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Simultaneous sonication-assisted extraction, and determination by gas chromatography–mass spectrometry, of di-(2-ethylhexyl)phthalate, nonylphenol, nonylphenol ethoxylates and polychlorinated biphenyls in sludge from wastewater treatment plants

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Abstract

Di-(2-ethyl-hexyl)phthalate (DEHP), nonylphenol, nonylphenol mono- and diethoxylates (NPEs) and polychlorinated biphenyls (PCBs) are organic pollutants in sewage sludge which have to be monitored in the European Union according to a future Sludge Directive. In the present work, an analytical method for the simultaneous extraction and determination of DEHP, NPEs and PCBs is proposed for the routine analysis of these compounds in sludge from wastewater treatment plants. All the compounds were simultaneously extracted by sonication with hexane and analysed by gas chromatography–mass spectrometry (GC–MS) in electronic impact mode. Recoveries achieved were 105% for DEHP, 61.4–88.6% for NPEs and 55.8–108.3% for PCBs with relative standard deviation bellow 10%. Limits of quantification were 65 μg kg^{-1} for DEHP, from 630 to 2504 μg kg^{-1} for NPEs and from 5.4 to 10.6 μg kg^{-1} for PCBs in dried sludge. The applicability of the proposed method was evaluated by the determination of these compounds in sludge from wastewater treatment plants in Seville (South Spain).
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1. Introduction

The quantity of sludge from wastewater treatment plants has been greatly increased in the recent years within the European Union (EU) because of the implementation of the Directives 91/271/EEC [1] and 98/15/EEC [2] concerning wastewater treatment. The production of sludge in the EU was predicted to be increased from 5.5 million tons in 1992 to about 8.3 millions in 2005 of which about 53% was estimated to be used as fertilizer on agriculture [3]. The application of sewage sludge to farmland is possibly often the cheapest sludge disposal option. It provides an opportunity to recycle beneficial plant nutrients and organic matter for crop production. However, care must be taken that chemical or pathogenic contaminants present in sludge do not cause adverse effects. For example, heavy metals and pesticides, industrial solvents, dyes, plasticizers, surfactants and many other complex organic molecules, generally with low water solubility and high adsorption capacity, tend to accumulate in sludge [4]. In spite of European Directive 86/278/EEC limits the total amount of several heavy metals depending on the pH of the soil, there are no limit values set for trace organic contaminants in sludge within the current European legislation concerning sewage sludge. So, in the 1990s, some countries as Denmark [5] and Germany [6] fixed limit concentrations of some organic compounds in sewage sludge to be used in agriculture to prevent contamination of agriculture lands. In 2000, the European Union produced a Working Document on Sludge (Third Draft, April 2000) [7], described as "an EU-initiative to improve the present situation for sludge management". It proposes that there would be "provisions on concentration limit values for heavy metals and organic compounds" and that ". . .if the concentration of one or more organic

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compounds in sludge is higher than the concentration limits propose, the use of sludge (on agricultural land) should not take place". The question of whether limits should be set for organic contaminants in sewage sludge is complex and controversial for several reasons. Amongst them is that there is still a general lack of accepted, validated analytical methods for the analysis of most classes of organic chemicals in sewage sludge and a lack of background or survey data on their occurrence [8–11]. Some of the organic compounds, with appreciable concentrations in sludge [12], that will have to be monitored according to this document are DEHP (di(2-ethylhexyl)phthalate), NPEs (sum of nonylphenol and nonylphenolethoxylates with one or two ethoxy groups) and PCBs (sum of the polychlorinated biphenyls components number 28, 52, 101, 118, 138, 153 and 180). The limits values established for these compounds in sludge dry matter (dm) for land application of sludge are 100 mg kg^{-1} for DEHP, 50 mg kg^{-1} for NPEs and 0.8 mg kg^{-1} for the sum of the seven PCB congeners [7]. Limits values established in Germany in 1992 were 0.2 mg kg^{-1} dm for each of the six PCB congeners [6]. Limits values established in Denmark in 1996 were 50 mg kg^{-1} dm for DEHP and 10 mg kg^{-1} for NPEs [5].

Phthalates are organic compounds produced in huge amounts in the whole world to be used as softeners in plastic (PVCs) and as additives in paints, glues and inks. In spite of the strong environmental impact of DEHP, it is the most used of the phthalates esters due to its stability, fluidity and low volatility [13]. NPEs are used as surfactant agent in cleaning, cosmetics and hygienic products. 4-Nonylphenol (NP) is a widespread toxic degradation product of non-ionic alkylphenol surfactants. PCBs have been used as coolants and lubricants in transformers, capacitors and other electrical equipment due to their non-flammability properties. Their production was banned in the 1980s in most countries but they still occur in the environment. For instance, concentration levels of PCBs in dried sludge samples were reported to be in the range from 0.003 to 0.596 mg kg^{-1} from Catalonia (NE Spain) WWTPs sludges during 2001–2003 [12].

In agreement with previously exposed, to test the suitability of sewage sludge for land application according to the future Sludge Directive, simple, reliable and fast analytical methods are needed. A few analytical methods have been reported for the determination of these compounds in sewage sludge, separately or simultaneously with other compounds but only one method has been found in literature for their simultaneous determination in sewage sludge [12]. This method involves extraction with dichloromethane, shaking for two hours, drying the supernatant, interaction of the extract with copper overnight and a further determination by GC–MS. Anticipating the need for easy quantification of these compounds in sludge samples, the aim of this work was to provide an alternative method for the simultaneous extraction and determination of DEHP, NPEs and PCBs in sewage sludge to be used for quality monitoritation of sludge according to the future European Directive. The proposed method was applied for the determination of DEHP, NPEs and PCBs concentrations in primary, secondary and digested-dehydrated sludge samples from four WWTPs in Seville (South Spain).

2. Experimental

2.1. Chemicals and reagents

DEHP, a PCBs congener mix (PCB 28, 52, 101, 118, 138, 153 and 180, 10 μg mL^{-1} of each component in cyclohexane) and *tert*-butylphenol, used as internal standard (IS), were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Nonylphenol technical grade Pestanal® was obtained from Riedel-de-Haën (Seelze, Germany), nonylphenol mono- and diethoxylated technical mixture Igepal® CO-210 was obtained from Aldrich (Milwaukee, WI, USA). Hexane and dichloromethane were purchased from Romil Ltd. (Barcelona, Spain). Working solutions of all compounds were prepared by diluting the stock standard solutions in hexane. Concentration of the internal standard in the calibration solutions was 1.0 μg mL^{-1}.

2.2. Chromatography

Chromatographic analysis was performed on an Agilent 6890N gas chromatograph (Palo Alto, CA, USA) coupled to an Agilent 5973N mass spectrometer and equipped with an Agilent 7683 autosampler and a PTV (programmed temperature vaporizer) injector. Separations were carried out using an Agilent HP-5 ms column (30 m × 0.25 mm i.d. × 0.25 μm film thickness (5%-phenyl-methylpolysiloxane).

An aliquot of 5 μL of sample was injected in solvent vent mode. Injector temperature was increased from 40 °C (held for 1.1 min) to 300 °C at 700 °C min^{-1} (held for 5 min at 300 °C) and then was decreased to 250 °C (held for 20 min) at −50 °C min^{-1} using liquid carbon dioxide. Helium was used as carrier gas at a constant pressure of 146 kPa to achieve retention time locking from a run to another. Oven temperature was programmed as follows: 70 °C for 2 min and then three temperature ramps, 25 °C min^{-1} from 70 °C to 150 °C, 3 °C min^{-1} from 150 °C to 200 °C and 8 °C min^{-1} from 200 °C to 280 °C (held for 15 min).

The mass spectrometer was operated in the electronic impact mode (70 eV). Two acquisition modes were employed. Selected ion monitoring mode (SIM) was used for quantitative analysis; the *m*/*z* values of the ions monitored are listed in Table 1. The presence of the compounds was confirmed by means of the mass spectra obtained in full scan acquisition mode in the *m*/*z* range from 50 to 400.

Calibration curves were constructed by linear regression of peak areas of standard solutions against their respective concentrations. Standard solutions were prepared in hexane at concentrations ranging from 0.14 to 1.6 μg mL^{-1} for DEHP, from 0.25 to 2.0 μg mL^{-1} for NPEs and from 0.020 to 0.10 μg mL^{-1} for PCBs.

2.3. Sample treatment

Sludges were lyophilized in a Cryodos-50 (Telstar, Terrassa, Spain) lyophilizer and sieved (particle size <100 μm). An amount of 0.5 g of the sieved lyophilized sludge was transferred to 10 mL glass tubes and 5 ml of hexane and 25 μL of 200 μg mL^{-1} IS solution were added. The tubes were shaken for 20 min in a mechanical shaker, sonicated for 15 min and

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