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PRESENCE AND REMOVAL OF ORGANIC MICROPOLLUTANTS IN 8 DIFFERENT WASTEWATER TREATMENT PLANTS AND RISK ASSESSMENT OF TREATED EFFLUENT

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Abstract Increasing attention has been paid in the recent years to the presence of Organic MicroPollutants (OMPs) in water, being considered a source of a high risk for public health and environment (Rodriguez-Narvaez et al., 2017). The present study belongs to a wide research activity carried out since 2018 and still ongoing having the aim to assess the occurrence with time and removal rate of OMPs in full-scale Wastewater Treatment Plants (WWTPs) (Di Marcantonio et al. 2020). The present paper shows the results of the monitoring activity conducted on the influent and effluent of 8 WWTPs focusing on 14 selected OMPs belonging to different classes (e.g. caffeine, illicit drugs, pharmaceuticals). The study activity included measuring in the same samples the traditional water quality parameters (e.g. COD, nitrogen species, TSS) to evaluate if there is any correlation between their removal and that of the selected OMPs. The investigated plants were chosen being representative of different treatment processes, of the type of final disposal of the treated water and the characteristics and extension of the area served by the sewage network. Finally, the environmental risk assessment was carried out based on the values of OMPs measured in the effluent of the plants.

Keywords: Caffeine, Emerging contaminants, Illicit drugs, Pharmaceuticals, Wastewater treatment plants.

1. Introduction

Organic MicroPollutants (OMPs) include a wide number of chemicals belonging to different classes, e.g. pharmaceuticals and personal care products (PPCPs), licit and illicit drugs and their metabolites, steroids and hormones, endocrine-disrupting compounds, surfactants, perfluorinated compounds, phosphoric ester flame retardants, industrial additives and agents, siloxanes, artificial sweeteners and gasoline additives (Bletsou et al. 2015; Barbosa et al. 2016; Chiavola et al. 2019). In the last two decades, increasing attention has been dedicated to OMPs, as a source of a high risk for public health and environment (Naidu et al. 2016; Rodriguez-Narvaez et al. 2017). These substances are widely found in the sewage systems where they are released along with their metabolites as a consequence of human consumption, internal adsorption, metabolization. Through the sewage the OMPs and their metabolites reach the wastewater treatment plants. The scientific community established that one of the main sources of release to the environment is represented by the wastewater treatment plants (WWTPs), since not specifically designed and operated to treat OMPs- containing sewage and therefore unable to remove them to a wide extent (Di Marcantonio et al., 2020; Luo et al., 2019). So far, the information about the removal processes and transformations occurring in the plants are not fully clear and must be further elucidated. This study aims to provide a better knowledge on the effects of the wastewater treatment plants on the removal of OMPs: particularly, the focus was put on the effects of 8 different layouts of plants with respect to 14 selected OMPs. Furthermore, the influence of operating, process and environmental conditions, and also influent characteristics was considered. This information is essential to evaluate the level of efficiency reached by the existing plants and if there is the need to implement new treatments or operating strategies to increase the abatement level of the selected OMPs. Finally, the environmental risk assessment was carried out for the release of the treated effluent of the WWTPs in the final receptors (European Medicines Agency 2018). The results herewith presented represent a part of a wider study which is still ongoing with the aim to provide all the data needed to achieve a full understanding of the problem.

2. Materials and methods

2.1. WWTPs and sampling campaign

The sampling campaign was conducted on 8 WWTPs located in the Central Italy from January 2020 to December 2020. Such plants were selected due to the high treatment capacity (in terms of Population Equivalent, PE) and the different type of the biological oxidation process (Di Marcantonio et al. 2020) (see Table 1). The campaign consisted of a total of 68 sampling days, distributed between 5 and 12 among the WWTPs. Sampling was performed by grab samples collected from the influent and effluent. The following contaminants, belonging to the classes of pharmaceuticals and illicit drugs, were considered:

· Benzoylecgonine (BEG)
· Carbamazepine (CBZ)
· Cocaine (COC)
· Ketoprofen (KTP)
· Lincomycin (LCN)
· Methamphetamine (MET)
· Sulfamethoxazole (SMX)
· Trimethoprim (TMT)
· 11-nor-9carboxy-Δ9-THC (THC-COOH)
· Amphetamine (APT)
· Caffeine (CAF)
· Sulfadiazine (SDZ)
· Warfarin (WRF)
· Sulfadimethoxine (SDM)

The quantitative analysis of OMPs was performed through Ultra-Performance Liquid Chromatography coupled to tandem Mass Spectrometry. The applied analytical method was based on EPA 538, which was optimized through previous studies conducted by the same research group. The analytical method was also accredited in 2020 by ACCREDIA for most of the analytes.

Table 1. Main characteristics of the monitored WWTPs. Abbreviations: BS=Bar Screening, DD=Degreasing Degritting, PS=Primary Sedimentation, O=Biological Oxidation, DN=Denitrification, SS=Secondary Sedimentation, F=Filtration, BF=Biofiltration, MBR=Membrane BioReactor, MBBR=Moving Bed Biofilm Reactor, UV=UV disinfection, DC=Hypochlorite disinfection, DP=Peracetic acid disinfection.

Name of the monitored WWTPs	Water treatment line	Av. flow rate [mc/s]	Design treatment capacity [PE]
WWTP 1	BS, DD, PS, DN, O, SS, F, UV, DC	0.22	90 000
WWTP 2	BS, DD, MBBR, SS, F, DP	0.17	90 000
WWTP 3	BS, DD, PS, DN, O, SS, DC	1.17	300 000
WWTP 4	BS, DD, PS, DN, O, SS, DC	1.83	600 000
WWTP 5	BS, DD, PS, O, SS, DC	2.96	520 000
WWTP 6	BS, DD, PS, DN, O, SS, DC	0.99	350 000
WWTP 7	BS, DD, PS, BF, O, SS, DP	9.23	1 090 000
WWTP 8	BS, DD, DN, O, MBR	0.06	18 000

2.2. Calculation methods

Frequency of detection (Fd) of each contaminant considering all the plants together has been calculated with the following equation:

$$Fd(\%) = \frac{n}{N} * 100$$

Where N is the total number of samples and n is the number of samples where the concentration of the contaminant is above the Minimum Reporting Level (MRL) of the analytical method.

The removal efficiencies were evaluated for each compound as follow:

$$R(\%) = \frac{Cin - Cout}{Cin} * 100$$

Where Cin and Cout stand for the concentrations measured in the influent and effluent of the plants for each contaminant in the different sampling days.

The standardized removal efficiency (SRE) has been calculated through the following equation:

$$SRE = \frac{x - \mu}{\sigma} * \frac{n}{N}$$

Where x represents each individual removal efficiency for a given contaminant in a specific WWTP and sampling day, μ is the average removal efficiency for the contaminant over all WWTPs, σ is the standard deviation of the removal efficiencies for a contaminant over all WWTPs, n is the number of measurements for the contaminant in the WWTPs class which the plant belongs to and N is the number of measurements across all WWTPs (Ben et al. 2018; Di Marcantonio et al. 2020).

The risk quotient (RQ) was calculated for each contaminant detected in the effluent of each WWTP using the following equation:

$$RQ = \frac{MEC}{PNEC}$$

The MEC was considered as the median concentration value of each OMP in the output. MEC values were divided by a dilution factor (posed equal to10) in order to take into account the concentration dilution when the effluent is released and mixed with the receiving waters (European Chemicals Agency, 2012).

3. Results and discussion

3.1. Statistical analysis of OMPs concentrations in the influents and effluents

Figure 1 shows the OMPs concentration in the influent (IN) and effluent (OUT) of the selected WWTPs. Among the OMPs searched, BEG, SMX, KTP, CBZ, COC, TMT and CAF were almost always detected in IN samples (Fd ranged from 98% to 100%). The Fd of BEG, COC, TMT, KTP and CAF was drastically reduced in the output; by contrast, CBZ and SMX were still present in most of the effluent samples. As far as the concentration is concerned, the CAF showed the highest input value; then, higher values were found for BEG and KTP with respect to other contaminants. However, the values measured in the output were much lower. As shown by Figure 1, the input and output concentration of CBZ were very similar. In the case of APT and SDM, both in the input and output, concentrations were lower than MRL. For WRF and THC-COOH, concentrations resulted to be below MRL in most measurements (Fd<10%). SDZ and MET showed a similar behaviour, with low input and output concentrations. The LCN value was also rather low in the input and output in all the plants (ranging from 0.01 to 0.17 μg/L). SMX was subjected to a significant reduction between the IN and the OUT samples. SMX, together with CBZ, was the OMP with the highest effluent Fd. These results agree with those presented by other studies of the scientific literature (Balakrishna et al. 2017; Couto et al. 2019).

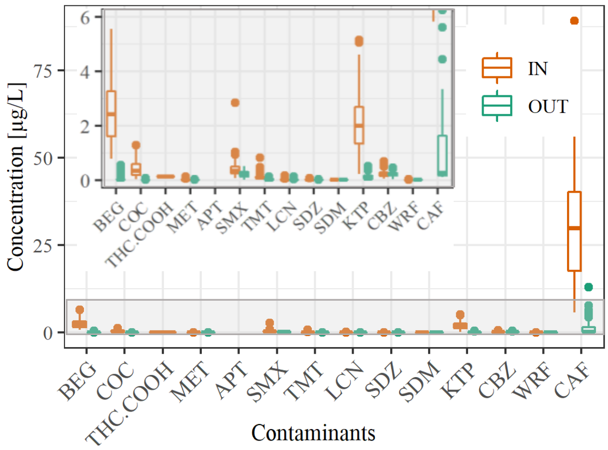

Figure 1. Statistical variation around the median value of influent (IN) and effluent (OUT) concentrations of each OMP in the 8 WWTPs.

3.2 Removal Efficiency

The calculated OMPs removal efficiencies between the influent to the plant and the final effluent are presented in Figure 2 for the investigated WWTPs.

As it can be seen from the boxplot, BEG and COC were characterized by a high removal (above 90% as median value), which is in accordance with the data reported by the scientific literature. Median removal of KTP was above the 85% for all the treatment plants. Despite the higher inlet concentration, CAF was fully or almost fully removed in all the WWTPs. Differently from the other OMPs, CBZ, showed a median removal always below 40%, with a prevalence of negative and null removal efficiencies.

As it can be seen from Figure 2, LCN showed a peculiar behaviour as compared to the other contaminants, with quite heterogeneous removal efficiencies among the plants. For instance, the removals were negative in WWTP1, WWTP3 and WWTP7, whereas higher values were measured in WWTP2 and WWTP8 (i.e. 42% and 65%, respectively).

For MET and TMT, the removals values were quite high, in most of the plants. SMX showed a removal between -8% (WWTP7) and 65% (WWTP2). For SDZ, similar removals were found in all the plants, with values exceeding 50%. For SDM, APT, THC-COOH and WRF, the removal trend was not considered reliable due to the low number of samples where they were detected above MLR (Fd<10%).

In order to make a better comparison between the various plants, the removals of the OMPs under study was evaluated based on the standardized removal efficiency (SRE). The calculated standardized removal efficiencies of all OMPs in the 8 WWTPs are shown in Figure 3.

From these statistical analyses, it can be seen that all plants behaved very similarly, although specific differences can be highlighted. This could depend on the different treatment capacity of the plants and plant layout. Based on the median value of the SRE (represented by the red dots) it is possible to groups WWTP6, WWTP7 and WWTP8 together, as the plants characterized by the worse performance as compared to the other plants. The best overall OMPs removal capability was observed by the WWTP1 and WWTP5; however, the former one was also characterized by a wide variability of the removal values. WWTP1 is actually a wastewater reclamation plant, equipped with the tertiary compartment; therefore, it is

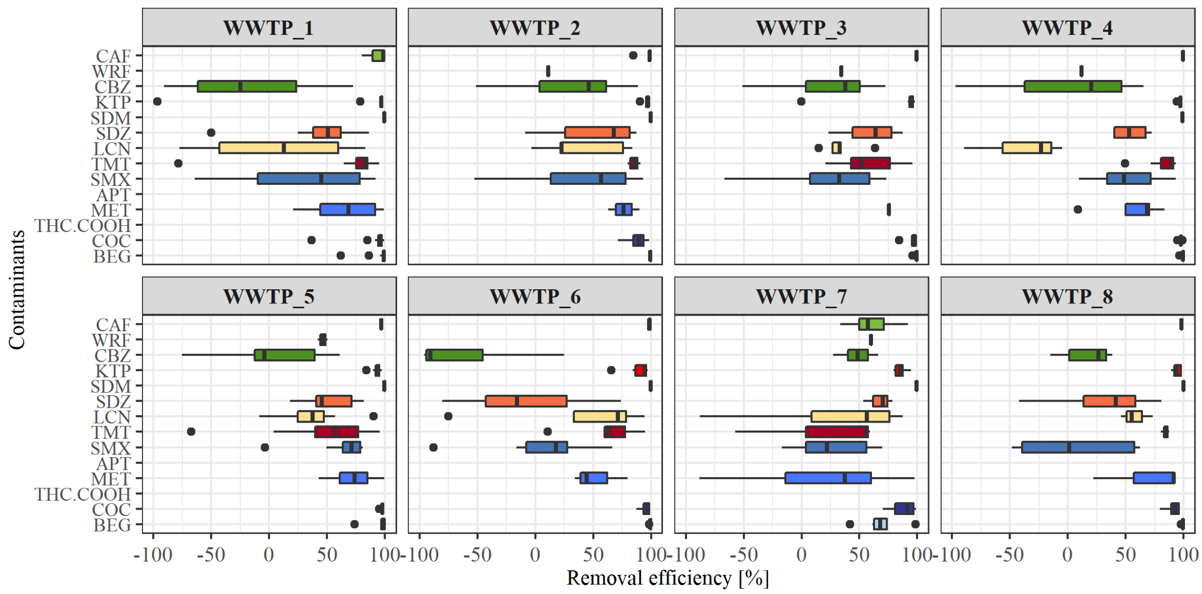

Figure 2. OMPs removal efficiencies in the different WWTPs.

likely that the better performance was due to the presence of this additional stage.

The WWTP2 also performed better than other plants in terms of SRE distribution. The biological compartment of this plant is an MBBR, which is known as a treatment technology capable of removing also the contaminants with a lower biodegradability due to a higher Sludge Retention Time (SRT) (Grandclément et al. 2017). WWTP4 and WWTP8 provided the tighter boxplot, which suggests that the performance of these plants was quite stable.

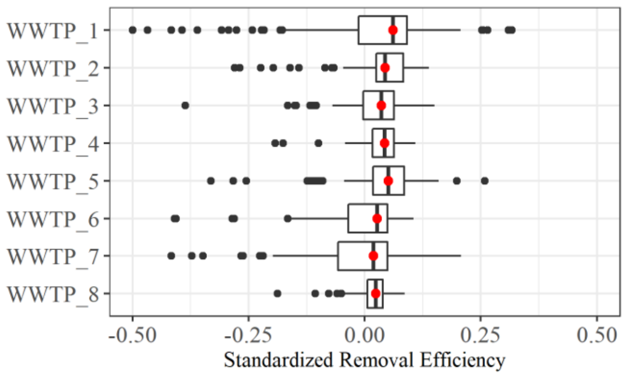

Figure 3. Standardized removal efficiency of the different of WWTPs related to all the OMPs together.

3.4 Environmental Risk Assessment (ERA)

The environmental risk assessment was carried out in order to evaluate whether the residual concentration of OMPs in the final effluent of the WWTPs is a risk for the aquatic ecosystems represented by the receiving water bodies. The results of the ERA provided RQ values always below 1 for all the OMPs. This indicates that the effluent from all the investigated WWTPs does not represent a source of environmental risk under the considered operating conditions. The highest value of RQ (0.6) was found for CBZ in WWTP1.

4. Conclusions

The results obtained provide an important overview of the treatment performance of different types of full-scale WWTPs with respect to selected classes of OMPs, chosen since frequently found in the influent to the plants. Based on these results, it can be concluded that most of the OMPs are removed efficiently by the common WWTPs for domestic sewage; the residual concentrations still present in the treated effluent does not pose a risk for the environment. According to other studies, only for CBZ the concentration does not change between the influent and the effluent; however, the related risk can be considered still low due to the limited concentrations.

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