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Influence of seasonal climate differences on the pharmaceutical, hormone and personal care product removal efficiency of a drinking water treatment plant

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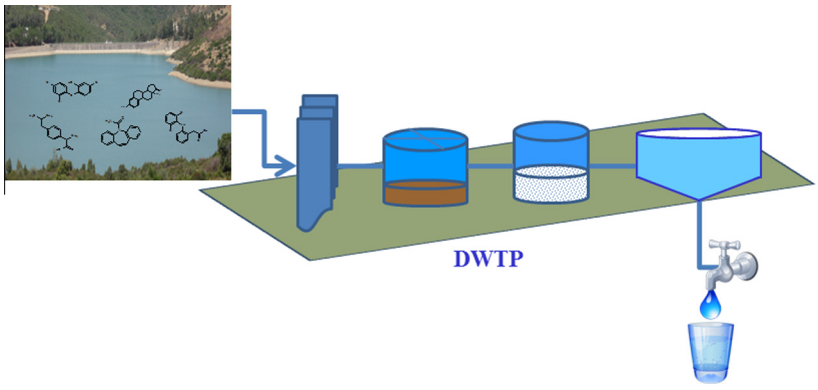
HIGHLIGHTS

- Pharmaceuticals, hormones and personal care products at different stages in the DWTP was studied.
- Raw water samples collected in warm periods contain lower levels of most of the analytes.
- Treatment steps most markedly contributing to removal were pre-oxidation and chloramination.
- The overall removal efficiency of the DWTP exceeds 99.8% for all target compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

The potential presence of pharmaceuticals, hormones and personal care products in drinking water supplies has raised concerned over the efficiency with which these substances are removed by water treatment processes. In this work, we analyzed samples of raw, unprocessed water collected in different periods and found them to contain higher levels of these contaminants in the colder periods (viz. 12–314 ng L^{-1} in autumn and winter as compared to 8–127 ng L^{-1} in spring and summer) as a result of their biodegradation being favoured by high temperatures and solar irradiance. We also assessed the efficiency with which these contaminants are removed from drinking water by a water treatment plant operating in south-eastern Spain. Preoxidation with potassium permanganate and chloramination with sodium hypochlorite in the presence of highly concentrated ammonia were found to be the treatment steps most markedly contributing to the removal of pharmaceuticals, hormones and personal care products from drinking water (especially in the warmer periods, where these contaminants were completely removed from the water). By contrast, water treated in the colder periods (autumn and winter) still contained small amounts of ibuprofen and carbamazepine (0.09–0.5 ng L^{-1}) which, however, accounted for less than 0.2% of their original concentrations in the water prior to treatment.

1. Introduction

Pharmaceuticals, personal care products and endocrine disrupting chemicals including hormones, many of which have adverse ecological and human health effects, have recently been identified as emerging organic contaminants in environmental waters (Ying, 2007; Benotti et al., 2009; Kumar and Xagoraraki, 2010). These substances are frequently detected in streams receiving agricultural, domestic and/or industrial wastewater effluents. The adverse effects of pollution by pharmaceuticals include aquatic toxicity, resistant development in pathogenic bacteria, genotoxicity and

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endocrine disruption (Ying, 2007; Kümmerer, 2009; Bruce et al., 2010). The frequent presence of these substances in streams (especially in those used as sources of drinking water) has raised concern over that in drinking water and hence over their potential effects on human health through chronic exposure. In response, environmental scientists are seeking ways to efficiently remove pharmaceuticals and other priority pollutants from sources such as hospital and domestic wastewater prior to discharge (Stackelberg et al., 2004). Sewage treatment processes were not initially designed to specifically remove pharmaceuticals, hormones and personal care products from sewage influents; as a result, their ability to remove these substances depends not only on that of sorbents to retain solid particles (activated sludge) or the contaminants to biodegrade naturally (Loraine and Pettigrove, 2006; Santos et al., 2009). Pharmaceuticals, hormones and personal care products not readily degraded by sewage treatment plants are discharged into receiving waters in modified or unchanged forms usually forming complex mixtures of many compounds in treated effluents. These compounds contaminate rivers, lakes, estuaries, and also, in some instances, drinking water. Effective removal of pharmaceuticals, hormones and personal care products in addition to other priority pollutants from wastewater prior to discharge has thus become an emerging issue in environmental science and engineering.

The efficiency of drinking water treatment plants (DWTPs) in removing pharmaceuticals, hormones and personal care product depends on the particular processes they use. Thus, coagulation, flocculation and precipitation are ineffective for removing many dissolved organic contaminants (Ternes et al., 2002; Westerhoff et al., 2005). On the other hand, oxidative processes based on ozone (Zwiener and Frimmel, 2000; Adams et al., 2002; Ternes et al., 2002; Huber et al., 2003, 2005; Snyder et al., 2006; Lee et al., 2008), chlorine (Pinkston and Sedlak, 2004; Chamberlain and Adams, 2006; Gibs et al., 2007; Stackelberg et al., 2007; Lee et al., 2008), chlorine dioxide (Lee et al., 2008), monochloramine or potassium salts of permanganate (Ma et al., 1997; Hu et al., 2009) and ferrate (Lee et al., 2008; Hu et al., 2009) effectively reduce the concentrations of several classes of microcontaminants including some pharmaceuticals, hormones and personal care products. However, the efficiency with which these substances are removed from water depends on their initial concentration, physico-chemical properties (e.g. octanol–water partition coefficient, solid–water partitioning characteristics) and degradation pathway (which may produce toxic metabolites), in addition to some characteristics of the water containing them and the operating conditions used at the treatment plant. Ternes et al. (2002) examined the ozone-based removal of five pharmaceuticals at both the laboratory and a full-scale drinking water treatment plant, and found only diclofenac and carbamazepine to be removed by more than 90% by the purification treatment. Soufan et al. (2012) succeeded in removing more than 95% of all diclofenac by chlorinating water. Zwiener and Frimmel (2000) conducted oxidation tests to degrade acetylsalicylic acid, ibuprofen, diclofenac, bezafibrate, clofibric acid and fenofibric acid with ozone and found that only about 3% of the initial amount of diclofenac was degraded; however, using ozone and hydrogen peroxide in combination boosted hydroxyl radical formation and improved the degradation efficiency for all compounds as a result.

In this work, we investigated in greater detail the efficiency of a conventional DWTP in removing a variety of pharmaceuticals (analgesics, non-steroidal anti-inflammatories, antibacterials, anti-epileptics, β-blockers and lipid regulators), personal care product and hormones, in order to identify the specific target compounds most susceptible and resistant to removal by water treatment. The removal efficiency of different treatment steps including preoxidation/coagulation, sedimentation, filtration and chloramination was examined separately. We also investigated the potential influence of the environmental conditions (temperature, rainfall, solar irradiance) on the overall removal efficiency and that of each individual step, and also on the concentrations of the target analytes in the water sources feeding the treatment plant. These environmental conditions have been found in several studies to be the most relevant to degradation of various organic compounds.

2. Materials and methods

2.1. Chemicals and reagents

All products were handled with care, using latex gloves, a respiratory protection device and fume foods. The pharmaceuticals (acetylsalicylic acid, carbamazepine, chloramphenicol, clofibric acid, diclofenac, florfenicol, flunixin, ibuprofen, ketoprofen, mefenamic acid, metoprolol, naproxen, niflumic acid, paracetamol, phenylbutazone, propranolol, pyrimethamine and thiamphenicol), hormones (17α-ethinylestradiol, 17β-estradiol and estrone) and a personal care product (triclosan) were supplied in the highest available purity by Sigma–Aldrich (Madrid, Spain). The internal standard (triphenylphosphate) and the derivatizing reagents [N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS)] were purchased from Fluka (Madrid, Spain). Oasis-HLB (particle size 50–65 μm) was obtained from Waters (Madrid, Spain). Methanol and ethyl acetate (chromatographic grade), were supplied from Merck (Darmstadt, Germany). Millex-LG filter units (hydrophilic, PTFE, pore size 0.20 μm, diameter 25 mm, filtration area 3.9 cm^2) were supplied by Millipore Ibérica, S.A. (Madrid, Spain).

Stock standard solutions of the individual pharmaceutical, hormones and personal care product at a 1 g L^{-1} concentration each were prepared in methanol and stored at 4 °C in the dark. Standard working-strength solutions were prepared by sequential dilution of each standard with water previously purified by passage through a Milli-Q System from (Millipore, Bedford, MA, USA) and adjusted to pH 7.

2.2. Instrumentation

All analyses were carried out on a Focus gas-chromatograph coupled to a DSQ II mass spectrometer equipped with an AI/AS 3000 autosampler and controlled by a computer running XCalibur software (Thermo Electron SA, Madrid, Spain). The target analytes were separated by using a DB-5 fused silica capillary column (30 m × 0.25 mm i.d., 0.25 μm) coated with 5% phenylmethylpolysiloxane (Supelco, Madrid, Spain). Helium (purity 6.0) at a flow of 1 mL min^{-1} was employed as the carried. For the analytes determination, the column temperature was initially kept to 70 °C for 1 min, raised to 150 °C at 14 °C min^{-1}, and then to 290 °C at 6 °C min^{-1}. The injection port and transfer line temperatures were kept at 270 and 280 °C, respectively. The ion source temperature for the 70 eV electron impact ionization mode was 200 °C. The mass spectrometer was operated in the selected ion monitoring (SIM) mode. The MS instrument was set in full scan mode (60–500 amu) for the quantification of the analytes. For each silyl derivative, $M^{+\cdot}$, $[M-15]^+$, and other additional ions were monitored which are included in Table 1, where $M^{+\cdot}$ is the molecular mass and $[M-15]^+$ is the molecular mass minor 15 corresponding to the loss of a CH_3 of the $Si(CH_3)_3$ group. The time of solvent delay was set to 8 min. In all analyses, a volume of 1 μL of the silylated derivatives was injected in the split mode (1:20 ratio) and the resulting peak area was used as analytical signal for quantification.

The continuous solid-phase extraction system was assembled from a Gilson Minipuls-3 peristaltic pump (Villiers-le-Bel, France) fitted with poly(vinylchloride) tubes, two Rheodyne 5041 injection