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Degradation of organic pollutants in Mediterranean forest soils amended with sewage sludge

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Abstract

The degradation of two groups of organic pollutants in three different Mediterranean forest soils amended with sewage sludge was studied for nine months. The sewage sludge produced by a domestic water treatment plant was applied to soils developed from limestone, marl and sandstone, showing contrasting alkalinity and texture. The compounds analysed were: linear alkylbenzene sulphonates (LAS) with a 10–13 carbon alkylic chain, and nonylphenolic compounds, including nonylphenol (NP) and nonylphenol ethoxylates with one and two ethoxy groups (NP1EO + NP2EO). These compounds were studied because they frequently exceed the limits proposed for sludge application to land in Europe. After nine months, LAS decomposition was 86–96%, and NP + NP1EO + NP2EO decomposition was 61–84%, which can be considered high. Temporal trends in LAS and NP + NP1EO + NP2EO decomposition were similar, and the concentrations of both types of compounds were highly correlated. The decomposition rates were higher in the period of 6–9 months (summer period) than in the period 0–6 months (winter + spring period) for total LAS and NP + NP1EO + NP2EO. Differences in decay rates with regard to soil type were not significant. The average values of decay rates found are similar to those observed in agricultural soils.
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1. Introduction

Large amounts of sewage sludge are generated each year from wastewater treatment plants, and their disposal represents a major environmental problem. Sewage sludge is applied to agricultural land as a soil conditioner and fertiliser, because the physical properties of the soil are improved, and nutrients such as nitrogen and phosphorus are supplied Hansson et al. (1999). In Spain, the National Sewage Sludge Plan (2001–2006) recommends land applications as the main use of this organic residue. In this country, the amount of sludge generated in 2005 was estimated at one million tons of dry matter, and 65% of this was expected to be reused in agriculture (Secretaría General de Medio Ambiente, 2001). In the European Union Member States, the total quantity of sewage sludge produced was expected to reach nine million tons of dry matter by the end of 2005, and around 45% is currently recycled to agricultural land (Joosten, 2005).

The use of organic residues such as sewage sludge in forest management has been receiving increasing attention (Benbrahim et al., 2006; Horswell et al., 2007). Sewage sludge may increase nutrient availability and tree growth, and thus it has been used in forest plantations (Jokela and Smith, 1991; Pibot, 1998). On the other hand, forest soils may be degraded because of disturbances such as wildfire, erosion, fuel-wood harvesting, etc. Improved soil

fertility by using sewage sludge may help to restore damaged ecosystems (White et al., 1997; Werner et al., 2000; Valdecantos et al., 2001).

Sludge application may lead to the accumulation of potentially hazardous components in soil, such as heavy metals and some organic compounds (Bright and Healey, 2003), and may increase the risk of these components entering the food chain. The use of sewage sludge in agriculture is regulated in the European Union by EU Council Directive 86/278/ECC (1986) in order to prevent harmful effects on soil, vegetation, animals and man. No European regulation is currently enforced on the use of sewage sludge on non-agricultural areas. The European Commission has proposed (without obligation) limit values of organic compounds in sludge for land application in a third draft of the "Working Document on Sludge" (EU, 2000), and some European countries – but not Spain – have introduced national regulations on this matter. In a future revision of the EU Sewage Sludge Directive, limits to some organic compounds, such as those showing high oxidative degradation potential in soils, may not be included (Amlinger, 2004). Some recent documents include limits for selected PAHs (polycyclic aromatic hydrocarbons) and PCBs (polychlorinated biphenyls), AOX (adsorbable organic halides), and NP + NP1EO + NP2EO (three nonylphenolic compounds) (EU, 2001; Leschber, 2004).

Two groups of organic pollutants are frequently found in sewage sludge: nonylphenolic compounds, including nonylphenol (NP) and nonylphenol ethoxylates with one or two ethoxy groups (NP1EO + NP2EO), and linear alkylbenzene sulphonates with an alkylic chain of 10–13 atoms of carbon (LAS).

NP, NP1EO and NP2EO are formed in wastewater treatment plants as degradation products from non-ionic surfactants such as those found in specialised cleaning agents. Their toxicity is a result of their ability to disrupt the normal function of the endocrine systems of various organisms (Laws et al., 2000; Todorov et al., 2002).

LAS are anionic surfactants widely used in cleaners and detergents for domestic and industrial applications. These may lead to increased skin penetration of other substances due to damage of the lipid layer, and there is limited evidence for reproductive and fetotoxic effects (Langenkamp et al., 2001).

The content of NP + NP1EO + NP2EO and LAS in European sewage sludge often exceeds the limits allowed by proposed regulations in the third draft of the "Working Document on Sludge" (Langenkamp et al., 2001), and thus they represent a major environmental problem. Legal limits for LAS have not been considered in recent documents, although the final version of these regulations has not been issued yet.

The degradation of LAS and NP + NP1EO + NP2EO in agricultural soils is high (Laturnus et al., 1999; Petersen et al., 2003). The decomposition rate depends on the type of application, and on soil conditions such as aeration rate and sorption capacity, and may be affected by the presence

of sewage sludge (De Wolf and Feijtel, 1998; Jensen, 1999; Mortensen and Kure, 2003). Most studies on the degradation of these compounds have been performed under laboratory conditions and with agricultural soils. Information on their decomposition dynamics in forest soils is scarce.

The objectives of this study are to analyse the degradation of NP + NP1EO + NP2EO and LAS in Mediterranean forest soils amended with sewage sludge, and to explore the drivers of degradation processes. The degradation of bulk (i.e., total) soil organic matter was studied as a reference for the degradation of organic pollutants. To our knowledge, no study on the degradation dynamics of the above two types of compounds in Mediterranean forest soils has been carried out so far.

2. Experimental

2.1. Sludge characterization

The sewage sludge used was produced by a domestic water treatment plant located in Relleu, a rural area of the Region of Valencia (SE Spain), with a water flow of 115 $m^3 d^{-1}$. The sludge was treated by gravity thickening, dewatered by air-drying (a common practice before agricultural application) and enriched in heavy metals. The concentrations of these heavy metals in the sludge were 5377 mg kg^{-1} dry weight (d.w.) for Zn, 2098 for Cu, 666 for Ni, 53 for Cr, 34 for Pb, 2.6 for Hg and less than 0.4 mg kg^{-1} for Cd. Sludge pH was 7.4 (Fuentes et al., 2007). The contents of NP + NP1EO + NP2EO, LAS, DEHP and organic matter in the sludge were determined before adding it to the soils (see below).

2.2. Soil types and characterization

The three soils used in this experiment were developed from limestone, marl and sandstone, respectively. These soils show contrasting alkalinity and texture, and they represent three of the most common forest soils in the Mediterranean basin (Table 1). The soil developed from limestone (*Rendzic Leptosol*; FAO, 1998) has a high con-

Table 1
Main physico-chemical features of the soils used in the experiment

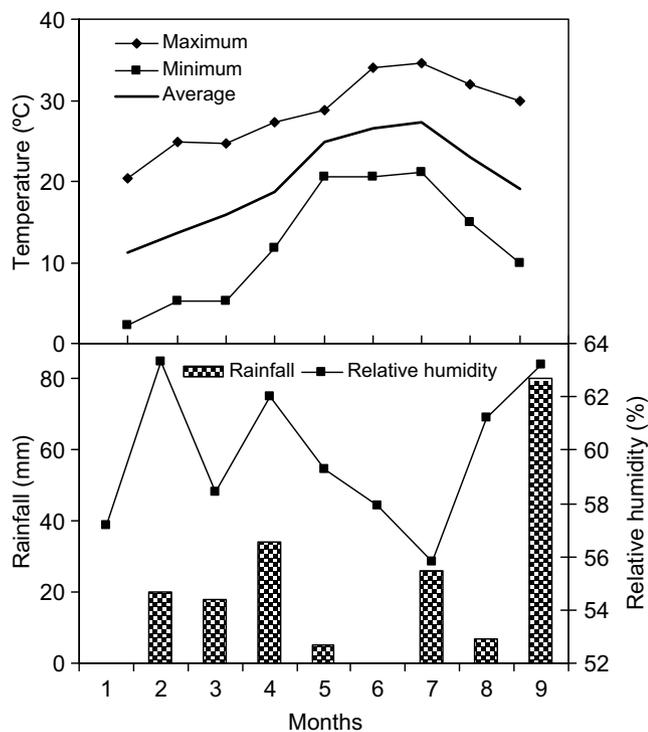| Characteristic	Soil developed from limestone	Soil developed from sandstone	Soil developed from marl
Texture class	Clay	Loam	Loam
Sand (g/100 g)	22.9	42.8	40.4
Silt (g/100 g)	33.5	40.4	40.0
Clay (g/100 g)	43.5	16.5	19.6
$CaCO_3$ (g/100 g)	15.5	4.0	51.0
pH	8.4	5.9	8.4
Organic carbon (g/100 g)	2.5	0.4	2.8
Bulk organic matter (g/100 g)	8.8	2.9	9.1

From Toribio and Romanyà (2006).

Fig. 1. Environmental conditions during the experiment: temperature, rainfall and relative humidity (the first month corresponds to February).

tent of clay as compared with those developed from sandstone and marl, and a basic pH. The soil developed from red sandstone (*Eutric Cambisol*; FAO, 1998) shows a very low percentage of organic carbon and acidic pH. Finally, the soil developed from marl (*Calcaric Regosol* according to FAO (1998)) has a very high content of $CaCO_3$ and a basic pH. LAS and $NP + NP1EO + NP2EO$ contents in the three soil types were negligible.

2.3. Experiment layout

The experiment was carried out in Alacant (SE Spain) under semi-arid conditions (Fig. 1), by using fifteen $70 \times 40 \times 40$ cm lysimeters (five replicates per soil type). In February 2003 lysimeters were filled with, from bottom to top, a 10 cm layer of limestone gravel, a 20 cm layer of

unamended soil, a 30 cm layer of soil mixed with dry sewage sludge, and a 2 cm surface layer of unamended soil. The sewage sludge was applied at a rate of 6000 g m^{-2} (60 mg ha^{-1}), corresponding to 1.79%, 1.60% and 1.22% of sludge in soil by weight for the limestone, marl and sandstone soils, respectively. The mixture was homogenized by hand before filling the lysimeters to achieve a mixture similar to the application of sludge in a full scale forest. Finally, one 1-year-old *Pinus halepensis* seedling per lysimeter was planted. The application of biosolid was localized, in planting holes, instead of widespread application as it is a technique which may help to minimize the surface area affected by plantation practices, thus minimizing the damages to the surrounding natural vegetation and reducing the risk of off-site contamination (Loch et al., 1995).

Soil moisture and temperature were measured at the upper layer (0–35 cm depth) by means of TDR probes and diodes, respectively (Fig. 2).

Soil samples were collected from the upper layer (0–30 cm depth) from each lysimeter at the onset of the experiment, and three and nine months after sludge application, for the analysis of LAS, NP, NP1EO and NP2EO, and organic matter. These samples were homogenized in a blender. Only initial samples and those incubated for nine months were analysed for the lysimeters containing sandstone soil, as samples incubated for six months had deteriorated.

2.4. Analysis of organic compounds

The contents of LAS, $NP + NP1EO + NP2EO$ and organic matter were analysed in sludge and soils before sludge application, and then in soil samples collected from the lysimeters. The limit of detection (LOD) for each analyte was determined as the mass of analyte which gave a signal that was $3 \times$ background noise, and the LOD for a group of analytes was determined as the sum of the LOD for each analyte.

2.4.1. LAS analysis
The technique described by Prats et al. (1997) was used. First, samples were stabilized with a formaldehyde solution,
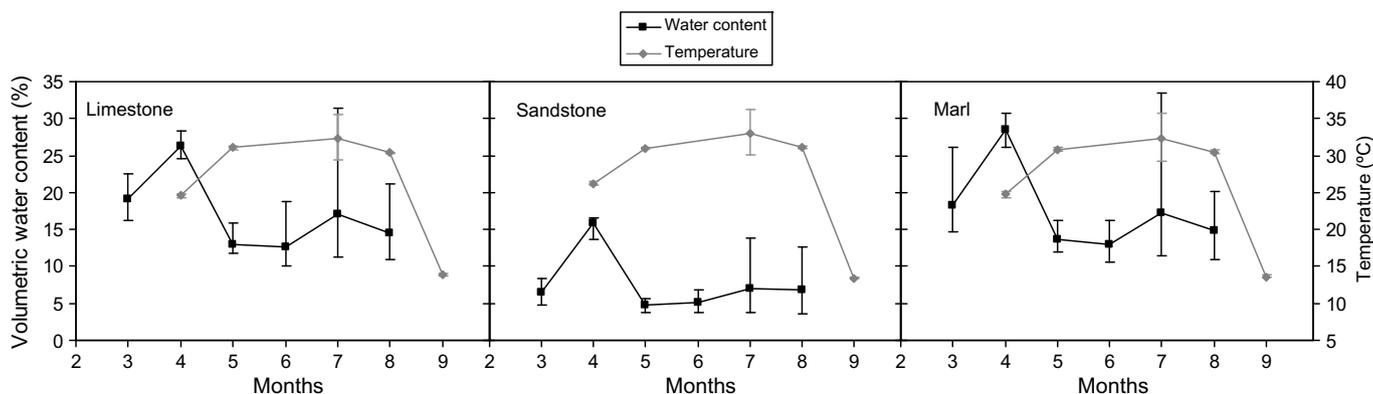

Fig. 2. Microclimatic conditions inside the lysimeters for the different soil types. Error bars refer to the maximum and minimum values.

and dried. LAS determination followed three steps. In the first step, around 10 g of sample were extracted with methanol using the Soxhlet method (US EPA method 3540C, 1996), where it is considered that most of the LAS retained in the solid pass to the fluid phase. This extraction method gives similar results as other techniques (Morales-Muñoz et al., 2004). The second step involved the purification of the extract with two columns: a quaternary amine column, where LAS were eluted with 4 N hydrochloric acid in methanol, and C-18 column, where LAS were eluted with methanol. Finally, the extract was analysed by high performance liquid chromatography (HPLC) and ultraviolet detection. The HPLC used was Shimadzu LC-6A with a UV SPD-6A detector (254 nm) and a chromatographic column LiChrosorb RP-18.5 mm diameter, 30 m in length and 5 μm particle size diameter. The mobile phase was methanol/water 80/20 0.1 M in $NaClO_4$, with a flow rate of 1 ml min^{-1}, the temperature in the column oven was 40 °C, and the injected volume of sample was 20 μL. The equipment was calibrated with several solutions of the standard Na-LAS P-550, supplied by Petresa (San Roque, Spain), with an average alkyl chain of 11.6 (CAS number: 68411-30-3). The homologue distribution was 12.1%, 34.1%, 30.6% and 23.2%, respectively for LAS with an alkylic chain of 10–13 carbon atoms. The content of impurities in this mixture was below 1%. The recovery rate was determined by considering two calibration curves: the first one with solutions of the standard that followed the extraction and purification explained above, and the other one directly, with no previous preparation. The variation of the results due only to the analytical method is around 10%.

2.4.2. Analysis of NP, NP1EO and NP2EO

First of all, an internal standard (4-*n*-Nonylphenol ring $^{13}C_6$; Cambridge Isotope Laboratories) was poured into around 10 g of sample. Then, the samples were dried by adding anhydrous sodium sulphate, and extracted with hexane:acetone (1:1) by using the Soxhlet method, following the recommendations of US EPA for soils, sediments and sludge samples (US EPA method 3540C, 1996). It has been found that this extraction method gives similar results as other techniques used by several authors (Croce et al., 2003). The solvent of the extracts was then changed to dichloromethane, and the extracts were cleaned by using size exclusion chromatography (Jordi GPC column, 680 mm × 22 mm I.D.), following US EPA method 3640A (1994). The column was eluted with dichloromethane at a flow rate of 5 ml min^{-1}, and a fraction was collected at 25–55 min. This fraction was concentrated to 2 ml and analysed with a Fisons GC8000 gas chromatograph (GC) coupled to a MS800 mass spectrometer (MS). The method used for the analysis was US EPA method 8270C (1996), with a DB-5 GC column (60 m × 0.25 mm ID). In the mass spectrometer, a positive electronic impact (EI+) source was employed and the SIR (selected ion recording) mode was used to detect exclusively the characteristic ions of the compounds of interest. In case of doubtful identity of compounds, the full scan mode was used to test the specific spectrum of the compounds detected.

The external standards used were 4-Nonylphenol (technical, Dr. Ehrenstorfer) and 4-Nonylphenol ethoxylate (technical, Dr. Ehrenstorfer). The internal standard (surrogate) was 4-*n*-Nonylphenol ring $^{13}C_6$, and the recovery standard, anthracene-D_{10} (AccuStandard). Phenanthrene-D_{10} (included in Internal Standards Mix 33, Dr. Ehrenstorfer) was initially used as internal standard (surrogate) for the analysis of NP, NP1EO and NP2EO, because some available labelled compounds interfered with the analysis. Nevertheless, considering the different polarity of phenanthrene-D_{10} and the nonylphenolic compounds, it was tested that the recovery rates of these compounds were similar for the entire process, including extraction and elution from the GPC column. The variation of the results due only to the analytical method is around 10%.

2.4.3. Organic matter

Samples were dried at 105 °C in an oven for 24 h, and then combusted at 550 °C for 12 h (Heron 12PR/300). Organic matter was estimated from the difference in weight of the samples before and after combustion.

2.5. Statistical analysis

We evaluated decomposition rate k for each compound as $k = -\ln(Xt/X_0)/t$, where Xt and X_0 correspond to the concentration of a particular compound at time t and 0, respectively, and t is the incubation time (in months). We evaluated the effect of soil type on decomposition rates by using one-way analysis of variance (ANOVA) with soil type as a fixed factor and $n = 5$ replicates.

We used repeated measures analysis of variance to evaluate the effect of time (within-subjects factor) and soil type (between-subjects factor) on the ratio between the concentration of different organic compounds.

When results showed a significant soil type effect, the Tukey's HSD test was used to perform pair-wise comparisons between soils. The statistical package used was SPSS 11.0 and the confidence limit was 95% ($P < 0.05$) in all cases.

3. Results and discussion

3.1. Organic pollutants and organic matter in soils and sludge

Soils contained negligible amounts of organic pollutants, and were always below the limit of detection (LOD). Blank samples had values lower than the LOD (Table 2).

LAS and NP + NP1EO + NP2EO concentrations in sludge were above the limits proposed by the EU for agricultural applications, and blanks were below the LOD for all compounds. Recoveries were high, ranging from 71% to

Table 2
Values of LOD, blanks and samples in the analysis of soils, sludge and soils amended with sludge

Compound	EU limit (mg kg^{-1} d.w.)	Soil				Sludge				Sludge + soil			
		LOD (mg kg^{-1} d.w.)	Blank (mg kg^{-1} d.w.)	Samples (mg kg^{-1} d.w.)	Recovery[a] (%)	LOD (mg kg^{-1} d.w.)	Blank (mg kg^{-1} d.w.)	Samples (mg kg^{-1} d.w.)	Recovery[a] (%)	LOD (mg kg^{-1} d.w.)	Blank (mg kg^{-1} d.w.)	Samples (mg kg^{-1} d.w.)	Recovery[a] (%)
TOTAL LAS	2600	1	<1	<1	82	40	<40	9660	83	1	<1	2–640	82
LAS C-10		0.1	<0.1	<0.1	86	4	<4	522	94	0.1	<0.1	<0.1–26	86
LAS C-11		0.3	<0.3	<0.3	85	12	<12	2700	92	0.3	<0.3	0.3–142	85
LAS C-12		0.3	<0.3	<0.3	84	12	<12	3556	71	0.3	<0.3	0.5–223	84
LAS C-13		0.3	<0.3	<0.3	75	12	<12	2882	77	0.3	<0.3	0.3–249	75
NP + NP1EO + NP2EO	50	0.1	<0.1	<0.1	40	43	<43	519	136	0.1	<0.1	0.1–6.2	62
NP		0.04	<0.04	<0.04	40	10	<10	68	136	0.04	<0.04	0.05–2.0	62
NP1EO		0.07	<0.07	<0.07	40	26	<26	385	136	0.07	<0.07	<0.07–3.6	62
NP2EO		0.03	<0.03	<0.03	40	7	<7	67	136	0.03	<0.03	0.05–2.6	62
Organic matter				29000–91000				390000				28000–115000	

[a] For LAS standard recovery (LAS C-10 + LAS C-11 + LAS C-10 + LAS C-13), for NP + NP1EO + NP2EO surrogate recovery (anthracene-D$_{10}$).

136%. The highest values of recovery in sludge probably resulted from the presence of compounds with the same ion as used for analysing the recovery standard. The values obtained agree with those found in a previous work for 16 sewage sludges from the same area (the Region of Valencia; Gomez-Rico et al., 2007). In this study LAS and NP + NP1EO + NP2EO exceeded the legal
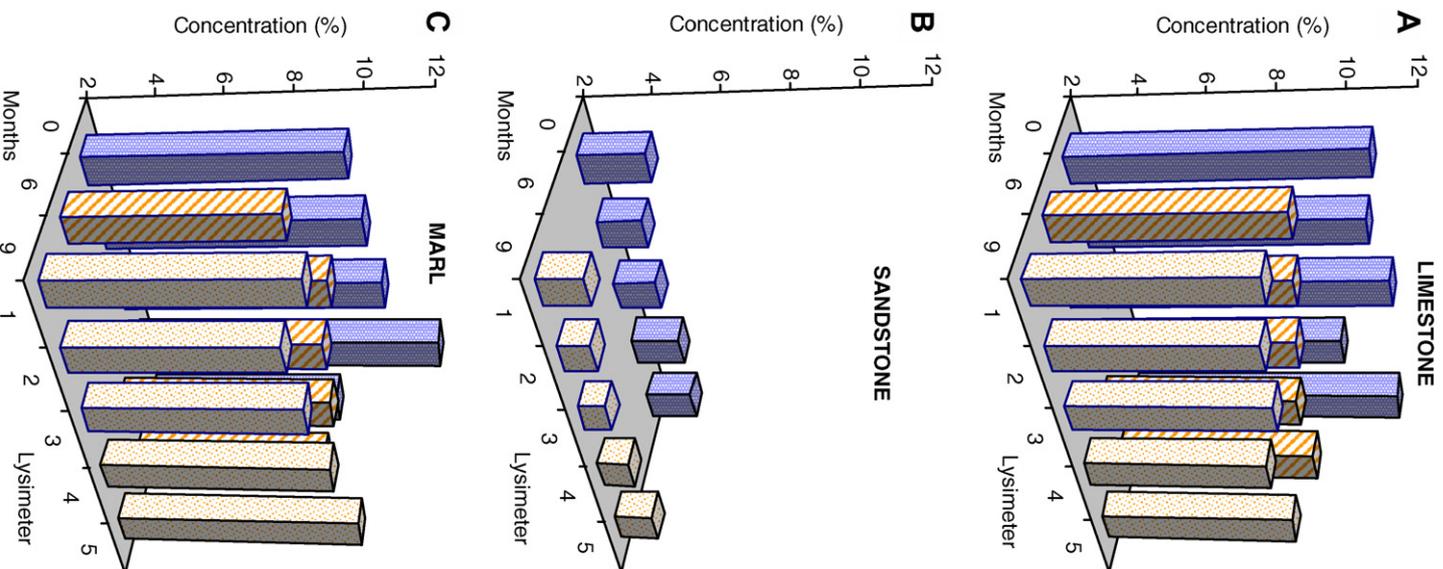

Fig. 3. Bulk organic matter degradation in soil developed from limestone (A), sandstone (B) and marl (C), with five curves in each graph corresponding to the five replicated lysimeters per soil type.

limits in most samples. Similar results are found in the literature for other countries (Jensen, 1999; Paulsrud et al., 2000; Marttinen et al., 2003). Nevertheless, the latest proposal for the revision of the EU Directive on sludge does not include any limit for LAS (Leschber, 2004), although this is not definitive.

3.2. Degradation of bulk organic matter

Soil organic matter decomposition for the whole study period was 23% for the limestone soil, 14% for the sandstone soil, and 16% for the soil developed from marl (Fig. 3A–C, Table 3). The degradation was higher for the period 0–6 months than for 6–9 months (Table 3) although the maximum temperatures were reached in the second period (Figs. 1 and 2).

Cogliastro et al. (2001) studied first year decomposition rates of sewage sludge applied on a deposit made of construction materials in the island of Montreal. In this clayey alkaline substrate, weight loss varied from 25% for applications equivalent to 125 kg N ha^{-1}, to 40% for application rates of 375 kg N ha^{-1}. Oleszczuk (2006) found that 18% of the total organic carbon decomposed after 50 months in a fallow soil planted with willow and amended with 75 mg sewage sludge ha^{-1}.

3.3. LAS degradation

Initial LAS contents were highly heterogeneous, probably due to the non-uniform mixing of sludge and soil. The mixture was homogenized by hand before filling the lysimeters to achieve a mixture similar to the application of sludge in a full scale forest. LAS decomposition was fast (Fig. 4A–C). Nine months after application, total LAS concentration ranged from less than 1% to ca. 40% of the original concentration.

All the values of decomposition are based on the analytical values obtained, and consequently assuming that the percentage of analytes absorbed in the solid after extraction is negligible or very small.

In a greenhouse experiment under constant climatic conditions and high moisture content, Laturnus et al. (1999) found that up to 62% of LAS inputs were degraded after 84 days in sandy soils receiving high rates of sludge (90 mg d.w. ha^{-1}). Degradation increased when the sludge application rate was lower (99% degraded at an application rate of 6 mg d.w. ha^{-1}), and when carrots were grown in the same soil. The plant LAS uptake of LAS has been studied and insignificant levels were found in roots (Grøn et al., 2001). High decomposition rates of LAS in soils have been observed elsewhere (Petersen et al., 2003), particularly

Table 3
Degradation of compounds and organic matter for the five replicate runs of each soil

Compound (mg kg^{-1}d.w.)	Degradation 0–6 months[a] (%)		Degradation 6–9 months[b] (%)		Total degradation after 9 months[a] (%)	
	Interval	Mean value	Interval	Mean value	Interval	Mean value
Limestone + 1.79% Sludge						
LAS						
Total LAS	0–97	56	73–97	90	90–100	96
LAS C-10	47–100	85	0–100	55	91–100	96
LAS C-11	0–97	57	63–97	87	86–100	95
LAS C-12	0–97	57	70–97	87	89–100	96
LAS C-13	0–96	51	84–98	93	94–100	97
NP + NP1EO + NP2EO	0–87	39	52–84	70	79–96	84
Organic matter	11–23	18	4–7	5	18–26	23
Sandstone + 1.22% Sludge						
LAS						
Total LAS					59–94	86
LAS C-10					46–90	83
LAS C-11					67–93	87
LAS C-12					47–94	83
LAS C-13					66–95	88
NP + NP1EO + NP2EO					47–67	62
Organic matter					8–17	14
Marl + 1.60% Sludge						
LAS						
Total LAS	0–84	45	49–97	84	63–99	86
LAS C-10	0–99	66	0–94	34	63–99	86
LAS C-11	0–92	48	51–97	82	61–99	84
LAS C-12	0–89	46	46–96	83	57–99	84
LAS C-13	0–80	41	54–98	87	67–100	88
NP + NP1EO + NP2EO	0–86	51	15–87	66	61–97	82
Organic matter	5–23	13	0–10	3	5–23	16

[a] Percentages referred to the experimental initial content.
[b] Percentages referred to the 6th month content.

under aerobic conditions (Jensen, 1999). The average values obtained in our work are similar to those obtained in other conditions, despite the differences in soil and climatic properties. In the present study, the forest soils used exhibited a texture class of clay or loam (Table 1), the water content for the mixture soil–sludge was 4.9–28.5% (Fig. 2), and the air temperature was relatively high. In contrast, in the literature the soils used were sandy, sandy loam and loamy

sand agricultural soils, the water content for the mixture soil–sludge was 60–75% of the water holding capacity (corresponding to a content of 7.5–12.0% approximately), and the temperatures were cooler.

Comparing the LAS degradation in two periods of the experiment separately, 0–6 months and 6–9 months (Table 3), it can be observed that the reduction was higher in the last period for total LAS and LAS with an alkylic chain of
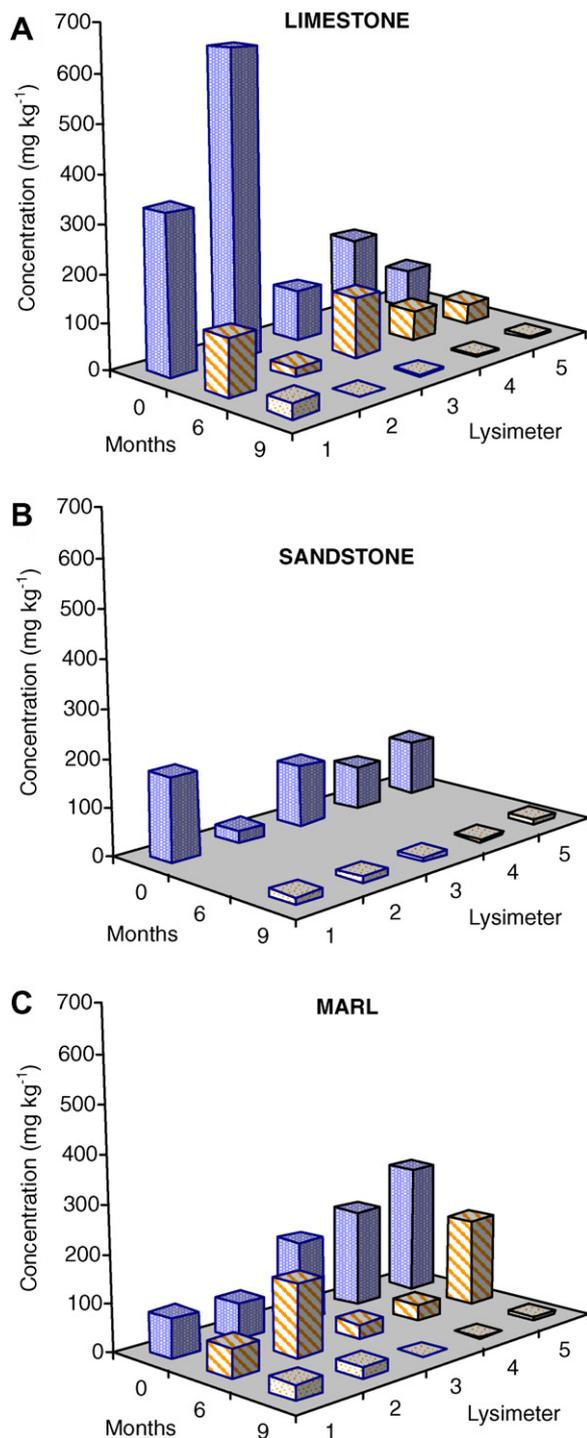

Fig. 4. Degradation of total LAS in soil developed from limestone (A), sandstone (B) and marl (C), with five curves in each graph corresponding to the five replicated lysimeters per soil type.
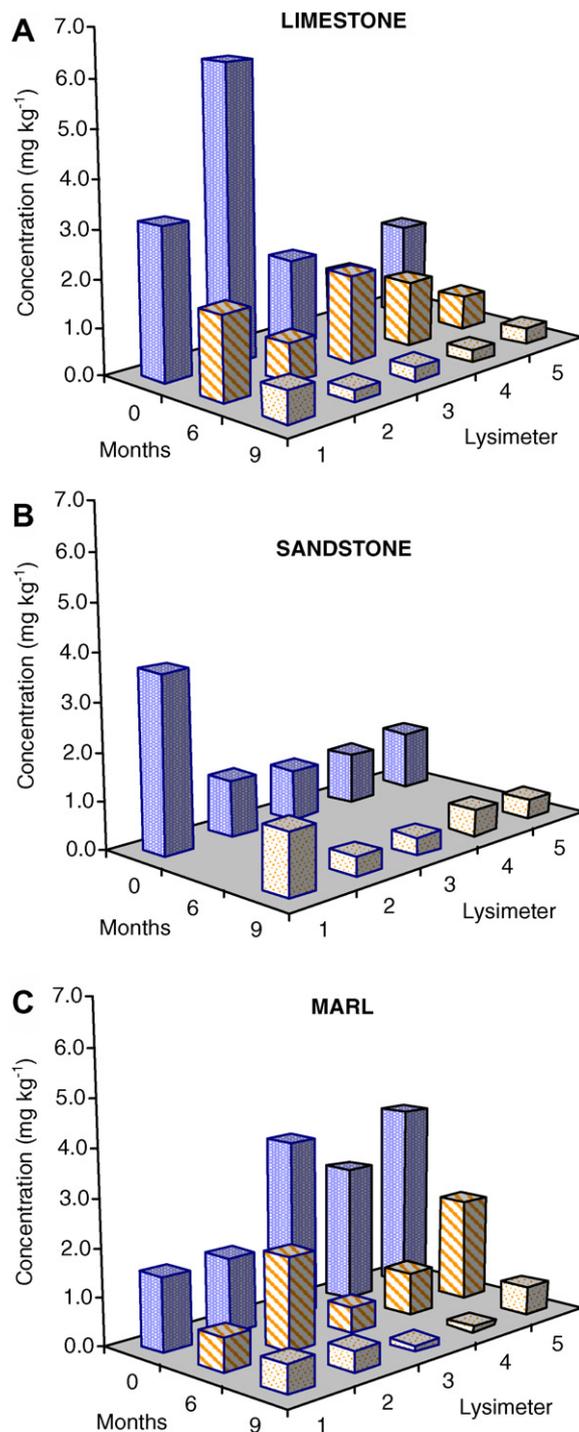

Fig. 5. Degradation of NP + NP1EO + NP2EO in soil developed from limestone (A), sandstone (B) and marl (C), with five curves in each graph corresponding to the five replicated lysimeters per soil type.

11–13 atoms of carbon. This could be due to the higher temperatures reached in that period (Figs. 1 and 2), which accelerated the process, or to the different soil sorption. It is worth noting that bulk organic matter did not follow the same pattern (the degradation in the first period was higher than in the second one).

3.4. NP, NP1EO and NP2EO degradation

NP2EO degrades to NP1EO, and then to NP. Later NP undergoes a ring cleavage and the oxidation of the alkyl chain (Ahel et al., 1994). Thus, it is not surprising that NP showed lower decay rates in the three types of soil (Fig. 5A–C). Variability in decay rates was high, as for LAS (furthermore LAS and NPEs varied in the same degree in a given sample for most of the experiments). Degradation of NP + NP1EO + NP2EO during the nine month incubation averaged 84% for limestone, 62% for sandstone, and 82% for marl (Table 3). We may note that estimations of the degradation rate for NP2EO may be subjected to substantial error, as the contents of this compound were close to LOD.

The degradation of NP + NP1EO + NP2EO and NP separately is commonly high in natural soils. Decomposition rates of as much as 70% after a three month incubation, and up to 95% after six months, with sludge application rates below 10 mg d.w. ha^{-1} have been reported in the literature (Laturnus et al., 1999; Petersen et al., 2003). The decomposition rate may increase in the presence of plants (Mortensen and Kure, 2003), and with small sewage sludge application rates (Laturnus et al., 1999). The results obtained in the present study are similar to those obtained under substantially different climatic conditions on agricultural soils.

Comparing the NP + NP1EO + NP2EO degradation in two periods of the experiment separately, 0–6 months and 6–9 months (Table 3), the reduction was higher in the last period, as for LAS, possibly as a result of higher temperatures reached or the different soil sorption.

3.5. Comparing decomposition rates

The temporal patterns of weight loss for LAS and NP + NP1EO + NP2EO were similar. These results were

Table 4
Decomposition rates of compounds and organic matter for the three different soils and results of an ANOVA analysis for the data

Compound	Limestone + 1.79% Sludge	Sandstone + 1.22% Sludge	Marl + 1.60% Sludge	1-way ANOVA (soil type)	
				F values	Significance
Decomposition rate k for 0–9 months (month^{-1})					
LAS					
Total LAS	0.42 ± 0.16	0.25 ± 0.09	0.35 ± 0.21	1.33	0.30
LAS C-10	0.46 ± 0.24	0.24 ± 0.10	0.34 ± 0.20	1.74	0.22
LAS C-11	0.40 ± 0.17	0.25 ± 0.07	0.33 ± 0.21	1.25	0.32
LAS C-12	0.41 ± 0.15	0.23 ± 0.09	0.34 ± 0.22	1.41	0.28
LAS C-13	0.45 ± 0.14	0.28 ± 0.08	0.37 ± 0.22	1.52	0.26
NP + NP1EO + NP2EO	0.22 ± 0.08	0.11 ± 0.02	0.24 ± 0.12	3.27	0.07
Total organic matter	0.028 ± 0.004	0.018 ± 0.004	0.016 ± 0.011	3.65	0.06
Organic matter due to the sewage sludge	0.21 ± 0.09	0.12 ± 0.06	0.21 ± 0.15	1.00	0.40
Decomposition rate k for 0–6 months (month^{-1})					
LAS					
Total LAS	<0.01–0.43		<0.01–0.40	0.44	0.53
LAS C-10	0.62 ± 0.42		0.71 ± 0.59	0.09	0.78
LAS C-11	<0.01–0.44		<0.01–0.38	0.15	0.71
LAS C-12	<0.01–0.45		<0.01–0.34	0.35	0.57
LAS C-13	<0.01–0.40		<0.01–0.37	0.46	0.52
NP + NP1EO + NP2EO	<0.01–0.37		0.14 ± 0.13	0.07	0.79
Total organic matter	0.032 ± 0.008		<0.001–0.039	0.71	0.42
Organic matter due to the sewage sludge	0.18 ± 0.04		0.29 ± 0.17	1.76	0.23
Decomposition rate k for 6–9 months (month^{-1})					
LAS					
Total LAS	0.84 ± 0.27		0.80 ± 0.37	0.05	0.83
LAS C-10	0.35± 0.33		<0.01–0.70	0.11	0.74
LAS C-11	0.79 ± 0.31		0.70 ± 0.33	0.22	0.66
LAS C-12	0.78 ± 0.29		0.74 ± 0.35	0.03	0.87
LAS C-13	0.99 ± 0.26		0.90 ± 0.42	0.15	0.71
NP + NP1EO + NP2EO	0.43 ± 0.15		0.43 ± 0.22	0.00	0.99
Total organic matter	0.014 ± 0.005		<0.001–0.035	1.94	0.20
Organic matter due to the sewage sludge	<0.01–0.56		<0.01–0.85	0.33	0.58

The values of decomposition rate are means ± standard deviation of $n = 5$ replicate runs, and results of a one-way ANOVA with the soil type as fixed factor are also shown.
The amount of organic matter added as sewage sludge was calculated as total organic matter minus initial organic matter of soils.

previously observed by Petersen et al. (2003) with agricultural soils.

LAS degraded more rapidly than NP + NP1EO + NP2EO considering the total length of the experiment (Table 4). Total organic matter of the mixture soil–sludge was weakly degraded since initial non-degradable organic matter of soil was much higher than organic matter introduced with sludge, but considering only the organic matter due to the sewage sludge the decomposition rate is similar to that of NP + NP1EO + NP2EO.

Large variability in decomposition rates of LAS and NP + NP1EO + NP2EO was observed by other authors working under field and greenhouse conditions (Petersen et al., 2003), and highlights the importance of spatial variability as experiments get closer to field conditions.

We found no significant effect of soil type on decomposition rate constants (Table 4). When considering the entire duration of the experiment, soil organic matter showed a trend towards higher decomposition rate in the limestone soil, and NP + NP1EO + NP2EO decomposition rates showed the same trend when applied on limestone and marly soils, but none of these was statistically significant.

The concentrations of LAS and NP + NP1EO + NP2EO were related by the following equation:

$$\log\left[\text{mg NP} + \text{NP1EO} + \text{NP2EO kg}^{-1}\right]$$
$$= 0.522 \times \log\left[\text{mg LAS kg}^{-1}\right] - 0.834 \quad (1)$$

with a coefficient of linear regression (R^2) of 0.847. The slope of the regression corresponds to the ratio between the decomposition constant k of NP + NP1EO + NP2EO and the decomposition constant of LAS. We found no significant relation between LAS and NP + NP1EO + NP2EO concentrations, and soil organic matter concentration.

After using a repeated measures analysis of variance, we found a significant effect of time on the [LAS]/[NP + NP1EO + NP2EO] ratio ($F_{1,12} = 27.86$, $P < 0.01$), indicating that degradations were different for LAS and NP + NP1EO + NP2EO, which is in accordance with the differences found in the decomposition rates (Table 4). At the onset of the experiment, the values of the [LAS]/[NP + NP1EO + NP2EO] ratios were 92, 75 and 58 for limestone, sandstone and marl soils, respectively; nine months after sludge application, the ratios were 18, 19 and 28 for the same soils.

Fast degradation of LAS and NP + NP1EO + NP2EO in Mediterranean forest soils amended with sewage sludge may result in a fast decrease in toxicity, and suggests that these compounds may represent a relatively low risk for the environment when applied in the conditions of our experiment. Further studies on the impact of LAS and NPs... on soil community composition and function are needed to fully understand their impact on Mediterranean forest soils.

4. Conclusions

The levels of two typical groups of organic contaminants (LAS and NP + NP1EO + NP2EO) in Mediterranean forest soils amended with contaminated sewage sludge decreased substantially over a nine month incubation period under semi-arid conditions. As much as 96% of the applied LAS and 84% of the nonylphenolic compounds disappeared during this period.

Soil type had a marginally significant effect on the NP + NP1EO + NP2EO decay rate; the soils with the highest pH and organic matter contents showed the highest decomposition rates, but not on the LAS decomposition rate. Differences between forest soils may have been obscured by heterogeneity in sewage sludge distribution within the soil.

This study, along with further research on heavy metal dynamics and plant growth in sludge-amended soils, can help to optimize the management of biosolids and minimize the environmental risks associated to their use.

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