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Assessment of the environmental fate of endocrine disrupting chemicals in rivers

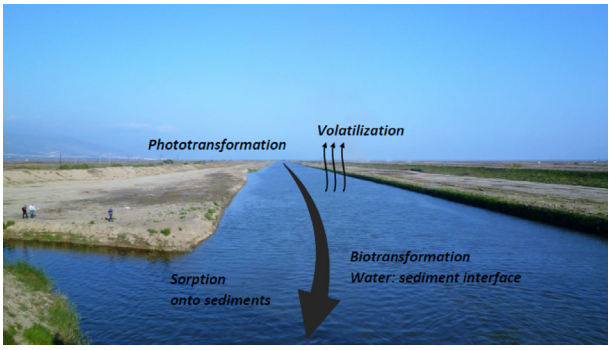
Elena Koumaki *, Daniel Mamais, Constantinos Noutsopoulos

Sanitary Engineering Laboratory, Department of Water Resources and Environmental Engineering, School of Civil Engineering, National Technical University of Athens, 5 Iroon Polytechniou, Zografou, 15780, Athens, Greece

HIGHLIGHTS

- Biotransformation rates of EDCs are faster under oxic than reduced oxygen conditions.
- Oxygen presence greatly affects EDCs' degradation pathway in river environment.
- EDCs are removed from water through sorption and biodegradation in oxygen presence.
- Bisphenol A biodegraded faster than triclosan and nonylphenols under oxic conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Laboratory tests were conducted with five endocrine disruptors (bishenol A, triclosan. nonylphenol, nonylphenol monoethoxylate and nonylphenol diethoxylate) under different redox conditions (aerobic, anoxic, anaerobic and sulfate-reducing conditions) to assess abiotic and biotic degradation in a river water/sediment system. The river water sample was collected from Spercheios River while the sediment was collected from the banks of a tributary of the river at the point where the discharge point of a wastewater treatment plant is located. To describe quantitatively elimination kinetics of the target compounds, pseudo first-order kinetics were adopted. According to the results from the microcosms studies, it can be stated that the substances are eliminated from the aqueous phase with relatively high rates under aerobic conditions due to both sorption and biotransformation processes. However, when reduced oxygen conditions were established in the microcosms incubations, biotransformation decreased, indicating the almost complete cease of the EDCs microbial degradation, while substances' sorption onto sediments showed no significant differences. All compounds were found to be biodegradable under aerobic conditions, and the low to high order of the calculated dissipation rate constants was $0.064 \pm 0.004\ d^{-1}$ (TCS) → $0.067 \pm 0.006\ d^{-1}$ (NP) →$0.076 \pm 0.009\ d^{-1}$ (NP2EO) → $0.081 \pm 0.007\ d^{-1}$ (NP1EO) → $0.103 \pm 0.011\ d^{-1}$ (BPA). Finally, regarding the biotransformation experiments, the elimination of the compounds limited in the absence of oxygen as compared to aerobic.

1. Introduction

During the last years, several studies have been published documenting the widespread presence of a great number of synthetic

* Corresponding author.
E-mail address: elenakoumaki@central.ntua.gr (E. Koumaki).

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organic compounds in surface waters, groundwater, wastewater and even in drinking water sources (Huang et al., 2014; Luo et al., 2014; Yu et al., 2013; Bueno et al., 2012; Loos et al., 2010; Barnes et al., 2008). Among synthetic organic compounds which are usually detected in the aquatic environment, endocrine disrupting chemicals (EDCs) are contained in various materials such as pesticides, metals, additives or contaminants in food, and personal care products, therefore presenting significant research interest. Although their continuous introduction in the environment might derive by several sources, such as agriculture and livestock, several studies connect directly the frequent detection of these compounds into the aquatic environment with the wastewater treatment plants (WWTPs) and indicate that wastewater is one of the most significant route for their transfer to the environment (Verlicchi et al., 2012; Stasinakis et al., 2008; Barceló and Petrovic, 2007; Nakada et al., 2006). This is explained by the fact that the detected concentrations of the substances are higher as the sampling points approach the WWTPs outfall (Kasprzyk-Hordern et al., 2009; Stasinakis et al., 2012; Barber et al., 2015). Beside the fact that these compounds are detected in low concentrations, some of them have become a significant environmental issue and have received great attention from the scientific community due to their toxicological and chemical characteristics (Song et al., 2014; Bedoux et al., 2012; Soares et al., 2008).

Regardless of the way and the route of entry of emerging pollutants into the natural environment, their concentration and persistence in aqueous systems is guided by various physicochemical processes. More specifically, the fate of such compounds might be influenced by transport, sequestration and degradation processes. Transport processes include the dispersion and dilution of substances, while turbulent mixing and aeration of water column may further reduce the concentration of the more volatile compounds. Sequestration includes processes where compounds may be transferred without any degradation and stored in other matrices or environmental compartments mainly through bioconcentration and sorption (Aga, 2008). Finally, the last category of processes in which the parent compounds are likely to be transformed or mineralized and therefore permanently removed from the aquatic environment include photolysis (Zacharakis et al., 2013; Sanchez-Prado et al., 2006; Li et al., 2013), biodegradation (Bradley et al., 2016; Zhang et al., 2013; Nie et al., 2012; Svenningsen et al., 2011; Stasinakis et al., 2010; Lu et al., 2009) and hydrolysis. However, it is important to emphasize that the elimination of the compounds is a transformation which leads to the formation of degradates that may be more mobile and persistent than the parent compounds and therefore, more frequently detected in the environment (Soares et al., 2008; Careghini et al., 2015; Murdoch and Sanin, 2016; Ma et al., 2016).

There are several studies report on the biotransformation of EDCs in the aquatic environment. However, in most cases these studies have been conducted either with synthetic water and not with real river water or with microorganisms inoculated from activated sludge or digested sludge samples and not with autochthonous bacteria from river sediments (Chiavola et al., 2016; Gangadharan Puthiya Veetil et al., 2012).

The compounds selected in this study as representatives of the EDCs are: Bisphenol A (BPA), Triclosan (TCS), Nonylphenol (NP) and Nonylphenols ethoxylates (NPEs) (mono-ethoxylate, NP1EO and di-ethoxylate, NP2EO). BPA was synthesized in 1891 and since then 3.2 million tonnes are produced per year (Okada et al., 2008), while its global production is concentrated in the US and the EU. Since its synthesis, BPA is used in the production of polycarbonate food packaging and beverages, dental sealants and epoxy resins (Chang et al., 2013). TCS is used since 1960 as an antibacterial and antifungal agent while its annual production has been estimated around 1500 t worldwide, of which 25% in Europe (Chen et al., 2009) for the production of personal care and hygiene products such as soaps, cleansers, toothpastes, mouthwashes, deodorants, foam baths, shampoos, etc. (Singer et al., 2002). Over the past 40 years, NP and NPEs have been widely used, mainly because of their surfactant properties in detergents, paints, pesticides, textiles and personal care products. In the EU, NP is mainly used (60%) as an intermediate to produce nonylphenol ethoxylates (NPnEOs), while its use to produce resins, plastics, stabilisers etc. amounts to 37% (European Chemical Bureau, 2002). The physicochemical properties of the target compounds are presented in Table 1. According to the Water Framework Directive (Directive 2013/39/EU, 2013) from the selected chemicals, nonylphenol (NP) is considered a priority substance with an annual environmental quality standards (EQS) equal to 0.3 μg L^{-1} and a maximum allowable concentration equal to 2 μg L^{-1}, while bisphenol A (BPA) is included in the list of substances under review for possible identification as a priority substance or hazardous substance (Directive 2008/105/EC, 2008).

In view of the above, the objective of this study was to assess the environmental transformation of five EDCs in river systems and more specifically to evaluate the role of sorption and biodegradation on their transformation under different redox conditions. In order to simulate closely natural conditions, we conducted microcosms experiments with river sediments collected in an area receiving WWTP effluent. Thus, the microbial community employed for the microcosms biodegradation experiments had been acclimatized in the presence of micropollutants commonly found in WWTP effluents.

2. Experimental methods

2.1. Chemicals and reagents

Methanol (MeOH) and ethyl acetate were of high performance liquid chromatography (HPLC) grade (Merck, Darmstadt, Germany) and were used as received. Bis(trimethylsilyl) trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS) and pyridine, used for silylation, were purchased by Supelco (Bellefonte, PA, USA) and Carlo Erba-SDS (Peypin, France), respectively. Analytical standards of NP, NP1EO, NP2EO, BPA, TCS and deuterated BPA (BPA-d16) were supplied by Sigma-Aldrich (USA). All compounds were used without further purification (minimum purity >99%). Stock solutions of individual compounds were prepared in methanol at 1000 mg L^{-1} and kept at −18 °C (Koumaki et al., 2017). HPLC grade water was prepared in the laboratory using a MilliQ/Milli-RO Millipore system (Millipore, Billerica, Massachusetts USA). Ultra-pure HCl (32%) was used for acidification of the samples (Merck, Germany).

2.2. Sediment and river water source

River water samples were collected from the Spercheios River water system, which is located in the Central-Eastern Greece. Although, the river does not closely relate with the discharge of effluents from WWTPs, it receives storm water discharges and run-offs from several anthropogenic activities (e.g. livestock, agricultural) thus exhibiting appreciable target compounds' background concentrations. The sediment samples were collected from the banks of a tributary of the Spercheios river at the point where the city of Lamia discharges treated wastewater, and so the microbial community is acclimated to the presence of the target compounds. A few kilometers downstream this tributary meets the Spercheios river (Koumaki et al., 2017).

Sediments were collected from the entire surface of the sediment layer (0–5 cm depth) and sieved to <2 mm, while river water was filtered under suction through 0.45 μm membranes to remove particulate and algal materials. Water and sediment were collected separately in glass bottles and stored at 4 °C until used and for no longer than 1 day. Background concentrations of target compounds as well as the major physicochemical parameters of river water and sediments samples are shown in Table 2.