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Temporal evolution of polycyclic aromatic hydrocarbons (PAHs) in sludge from wastewater treatment plants: Comparison between PAHs and heavy metals

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Abstract

This paper presents results on the presence and temporal variability of the 16 PAHs recommended by the EPA in primary, secondary and digested sewage sludge over a year. The sewage sludges originated from the Guadalete wastewater treatment plant (WWTP) site in Jerez de la Frontera (Cádiz, Spain). These organic pollutants have been extracted from the sewage sludge by microwave energy. High performance liquid chromatography coupled with diode array (HPLC-DAD) or fluorescence (HPLC-FL) detectors have been used. The results showed that total PAHs concentration varied between 1945 ng g^{-1} dry matter (DM) for primary sludges collected in March and 10100 ng g^{-1} DM for primary sludge collected in June. Generally, concentrations of PAHs were higher in compost and digested sludge than in fresh one. On the other hand, the highest concentration of PAHs were found on summer. This thing is associated to the traffic increase from inland zones to the coast (Jerez de la Frontera is very near to beaches). Finally, this paper present a comparative study of the American an European legislation concluding that the limits of concentrations established are not exceeded. In addition heavy metals were analysed. The origin of PAHs and heavy metals seems to be different.

Keywords: PAHs; Sewage sludge; HPLC; Microwave-assisted solvent extraction; Heavy metals; Compost

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1. Introduction

The determination of hazardous substances in sewage sludge is becoming an important issue due to increased amounts of sewage sludge produced as a consequence of the rising number of wastewater treatment plant. Inorganic pollutants are regularly controlled but organic pollutants have received a few attentions up to now.

Once the sludge has been treated in the depuration station it can be disposed of in different ways. The most commonly used procedures are: the controlled waste landfill site; application as a fertilizer; and incineration and subsequent discharge to coastal system. The first two options are the preferred choice in the European Union.

The application of these sludges in agriculture can be advantageous to the soil because they modify soil structure and provide organic matter and nutrients. On the other hand, utilization as a fertilizer has some risks namely, the accumulation of pollutants in soils, plants, animal pastures and the subsequent entry into the food chain of dangerous compounds (Mangas et al., 1998; McGowin et al., 2001; Bright and Healey, 2003).

Application of these sludges to agricultural land could increase the PAHs content of agricultural soils (Pino et al., 2000; Shu et al., 2000; McGowin et al., 2001). There are possible loss mechanism of PAHs in the soil, such as volatilisation, abiotic degradation, biodegradation, transboundary transfer and via crops (Moreda et al., 1998) what could generate potential problems via human food-chain contamination; therefore, it is necessary to known the levels of these contaminants when applied as a fertilizer.

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Considering these problems, it is necessary to control pollutants levels. Relevant organic contaminants present in sewage sludge are PAHs. PAHs constitute a large class of organic compounds. They are formed and released into the environment through natural and man-made sources. Natural sources include volcanoes and forest fire, while the man-made sources come mainly from the combustion of fossils fuels. These pollutants have a high persistence in the environment, low biodegradability and high lipophility, some of them being highly toxic (Vo-Dinh et al., 1998; Dabestani and Ivanov, 1999).

The determination of PAHs in sewage sludges has become a relevant topic in Europe since the 3rd draft directive of the European Union released regulating the total PAHs values allowed in sewage sludge used for agriculture (6000 ng g^{-1} calculated as the sum of acenaphthene, phenanthrene, fluorene, fluoranthene, pyrene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*g*,*h*,*i*]perylene and indeno [1,2,3-cd]pyrene) (European Commission, 2001). Other countries marked other limit values, for example, the maximum level admitted for the EE.UU. legislation is 4600 ng g^{-1} (calculated as the sum of benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a*,*h*]anthracene and indeno[1,2,3-cd]pyrene) but it is not allowed concentration higher than 1000 ng g^{-1} for benzo[*a*]pyrene.

In this paper, we have studied the temporal evolution of the 16 PAHs listed in the US Environmental Protection Agency (US EPA) priority list. These 16 PAHs are: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*] anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a*,*h*]anthracene, benzo-[*g*,*h*,*i*]perylene and indeno[1,2,3-cd]pyrene. Sewage sludges were collected from the Jerez de la Frontera WWTP for a year. On the other hand, Directive 86/278/EEC introduced limit values for heavy metals concentrations in sludge for use in agriculture. Heavy metals were analysed in order to know if the origin of PAHs and heavy metals is the same.

The contaminant levels (PAHs and heavy metals) of studied sludges which could be used as fertilizer (digested sludge and compost) are lower than the maximum admissible levels proposed in the 3rd draft European Directive and American legislation.

2. Materials and methods

2.1. Standards, solvents and reagents

Standard mixtures of 16 EPA PAHs at a concentration of 500 μg ml^{-1} in acetonitrile/toluene/hexane (6:3:1, v:v:v) were purchased from Hewlett–Packard (Waldbronn, Germany). These standards were stored at 4 °C and were used for the preparation of working standard solution in HPLC gradient grade acetonitrile (Merck, Darmstadt, Germany). HPLC grade acetone was also purchased from Merck. HPLC grade *n*-hexane and methanol were obtained from Romil (Barcelona, Spain). Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Aqueous stock solutions of Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Ti, Zn, B, Ca, Mg and Na were prepared by dilution of the respective standard 1000 mg l^{-1} solutions (Merck, Germany). All standard and reagent solutions were stored in polyethylene bottles. All reagents were of analytical-reagent grade.

2.2. Equipment

All measurements were made with a high performance liquid chromatograph consisted of a L-7100 Pump (Merck Hitachi), a L-7455 diode array detector and a L-7485 fluorescence detector (Merck Hitachi). The injector is a Rheodyne, Model 7725i (Cotati, CA, USA) fitted with a 20 μl external loop. The analytical cartridge column was a LichroCART 250-3 Lichrospher PAH column, 250 mm × 4.6 mm ID, 3 μm particle size. To protect it from contamination a LiChroCART 4-4 LiChrospher 100 RP-18,5 μm particle size, guard column, was installed.

The microwave extraction system was a Microwave Ethos 900 apparatus (Milestone, Sorisole, Italy) with a programmable power and irradiation time. The Microwave Ethos 900 apparatus is equipped with a carousel that is able to hold six extraction vessels.

An ICP Applied Research Laboratories (Fisons Instruments) model 3410+ was used for the elemental determination of Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Ti and Zn. B, Ca, Mg, K and Na were also analysed by ICP-AES.

2.3. Sewage sludge collection

Sewage sludges were collected from the Jerez de la Frontera (Cádiz, Spain) WWTP. The Jerez de la Frontera WWTP receives mainly domestic sewage water although there are some contributions from industrial one, principally from wine industries. Fig. 1 shows a scheme of the operation conditions in the depuration plant.

Primary and secondary sludge: 250 ml sample of sludge were collected twice a week for a month in order to obtain a representative sample for this period of time. Samples were collected from the nearest point stabilization system (maximum mixed), direct into the transport pipes to digestor reactor by means of collected samples valves. Samples were frozen until analysis.

Digested sludge: 1000 ml of sample of homogenous sludge was collected once a month. Samples were collected from discharge zone of positive displacement bombs which throw out sludges from the reactor. Samples were collected into the transport pipes to the store zone.

It is not necessary collect digested samples every day due to high retention time of the stabilized process of sludges