Pharmaceuticals and endocrine disrupting compounds (EDCs) in the Tiber River (Rome, Italy)

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Introduction

Emerging contaminants (ECs) and endocrine disrupting compounds (EDCs) are commonly found in surface waters, waste water and treated effluents at concentrations ranging from ng/L to few mg/L (1, 2 and references therein). Pharmaceuticals, and in particular synthetic antibiotics, are ECs extensively used in human and veterinary applications. The most important source of pharmaceuticals in the water cycle is via the body excretion, through urine (generally 55–80% of the total) and partially in the feces. In fact, pharmaceuticals are only partially metabolized and therefore enter the water cycle both as parent (unchanged) compounds and as a mixture of metabolites and/or as conjugated form. Latest studies focus on the effect of pharmaceuticals and their metabolites on aquatic ecosystem diversity, functioning and on the possible development of antibiotic resistance (AR) by the microbial community (3 and references therein).

Among EDCs, nonylphenols (NPs) and their precursors mono- and di-ethoxylates (NP1EO, NP2EO respectively) are metabolites of nonylphenol polyethoxylates (NPEOs), non-ionic surfactants widely used as detergents and emulsifying agents in industrial applications. NPs are included in the European list of priority hazardous substances for surface waters in the Water Framework Directive (WFD).

Pharmaceuticals and EDCs are not efficiently removed by most wastewater treatment plants (WWTPs) and through their effluents can reach surface waters (2, 4 and their references).

In this context, the present study investigated the occurrence of selected pharmaceuticals and EDCs in the principal WWTPs serving the city of Rome (Italy) and in the receiving River Tiber and River Aniene, in order to assess the possible risks for the aquatic ecosystem.

Materials and methods

Water samples (2 L) were collected in pre-cleaned brown bottles in January and June 2015 from five river sites and four WWTP effluents (Figure 1). The river sites were: Site 1 located upstream from the urban stretch of the River Tiber; Sites 2 and 3 located in the northern and southern urban stretch of the river, respectively; Site 4 near to the basin closure and Site 5 located along the River Aniene. The investigated WWTP effluents were: WWTP-Site 2 collecting slurry from the north of Rome mixed to industrial sewage, WWTP-Site 3 from the southern area of the city, WWTP-Site 4 from coastal districts and WWTP-Site 5 from the eastern part of the city mixed to industrial discharges.

The extraction/clean-up of pharmaceuticals and NPs from aqueous samples was performed by solid-phase extraction (SPE), by using Oasis MCX and Supelco C18 (Bellefonte, USA) cartridges, respectively, previously conditioned with methanol (6 mL) and ultrapure water acified at pH=2 (3 mL). Samples were then passed through the cartridges under vacuum and the cartridges were vacuum-dried for 5 minutes. Elution was made with methanol (3 mL) and 2% ammonia solution in methanol (3 mL).

All the eluates were pooled and dried under a gentle nitrogen stream. Analysis of pharmaceuticals was performed using HPLC/MS–MS, while NPs were determined by HPLC-fluorescence.

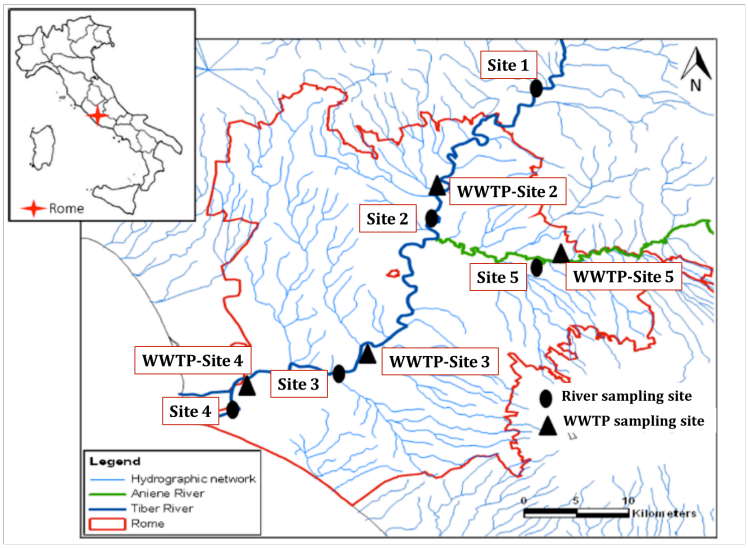

Figure 1. Map of the WWTPs, River Tiber and River Aniene sampling sites.

Results and discussion:

Figure 2 reports the average concentrations of the pharmaceuticals measured in the effluents of four WWTPs serving the city of Rome. Diclofenac (DIC), Gemfibrozil (GEM), Carbamazepine (CBZ), Ciprofloxacine (CIP), Sulfamethoxazole (SMX), Chlortetracycline (CTC) and Ibuprofen (IBP) concentrations were in the hundreds of ng/L, while Naproxen (NAP), Erythromycin (E-mycin), Estrone (E1), Fenoprofen (FPF), Clofibric acid (CFA) concentrations were in the tens of ng/L (Figure 2). These concentration values were in line with previously published data on the occurrence of pharmaceuticals in Italian urban wastewaters (5-8). Highest levels were detected for DIC, GEM, CBZ and CIP, as a result of both their high prescription extent and wide usage by the resident population. However, Amoxicillin (AMX), which is among the most prescribed antibiotics, occurred at low concentrations in WWTP effluents, probably because of its rapid natural degradation (8).

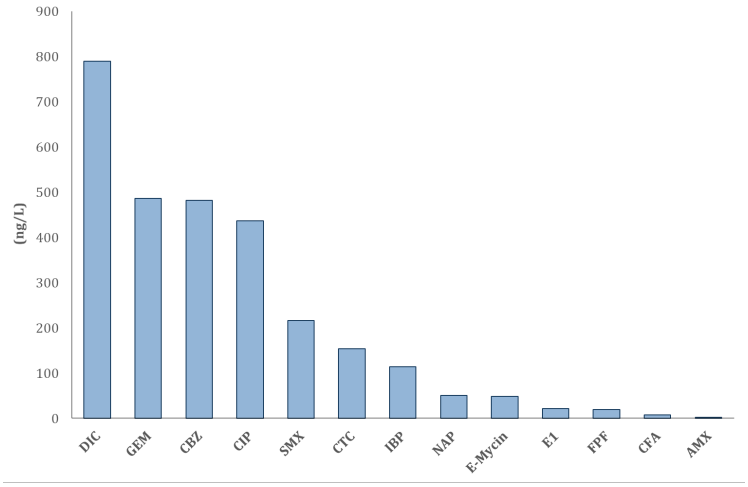

Figure 2. Average concentrations of the selected pharmaceuticals in the WWTP effluents of Rome.

Almost all the pharmaceuticals (with the only exception of FPF, CFA and AMX) were detected in the WWTP effluents and in River Tiber and River Aniene in both periods, although these chemicals were subjected to dilution (Figures 3 and 4, respectively). In the Site 1, located upstream of the urban area of Rome (Figure 1), was found the lowest pharmaceutical concentrations, which tended progressively to increase along the River Tiber

stretch crossing the city of Rome (Sites 3 and 4). These results confirm that WWTP effluents can act as a significant source of pharmaceuticals in surface waters.
The concentrations of target compounds showed a general increase during the summer period compared with those detected in the winter period, with the only exception of Ibuprofen and some antibiotics, such as CIP, SMX, CTC, E-mycin and AMX, which, on the contrary, showed an opposite seasonal variation (Figures 3 and 4). These results can be explained considering that the main removal processes in the investigated WWTPs are biodegradation and sorption, which are both temperature-dependent. For many compounds, sorption increases with a decreasing temperature, whereas biological removal efficiency decreases at lower temperatures. Therefore, in the two investigated periods, the one or the other removal mechanism can prevail due to the different seasonal temperatures and to the different physico-chemical characteristics of the compounds (9). In addition, the different occurrence of IBP and most of the detected antibiotics between the two sampling periods can be also related to their major human consume during the winter period, causing higher loads entering the treatment plants (10).

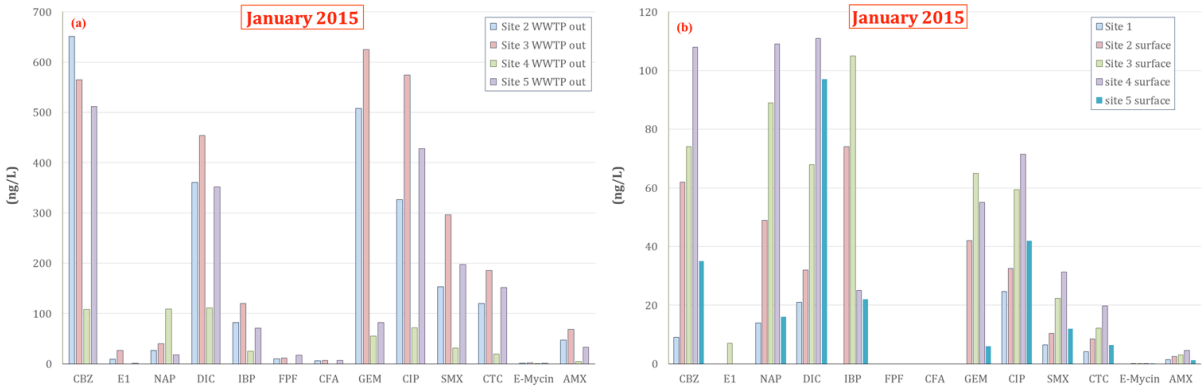

Figure 3. Average concentrations (ng/L) of the selected pharmaceuticals in the WWTP effluents (a) and surface waters (b) in January 2015.

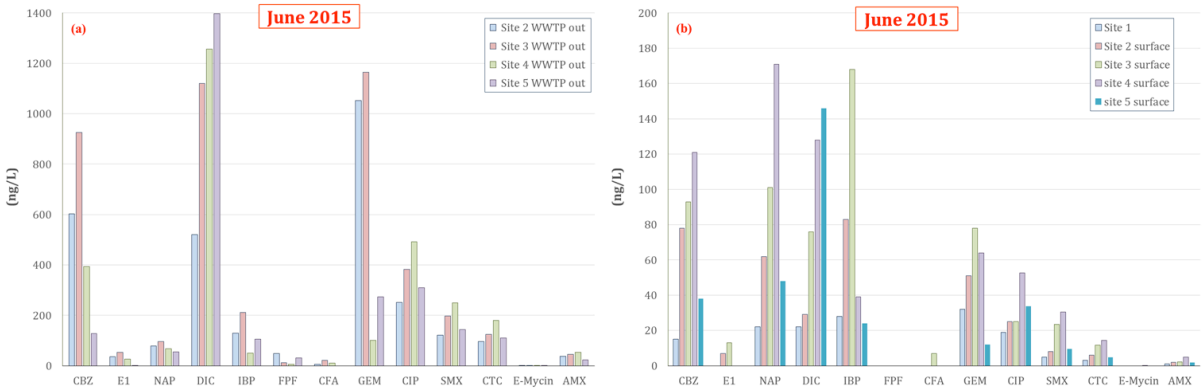

Figure 4: Average concentrations (ng/L) of the selected pharmaceuticals in the WWTP effluents (a) and surface waters (b) in June 2015.

The concentration values of bisphenol A (BPA), nonylphenol (NP), nonylphenol mono- (NP1EO) and di-ethoxylate (NP2EO) measured in the river waters in January and June 2015, are reported in Figure 5. BPA concentrations were rather constant along the river sites in both periods (Figure 6), ranging from 0.06 to 0.09 µg/L in summer and from <LOD (0.03 µg/L) to 0.14 µg/L in winter (Figure 5). Vitali et al. (2004) reported NP concentrations in the upper part of the River Tiber basin generally lower than 0.1 µg/L, although concentrations up to 1.6 µg/L were occasionally measured in samples collected downstream wastewater inputs (11). In our study, NP concentrations upstream Rome (Site 1) were higher than 0.30 µg/L in both seasons. These values

suggested the occurrence of NP sources in this rural area, where agriculture activities can cause the environmental input of nonylphenol ethoxylates surfactants contained in pesticide formulations. Furthermore, several textile, painting or paper mills industries sited in this area can discharge NP. Flowing through Rome, NP concentrations in the river remained almost constant in both seasons (Figure 5), indicating that WWTP effluents and urban drainage were the most important NP sources in the urban environment.
Higher surface water NP1EO and NP2EO concentrations were detected in summer than in winter season, especially at Site 3 and Site 4 located downstream the southern municipal WWTP effluent. In both seasons, the highest values of NP1EO and NP2EO (NP2EO>NP1EO) were determined in Site 5 (River Aniene), which is located near to an industrial area.

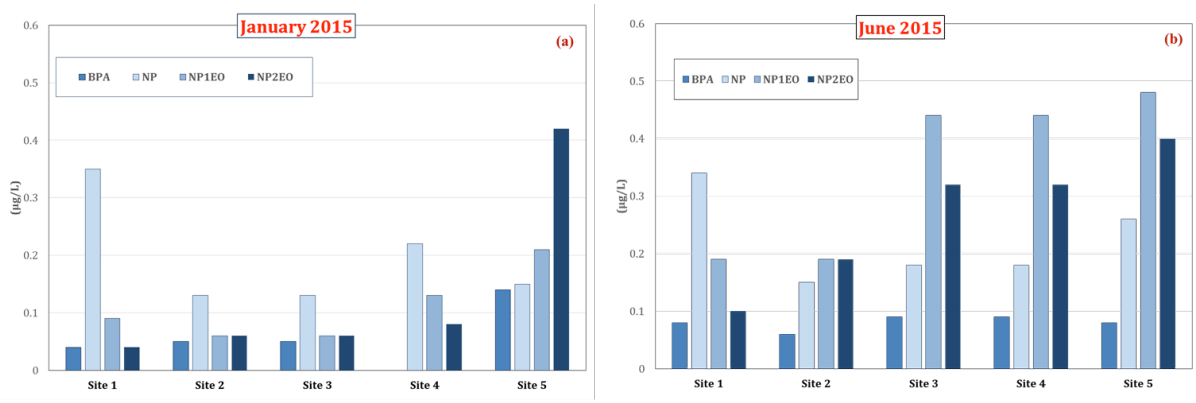

Figure 5. Concentration of bisphenol A (BPA), nonylphenol (NP), nonylphenol mono- (NP1EO) and di-ethoxylate (NP2EO) along River Tiber and River Aniene in January (a) and June (b) 2015.

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