case of River Ely no cocaine was present in wastewater effluent and receiving waters. Lower concentrations of illicit drugs in the River Ely are strongly associated with lower concentrations (even despite the lower dilution factor) of illicit drugs in final effluent resulting from better efficiency of treatment in WWTP Coslech than WWTP Cilfynydd. As can be observed from Fig. 3 activated sludge treatment gives almost 100% removal of amphetamine, cocaine and benzoylecgonine, while trickling filter beds resulted in 95% removal of amphetamine, only 25% removal of cocaine and no removal of benzoylecgonine. This again indicates the poor efficiency of trickling filter beds technology when compared to activated sludge.

Very limited information exists on the presence of illicit drugs in environmental matrices. Castiglioni et al. (2006b) reported 88–100% degradation of benzoylecgonine, 95–100% degradation of cocaine and 100% degradation of amphetamine. Bones et al. (2007) reported 92% removal of benzoylecgonine and 72% removal of cocaine during activated sludge treatment.

3.1.3. *Personal care products and endocrine disruptors*

Among studied benzophenones, only benzophenone-4 was found at high concentrations exceeding 100 ng L^{-1} in both rivers. This was also the only benzophenone found at high concentrations in treated wastewater effluent due to

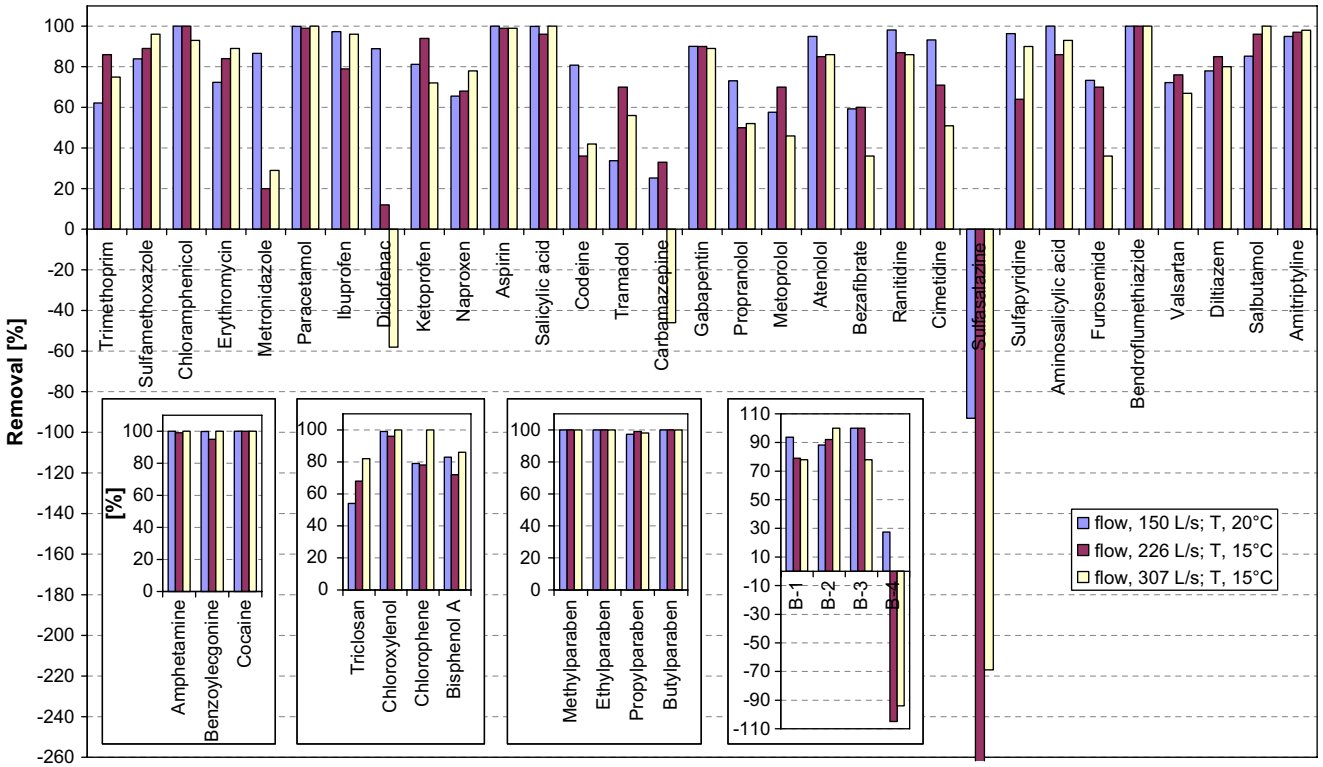

Fig. 5 – Efficiency of PPCPs degradation in WWTP Coslech at variable flow conditions (samples collected during four consecutive weeks: 12 June, 26 June, 03 July 2007).

insufficient wastewater treatment (Tables 7 and 8). Both activated sludge and trickling filter beds were found to have limited efficiency (<15%) in the removal of this compound from wastewater (Fig. 3). It is assumed that the above results from higher polarity of bnzophenone-4 than benzophenone-1, benzophenone-2 and benzophenone-3.

Both WWTP Coslech and Cilfynydd were found to remove preservatives (parabens) with a very high efficiency exceeding 90% and therefore these compounds were found in receiving waters less frequently and at lower concentrations (Fig. 3). Because methylparaben was frequently present in the raw sewage at the highest concentrations reaching 30 $\mu g\,L^{-1}$, it was also the most ubiquitous preservative found in the studied rivers. Much higher concentrations of parabens were recorded in raw wastewater treated in WWTP Coslech than in WWTP Cilfynydd, but due to more efficient activated sludge treatment these compounds were found in the River Ely at lower concentrations and with lower frequency than in the River Taff.

Among the disinfectants/antiseptics and endocrine disruptors studied only 4-chloroxylenol and 4-tert-octylphenol were found at concentrations exceeding 100 $ng\,L^{-1}$ in both rivers (Tables 7 and 8). These compounds were also found at high concentrations in raw sewage. Most disinfectants/antiseptics and endocrine disruptors were, with the exception of 3,4,5,6-tetrabromo-o-cresol and 4-tert-octylphenol, removed to a high extent during wastewater treatment (Fig. 3).

The comparison of the two wastewater treatment technologies utilised indicated that both technologies were efficient in the removal of the majority of personal care products and endocrine disruptors studied. While activated sludge treatment was found to provide higher efficiency in the removal of parabens (>99% efficiency) and some benzophenones, it was, however, identified as less efficient than trickling filter beds in the removal of *p*-benzylphenol belonging to the group of disinfectants/antiseptics (46% activated sludge; 93% trickling filters) and bisphenol A, an endocrine disruptor (85% activated sludge; 91% trickling filters). An advantage of trickling filters is that stable populations can become established or immobilised which are capable of degrading recalcitrant compounds whilst in activated sludge these particular bacterial species are washed out.

Only limited data is available for the occurrence and fate of personal care products during wastewater treatment. Bendz et al. (2005), Yu et al. (2006), Gómez et al. (2007) and Lishman et al. (2006) revealed, respectively, 58%, 69%, 88% and 93% degradation efficiency of triclosan during activated sludge treatment, which is in agreement with the data presented here. Triclosan undergoes biodegradation but due to its relatively high partition coefficient ($K_{ow} = 5.4$) it is also adsorbed to sludge (Gómez et al., 2007). Yu et al. (2006) also studied the removal of chlorophene. The obtained efficiency of 73% was lower than the one observed in this research. Gómez et al. (2007) reported results comparable with this research for bisphenol A (81%). Due to the particular properties of bisphenol A significant sorption to sludge is also expected. It has to be emphasised here that despite high removal efficiency of some personal care products, their possible effect on aquatic

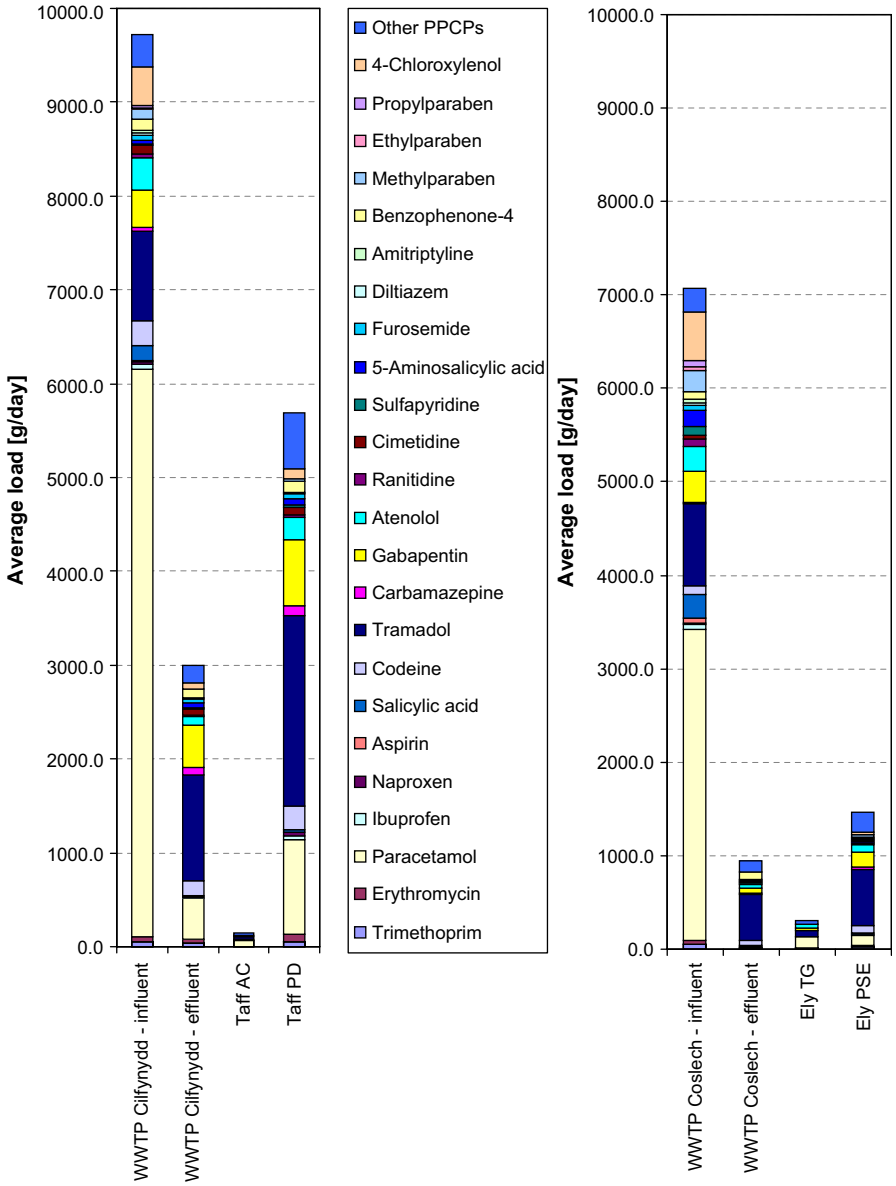

Fig. 6 – PPCPs average loads in WWTPs and receiving waters (calculated for the results obtained over the 5-month sampling period).

life cannot be underestimated as these compounds, as opposed to pharmaceuticals, can enter surface water directly as a result of human recreational activities.

3.2. *Influence of variable flow conditions on PPCPs concentration in wastewater and receiving waters*

The 5-month monitoring programme revealed that concentrations of the studied PPCPs directly depended on wastewater flow, which strictly related to the level of rainfall. The results for chosen PPCPs (those of the highest recorded average concentrations) analysed during the 4 weeks sampling regime at WWTP Coslech and the River Ely are presented in Fig. 4. Air temperatures during the sampling regime were 15–20 °C; pH values depended on the type of sample and are presented in Fig. 4. It can be observed for the majority of PPCPs that a twice as low flow of WWTP influent doubles the amount of studied contaminants. Similarly, rainfall affected concentrations of PPCPs in receiving waters, where in general, concentrations of PPCPs were found to be considerably higher during dry weather conditions and substantially decreased during wet weather conditions due to a significant dilution of river water with rain water.

The efficiency of the removal of PPCPs during wastewater treatment at WWTP Coslech was also found to be affected by variable flow conditions (Fig. 5), although more research is needed to draw explicit conclusions. In general lower efficiencies of PPCPs treatment were observed during wet weather conditions (e.g. metronidazole, ibuprofen, diclofenac, codeine, carbamazepine, beta-blockers, cimetidine and furosemide). However, in the case of several compounds (trimethoprim, erythromycin-H_2O, naproxen, salbutamol,

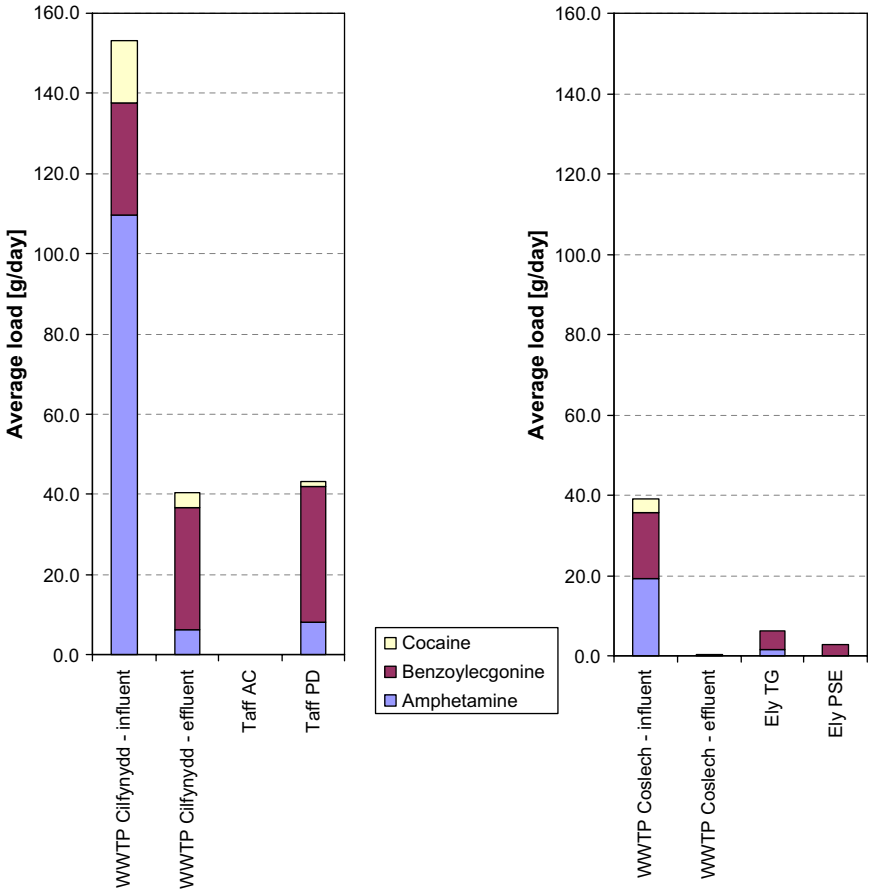

Fig. 7 – Illicit drugs average loads in WWTPs and receiving waters (calculated for the results obtained over the 5-month sampling period).

amitriptyline, triclosan and chlorophene) an increase of degradation efficiency was noted with an increase of flow rate of wastewater. This variation of treatment efficiency might be also affected by other parameters such as loading rate, solids retention time, sludge growth rate, temperature and light intensity. In the case of WWTP Cilfynydd, due to much poorer performance it was very difficult to find correlation between flows of wastewater and efficiency of trickling filter beds technology in the removal of PPCPs.

3.3. *Loads of PPCPs in WWTPs*

The calculated loads of all PPCPs in WWTP influent, effluent and rivers are presented in Figs. 6 and 7. The results clearly prove that WWTP effluent discharged into rivers is the main source of environmental contamination (see points Taff AC and Ely TG positioned before WWTPs and points Taff PD and Ely PSE located after WWTPs in Figs. 6 and 7). The comparison of the loads of PPCPs in the two rivers and WWTPs confirms the former discussion. WWTP Cilfynydd, a large wastewater plant serving over 100 000 inhabitants, receives sewage with higher loads of PPCPs than WWTP Coslech. Additionally, the less efficient trickling filter beds treatment system utilised in WWTP Cilfynydd is characterised by lower removal of PPCPs resulting in higher loads of PPCPs entering the river water. It is worth emphasising that the higher load of PPCPs in PD sampling point when compared with final WWTP effluent results from the fact that nearby there is also another WWTP (not discussed in this paper, see Section 2) that discharges treated effluent into the River Taff and contributes to the loads of PPCPs in receiving waters (PD sampling point).

It can be observed from Fig. 6 that a few kilograms of the studied PPCPs enter wastewater plants every day. The efficiency of their removal strongly depends on the wastewater technology implemented in WWTPs. In general, WWTP Cilfynydd resulted in on average less than 70% removal of 55 PPCPs studied. WWTP Coslech gave much higher removal efficiency of over 85%. As a result over 3 kg of studied PPCPs enter the River Taff with treated wastewater effluent from WWTP Cilfynydd while only on average 1 kg of PPCPs enters the River Ely with treated wastewater effluent from WWTP Coslech every day.

Loads of illicit drugs in WWTPs and receiving waters are presented in Fig. 7. Similar to the discussion above, much higher loads of illicit drugs are observed in WWTP Cilfynydd (influent: $>140\ g\ day^{-1}$; effluent: $>40\ g\ day^{-1}$) when compared to WWTP Coslech (influent: $<40\ g\ day^{-1}$; effluent: $<1\ g\ day^{-1}$). WWTP Cilfynydd is also characterised by lower efficiency. As a result high loads of illicit drugs are observed in the River Taff ($>40\ g\ day^{-1}$).

4. Conclusions

The manuscript presents the results obtained during the 5-month monitoring programme of PPCPs in wastewater and receiving waters in South Wales. Two contrasting wastewater treatment plants (WWTP Cilfynydd and WWTP Coslech) discharging treated wastewater effluent into two contrasting rivers (the rivers Taff and Ely) were the subject of the research. The research revealed that PPCPs are present at very high concentrations in raw sewage: average total 10 kg of 55 studied PPCPs in wastewater entering WWTP Cilfynydd and average 7 kg of PPCPs in wastewater entering WWTP Coslech every day, which indicates their high usage. The majority of PPCPs were abundant in both wastewater and receiving waters. Concentrations of PPCPs in raw sewage were found to correlate with consumption patterns in Wales and metabolism. Out of all the PPCPs studied here the following pharmaceuticals were found at the highest concentrations ($>10\,\mu g\,L^{-1}$) in raw wastewater: paracetamol, tramadol, codeine, gabapentin and atenolol. These compounds were also dispensed in the Welsh community in high quantities and/or were excreted by humans as unchanged drugs or conjugates. Rainfall was found to be another important factor influencing the level of concentrations of PPCPs in wastewater.

The efficiency of the removal of PPCPs strongly depended on the wastewater technology implemented in WWTPs. In general, WWTP Cilfynydd resulted in on average less than 70% removal of 55 PPCPs studied. WWTP Coslech gave much higher removal efficiency of over 85%. This is because WWTP Coslech utilises more efficient activated sludge treatment as opposed to WWTP Cilfynydd, where trickling filter beds are used to treat wastewater. In general, activated sludge technology was found to be more effective in the removal of all pharmaceuticals, illicit drugs and some personal care products and endocrine disruptors. The only PPCPs which were characterised by higher removal efficiency after trickling filter beds belong to the group of disinfectants/antiseptics (*p*-benzylphenol), endocrine disruptors (bisphenol A) and sunscreen agents (benzophenone-4). However, it has to be emphasised here again that successful removal of PPCPs from wastewater during activated sludge treatment does not indicate their degradation, as some PPCPs (especially non-polar compounds) might only undergo partitioning from wastewater into activated sludge without their complete mineralization. Therefore further study is needed to confirm set conclusions and fully understand the fate of PPCPs during wastewater treatment through extensive studies involving analysis of PPCPs not only in wastewater but also in sludge.

As a result of a discharge of treated wastewater over 3 kg of PPCPs were found to enter the River Taff every day with WWTP effluent from WWTP Cilfynydd, and on average 1 kg of PPCPs per day was found to enter the River Ely with WWTP effluent from WWTP Coslech. The monitoring programme revealed that wastewater effluents are the main contributors to PPCPs concentrations in the rivers studied. Bearing in mind that WWTP effluents are also the main contributors to rivers' flows (dilution factor for the rivers: only 23 times in River Taff and 13 times in River Ely) the effect of WWTP effluent on the quality of river water is significant and cannot be underestimated. An additional aspect that requires attention is that although both WWTPs treat wastewater to the required standards, an unsatisfactory removal of PPCPs is observed. This is of particular importance in water reuse, which is or will have to be implemented, especially in places with low water resources.

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