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Assessing the risk associated with the presence of emerging organic contaminants in sludge-amended soil: A country-level analysis

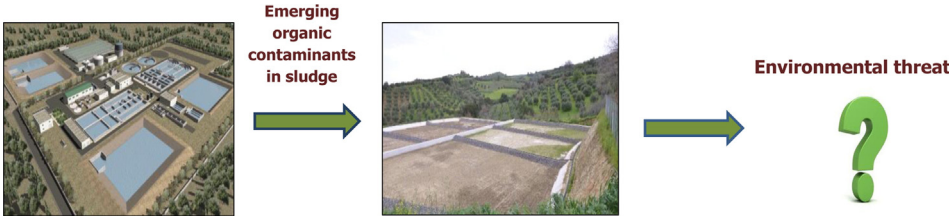
Vasiliki S. Thomaidi [a], Athanasios S. Stasinakis [a,*], Viola L. Borova [b], Nikolaos S. Thomaidis [b]

[a] Department of Environment, University of the Aegean, 81100 Mytilene, Greece
[b] Department of Chemistry, National and Kapodistrian University of Athens, 15771 Athens, Greece

HIGHLIGHTS

- The risk due to 99 EOCs in sludge-amended soil was evaluated in Greece.
- Risk assessment was based on terrestrial and aquatic toxicity data.
- $RQ_{soil} > 1$ was calculated for 12 compounds.
- Synthetic phenolic compounds and siloxanes seem to pose the highest risk.
- The mixture of EOCs seems to possess a possible risk to terrestrial environment.

GRAPHICAL ABSTRACT



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ABSTRACT

Greece was used as case study and the environmental risk associated with the existence of 99 emerging organic contaminants (EOCs) in sludge-amended soil was estimated using risk quotient (RQ) approach. Data on the concentration levels of EOCs in sewage sludge was collected after literature review. Chemical analyses were also conducted for 50 pharmaceuticals and illicit drugs in sludge samples from Athens Sewage Treatment Plant. Risk assessment was based on both terrestrial and aquatic acute toxicity data, using both the maximum and the average measured concentrations of the target compounds. EC_{50}/LC_{50} values were collected through literature review or using the ECOSAR program in cases that experimental values were not available. Triclosan seems to pose an environmental risk on the soil environment, as its RQ values exceeded 1, both in terrestrial and aquatic toxicity data based risk assessment. Calculations based on aquatic toxicity data showed that another eleven compounds had RQs higher than 1, most of them belonging to the classes of synthetic phenolic compounds and siloxanes. Tetradecamethylhexasiloxane presented the highest RQ, while high RQs were also calculated for decamethylcyclopentasiloxane and caffeine. No environmental risk for the terrestrial environment is expected due to the individual action of illicit drugs, perfluorinated compounds and benzotriazoles. The sludge source and the day of sampling affected the estimated threat due to nonylphenolic compounds; however these factors did not affect the estimated risk for siloxanes, caffeine and ofloxacin. Calculation of RQ values for the mixture of EOCs, using either the maximum or the average concentrations, far exceeded 1 (253 and 209, respectively), indicating a presumable threat for the terrestrial environment due to the baseline toxicity of these compounds. Countries that reuse sludge for agricultural purposes should include specific EOCs in national monitoring campaigns and study more thoroughly on their effects to the terrestrial environment.

1. Introduction

The term 'emerging organic contaminants' (EOCs) includes a broad spectrum of chemicals that have not yet been regulated. Among others, they include pharmaceuticals (PhCs), illicit drugs (IDs), synthetic

* Corresponding author.
E-mail address: astas@env.aegean.gr (A.S. Stasinakis).

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phenolic compounds (SPCs), perfluorinated compounds (PFCs), benzotriazoles (BTRs), benzothiazoles (BTHs) and siloxanes (SLXs) (Murray et al., 2010). These compounds are contained in everyday products, they are detected in domestic wastewater worldwide and many of them have been identified as endocrine disruptors (Farré et al., 2008; Bletsou et al., 2013; Stasinakis et al., 2013). Due to their physicochemical properties, some of them tend to adsorb on the suspended solids during wastewater treatment, and they are thus transferred to sewage sludge (Clarke and Smith, 2011; Stasinakis, 2012; Petrie et al., 2014).

Agricultural reuse of treated sludge is one of the most common sludge management practices. In EU-27, 21 Member States have adopted agricultural reuse, while 53% of the total produced sludge is recycled in agriculture directly or after composting (Kelessidis and Stasinakis, 2012). In USA and Canada, more than 50% and 40%, respectively, of the produced biosolids are applied to land (Citulski and Farahbakhsh, 2010; Venkatesan et al., 2015), while in China the land application of treated sewage sludge is suggested as the optimal solution for efficient sludge management (Yang et al., 2015). So far, literature has focused on the environmental threats due to the existence of heavy metals and pathogens in sludge-amended soils (Lewis and Gattie, 2002; Smith, 2009; Pritchard et al., 2010). Based on this information, the EU and several countries have set limit values and have suggested practices to prevent harmful effects on soil, vegetation, animals and humans (Alvarenga et al., 2015; Verlicchi and Zambello, 2015).

On the other hand, there is much less information on the environmental risk to the terrestrial environment due to the occurrence of EOCs in sewage sludge. Most of the relevant studies concern specific Sewage Treatment Plants (STPs) and a limited number of compounds or specific groups of contaminants. Additionally, due to the limited available soil toxicity data, in most of the relevant articles the potential risk for the soil environment has been estimated using only aquatic toxicity data and the methodology proposed by EC (2003). Specifically, González et al. (2010) evaluated the toxicological risk of 3 SPCs in the terrestrial environment in the South Spain, while Martín et al. (2012b, 2015) assessed the ecological hazard associated with the presence of 16 and 22 PhCs respectively, in sludge-amended soil in the same area. Three related studies have also been conducted in China. The potential risk due to the presence of 4 SPCs and 5 PhCs (Chen et al., 2011), 4 PhCs (Wu et al., 2014) and 2 synthetic musks and 2 SLXs (Liu et al., 2014) was estimated in sludge-amended soil, in the North, South and East of China, respectively. Although risk assessment is more reliable if a large number of compounds belonging to different classes are taken into account, to the best of our knowledge, so far, there is only one relevant study estimating the risk from the occurrence of a significant number of pharmaceuticals and personal care products in sewage sludge (Verlicchi and Zambello, 2015). On the other hand, the potential risk related to the presence of individual EOCs in sludge as well as with their mixture toxicity on the terrestrial environment has not been estimated at country level. Bearing in mind that the EOCs that are detected in sewage sludge are generally the same compounds in all developed countries and their concentration values range at similar levels (González et al., 2010; Arvaniti and Stasinakis, 2015), studies that would clarify the above risk-related issues could be useful for researchers and policymakers in identifying those micropollutants that have to be a) removed more efficiently during wastewater and sludge treatment, b) periodically monitored in national sludge campaigns and c) included in relevant future legislations.

The main objective of the current study was to estimate the potential environmental risks from the disposal of sewage sludge containing EOCs in soil, selecting Greece as a case study. For this reason, soil and aquatic toxicity data were collected and the possible threat due to the occurrence of single compounds and mixture of EOCs was estimated using risk quotient (RQ) approach. The effect of daily and source-origin variation of selected EOCs concentrations on estimated threat was investigated, while the role of maximum and average measured concentrations of target compounds in calculated RQ values was checked. Moreover, suggestions on the environmental policy that has to be followed in the future on this issue were made.

2. Materials and methods

2.1. Concentration data collection: literature review and chemical analysis

An extended literature review was initially conducted to investigate the EOCs that have been detected in dewatered sewage sludge samples, originating from Greek STPs (Table S1). Their concentrations were recorded and the maximum concentration was selected for each compound (Table S2), as the worst-case scenario was initially applied in this study.

Moreover, the occurrence of 50 further PhCs and IDs was investigated in sewage sludge samples from Athens STP, Greece. This plant serves 3,700,000 inhabitants and the wastewater treatment process involves primary sedimentation, activated sludge process with biological nitrogen/phosphorus removal and secondary sedimentation. The produced sludge is treated via thickening, anaerobic digestion, mechanical dewatering and thermal drying (Samaras et al., 2013). To determine the concentrations of selected PhCs and IDs, grab samples of dewatered sludge were taken during eight consecutive days. All samples were collected in glass jars, transferred to refrigerated coolers in the laboratory, freeze-dried and stored in the dark (−20 °C) until analysis. Detailed information about the analytical procedure can be found in Gago-Ferrero et al. (2015).

In brief, ultrasonic extraction was employed on freeze-dried sewage sludge with 3 × 2 mL MeOH-water (pH 2.5, formic acid 0.5% and 0.1% EDTA) 50:50 (v/v) and the extract was evaporated to dryness. Reconstitution of the analytes was performed with 0.5 mL MeOH-water (0.05% formic acid), 25:75 (v/v). Finally, the extract was filtered through a 0.2 μm RC syringe filter and the samples were transferred to a glass vial for HPLC-MS/MS analysis. Instrumental analysis was performed with a Thermo UHPLC Accela system connected to a TSQ Quantum Access triple-quadrupole mass spectrometer from Thermo Electron Corporation (San Jose, CA, USA), equipped with an electrospray-ionization (ESI) source (Thermo IonMAX) and operated in both positive and negative mode. The analytical method presented satisfactory repeatability; sufficient recoveries were obtained for most of the target compounds, while method detection limits (MDLs) and limits of quantification (LOQs) allowed a reliable detection and quantification of the target compounds at the levels they are typically present in sewage sludge samples (Table S3). The seven-point calibration curves (0.5–100 ng mL^{-1}) which were obtained for the SRM transitions were linear with $r^2 > 0.99$ in all cases. The trueness of the method was assessed by spiking experiments at one concentration level (40 ng g^{-1} dw) in sewage sludge samples. Analytical variability from repeated analyses within the laboratory was evaluated by spiking sewage sludge samples with 40 ng g^{-1} dw of each compound (n = 6). Intermediate precision was determined as relative standard deviation (% RSD) from the recovery experiments (n = 6, 40 ng g^{-1} dw), processed with the method described. MDLs and LOQs were calculated by analyzing five times the spiked samples. Matrix effects (ME, %) were also assessed and were expressed as percentage of suppression or enhancement.

2.2. Toxicity data collection

According to the Technical Guidance Document (EC, 2003), risk assessment in soil could be based on the short-term toxicity data of terrestrial organisms, such as plants, earthworms or/and soil microorganisms. Thus, experimental acute toxicity data (EC_{50} or LC_{50}) for these groups of organisms were collected through literature review and the lowest value was chosen in order to estimate the environmental risk for worst-case scenario (Table S4). EC_{50}/LC_{50} values given in mg L^{-1} were