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Review

Urban Sludges Utilization in Agriculture: Possible Limitations Due to Their Contamination with Polycyclic Aromatic Hydrocarbons

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Abstract

The objective of the present study was to assess the polycyclic aromatic hydrocarbons' (PAH) contamination of urban sewage sludge – a potential agricultural fertilizer, as a result of the increasing environmental concern regarding the fate of biodegradable solid wastes generated by wastewater treatment processes. PAHs were determined by an Agilent 1100 high performance liquid chromatograph with fluorescence and diode-array detection, separations being accomplished using an Envirosep PP column with a mixture of acetonitrile: water as mobile phase. This study revealed a low contamination of sewage sludge originating from Cluj Napoca wastewater treatment plant with PAHs (15.61 µg/kg dry weight for overall PAHs concentration) during a four-month monitoring period, with individual concentrations ranging from 0.06 to 11.50 µg/kg dry weight, the highest recorded values being for naphthalene (11.50 µg/kg dry weight), phenantrene (1.39 µg/kg dry weight) and benzo (g, h, i) perylene (0.63 µg/kg dry weight). As the recorded values during the study period were low, we can conclude that the environmental risks related with PAHs contamination is quite low; due to their hydrophobic character, groundwater pollution by levigation can be also excluded. However, seasonal variations of PAHs contamination are possible and for this reason this study will be extended for a full-year period.

Keywords: soil, sludge, polycyclic aromatic hydrocarbons, PAH, pollution.

1. Introduction

The amounts of sewage sludge produced in wastewater treatment plants raises constantly as human society develops, generating environmental problems due to an increase need to provide the proper disposal requirements. A possibility to solve this problem is the land application technique; sludge may be applied to agricultural or dedicated surfaces and hence sewage sludge from municipal wastewater treatment can be used in agriculture as a nutrient source and to aid in moisture retention [2, 4]. However, as many wastewater treatment plants (especially those one from big cities) receive discharges from both residential and industrial sources, such residues need to be controlled carefully in order to protect human health and the environment, because sewage sludge is a carrier of chemical pollutants such as heavy metals and organic pollutants [3].

Polycyclic aromatic hydrocarbons (PAHs) occur ubiquitously in the environment from both natural sources and anthropic pollution (generated as by-products of incomplete combustion in certain

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industries such as iron, steel or rubber industries), being high concern pollutants because some of them have been identified as carcinogenic, mutagenic and teratogenic [6]. Due to their low solubility in water and their lipophilic nature, these compounds are concentrated strongly in the sewage sludge during wastewater treatment process, being then only little degraded by biological processes from the treatment plant. PAHs from sludge can originate from three types of sources: exhaust gas and the runoff of raining water on roads, the fumes of industrial thermal units and may reach the soil through raining water and the industrial effluents. Besides sludge disposal from public sewage treatment plants, other potential sources of PAHs in soil include automotive exhaust, irrigation with coke oven effluent, leachate from bituminous coal storage sites and use of soil compost and fertilizers [7, 8, 13]. Possible contamination pathways of the human food chain with these compounds would be food crops or grazing livestock that eat contaminated feed grown on sludge-amended soil or ingest contaminated soil directly while grazing [5].

The purpose of this paper is to assess the level of contamination with PAHs for the urban sludge resulted from the wastewater treatment plant located in Cluj Napoca, Romania, and to establish if it is appropriate to continue a more detailed research, knowing that residues of some PAHs can persist in the soils for many years [10-12]. The results from this study can be very useful for the proper application of sewage sludge into agriculture soils.

2. Material and Methods

Samples of sewage sludge were collected from Cluj Napoca's wastewater treatment plant in polyethylene bags, after dewatering stage, over a 4-month period (August –November 2012). Samples were dried at 105°C, then extracted using a Soxhlet extractor with dichloromethane according to the EPA's method 8275A [13]; the obtained extract were evaporated to dryness in a rotary evaporator, then re-dissolved in 1.5 mL acetonitrile and subjected to high performance liquid chromatographic (HPLC) analysis.

PAHs were purchased from Supelco (Bellefonte, PA, USA) as a TCL PAHs Mix at concentration of 20-1000 µg/mL in acetonitrile: methanol (90:10). Calibration solutions were prepared by diluting the standard solution with acetonitrile. Solvents used were all HPLC grade, being supplied by Merck (Darmstad, Germany). Ultrapure water was obtained from a WATEK IWA 20 water purification system.

PAHs were determined by an Agilent 1100 high performance liquid chromatograph consisting in a solvent degasser, a quaternary pumping system, an autosampler, a column oven, a diode-array detector and a fluorescence detector. Separations were accomplished using an Envirosep PP column (125 mm x 4.6 mm I.D) using acetonitrile: water as mobile phase [1, 9]. The quantitative analysis was accomplished by the external standard calibration method; PAHs' identification was performed by comparison of their retention time with those of authentic standards. For peak identity confirmation, the diode-array detector's spectra were compared with reference compounds spectrum in the spectrum library. The procedure been checked for recovery efficiencies using spiked PAH samples; recoveries ranged between 27% and 83% and the reported data are corrected accordingly, considering the means of triplicate determinations. Data processing was accomplished using Chemstation 08.03 Software.

3. Results and Discussion

Table 1 summarizes the obtained data, emphasizing a total PAHs concentration of 15.61 µg/ kg (Cluj Napoca – city center), naphthalene being the major component (11.50 µg/ kg dry weight), followed by phenantrene (1.39 µg/ kg dry weight) and benzo (g,h,i)perylene (0.63 µg/ kg dry weight); chrysene was not detected in any of the analyzed samples..

Table 1. Average concentrations of the determined in sewage sludge

PAHs	µg PAHs / kg dried weight	Standard deviations
Naphthalene	11.50	0.78
Acenaphtene	0.07	0.01
Fluorene	0.45	0.03
Phenanthrene	1.39	0.07
Anthracene	0.10	0.01
Pyrene	0.48	0.05
Benz(a)anthracene	0.17	0.02
Chrysene	Not detected	-

Table 1. Average concentrations of the determined in sewage sludge - continued

PAHs	µg PAHs / kg dried weight	Standard deviations
Benzo(b)fluoranthene	0.09	0.02
Benzo(k)fluoranthene	0.03	001
Benzo(a)pyrene	0.06	0.01
Dibenzo(a,h)anthracene	0.19	0.04
Benzo(g,h,i)perylene	0.63	0.12
Indeno(1,2,3-c,d)pyrene	0.44	0.09
Total/ site	15.61	

As PAHs from petrogenic sources have lower molecular weight with depletion of higher molecular weight, while pyrogenic sources generate higher molecular weight PAHs, analyzing the obtained data we can conclude that pyrogenic sources are mostly responsible for contamination of the analyzed samples of sewage sludge with PAHs

4. Conclusions

This study revealed a low contamination of sewage sludge originating from Cluj Napoca wastewater treatment plant with PAHs (15.61 µg/ kg dry weight for overall PAHs concentration), with individual concentrations ranging from 0.06 to 11.50 µg/ kg dry weight, the highest recorded values being for naphthalene (11.50 µg/ kg dry weight), phenantrene (1.39 µg/ kg dry weight) and benzo (g, h, i) perylene (0.63 µg/ kg dry weight). As the recorded values during the study period were low, the environmental risks related with PAHs contamination is quite low in the studied case; due to their hydrophobic character, potential adverse effects such as groundwater pollution by levigation can be also excluded. However, seasonal variations of PAHs contamination are possible and for this reason this study will be extended for a full-year period.

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