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Presence of organic pollutants in sludge from anaerobic wastewater stabilization ponds

J.L. Santos, I. Aparicio, A. Santos, F. Álvarez, M. López-Artíguez, D. Olano, S. García, E. Alonso*

Department of Analytical Chemistry, University of Seville, C/ Virgen de África 7, E-41011 Seville, Spain
Tel. +34 (9) 5455-2858; Fax +34 (9) 5428-2777; email: ealonso@us.es

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ABSTRACT

One of the most common disposal options of sewage sludge is its application to agricultural lands. During wastewater treatments, pollutants tend to be concentrated into sludge so it is important to evaluate the concentration of those pollutants to avoid negative effects to the environment. To control the quality of the sludge that is going to be applied to soil, the European Union (EU) published in 2000 the third draft of a future sludge Directive entitled “Working Document on Sludge” where concentration limit values for some organic compounds (AOX, DEHP, LAS, NPE, PAH, PCB and PCDD/F) are fixed. The implementation of the future Directive could imply the application of post-treatment processes to sludge to reduce the concentration levels of the organic pollutants to levels that enable safe application of sewage sludge as soil fertilizer. Several authors have reported concentration levels of the above cited pollutants in anaerobic and aerobic treatment plants. However, there is no much information about concentration levels in lagoon sludge from anaerobic wastewater stabilization ponds which are the most common wastewater treatments applied in small communities with equivalent inhabitants in the range up to 10,000. In the present work, concentration levels of several of the organic compounds included in the EU directive draft have been measured in sewage sludge samples from three wastewater stabilization ponds operating in small communities located in the south of Spain. Organic compounds measured were di-(2-ethylhexyl)phthalate (DEHP), sum of nonylphenol and nonylphenol ethoxylates with 1 and 2 ethoxy groups (NPEs), linear alkylbenzene sulphonates (LAS), sum of nine polycyclic aromatic hydrocarbons (PAHs) and sum of seven polychlorinated byphenyls (PCBs). Sludge applicability to soil, in relation with the limit values fixed in the EU sludge directive draft, has been evaluated. The highest concentration levels were found for LAS (mean value 5373 mg/kg dry matter), NPE (mean value 177.1 mg/kg dry matter) and DEHP (mean value 72.3 mg/kg dry matter), in this order. PAHs were detected at lower concentration levels (concentrations lower than 0.80 mg/kg dry matter) whereas no PCB was detected in the analyzed samples.

Keywords: Organic pollutant; Sewage sludge; Working document on sludge; Wastewater stabilization ponds

1. Introduction

The quantity of sewage sludge generated from wastewater treatment plants has considerably increased in the last years due to the increase of wastewater treatment processes. One of the main disposal options of the generated sludge is its use as a fertilizer in soils being this option the most often application in countries as Spain. Nevertheless, sewage sludge can provide to soils not only organic matter and nutrients [1–3] but also pollutants

* Corresponding author.

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which tend to be concentrated into sludge during wastewater treatment [4,5]. Some of these pollutants are heavy metals, pesticides, industrial solvents, dyes, plasticizers, surfactants and many other complex organic molecules. To control the quality of sewage sludge that it is going to be applied to soils, the European Union (EU) published in 2000 the third draft of a future sludge directive entitled "Working Document on Sludge" [6]. This text, which complements the European Directive 86/278/CEE [7], promotes the use of sludge on soils as fertilizer and establishes conditions and limit values of concentration of heavy metals and organic compounds for land application of sludge. The organic compounds that will have to be monitored according to the EU Directive draft are the sum of halogenated organic compounds (AOX), linear alkylbenzene sulphonates (LAS), di(2-ethylhexyl) phthalate (DEHP), nonylphenol and nonylphenol ethoxylates with 1 or 2 ethoxy groups (NPEs), the sum of nine polycyclic aromatic hydrocarbons (PAHs), the sum of seven polychlorinated biphenyls congeners (PCBs) and polychlorinated dibenzodioxins (PCCDs) and dibenzofuranes (PCDFs). Concentration limits fixed in the directive draft for land application of sludge are 500 mg/kg dry matter (dm), 2600 mg/kg dm, 100 mg/kg dm, 50 mg/kg dm, 6 mg/kg dm and 0.8 mg/kg dm for AOX, LAS, DEHP, NPE, sum of nine PAH congeners and sum of seven PCB congeners, respectively, and 100 ng TE/kg dm for PCDD/PCDF.

The implementation of the future sludge Directive could have serious implications in wastewater treatment plant management because post-treatment processes will have to be applied to sludge in order to reduce organic pollutants to concentration levels that enable its use as fertilizer in soils. This fact will be even more significant in small communities with equivalent inhabitants in the range up to 10,000 where low-cost treatments are needed. The number of towns with low equivalent inhabitants is extremely in high in some countries. For example, in Andalusia region (south of Spain), the 85% of the towns have less than 2000 inhabitants [8]. In such communities, wastewater treatments use to be based on wastewater stabilization ponds (WSPs) because of their low cost and low energy consumption. The increase of the cost associated to desludge, disposal, transport and treatment of the sludge to reduce the content of organic pollutants could be not affordable by those small communities. At present, there is some information available in literature about the concentration levels of the organic pollutants in wastewater treatment plants based on anaerobic or aerobic digestion of sludge which treat wastewater from big cities. Nevertheless, there is a lack of information about the concentration levels of these organic pollutants in lagoon sludge from WSPs.

In this paper, two developed and validated methods have been applied to the monitorization of DEHP, NPEs, LAS, PAHs and PCBs in lagoon sludge samples from three anaerobic WSPs located in Cádiz (south of Spain). From the concentration levels measured, the applicability of lagoon sludge to agriculture in relation with the limit values fixed in the EU sludge directive draft has been evaluated.

2. Experimental

2.1. Wastewater stabilization ponds and sampling

Sludge samples were collected from three anaerobic WSPs sited in Cádiz (south of Spain) which treated wastewater from small communities. Samples were obtained by mixing aliquots collected from four sampling sites at the bottom of each WSP. Samples were stored in glass bottles and frozen after collection. Before analysis they were lyophilized and sieved (particle size <100 mm). Characteristics of the analyzed sludge samples are shown in Table 1.

Table 1
Characterization parameters of the analyzed lagoon sludge samples

Characterization parameter	Range	Mean value	RSD (%)
pH	5.9–7.9	6.9	14.5
Water content (%)	91.8–99.6	95.7	4.07
Organic matter content (%)	38.3–49.5	42.3	14.8
Total Kjeldahl nitrogen (%)	1.6–2.4	2.1	21.7
Total phosphorous (%)	0.7–1.6	1.0	52.0
Potassium (%)	0.2–0.8	0.5	57.3
Ammonium (mg/kg)	6495–9102	8020	16.9

2.2. Chemicals and reagents

Commercial LAS mixture [C_{10} (12.3%), C_{11} (32.1%), C_{12} (30.8%) and C_{13} (23.4%)] was supplied by Petroquímica Española (PETRESA). DEHP and nonylphenol technical grade Pestanal® were obtained from Riedel-de-Haën (Seelze, Germany), nonylphenol mono- and diethoxylated technical mixture Igepal® CO-210 was obtained from Aldrich (Milwaukee, WI, USA). A standard mixture of the 16 EPA PAH (naphthalene, acenaphthylene, acenaphthene, fluorene, 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) at a concentration of 500 µg/mL in acetonitrile/toluene/hexane (6:3:1; v/v/v) was purchased from Hewlett-Packard (Waldbronn, Germany).A PCB congener mix (PCB 28, 52, 101, 118, 138, 153 and 180, 10 µg/mL of each component in cyclohexane) was obtained from Dr. Ehrenstorfer (Augsburg, Germany).

2.3. Analytical determination

DEHP, NPEs and PCBs were simultaneously extracted from sewage sludge with n-hexane by sonication-assisted extraction and simultaneously determined by gas chromatography-mass spectrometry according to a previously reported method [9].

LAS and PAHs were simultaneously extracted from sewage sludge with methanol by sonication-assisted extraction, extracts were cleaned up by solid phase extraction and LAS and PAH were separately determined by high performance liquid chromatography with ultraviolet and fluorescence diode array detectors according to Santos et al. [10]. Limits of detection (LODs), limits of quantification (LOQs) and recoveries of each compound are summarized in Table 2.

3. Results and discussion

Concentration ranges of each organic compound are summarized in Table 3. Concentration levels of DEHP, sum of NP, NP1EO and NP2EO, sum of LAS C10, C11, C_{12} and C_{13} and sum of the nine PAH congeners regulated in the EU sludge directive draft are represented in Fig. 1 as boxplots. No boxplot is show for PCB because no PCB was detected in the measured samples. Each box shows the lower (≦25%), median (≦50%) and upper quartile (≦75%). Lines from each box show maximum

Table 2
Limits of detection (LOD), limits of quantification (LOQs) and recoveries from sewage sludge of DEHP, NPEs, LAS, PAHs and PCBs

Compound	LOD (mg/kg dm)	LOQ (mg/kg dm)	Recovery (%)
DEHP	0.02	0.07	105
NPE			
NP	0.19	0.63	77.9
NP1EO	0.75	2.50	88.6
NP2EO	0.42	1.40	61.4
LAS			
C10	3	8	85
C11	9	15	80
C12	9	18	84
C13	2	5	97
PAH			
Naphthalene	0.029	0.092	90
Acenaphthylene	0.093	0.160	76
Acenaphthene + fluorene	0.004	0.010	72
Phenanthrene	0.005	0.010	99
Anthracene	0.001	0.002	70
Fluoranthene	0.004	0.012	68
Pyrene	0.078	0.029	75
Benzo[a]anthracene	0.006	0.021	93
Chrysene	0.0002	0.001	91
Benzo[b]fluoranthene	0.001	0.002	84
Benzo[k]fluoranthene	0.002	0.008	55
Benzo[a]pyrene	0.024	0.040	50
Dibenzo[a,h]anthracene	0.011	0.036	82
Benzo[ghi]perylene	0.045	0.150	87
Indeno[1,2,3-cd]pyrene	0.029	0.092	51
PCB			
PCB 28	0.002	0.006	91.7
PCB 52	0.002	0.005	80.2
PCB 101	0.003	0.010	85.6
PCB 118	0.002	0.007	91.9
PCB 138	0.002	0.006	108
PCB 153	0.002	0.007	105
PCB 180	0.003	0.011	55.8

Table 3
Concentration levels of DEHP, NPEs, LAS, PAHs and PCBs in sewage sludge from anaerobic wastewater stabilization ponds

Compound	Range (mg/kg dm)	Mean (mg/kg dm)	RSD (%)
DEHP	25.0–145	72.3	51.1
NPE			
NP	33.0–199	103	61.4
NP1EO	13.0–145	59.0	50.0
NP2EO	<LOD–30	15.1	13.1
LAS			
C10	<LOD–602	200	57.0
C11	<LOD–3563	1164	59.7
C12	<LOD–5902	1954	61.5
C13	<LOD–5948	2055	62.9
PAH			
Naphthalene	<LOD–0.185	0.057	132
Acenaphthylene	<LOD	<LOD	—
Acenaphthene + fluorene	<LOD–0.024	0.008	156
Phenanthrene	<LOD–0.266	0.168	55.0
Anthracene	<LOD–0.055	0.009	245
Fluoranthene	<LOD–0.204	0.114	74
Pyrene	<LOD	<LOD	—
Benzo[a]anthracene	<LOD–0.491	0.120	168
Chrysene	<LOD–0.177	0.041	173
Benzo[b]fluoranthene	<LOD–0.035	0.006	230
Benzo[k]fluoranthene	<LOD	<LOD	—
Benzo[a]pyrene	<LOD	<LOD	—
Dibenzo[a,h]anthracene	<LOD	<LOD	—
Benzo[ghi]perylene	<LOD	<LOD	—
Indeno[1,2,3-cd]pyrene	<LOD	<LOD	—
PCB			
PCB 28	<LOD	<LOD	—
PCB 52	<LOD	<LOD	—
PCB 101	<LOD	<LOD	—
PCB 118	<LOD	<LOD	—
PCB 138	<LOD	<LOD	—
PCB 153	<LOD	<LOD	—
PCB 180	<LOD	<LOD	—

and minimum concentration values. The most contaminated sludge samples were obtained from WSP3. This fact could be explained by the high industrial activity in this area, mainly based on textile industry.

3.1. DEHP

DEHP was found in all of the analyzed samples at concentrations in the range of 25.0–145 mg/kg dm, mean concentration 72.3 mg/kg dm (Table 3). The 34% of the analyzed lagoon sludge samples contained concentration levels of DEHP higher than the limit value fixed in the EU directive draft (100 mg/kg dm).

There is no much information in literature about concentration levels of DEHP in lagoon sludge. Amir et al. reported concentration levels of DEHP of 28.67 mg/kg dm in lagoon sludge samples from an anaerobic lagoon of an experimental treatment plant in the Marrakech city (Morocco) [11]. The reason of the low concentration level measured was explained because of the low industrial activities of the country. Concentration levels measured were similar to those reported in other kind of WWTPs as for example, WWTPs with anaerobic digestion of sludge [12,13] or with aerobic digestion of sludge [5,13].

3.2. NPEs

NP and NP1EO were detected in all of the analyzed samples. NP was present at the highest concentration levels (mean concentration 103 mg/kg dm) followed by

NP1EO and NP2EO, in this order (mean concentrations of 59.0 and 15.1 mg/kg dm, respectively) (Table 3). The higher concentration of NP compared with the concentrations of NP1EO and NP2EO, could be explained by the formation of NP as a degradation product from nonylphenolic compounds under the anaerobic conditions in WSPs [14]. NPEs (sum of NP, NP1EO and NP2EO) were in the concentration range from 61.4 to 82.0 mg/kg dm what implies that NPE concentration was higher than the limit value of 50 mg/kg dm fixed in the EU directive draft in the all of the analyzed samples (Fig. 1).

No information has been found in literature about the concentration levels of NPEs in lagoon sludge samples. Concentration levels are in concordance with those reported by other authors in WWTPs based on activated sludge processes [15,16] and with those reported in anaerobically-digested and thermal-dried sludge samples from WWTPs operating in France [17], Spain [5] and Greece [18] with served population and industrial discharges higher than those corresponding to the WSPs evaluated in this paper.

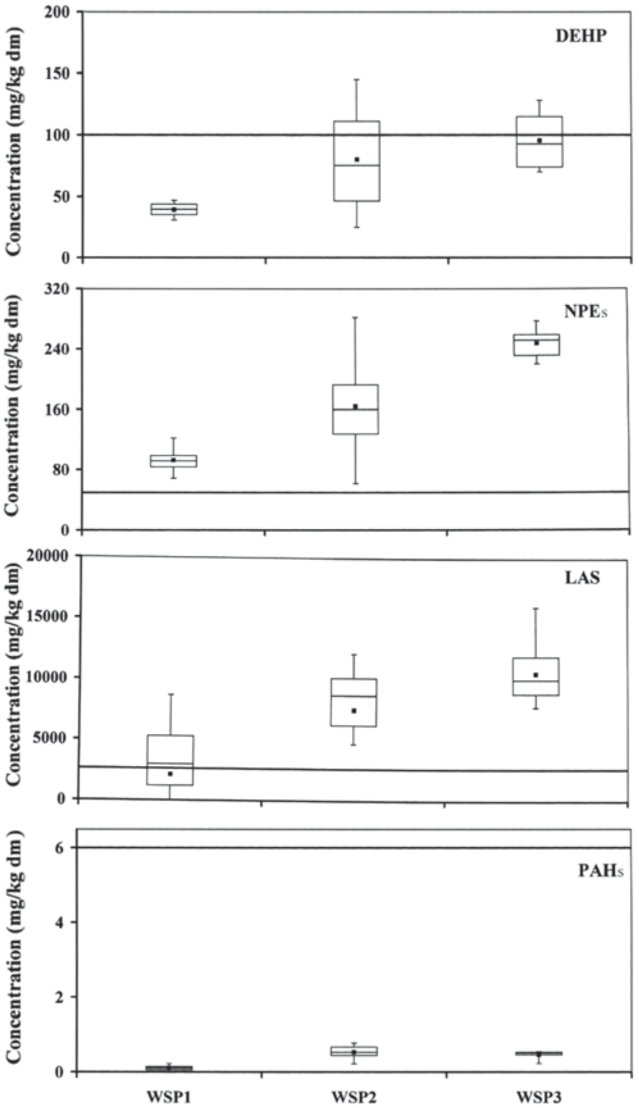

Fig. 1. Box and whisker plots of DEHP, NPE, LAS and PAH concentrations in the analyzed lagoon sludge samples. Horizontal lines show concentration limit values fixed in the EU directive draft for land application of sludge [6].

3.3. LAS

LAS were the organic pollutants present at the highest concentration levels in the analyzed sludge samples (Table 3). LAS congeners were not detected in some of the analyzed samples whereas in others concentration levels up to 16015 mg/kg dm were measured (Fig. 1). These high concentration levels could be associated to the poor degradation of these compounds under anaerobic conditions [15,19]. 83% of the analyzed lagoon sludge samples contained concentration levels of LAS higher than the limit value of 2600 mg/kg dm fixed in the EU sludge directive draft.

No data was found in literature about concentration levels of LAS in lagoon sludge samples. Concentration levels measured are similar to those reported by other authors in sludge samples from WWTPs with anaerobic digestion of sludge from England [20] and Spain [21].

3.4. PAHs

Some of the PAH included in the Third Draft of the future sludge Directive, benzo[a]pyrene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene and others as acenaphthylene, pyrene, dibenzo[a,h]anthracene and benzo [g,h,i]perylene, were not detected in the lagoon sludge samples measured (Table 3). Total PAH concentration, expressed as the sum of acenaphthene, phenanthrene, fluorene, fluoranthene, pyrene, benzo[b]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene was below the limit of detection of the method in some samples and up to 0.78 mg/kg dm in others what implies that PAH total concentration was lower than the limit value of 0.8 mg/kg dm fixed in the EU directive draft in the all of the analyzed samples (Fig. 1).

No information was found in literature about the concentration levels of PAHs in lagoon sludge. Concentration levels measured were lower than those reported by other authors in sludge samples from WWTPs with anaerobic digestion of sludge from Spain [5,22,23], France [24] and Italy [25].

3.5. PCBs

No PCB congener was detected in the lagoon samples analyzed (Table 3). This fact can be explained because PCBs are compounds widely related to industrial activity what is not usual in the small communities evaluated.

4. Conclusions

The organic pollutants DEHP, NPE, LAS and PAH were detected in the lagoon sludge samples analyzed while no PCB congener was detected. The compounds at the highest concentration levels were LAS, NPEs and DEHP, in this order. NPEs, LAS and DEHP concentrations were above the limit fixed in the EU directive draft in the 100%, 83% and 34% of the analyzed samples whereas PAHs and PCBs were always at concentration levels lower than their concentration limit. These results show the need of several technological changes in sludge management in small communities to reduce the concentration of the organic pollutants to levels that allow land application of sewage sludge according to the future EU Directive. This fact can be of major importance in small communities because the cost associated to sludge treatments could be no affordable in such communities.

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