ARTICLE IN PRESS
STOTEN-22122; No of Pages 11
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

Contamination sources and distribution patterns of pharmaceuticals and personal care products in Alpine rivers strongly affected by tourism

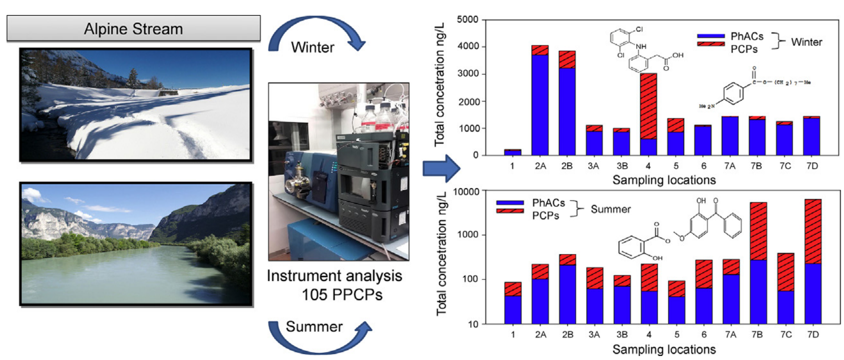
Ladislav Mandaric [a], Elena Diamantini [d], Elisa Stella [d], Karina Cano-Paoli [d], Jennifer Valle-Sistac [b], Daniel Molins-Delgado [b], Alberto Bellin [d], Gabriele Chiogna [e,g], Bruno Majone [d], M. Silvia Diaz-Cruz [b], Sergi Sabater [a,c], Damia Barcelo [a,b], Mira Petrovic [a,f,]*

[a] Catalan Institute for Water Research (ICRA), C/Emili Grahit, 101 E, 17003 Girona, Spain
[b] Department of Environmental Chemistry IDAEA-CSIC, C/Jordi Girona, 18-26, 08034 Barcelona, Spain
[c] Institute of Aquatic Ecology, University of Girona, Campus de Montilivi, 17071 Girona, Spain
[d] Department of Civil, Environmental and Mechanical Engineering, University of Trento, Via Mesiano, 77, Trento I-38123, Italy
[e] Faculty of Civil, Geo and Environmental Engineering, Technical University of Munich, Arcistrasse 21, Munich 80333, Germany
[f] Catalan Institution for Research and Advanced Studies (ICREA), Lluis Company 25, 08010 Barcelona, Spain
[g] Institute of Geography, University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria

HIGHLIGHTS

- The occurrence patterns of pharmaceuticals and personal care products have been investigated in the Alpine river basin.
- Correlations between tourist arrivals and concentrations of pharmaceuticals and personal care products have been performed.
- High concentrations of pharmaceuticals and personal care products have been observed at sampling sites affected by tourism.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 December 2016
Received in revised form 22 February 2017
Accepted 22 February 2017
Available online xxxx

ABSTRACT

Knowledge regarding the impact of tourism on the emergence of pharmaceuticals and personal care products (PPCPs) in Alpine river waters is limited and scarce. Therefore, a study on the occurrence patterns and spatiotemporal variability of 105 PPCPs in an Alpine river basin located in the Trentino-Alto Adige region (North-Eastern Italy) has been conducted. We observed that the total concentration of analyzed PPCPs was generally higher in all sampling sites during winter than in the summer. The analysis of tourist data revealed that during both

Abbreviations: ADAF, Anti-icer fluid; APPI, Atmospheric pressure photo-ionization; AVB, Avobenzone; BP1, Benzophenone 1; BP3, Benzophenone 3; BZT, 1-H-Benzotriazole; DHMB, 2,2′-Dihydroxy-4-methoxybenzophenone; DMeBZT, 5,6-Dimethyl-1-H-benzotriazole; EPB, Ethyl paraben; ESI, Electrospray ionization; Et-PABA, Ethyl-*p*-aminobenzoic acid; LOD, Limit of detection; LOQ, Limit of quantification; MeBZT, 4-Methyl-benzotriazole; NI, Negative electrospray ionization; NSAID, Non-steroidal anti-inflammatory drug; OC, Octocrylene; ODPABA, Octyl-dimethyl-*p*-aminobenzoic acid; p, Probability; PCPs, Personal care products; PhACs, Pharmaceutically active compounds; PI, Positive electrospray ionization; PLE, Pressurized liquid extraction; PPCPs, Pharmaceuticals and personal care products; r, Pearson moment correlation factor; ROS, Reactive oxygen species; SM, Supplementary material; SPE, Solid phase extraction; SPE-HPLC-MS^2, Solid phase extraction- high performance liquid chromatography–tandem mass spectrometry; SRM, Selected reaction monitoring; UHPLC-QqLIT-MS^2, Ultra-high-performance liquid chromatography coupled to triple quadrupole linear ion trap mass spectrometry; WWTPs, Wastewater treatment plants; 4HB, 4-Hydroxybenzophenone; 4MBC, 3-(4′-Methylbenzylidene) camphor.

* Corresponding author at: Catalan Institute for Water Research, H_2O Building, Science and Technology Park of the University of Girona, Emili Grahit, 101, 17003 Girona, Spain.
E-mail address: mpetrovic@icra.cat (M. Petrovic).

http://dx.doi.org/10.1016/j.scitotenv.2017.02.185

Editor: Kevin V. Thomas

Keywords:
Alpine ecosystems
Adige River
Pharmaceutical compounds
Personal care products
Tourism
Spatiotemporal variability

sampling campaigns the number of tourists was lower in the downstream sites in comparison with the upstream area of the basin (Val di Sole). Particularly, sampling sites located near important tourist resorts have shown the highest abundance of the PPCPs during winter, being analgesics/anti-inflammatories, antihypertensives and antibiotics the most abundant pharmaceutically active compounds (PhACs). Diclofenac showed the highest concentration amongst PhACs, reaching concentrations up to 675 ng L^{-1} in the sampling site situated downstream of the Tonale wastewater treatment plant (WWTP). Antihypertensives were found at concentrations >300 ng L^{-1}, while antibiotics were quantified up to 196 ng L^{-1}, respectively. Amongst personal care products (PCPs), the most abundant compound was octyl-dimethyl-*p*-aminobenzoic acid (ODPABA) with concentrations reaching up to 748 ng L^{-1} in the sampling site situated within the Rotaliana district. In general, concentrations and detection frequencies were higher in water than in the sediment samples. The most frequently detected PhACs in sediments from both sampling campaigns were antibiotics, while amongst PCPs in sediments, octocrylene (OC) showed the highest concentration in both sampling campaigns. As a result, this study highlights the potential impact of tourism on the water quality of the Alpine aquatic ecosystems.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) include prescription drugs, non-prescription drugs, veterinary drugs and consumer chemicals typically found in fragrances, sun-screen agents, lipsticks, shampoos, hair colors and cosmetic products (Daughton and Ternes, 1999; Boxall et al., 2012). PPCPs are considered emerging contaminants and can enter the aquatic ecosystem via multiple pathways, including human excretion, unused drugs and products, agricultural and livestock practices (Jorgensen and Halling-Sorensen, 2000; Ort et al., 2010; Rosi-Marshall and Royer, 2012; Boxall et al., 2012; Tijani et al., 2016). However, the main pathway for PPCPs to freshwaters is through wastewater effluents as a result of incomplete removal in the wastewater treatment (Hirsch et al., 1999; Daughton and Ternes, 1999; Giger et al., 2003; Ternes et al., 2004). Because of their continuous release into the aquatic environment via waste water treatment plants (WWTP) effluents, PPCPs may act as pseudo-persistent contaminants (Ellis, 2006), and as such may cause unwanted and unexpected effects on the living organisms and environment (Daughton and Ternes, 1999; Ferrari et al., 2003; Stackelberg et al., 2004; Fent et al., 2006; Ortiz de García et al., 2014). PPCPs in the aquatic environment have been recognized as one of the most urgent environmental issues during the last decade (Jones et al., 2001; Richardson and Ternes, 2005). Concentrations of PPCPs range from ng L^{-1} to μg L^{-1}, while their occurrence in water varies across different regions and seasons (Moldovan, 2006; Kasprzyk-Hordern et al., 2008; Fernández et al., 2010; Yoon et al., 2010; Spongberg et al., 2011). It is therefore highly relevant to understand their temporal and spatial variability and distribution (Musolff, 2009).

The relevance of PPCPs associated with touristic activity in Alpine ecosystems is however largely unknown. So far, the impact of tourism on river water quality has mostly been approached through the monitoring of the physicochemical and microbiological parameters (White et al., 1978; Rodriguez, 1987; Almeida et al., 2007; Rashid and Romshoo, 2013; Bhadula et al., 2014). Even though several studies have reported concentrations of PPCPs in large rivers (Celano et al., 2014; Meffe and de Bustamante, 2014), studies regarding the occurrence of PPCPs in the Alpine streams remain limited (see e.g., Repice et al., 2013). Therefore, the potential environmental threats to the aquatic environment associated with touristic fluxes and PPCPs in the Alpine regions requires investigation. In this context the Adige river basin, which is located in the South-Eastern Italian Alps, may be considered representative of the situation characterizing Alpine regions with intense touristic activity; hundreds of kilometers of ski slopes and an extraordinary variety of landscapes make this region a cutting-edge tourist destination during summer and winter months. As a consequence, a strong seasonality on consumption and use of PPCPs and their arrival to the river system is likely to be expected. Waste water treated effluents have been identified as the main sources of contamination in the Adige catchment (Caserini et al., 2004; Repice et al., 2013), while extensive hydropower exploitation (Zolezzi et al., 2009, 2011), which has induced significant alterations of the streamflow regimes in both the main stem and tributaries (Majone et al., 2016), is likely to enhance the sensitivity of the river ecosystem to PPCP loads.

Therefore, the present study aims (1) to define the occurrence patterns of contaminants in relation to their sources (tourist arrivals, resident population), and (2) to relate the temporal variability (summer–winter) of PPCPs to the varying environmental variables (water flow, temperature), in water and sediments.

2. Materials and methods

2.1. Basin and sampling sites description

The Adige River has a total length of 410 km, being the second longest river in Italy after the Po. It rises from 1586 m a.s.l. (46.834444, 10.514722) in the proximity of Lake Resia, flows in the Southern-East Alps, and reaches the Adriatic Sea at Rosolina a Mare, south of Venice (45.149722, 12.320278) (Chiogna et al., 2016). The catchment includes 298 glaciers with a total surface of 128 km^2, which is reducing rapidly as a consequence of the observed rising trend of temperature (Lutz et al., 2016). Streamflow shows a typical Alpine character, with a principal maximum in summer, due to snow melting, and a secondary maximum in autumn, which may become dominant depending on the intensity of cyclonic storms. The minimum and maximum river flows of Adige and Noce rivers are shown in the Table 1S (SM) of the Supplementary material (SM). The mean streamflow at Trento gauging station is 203 $m^3 s^{-1}$ with a contributing area of 9763 km^2. This gauging station is the most representative of streamflow at the sampling location 6 and locations downstream city of Trento. Two sampling campaigns were conducted at 12 locations in the Adige main stem and the Noce tributary (See Fig. 1). The WWTPs located immediately upstream of the sampling locations are also shown in Fig. 1. Daily outflows from WWTPs were obtained from Agenzia per la Depurazione of the Province of Trento (https://adep.provincia.tn.it/Agenzia-per-la-Depurazione-ADEP). Finally, the main characteristics of the treatment process, population served and average daily WWTP outflows for sampling periods (Feb 15th–17th and Jul 3rd–5th, 2015) are provided in the Table 2S (SM). Tourist arrivals can be expected to be one of the most relevant driving factors influencing PPCPs concentrations. Tourist arrivals were retrieved from the dataset provided by ISPAT, http://www.statistica.provincia.tn, at a monthly resolution for the year 2015 (Fig. 2). Resident population in each municipality was downloaded from http://www.istat.it/it/ at the available time step of 1 year. The sub-catchment draining to each sampling point was identified (Table 1). Tourist arrivals were used as a proxy for tourism impact while the resident population was used as a proxy for urban centers.

Please cite this article as: Mandaric, L., et al., Contamination sources and distribution patterns of pharmaceuticals and personal care products in Alpine rivers strongly affected b..., Sci Total Environ (2017), http://dx.doi.org/10.1016/j.scitotenv.2017.02.185