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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.

Keywords: Linear alkylbenzene sulphonates; Nonylphenol; Nonylphenol ethoxylates; Organic matter

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

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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).