Risk assessment associated with the presence of emerging organic contaminants released from wastewater treatment plants in sludge amended soil and effects on terrestrial life: Greece as a case study.

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Abstract: The purpose of this study was to estimate the environmental risk associated with the existence of 99 emerging organic contaminants released from municipal wastewater in the terrestrial environment. Chemical analyses were carried out for 50 pharmaceuticals and illicit drugs; whereas a literature review was held to record the concentration levels of the target compounds in sewage sludge. Risk assessment was based on both terrestrial and aquatic toxicity data. An extensive literature review was also conducted in order to record the experimental acute toxicity data of these compounds (EC_{50}/LC_{50} values). In cases that no experimental toxicity data was available, ECOSAR model (U.S. EPA) was used. According to the results, triclosan presented the highest possibility for ecological threat both in terrestrial and aquatic data based risk assessment. Additionally, another 11 organic micropollutants, belonging to the groups of pharmaceuticals, synthetic phenolic compounds, siloxanes and benzothiazoles, exhibited environmental hazard, as their RQ values exceeded 1. Illicit drugs, perfluorinated compounds and benzotriazoles presented no environmental risk for the terrestrial organisms. The estimated threat due to nonylphenolic compounds seemed to be affected by the sludge source and the day of sampling, while these factors did not affect the risk presented by the rest of the compounds.

Keywords: emerging contaminants, wastewater, sludge-amended soil, risk assessment.

1. Introduction

Emerging organic contaminants (EOCs), are chemicals contained in manufactured products, such as human pharmaceuticals and veterinary drugs, personal care products, disinfectants, detergents, non-stick pans and cooking utensils, fabrics for furniture, foods for diabetics and emulsifiers. They include a range of organic substances; for example pharmaceuticals (PhCs), illicit drugs (IDs), synthetic phenolic compounds (SPCs), perfluorinated compounds (PFCs), benzotriazoles (BTRs), benzothiazoles (BTHs) and siloxanes (SLXs) (Farré *et al*., 2008; Bletsou *et al*., 2013; Stasinakis *et al*., 2013). As a result of their physicochemical properties, a certain number of them present a forcible tendency to adsorb on sewage sludge during wastewater treatment processes (Stasinakis, 2012; Petrie *et al*., 2014).

Although agricultural reuse of sewage sludge is a prevalent practice in the United Europe (Kelessidis and Stasinakis, 2012), there are a limited number of studies relevant to the presence of EOCs in sewage sludge and soil (Gago-Ferrero *et al*., 2015). Moreover, there is a lack of data associated with the environmental risk of these compounds in country level, as the majority of the previous studies are referred to specific Sewage Treatment Plants (STPs), or to a limited number of compounds and specific groups of contaminants (e.g. PhCs, SPCs) (González *et al*., 2010; Martín *et al*., 2012b; Liu *et al*., 2014). Supposing that the EOCs that are transferred in soil through agricultural use of sewage sludge are generally the same in all developed countries and their concentration values are ranged at similar levels, studies that would clarify the above issues could be useful for researchers and policymakers to identify those micropollutants that have to be removed more efficiently from STPs and included in relevant legislation.

The aim of this study was to estimate the environmental risks associated with the presence of EOCs in soil, in country level, choosing Greece as a case study. After literature review, all the published concentration data of EOCs in dewatered sewage sludge for Greek STPs was recorded; whereas sewage sludge samples originating from Athens STP,

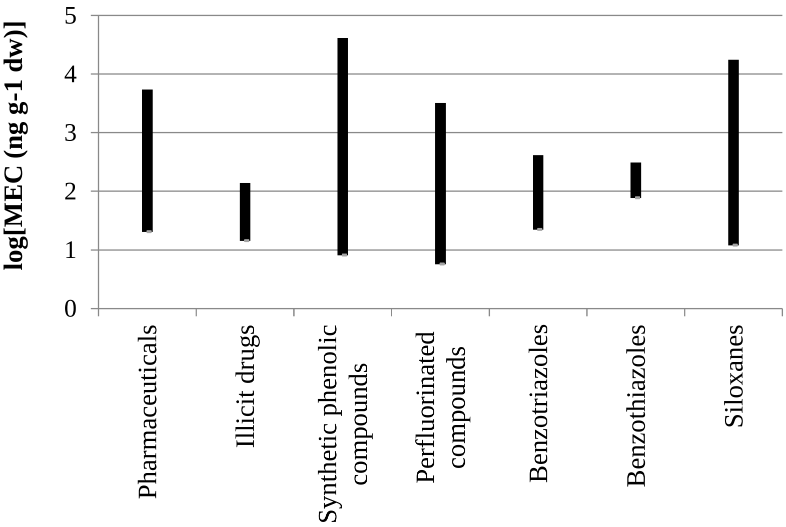

Figure 1. Maximum concentration levels of 7 classes of organic emerging contaminants in dewatered sewage sludge from Greek STPs.

Greece, were analyzed for 50 PhCs and IDs. According to the Technical Guidance Document (TGD) on Risk Assessment (EC, 2003), the Risk Quotients (RQs) of the individual compounds were calculated in soil, based on the maximum concentrations and the minimum acute toxicity data (literature or ECOSAR values).

2. Materials and methods

2.1. Occurrence of EOCs in Greece STPs

Literature review was held to collect the sludge concentrations of EOCs in Greek STPs and the maximum values were recorded in order to assess the risk for worst-case scenario. The occurrence of further 50 PhCs and IDs was investigated in dewatered sewage sludge samples collected from Athens STP, Greece. Detailed information about the sampling, the sample preparation and all the analytical procedures has been reported in a previous study (Gago-Ferrero *et al*., 2015).

2.2. Toxicity data collection

Terrestrial acute toxicity data (EC/LC50) for three groups of organisms (plants, earthworms and soil microorganisms) was collected, either after literature review or using the ECOSAR model; while aquatic toxicity data (EC/LC50) was collected for algae, *daphnia magna* and fish, as well. The lowest value was chosen in order to predict the ecological risk based on the worst-case scenario. The corresponding PNEC values ($PNEC_{soil,terrestrial}$ and $PNEC_{soil,aquatic}$) were calculated by Eqs (1), (2) and (3):

$$PNEC_{soil,terrestrial} = \frac{EC_{50}\ or\ LC_{50}}{1000} \quad (1)$$

$$PNEC_{soil,aquatic} = PNEC_{water} \text{ x } K_d = PNEC_{water} \text{ x } K_{oc} \text{ x } f_{oc} \quad (2)$$

$$PNEC_{water} = \frac{EC_{50}\ or\ LC_{50}}{1000} \quad (3)$$

2.3. Environmental risk assessment

To estimate the ecological risks posed by EOCs to the terrestrial organisms, risk quotients ($RQ_{soil,terrestrial}$ or $RQ_{soil,aquatic}$) were calculated, according to Eq. (4):

$$RQ_{soil} = \frac{PEC_{soil}}{PNEC_{soil}} \quad (4)$$

where PEC_{soil} (ng g^{-1} dw) is the concentration of the compounds in soil, estimated one year after a single sludge application (EU, 2003; Martín *et al*., 2012b).

The PEC_{soil} values were calculated applying the Eq. (5), (EU, 2003):

$$PEC_{soil} = \frac{\mathrm{MEC_{sludge}} \times \mathrm{APPL_{sludge}}}{\mathrm{DEPTH_{soil}} \times \mathrm{RHO_{soil}}} \quad (5)$$

where MEC_{sludge} (ng g^{-1} dw) is the maximum concentration values of the EOCs in sludge samples, $APPL_{sludge}$ is the dry-sludge application rate (0.5 kg m^{-2} $year^{-1}$, for agricultural soil), $DEPTH_{soil}$ is the mixing depth of soil (0.20 m, for agricultural soil) and RHO_{soil} is the bulk density of wet soil (1700 kg m^{-3}, for agricultural soil) (González *et al*., 2010; Martín *et al*., 2012b). If RQ is greater than 1, a possible environmental risk is assumed, while if RQ value is lower than 1, no risk is indicated.

3. Results and discussion

3.1. EOCs in Greece STPs' sludge

According to the literature and experimental data collected in this study, 99 EOCs have been detected in Greek STPs, belonging to 7 classes of organic micropollutants: PhCs, IDs, SPCs, PFCs, BTRs, BTHs, and SLXs. Their maximum concentration levels ranged from less than 10 ng g^{-1} dw (SPCs and PFCs) to some tens of μg g^{-1} dw (SPCs), as it is shown in Fig. 1. The majority of SPCs and SLXs presents high concentrations values in sludge samples due to their widespread domestic and industrial use and their physicochemical properties (low water solubility and high sorption coefficients) that enhance their accumulation onto sludge (González *et al*., 2010).

3.2. Environmental risk assessment

As terrestrial acute toxicity data was scarce, risk assessment based on relevant data was carried out for 18 out of the 99 target compounds. Amongst them, only triclosan, belonging to the group of SPCs, presented an $RQ_{soil,\ terrestrial}$ value higher than 1, specifically 8.1, indicating a possible threat for earthworms. The rest of the target compounds (12 PhCs, 2 SPCs, 2 PFCs and 1 SLX) did not seem to pose an environmental risk to the terrestrial organisms (plants, earthworms and soil microorganisms).

According to the results of risk assessment based on aquatic toxicity data, calculations were carried out for 68 out of the 99 detected EOCs, as no information on their toxicity nor their K_{oc} value could be obtained in the literature or *via* ECOSAR model. As it is shown in Fig. 2, for 12 compounds calculated $RQ_{soi,\ aquatic}$ higher than 1, in sludge-amended soil. The classes of EOCs that seemed to pose the greatest risk to the terrestrial environment were SPCs and SLXs; while the highest quotients were calculated for tetradecamethylhexasiloxane, decamethylcyclopenta-siloxane, caffeine and triclosan, equal to 66, 50, 46 and 28, respectively. Regarding IDs, PFCs and BTRs, no compounds in these groups presented a possible threat to terrestrial organisms; while the most of the PhCs had $RQ_{soil,aquatic}$ lower than 1, indicating no individual environmental threat due to their occurrence in sewage sludge.

3.3. Effect of variations in EOCs sludge concentrations on the predicted environmental risk

For those compounds presented $RQ_{soil,\ terrestrial}$ or $RQ_{soil,\ aquatic}$ higher than 1, further calculations were held in order to check whether variations in concentration due to the sludge source and day of sampling affect the predicted environmental risk. Thus, all the available concentration values in sludge originated from Greek STPs were used and additional RQ_{soil} values were calculated. SPCs was the group of EOCs for which the most concentration values were available, as they have been detected in six Greek STPs, during four sampling periods; whereas SLXs were the micropollutants with limited concentration data, as they have been detected only in one STP, during one sampling period. In Fig. 3, box-and-whisker plots of $LogRQ_{soil}$ values for the target compounds are shown. Apart from triclosan, for which calculations were based both on terrestrial and aquatic toxicity data, all the other calculations were based merely on aquatic toxicity data. According to the results, all SLXs and the PhCs caffeine and ofloxacin presented $RQ_{soil,\ aquatic}$ higher than 1, indicating that they may pose a serious threat to the terrestrial organisms, despite the daily variation in concentrations and the differences in plant capacity and treatment processes. Amongst SPCs, triclosan seemed to pose the greatest threat to the terrestrial environment, as 91% and 60% of the analyzed samples presented $RQ_{soil,aquatic}$ and $RQ_{soil,terrestrial}$ values, respectively, higher than 1. The corresponding rate for the rest of the SPCs (nonylphenol, nonylphenol

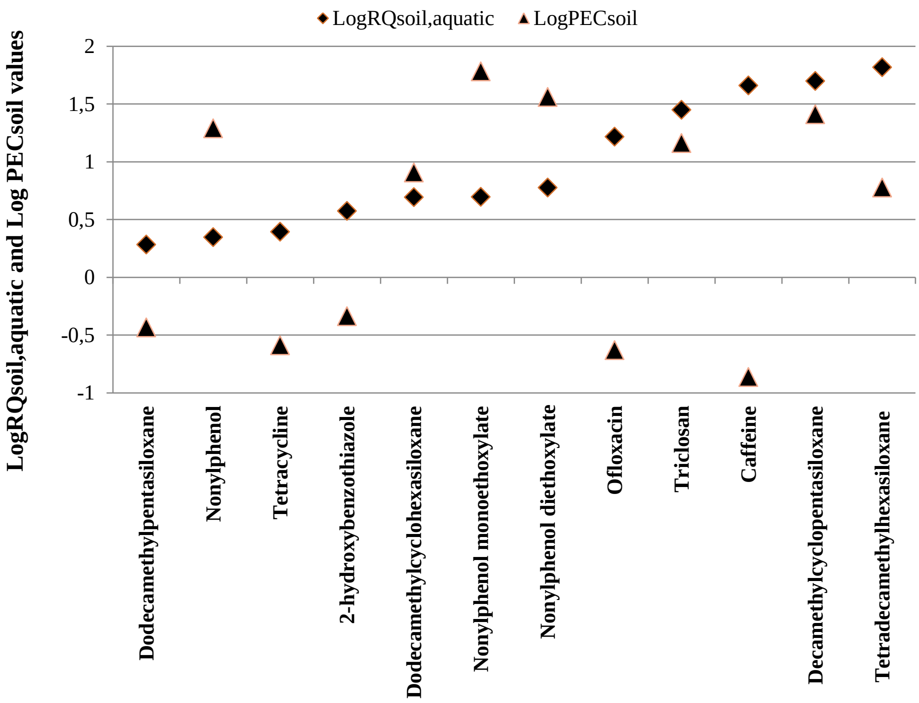

Figure 2. Risk quotients ($RQ_{soil,aquatic}$) and predicted soil concentration (PEC_{soil}) levels of 12 emerging organic contaminants (EOCs) that present environmental threat in sludge-amended soil. ($RQ_{soil,aquatic}$ values are ranked with increasing value; their calculations were based on aquatic acute toxicity data and worst-case scenario).

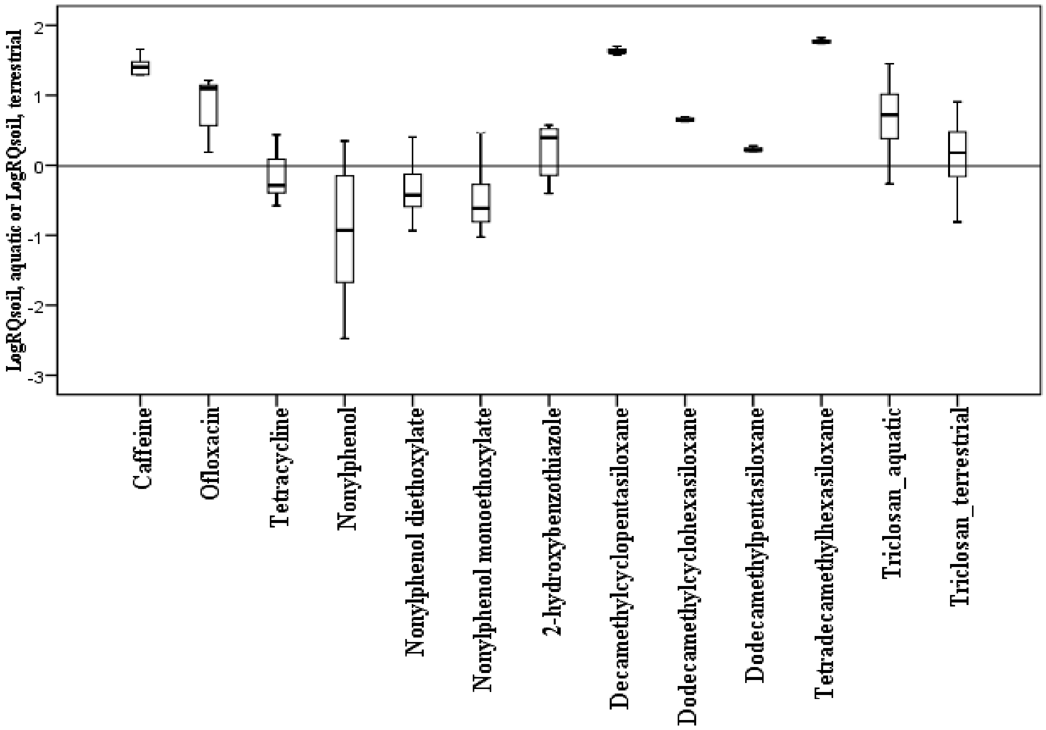

Figure 3. Box-and-whisker plots of $logRQ_{soil}$ values of those emerging organic compounds (EOCs) that had RQ_{soil} values higher than 1 for the worst-case scenario. (The horizontal black line in the boxes represents the median value, the low and upper lines in each box correspond to the lower and upper quartile, the lines extending from each box show the highest and lowest $logRQ_{soil}$ values).

monoethoxylate and nonylphenol diethoxylate) was 21%.

4. Conclusions

The concentrations of 99 EOCs in Greek STP's sludge have been monitored. Their levels ranged from less than 10 ng g^{-1} dw (SPCs and PFCs) to some tens of μg g^{-1} dw (SPCs). According to the results of risk assessment, SPCs and SLXs presented the highest risk of all EOCs in sludge-amended soil; while triclosan seemed to pose a significant environmental hazard to the terrestrial organisms, as both $RQ_{soil,aquatic}$ and $RQ_{soil,terrestrial}$ values exceeded 1. The results of the study indicate that sludge treatment methods should be improved to reduce the load of organic micropollutants in soil, while specific EOCs, such as EDCs and SLXs should be included in future national monitoring campaigns.

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