

Occurrence and seasonal variability of personal care products (PCPs) in wastewater treatment and receiving soils

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Abstract. Clean water is a key resource for a series of activities, such as agriculture, power generation and public and industrial supplies. However, wastewater generated by these activities is released into the environment and may represent a potential risk to ecosystems and even human health depending on the presence of certain types and levels of contaminants. This study is focused on personal care products (PCPs), a class of emerging contaminants which includes commonly used cosmetic and personal hygiene products (e.g., fragrances, UV-filters, antimicrobials, surfactants and many others). We have monitored the concentrations of 66 PCPs in influent and effluent wastewater, sludge and compost samples from a wastewater treatment plant (WWTP) at Jerez de la Frontera (SW Spain) over a period of 1 year. Simultaneous analysis of target compounds was performed by means of stir bar sorptive extraction (SBSE) followed by gas chromatography/tandem mass spectrometry (GC-MS/MS). Pressurized liquid extraction (PLE) was used for solid samples. Most target compounds (> 60%) were frequently detected in influent wastewater samples. The highest concentrations were detected in summer and spring, probably related to higher human consumption and intense use of these compounds. Due to the low removal efficiencies for most chemicals (< 60%), 60 of them were always detected in the final effluent. The highest concentrations here were observed for octocrylene, tonalide, OTNE and galaxolide, an UV-filter and three synthetic fragrances, showing average concentrations of 13, 7, 6, 4 $\mu\text{g L}^{-1}$, respectively. Some target compounds such as nitro musks and galaxolide also showed removal efficiencies that were extremely low (< 10%). Concentration of these compounds in sludge and compost from Jerez de la Frontera WWTP were up to 3000 ng g^{-1} . Additionally, we carried out several sampling campaigns to collect soils samples from the area, where effluent wastewater from the WWTP is used for irrigation. Many of the same compounds often detected in effluent samples were detected at concentrations between < 1 and 300 ng g^{-1} in these soils samples.

Keywords: personal care products, sludge, compost, wastewater, soil.

1. Introduction

Over the past decade, several studies have shown evidence of personal care products (PCPs) being ubiquitous in surface water, groundwater, and even in receiving soils (Snyder *et al.*, 2003; Chase *et al.*, 2012). Improved analytical methodologies have lowered detection limits for these compounds to parts per trillion (ppt) levels even in the most complex of environmental matrices, leaving little doubt of their occurrence in water supplies around the globe. What remains, however, is a growing list of questions pertaining to the environmental fate of PCPs, the ecotoxicological and human health risks associated with their occurrence, and the ability of current water and wastewater treatment infrastructures to effectively remove these compounds.

The dominant route for PCPs entry into the environment is through effluents from domestic wastewater treatment plants. Accordingly, PCPs and their metabolites are often referred to as “effluent-derived” contaminants, originally present in wastewater from their use in medicinal and personal care products and ultimately discharged into municipal sewer systems as human waste products. The tendency for these compounds to persist or be only partially degraded during treatment or to bypass treatment altogether via sewage overflows will, therefore, contribute to their load in receiving waters, many of which serve as recreational and drinking water sources.

This research is focused on the detection of PCPs (and some regulated contaminants), in influent and effluent wastewater and sludge samples from Jerez de la Frontera WWTP (SW Spain) over a period of 1 year. Soil columns from an adjacent area irrigated with the final effluent of the WWTP were also analyzed. We aimed to identify those compounds most likely to persist during wastewater treatment and, therefore, to pose the greatest probability of exposure after effluent discharge.

2. Materials & Methods

2.1. Reagents

Water and solid samples were analyzed for 16 fragrances, 14 UV-filters, 16 PAHs, 12 organophosphate compounds, 6 PCBs, 1 antibacterial (TCS) and 1 insect repellent (DEET). Mixed standard solutions of PCPs were

purchased from different vendors; more details can be found in Pintado-Herrera *et al.* (2015).

2.2. Sampling Site and Sample collection

The sampling site selected for this work is the wastewater treatment plant (WWTP) at Jerez de la Frontera (SW Spain). Water samples were collected at the inlet and outlet of the WWTP (215 000 inhabitants) after secondary (activated sludge) and tertiary (UV irradiation) wastewater treatment processes. Sludge samples were obtained from a reactor carrying out the anaerobic digestion of primary and secondary sludge mixture. The resulting sludge is later composted and the final effluent is used for irrigation of adjacent green areas. Samples were also taken in these spots.

Sewage and sludge samples were collected on a monthly basis, whereas soil samples were taken every season from summer 2014 to summer 2015. Influent and effluent water samples were collected in 1L clean amber glass bottles. Sludge and compost samples were stored in glass containers previously rinsed. Soil samples at different depths from the surface (20, 40, 60, 90, 120 and 150 cm) were collected using hand auger equipment (Eijkelkamp). All samples were stored at 4 °C until analysis, performed within 24 hours.

2.3. Sample preparation

Water samples were filtered through 45 µm pore size glass fiber filters and extracted by stir bar sorptive extraction (SBSE) following the protocol described by Pintado-Herrera *et al.* (2014). On the other hand, extraction of analytes from solid matrices (sludge, compost and soil samples) was achieved by pressurized liquid extraction (PLE) using an accelerated solvent extractor ASE 200. Likewise, details on the extraction method can be found in Pintado-Herrera *et al.* (2016).

2.4. GC-MS/MS determination

The separation, identification and quantification of analytes were performed using gas chromatography (SCION 456-GC, Bruker) coupled to triple quadrupole mass spectrometry (SCION TQ from Bruker with CP 8400 Autosampler). Capillary gas chromatography analysis was carried out on a BR-5 ms column (30 m × 0.25 mm i.d. × 0.25 µm film thickness), keeping the carrier gas flow (helium) at 1 mL min⁻¹, and the transfer line and the injection port temperatures at 280°C. The column temperature ramp was as follows: 70°C for 3.5 min, increased at 25°C min⁻¹ to 180°C, then at 10°C min⁻¹ to 300°C, and held for 4 min. Injection volume was 1 µL in splitless mode and the solvent delay was set to 4.5 min.

3. Results and discussion

In the literature, the removal efficiency is generally computed as the percentage of reduction between the dissolved aqueous phase concentration of the contaminant in the influent and the dissolved aqueous phase concentration of the contaminant in the effluent.

Table 1 shows concentrations of PCPs by group in the influent and effluent of Jerez de la Frontera WWTP and the removal efficiencies (%) for these compounds.

The total concentrations of PCPs in the WWTP influent were higher than concentrations in the final effluent. The classes with the highest concentrations were fragrances (especially galaxolide, tonalide and OTNE) with values over 10 µg L⁻¹ on average, followed by UV-filters (4 µg L⁻¹) and organophosphate compounds (0.3 µg L⁻¹).

Due to the higher consumption of fragrances all year round, these chemicals showed higher concentrations in wastewater during all seasons. On the contrary, the highest concentrations of UV-filters (homosalate and octocrylene) and the insect repellent DEET were measured during the summer months. PCBs and PAHs were less relevant because their uses are restricted and were always at concentrations < 350 ng L⁻¹.

Figure 1 shows the annual average concentration ranges (box plots) for the top 8 most abundant PCPs in wastewater and sludge samples from Jerez de la Frontera WWTP. The greatest concentrations in water samples were observed at influent treatment and were one to two orders of magnitude higher than those for final effluents. Octocrylene (OC) showed the highest concentration due to UV-filter human consumption in summer months but, on average, OTNE showed the highest concentration (3630 ng L⁻¹) because fragrances are continuously used along the entire year. Differences were also observed between wastewater influent concentrations, which exhibited PCP levels between 96 – 3630 ng L⁻¹ (on average), and the average concentrations measured at the inlet sludge anaerobic tank, between 835 and 295602 ng g⁻¹. These results denote the hydrophobicity of these compounds and their strong sorption capacity to solid matrices.

Regarding the occurrence of PCPs in soils irrigated with effluent from the WWTP, this issue has been previously pointed out in sediments from the same area (Guadalete River) that are also impacted by sewage. In that sense, the levels of PAHs and PCBs reported here (Figure 2) were within the same range than those previously published by Lara-Martin and co-workers in a previous study with sediments from Cadiz Bay (2005), and very close to the levels reported and Pintado-Herrera *et al.* (2016).

Finally, the leaching potential for PCPs from the surface to deeper horizons in soils was assessed by comparing their vertical distributions at different depths (Figure 2) in soil columns from Jerez de la Frontera WWTP. These data suggest historical depositions over the last years as these compounds were detected along the entire length of the columns. Fragrances and UV-filters were predominant in these soils irrigated with effluents. Faster degradation processes in summer may explain the lowest values for fragrances in soils, which could be counteracted by highest inputs of UV-filters during that period. Regulated compounds such as PCBs show no variation and their presence could be also related to atmospheric inputs, as well as for PAHs.

4. Conclusions

The occurrence and removal of PPCPs in a WWTP was investigated during several seasons. Relatively poor removal efficiency (lower than 60%) was achieved for most of the target contaminants. The highest

concentrations were measured in sludge from the anaerobic reactor due to the strong PCP adsorption capacities derived

Table 1. Seasonal variability in the concentrations (ng L^{-1}) of target compounds in wastewater from the influent and effluent of Jerez de la Frontera WWTP. Removal efficiencies (%) are also shown.

		Fragrances	UV-filters	DEET	TCS	Organophosphate compounds	PCBs	PAHs
Summer	Influent	11957	2749	367	440	509	<LOQ	127
	Effluent	8974	1230	393	325	157	<LOQ	38
	Removal	25	55	0	26	69	-	70
Autumn	Influent	8802	1458	138	615	239	0	334
	Effluent	9198	97	398	209	187	0	177
	Removal	0	93	0	66	22	-	47
Winter	Influent	8755	308	0	514	201	<LOQ	75
	Effluent	11238	49	0	231	88	<LOQ	19
	Removal	0	84	-	55	56	-	75
Spring	Influent	12178	12323	460	424	655	-	237
	Effluent	8433	1902	331	174	209	-	80
	Removal	31	85	28	59	68	-	66
Year	Influent	10423	4209	241	498	401	<LOQ	193
	Effluent	9461	820	280	235	160	<LOQ	78
	Removal	9	81	0	53	60	-	60

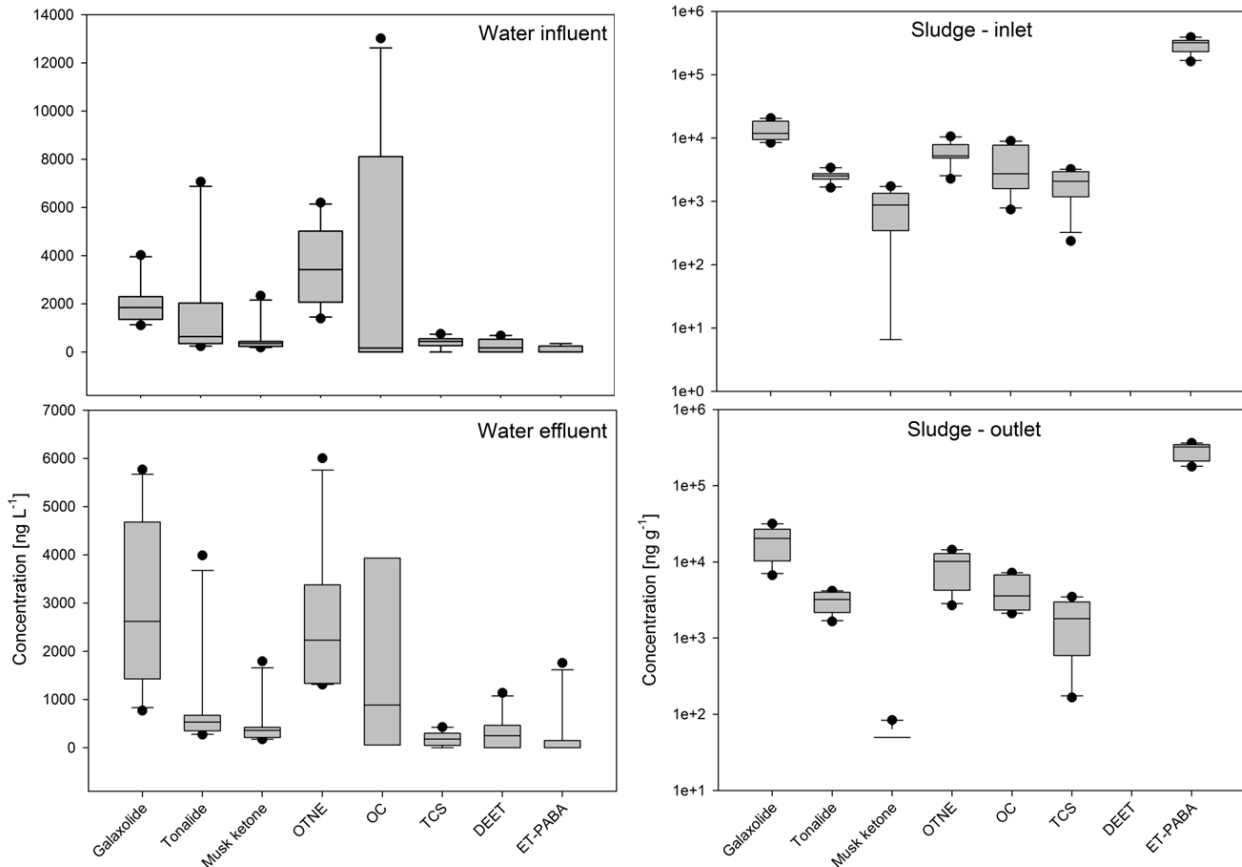


Figure 1. Top 8 most abundant PCPs (ng L^{-1}) in the influents and effluents on annual averages.

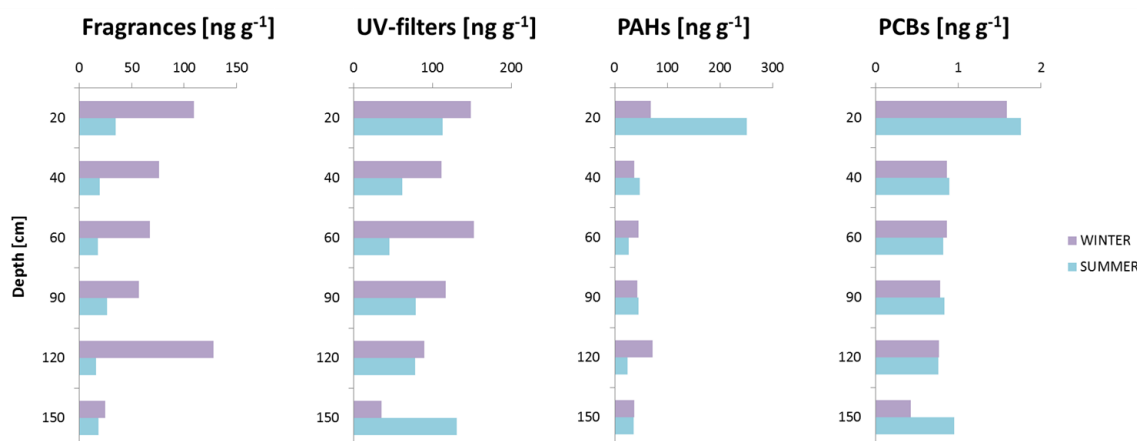


Figure 2. Vertical concentration profiles (ng g^{-1}) of emerging and priority contaminants in soil irrigated with the final effluent from Jerez de la Frontera WWTP.

from their high hydrophobicity. Fragrances and UV-filters were the most prominent groups of PCPs due to its highest consumption. Their occurrence not only in treated wastewater and sludge, but also in surface soils impacted by sewage and deeper layers revealed their potential for leaching after years of disposal into the terrestrial environment, which could lead to contamination of aquifers.

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