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Occurrence of pharmaceutically active compounds in surface waters of the henares-jarama-tajo river system (madrid, spain) and a potential risk characterization

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ABSTRACT

The Henares-Jarama-Tajo river system is the largest drainage basin in the Province of Madrid, Spain. This area is characterized by the presence of intensive urban and industrial activities influenced by a continental Mediterranean climate with rainfalls presenting substantial fluctuations along the different seasons. This research aimed to monitor seasonal variations in concentrations of 22 pharmaceutically active compounds (PhACs) in this river system and to establish the potential risk of sublethal effects on aquatic organisms. A total of 10 sampling sites were selected along the river system with samples collected in each of the four seasons during a year-round schedule. Most of the PhACs detected were present in sampling sites downstream in the vicinity of the most populated cities (i.e. Madrid, Guadalajara and Alcalá de Henares). Only two PhACs, fluoxetine and paraxantine, were detected in all sites regardless of the season, and showed median (± interquartile range) concentrations of 21.4 (±31.2) ng L^{-1} and 8.5 (±5.3) ng L^{-1}, respectively. Other PhACs were detected with a frequency >80% and included, caffeine, diphenylhydantoin, hydrochlorotiazide, ibuprofen, ketoprofen, diclofenac, sulfamethoxazole, atenolol, naproxen, carbamazepine and propanolol. Seasonal variations were observed with the highest concentrations in December and the lowest in September. By combining measured environmental concentrations with toxicity data (either publicly available or obtained experimentally in our laboratory), and by calculating an Maximum Risk Index (MaxRI) that each combination of PhACs should have for non exceeding the risk threshold, a high potential for long-term risk (MaxRI<10) was estimated for most of the sampling sites and sampling dates. This research allowed the characterization of the potential risk for each of the PhACs to exert sublethal effects on aquatic organisms using acute screening methods, justifying the need for chronic data in order to refine the risk of these compounds to aquatic organisms.

1. Introduction

The presence of pharmaceutically active compounds (PhACs) in the environment can pose significant human and wildlife health threats. As with other anthropogenic substances, aquatic systems become the final recipient of PhACs, being found in sewage treatment plant effluents (Bendz et al., 2000; Spongberg and Witter, 2008), surface waters and even in drinking waters (Kümmerer, 2001; Benotti et al., 2009). For instance, more than 100 pharmaceuticals and personal care products have been detected in effluents of wastewater treatment plants (WWTPs) in several countries of the European Union (Kümmerer, 2001). These compounds and their metabolites continuously enter the aquatic environment largely through effluents from WWTPs due to incomplete elimination or sporadic direct wastewater discharge (Daughton, 2004). Even low concentrations of these substances may lead to unwanted effects in aquatic systems (Daughton and Ternes, 1999; Fent et al., 2006; Jones et al., 2007). Although pharmaceuticals are designed as bioactive molecules to treat diseases, they can affect non-target organisms (Van der Ven et al., 2006) with harmful effects reported at environmentally relevant concentrations (Madsen et al., 2004). Concern is such that several reviews recently published have dealt with the exposure of humans or biota to pharmaceuticals (Larsen et al., 2004; Jones et al., 2004; Kuster, 2004; Garric and Ferrari, 2005; Hernando et al., 2005; Fent et al., 2006; Zuccato et al., 2006).

Pharmaceuticals were initially identified in the mid-1970s associated with SWTP effluents in the USA (Higinite and Azarnoff, 1977). It has not been until this last decade when social concern has aroused for a potential risk to ecosystems (Fent et al., 2006: Jjemba, 2006; Kolpin et al., 2002). In Spain, municipal wastewater discharge has

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become a major contributor to the pollution in urban riverine waters (Martínez et al., 2007) with concentrations dependent mainly on rainfall. With the exception of the Ebro river basin (AquaTerra), an integrated project of the 6th EU RTD Framework Programme, to our knowledge no other data are available for other basins.

The Henares-Jarama-Tajo river system makes up the largest drainage basin located in the Province of Madrid, Spain, covering an area of approximately 3,100 km^2 (Fig. 1). Basically, its course in the Province of Madrid starts with the Henares river flowing to the Jarama from the north-eastern part of the province, just before the Jarama runs through the vicinity of the city of Madrid. The Tajo is then joined by the Jarama river, runs straight through the city of Toledo and leaves the province by its south-western margin. The particularity of this basin lies in two aspects: 1) it is located in one

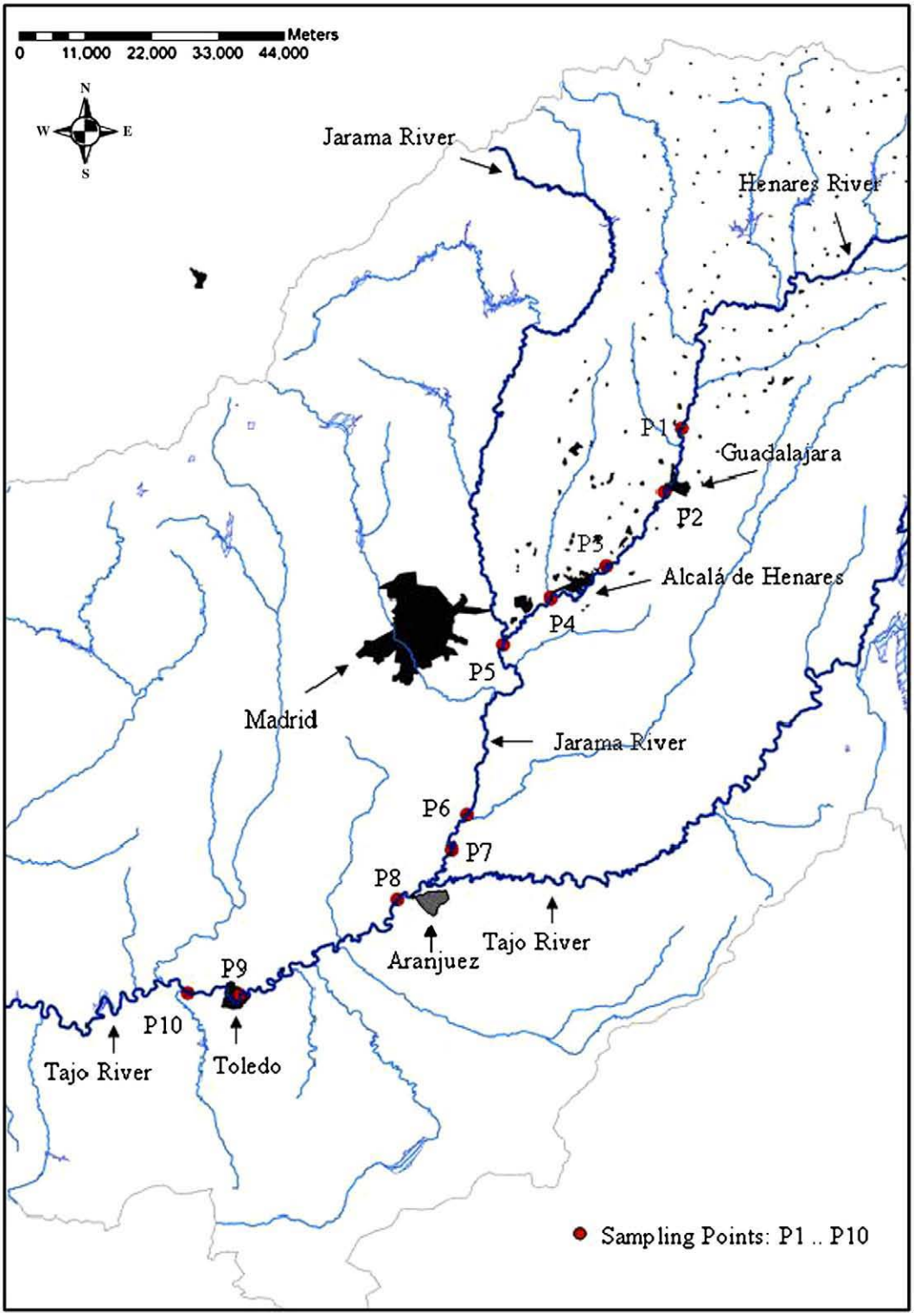

Fig. 1. Henares-Jarama-Tajo basin. Map pf the sampling sites, indicating the principal populous cities.