Fate of Pharmaceuticals and Personal Care Products (PPCPs) from discharge to drinking water: a modelling and monitoring integrated framework

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Abstract
Pharmaceuticals and Personal Care Products (PPCPs) presence in drinking water is gaining growing concern for potential negative effects on human health. This study combined modelling of river transport with monitoring campaigns performed over one year at a drinking water treatment plant (DWTP) located at the closure section of Po river basin, to evaluate the types of released PPCPs, their concentrations and fate in both the river and the DWTP. Over the 114 monitored PPCPs, maximum 23 compounds have been detected at the DWTP inlet with concentrations from 10 to 1800 ng/L, varying among PPCPs and in time. The transport in Po river of iopamidol, with the highest concentration at the DWTP inlet, was simulated combining hydrological and quality data and models. Finally, DWTP monitoring showed that ozonation and adsorption onto activated carbon have the main impact in reducing a wide variety of PPCPs, with performances influenced by their characteristics.

Keywords
Drinking water; Full-scale monitoring; Holistic framework; Pharmaceuticals and Personal Care Products (PPCPs); Transport modelling

INTRODUCTION

In recent decades, the presence of pharmaceuticals and personal care products (PPCPs) in the aquatic environment has become an issue of growing global concern. PPCPs are commonly present in water in trace concentrations (from ng/L to μg/L), complicating their detection and analytical procedures (Luo et al., 2014). These substances can enter the aquatic environment through various sources. When discharged in surface waters, PPCPs are subjected to various degrees of natural attenuation, such as dilution in water, adsorption on suspended solids and sediments, direct and indirect photolysis and aerobic biodegradation (Pal et al., 2010). Transport models have become an important tool to study water quality and are widely used to simulate contaminants fate in water bodies providing valuable support to decision makers to define appropriate remediation strategies. However, quantitative data regarding PPCPs emission from different sources and attenuation phenomena are not available (Mompelat et al., 2009), resulting in high uncertainty of PPCPs concentrations in the natural sources feeding drinking water treatment plants (DWTPs). Finally, PPCPs concentration in treated drinking water is influenced by treatment processes present in the DWTPs and their removal efficiencies. Studies related to removal efficiencies towards PPCPs refer mainly to full-scale monitoring in urban wastewater treatment plants or to laboratory scale tests in synthetic water (Deegan et al., 2011), while full-scale DWTPs monitoring are limited (Huerta-Fontela et al., 2011). For these reasons, it is difficult to accurately assess PPCPs distribution, fate in the natural sources and in DWTPs, as input for environment and human health risk assessments.
The objective of this study, supported by the Interreg Central Europe 2014-2020 project "CE1412 boDEREC-CE", is to combine hydrological data and modeling of PPCPs river transport with a field monitoring campaign performed at a DWTP located at the closure section of its basin, to evaluate the types of PPCPs released in the basin and fate in the river and in the DWTP.

MATERIALS AND METHODS

The selected case study is the DWTP located in Pontelagoscuro (Italy), that represents the closure section of the Po river basin, that is the largest Italian watershed with a surface of about 74,000 km^2. The Po river basin is a highly populated area (population density of 423 inhab/km^2), that is highly industrialized, intensely cultivated, and hosts vastly developed transport infrastructures.

Pontelagoscuro DWTP is located directly on Po river and withdraws raw waters directly from Po river and from groundwater (GW) extracted at 100 m from the river after bank filtration, producing about $27 \cdot 10^6$ m^3/year of drinking water. Surface water is treated through a lagoon basin (Lag), a clariflocculation step followed by sand filtration and ozonation (O_3). Groundwater undergoes an aeration step followed by sedimentation and sand filtration. The two streams are then merged and treated on granular activated carbon (GAC) filters and disinfected by chlorine dioxide before drinking water is distributed in the network.

Six monitoring campaigns have been performed at the DWTP from September 2020 to July 2021, collecting six samples in each campaign: at the two raw waters, at the inlet and outlet of several treatment processes treating the surface water, and at the outlet of GAC filters. The following parameters have been monitored: 114 PPCPs, pH, redox potential, conductivity, total dissolved solids (TDS), turbidity, absorbance at 254 nm and total organic carbon (TOC).

As for the surface water transport model for Po river, an operational and calibrated HEC-RAS unsteady flow model was used. The simulated hydraulic scheme includes three branches: (i) Po river from the Secchia river confluence to Panaro river confluence, (ii) Panaro river, and (iii) Po river from Panaro confluence to Po river delta, where Pontelagoscuro DWTP is located. The water quality analysis performed by the HEC-RAS model uses the QUICKEST-ULTIMATE explicit numerical scheme to simulate surface water solving the One-Dimensional Advection-Dispersion Equation. Iopamidol was selected among the monitored PPCPs. The following assumptions were made in order to approximate the behaviour of the compound in the river: (i) the release of the contaminant is continuous, (ii) the initial concentration is constant in the whole river, (iii) the river branches are modelled as one-dimensional channels, and (iv) the downstream boundary condition does not influence the mass flow in the channel.

RESULTS AND DISCUSSION

The monitoring campaign performed at the DWTP allowed, firstly, to evaluate the pollution levels of the two raw waters (Po river and bank filtration wells) and the most critical contaminants for Po river basin. Over the 114 monitored PPCPs, in Po river raw water at maximum 23 compounds have been detected, while 7 PPCPs have been detected in the bank filtration wells raw water. Figure 1 shows the detected PPCPs in the two raw waters and their concentrations for the six monitoring campaigns. It is interesting to note the types of PPCPs that can be found in Po river raw water at the inlet of Pontelagoscuro DWTP, since it can provide an overview of the contamination sources over the entire Po river basin. Po river raw water is characterized by a wide variety of PPCPs. The PPCP with the highest concentration in both Po river and the bank filtration wells is iopamidol, that is a X-ray contrast agent. Also other X-ray contrast agents have been found in Po river (iomeprol, iopromide and iohexol), but they were not detected in the wells. Other types of PPCPs found in Po river are one drug against diabetes (metformin), two stimulants (caffein and paraxanthine), one purine (oxypurinol), two artificial sweeteners (acesulfame and saccharin), two anticorrosion agents (benzotriazole and benzotriazole methyl), one painkiller (paracetamol), four antihypertensives (valsartan, telmisartan, valsartan acid, irbesartan), one antiepileptic (gabapentin) and two anti-inflammatory drug (diclofenac, ibufrofen). PPCPs concentrations in Po river ranged from about 10 to 1800 ng/L. This contamination is higher, in terms of both PPCPs number and concentration, compared to water extracted by the wells, where iopamidol is still the PPCP with the highest concentration, followed by oxypurinol and acesulfame, which have no significant difference in concentrations compared to Po river raw water. Two anticorrosive agents were found in groundwater at half the concentration of Po river raw water. As for the antiepileptic drugs, gabapentine's concentration is about 30% of that measured in Po river, while carbamazepine was found in the bank filtration wells at concentration levels close to the ones in Po river. A significant variability in PPCPs concentration in the six campaigns has been observed, which can be due, among others, to seasonal use of the analysed PPCPs, hydrological conditions of Po river, analytical method uncertainty.

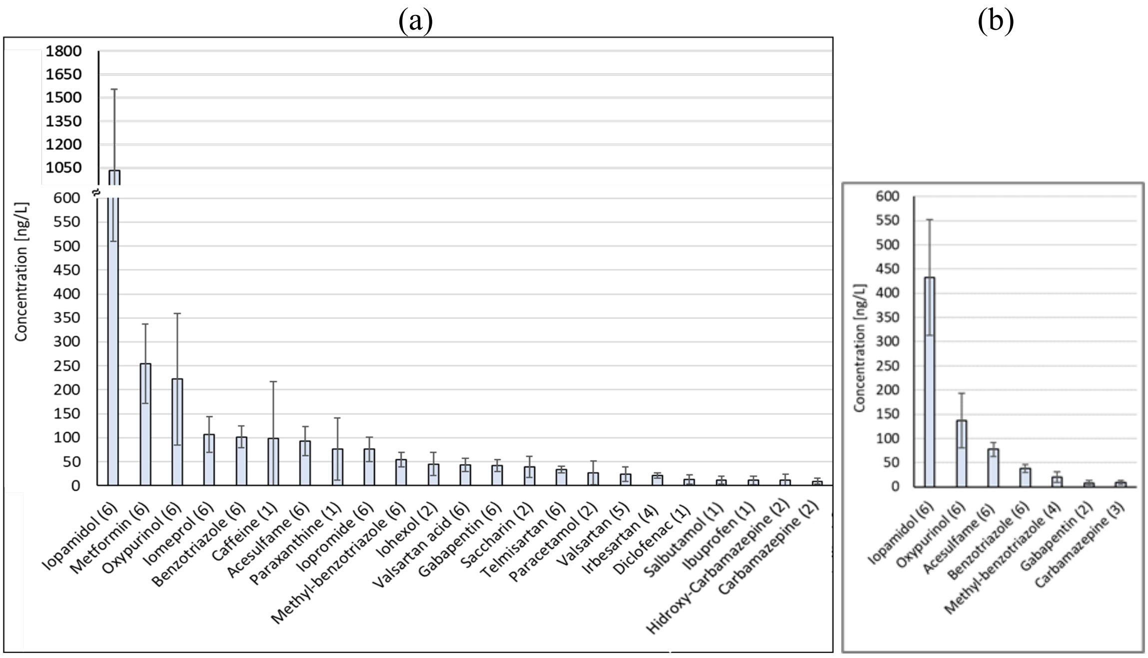

Figure 1. PPCPs concentration (mean ± standard deviation) in the raw waters captured by Po river (a) and from bank filtration wells (b). The number of times each compound was detected during the 6 campaigns is reported in brackets and the respective abbreviations are also reported.

To evaluate whether the hydrological conditions of Po river during the sampling campaigns can justify the variability in PPCPs concentrations at the DWTP inlet, the hydraulic and water quality models were coupled in the prototypal surface water transport model for iopamidol, that was the most critical PPCP, being detected with the highest concentration at the DWTP inlet. An example of the results of Po river transport simulation are displayed in Figure 2.

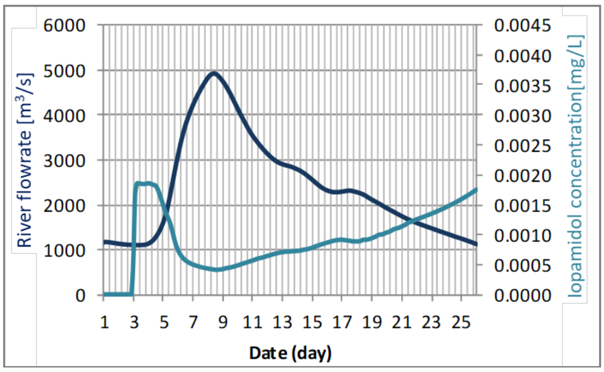

Figure 2. Hourly time series of iopamidol concentration compared with the flood hydrograph, simulated for the period from 1 to 25 October 2020.

It can be observed that the simulated iopamidol concentration is influenced by Po river hydrological conditions varying from 0.5 to 1.8 µg/L, that is in the measurements range observed. This range was found assuming upstream (154 kg/day) and lateral (26 kg/day) mass injection, coherent with the total mass injection (180 kg/day) calculated from the first sampling measurements at the DWTP (iopamidol concentration of 1.74 µg/L; Po river flowrate of 1,190 m^3/s).
Being able to estimate the concentration at the inlet of the DWTP, knowing Po river hydrological conditions, it is important to analyse the fate of PPCPs in the DWTP to evaluate their concentrations in the treated drinking water. Looking at the sum of PPCPs concentrations throughout the DWTP line treating Po river raw water (Figure 3), it can be observed the wide variability of concentration in the water leaving the lagoon and entering the ozonation section, confirming that there is no a significant reduction in PPCPs concentration in clariflocculation and sand filtration (Luo et al., 2014). Actually, the two main processes that showed an impact in

reducing a wide variety of PPCPs are ozonation and adsorption on activated carbon, with also a significant reduction in variability, resulting in a PPCPs sum concentration from 0.5 to 1.0 µg/L.

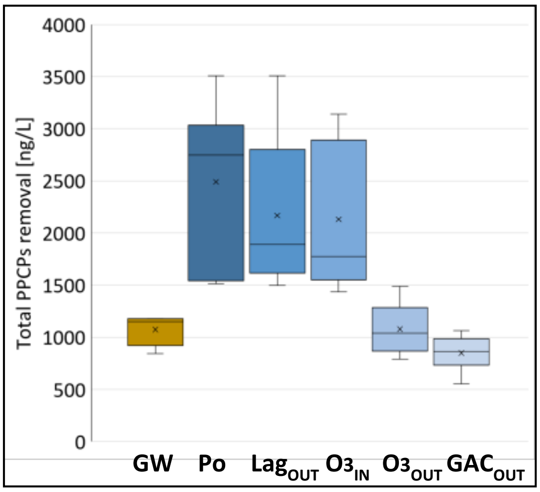

Figure 3. Boxplot of the sum of PPCPs concentrations in each sampling point through the DWTP.

The effectiveness of the different treatment in reducing the PPCPs depends on the operating conditions and compounds characteristics. Only two PPCPs were detected at the outlet of the GAC filters: iopamidol and metformin, having the highest concentrations, and which are characterized by low reactivity with ozone (low log K_{O3}) and low affinity with activated carbon, being hydrophilic compounds (low log D_{OW}).

In conclusion, the combination of field monitoring campaigns at the DWTP and the river transport modelling allowed to evaluate PPCPs pollution in the Po river basin and their fate from discharge to drinking water.

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