Behaviour of pharmaceuticals and personal care products in a sewage treatment plant of northwest Spain

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Abstract Thirteen pharmaceutical and cosmetic compounds have been surveyed along the different units of a municipal sewage treatment plant (STP) to study their fate across each step and the overall removal efficiency. The STP studied corresponds to a population of approximately 100,000 inhabitants located in Galicia (northwest Spain), including three main sections: pre-treatment (coarse and fine screening, grit and fat removal); primary treatment (sedimentation tanks); and secondary treatment (conventional activated sludge). Among all the substances considered (galaxolide, tonalide, carbamazepine, diazepam, diclofenac, ibuprofen, naproxen, estrone, estradiol, ethinylestradiol, roxitromycin, sulfamethoxazole and iopromide), only significant concentrations were found for two musks (galaxolide and tonalide), two antiphlogistics (ibuprofen and naproxen), two natural estrogens (estrone, estradiol), one antibiotic (sulfamethoxazole) and the X-ray contrast media (iopromide), being the other compounds below the quantification level. In the primary treatment, only the fragrances were partly removed, with efficiencies of 20–50% for galaxolide and tonalide. However, the aerobic treatment caused an important reduction in all compounds detected, between 35 and 75%, with the exception of iopromide. The overall removal efficiency of the STP ranged between 70 and 90% for the fragrances, 45 and 70% for the acidic compounds, around 67% for estradiol and 57% for the antibiotic sulfamethoxazole.

Keywords Pharmaceuticals; cosmetics; PPCPs; wastewaters; sewage treatment plant; adsorption

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Introduction

Municipal wastewater contains a multitude of persistent organic compounds derived from domestic application such as active ingredients in pharmaceuticals and personal care products, which are used in large quantities throughout the world. Here both groups will be collectively referred to as 'pharmaceuticals and personal care product ingredients' (PPCPs).

Some of the most representative PPCPs found in sewage treatment plants (STPs) are antibiotics, lipid regulators, anti-inflammatories, antiepileptics, tranquillizers, contrast media and contraceptives with very different chemical structures. Because of them, a considerable effort is being made in order to develop the analytical techniques needed to quantify their occurrence in effluents, but also to assess their chemical properties, their biodegradability potential, etc.

Recent studies have reported the presence of a large variety of PPCPs in STP effluents and surface waters, with concentrations up to several micrograms per litre (Hirsch *et al.*, 1999). In fact, more than 50 PPCPs have been detected during the last years in different environmental samples, due to the continuous improvement of the analytical techniques.

Many of these samples have been taken from wastewater (Buser *et al.*, 1999; Ternes, 1998), but also from surface or groundwaters (Buser and Müller, 1998).

PPCPs passing wastewater treatment systems are continuously infused to the environment via STPs discharges and are present in the feeding water (groundwater, bank filtrates, surface water) of waterworks. In some cases even drinking water is contaminated with PPCPs.

The continuous, widespread, long-term exposure of PPCPs to the environment and humans, although at low concentration levels, may result first in gradual almost hardly detectable changes. However, in the long run significant impacts on the environmental and human health cannot be excluded. In this way, within the V Marco Program of the European Commission, diverse research groups and companies from different countries have started up a project (POSEIDON) with the objective of determining the occurrence of PPCPs in the environment and to asses and improve the technologies for the removal of these compounds in STPs to prevent the contamination of receiving waters and groundwater.

Objectives

The objective of this work is to investigate the presence and behaviour of some PPCPs in an STP corresponding to a population of approximately 100,000 inhabitants. Compounds belonging to different therapeutical classes have been considered, such as anti-inflammatories (ibuprofen, naproxen, diclofenac); tranquillisers (diazepam); anti-epileptics (carbamazepine) and polycyclic musks (galaxolide, tonalide).

Materials and methods

The sewage treatment plant studied in this work corresponds to a population of approximately 100,000 inhabitants located in Galicia (northwest Spain). The plant includes three main sections: pre-treatment, primary treatment and secondary treatment (Figure 1). After the reception and pumping of the inlet wastewaters, the pre-treatment section comprises units for coarse screening (bar racks), fine screening and aerated chambers for grit and fat removal. The primary treatment is carried out in circular sedimentation tanks. Finally, the secondary treatment is carried out in biological reactors using the conventional activated sludge process (mixed reactors followed by a sedimentation tank). The supernatant of the

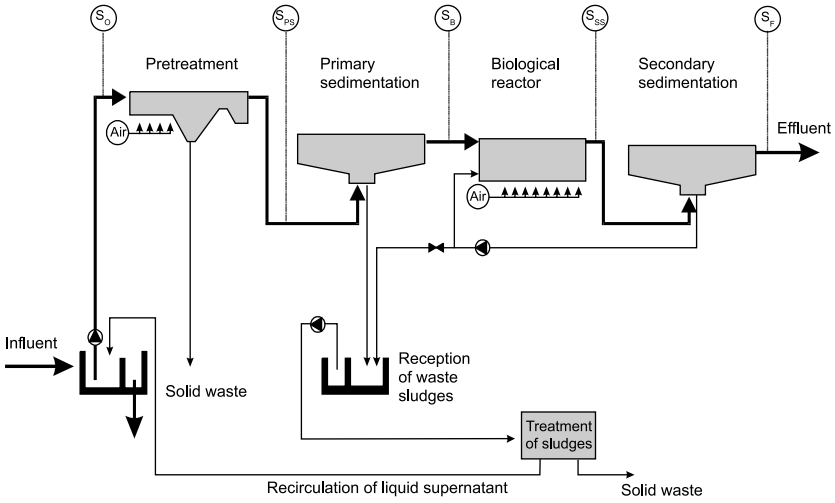

Figure 1 Flow sheet of the STP studied

secondary sedimentation unit constitutes the final effluent of the plant. The excess of secondary sludges, together with the solids obtained from the primary sedimentation, are treated in a specific unit from which a solid waste and a liquid stream, recycled to the inlet of the plant, are obtained (Figure 1). The sludge treatment comprises three steps: concentration (thickening or flotation), stabilisation (flocculation) and drying (filtration).

Total Solids (TS), volatile solids (VS), total suspended solids (TSS), volatile suspended solids (VSS), pH and total and soluble chemical oxygen demand (COD) were determined by *Standard Methods* (APHA–AWWA–WPCF, 1999). Total organic carbon (TOC) was measured with a Shimazdu model TOC-5000 total organic carbon analyzer, TOC concentrations were calculated by the difference between Total Carbon (TC) and Inorganic Carbon (IC). NO_2^-, NO_3^-, Cl^-, PO_4^{3-} and SO_4^{2-} were analyzed by Capillary Electrophoresis (Waters Capillary Ion Analyzer, CIA model). Sodium chromate was used as electrolyte (0.005 mol l^{-1}) as well as an electro-osmotic modifier CIA-PakTM OFM Anion BT (Waters) 0.46 mM (Ewing *et al.*, 1989).

The soluble content of the fragrances, anti-inflammatories, carbamazepine and diazepam was determined after solid-phase extraction (SPE) of 500 ml samples using 60 mg OASIS HLB cartridges (Waters, Milford, MA, USA). Meclofenamic acid and dihydrocarbamazepine were added to the samples as surrogate standards. All compounds were quantitatively eluted from the cartridge using 3 ml of ethyl acetate. This extract was then divided into two fractions: one of them was used for the direct determination of the soluble content of carbamazepine, diazepam and fragrances; the second one was employed for the determination of the anti-inflammatory species. In this case compounds were silylated previously to their gas chromatographic separation according to a previously published method (Rodríguez *et al.*, 2003). In both cases, GC/MS was used to determine the concentration of the investigated compounds in the SPE extract.

In the cases of galaxolide and tonalide, complementary methodology was used to determine the overall amount present in samples containing solids: the total load. A previously developed method (García-Jares *et al.*, 2002; Llompart *et al.*, 2003), based on an SPME (Solid Phase Micro Extraction) technique using PDMS/DVB fiber was used for this purpose. The whole sample, including the soluble fraction and the solid particles, was thermostatised and magnetically stirred during the extraction process. The SPME fibre was exposed to the headspace over the sample. After the sampling time (30 min), the fibre was desorbed into the GC injector and GC-MS analysis was performed.

Antibiotics, X-ray contrast media and estrogens were analyzed in Germany by the group of Dr. Ternes. For the first two groups, analyses were carried out by LC electrospray tandem MS after an enrichment step using an SPE method and elution with methanol (Hirsch *et al.*, 1999). Estrogens were analyzed by GC (ion trap) MS/MS after an enrichment step using an SPE method, elution with acetone and derivatisation with MSTFA/DTE/TMSI for 1 h at 60 °C (Ternes *et al.*, 1999a).

Quantification limits and recoveries are given in Table 1. Values given for the different samples of the STP considered in this work correspond to the mean value of two aliquots of each composite sample.

Results and discussion

Four integrated-sampling campaigns (24 hour samples) were carried out in different seasons: autumn (October 2001), winter (January 2002), spring (April 2002) and summer (June 2002). The points were liquid samples were taken are the following (Figure 1): (i) inlet to the grit removal unit (So); (ii) inlet to the primary clarification (Sps); (iii) inlet to the biological reactor (Sb); (iv) inlet to the secondary clarification (Sss), and (v) effluent of the plant (Sf).

The overall efficiencies achieved for COD and TSS along the entire STP were 80–94% and 92–94%, respectively.

Among all the substances considered in this work, the following have been detected in the investigated wastewaters: galaxolide and tonalide (musks), ibuprofen and naproxen (antiphlogistics), sulfametoxazole (antibiotic), estrone and estradiol (natural estrogens) and iopromide (contrast media). However, diazepam, carbamazepine, diclofenac, roxithromycin and ethinylestradiol were below the quantification limit (Table 1).

Apart from the usual variation between samples at the inlet of the STP (point So), all these compounds are present in the range of 0.6–6.6 $\mu g\,l^{-1}$. The two polycyclic musks, galaxolide and tonalide, were detected in the ranges 2.1–3.4 and 0.9–1.7 $\mu g\,l^{-1}$ respectively. These values are lower than those reported by Heberer *et al.* (1999) in surface waters in Berlin, which had high percentages of treated sewage (maximum concentrations of 10 $\mu g\,l^{-1}$). The acidic compounds, ibuprofen and naproxen, were detected in the ranges 2.6–5.7 and 1.8–4.6 $\mu g\,l^{-1}$, significantly higher than the ones previously reported by Stumpf *et al.* (1999) in a Brazilian STP influent, with concentrations around 0.3 and 0.6 $\mu g\,l^{-1}$, respectively.

In the cases of selected antibiotics, sulfamethoxazole was quantified with concentrations of around 0.6 $\mu g\,l^{-1}$ whereas roxithromycin was below the LOQ. According to the results reported by Hirsch *et al.* (1999) these values are in the same range as those reported for German wastewaters. Iopromide was found in the range of 6–7 $\mu g\,l^{-1}$, quite a high value comparing it with other studies (Ternes and Hirsch, 2000). Finally, the natural estrogens detected in these wastewaters were in the range of 2–3 $ng\,l^{-1}$ whereas ethinylestradiol was below the LOQ. These values are low, even in the case of natural estrogens, since previous works have given 15 and 27 $ng\,l^{-1}$ for estradiol and estrone, respectively, in municipal German STPs; or 21 and 40 $ng\,l^{-1}$, respectively, in Brazilian STPs (Ternes *et al.*, 1999a).

Fragrances are well removed during primary treatment, with most of the values around 40%, as well as the hormone estradiol (20%). These efficiencies calculated for both types of PPCP are closely related to those obtained for suspended solids which points that adsorption onto solid particles is the key mechanism involved. However, no significant reduction was observed in the pre-treatment and sedimentation steps for ibuprofen, naproxen, sulfametoxazole, estrone and iopromide, which is concordant with their acidic nature, with very low solid-liquid partition coefficients, which makes them to be present mainly in the liquid phase.

Table 1 Selected PPCPs and limits of quantification (LOQ) in nanograms per litre

Name	Application	CAS	Formula	LOQ	Recov.
Galaxolide	fragrance	1222-05-5	$C_{18}H_{26}O$	4	88%
Tonalide	fragrance	1506-02-1	$C_{18}H_{26}O$	6	90%
Diazepam	tranquilliser	439-14-5	$C_{16}H_{13}ClN_2O$	63	99%
Carbamazepine	antiepileptic	298-46-4	$C_{15}H_{12}N_2O$	74	67%
Diclofenac	anti-inflammatory	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	50	105%
Ibuprofen	anti-inflammatory	15687-27-1	$C_{13}H_{18}O_2$	20	90%
Naproxen	anti-inflammatory	22204-53-1	$C_{14}H_{14}O_3$	20	88%
Estrone	estrogen	53-16-7	$C_{18}H_{22}O_2$	1	75%
17β-Estradiol	estrogen	50-28-2	$C_{18}H_{24}O_2$	1	75%
17α-Ethinylestradiol	estrogen	57-63-6	$C_{20}H_{24}O_2$	1	75%
Roxitromycin	antibiotic	80214-83-1	$C_{41}H_{76}N_2O_{15}$	20	84%
Sulfamethoxazole	antibiotic	723-46-6	$C_{10}H_{11}N_3O_3S$	20	80%
Iopromide	contrast media	73334-07-3	$C_{18}H_{24}I_3N_3O_8$	20	82%

All the PPCPs detected, with the exception of iopromide, are removed during biological treatment with efficiencies between 30–75% for musks, 40–75% for antiphlogistics, around 70% for the antibiotic and 50% for the natural estrogen, estradiol.

With respect to the estrogens, estradiol was removed during the biological treatment (47%), being both the effluent of this unit and of the overall plant below LOQ. On the contrary, estrone concentrations were higher along all the different units, which agree with the fact that under oxidation conditions, estradiol is quickly converted into estrone, which is much slower degraded (Ternes *et al.*, 1999b). Taking into account the initial concentration of the estradiol (3 ng/l) and the limit of quantification (LOQ) of 1 ng/l, it can be assumed that 2 ng/l were removed, value that agrees with the concentration detected for the estrone.

Figure 2 shows the average removal efficiencies obtained for the compounds which were significantly affected by primary or secondary treatment. In the case of estrone, the values are negative since the fast reaction of estradiol causes the generation of estrone.

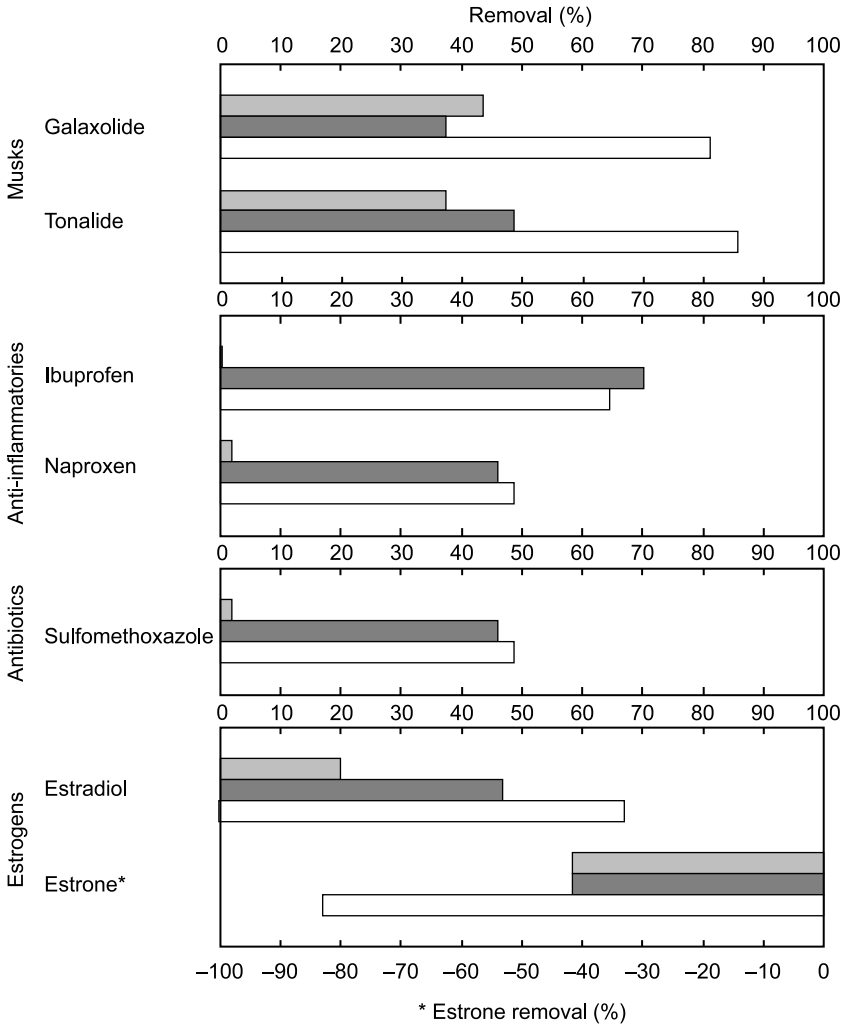

Figure 2 Removal efficiencies obtained for the PPCPs detected in the STP during primary (▒), secondary (■) and overall (□) treatment

A differentiation between adsorption and degradation during the removal process was not performed. However, for the investigated drugs no significant adsorption on sludge is expected, due to its physical-chemical properties.

Conclusions

The municipal wastewaters generated by a city of around 100,000 inhabitants in Galicia (NW Spain) have been screened for 13 PPCPs corresponding to different therapeutical groups (musks, antibiotics, tranquillisers, antiepileptics, antibiotics, estrogens and contrast media). Only 8 compounds were quantified (galaxolide, tonalide, ibuprofen, naproxen, sulfamethoxazole, estrone, estradiol and iopromide), being the others below the limits of quantification (carbamazepine, diazepam, diclofenac, roxithromycin and ethinylestradiol).

The eight compounds which were detected in raw wastewaters (galaxolide, tonalide, ibuprofen, naproxen, sulfamethoxazole, estrone, estradiol and iopromide) had a different behavior along the units of the STP.

During the primary treatment, the lipophilic properties of fragrances and estradiol facilitate their removal within fat separation. Besides, their good adsorption onto solid surfaces allows an important elimination in the primary settler to be obtained.

During the secondary treatment (conventional activated sludges) all compounds detected have been partially removed, with the exception of iopromide, which remained in the water phase. Most of estradiol was partially oxidized in the aeration tank, which explains the increase of estrone concentration in the effluent.

Acidic compounds, antibiotics, estrone and contrast media are not affected along primary treatment. However, musks and estradiol are significantly removed in the sedimentation steps with efficiencies between 20–50%. All substances, with the exception of iopromide, are partially eliminated during biological treatment, with efficiencies up to 30 and 75%. The overall removal ranged between 70–90% for the fragrances, 40–70% for the acidic compounds, around 67% for estradiol and 57% for the antibiotic sulfamethoxazole.

Adsorption of compounds onto solid particles plays an important role on the elimination of these substances, especially fragrances, since much higher concentrations of them have been detected in non filtered samples with high solids content. This adsorption mechanism is currently not completely understood and requires further studies.

According to these results, some modifications or improvements can be implemented in existing STPs. In the primary treatment (coagulation-flocculation and flotation units) the use of some additives as well as the proper adjustment of the operating conditions could be a tool to remove PPCPs from the water phase prior to the biological treatment. During biological treatment, the variation of operational parameters, such as solids retention time (SRT), or the combination of anoxic/aerobic steps could improve the efficiency.

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