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Influence of seasonality and vegetation on the attenuation of emerging contaminants in wastewater effluent-dominated streams. A preliminary study

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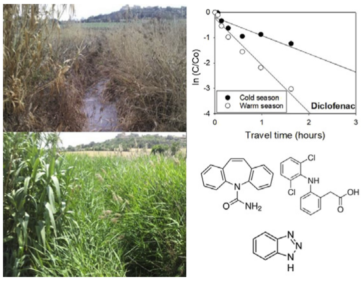
HIGHLIGHTS

- The attenuation of ECs 1 km downstream ranged from no removal to up to 80%.
- The half-lives of ECs in the 4 streams ranged from 0.4 to 20 h (3.9 ± 3.5 h).
- The in-stream attenuation of ECs showed a high seasonality.
- The stream covered by vegetation had the shortest half-lives for most of the ECs.
- All streams were capable of decreasing the cumulative acute HQ 1 km downstream.

GRAPHICAL ABSTRACT



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ABSTRACT

Treated wastewater from small communities is discharged into rivers or streams with a high biodiversity value. This is particularly important in Mediterranean countries, where most of the streams are dry almost all year round. This preliminary study assessed the occurrence and attenuation of 23 emerging contaminants (ECs) in 4 wastewater-dominated streams in which treated wastewater accounted for the entire stream flow. The concentration of ECs was monitored in the warm and cold seasons in the wastewater treatment plant (WWTP) effluent and at 6 downstream locations. The concentration of ECs in the WWTP effluents ranged from undetected to 12 μg L^{-1}. The attenuation of ECs 1 km downstream ranged from no removal to up to 80% (48% on average). The half-lives of ECs in the 4 streams ranged from 0.4 to 20 h (3.9 ± 3.5 h on average). Compounds such as benzodiazepine drugs and flame retardants were the most recalcitrant (half-lives >5 h). The highest attenuation of ECs and ammonia was observed in the stream completely covered by vegetation. The cumulative hazardous quotient 1 km downstream was reduced on average by more than 60%. Therefore, the results suggest that both seasonality and vegetation play an important role in in-stream attenuation of ECs.

1. Introduction

A large part of the world's population lives in small communities located in remote areas, where sewage is still generally poorly treated or even untreated and is usually discharged into rivers or streams with a high biodiversity value (Molinos-Senante et al.,

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2014). This is particularly important in Mediterranean countries, where streams are dry almost all year round. Such wastewater-effluent-dominated streams support perennial-stream ecosystems that would not otherwise exist. At the same time, ecosystems downstream of effluent discharges can improve water quality, support water re-use, and offer various societal benefits, including enhanced and novel riparian and aquatic habitats, improved aesthetic values, and higher rates of groundwater recharge (Luthy et al., 2015). However, biota in wastewater-dominated streams is exposed to high concentrations of pollutants (in the ng L^{-1} to low μg L^{-1} range), such as emerging contaminants (ECs) (Brooks et al., 2005; Lee and Rasmussen, 2006; Acuña et al., 2015). Some of the potential environmental effects of the presence of ECs in surface waters are the reduction of the biological community structure in rivers (Muñoz et al., 2009), declining fish populations in lakes (Kidd et al., 2007), and physiological stress in freshwater mussels (Gillis et al., 2014). The evaluation of the hazard quotient (HQ) between the chemical composition of the water samples and the predicted no-effect concentration (PNEC) for different water organisms (*Daphnia* sp., green algae, and fish) has been used extensively to assess the effect of the presence of these compounds in surface water bodies (EPA, 1998).

Once ECs are discharged into the aquatic environment they are exposed to different attenuation processes such as photodegradation, sorption, and biodegradation, but these processes are highly dependent on environmental conditions such as solar radiation, sediment characteristics, or the presence of microbial communities (Kunkel and Radke, 2012; Al-Khazrajy and Boxall, 2016). In this regard, in-stream attenuation has received considerable attention in recent years due to its high capacity for removing ECs (Fono et al., 2006; Writer et al., 2013; Acuña et al., 2015; Li et al., 2016). For instance, Acuña et al. (2015) observed that the in-stream attenuation half-life of ECs in 4 Iberian streams ranged from less than 2 h for compounds such as ibuprofen and acetaminophen to more than 28 h for compounds such as diazepam. Different results have been reported in other countries. For example, carbamazepine, which has been shown to have a half-life of 4.1 h in Iberian rivers (Spain), has been found to have a half-life of up to 21 h in a river in Colorado (USA) (Writer et al., 2013). In general, the results show a high variability, which may be due to the different climate conditions or to river size, shape, or structure. In fact, little attention has been paid to the effect of seasonality and the presence of vegetation on such attenuation. Moreover, most of the studies performed to date assess streams in which treated wastewater effluent accounts for between 1 and 80% of the total stream flow.

This study aimed to evaluate the effect of seasonality and the presence of vegetation on the attenuation of 23 ECs in 4 Mediterranean streams (NE Spain) in which treated wastewater accounts for the entire stream flow. Additionally, an aquatic risk assessment study was performed based on the HQs for *Daphnia* sp., green algae, and fish at acute and chronic levels.

2. Material and methods

2.1. Description of the sampling sites

The studied streams received treated wastewater from 4 WWTPs located in north-east Spain. The WWTP systems were as follows: an extended aerated system located in Mon Roig del Camp (BP stream), a waste stabilization pond located in Guissona (TP stream), an extended aerated system located in Calaf (TA stream), and a CW located in Sant Martí de Sesgueioles (RG stream). All WWTPs discharged their treated wastewater into seasonal streams that are dry almost all year round upstream of the WWTP. Table 1 shows the main characteristics of the studied WWTPs and streams. Further details on the description of the WWTPs are described elsewhere (Matamoros et al., 2016a). The main difference between streams is the water flow velocity and vegetation coverage. The RG stream was completely covered by vegetation (data obtained from Google earth image analysis) and the system with the lowest water velocity.

2.2. Sampling strategy

Two sampling campaigns were carried out, the first in July 2015 (warm season) and the second in February 2015 (cold season). In each campaign, grab water samples were collected from the effluent of all the treatment systems and at 6–10 points at increasing distances from the WWTP. The total number of samples collected was of 56. Only one sampling campaign was carried out by season and stream, except the RG stream that was sampled by triplicate during the warm season. The 7–10 locations were sampled within a 1 h time span in each stream. No rainfall events were recorded at any time one week before or during the sampling period. All the water samples were collected in 1000 mL amber glass bottles, which were transported under refrigeration to the laboratory, where they were stored at 4 °C until analysis. The sample holding time was less than 6 h. All streams were dry upstream of the WWTP during the sampling campaigns.

2.3. Chemicals and reagents

Gas chromatography (GC) grade (Suprasolv) hexane, methanol, and ethyl acetate were obtained from Merck (Darmstadt, Germany). Analytical-grade hydrogen chloride was obtained from Panreac (Barcelona, Spain). Benzotriazole, carbamazepine, diclofenac, ibuprofen, ketoprofen, MCPA, methylparaben, naproxen, oxazepam, triclosan, 1-methylbenzotriazole, atrazine, OH-benzothiazole, caffeine, DEET, diazepam, galaxolide, tris(2-chloroethyl) phosphate (TCEP), triphenyl phosphate (TPP), tributyl phosphate (TBP) and Tris (1-chloro-2-propyl phosphate) (TCPP), atrazine D5, ibuprofen D3, tonalide D3 and carbamazepine 13C were purchased from Sigma-Aldrich (Steinheim, Germany). Trimethylsulfonium hydroxide (TMSH) was obtained from Fluka (Buchs, Switzerland). Strata-X polymeric SPE cartridges (200 mg) were purchased from Phenomenex (Torrance, CA, USA) and the 0.7 μm glass fibre filters (ø 47 mm) were obtained from Whatman (Maidstone, UK).

2.4. Analytical procedures

Conventional wastewater quality parameters, including ammonium nitrogen ($NH^{+}{}_4$-N), total suspended solids (TSS), and chemical oxygen demand (COD), were determined in all the water samples. The COD was measured with Hach Lange COD cell tests (LCK 314 and LCK 614) on a spectrophotometer (Hach Lange Pocket Colorimeter II at 450 nm). Onsite measurements of water temperature and dissolved oxygen (DO) were taken using a Checktemp-1 Hanna thermometer and a Eutech Ecoscan DO6 oxygen meter, respectively.

All water samples were filtered and processed as previously reported (Matamoros and Bayona, 2006). A 500 mL sample (pH = 3 with HCl) was spiked with 50 ng of a surrogate standard (atrazine D5, ibuprofen D3, tonalide D3, and carbamazepine 13C). The spiked sample was percolated through a previously activated polymeric solid-phase extraction cartridge (200 mg Strata X). The cartridges were dried under vacuum (400 mbar) using a Baker SPE-12G manifold (J.T. Baker, USA) for 1 h and then eluted with 10 mL of hexane/ethyl acetate (1:1). The eluted extract was evaporated