OCCURRENCE OF EMERGING ORGANIC CONTAMINANTS RELEASED FROM WASTEWATER TREATMENT PLANTS IN THE AQUATIC ENVIRONMENT AND EFFECTS ON AQUATIC LIFE: THE CASE OF GREECE

THOMAIDI V.S.[1], STASINAKIS A.S.[1], BOROVA V.L.[2] and THOMAIDIS N.S.[2]

[1] Department of Environment, University of the Aegean, 81100 Mytilene [2] Department of Chemistry, University of Athens, Panepistimioupolis, 157 71 Athens.
E-mail: astas@env.aegean.gr

ABSTRACT

Emerging organic contaminants (EOCs) are widely used compounds that have gained scientific interest during the last decade. Despite the frequent detection of these compounds in treated wastewater and surface water, there is a lack of data relevant to the hazard they exhibit to aquatic organisms.

The main objective of this study was to estimate the risk associated with the occurrence of the EOCs released from municipal wastewater in the aquatic environment. For this reason Greece was chosen as a case study. Treated wastewater was analyzed for 105 pharmaceuticals and illicit drugs; whereas a literature review was held to record the concentration levels of all emerging micropollutants determined in Greek Wastewater Treatment Plants (WWTPs). An extensive literature review was also conducted in order to record the experimental acute toxicity data of these compounds (EC_{50} or LC_{50} values) for 3 different aquatic organisms (fish, daphnia magna and algae). In cases that no experimental toxicity data was available, ECOSAR model (U.S. EPA) was used. The risk quotients (RQ) were calculated for treated wastewater and 25 Greek rivers, taking into account the Measured Environmental Concentration (MEC), the Predicted No Effect Concentration (PNEC) and the dilution the wastewater undergoes when it is released in rivers. The possible risk due to the mixture of the target compounds was estimated as well, using the baseline toxicity values calculated by the ECOSAR model.

According to the literature and experimental data, 207 EOCs have been detected in treated wastewater originated from Greek WWTPs, belonging to 8 different groups: pharmaceuticals, illicit drugs, phenolic endocrine disruptors (EDCs), perfluorinated compounds, benzotriazoles, benzothiazoles, artificial sweeteners and siloxanes. Their concentration levels ranged from less than 1 ng L^{-1} (pharmaceuticals) to some tens of μg L^{-1} (artificial sweeteners). EDCs seem to be the most dangerous class of the emerging pollutants, since 4 compounds (nonylphenol, nonylphenol diethoxylate, nonylphenol monoethoxylate and triclosan) presented high RQ values even after significant wastewater dilution to river water. Specifically, triclosan presented RQ > 1 (in algae) for all studied rivers (dilution factor up to 2388), while decamethylcyclopentasilane (in daphnia magna), caffeine (in algae) and nonylphenol (in fish) presented RQ values higher than 1, for 23 (dilution factor ≤ 1910), 22 (dilution factor ≤ 913) and 20 rivers (dilution factor ≤ 824), respectively. The mixture of the micropollutants presents a serious hazard for aquatic organisms, as its RQ remains high (98 for fish, 123 for daphnia magna and 42 for algae), even in river with the highest dilution factor. The group of micropollutants that contribute the most in the mixture's RQ is EDCs, as its contribution came up to 99 % in fish and daphnia magna and 98 % in algae.

Keywords: emerging contaminants; wastewater; risk assessment; rivers; mixture.

1. Introduction

Although emerging organic micropollutants have often been detected in the environment during the last decades, they have not been sufficiently studied so far. These compounds are present in everyday products, such as personal care products and cosmetics, disinfectants, detergents, non-stick pans and cooking utensils, fabrics for furniture, foods for diabetics and emulsifiers and include a wide variety of compounds; among others, pharmaceuticals (PhCs), illicit drugs, endocrine disrupters (EDCs), artificial sweeteners, perfluorinated compounds (PFCs), benzotriazoles (BTRs), benzothiazoles (BTHs), siloxanes, nanomaterials and water disinfection by-products (Farré *et al*., 2008; Bletsou *et al*., 2013; Stasinakis *et al*., 2013; Robles-Molina *et al*., 2014). According to the previous studies, EOCs are partially removed during wastewater treatment, so they are present in the aquatic environment, worldwide.

The presence of the EOCs in the aquatic environment may cause adverse effects to both aquatic organisms and humans, as there is evidence that these compounds are toxic and through the food chain, accumulate in biota (Farré *et al*., 2008). For example, EDCs have the potential to cause negative effects to the endocrine system of terrestrial and aquatic organisms and humans, as well (Liu *et al*., 2009). Due to the high consumption of the EOCs, many studies have been published, related to the environmental risk they pose when they are released to the environment. However, most of these studies are referred to a limited number of compounds and specific groups of micropollutants (e.g. PhCs, EDCs), or to specific pollution areas (e.g. rivers, lakes) and to specific pollution sources (e.g. hospitals) (Escher *et al*., 2011; Stasinakis *et al*., 2012; Kosma *et al*., 2014).

The aim of this study was to estimate the environmental risks associated with the presence of EOCs to treated wastewater and rivers, in country level, choosing Greece as a case study. The occurrence of 150 PhCs and illicit drugs in treated wastewater was investigated; whereas a literature review was conducted to record the concentration levels of all EOCs determined in Greek WWTPs during the last decade. According to the Technical Guidance Document (TGD) on Risk Assessment (EC, 2003), the Risk Quotients (RQs) of the individual compounds were calculated in treated wastewater and rivers, based on the maximum concentrations, acute toxicity data (literature or ECOSAR values) for three classes of aquatic organisms (fish, daphnia magna and algae) and Dilution Factor (DF). The possible risk due to the mixture of the target compounds was estimated as well, using the baseline toxicity values calculated by the ECOSAR model.

2. Materials and methods

2.1. Occurrence of EOCs in Greek WWTPs

Literature review was held to collect the effluent concentrations of EOCs in Greek WWTPs and the maximum values were reported in order to assess the risk for worst-case scenario. The occurrence of further 150 PhCs and illicit drugs was investigated in secondary treated wastewater samples collected from a WWTP in Athens, Greece. Detailed information about the sampling, the sample preparation and all the analytical procedures has been reported in previous studies (Borova *et al*., 2014; Dasenaki *et al*., 2014).

2.2. Environmental risk assessment

As EOCs are widely used in every day products worldwide, the risk assessment was based on the hypothesis that the effluents of the Greek WWTPs contain all the detected target compounds. Acute toxicity data (EC_{50} or LC_{50}) for three groups of aquatic organisms (fish, daphnia magna and fish) was collected, either after literature review or using the ECOSAR model and the lowest value was chosen in order to predict the ecological risk based on the worst-case scenario.

The RQs were calculated by dividing the MEC to PNEC values, for three aquatic organisms (fish, daphnia magna and algae). If RQ is greater than 1, a possible environmental risk is assumed, while if RQ value is lower than 1, no risk is indicated. PNEC values were calculated by dividing the LC_{50} or EC_{50} value by an assessment factor equal to 1000 (EC, 2003).

As pollutants in wastewater are usually present in mixtures, an additional risk assessment for the mixture of the emerging contaminants should be carried out. According to the literature (Escher *et al*., 2011), the mixture's RQ can be calculated using Eq. (1), while baseline toxicity, predicted by the ECOSAR model, was used to calculate PNEC values:

$$RQ_{mix} = \sum_{i=1}^{n} RQ_i = \sum_{i=1}^{n} \frac{MEC_i}{PNEC_i} \qquad (1)$$

To calculate risk quotients in Greek rivers (RQ_r), the RQs in treated wastewater were divided by the respective DF value (Eq. 2):

$$RQ_r = \frac{RQ}{DF} \qquad (2)$$

The DF of the Greek rivers was calculated taking into account the average effluents flows (Q_e) of 25 Greek WWTPs and the average water flows of the corresponding rivers (Q_r), according to Eq. 3:

$$DF = \frac{Q_r}{Q_e} \qquad (3)$$

3. Results and discussion

3.1. EOCs in Greek WWTPs

According to the literature and experimental data collected in this study, 207 EOCs have been detected in Greek WWTPs, belonging to 8 different classes of organic micropollutants: PhCs, illicit drugs, EDCs, PFCs, BTRs, BTHs, artificial sweeteners and siloxanes. Their concentration levels range from less than 1 ng L^{-1} (PhCs) to some tens of μg L^{-1} (artificial sweeteners), as it is shown in Figure 1.

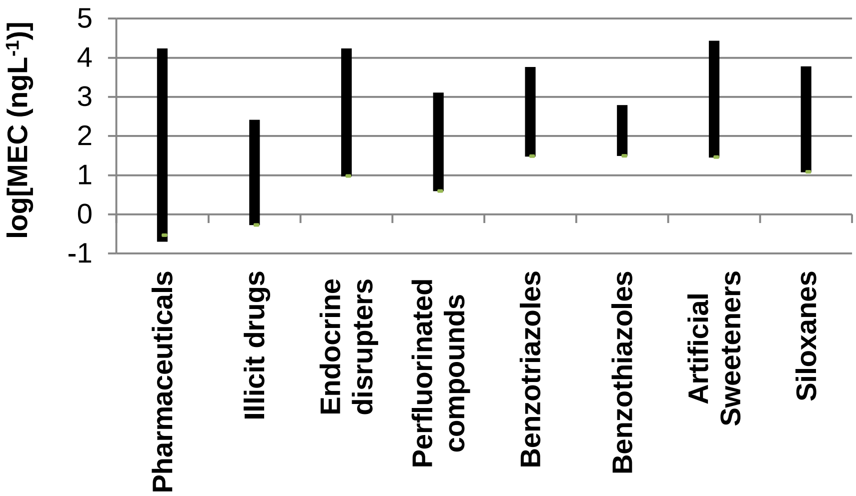

Figure 1: Concentration levels of 8 classes of organic emerging contaminants in Greek WWTPs (secondary treated wastewater).

3.2. Environmental risk assessment

According to the results of risk assessment, 30 compounds in secondary treated wastewater had RQ values higher than 1, while the most sensitive aquatic organisms were algae (Figure 2). The class of EOCs that seems to pose the greatest threat to aquatic environment was EDCs, as all substances in this class had RQ > 1 for fish. Regarding PhCs, 19 compounds presented a possible threat to aquatic organisms; whereas tolytriazole (BTHs), sucralose (artificial sweeteners) and 3 siloxanes seem to pose environmental risk to aquatic organisms, as well. All illicit drugs, PFCs and BTRs had RQ < 1.

Calculation of RQ values in rivers (RQ_r), showed RQ_r higher than 1 for 17 substances in algae and for 7 substances in fish and daphnia magna. The class of EOCs with the highest risk in rivers was EDCs, since 4 compounds presented high RQ_r, even after wastewater dilution (DF up to 2388).

To estimate the toxicity of the mixture of the compounds, the risk quotient RQ_{mix} was calculated. According to the results, the most sensitive aquatic organisms in the presence of the mixture seem to be daphnia magna (RQ_{mix} = 294585), as the RQ_{mix} values for fish and algae are 233846 and 101112, respectively. The group of EOCs that has the highest contribution to the mixture toxicity is EDCs. Treated wastewaters seem to cause a significant hazard to aquatic organisms, even after they are released into rivers. As it is shown in Figure 3, even in rivers with high DF, $RQ_{mix,river}$ remains higher than 1.

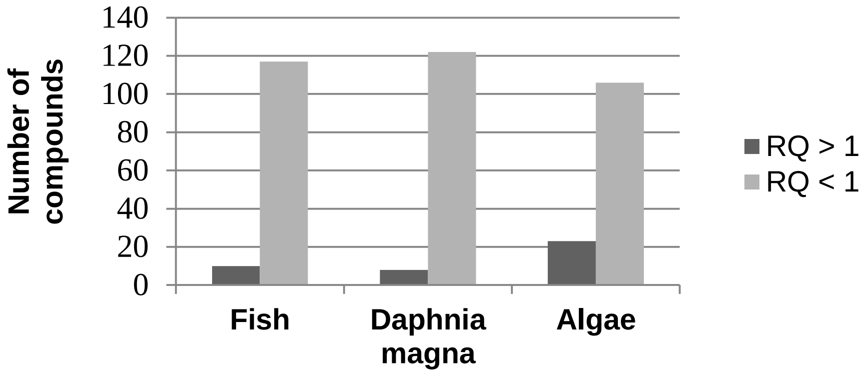

Figure 2: Emerging organic contaminants that present RQ values higher than 1 and lower than 1, in Fish, Daphnia magna and Algae.

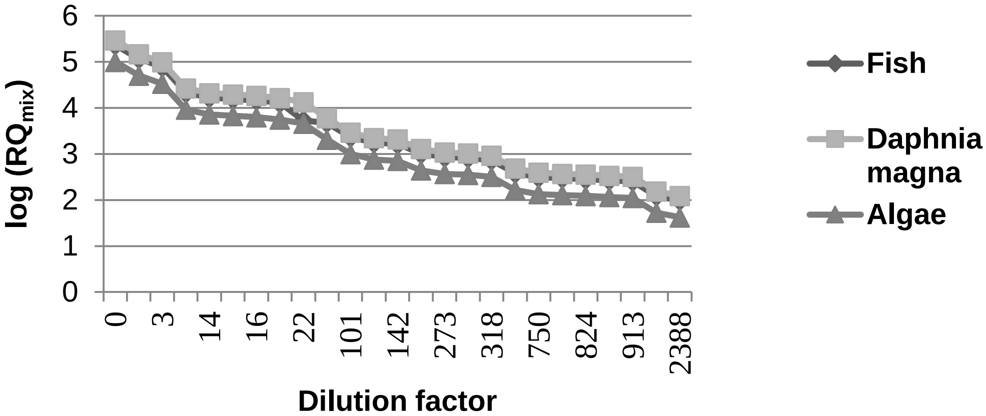

Figure 3: Effect of dilution factor (DF) on risk due to the existence of mixture of emerging organic contaminants in Greek rivers ($RQ_{mix, river}$).

4. Conclusions

The concentrations of 207 EOCs in Greek WWTP's effluents have been monitored. Their levels range from less than 1 ng L^{-1} (PhCs) to some tens of μg L^{-1} (artificial sweeteners). According to the results of risk assessment, EDCs presented the highest risk among all the studied EOCs in both wastewater and rivers. Moreover, they had the greatest contribution to the mixture toxicity. A possible ecological threat due to the presence of the mixture of EOCs seems to exist, even in rivers with high dilution factors.

ACKNOWLEDGMENTS

This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALES. Investing in knowledge society through the European Social Fund. (WATERMICROPOL, www.aegean.gr/environment/watermicropol)

REFERENCES

1. Bletsou A.A., Asimakopoulos A.G., Stasinakis A.S., Thomaidis N.S., Kannan K. (2013), Mass Loading and Fate of Linear and Cyclic Siloxanes in a Wasrewater Treatment Plant in Greece. Environ Sci Technol, **47**, 1824-1832.
2. Borova V.L. Maragou N.C, Gago-Ferrero P., Pistos C., Thomaidis N.S. (2014), Highly sensitive determination of 68 psychoactive pharmaceuticals, illicit drugs, and related human metabolites in wastewater by liquid chromatography-tandem mass spectrometry, Anal Bioanal Chem, **406(17)**, 4273-4285.
3. Dasenaki M.E., Chatzipanagi N., Dede D., Thomaidis N.S. (2014), Multiresidue analytical method for the determination of pharmaceuticals in wastewater samples using Solid-Phase Extraction and liquid chromatography–tandem mass spectrometry. Anal Bioanal Chem, submitted 2014.
4. European Commission (EC), 2003. Technical Guidance Document in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances, Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market, Part II. Office for Official Publications of the European Communities, Luxembourg.
5. Escher B., Baumgartner R., Koller M., Treyer K., Lienert J., McArdell C (2011), Environmental toxicology and risk assessment of pharmaceuticals from hospital wastewater. Water Res, **45**, 75-92.
6. Farré M., Pérez S., Kantiani L., Barceló D. (2008), Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment. Trends Anal Chem, **27**, 991-1007.
7. Kosma C.I., Lambropoulou D.A., Albanis T.A. (2014), Investigation of PPCPs in Wastewater Treatment Plants in Greece: Occurrence, removal and environmental risk assessment. Sci Total Environ, **466-467**, 421-438.
8. Liu Z., Kanjo Y., Mizutani S. (2009), Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment – physical means, biodegradation and chemical advanced oxidation: A review. Sci Total Environ, **407**, 731-748.
9. Robles-Molina J., Gilbert-López B., García-Reyes J., Molina-Díaz A. (2014), Monitoring of selected priority and emerging contaminants in the Guadalquivir River and other related surface waters in the province of Jaén, South East Spain. Sci Total Environ, **479-480**, 247-257.
10. Stasinakis A.S., Mermigka S., Samaras V.G., Farmaki E., Thomaidis N.S. (2012), Occurrence of endocrine disrupters and selected pharmaceuticals in Aisonas River (Greece) and environmental risk assessment using hazard indexes. Environ Sci Poll Res, **19**, 1574-1583.
11. Stasinakis A.S., Thomaidis N.S., Arvaniti O.S., Asimakopoulos A.G., Samaras V.G., Ajibola A., Mamais D., Lekkas T.D. (2013), Contribution of primary and secondary treatment on the removal of benzothiazoles, benzotriazoles and three other classes of emerging contaminants in Sewage Treatment Plant. Sci Total Environ, **463-464**, 1067-1075.