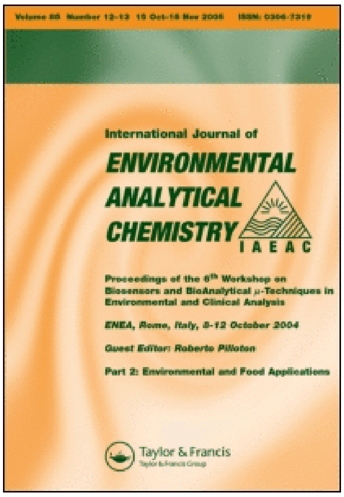

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Monitoring of di-(2-ethylhexyl)phthalate, nonylphenol, nonylphenol ethoxylates, and polychlorinated biphenyls in anaerobic and aerobic sewage sludge by gas chromatography-mass spectrometry

Juan L. Santos[a]; María Del Mar González[a]; Irene Aparicio[a]; Esteban Alonso[a]
[a] Department of Analytical Chemistry, University of Sevilla, E-41011 Sevilla, Spain

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Monitoring of di-(2-ethylhexyl)phthalate, nonylphenol, nonylphenol ethoxylates, and polychlorinated biphenyls in anaerobic and aerobic sewage sludge by gas chromatography–mass spectrometry

JUAN L. SANTOS, MARÍA DEL MAR GONZÁLEZ,
IRENE APARICIO and ESTEBAN ALONSO*

Department of Analytical Chemistry, University of Sevilla,
C/Virgen de África 7, E-41011 Sevilla, Spain

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The occurrence of di-(2-ethyhexyl)phthalate (DEHP), nonylphenol and nonyphenol mono- and diethoxylates (NPEs) and seven polychlorinated biphenyl (PCB) congeners in different types of sludge samples is reported. The analysis of these compounds was carried out by sonication-assisted extraction and analytical determination by gas chromatography coupled with a mass spectrometry detector, following a previously described method. The applicability of the method was tested by monitoring the organic pollutants in primary, secondary, mixed, and digested-dehydrated sludge samples from two wastewater treatment plants (WWTPs) based on aerobic and on anaerobic biological stabilization. The occurrence of these compounds in sewage sludge and the influence of sludge stabilization process on the further farmland application of the sludge were evaluated. DEHP and NPEs were detected in all analysed sludge samples from both WWTPs at concentration levels in the range of 22.3–601 $\mathrm{mg\,kg^{-1}}$ and 136–2357 $\mathrm{mg\,kg^{-1}}$ dm (dry matter), respectively. PCBs were detected in all types of sludge analysed from the anaerobic WWTP but was not detected in any sludge sample from the aerobic WWTP. Concentration levels of the sum of the seven PCBs congeners were up to 1.5 $\mathrm{mg\,kg^{-1}}$ dm. The concentration of DEHP, sum of NPEs, and sum of the seven PCB congeners were higher than the limits fixed in the third draft of the future Sludge Directive for land application of sludge in the 67%, 100%, and 11% of samples from the anaerobic WWTP and in the 83%, 92%, and 0% of samples from the aerobic WWTP, respectively.

Keywords: DEHP; NPEs; PCBs; Sludge; Anaerobic and aerobic digestion

1. Introduction

In recent years, the implementation of the Directives 91/271/EEC [1] and 98/15/EEC [2] concerning urban wastewater treatment has increased the number of wastewater treatment plants (WWTPs) operating in the European Union. This fact has led, in most countries, to an increase in the production of sewage sludge. Nowadays, the three most common final destinations of sludge are incineration, landfills, and agricultural use [3]

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*Corresponding author. Fax: +34-9-5428-2777. Email: ealonso@us.es

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with the application of sewage sludge to farmland usually being the cheapest sludge disposal option. However, as sewage sludge is a by-product of wastewater treatment, it inevitably contains a wide range of potential contaminants, including nutrients, metals, pathogens, and organic chemical residues [4]. Consequently, high concentrations of several xenobiotic compounds have been reported to be present in sludge [5, 6]. In the European Directive 86/278/EEC [7], limit values of the total amount of several heavy metals are established for sludge land application depending on the soil's pH. In 2000, the European Union published the third draft of a future sludge Directive entitled 'Working Document on Sludge' [8] where more restricted concentration limit values of heavy metals are fixed and where concentration limit values of some organic compounds are included for the first time. Some of the organic compounds included in this document are di-(2-ethylhexyl) phthalate (DEHP), nonylphenol and nonylphenol ethoxylates with one or two ethoxy groups (NPEs), and polychlorinated biphenyl (PCBs) congener numbers 28, 52, 101, 118, 138, 153, and 180. The concentration limits established in sludge dry matter (dm) for land application of sludge are $100\,\mathrm{mg\,kg^{-1}}$ for DEHP, $50\,\mathrm{mg\,kg^{-1}}$ for the sum of nonylphenol and nonylphenolethoxylates, and $0.8\,\mathrm{mg\,kg^{-1}}$ for the sum of the seven PCBs congeners.

DEHP is the most common of the phthalates esters, extensively used as a plasticizer in polyvinylchloride (PVC) and as additive in various other daily products [9]. NPEs are degradation products of non-ionic alkylphenol polyethoxylates surfactants, which are widely used in detergents owing to their rapid biodegradability [5]. PCBs are a family of 209 congeners based on the biphenyl molecule and a different rate of chlorination and positioning of the chlorine atoms with a pronounced persistence against chemical and biological degradation [10, 11]. Their high persistence in the environment and high toxicological risks to wildlife caused their withdrawal from commercial production in Europe during the 1980s and 1990s. Nowadays, the main source of emissions of PCBs, 90% of emissions, is volatilization from soil [12].

Sludges destined for land applications normally require stabilization before use to control the accumulation of chemicals, odours, and microbes. The most common methods for sludge stabilization are aerobic and anaerobic biological digestion. Aerobic digestion is based on biological decomposition and stabilization of organic substances in the presence of oxygen, while anaerobic digestion consists in the biological degradation of the organic matter under anoxic conditions. After stabilization, digested sludge is usually dehydrated or/and composted. Anaerobic digestion is the treatment applied in most of the WWTPs [13] as a low-organic loaded effluent is achieved with an acceptable economic cost.

To test the suitability of anaerobically and aerobically digested sewage sludge for land application of sludge according to the future Sludge Directive, simple, reliable, and fast analytical methods are needed. However, there is still a general lack of accepted and validated analytical methods for the analysis of most kind of organic chemicals in sewage sludge and a lack of background or survey data of their occurrence [14–16]. A few analytical methods have been reported for the determination of these compounds in sewage sludge, separately or simultaneously with other compounds, but only two methods have been found in the literature for their simultaneous determination in sewage sludge [5, 17].

In this article, a previously developed and validated method [17] has been applied for routine monitoring of DEHP, NPEs and PCBs in primary, secondary, mixed and digested-dehydrated sludge samples from two WWTPs, one based on aerobic biological stabilization of sludge and another based on anaerobic stabilization to test the applicability of the method to the analysis of these pollutant in different types of sludge. The analytical method applied is based on sonication-assisted sample extraction and further analytical determination by gas chromatography coupled to mass spectrometry. The influence of the aerobic and anaerobic treatments of sludge in the elimination of DEHP, NPEs and PCBs has been evaluated and related to the application of sewage sludge to farmland according to the third draft of the future European Sludge Directive [8].

2. Experimental

2.1 *Chemicals and reagents*

DEHP, a PCB 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 an internal standard (IS), were obtained from Dr Ehrenstorfer (Augsburg, Germany). Nonylphenol technical grade Pestanal® was obtained from Riedel-de-Haën (Seelze, Germany), and nonylphenol mono- and diethoxylated technical mixture Igepal® CO-210 was obtained from Aldrich (Milwaukee, WI). *n*-Hexane was purchased from Romil Ltd (Barcelona). Working solutions of all compounds were prepared by diluting the stock standard solutions in *n*-hexane. The concentration of the internal standard in the calibration solutions was 1.0 μg mL^{-1}.

2.2 *Analytical procedure*

The analytical procedure was based on a previously reported validated method for the simultaneous determination of DEHP, NPEs, and PCBs in WWTP sewage sludge [17]. Quantification was carried out by the internal standard method. The recoveries and limits of detection (LOD) of the applied analytical method are summarized in table 1.

Table 1. Some characteristics of the method applied to DEHP, NPEs, and PCBs determination in sewage sludge [17].

Compound (mg kg^{-1} dm)	Ions monitored (*m*/*z*)	Retention time (min)	LOD	Recovery (%)
DEHP	149[a], 162, 167	29.60	0.020	105.4 ± 8.3
NPEs				
NP	107, 121, 135[a], 149	12.28	0.189	77.9 ± 9.9
NP1EO	135, 165, 179[a], 193	18.83	0.751	88.6 ± 7.2
NP2EO	223[a]	26.42	0.421	61.4 ± 9.1
PCBs				
PCB 28	186, 256[a], 258, 260	16.05	0.002	91.7 ± 7.3
PCB 52	220, 290, 292[a], 294	17.85	0.002	80.2 ± 9.4
PCB 101	254, 256, 326[a], 328	22.55	0.003	85.6 ± 7.1
PCB 118	254, 324, 326[a], 328	25.27	0.002	91.9 ± 8.9
PCB 138	288, 290, 360[a], 362	27.07	0.002	108.3 ± 7.8
PCB 153	288, 290, 360[a], 362	26.13	0.002	105.3 ± 5.6
PCB 180	162, 324[a], 394, 396	29.13	0.003	55.8 ± 6.8

[a] Ion used for quantification.

2.2.1 Sample treatment. Dried sludge (0.5 g) was extracted with hexane by sonication-assisted extraction and finally diluted to 5 mL, as described in the previously reported method [17].

2.2.2 Gas chromatography–mass spectrometry. Analytical determination was performed on an Agilent 6890N gas chromatograph coupled to an Agilent 5973N mass spectrometer and equipped with an Agilent 7683 autosampler and a programmed temperature vaporizer injector. Separations were carried out using an Agilent HP-5ms column (30 m × 0.25 mm i.d. × 0.25 µm film thickness, 5%-phenyl-methylpolysiloxane). The operational conditions used were those reported previously [17]. The ions monitored and retention times of each of the analysed pollutants are shown in table 1.

2.2.3 Sewage treatment plants and sampling. Anaerobically and aerobically digested sludge grab samples were collected from two WWTPs located in the south of Spain, one based on anaerobic stabilization (AnWWTP) and the other based on aerobic stabilization (AeWWTP). AnWWTP is sited in Jerez de la Frontera (Cádiz, Spain) and has a population equivalent (measure of pollution representing the average organic biodegradable load per person per day) of 100, 000 inhabitants. AeWWTP is situated in Chiclana de la Frontera (Cádiz, Spain) and has a population equivalent of 35,000 inhabitants. Wastewater treatment in both WWTPs includes primary treatment based on settling and flotation and secondary treatment based on biological treatment with activated sludge. Then, the primary and secondary sludge are combined (mixed sludge) and digested anaerobically (AnWWTP) or aerobically (AeWWTP). Finally, in both WWTPs, the digested sludge is chemically conditioned and dehydrated.

For AnWWTP, primary, secondary, and dehydrated digested sludge samples were collected, and for AeWWTP, mixed and dehydrated digested sludge samples were collected. A sample of each kind of sludge was collected monthly from March to August 2006. Samples were stored in glass bottles and kept frozen until processing. To avoid any contamination of samples with DEHP during sampling and sample processing [3], no plastic equipment was used, and all glassware was washed prior to use with solvents used in sample treatment and then dried at 130°C.

3. Results and discussion

3.1 *Applicability of the analytical method*

No significant interference from matrix components was observed for the determination of DEHP, NPEs, and PCBs in the types of sewage sludge evaluated at the concentration levels of the organic pollutants in sewage sludge. In figures 1 and 2, GC/MS total ion chromatograms of anaerobically digested sludge and aerobically digested sludge samples, respectively, are shown. Lower abundances of matrix constituents were observed in chromatograms from anaerobic sludge samples compared with chromatograms from aerobic sludge samples. The lower presence of matrix constituents in anaerobic sludge samples is due to the higher degradation of more (non-polar) organic

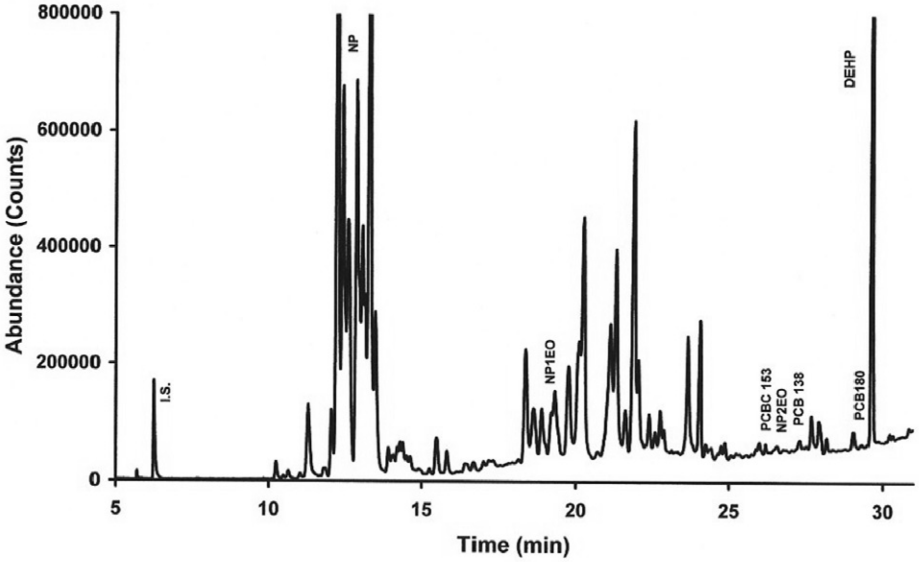

Figure 1. GC/MS total ion chromatogram of an anaerobically digested sludge sample.

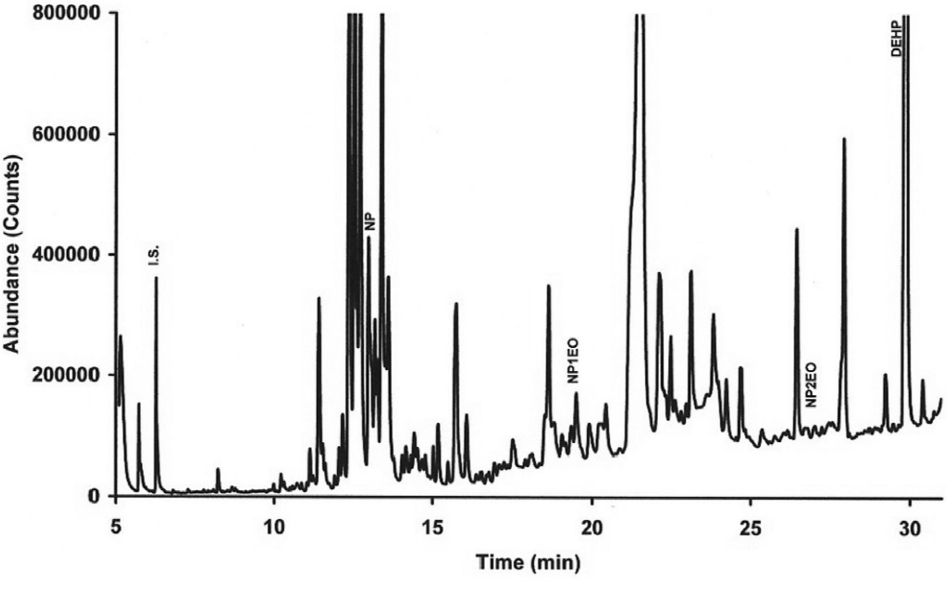

Figure 2. GC/MS total ion chromatogram of an aerobically digested sludge sample.

chemicals under anaerobic stabilization, and so the chromatogram is less loaded than the chromatogram from aerobic sludge samples.

The low limits of detection of PCBs compared with limits of detection of DEHP and NPEs should be mentioned, a finding also described by Gibson *et al.* [4] in a similar sludge. This could be due to a low degree of matrix interference in PCBs determination.

3.2 *Concentration levels of the monitored pollutants in the evaluated WWTPs*

Table 2 shows the range of concentrations of the organic pollutants in each type of sludge analysed. Most of the compounds were in higher concentrations in sewage sludge from AnWWTP than in sewage sludge from AeWWTP mainly due to the different influent wastewater in each WWTP. The concentration of the compounds in each type of sludge depends on the concentration of the compound in the influent wastewater, the degradation of the compound during sludge treatments, mainly after aerobic digestion, and the enrichment factor achieved during stabilization processes due to the decrease in sludge weight. In the AnWWTP, in general, the highest concentrations were achieved in digested-dehydrated sludge, then in primary sludge, and finally in secondary sludge. In the AeWWTP, the highest concentrations were achieved in digested-dehydrated sludge. The enrichment factor achieved after the stabilization processes depends not only on the loss of weight of sludge but also on the degradation of the organic pollutant during the stabilization treatment.

3.2.1 DEHP. DEHP was found in all sludge samples analysed (table 2). The concentrations in most of the samples were somewhat higher than the limit value of 100 mg kg^{-1} dm fixed in the third draft of the future EU Sludge Directive [8] (figure 3). The concentrations, in most of the samples analysed, were in the range previously reported by other authors in Catalonia (Spain) in 2000 (180–267 mg kg^{-1}) [18] and during 2001–2003 (2–258 mg kg^{-1}) [5] and in the Valencian Community (Spain) during 2002–2003 (8–350 mg kg^{-1}) [19].

The concentration of DEHP was higher than the limit value specified in the draft of the future EU sludge directive in 100%, 33%, and 67% of primary, secondary, and digested-dehydrated sludge samples, respectively, from AnWWTP and in 83% of both mixed and digested-dehydrated sludge samples from AeWWTP. In AnWWTP, the mean concentrations in primary, secondary, and anaerobically digested and dehydrated

Table 2. Concentrations of DEHP, NPEs, and PCBs in primary (P), secondary (S), mixed (M), and digested-dehydrated (D) sludge samples from anaerobic and aerobic WWTPs in Cádiz (Spain).

	AnWWTP (mg kg^{-1} dm)			AeWWTP (mg kg^{-1} dm)	
Compound	P ($n=6$)	S ($n=6$)	D ($n=6$)	M ($n=6$)	D ($n=6$)
DEHP	227−554	22.3−553	59.8−280	44.0−409	95.2−601
NP	185−777	52.9−611	816−1385	12.9−745	9.6−1041
NP1EO	342−1250	284−1129	232−640	13.8−125	20.3−106
NP2EO	39.9−829	89.4−1375	35.6−331	< LOD[a]−102	< LOD−130
ΣNPEs[b]	759−2319	529−2457	1083−2357	158−837	136−1278
PCB 28	< LOD	< LOD	< LOD	< LOD	< LOD
PCB 52	< LOD	< LOD	< LOD	< LOD	< LOD
PCB 101	< LOD	< LOD	< LOD	< LOD	< LOD
PCB 118	< LOD	< LOD	< LOD	< LOD	< LOD
PCB 138	< LOD−0.2	< LOD−0.2	< LOD−0.3	< LOD	< LOD
PCB 153	< LOD−0.2	< LOD−0.2	< LOD−0.7	< LOD	< LOD
PCB 180	< LOD−0.1	< LOD−0.1	0.1−0.5	< LOD	< LOD
ΣPCBs[c]	0.1−0.5	< LOD−0.4	0.3−1.5	< LOD	< LOD

[a] < LOD: concentration below the limit of detection of the method.
[b] Sum concentration of NP, NP1EO, and NP2EO.
[c] Sum concentration of the seven PCB congeners.

sludge were 332, 169, and 142 mg kg^{-1} dm, respectively. In AeWWTP, the mean concentrations in mixed and aerobically digested and dehydrated sludge were 228 and 283 mg kg^{-1} dm, respectively. The reduction in the content of DEHP from primary sludge to secondary sludge in about 50% can be explained by the high retention

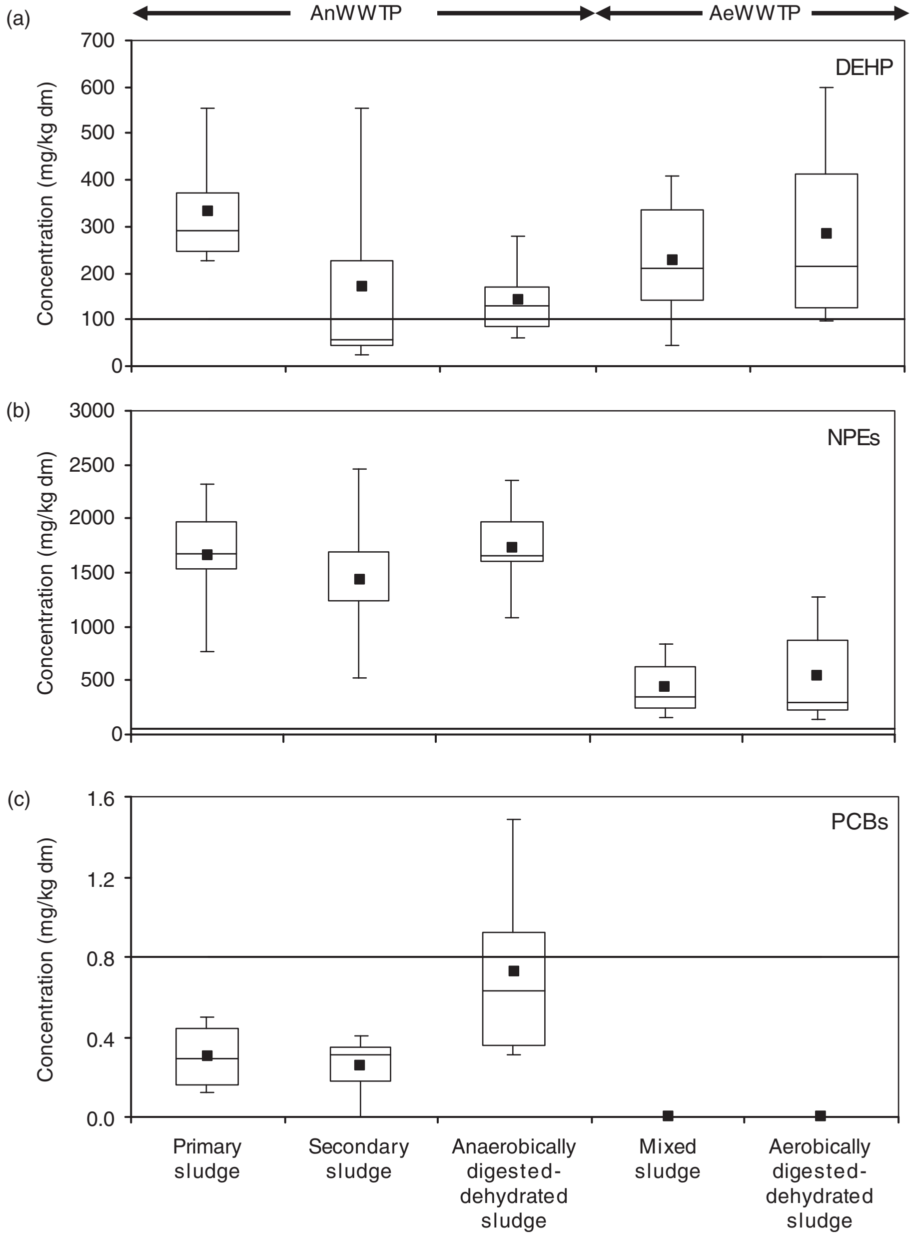

Figure 3. Box-and-whisker plots of DEHP, NPEs, and PCBs concentrations in primary, secondary, and anaerobically digested sludge samples from AnWWTP and in mixed and aerobically digested sludge samples from AeWWTP. Horizontal lines show limit concentration of each compound fixed in the third draft of the future EU Sludge Directive [8].

capacity of this compound onto particle matter during primary settlement of sludge, so it is mainly eliminated by retention on primary sludge [13]. Moreover, a high biodegradation of DEHP in the activated sludge process [20] where secondary sludge is obtained explains the reduction in DEHP concentration from primary sludge to secondary sludge. Then, DEHP is degraded under anaerobic digestion as previously observed by other authors [13, 21]. Its further degradation during biological digestion depends on its bioavailability that is limited by the transfer of DEHP within the solid matter [13].

3.2.2 NP, NP1EO, and NP2EO. NP and NP1EO were found in all sludge samples analysed (table 2). NP2EO was found in all samples from AnWWTP and in one mixed sludge sample and three aerobically digested sludge samples from AeWWTP. Concentration values were in the range previously reported by other authors in New York (USA) during 1997–2000 (1100–1800 mg kg^{-1}) [22], Catalonia (Spain) during 2001–2003 (14–3150 mg kg^{-1}) [5], and the Valencian Community (Spain) during 2002–2003 (190–3500 mg kg^{-1}) [19]. The concentration of the sum of NP, NP1EO, and NP2EO was considerably higher than the limit value of 50 mg kg^{-1} dm fixed in the third draft of the future European Sludge Directive in all samples analysed (figure 3).

It has been reported that under anaerobic conditions, NP2EO is degraded to NP1EO, and NP1EO is degraded to NP [23, 24]. This fact explains the decrease in concentrations for NP1EO and NP2EO from primary and secondary sludge to anaerobically digested sludge (figure 4a) and the high concentration of NP in anaerobically digested sludge compared with the concentrations in primary and secondary sludge samples.

Under aerobic conditions, besides the transformation of NP2EO into NP1EO and NP1EO into NP, the formation of nonylphenoxy acetic acids occurs. The nonylphenoxy acetic acids are finally decomposed to nonylphenol carboxylate [24], which could explain the smaller increase in the concentration of NP observed after the aerobic digestion (figure 4b) compared with that obtained after the anaerobic digestion (figure 4a), consistent with the study of Knudsen *et al.* [23].

3.2.3 PCBs. As can be seen in table 2, the concentrations of the PCB congeners 28, 52, 101, and 118 were below the limits of detection of the method in all sludge samples analysed. The concentration of PCBs in most of the samples analysed were in the range previously reported by other authors in Catalonia (Spain) during 2001–2003 (0.003–0.596 mg kg^{-1}) [5], in Thessaloniki (Greece) during 2001–2003 (0.12–1.00 mg kg^{-1}) [25], in the Valencian Community (Spain) during 2002–2003 (0.02–0.31 mg kg^{-1}) [19].

PCB congeners 138, 153, and 180 were detected in the 72%, 50%, and 83%, respectively, of the analysed samples from AnWWTP. The concentration of the sum of the seven PCB congeners was higher than the limit value specified in the directive draft in only two of the 30 samples analysed; both were digested-dehydrated sludge from AnWWTP (figure 3). No PCB congener was detected in sludge samples from AeWWTP (table 2). The different PCBs concentration in sewage sludge from each WWTP can be explained by a dramatic influence of the quality of influent wastewater and the performance characteristics of each system on the concentration of PCBs in sewage sludge [25]. Biodegradation of PCBs has been described to be dependent on their bioavailability that is limited by the strong sorption of PCBs onto sludge particles [26].

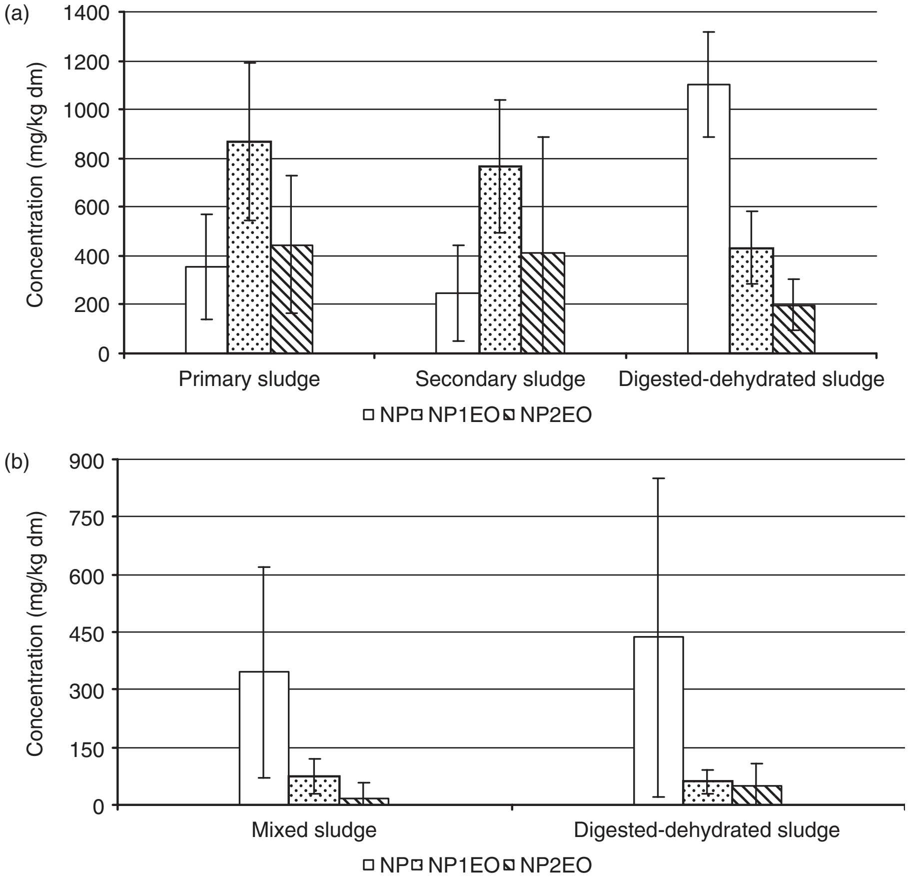

Figure 4. Mean concentrations and standard deviations of NP, NP1EO, and NP2EO in primary, secondary, and anaerobically digested sludge samples from AnWWTP (a) and in mixed and aerobically digested sludge samples from AeWWTP (b).

This sorption could explain the increase in PCBs concentration from primary and secondary sludge to digested sludge.

4. Conclusions

The applied method has been demonstrated to perform well for the intended use of routine quality control of anaerobically and aerobically digested sewage sludge according to the future European Union Sludge Directive of land application of sewage sludge.

In 73%, 100%, and 7% of the sludge samples analysed, the concentration levels of DEHP, NPEs, and PCBs, respectively, were above the limit proposed by the European Union for land application of sludge. Thus, post-treatment processes are necessary to reduce these concentrations to levels that enable the safe application of sewage sludge as a soil fertilizer.

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