Wide-scope target analysis of >2,100 emerging contaminants in landfill leachates by LC-QTOFMS and investigation of their potential ecological threat

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Abstract

Organic micropollutants are compounds which are normally detected at concentrations up to microgram per liter in the aquatic environment and they are considered to be potential threats to the ecosystem. Some of them have been studied in detail since 1980s and are already included in existing national or international legislative documents, while others are characterized as emerging contaminants (ECs) and no regulations currently require their environmental monitoring. During the last decade, several studies have been focused on the investigation of possible sources of emerging contaminants' distribution into the environment. According to the literature, sewage treatment plants are considered as major point sources of these compounds into the environment, as they receive domestic and industrial wastewater, as well as urban and - in some cases- agricultural runoff (Ratola et al., 2012; Luo et al., 2014; Arvaniti and Stasinakis, 2015). On the other side, the contribution of landfills, via the produced leachates, in transferring emerging pollutants to the environment, is not well reported so far (Oturan et al., 2015). Besides European policy for recycling and waste-to-energy, landfilling still remains one of the alternative options for municipal solid waste management in EU-28, where 58×10^6 tonnes of municipal solid waste were disposed to landfills in 2017 (Eurostat, 2018). Concerning Greece, more than 80% of the produced municipal solid waste is dumped to central landfills which are located in the mainland and islands.

The occurrence of ECs in leachates samples originated from different Greek landfills was investigated in this study and the possible threat for the aquatic environment was evaluated using risk quotient (RQ) methodology. For this reason, raw and treated leachate samples (after biological treatment with activated sludge process or/and advanced treatment with reverse osmosis, RO) were collected from eight (8) landfills around Greece, in June 2018. All studied landfills receive municipal solid waste but present different characteristics regarding their capacity and the technology applied for leachates' treatment. The samples were initially analyzed for conventional pollutants and afterwards for the existence of ECs using LC-ESI(+/-)-QTOFMS. For the determination of emerging contaminants, Solid-Phase Extraction using mixed-mode sorbents was used for the extraction and pre-concentration of compounds with different physicochemical properties. The HRMS chromatograms were screened with an in-house wide scope database of more than 2,100 organic pollutants including compounds of different classes (such as pharmaceuticals, personal care products, drugs of abuse, pesticides, stimulants, sweeteners, perfluorinated compounds, benzotriazoles, benzothiazoles, phthalates and surfactants), as long as their transformation products and metabolites. The concentrations of the contaminants in leachates were calculated based on standard addition method. For estimating the ecological threat for the aquatic environment, toxicity data was collected after literature review or using ECOSAR and RQs were found for the detected ECs according to the Technical Guidance Document on Risk Assessment (EC, 2003; Thomaidi et al., 2015) for raw, biologically treated and RO treated leachates. According to this methodology, in cases that RQ is less than 1, no ecotoxicological risk for the aquatic environment is indicated, while in cases that RQ is greater than 1, ecotoxicological risk is possible for the aquatic environment.

According to the results, the pH of the samples was ranged between 5.28 and 8.98 and their conductivity between 0.21 mS/cm (sample treated with RO) and 27.9 mS/cm (raw leachate sample). The average COD and the NH_4-N concentrations of the raw leachate samples was 7,261 ± 2,953 mg/L and 962 ± 451 mg/L, respectively, while the application of biological treatment resulted to a partial decrease of these pollutants to 2,665 ± 2,902 mg/L and 212 ± 185 mg/L, respectively. The advanced treatment of leachates with RO resulted to significant decrease of conventional pollutants to 24 ± 9 mg/L for COD and 25 ± 24 mg/L for NH_4-N.

Concerning the occurrence of ECs, 62 compounds were detected in total belonging to different chemical groups such as pharmaceuticals, food additives, plant protection products, industrial chemicals and perfluorinated compounds, while 14 of them were found at more than 50% of collected samples. The compounds that were detected with the higher frequency were 2-OH-benzothiazole (84% of samples), PFOA (68% of samples), bisphenol A, bentazone and propamocarb (64%

of samples). The number of detected compounds, as well as their concentrations varied significantly based on the matrix and the applied treatment process. More ECs and at higher concentration levels (up to some hundreds μg/L) were detected in raw leachate samples, while the application of biological treatment removed totally some of them and partially decreased the concentrations of the rest. The elimination of ECs was much more important when RO was applied. In these samples, only few compounds were detected per sample and their concentrations did not exceed levels of ng/L. The results of risk assessment showed that the possibility of ecological threat for the aquatic environment cannot be rejected for the cases that raw or biologically treated leachates are discharged into rivers with small flow.

Keywords: emerging pollutants; occurrence, leachates; HRMS; environmental risk assessment;

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