OCCURRENCE AND FATE OF EMERGING TRACE ORGANIC CONTAMINANTS IN TWO SEMI-URBANIZED CATCHMENT BASINS IN SICILY (ITALY): FROM SOURCE TO SINK

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ABSTRACT

Many studies indicate that several classes of emerging trace organic contaminants (ETrOCs) are widely distributed in the environment. Some ETROCs have shown estrogenic and other effects to wildlife and potentially to humans while the release of antibiotics in the environment has been shown to cause the development of bacterial resistance. In this study, water samples were collected from the source to sink in two semi-urbanized catchment basins in Sicily, and analyzed for several ETROC classes, including pharmaceuticals, personal care products, and endocrine disrupting compounds. In both catchment basins, wastewater treatment plants (WWTPs) were identified as the major sources of ETROCs. More recalcitrant ETROCs, notably acesulfame and sucralose were found in all sampling points along the rivers, whereas the highest total ETrOC concentrations were found in samples collected directly downstream from wastewater discharge. No ETrOCs were detected in sea water. Acesulfame and caffeine were detected at low concentration in sea water samples collected close to the rivers' mouth. Discharges of WWTP effluents in the rivers were found to cause an increase of dissolved organic carbon concentration (DOC) in affected water. Fluorescence excitation-emission spectroscopy confirmed the presence of a significant fraction of effluent organic matter in river water. UV absorbance at 254 nm, total fluorescence and DOC were well correlated (R^2 > 0.7) with sucralose concentrations found in sample taken along the course of the investigated rivers. This supports the notion that these surrogate parameters can be useful tools to evaluate wastewater impact in river.

Keywords: Emerging pollutants, River, Sea, Wastewater discharge, Monitoring, Fluorescence, Sucralose

1. Introduction

More than 65 million chemicals and chemical formulations are available commercially and approximately 15,000 new chemicals are given Chemical Abstract Service (CAS) numbers each day (Snyder, 2014). Thus, it is not surprising that an ever increasing number of synthetic chemicals are being detected in water. In recent years, a large number of studies have focused on pharmaceuticals, endocrine disrupting chemicals, and other emerging trace organic compounds (ETOrCs) which can be identified and quantified in nanogram per liter concentrations, or lower, in water using modern analytical techniques (Anumol and Snyder, 2015). While effects of many ETOrCs on public health remains largely unknown, studies have shown that some of these contaminants can have drastic effects on aquatic organisms at concentrations of these compounds typical for wastewater (Daughton and Ternes, 1999). Other studies have demonstrated that a combination of ETOrCs can have synergistic effects on some organisms (Carlsson *et al*., 2006). Despite this awareness, legal limits have not yet been set for ETOrCs in water.

Wastewater treatment plants (WWTPs) have been shown to be significant source of ETOrCs in river water (Niina *et al*., 2005). Anthropogenic compounds such as artificial sweeteners (e.g. sucralose and acesulfame), caffeine, carbamazepine and primidone have been proposed and demonstrated to be useful tracers or indicators of domestic and municipal wastewater in surface water (Jekel *et al*., 2015) but the analysis of ETOrCs at their actual levels in water is laborious, time-consuming and expensive. Also, given the number of ETOrCs introduced to the environment constantly increasing, it is impossible to monitor each one of them individually. While the use of indicator compounds is relevant and appealing, it is still affected by similar analytical problems and this approach reduces the time and cost of analysis only slightly. Consequently, interest is increasing in using easily measurable bulk organic parameters (BOPs) of water as surrogates useful for ETOrCs monitoring. For example, UV absorbance and fluorescence excitation/emission spectroscopy has shown good promise in predicting the removal of ETOrCs during advanced wastewater treatments (Gerrity *et al*., 2012).

Objectives of this study were: i) to evaluate the occurrence and fate of selected ETROCs, including pharmaceuticals and personal care products, endocrine disrupting compounds, and sweeteners, in two catchment basins that receive different point sources of ETROCs; ii) to explore the use of spectroscopic surrogate parameters to monitor the fate of ETROCs in wastewater-affected rivers.

2. Materials and methods

2.1. Sampling site and samples collection

Simeto and San Leonardo rivers flow in the East Coast Region of Sicily (Italy). The Simeto River with a length of 101 km and a basin catchment extension of 4193 km^2 is one of the main rivers in Sicily. Its main influents are from the source to the mouth: the Troina, Salso, Dittaino and Gornalunga Rivers. The San Leonardo is a much smaller river with a length of 43 km and a basin catchment surface of 559 km^2. Both rivers receive discharges of different WWTPs effluents. Grab samples were collected along the Simeto and San Leonardo rivers trying to follow the same plume of water. Grab samples from the tributaries Troina and Dittaino rivers were also collected. Samples were collected in the Mediterranean Sea close the rivers' mouths as well (Figure 1). The untreated sewage from a non-operating WWTP (point C3 in Figure 1) was collected as a grab sample at the point prior to reaching the San Leonardo River.

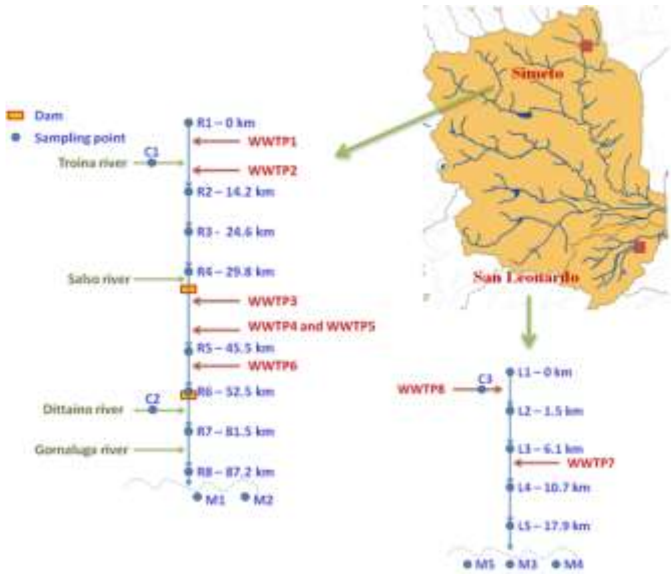

Figure 1: General scheme of the Simeto and San Leonardo watersheds and locations of the sampling points. M symbol correspond to samples collected in the Mediterranean Sea close to the rivers' mouths. C points denote tributary rivers. Square symbols located in the river catchments correspond to R1 and L1 sampling points. Progressive distance is reported for collection points in the Simeto and San Leonardo watersheds.

2.2. Analytical methods

Twelve pharmaceuticals (atenolol, carbamazepine, N,N-Diethyl-m-toluamide (DEET), diclofenac, diltiazem, gemfibrozil, ibuprofen, meprobamate, naproxen, primidone, sulfamethoxazole), four personal care products (tris (2-chloroethyl) phosphate (TCEP), (tris (2-chloropropyl) phosphate) TCPP, triclocarban, triclosan), two sweeteners (acesulfame, sucralose), one stimulant (caffeine) and two industrial products (benzotriazole, perfluoro octanoic acid PFOA) were analyzed using an automated liquid chromatography online SPE system coupled to an Agilent 6460 triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA). Further details of the analytical method are available in prior related publications (Anumol and Snyder, 2015). A Shimadzu TOC-LCSH (Kyoto, Japan) total carbon analyzer was used for DOC quantification. Conductivity and pH were measured at room temperature in the laboratory. UV absorbance spectra were measured using a Shimadzu UV spectrophotometer. Fluorescence excitation-emission matrix (EEM) measurements were conducted using a Shimadzu fluorometer that employs a xenon excitation source. Regional integration was conducted according to published literature (Gerrity *et al*., 2012) to calculate the total fluorescence (TF) intensities (in Raman unit) for each sample.

3. Results and discussion

3.1. ETROCs concentrations in rivers

Concentrations of some of the investigated ETROCs in the river water are reported in Table 1 and Table 2 for the Simeto and San Leonardo rivers, respectively. In the Simeto River, the highest total concentrations of ETROCs were found in points R2, R5 and R6, which are located downstream of the corresponding wastewater discharges (Figure 1). These points are also characterized by elevated DOC concentrations. In accord with this, analysis of the EEM spectra confirmed the presence of a significant fraction of wastewater organic matter in water samples collected downstream from WWTP discharges. Acesulfame and sucralose were the only two compounds to be detected in all the sampling points along the Simeto river, except in the sampling points that are non-impacted by wastewater (point R1 in Figure 1). Acesulfame and caffeine were the only compounds detected in sea water.

Table 1: ETROCs concentration in different points of Simeto river.

	R1	C1	R2	R3	R4	R5	R6	C2	R7	R8	M1	M2
DOC	2.6	2.7	3.2	2.8	2.7	5.1	5.2	5.9	4.4	4.8	3.5	2.2
Acesulfame	<MRL	433	574	749	130	582	709	178	428	353	117	<MRL
Sucralose	<MRL	<MRL	271	362	na	174	211	234	247	215	<MRL	<MRL
Caffeine	<MRL	45	176	<MRL	80	228	491	34	73	76	110	65
Sulfamethoxazole	<MRL	<MRL	<MRL	17	<MRL	26	27	<MRL	21	17	<MRL	<MRL
Carbamazepine	<MRL	<MRL	36	24	<MRL	<MRL	24	<MRL	<MRL	<MRL	<MRL	<MRL
Naproxen	<MRL	<MRL	39	<MRL	<MRL	30	17	<MRL	6	9	<MRL	<MRL
DEET	<MRL	<MRL	68	13	<MRL	22	53	<MRL	7	32	<MRL	<MRL
Primidone	<MRL	6	10	7	9	<MRL	<MRL	49	33	<MRL	<MRL	<MRL
Gemfibrozil	<MRL	<MRL	30	<MRL	<MRL	6	8	<MRL	2	<MRL	<MRL	<MRL

na, non-available. MRL, minimum reporting level

In the San Leonardo river water, the highest total ETROC concentrations and DOC levels were measured after the wastewater discharge entered the stream (Table 2). Due to the short length of the San Leonardo river, carbamazepine, DEET, gemfibrozil, sulfamethoxazole were detected together with acesulfame and sucralose in all the sampling points impacted by wastewater.

Significant dilution at point L5 (i.e. river estuary) for all the ETROCs is attributable to sea water intrusion. On the contrary, an increase in DOC concentration was observed in this point.

Table 2: ETROCs concentration in different points of San Leonardo river.

	C3	L1	L2	L3	L4	L5	M3	M4	M5
DOC	9.0	3.5	7.2	5.3	5.7	6.6	1.3	1.0	0.9
Acesulfame	4689	<MRL	2566	2184	1816	874	96	<MRL	<MRL
Sucralose	899	<MRL	713	600	852	493	<MRL	<MRL	<MRL
Caffeine	18834	34	12838	407	157	88	28	77	24
Sulfamethoxazole	41	<MRL	28	36	51	23	<MRL	<MRL	<MRL
Carbamazepine	66	<MRL	43	31	76	44	<MRL	<MRL	<MRL
Naproxen	323	<MRL	149	103	70	<MRL	<MRL	<MRL	<MRL
DEET	1364	<MRL	694	343	428	109	<MRL	<MRL	<MRL
Primidone	<MRL	<MRL	<MRL	<MRL	54	<MRL	<MRL	<MRL	<MRL
Gemfibrozil	152	<MRL	325	21	94	7	<MRL	<MRL	<MRL
MRL, minimum reporting level									

3.2. Correlation models between surrogates and ETrOCs

In the Simeto and San Leonardo river watersheds, good correlations were observed between sucralose concentrations and UV absorbance at 254 nm (UV_{254}), TF and, only for the Simeto river, DOC measurements (Table 3). This is in agreement with the point that organic matter in the river water is likely to be impacted by wastewater. No correlation was observed for other ETROCs. In Table 3, data from the river tributaries and sea water (i.e. C points, and M points) were not used for linear regression analysis, but good correlations for sucralose with UV_{254}, TF and, only in Simeto river, DOC were still observed in both basin catchments (R^2>0.7) even if samples from the tributaries were included in the analysis. For the San Leonardo river, sample collected in the estuary (point L5) was not used for linear regression analysis. In this point where very high DOC concentration was measured, sea water intrusion and different organic matter fractions typical of estuarine environment (Hundson *et al*., 2007) may skew the R^2 values.

Table 3: Linear correlation (R^2) between surrogate parameters and sucralose concentrations in Simeto and San Leonardo rivers.

	Simeto river	San Leonardo river
UV_{254}	0.873	0.955
TF	0.726	0.958
DOC	0.840	0.017
Conductivity	0.320	0.512
N. correlation points	6	3

It is noteworthy to observe that in San Leonardo river only a very limited number of points can be used for linear regression analysis.

4. Conclusions

This study resulted in the following findings:

- Wastewater treatment plants were identified as the major sources of ETROCs in river;
- Increase of DOC concentrations in river was determined to be related to wastewater discharge;
- Good correlations were found to exist between DOC, UV_{254} and TF and the wastewater tracer sucralose suggesting the possibility to use surrogate parameters measurement to evaluate wastewater impacts in rivers and watershed.

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