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Evaluation of polar organic micropollutants as indicators for wastewater-related coastal water quality impairment☆

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ABSTRACT

Results from coastal water pollution monitoring (Lesvos Island, Greece) are presented. In total, 53 samples were analyzed for 58 polar organic micropollutants such as selected herbicides, biocides, corrosion inhibitors, stimulants, artificial sweeteners, and pharmaceuticals. Main focus is the application of a proposed wastewater indicator quartet (acesulfame, caffeine, valsartan, and valsartan acid) to detect point sources and contamination hot-spots with untreated and treated wastewater. The derived conclusions are compared with the state of knowledge regarding local land use and infrastructure. The artificial sweetener acesulfame and the stimulant caffeine were used as indicators for treated and untreated wastewater, respectively. In case of a contamination with untreated wastewater the concentration ratio of the antihypertensive valsartan and its transformation product valsartan acid was used to further refine the estimation of the residence time of the contamination. The median/maximum concentrations of acesulfame and caffeine were 5.3/178 ng L^{-1} and 6.1/522 ng L^{-1}, respectively. Their detection frequency was 100%. Highest concentrations were detected within the urban area of the capital of the island (Mytilene). The indicator quartet in the gulfs of Gera and Kalloni (two semi-enclosed embayments on the island) demonstrated different concentration patterns. A comparatively higher proportion of untreated wastewater was detected in the gulf of Gera, which is in agreement with data on the wastewater infrastructure. The indicator quality of the micropollutants to detect wastewater was compared with electrical conductivity (EC) data. Due to their anthropogenic nature and low detection limits, the micropollutants are superior to EC regarding both sensitivity and selectivity. The concentrations of atrazine, diuron, and isoproturon did not exceed the annual average of their environmental quality standards (EQS) defined by the European Commission. At two sampling locations irgarol 1051 exceeded its annual average EQS value but not the maximum allowable concentration of 16 ng L^{-1}.

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1. Introduction

The European Union's Marine Strategy Framework Directive (MSFD) (EC, 2008) establishes a framework, within which the EU member states shall take the necessary measures to achieve and maintain good environmental status in marine waters by developing strategies to monitor, protect, and restore the marine environment, and reduce inputs, pressures or impacts of human activities in each marine region. Within the MSFD the good environmental status is defined by eleven qualitative descriptors focusing on — among other concerns — concentrations of defined contaminants and human-induced eutrophication.

Recent multi-residue monitoring studies demonstrate the wide occurrence of micropollutants such as biocides, corrosion inhibitors, pharmaceuticals, and stimulants in European coastal waters (Loos et al., 2013; Munaron et al., 2012; Nödler et al., 2014a). However, in contrast to priority pollutants such as organochlorine pesticides, PCBs, and PAHs there is a knowledge gap regarding the environmental effects of micropollutants. Consequently, for most of these compounds there are no environmental quality standards

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(EQS) defined by the European Commission and especially the group of pharmaceutically active compounds is underrepresented (EC, 2013).

Selected anthropogenic micropollutants can serve as indicators for certain processes (e.g., mixing, water treatment techniques) and their major sources and entry routes, such as wastewater, agriculture, and surface runoff (Jekel et al., 2015; Reh et al., 2015). Therefore, their presence indicates potential water quality impairment associated with the respective contamination source, which offers a great potential to be used within a refined monitoring paradigm towards a successful implementation of the MSFD. Due to its low elimination rates in WWTPs and high stability in the environment, the artificial sweetener acesulfame has been proposed as wastewater indicator (sometimes referred to as *population marker*) (Buerge et al., 2009). There is no natural background of this compound. Therefore, its detection is tantamount to an anthropogenic impact on the investigated water body. In Swiss lakes Buerge et al. (2009) observed good correlation of acesulfame and the anthropogenic burden of the lakes (ratio of population and water through flow).

Because of its low removal rates in WWTPs and environmental stability acesulfame does not discriminate between treated and untreated wastewater (Buerge et al., 2009). However, as raw sewage in coastal waters is closely linked with human-induced eutrophication and further risks for environmental and human health (Lipp et al., 2001; Heisler et al., 2008), this distinction is particularly desirable. Especially EU-member states, which have a considerable interest in fishery and marine-based tourism, have an instant and particular interest in all reasonable measures to decrease these risks to an acceptable level. For the detection of untreated wastewater in freshwater environments the stimulant caffeine has been proposed. Caffeine is present in high concentrations in raw sewage (mostly >20,000 ng L^{-1}) but at sludge retention times (SRT) >5 d elimination of >99% and thus very low caffeine concentrations in WWTP effluents can be achieved by activated sludge treatment (Buerge et al., 2003). Therefore, in absence of natural caffeine sources such as tea or coffee plantations the detection of caffeine in a water body is a strong indication for the presence of untreated sewage and this approach has further been applied for quantitative assessments (Buerge et al., 2006; Hillebrand et al., 2012). Buerge et al. (2006) calculated fractions of untreated wastewater introduced to Swiss surface waters via combined sewer overflow. Their approach worked very well as the population not connected to wastewater treatment was negligible (<0.5%). Conversely, in absence of combined sewer overflow the caffeine concentration in a water body reflects the population not connected to wastewater treatment. Due to biodegradation processes in the environment this indicator function is limited to recent contaminations (Hillebrand et al., 2015). Lately, a large-scale monitoring study revealed the widespread presence of caffeine (95% detection frequency, maximum concentration >3000 ng L^{-1}) and thus untreated wastewater recently introduced into the coastal environment of different marine systems (e.g., the Aegean Sea, Baltic Sea, Dardanelles, Northern Adriatic Sea, San Francisco Bay) (Nödler et al., 2014a).

The antihypertensive valsartan was further detected in the marine environment (Klosterhaus et al., 2013; Moreno-González et al., 2015). Moreover, of the 108 target compounds monitored by Klosterhaus et al. (2013) (including caffeine) this compound was detected in all samples from San Francisco Bay and at the highest individual concentration (92 ng L^{-1}). High concentrations of valsartan (>20,000 ng L^{-1}) can be detected in raw sewage (Gurke et al., 2015). In WWTPs the compound is biotransformed to the transformation product valsartan acid, which is more persistent to further degradation compared to the parent compound (Kern et al., 2010). In raw sewage valsartan acid is only occasionally present and at low concentrations (Nödler et al., 2013a). The transformation can also be observed in river water microcosms, but at much lower reaction speeds (>10 days vs. <1 day in WWTP) (Nödler et al., 2014b). Therefore, a high ratio of valsartan/valsartan acid in the environment indicates a recent contamination of untreated wastewater, which is similar to the detection of caffeine. However, regarding longer residence times of untreated sewage (>7 days) laboratory experiments with river water microcosms suggest higher biodegradation rates for caffeine than for valsartan (Nödler et al., 2014b). For this reason it is very likely that the ratio of valsartan/valsartan acid is still in favor of the parent compound while most of the caffeine is already degraded.

The described indicator functionalities derived from previous studies can be summarized as presented in Table 1. The information derived from a combined use of this indicator quartet is helpful for identifying or allocating respective contamination sources, for suggesting the prioritization of significant monitoring after the implementation of measures, and also for risk assessment. Moreover, the application of the here proposed indicator concept is a highly promising tool to support the evaluation of the environmental status within the MSFD. In contrast to direct nutrient measurement (PO_4^{-3}, NH_4^+, NO_3^-) or analysis for microbial indicators (e.g., *E. coli*), the analysis of the indicator quartet allows for instantly addressing domestic wastewater as the contamination source. Main focus of the presented work is the application of the proposed wastewater indicator quartet in the coastal environment of a Mediterranean island to detect point sources and contamination hot-spots and to compare the derived conclusions with the state of knowledge regarding local land use and infrastructure.

In saline environments such as coastal waters or estuaries the substantial inflow of wastewater leads to decreasing electrical conductivity (EC) (Lara-Martín et al., 2014; Siegener and Chen, 2002). Therefore, the possibility to detect wastewater inflow by EC-monitoring is evaluated by the comprehensive approach of using acesulfame, caffeine, and EC. In order to provide a wider perspective on the contamination of coastal ecosystems with micropollutants, the samples were analyzed for additional compounds such as selected herbicides, biocides, corrosion inhibitors, and pharmaceuticals. Among others, the list included compounds of current interest to the European Commission such as atrazine, diuron, irgarol 1051, isoproturon, diclofenac, erythromycin, and clarithromycin (EC, 2013, 2015).

As a representative location for the study, Lesvos Island (Aegean Sea, Greece) was chosen. The island, being typical for many others in the Aegean Archipelago and elsewhere, highly depends on marine-based tourism and fishery and does not suffer from severe pollution problems (i.e., industrial activity, intensive agriculture or large urban settlements). An earlier study addressing the impact of anthropogenic organic pollutants on the coastal area of Lesvos found no evidence for substantial pollution of fish, sediment, and water by lipophilic compounds such as PAHs and organochlorine pesticides (Aloupi et al., 2007). However, despite substantial infrastructural development the water quality in certain areas (e.g., eutrophic episodes in the area of the main city Mytilene) is still affected by untreated wastewater (Aloupi et al., 2007). Lesvos Island provides two semi-enclosed shallow coastal environments (Kalloni and Gera), which are typical for Eastern Mediterranean embayments. The water exchange with the open sea is limited in these gulfs and the situation concerning water residence times and associated nutrient-related problems such as algal blooms will most likely aggravate due to the present and future climate change (Spyropoulou et al., 2013). The connection rate to the sewerage system is different at both gulfs and this situation is supposed to be reflected by the concentration patterns of the indicator set.

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