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Contamination patterns and attenuation of pharmaceuticals in a temporary Mediterranean river

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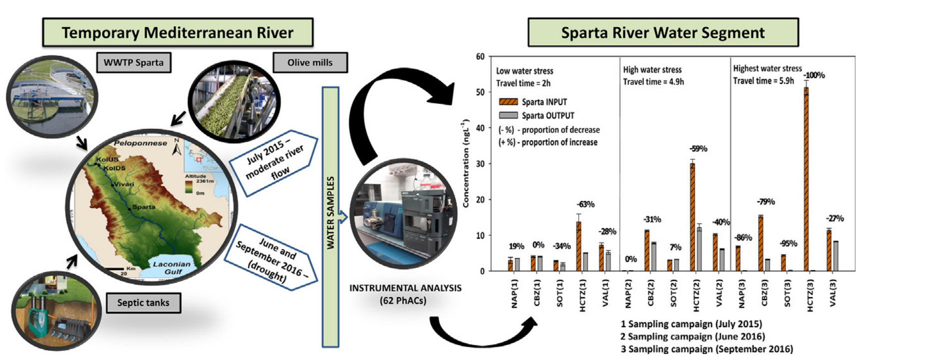
HIGHLIGHTS

- Variation of PhAC and nutrient concentrations relates to river flow variability.
- PhACs and nutrients are considerably higher downstream of the WWTP Sparta.
- Longer residence times accounts for higher in-stream attenuation of most PhACs.

GRAPHICAL ABSTRACT



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ABSTRACT

The contamination patterns and fate of pharmaceutically active compounds (PhACs) were investigated in the Evrotas River (Southern Greece). This is a temporary river with differing levels of water stress and water quality impairment in a number of its reaches. Three sampling campaigns were conducted in order to capture different levels of water stress and water quality. Four sampling sites located on the main channel of the Evrotas River were sampled in July 2015 (moderate stream flow), and June and September 2016 (low stream flow). Discharge of urban wastewater has been determined as the main source of pollution, with PhACs, nutrients and other physicochemical parameters considerably increasing downstream the wastewater treatment plant (WWTP) of Sparta city. Due to the pronounced hydrological variation of the Evrotas River, generally, the highest concentrations of PhACs have been detected during low flow conditions. Simultaneously, low flow resulted in an increased water travel time and consequently longer residence time that accounted for the higher attenuation of most PhACs. The average decrease in total concentration of PhACs within the studied waterbody segment (downstream of Sparta city) increased from 22% in July 2015 to 25% in June 2016 and 77% in September 2016. The PhACs with the highest average concentration decrease throughout the sampling campaigns were hydrochlorothiazide, followed by sotalol, carbamazepine, valsartan, and naproxen.

Abbreviations: D.F., average detection frequency; D.O., dissolved oxygen; Dow, octanol-water distribution coefficient; ESI, electrospray ionization; Kow, octanol-water partition coefficient; LOD, limits of detection; LOQ, limits of quantifications; NI, negative electrospray ionization; OTC, over-the-counter; PCA, Principal Component Analysis; PhACs, pharmaceutically active compounds; PI, positive electrospray ionization; r, Pearson's moment correlation factor; SM, Supplementary material; SPE, solid phase extraction; SRM, selected reaction monitoring; UHPLC-QqLIT-MS/MS, ultra-high-performance liquid chromatography coupled to triple quadrupole linear ion trap tandem mass spectrometry; WWTP, wastewater treatment plant.

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1. Introduction

Mediterranean streams and rivers are characterized by inter-annual hydrological variations encompassing floods in spring and autumn and droughts in summer (Sabater et al., 2008), which in turn can cause headwater and middle-order streams to become intermittent, or even to dry out for an extended period (Lake, 2003). Consequently, temporary streams and rivers in the Mediterranean basin are amongst the most complex and dynamic freshwater ecosystems, and at the same time, highly fragile (Larned et al., 2010; Acuña et al., 2014a). These systems are affected by strong hydrological and anthropogenic pressures resulting from extensive water abstraction, river fragmentation and climate change (Larned et al., 2010; Acuña et al., 2014a; Skoulikidis et al., 2017). Water quantity pressures are further accentuated by nutrient enrichment and microcontaminants pollution from urban and industrial wastewaters, and by organic pollution from municipal wastewaters and agricultural activities (Meybeck, 2004; Vörösmarty et al., 2010). Amongst the microcontaminants, the use of pharmaceutically active compounds (PhACs) for both human and veterinary applications results in a vast array of products reaching aquatic environments. PhACs are a group of chemical substances with pharmacologic and physiologic properties and include all prescription, nonprescription, and over-the-counter (OTC) therapeutic drugs, in addition to veterinary drugs (Richardson and Ternes, 2005). Following their administration, PhACs are excreted as a mixture of parent compounds and metabolites that are usually more polar and hydrophilic than the original drug, while large fraction of these substances is discharged into the wastewater in the form of degradation products that are often poorly eliminated in conventional wastewater treatment plants (WWTPs, Gros et al., 2010; Ratola et al., 2012). PhACs are being discharged into the aquatic environment through different sources, i.e. human excretion, disposal of unused and expired drugs, agricultural and livestock practices (Halling-Sørensen et al., 1998; Boxall et al., 2012; Tijani et al., 2016), and reach the environment as treated or untreated wastewater discharges (Heberer, 2002; Vieno et al., 2005). Their continuous discharge into the aquatic environment makes the PhACs pseudo-persistent contaminants (transformation and removal rates are compensated by their continuous discharge into the environment), and as such may cause adverse effects on living organisms and the environment (Daughton and Ternes, 1999; Halling-Sørensen et al., 1998). For example, there is evidence that PhACs, such as antidepressants, psychiatric drugs, hormones, and antihistamines can induce behavioral changes in fish, affecting fish aggression, reproduction and feeding activity, thus, in turn, directly affecting individual fitness and indirectly affecting food webs and ecosystem processes (Schultz et al., 2011; Brodin et al., 2014; Sharifan and Ma, 2017).

Once released into the aquatic environment, PhACs undergo different in-stream attenuation processes (i.e. biotransformation, photolysis, sorption, volatilization). These processes are related to the specific characteristics of the PhACs, the physicochemical and biological parameters of the river (Gurr and Reinhard, 2006; Kunkel and Radke, 2008), and to the specific dilution capacity and water travel time within the study reach or waterbody (Rueda et al., 2006; Keller et al., 2014). There is, however, limited knowledge regarding the fate, behavior, and transport of PhACs in Mediterranean aquatic ecosystems, compared to other pollutants (Halling-Sørensen et al., 1998; Kolpin et al., 2002; Golet et al., 2002; Moldovan, 2006; Acuña et al., 2014b), while the functioning of in-stream attenuation mechanisms is not completely understood (Kunkel and Radke, 2011), particularly in the Mediterranean river systems (Al Aukidy et al., 2012; López-Serna et al., 2012; Stasinakis et al., 2012; Stamatis et al., 2013; Nannou et al., 2015). Also, few studies have detailed the fate and in-stream attenuation of PhACs during different seasons (Pal et al., 2010), especially together with the other organic micropollutants (Biales et al., 2015; Fairbairn et al., 2016; Garrido et al., 2016) and during heavy rainfall and floods (Pailler et al., 2009). However, concentration levels of PhACs in the Mediterranean streams and rivers depend as well on numerous factors such as the land uses and the hydrometeorological conditions. Therefore, reduced dilution capacity of Mediterranean streams and rivers during dry periods may result with the increased concentration levels of PhACs and other organic micropollutants (Almeida et al., 2014; Sabater et al., 2016), while due to an increased rainfall and subsequent dilution capacity during wet periods, generally lower concentration levels of PhACs may be expected (Kasprzyk-Hordern et al., 2009; Lacey et al., 2012; Papageorgiou et al., 2016). Though, during heavy rainfall events in the Mediterranean, flow augmentation, sediments resuspension, combined sewer overflows resuspension, and reduced hydraulic retention time in the WWTPs, leads to a particularly increased in-stream concentration levels of PhACs (Cowling et al., 2005; Sui et al., 2011; Osorio et al., 2012; Osorio et al., 2014; Corada-Fernández et al., 2017; Reoyo-Prats et al., 2018). Therefore, determining the PhACs concentrations and their fate mechanisms in the Mediterranean aquatic environment is important in order to assess their environmental risk (Boxall et al., 2012), particularly during drought and heavy rainfall events.

The main objectives of this study were to i) determine the concentration patterns of PhACs in a temporary Mediterranean river affected by agricultural and urban pollution; ii) estimate the recovery potential (natural in-stream attenuation of contaminants) in the water bodies studied, and iii) define the joint effects of hydrological (river flow) and chemical stressors (urban and agricultural pollution) on the occurrence and distribution of PhACs in this Mediterranean river.

2. Materials and methods

2.1. Study area

The study was conducted at the Evrotas River, a biogeographically isolated basin in the southernmost Balkan Peninsula, in Southern Peloponnese, Greece (Fig. 1). The Evrotas River is a large (2418 km^2), mid-altitude Mediterranean basin, with the river flowing unobstructed between the mountain ranges of Taygetos (2407 m a.s.l.) and Parnon (1904 m a.s.l.), and entering after 90 km into the Lakonian Gulf. Along the course of the Evrotas, numerous permanent and temporary karstic springs contribute to river runoff (Vardakas et al., 2015). The mountainous area of the basin is mostly formed by Mesozoic-Palaeogene limestone and impermeable rocks (schists and flysch), while the lower parts of the river basin are formed of extensive alluvial aquifers (Pliocene and Quaternary sediments, Skoulikidis et al., 2011). The Evrotas River Basin has an average annual temperature of 16 °C and a mean annual precipitation of 803 mm (2000–2008), with wet and cool winters and warm and dry summers (Nikolaidis et al., 2009). The combined effects of water abstraction and natural drought result in the partial desiccation of the river in late summer-early autumn (Skoulikidis et al., 2011).

The main sources of municipal sewage in the study area is the city of Sparta (population of 16,239), which has a sewage collection system (with not all of the households, however, connected to it) and WWTP that discharges treated effluents into the Evrotas River. The smaller communities upstream are served by septic tanks and cesspools. The Evrotas River, therefore, receives the treated sewage of Sparta and untreated wastewaters from nearby communities. However, during the dry period, the WWTP may not operate sufficiently and/or cesspool waste dumping may occur, as evident by the zero dissolved oxygen (D.O.) values recorded repeatedly and for periods of several days downstream the WWTP effluent discharge point (Lampou et al., 2015). These add to the disposal of agro-industrial wastes and agrochemical pollution (oil mill wastes, wastes from orange juice production, Markantonatos et al., 1996; Skoulikidis et al., 2011).

2.2. Sampling sites and collection

Three sampling campaigns were conducted by scientists of the Hellenic Centre for Marine Research in order to capture different levels of