

Article

Occurrence of Linear Alkylbenzene Sulfonates, Nonylphenol Ethoxylates and Di(2-ethylhexyl)phthalate in Composting Processes: Environmental Risks

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Abstract: Composting is an important waste management strategy, providing an economical and environment-friendly approach to sanitizing and stabilizing biosolids for land soil amendment. However, the resulting product can contain a large number of organic pollutants that may have adverse effects on the ecosystem. This paper presents the occurrence of eight widely used organic pollutants (four linear alkylbenzene sulfonates (LAS C10-C13), nonylphenol and its mono- and di-ethoxylates (NPE) and a di(2-ethylhexyl)phthalate (DEHP)) in full-scale composting processes. LAS homologues were detected at the highest concentrations (range of Σ LAS: 2068–9375 mg kg⁻¹ dm), exceeding the limit fixed in the EU Directive draft. The concentration levels of the NPE and DEHP were significantly lower (up to 27.5 and 156.8 mg kg⁻¹ dm, respectively) and did not exceed their fixed limits in the EU Directive draft. Ecotoxicological risk assessment for when compost is amended onto soils has also been evaluated. The concentrations measured represented a medium-low risk for most compounds, although it was not enough in the case of LAS C11 and C13 and NP.

Keywords: linear alkylbenzene sulfonate; nonylphenol ethoxylates; di(2-ethylhexyl)phthalate; occurrence; composting processes; risk assessment



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1. Introduction

Every year, a large amount of sewage sludge (\approx 15 million tons of sludge (dry matter [dm]) in the European Union (EU) 28) requiring disposal is produced as a result of wastewater treatments [1]. Approximately 40% of the produced sludge is used for agricultural purposes as a source of organic matter and nutrients. However, this percentage has large variations between the EU member states (from 0% in Malta or the Netherlands to more than 50% in countries like Spain or France) [1,2]. In Spain, particularly in the Andalusia region, this practice is even more pronounced (64%), since the decline in soil quality occurs due to loss of the organic fraction [1–3].

Sewage sludge is rich in nutrients such as nitrogen and phosphorus and contains valuable organic matter. Composting provides an economical and environment-friendly approach to sanitizing and stabilizing biosolids for land soil amendment and enrichment, since its agronomic value is increased as a result of fermentation and maturation [4]. However, one of the issues with this practice is the presence of a large number of organic pollutants that, even when present at low concentrations, may have adverse effects on the ecosystem and which may even be concentrated during the process. In the European Union, the application of sludge onto soil is regulated by Directive 86/278/CEE, which establishes a limit of 10 tons (Tn) of dry matter (dm) of treated sewage sludge per hectare and year. This directive sets limit values for seven heavy metals in sewage sludge used in agriculture. Currently, it is considered out of date and has been earmarked by the commission as a candidate for revision for around 10 years [3,5]. In 2000, the elaboration of the “3rd draft of the working document on sludge” set stricter limits on heavy metals and

also studied the possibility of analyzing some priority organic compounds such as linear alkyl sulfonates (LAS), nonylphenol (n)ethoxylates (NPE) and phthalates, among others, in sludge [6–9]. These compounds can enter the sewage system through both industrial and domestic sources. One of the most controversial aspects of the document is the question of which organic contaminants should be monitored and if limit values for these compounds in sludge should be set for land applications of sludge. There are no unanimous criteria for the classes of pollutants that must be controlled in sewage sludge or for limiting the concentrations that determine the applicability or lack thereof for these sludges with crop soils. Some limit values for the concentrations of these compounds in sewage sludge applied to the soil have been fixed in some particular countries, such as Denmark (DEHP, LAS, NPE and PAH), Sweden (NPE, PAH and PCBs) or Austria and Germany (PCBs and PCDD/F) [2].

The presence of these organic compounds at detectable amounts (from $\mu\text{g kg}^{-1}$ to mg kg^{-1} dm) in treated sewage sludge has led to concerns that land applications of biosolids may result in the accumulation of contaminants in the soil and their subsequent translocation through the food chain [10]. With this work, we wanted to reveal the necessity of introducing programs to monitor the presence of priority organic pollutants in sewage sludge and reduce the potential sources that may enter the environment. The aim of this work was to investigate the occurrence, removal and environmental risk assessment of eight priority organic pollutants (four LAS homologues (C10–C13), nonylphenol (NP) and its mono- and di-ethoxylates (NP1EO and NP2EO) and a di(2-ethylhexyl)phthalate (DEHP)) in two piles of sewage sludge along the composting process in a full-scale study.

2. Materials and Methods

2.1. Chemicals and Reagents

HPLC-grade acetone, acetonitrile, methanol and water were supplied by Romil Ltd. (Barcelona, Spain). Analytical grade formic acid and ammonium formate were obtained from Panreac (Barcelona, Spain).

A commercial LAS mixture containing C10 (12.3%), C11 (32.1%), C12 (30.8%) and C13 (23.4%) was obtained from Petroquímica Española (PETRESA). Technical-grade NP and DEHP were supplied by Riedel-de Haën (Seelze, Germany). The solutions, individual stock (1000 mg L^{-1}) and mixture (10 mg L^{-1}) were prepared in methanol and stored at $4 \text{ }^\circ\text{C}$.

Oasis MCX cartridges (60 mg) for solid phase extraction (SPE) were acquired from Waters (Milford, MA, USA).

2.2. Biosolid Samples

The composting process for two piles of biosolids (pile A and B) was carried out in dynamic full-scale batteries that were thermally controlled. Aeration was facilitated by mechanical turning. This composting system is the most widely used system. The material is piled up, mixed and turned periodically, thus avoiding compaction and delivering oxygen to the system. Each pile of biosolid was composted for 127 days. The two piles were equal and were measured to ensure the representativeness of the results. Eight samples of each composting pile were taken during the composting process: 3 during the dryness phase on days 0 (initial product), 10 and 21, 3 during the fermentation phase on days 37, 65 and 85 and 2 during the maturation phase on days 99 and 127 (final product). Each sample (1 kg) was composed of 5 aliquots of biosolids (using a gripping device) from different parts of the pile. Once in the lab, the samples were lyophilized (0.01-mbar vacuum after being frozen at $-18 \text{ }^\circ\text{C}$ for 24 h) and sieved ($<0.1 \text{ mm}$).

2.3. Determination of Sludge Characterization Parameters

The parameters measured to characterize the sludge samples were the pH, conductivity, soluble salts, nitrogen Kjeldahl (NK), crude protein, carbon (C), organic matter, C/N, Ca, Mg, total phosphorus (TP), extracted phosphorus (EP), total potassium (TK), extracted potassium (EK), moisture, temperature and heavy metals Pb, Fe, Mn, Ni, Cu, Cr, Cd, Zn, Co,

Al and Hg. Standard methods for wastewater analysis and standard techniques compiled by APHA-AWWA-WPCF were used [11].

2.4. Analysis of LAS, NPE and DEHP

LAS, NPE and DEHP were extracted by ultrasonic solvent extraction (USE) following a previously published method [12]. Aliquots of 2 g of biosolids were put in contact with two aliquots of acetone (3 mL) and one aliquot of methanol (3 mL) for each extraction step (10 min). The supernatants were separated by centrifugation (4000 rpm, 20 min), combined and cleaned up by SPE with Oasis MCX cartridges. The samples were passed through the SPE cartridges (previously conditioned) at a flow rate of 1 mL min⁻¹. Next, an aliquot of 5 mL of the cleaned extract was evaporated to dryness and reconstituted in 1 mL of a methanol:water mixture (1:1, *v/v*).

Analytical determination was performed on an Agilent 1200 series HPLC coupled to a 6410 triple quadrupole (QqQ) mass spectrometer (MS) (Agilent, USA) using a previously developed method [13]. For compound separation, a Zorbax Eclipse XDB-C18 Rapid Resolution HT (50 × 4.6 mm i.d.; 1.8 μm) column (Agilent, USA) was used. The mobile phase was composed of an aqueous 15 mM ammonium formate solution (0.1% *v/v* formic acid) (solvent A) and acetonitrile (0.1% *v/v* formic acid) (solvent B). Chromatographic elution started with a linear gradient from 75% to 100% of solvent B in 5 min at a flow-rate of 0.6 mL min⁻¹ and held to 5 min. The column was thermostated at 35 °C.

The analytical method was previously validated. Table 1 shows a summary of some of the most significant parameters of the method. Method detection (MDL) and quantification (MQL) limits were calculated as the concentrations corresponding to signal-to-noise ratios of 3 and 10, respectively, by means of spiked samples at low concentration levels. External calibration was used for quantitation. Quality control was applied by analyzing the procedural blanks, standard solutions and spiked samples in duplicate every 10 samples to evaluate possible contaminations and instrumental analysis variability.

Table 1. Recovery (R), precision (% expressed as relative standard deviation (RSD)), method detection limits (MDLs) and method quantification limit (MQL) in compost samples.

Compound	R (%)	RSD (%)	MDL (μg kg ⁻¹ dm)	MQL (μg kg ⁻¹ dm)
LAS C ₁₀	79	4.4	0.18	0.61
LAS C ₁₁	97	4.5	0.51	1.69
LAS C ₁₂	97	4.2	0.50	1.66
LAS C ₁₃	99	5.0	0.39	1.32
NP ₁ EO	77	8.6	1.52	5.07
NP ₂ EO	94	1.5	0.32	1.05
NP	73	4.8	0.31	1.04
DEHP	76	8.3	6.94	23.1

2.5. Ecotoxicological Risk Assessment

Ecotoxicological risk assessment (ERA) was assessed using risk quotient (RQ) values in soil amended with compost. The RQ was calculated as the quotient between the predicted environmental concentration in the soil (PEC_{soil}) and the predicted no-effect concentration (PNEC). The PEC_{soil} values provided an estimation of the concentration of a substance expected in the soil after a one-dose application of compost (Equation (1)):

$$PEC_{soil} = C_{compost} \cdot APPL_{compost} / DEPTH_{soil} \cdot RHO_{soil} \quad (1)$$

where, according to the European Union Technical Guideline Document [14], $C_{compost}$ is the concentration measured in the compost (μg kg⁻¹ dm), $APPL_{compost}$ is the application rate of dry compost onto soils (0.5 kg m⁻² year); $DEPTH_{soil}$ is the mixing depth (0.20 m) and RHO_{soil} is the bulk density of wet soil (1700 kg m⁻³) for agricultural soils.

PNECs are usually calculated using the lowest acute Lethal Concentration 50 (LC₅₀) or Effective Concentration 50 (EC₅₀) toxicity data in fish, *Daphnia magna* or algae and dividing them by an assessment factor of 1000 to consider the worst case scenario.

It should be noted that the data collected from the literature on the toxicity of the selected compounds in terrestrial organisms were very limited. According to the European Union Technical Guideline Document, PNEC_{soil} was estimated through the PNEC_{water} and partition coefficients (K_d) approach (Equation (2)) [15], assuming that the sensitivity of the terrestrial organisms was comparable:

$$\text{PNEC}_{\text{solid}} = \text{PNEC}_{\text{water}} \cdot K_d \quad (2)$$

The ecotoxicological data and K_d values from the literature are compiled in Table 2. RQ values >1 would indicate that the compound did imply a significant risk to the terrestrial microorganisms in the soil.

Table 2. Ecotoxicological data, solid water partition coefficient (K_d) and predicted no-effect concentration (PNEC) of each compound in water and soil.

Ecotoxicological Data			PNEC _{water}		PNEC _{soil}	
Organism	Test	Toxicological Value (mg L ⁻¹)	(µg L ⁻¹)	Log K _d	(µg kg ⁻¹)	
C10	<i>Daphnia magna</i> (invertebrate)	LC ₅₀ (48 h)	13.9 ¹	13.9	2.72 ¹	7294.8
C11	<i>Nannochloropsis gaditana</i> (algae)	EC ₅₀ (72 h)	1.38 ²	1.38	2.60 ¹	549.4
C12	<i>Pimephales promelas</i> (fish)	EC ₅₀ (48 h)	3.2 ²	3.2	3.53 ¹	10,843.0
C13	<i>Nannochloropsis gaditana</i> (algae)	EC ₅₀ (72 h)	0.18 ²	0.18	2.09 ⁵	22.1
NP ₂ EO	<i>Mysidopsis bahia</i> (invertebrate)	LC ₅₀ (48 h)	0.11 ³	0.11	3.76 ⁶	633.0
NP ₁ EO	<i>Mysidopsis bahia</i> (invertebrate)	LC ₅₀ (48 h)	0.11 ³	0.11	3.64 ⁷	480.2
NP	<i>Mysidopsis bahia</i> (invertebrate)	LC ₅₀ (96 h)	0.02 ³	0.02	2.67 ⁷	9.4
DEHP	<i>Selenastrum capricornutum</i> (algae)	LC ₅₀ (48 h)	0.1 ⁴	0.1	3.90 ⁸	794.3

¹ Ying, 2006 [16]. ² Garrido-Perez et al., 2008 [17]. ³ Fenner et al., 2002 [18]. ⁴ Rhodes et al., 1995 [19]. ⁵ Feijtel et al., 1999 [20]. ⁶ During et al., 2002 [21]. ⁷ Yu et al., 2008 [22]. ⁸ <http://echa.europa.eu/documents/10162/060d4981-4dfb-4e40-8c69-6320c9debb01>; Accessed December 2021 [23]. LC₅₀: Lethal Concentration 50; EC₅₀: Effective Concentration 50.

3. Results

3.1. Characterization Parameters

Temperature plays an important role in composting efficiency. In both compost piles, the temperature reached its maximum at the beginning of the fermentation step in about 37 days (41 °C in pile A and 49 °C in pile B). However, while the temperature of pile B was higher than 40 °C during days 21–65, the temperature measured in pile A was higher than 40 °C only in the first days of the fermentation step. The rise in temperature during composting was mainly due to the evolution of metabolic heat and the initial temperature of the pile, so this would indicate that the transformation of readily available substrates in pile B was higher than in pile A.

Table 3 shows those values at the initial and final stages of composting of the two biosolid piles. The initial moisture content was 79 and 73% in pile A and B, respectively. These values decreased continuously over 85 days, reaching their minimum values (8% and 6% in pile A and B, respectively) and then remaining almost constant until the end of the composting process (11% moisture content in both piles). The moisture content varied as a function of the aeration rate, agitation, the bulking agent used and the metabolic production of heat. Therefore, the similar progression of the moisture content in both piles would indicate similar conditions.

Table 3. Characterization parameters of the two biosolid piles.

Parameter	Units	Pile A		Pile B	
		Day 0	Day 127	Day 0	Day 127
Kjeldahl nitrogen	% dm	5.7	2.8	4.8	2.8
Crude protein	% dm	35.8	17.4	29.8	17.4
Carbon	% dm	41	17	40	21
Organic matter	% dm	71	30	69	37
C/N	-	7.2	6.1	8.4	7.6
Ca (CaO)	% dm	1.1	1.6	1.6	1.5
Mg (MgO)	% dm	0.65	0.17	0.41	0.34
Extracted P (P ₂ O ₅)	% dm	2.9	0.972	1.96	0.589
Total P (P ₂ O ₅)	% dm	6	4.7	5	4.5
Extracted K (K ₂ O)	% dm	0.21	0.16	0.12	0.11
Total Pb	mg kg ⁻¹ dm	135	99	89	81
Total K (K ₂ O)	% dm	0.36	0.54	0.28	0.55
Conductivity	mS cm ⁻¹ 25 °C dm	4.7	4.2	4.2	4.8
Soluble salts	%	0.30	0.27	0.27	0.31
Total Fe	mg kg ⁻¹ dm	9054	16,099	14,054	18,345
Total Mn	mg kg ⁻¹ dm	223	418	181	324
Total Ni	mg kg ⁻¹ dm	<20	23	28	30
Total Cu	mg kg ⁻¹ dm	249	182	300	223
Total Cr	mg kg ⁻¹ dm	49	56	55	63
Total Cd	mg kg ⁻¹ dm	1.0	0.8	1.3	1.1
Total Zn	mg kg ⁻¹ dm	771	643	1043	859
Total Co	mg kg ⁻¹ dm	<10	<10	<10	25
Total Al	mg kg ⁻¹ dm	12,509	26,984	14,843	28,639
Total Hg	mg kg ⁻¹ dm	1.20	-	1.30	-
pH	Und pH dm	8.2	8.3	8.1	8.0
Moisture	%	79	11	73	11

–: no detected.

The metal content showed a different behavior. The concentrations of K, Fe, Mn, Ni, Cr and Al increased during the composting process in both piles. This could be explained by the lost weight of the studied piles due to the degradation of the organic matter (between 30 and 40%). This fact was previously explained by other authors [24,25]. The total N in pile A decreased from 5.7 to 2.8% dm, and this decrease was notably lower in pile B (from 4.8 to 2.8% dm).

The sludge to be composted had a pH between 8.1 and 8.2 and was slightly acidic (between 6) a few days later. During fermentation, the pH value dropped to 4.5–5.5 due to bacterial activity and the formation of weak acids. Subsequently, the fermentable material produced an alkaline reaction due to the formation of ammonia resulting from the degradation of proteins and amino acids. The pH reached values close to neutral or slightly alkaline at the end of the process (pH 8.0–8.3).

The C/N ratio was reduced by the loss of C as CO₂ and N during composting. This reduction was a bit more notable in pile A (15%) than in pile B (9%), which was related to the higher decrease in the C (59%) and N (51%) content in pile A. Other parameters, such as conductivity, remained almost constant during the composting process in both piles.

The appropriate characteristics of the initial product and the composting process contributed to the increase in the agronomic value of the compost obtained in both piles.

3.2. Concentrations of Organic Compounds

All of the studied priority organic compounds (LAS, NPE and DEHP) were detected in all samples analyzed (Table 4) regardless of the pile of compost, except in one sample from pile B, where the concentration of NP was lower than the MQL of the applied analytical method.

Table 4. Mean and range concentration levels of priority organic compounds.

Group	Compound	Pile A		Pile B	
		Mean mg kg ⁻¹ dm	Range mg kg ⁻¹ dm	Mean mg kg ⁻¹ dm	Range mg kg ⁻¹ dm
LAS	C ₁₀	127	67.9–214	242	128–371
	C ₁₁	889	502–1451	1690	888–2520
	C ₁₂	1478	793–2462	2585	1395–3647
	C ₁₃	1207	705–1926	2093	1159–2836
NPE	NP ₁ EO	1.39	0.93–2.28	1.93	1.23–2.79
	NP ₂ EO	13.6	11.2–16.8	14.8	8.68–20.1
	NP	6.45	4.89–9.26	5.26	<MQL-10.6
Phthalate	DEHP	7.61	4.91–12.8	12.4	6.56–15.8

LAS homologues were detected at the highest concentrations in all compost samples, being lower in pile A (range of Σ LAS: 2068–6033 mg kg⁻¹ dm) than in pile B (range of Σ LAS: 3569–9375 mg kg⁻¹dm), especially in the case of the homologues C11, C12 and C13. The highest concentrations were found in the case of the homologue C12, followed by the homologues C13, C11 and C10. This distribution was similar to those found in household products such as laundry detergents, dishwashing liquids, shampoos and other personal care products, which points to the domestic contribution to the samples. These elevated concentrations could be attributed to their intense usage and the strong tendency to partition into and persist in compost, despite being largely removed to the water phase in wastewater treatment plants [26,27]. Taking into consideration the limit values fixed by the Working Document on Sludge in the case of LAS (2600 mg kg⁻¹dm), the concentrations of LAS measured in both piles of compost were higher than this limit in all steps of the composting processes.

The concentration levels of NPE and DEHP were similar in both piles of compost. Considering NPE, the higher concentrations were found in the case of NP₂EO, followed by NP and NP₁EO. In both cases, the concentrations measured were lower than the limit values fixed in the Working Document on Sludge (50 mg kg⁻¹dm for NPE and 100 mg kg⁻¹dm for DEHP). In the case of pile A, concentrations ranged from 18.7 mg kg⁻¹dm to 26.9 mg kg⁻¹dm for NPE, and in pile B, they ranged from 17.8 to 27.5 mg kg⁻¹dm. In the case of DEHP, these concentrations ranged from 4.91 to 12.8 mg kg⁻¹dm and from 6.56 to 15.8 mg kg⁻¹dm in pile A and B, respectively.

3.3. Occurrence of Organic Pollutants during the Composting Process

The concentrations of the studied compounds measured during the composting process in piles A and B are shown in Figure 1. The concentrations measured in pile A showed 2 punctual rises at days 10 (dryness phase) and 99 (maturation phase), especially in the case of the LAS homologues. As a result, only a slight decrease in the concentrations was observed during composting. Regarding pile B, a continuous decrease in the concentrations was observed, reaching higher global removal in pile B.

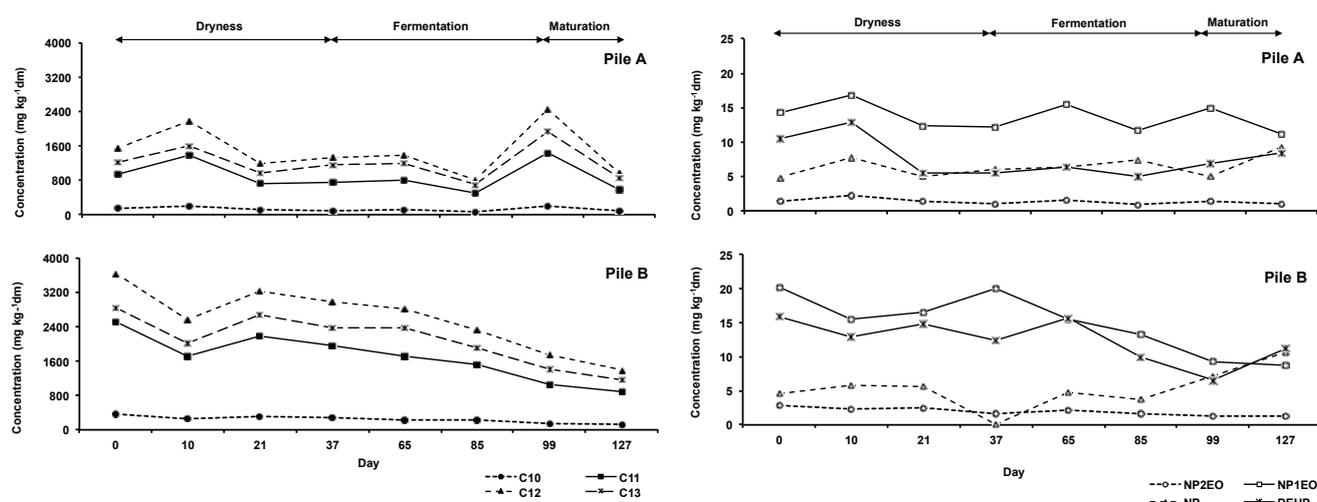


Figure 1. Evolution of the concentrations of LAS homologues, NPE and DEHP during composting in piles A and B (each sample was measured in triplicate, and the RSD was $\leq 1.5\%$ in all cases).

Regarding the LAS homologues, their concentrations were reduced by between 20 and 31% during the dryness step in pile A (Figure 2). However, due to the increase in the concentrations measured at day 99, these concentrations were increased (28–36%) during the fermentation step and finally decreased during the maturation process. Globally, the reduction in the concentrations of the LAS homologues achieved during composting was from 30 to 50%. In the case of pile B, the concentrations measured for the LAS homologues decreased as follows: dryness by 6–16%; fermentation by 28–30%; maturation by 40–43%; and global by 59–66%. The higher global decrease in the concentrations of the LAS homologues was observed in pile B, probably due to the higher temperature achieved in pile B during composting (thermophilic phase), because thermophilic temperatures are more favorable to biological activity associated with the removal of these compounds. In a similar study, Pakou et al. [28] achieved removal efficiencies between 77 and 91%. The authors concluded that the initial concentration of the LAS affected the removal percentage. However, at low LAS concentration values, limited bioavailability led to a residual concentration of LAS that was difficult to reduce any further. The maturation stage's duration is important for achieving a complete removal of these compounds.

Unlike in the case of the LAS homologues, NPE showed a similar behavior during the composting process of pile A (Figure 2), in which their concentration did not vary significantly. The concentration of NP during composting increased from 4.89 to 9.26 $\text{mg kg}^{-1} \text{dm}$ and from 4.59 to 10.6 $\text{mg kg}^{-1} \text{dm}$ in pile A and pile B (Figure 1), respectively, probably due to the degradation of NPEO. A similar observation was published by several authors [8,28,29], and a considerable removal of NPEs (64–95%) was reached in some cases [28,29].

The mesophilic temperatures in the fermentation phase of pile B favored the removal of NP (33%), but this effect was counteracted by the generation of NP from the degradation of NPEO. This effect was also observed by Moeller and Reeh [30], in whose study the effect of the thermophilic conditions resulted in a net accumulation of NP, with transitory elevated concentrations of the degradation products. However, some authors have reported losses of NP during composting [31]. The removal (%) depends on their initial concentrations in the compost mixture [28], bulking agents and mesophilic phase [29]. Some conditions during the process such as the ventilation, the pH or the microbial community can influence the degradation and removal of NP. Zheng et al. [29] observed an increase in the removal % of NP from 19.7% to 41.6% with prolonged ventilation from 5 to 15 min during composting.

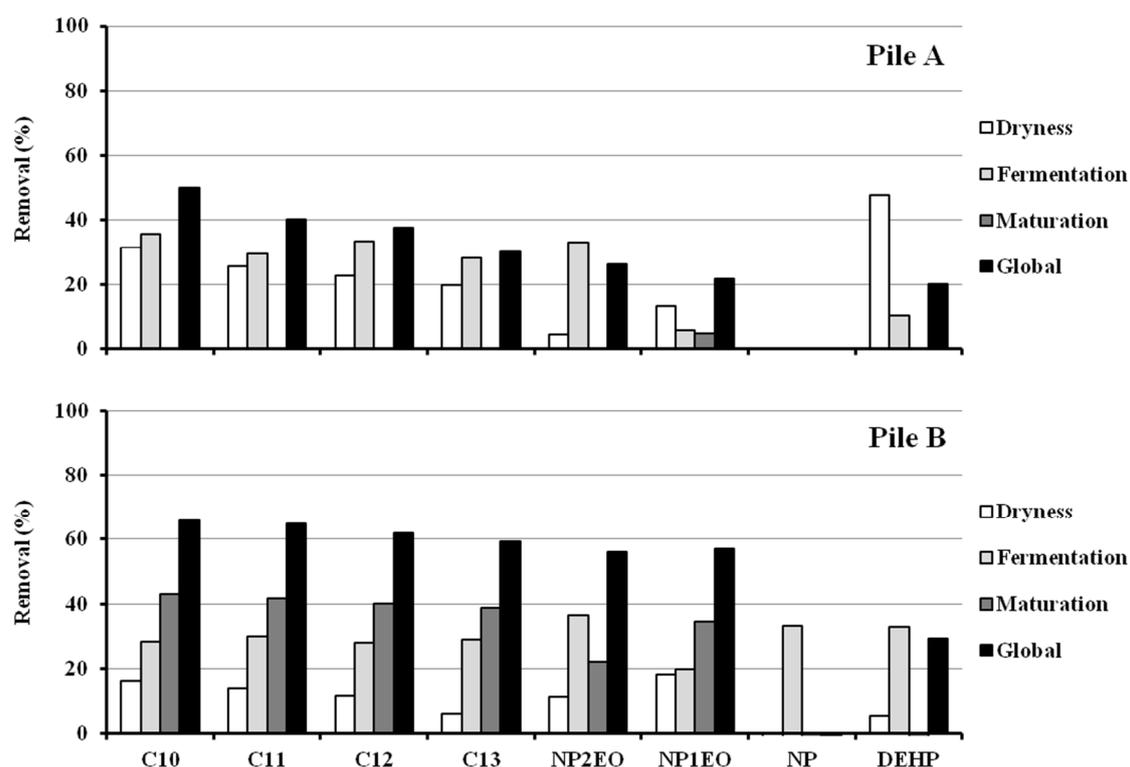


Figure 2. Removal rates of LAS homologues, NPEs and DEHP during the different phases of composting in piles A and B.

In the case of DEHP, its concentration decreased during composting from 10.5 to 8.35 mg kg⁻¹dm in pile A and from 15.8 to 11.2 mg kg⁻¹dm in pile B. Similar results were previously reported by Gibson et al. [31] and Poulsen and Bester [32]. The concentration levels of DEHP in the final product of composting were generally <100 mg kg⁻¹, with removal percentages between 50 and 97% [33].

Like what happened for the rest of the pollutants studied, the losses of this pollutant were higher in pile B (29%), especially during the fermentation step (33%), than in pile A (20%), where the higher losses were achieved in the dryness step (48%) (Figure 2). This suggests that as much microbial degradation, favored by mesophilic temperatures, as volatilization driven by water loss is possible, as DEHP is semi-volatile.

3.4. Risk Assessment

The calculated RQs in soil amended with compost from piles A and B are shown in Figure 3. The red horizontal line drawn at RQ 1 denotes the limit between medium and high risk. Overall, the risk associated with the presence of the selected compounds was medium-low for most of them. However, it was not enough to not represent a potential risk to the environment in the case of LAS C11 and C13 in both piles. These homologues had a PNEC_{soil} value lower than the other homologues, mainly due to the low toxicity data reported in the literature for these compounds. Regarding NPE and DEHP, in general, their RQ values were lower than those found in the case of LAS homologues. For the NPE group, an increase in the risk was observed with the decrease in the number of ethoxy groups. The only toxicological effect expected was the one caused by NP in pile B. González et al. [8] estimated the ERA of the selected compounds after the application of compost to the soil, and their results also revealed a potential toxic effect in the case of LAS C13 and NP during the first 23 and 56 days, respectively, after the application of sewage sludge to the soil.

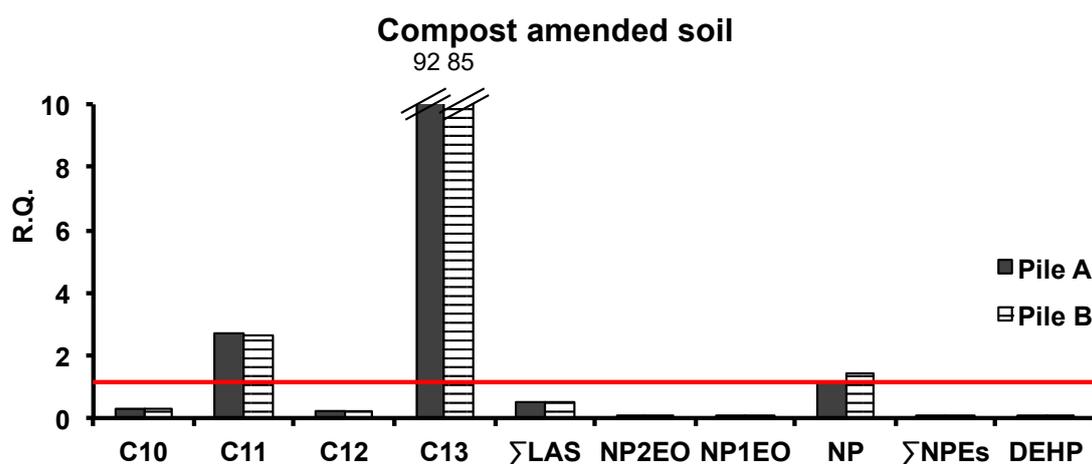


Figure 3. Risk quotients (RQs) of studied compounds in soil amended with compost.

Up to now, the lack of legislation on the content of the selected organic pollutants in sludge-amended soil made it impossible to state with certainty that the results obtained so far were sufficient to avoid medium-to-long-term damage to living microorganisms. Future advances in this area require the collection of ecotoxicological data from terrestrial microorganisms and the incorporation of additional endpoints (including chronic exposure), as well as the analysis of these compounds at lower, environmentally relevant concentrations. Additionally, other treatments can be used prior to sludge application to agriculture land in order to reduce the load of organic pollutants. Hydrothermal carbonization, biodrying or hydrothermal liquefaction have been recently investigated as potential technologies [1].

4. Conclusions

The occurrence of eight priority organic pollutants in two piles of sewage sludge along the composting process in a full-scale study was evaluated. All the studied priority organic compounds (LAS, NPE and DEHP) were detected in all samples analyzed. While LAS homologues were detected at the highest concentrations (Σ LAS: 2068–9375 mg kg⁻¹dm), exceeding the limit fixed in the EU Directive draft and also pointing out the domestic contribution to the samples, the concentration levels for NPE and DEHP were significantly lower and did not exceed their fixed limits in the EU Directive draft.

A decrease in the concentrations was observed along the composting process for all compounds, except for NP, probably as consequence of the degradation of NPEO. Overall, the removal was higher in the pile that reached the thermophilic phase (pile B), which probably involved specific microorganisms present at this temperature. The environmental risk assessment showed, in spite of the decrease in the concentrations of these compounds, a potential risk due to LAS homologues C11 and C13 and NP and highlighted the need to carry out a more accurate and comprehensive environmental risk assessment taking into consideration ecotoxicological data in terrestrial microorganisms for these pollutants, as well as the incorporation of additional endpoints.

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