Science of the Total Environment xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Integrated environmental risk assessment of chemical pollution in a Mediterranean floodplain by combining chemical and biological methods

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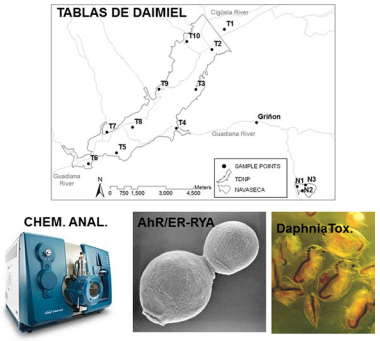
HIGHLIGHTS

- We analyzed risk of micropollutants in Las Tablas de Daimiel floodplain
- Foodplain water samples showed low levels of pollutants and of toxic effects
- High pollution levels in Navaseca pond, impacted by waste water discharges
- Navaseca water samples were toxic to Daphnia and showed a moderate estrogenicity
- Results showed a good chemical status for Las Tablas de Daimiel

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 October 2016
Received in revised form 10 January 2017
Accepted 10 January 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Contaminant
Endocrine disruption
Freshwater
UNESCO biosphere reserve
Ramsar site

ABSTRACT

The Tablas de Daimiel National Park (TDNP) is a unique floodplain ecosystem in central Spain, serving as permanent resting and breeding areas for many waterbird species. In the last decades, this biodiversity hotspot has been severely endangered by poorly treated wastewater discharges from upstream urban communities arriving through its two major contributors, the Cigüela and Guadiana rivers. In this work, we analysed the potential risk of this constant input of micropollutants (estrogens, dioxin-like compounds and other endocrine disruptors) for the resident wildlife. We sampled 12 locations in TDNP and in the nearby Navaseca Pond during 2013, and performed a series of in-vivo and in-vitro bioassays, including *Daphnia magna* post-exposure feeding inhibition and recombinant yeast-based assays for dioxin-like and estrogenic activities. These results were then compared with the chemical composition of the samples, analysed by GC–MS/MS and LC-MS/MS, and evaluated according to their toxic potential as toxic equivalents or TEQ. The Navaseca Pond, heavily impacted by wastewater from the town of Daimiel, showed the highest levels of toxic compounds, estrogenic activity, and *Daphnia* toxicity. Conversely, the less impacted TDNP sites showed low residue levels of contaminants, low estrogenicity and dioxin-like activity and negligible toxicity. The results indicates that the current good chemical status of TDNP is menaced by both the inflow of wastewater treatment plants effluents from Guadiana and Cigüela rivers into TDNP tributaries and, as it occurs in the Navaseca Pond, by direct sewage discharges.

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http://dx.doi.org/10.1016/j.scitotenv.2017.01.061
0048-9697/

1. Introduction

River floodplains provide human society with many important ecosystem services (Postel and Carpenter, 1997), but their ecological status is determined by several complex parameters, including fluvial dynamics and groundwater and man-made processes (Alvarez-Cobelas et al., 2001). In recent times, intensive agriculture combined with groundwater extraction for irrigation, and overall decreases in surface and groundwater quality have appeared as major threats for river floodplains (Tockner and Stanford, 2002). As a consequence, most floodplains are functionally extinct nowadays in North America and Europe, including the Mediterranean (Brinson and Malvárez, 2002; Tockner and Stanford, 2002). In Spain, floodplains present the worst conservation situation among all wetlands, as >79% of the surface they possessed in the 19th century has been lost by draining for cultivation (Casado et al., 1992). A worse-case scenario of a severely impacted Mediterranean floodplain are Tablas de Daimiel National Park (TDNP), which is located at the centre of Spain, and it is considered a Biosphere reserve by UNESCO, a Ramsar site and refuge for migratory birds and aquatic plants. Its many valuable features come from the structure of submerged vegetation communities, dominated by a mosaic of *Cladium mariscus* sawgrass-emergent stands and open water habitats ("tablas") (Cirujano et al., 1996), and of extensive stonewort (Charophyceae) communities. The latter plant community is extremely important for the survival of many migratory and resident waterbirds (Cirujano et al., 1996). The waterbird community in TDNP has been famous since at least the Middle Ages, being cited in the ancient hunting literature sources (Coronado et al., 1974). Almost 200 bird species have been recorded in this wetland and its surrounding terrestrial habitats; this figure includes practically every inland waterbird species known in southern Europe. Registers of ichthyofaunal diversity in TDNP from the 16th Century onwards reflected a richness of species that remained so at the turn of the 20th Century. However, recent invasive events of freshwater fish, such as the common carp (*Cyprinus carpio*), are negatively affecting aquatic vegetation, both directly by consuming macrophytes, and indirectly by changing water quality (Laguna et al., 2016)

The wetlands of TDNP are the result of the mixture of inputs from Cigüela and Guadiana rivers, together with groundwater discharge from the West Mancha aquifer (Alvarez-Cobelas et al., 2001; Berzas et al., 2000). The reduction of the drainage area and an overexploitation of groundwater for irrigation purposes lead to the near desiccation of TDNP and, finally, to the ignition of a smouldering peat fire inside the TDNP in August 2009. This fire posed an enormous risk for both the physical structure supporting the ecosystem and the quality of groundwater beneath it (Moreno et al., 2011), especially considering that fires are an important source of pollution by polycyclic aromatic hydrocarbons (PAHs) for Mediterranean rivers (Vila-Escale et al., 2007). A TDNP Hydric Regeneration Plan was implemented to stop or at least mitigate this environmental degradation. The plan includes the artificial recharge of the wetlands by pumping groundwater from nearby wells and, occasionally, by diverting water from the Tajo River to the Cigüela River (Berzas et al., 2000).

TDNP also suffers from water pollution associated with human population growth and the subsequent agriculture and industry developments (Berzas et al., 2000; Sanchez-Ramos et al., 2016). Pollution sources include dispersed-source pollution from surrounding agriculture and industrial activities, and point-source pollution from wastewater treatment plants (WWTPs) discharging treated or untreated effluents into the Cigüela and Guadiana rivers (Sanchez-Ramos et al., 2016). One of such contaminated sites is the Navaseca Pond, which is located at the Guadiana River basin and that receives wastewater effluents from the town of Daimiel, both treated and untreated, particularly during heavy rain episodes. Besides the town of Daimiel, Villarrubia de los Ojos town discharges wastewater effluents to Cigüela River from its wastewater treatment plant. Another nearby town, Fuente el Fresno, has been discharging untreated effluents into Cañada Lobosa stream until 2013 when its wastewater treatment plant started to operate. This means that there is potential risk of contaminants to cause detrimental effects on living biota in the TDNP. In recent years, the populations of herbivorous waterfowl have shown a marked decrease, potentially linked to the deterioration of submerged macrophyte stands by introduced fish species, such as the common carp *Cyprinus carpio* (Laguna et al., 2016). There is, however, the possibility that some noxious contaminants are affecting birds directly or indirectly being toxic to aquatic invertebrates and plants, which are food sources for aquatic birds. The aim of the present study is to characterize noxious organic contaminants in TDNP and their main water sources, by sampling 14 locations in the wetland of TDNP and its nearby Navaseca Pond during 2013. We determined residue levels of up to 31 different organic compounds including estrogens, antimicrobials, preservatives, plasticizers, alkylphenols, anticorrosives and flame retardants, that are often found in treated wastewater effluents, some of them with known estrogenic activity to vertebrates (Gorga et al., 2013). Additionally, PAHs present in suspended solids of water samples were determined, since some of them are known to have dioxin-like activity (Misaki et al., 2007). Chemical determinations were complemented with measurements of total estrogenicity and dioxin-like activity using in vitro recombinant yeast assays (RYAs) (Bosch et al., 2009; Céspedes et al., 2004; Noguerol et al., 2006a) and of general toxicity to aquatic invertebrates using post-exposure *Daphnia magna* feeding toxicity tests (Bosch et al., 2009; Rivetti et al., 2015b). Combining chemical and toxicity assays will allow identifying chemicals causing toxic effects, which may help the implementation of future remediation strategies in the TDNP.

2. Material and methods

2.1. Study area

TDNP is situated in central Spain at the SW corner of the Mancha Húmeda Biosphere Reserve (MAB program, UNESCO), within the province of Ciudad Real (39° 08′17″N, 3° 41′50″S, Fig. 1A, B). The Park covers an area of 3030 ha, of which almost 2000 ha consists of a fluctuating Mediterranean floodplain, which is fed by water from the Guadiana and Cigüela rivers and the underlying aquifer (Fig. 1C). This region has a semiarid continental Mediterranean climate, with an extremely irregular rainfall regime, the average annual rainfall being between 400 and 500 mm, and having an average temperature of 14 °C (Alvarez-Cobelas et al., 2001; Cirujano et al., 1996).

2.2. Experimental design and water sampling

Organic contaminants from both diffuse (e.g., historical smouldering peat fires) and point (WWTP) pollution sources were analysed in ten experimental stations sampled after the main rain season in May 2013 throughout TDNP, and representing different hydrogeological areas (Fig. 1C). In TDNP, the stations T1, T2, T3, T9 and T10 are mostly influenced by the Cigüela River, as they are located upstream the join with Guadiana River, whereas stations T4, T5, T6, T7 and T8 are downstream that join and have the influence of Guadiana River too (Fig. 1C). Stations T4–8 may also be affected by diffuse pollution of PAHs coming from historical smouldering peat fires (Moreno et al., 2011). To study seasonal variation, the ten stations were also sampled during the main dry season in July 2013. Unfortunately station T8 was dry and samples from station T3 were accidentally lost. Furthermore, July sampling included an additional station from the Guadiana River (Griñon station), and three stations at the Navaseca Pond, one at the discharging point of the Daimiel WWTP (N1), and two more sites at both extremes of the pond (N2, N3, Fig. 1C). Fig. 1C depicts different sources of diffuse pollution influencing the TDNP, coming from agricultural activities, from Villarubia de los Ojos WWTP discharges through the Cigüela river,

Please cite this article as: Rivetti, C., et al., Integrated environmental risk assessment of chemical pollution in a Mediterranean floodplain by combining chemical and biological ..., Sci Total Environ (2017), http://dx.doi.org/10.1016/j.scitotenv.2017.01.061