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Occurrence and removal of pharmaceuticals in a municipal sewage treatment system in the south of Sweden

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ABSTRACT

The occurrence and removal rate of seven pharmaceuticals (ibuprofen, naproxen, diclofenac, fluoxetine, ofloxacin, norfloxacin, ciprofloxacin), two metabolites (norfluoxetine, clofibric acid), one degradation product (4-isobutylacetophenone) and 3 estrogens (17α-ethinylestradiol, 17β-estradiol, estrone) were studied in the inlet and outlet of a tertiary sewage treatment plant (STP) in Sweden as well as between different treatment steps in the STP which includes a conventional activated sludge step. Pharmaceuticals in raw household and raw hospital sewage streams leading to the STP were as well investigated. Hydraulic retention times (HRT) of each treatment step was considered for sampling and for the calculation of the removal rates. These rates were above 90%, except for diclofenac, clofibric acid, estrone and ofloxacin. However, only diclofenac and naproxen showed significant effluent loads (>145 mg/d/1000 inh). Diclofenac was not eliminated during the treatment and in fact even higher concentrations were found at the effluent than in the inlet of the STP. 17α-Ethinylestradiol was not detected in any of the samples. Results indicate that a STP such as the one in Kristianstad, Sweden, with a tertiary treatment is sufficient to remove significantly most of the investigated pharmaceuticals. The chemical treatment improved the removal of several pharmaceuticals especially the antibiotics, which showed step removal rates between 55 and 70%. The expected concentration levels of the pharmaceuticals in the surface water (dilution 1 to 10) close to the outlet of the STP are below the no-observed effect-concentration (NOEC). However, despite that this would imply no important effects in the aquatic environment one cannot rule out negative consequences nearby the STP because most of the NOEC values are derived from acute toxicity data. This may underestimate the real impact of pharmaceuticals in the aquatic ecosystem.

1. Introduction

Sewage treatment plants (STPs) are designed to clean urban and industrial wastewater. The quality of the outgoing water is usually measured by parameters which quantitate the removal of nitrogen, phosphate, pathogens, particulate matter and metal ions (Lindquist, 2003). However, nowadays these operating plants are not designed to quantitatively remove other pollutants such as pharmaceuticals. Several studies have proved that a number of organic micropollutants, including pharmaceuticals and steroid hormones, are found in the effluent of STPs as well as in surface and groundwater (Halling-Sørensen et al., 1998; Kolpin et al., 2002; Kümmerer, 2004; Ternes, 1998). As a result, the impact of pharmaceuticals on aquatic life has been under debate for a number of years because the concentrations in treated wastewater streams of certain chemicals, *e.g.* steroid hormones, have been sufficiently high to induce adverse effects on fish or other aquatic

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organisms (Nagler et al., 2001). Therefore, in the last few years, large efforts have been made to improve STPs, often by introducing new steps designed to remove more efficiently contaminants like pharmaceuticals (Batt et al., 2007; Clara et al., 2005b; Jones et al., 2007; Kosjek et al., 2007; Nakada et al., 2007; Ternes et al., 2003). Nevertheless, many STPs in Europe include only two treatments steps (physical and biological) while few of them use a tertiary treatment or an advanced sewage treatment (*e.g.* ultrafiltration, flocculation, ozonation, advanced oxidation, or osmosis). The later treatments are seldom used because of their high cost. However, they are under extensive investigation due to the improvements they yield in the removal of organic micropollutants. The large differences among the STPs make the knowledge about treatment efficiency for pharmaceuticals imprecise. The removal rate (RR) of pharmaceuticals in STPs can, indeed, vary to a large extent. The treatment efficiency in STPs is significantly affected by several factors (Cirja et al., 2008), such as the physico-chemical properties of pharmaceuticals, the treatment processes employed, the age of the activated sludge (Clara et al., 2005a), the hydraulic retention time (HRT), and environmental conditions such as temperature and light intensity (Andreozzi et al., 2003). Knowing only the removal efficiency is not sufficient to understand if the pharmaceuticals are adsorbed into sludge (often used for soil amending), or whether they are biodegraded or abiotically degraded. Additionally, toxic degradation products occurring in the treated waste may not be identified if they are not explicitly addressed. Finally several pharmaceuticals are excreted as conjugates and can make a significant, but poorly understood, contribution after release of the active moiety by cleavage during treatment in STPs.

One of the first studies about the occurrence and removal rates of drugs in an STP was carried out by Ternes et al. (1999). They reported concentrations of estrogens in German and Canadian STP effluents. The elimination load (g/d) was measured comparing the influent and effluent of an STP in Brazil and one in Germany over a period of 6 d. Not until recent years this research area has become of greater interest resulting in many publications. Generally removal rates, mostly described as the difference in gram per day per 1000 inhabitants between influent and effluent (Castiglioni et al., 2006; Gros et al., 2007; Vieno et al., 2007), are investigated. However, other information can occasionally be found, such as the contribution of STP effluent to the presence of pharmaceuticals in natural waters (Gros et al., 2007), the ratio of removal by sorption or biological transformation (Joss et al., 2005), the removal rate by activated sludge process (Jones et al., 2007), the concentration of pharmaceuticals after a treatment involving activated sludge, sand filtration and ozonation (Nakada et al., 2007), seasonal variations, and/or pharmaceutical concentration comparisons between the inlets and outlets of different STPs (Castiglioni et al., 2006; Clara et al., 2005b; Vieno et al., 2007).

In work reported in this paper we have studied the occurrence of a number of priority pharmaceuticals, two metabolites and one toxic degradation product, in the sewage treatment system of Kristianstad (Sweden). To facilitate a general discussion about the fate of pharmaceuticals in a sewage system, the chosen substances also represent a wide range of physicochemical properties (Table 1). As a consequence, the methodology for analysing them has demanded the development of several analytical methods, which are thoroughly described in our previous work (Zorita et al., 2008a,b,c; 2007a,b). For the first time, samples have been taken from sewage pipes from a residential area and from hospital outlet leading to the treatment plant, as well as at the inlet, the outlet, and between different treatment steps within the STP, giving additional and useful information on the effects of the different treatment steps on the removal of pharmaceuticals. Overall rates were monitored as well. For some of the target compounds, the removal rates in STPs have not been previously determined.

2. Materials and methods

2.1. Chemicals

Ibuprofen, naproxen, diclofenac sodium salt, clofibric acid, norfloxacin, ofloxacin, 4-isobutylacetophenone (4-IBAP), estrone and 17α-ethinylestradiol, fluoxetine and norfluoxetine were obtained from Sigma-Aldrich (Stenheim, Germany). Ciprofloxacin and 17β-estradiol were purchased from Fluka (Buchs, Germany). Surrogate internal standards (IS) were enrofloxacin from Fluka, 4-butylacetophenone, estrone-d4 and 17β-estradiol-d3 from Aldrich, and ibuprofen-d3 and 17β-ethinylestradiol-d4 from CDN isotopes (Point-Claire, Quebec, Canada). All other chemicals were obtained as previously reported. Physicochemical characteristics of the analytes are given in Table 1.

2.2. Sampling and description of the sewage treatment plant

Samples were collected from streams from a household sewage pipe (*ca.* 800 m^3/d, O samples), from a city hospital sewage pipe (*ca.* 450 m^3/d, H samples) and from the STP in Kristianstad, South Sweden (samples STP 1-STP 5). STP water quality parameters are given in Table 2. The plant handles a 150,000 population equivalent, due to the large food industry present in the area *e.g.* slaughter house, dairy and distillery, although the STP only serves 55,000 inhabitants. The average flow on a yearly basis through the plant is *ca.* 20,000 m^3/d. Based on this flow, the average total hydraulic retention time (HRT) was calculated as *ca.* 35 h. The total removal of nitrogen is about 75%, BOD 99% and COD 99%. The STP is designed to encompass three treatment steps (Fig. 1).

The primary step, known as *mechanical treatment*, removes coarse particles. The sewage water entering the plant first passes through a set of screens with openings of 3 mm followed by a grit-aerated chamber (sand trap). After this the remaining suspended contaminants settle in a larger sedimentation basin, which has a volume of 2600 m^3. The second step is the *biological treatment* that separates and breaks down organic contaminants, *e.g.* nitrogen and BOD/COD, with the aid of microorganisms. The biological process consists of an anoxic step followed by larger aerobic decomposition. In order to obtain a more efficient biological process in the aeration basin, an activated sludge process is used involving recycling of *ca.* 90% of the sludge giving an average solid retention time (SRT) of 8±2 d. The biological step has a volume of 10,530 m^3. The flow entering the biological treatment is half of the incoming flow due to a parallel treatment step. For removal of phosphorus a *chemical treatment* is used as the third step. In