



# Polar organic micropollutants in the coastal environment of different marine systems



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## ABSTRACT

Polar anthropogenic organic micropollutants are frequently detected in freshwater and discharged on large scale into marine systems. In this work the results of 153 samples collected from the shorelines of the Baltic Sea (Germany), Northern Adriatic Sea (Italy), Aegean Sea and Dardanelles (Greece & Turkey), San Francisco Bay (USA), Pacific Ocean (USA), Mediterranean Sea (Israel), and Balearic Sea (Spain) are presented. The samples were analyzed for various classes of micropollutants such as pharmaceuticals, corrosion inhibitors, biocides, and stimulants. Caffeine, paraxanthine, theobromine, tolyltriazole, 1H-benzotriazole, and atrazine were detected in >50% of all samples. The detection frequencies of carbamazepine, iopamidol, diuron, sulfamethoxazole, paracetamol, theophylline, and atenolol were between 20% and 32%. As caffeine is linked to untreated wastewater, the widespread occurrence of raw sewage in marine environments and thus potentially elevated nutrient concentrations and risk for the presence of wastewater-related pathogens is remarkable.

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## 1. Introduction

Polar anthropogenic organic micropollutants such as pharmaceuticals, corrosion inhibitors, biocides, and stimulants are frequently detected in raw sewage and wastewater treatment plant (WWTP) effluents (Loos et al., 2013a; Margot et al., 2013). Therefore, these compounds are omnipresent in the aquatic environment including groundwater (Loos et al., 2010; Reh et al., 2013) and surface water (Loos et al., 2009; Hughes et al., 2013) and, consequently, discharged on large scale into marine environments. Regarding the corrosion inhibitors 1H-benzotriazole and tolyltriazole, Wolschke et al. (2011) calculated an annual input into the North Sea of ~60 t by the River Rhine alone. Xu et al. (2013) determined the concentrations of nine selected antibiotics in the Pearl River and concluded that a total of 193 t a<sup>-1</sup> is transported by the Pearl River to the South China Sea. In addition to riverine contributions, micropollutants are also released by atmospheric input, direct discharge of raw and treated domestic and industrial wastewater, shipping, harbor and port activities, offshore oil exploration, and aquaculture (EEA, 2011). Depending on the persistency of a compound and the water exchange and evaporation rate in the receiving water body, a compound may significantly accumulate in

marine and especially coastal environments. This was demonstrated by Biselli et al. (2000) who compared the concentrations of antifouling agents in German marinas of the North and Baltic Sea and attributed the significantly lower concentrations in North Sea marinas to their higher water exchange rate.

The European Water Framework Directive (EC, 2000) sets environmental objectives for the proper quality of inland, surface, transitional, coastal, and ground waters. Moreover, the Marine Strategy Framework Directive (MSFD) (EC, 2008) establishes a framework, within the member states shall take the necessary measures to achieve and maintain good environmental status in the marine environment by developing strategies to monitor, protect, and restore the marine environment and reduce inputs, pressures or impacts of human activities in each marine region. The very recently published report regarding the first phase of the MSFD stated that “pollution in the marine environment has decreased in some places but levels of nutrients and certain hazardous substances are overall still above acceptable limits. Oxygen depletion, as a result of nutrient pollution, is particularly serious in the Baltic and Black Seas.” (EC, 2014) and it was concluded that more efforts need to be made to meet the objective of reaching good environmental status until 2020.

In view of the above and considering observable detrimental effects in the environment caused by complex mixtures of chemicals (EEA, 2011; Kortenkamp et al., 2009), intensive global

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monitoring studies covering a large variety of different substances representing various contamination sources are implied. Loos et al. (2013b) monitored 67 micropollutants in the Northern Adriatic Sea 16 km offshore from Venice (Italy) and detected 45 above the limit of quantification. Among the compounds detected in highest concentrations were caffeine, tolyltriazole, 1H-benzotriazole, and terbuthylazine. Of the 108 target compounds monitored by Klosterhaus et al. (2013) in San Francisco Bay, 32 were detected at least at one and 12 at all five sampling locations. Among the compounds with 100% detection frequency were valsartan, sulfamethoxazole, carbamazepine, caffeine, gemfibrozil, and atenolol. The French Mediterranean coast was investigated by Munaron et al. (2012) and again, caffeine, carbamazepine, and terbuthylazine were among the most abundant compounds. These are recent examples demonstrating the wide distribution of anthropogenic organic micro-pollutants in marine environments. However, comprehensive data sets in coastal or open marine waters are still relatively scarce and mostly isolated studies covering very specific and relatively small areas, usually represented by limited sampling locations, can be found in the literature.

In this work monitoring data represented by more than 150 samples collected from the shorelines of the Baltic Sea (Germany), Northern Adriatic Sea (Italy), Aegean Sea and Dardanelles (Greece & Turkey), San Francisco Bay (USA), Pacific Ocean (from Muir Beach to Monterey Bay; USA), Mediterranean Sea (Israel), and Balearic Sea (Spain) are presented. The monitoring study was conducted from 2009 to 2011. Water samples were analyzed for various classes of micropollutants such as non-steroidal anti-inflammatory drugs (NSAIDs), stimulants, antihypertensives, iodinated X-ray contrast media, antibiotics, lipid regulators, antiallergics, anticonvulsants, sedatives, antidepressants, herbicides, biocides, corrosion inhibitors, one gastric acid regulator, one antipsychotic, one breast cancer drug, and selected transformation products of compounds from the aforementioned classes. The aim of this study is to provide an overview regarding the occurrence of polar anthropogenic organic micropollutants in coastal environments, the identification of the most abundant compounds and sources, and the observed concentration ranges.

## 2. Material and methods

### 2.1. Water sampling and sample pre-treatment

Locations, sampling periods, and the number of seawater samples are presented in Table 1. Grab samples were taken from beach

**Table 1**  
Locations, sampling periods, and numbers of samples.

Location	Sampling period	No. of samples
Baltic Sea, Germany	May 2009	30
Northern Adriatic Sea, Italy	May 2010	7
Northern Adriatic Sea, Italy (Venice)	May 2010	5
Northern Aegean Sea, Greece	May 2010	53
	May 2011	14
Northern Aegean Sea, Turkey	May 2011	3
Dardanelles, Turkey	May 2011	3
San Francisco Bay, USA	February 2010	20
Pacific Ocean (from Muir Beach to Monterey Bay; USA)	February 2010	10
Mediterranean Sea, Israel <sup>a</sup>	July 2009	4
Mediterranean Sea, Israel <sup>b</sup>	January 2011	2
Balearic Sea, (Ebro estuary and Barcelona, Spain)	October 2010	2
Total		153

<sup>a</sup> Between Haifa and the Lebanese border.

<sup>b</sup> Ashkelon and Herzliya.

areas, seaside promenades or long piers (maximum distance to the coastline ~200 m). Sampling locations of selected areas are presented in Figs. 1–4. The water samples were collected in 0.5 L (clear glass, screw cap) glass bottles and kept in a portable refrigerator (4 °C) or cooling box during transportation or shipping to the laboratory. Solid phase extraction (SPE) with OASIS HLB cartridges (Waters; Eschborn, Germany) was employed within 72 h after sampling according to Nödler et al. (2010). The SPE cartridges were stored at –18 °C until analysis. The used materials for sampling and sample pre-treatment and the method of sample pre-treatment and analyte stabilization were proved to be most suitable regarding analyte stability and recovery (Hebig et al., 2014; Hillebrand et al., 2013).

### 2.2. Analysis

The monitored compounds and their applications are presented in Table 2. The analysis was conducted by high-performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS). Isotopically labeled internal standards were chosen as a powerful tool for matrix compensation (Bester, 2008). Compounds without isotopically labeled standard were referred to the closest-matching internal standard according to retention time, ionization mode (+/–ESI), and chemical structure. Details regarding the analytical method (internal standards, mobile and stationary phase, suppliers, instrumentation, MS/MS-parameters, etc.) are presented in Nödler et al. (2010) and Reh et al. (2013). For the calibration, artificial samples were prepared by spiking 500 mL aliquots of ultra-pure water with the analytes. The calibration levels were processed similar to the real samples. The method quantitation limits (MQLs) were 1–28 ng L<sup>-1</sup> and the recovery in seawater (40/400 ng L<sup>-1</sup> concentration levels for the X-ray contrast media and the mono-methylxanthines and 20/200 ng L<sup>-1</sup> for all other compounds; triplicates) ranged from 80% to 110% except for 1-methylxanthine (69%) and cotinine (62%). Relative standard deviations were ≤10%. Regular blank samples were analyzed to confirm contamination-free work processes.

## 3. Results and discussion

The results of the monitoring studies are presented in Tables 3 and 4. In Fig. 5 compounds with detection frequencies >10% in all analyzed samples are presented. The wide distribution of polar organic micropollutants in the coastal environment is clearly demonstrated. There was only one sample (Pacific Ocean) where none of the analytes were detected. Of the monitored 53 compounds the following 10 were not detected above the MQL in any sample: 4-nitro-SMX (<1 ng L<sup>-1</sup>), atenolol acid (<4 ng L<sup>-1</sup>), clofibric acid (<3.4 ng L<sup>-1</sup>), desamino-SMX (<1.5 ng L<sup>-1</sup>), desisopropylatrazine (<5.6 ng L<sup>-1</sup>), diazepam (<1.4 ng L<sup>-1</sup>), pantoprazole (<4.8 ng L<sup>-1</sup>), sertraline (<16 ng L<sup>-1</sup>), tetrazepam (<2.5 ng L<sup>-1</sup>), and trimethoprim (<2.5 ng L<sup>-1</sup>). All other analytes were detected at at least one location and selected compounds are discussed in the following.

### 3.1. Stimulants

Caffeine and selected caffeine metabolites (paraxanthine, theobromine) were the most abundant analytes and present at concentrations up to 3068 ng L<sup>-1</sup> (caffeine; seafloor of Thessaloniki, Greece). It is furthermore noticeable that in 146 samples from 153 samples caffeine was present (Fig. 5). This compound is usually present at high concentrations in raw sewage and efficiently eliminated in WWTPs (>90%; Buerge et al., 2003). Therefore, it can be used as (semi-quantitative) indicator for untreated domestic wastewater in freshwater systems (Buerge et al., 2003;

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