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EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents

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ABSTRACT

In the year 2010, effluents from 90 European wastewater treatment plants (WWTPs) were analyzed for 156 polar organic chemical contaminants. The analyses were complemented by effect-based monitoring approaches aiming at estrogenicity and dioxin-like toxicity analyzed by in vitro reporter gene bioassays, and yeast and diatom culture acute toxicity optical bioassays. Analyses of organic substances were performed by solid-phase extraction (SPE) or liquid–liquid extraction (LLE) followed by liquid chromatography tandem mass spectrometry (LC-MS-MS) or gas chromatography high-resolution mass spectrometry (GC-HRMS). Target microcontaminants were pharmaceuticals and personal care products (PPCPs), veterinary (antibiotic) drugs, perfluoroalkyl substances (PFASs), organophosphate ester flame retardants, pesticides (and some metabolites), industrial chemicals such as benzotriazoles (corrosion inhibitors), iodinated x-ray contrast agents, and gadolinium magnetic resonance imaging agents; in addition biological endpoints were measured. The obtained results show the presence of 125 substances (80% of the target compounds) in European wastewater effluents, in concentrations ranging from low nanograms to milligrams per liter. These results allow for an estimation to be made of a European median level for the chemicals investigated in WWTP effluents. The most relevant compounds in the effluent waters with the highest median concentration levels were the artificial sweeteners acesulfame and sucralose, benzotriazoles (corrosion inhibitors), several organophosphate ester flame retardants and plasticizers (e.g. tris(2-chloroisopropyl)phosphate; TCPP), pharmaceutical compounds such as carbamazepine, tramadol, telmisartan, venlafaxine, irbesartan, fluconazole, oxazepam, fexofenadine, diclofenac, citalopram,

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codeine, bisoprolol, eprosartan, the antibiotics trimethoprim, ciprofloxacine, sulfamethoxazole, and clindamycine, the insect repellent N,N′-diethyltoluamide (DEET), the pesticides MCPA and mecoprop, perfluoroalkyl substances (such as PFOS and PFOA), caffeine, and gadolinium.

1. Introduction

European Commission Directive 91/271/EEC (EC, 1991) concerns the collection, treatment and discharge of urban wastewater and the treatment and discharge of wastewater from certain industrial sectors. Its aim is to protect the environment from any adverse effects caused by the discharge of such waters. The increasing extent and level of municipal wastewater treatment in Europe in the past decades has significantly improved the quality of surface waters, even though obligations set for the European Union are not equally fulfilled by all its members (EC, 2004; Reemtsma et al., 2006). However, priority substances or other organic compounds are not regulated in wastewater treatment plant (WWTP) effluents (EC, 1991), but in surface waters under the Water Framework Directive (EC, 2000).

Whilst household and industrial wastewater treatment has been implemented progressively across Europe, and existing treatment technologies produce water that meets current legislation on water-quality standards, it has been demonstrated that the removal of many emerging (i.e. not yet regulated) contaminants, including pharmaceuticals and personal care products (PPCPs), hormones, and other industrial chemicals is incomplete. Various studies over recent years have shown that treated municipal wastewater contributes significantly to water pollution from micropollutants (e.g.: Ashton et al., 2004; Castiglioni et al., 2006; Clara et al., 2005; De la Cruz et al., 2012; Gabet-Giraud et al., 2010; Gracia-Lor et al., 2010, 2012; Gros et al., 2010; Hollender et al., 2009; Jelic et al., 2012; Joss et al., 2005, 2006; Kasprzyk-Hordern et al., 2009; Köck-Schulmeyer et al, 2011; Lindqvist et al., 2005; Martínez Bueno et al., 2012; Micropoll, 2011, 2012; Miège et al., 2009; Nakada et al., 2006; Paxéus, 2004; Radjenović et al., 2007a,b; Reemtsma et al., 2006; Ternes, 1998; Vieno et al., 2007; Verlicchi et al., 2012; Zhang et al., 2008a).

Conventional WWTPs are designed to remove pathogens and coliforms and to reduce loads of carbon, nitrogen, and phosphorus. In addition, many non-polar chemical compounds are well removed by sorption to sludge. Other important removal pathways of organic compounds during wastewater treatment are biotransformation/biodegradation, and stripping by aeration (volatilization) (Radjenović et al., 2007a). Several polar compounds, especially those which are poorly degradable, may however be discharged with WWTP effluents into receiving waters and then occur in surface waters (Reemtsma et al., 2006). Some polar chemical compounds such as nonylphenol (Yu et al., 2009; Zhang et al., 2008b) or perfluoroalkyl substances (PFASs) such as perfluorooctansulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (Becker et al., 2008) are even formed in WWTPs from precursor compounds.

In 2006, Reemtsma and co-workers published the first EU-wide study on the occurrence of polar organic pollutants in WWTP effluents and the receiving surface waters. In their study, the effluents of eight municipal WWTPs in Western Europe were analyzed by liquid chromatography – mass spectrometry (LC-MS) for the occurrence of 36 polar pollutants, comprising PPCPs and other household and industrial chemicals. Half of the determined compounds were not significantly removed in tertiary wastewater treatment with enhanced nutrient removal (Reemtsma et al., 2006).

In the last years, several fate studies on the occurrence and behavior of PPCPs, endocrine disruptors, illicit drugs, and other industrial chemicals have been performed. The efficiency of the removal of PPCPs (and other compounds) was found to be strongly dependent on the technology implemented in the WWTP (Hollender et al., 2009; Kasprzyk-Hordern et al., 2009; Vieno et al., 2007).

The main objective of this study was to assess the occurrence of as many as possible polar organic chemical contaminants in WWTP effluents as well as relevant biological endpoints such as estrogenicity, on a European scale (Gawlik et al., 2012). In this study 90 WWTPs across Europe were sampled, 156 chemicals were measured and four different toxicity assays were conducted on selected samples.

2. Materials and methods

2.1. *EU-wide sampling campaign, sample transport and storage*

The identity of the individual 90 WWTPs investigated in this study cannot be disclosed in this publication. The samples came from Austria (number of samples: 6), Belgium (18), Czech Republic (7), Cyprus (2), Finland (6), France (5), Germany (2), Greece (2), Hungary (2), Ireland (2), Italy (2), Lithuania (3), Netherlands (11), Portugal (2), Slovenia (1), Spain (3), Sweden (11), and Switzerland (5). The selection of the WWTPs was done autonomously by the participating EU Member States; no selection criteria were given by the JRC (Joint Research Centre). On the other hand, the participants were aware of the aims of the study and therefore most of them provided samples of wastewaters treated by WWTPs of different/variable capacities and wastewater sources (domestic, industrial, rain). Around half of the plants provided us with information on the plant capacity (m^3/d) and the population equivalents, which was in the range of <1000 up to over 1 million (for at least 3 plants); i.e. WWTPs of all sizes were investigated in this study. Thus, the selection of the plants was quite representative of the EU. Mainly municipal WWTPs were investigated, but some plants were dominated by industrial wastewaters. Sampling