

Environmental and Soil Safety of Major Surfactants: Alcohol Ethoxylates and Alkylphenol Ethoxylates

V. Andreu¹, E. Ferrer², J.L. Rubio¹, G. Font² & Y. Picó²

¹ Centro de Investigaciones sobre Desertificación-CIDE (CSIC,UV, GV), Camí de la Marjal s/n, Apdo. Oficial, 46470 Albal, Valencia, Spain

Teléfono: 3496 1220540, fax: 3496 1270967, e-mail: vicente.andreu-perez@uv.es

²Laboratori de Bromatologia / Toxicologia, Facultat de Farmàcia, Universitat de València, Av. Vicent Andrés Estellés sin, 46100 Burjassot, València, Spain.

Abstract

Alkylphenols (octyl and nonylphenol), alkylphenol polyethoxylates (APEOs), and alcohol ethoxylates (AEOs) have been determined in soil treated with sewage sludge from different locations. These compounds were isolated from soil by pressurized liquid extraction (PLE) using a mixture acetone-hexane (50:50 v/v), the extracts were cleaned up by solid-phase extraction (SPE) with C₁₈, and determined by liquid chromatography atmospheric pressure chemical ionization-mass spectrometry (LC-APCI-MS). The method enabled high-reliable identification by monitoring the corresponding ammonium adduct [M+NH₃]⁺ for AEOs and APEOs, and the deprotonated molecule [M-H]⁻ for octyl and nonylphenol. Recoveries, calculated spiking soil samples at different concentrations, ranged from 89 to 94 %, with limits of quantification from 1 to 100 µg/kg. The procedures was applied for determining octylphenol, nonylphenol, AEOs, and APEOs in soils amended with sludges from different waste water treatment plants located in the Valencian Community. Data obtained showed that these compounds are present in the treated soils.

Introduction

In Europe, about 8 million tons of sewage sludge are generated annually by waste water sewage treatment plants (WWSTPs), its use in soils to improve the organic matter content is one of the most popular actions for their elimination, reaching during the year 2005 as elevated percentages as 50% in Germany, 54% in Spain, 65% in France, and 71% in United Kingdom.

Alkylphenol ethoxylates (APEs) and alcohol ethoxylates (AEOs) are non-ionic surfactants widely used in paints, herbicides, pesticides, pulp and paper production, textile manufacturing, adhesives, leather products, rubber and plastics, as well as, in metalworking (as lubricants). Their main use remains, however, as detergents, for both household and industrial applications, because of properties such as relative ionic insensitivity and high absorptive behaviour. Degradation products (alkylphenols, alkylphenol monoethoxylates and alkylphenol diethoxylates) have endocrine disrupting effects (Magoarou, 2000; Kroght et al., 2003; La Guardia et al. 2001).

The European Commission (EU, 2000), to maintain or to improve the present rate of recycling and the organic matter content in sludge, has elaborated a draft called "Working Document on Sludge" to broaden the scope of the existing regulation. It proposes maximum concentration limits for various micro-contaminants, among them AEOs and APEOs. The limit value for the sludge concentration for agricultural use is 50 mg/kg dry matter, and comprises substances like nonylphenol and nonylphenol ethoxylates with one or two ethoxy groups.

The aim of this work was to develop and to optimise an analytical method for the simultaneous determination of octylphenol, nonylphenol, alkylphenol ethoxylates and alcohol

ethoxylates in soils treated with sewage sludge, by utilizing pressurized liquid extraction (PLE), the unambiguous identification of these kind of compounds by LC-MS, and to compare the concentrations of these compounds in forest soil treated with sewage sludge (the organic matrix) generated by different Waste Water Sewage Treatment Plants (WWSTPs) in the Valencian Community (Spain).

Material and Methods

Reagents.- Alkylphenols: octylphenol (OP) and nonylphenol (NP); alkylphenol ethoxylates: Nonidet 40 (NP₆₋₁₅EOs), Triton X-100 (OP₆₋₁₅EOs), nonylphenol monoethoxylate (NP₁EO), and the technical mixtures of nonylphenols (NP₁₋₅EOs) and octylphenols (OP₁₋₅EOs) with low ethoxylate grade; alcohol ethoxylates: hexaethylene glycol mono-octadecyl ether (C₈EO₆), hexaethylene glycol monodecyl ether (C₁₀EO₆), hexaethylene glycol monododecyl ether (C₁₂EO₆), hexaethylene glycol monotetradecyl ether (C₁₄EO₆) and hexaethylene glycol monohexadecyl ether (C₁₆EO₆) were provided by Aldrich (Madrid, Spain) and Symta (Madrid, Spain). Methanol and dichloromethane were from Merck (Darmstadt, Germany) and the deionized water was obtained with a system MilliQ. The solid phase used, C₁₈, was acquired from Analysis Vínicos (Tomelloso, Spain). Ammonium acetate and anhydrous sodium sulfate were provided by Scharlau (Barcelona, Spain).

Soils.- Six samples of the superficial horizon (A) of a forest soil (Rendzic Leptosol) were taken from a hillside degraded by forest fire and erosion, with orientation South-East. This soil presented a total carbonates content of 45.2, pH of 7.1 and Sandy-Loam texture. Once in the laboratory they were left to dry at room temperature 24 hours, passed through a 2mm sieve, homogenised and stored in polyethylene boxes sealed until analysis. Laboratory standard analytical methods were applied for the determination of the most important physical and chemical characteristics of these samples.

Each sample was treated with a 10% of sludges coming from a purifying plant, located in different areas of the Valencian Community and after 24 hours analyzed.

Extraction.- Five grams of soil were homogenized with anhydrous sodium sulfate, placed in a cylindrical cell of 22 ml of capacity, and extracted using PLE with an ASE system of Dionex (CA, USA) and a mixture of acetone-hexane (50:50, v/v) at 60°C and 550 psi. The 40 ml extract was evaporated to dryness, redissolved in 100 ml of water and extracted with a glass column that contained 500 mg of previously activated C₁₈ with 10 ml of methanol and 10 ml of water. The retained surfactants were eluted with 10ml of methanol. The extract was evaporated to 1 ml.

Liquid chromatography- mass spectrometry. - The chromatographic separation was carried out with a column Luna C₁₈ (150 x 4.6 mm), 5 µm Phenomenex (Madrid, Spain), using a methanol-water gradient (both solvents contain 5 mM ammonium acetate to obtain the ammonium adduct) with a flow of mobile phase of 1 ml/min. The gradient begins with 70% methanol in water during 16 min and next the methanol percentage increases to 95% up to 30 min and remains for 15 more min. Detection was carried out using a mass spectrometer equipped with an APCI source. The conditions of the APCI were for the alkylphenol ethoxylates and the alcohol ethoxylates: source in positive ionization mode, capillary voltage of 4000 V, corona current 4 µA, fragmentor 140 V, temperature of the APCI 400 °C and, temperature and flow of the drying gas, 350 °C and 3 l/min respectively. Nonylphenol and octylphenol, were detected in negative ionization mode and with corona current of 25 µA. The rest of conditions were identical.

Results and Discussion

The analytical parameters of the method are listed in Table 1. PLE followed by SPE clean-up provides high recoveries for all the compounds from soil samples spiked at the limit of quantification (LOQ), which was considered as the minimum concentration that provides recoveries >70%, and relative standard deviations (RSDs,%) < 20% and oscillated between 1 and 100 µg/kg. Recoveries were from 89 to 102%. The linearity was calculated for an interval of concentrations between the LOQ and hundred times the LOQ (although the linearity interval is bigger, it is difficult to find real samples with higher content of surfactants). The correlation coefficient was in all cases > 0.994.

Table 1. Mean Recoveries (R,%), relative standard deviation (RSDs,%), linear concentration range, correlation coefficient (r), and limit of detection (LODs) obtained for spiked soil samples (n=5).

AEOs	Accuracy and precision			Linearity		LODs (µg/kg)
	Concentration (mg/kg)	R (%)	RSDs (%)	Range (mg/kg)	R	
C ₈ EO ₆	0.01	90	16	0.01-1	0.997	3
C ₁₀ EO ₆	0.01	94	14	0.01-7.4	0.999	3
C ₁₂ EO ₆	0.01	91	14	0.01-1.0	0.999	3
C ₁₄ EO ₆	0.01	96	12	0.01-1.0	0.998	3
C ₁₆ EO ₆	0.01	96	12	0.01-1.0	0.998	3
NP	0.1	97	19	0.1-10	0.997	30
NP ₁ EO	0.01	89	13	0.01-1.0	0.998	3
NP ₂ EO	0.005	90	15	0.005-0.5	0.997	1
NP ₃ EO	0.005	94	12	0.005-0.5	0.999	1
NP ₄ EO	0.005	91	17	0.005-0.5	0.999	1
NP ₅ EO	0.005	89	13	0.005-0.5	0.994	1
NP ₆ EO	0.005	92	13	0.005-0.5	0.997	1
NP ₇ EO	0.001	89	15	0.001-0.1	0.998	0.3
NP ₈ EO	0.001	90	16	0.001-0.1	0.997	0.3
NP ₉ EO	0.001	94	15	0.001-0.1	0.999	0.3
NP ₁₀ EO	0.001	91	14	0.001-0.1	0.999	0.3
NP ₁₁ EO	0.001	95	10	0.001-0.1	0.995	0.3
NP ₁₂ EO	0.001	94	9	0.001-0.1	0.998	0.3
NP ₁₃ EO	0.001	89	19	0.001-0.1	0.998	0.3
NP ₁₄ EO	0.001	90	16	0.001-0.1	0.997	0.3
NP ₁₅ EO	0.001	94	17	0.001-0.1	0.999	0.3
OP	0.1	91	15	0.1-10	0.999	30
OP ₁ EO	0.01	89	18	0.01-1.0	0.998	3
OP ₂ EO	0.005	90	17	0.005-0.5	0.997	1
OP ₃ EO	0.005	94	12	0.005-0.5	0.999	1
OP ₄ EO	0.005	91	12	0.005-0.5	0.999	1
OP ₅ EO	0.005	97	11	0.005-0.5	0.994	1
OP ₆ EO	0.005	99	12	0.005-0.5	0.996	1
OP ₇ EO	0.001	89	19	0.001-0.1	0.998	0.3
OP ₈ EO	0.001	90	16	0.001-0.1	0.997	0.3
OP ₉ EO	0.001	94	14	0.001-0.1	0.999	0.3
OP ₁₀ EO	0.001	91	14	0.001-0.1	0.999	0.3
OP ₁₁ EO	0.001	102	11	0.001-0.1	0.997	0.3
OP ₁₂ EO	0.001	99	10	0.001-0.1	0.996	0.3
OP ₁₃ EO	0.001	89	19	0.001-0.1	0.998	0.3
OP ₁₄ EO	0.001	90	16	0.001-0.1	0.997	0.3
OP ₁₅ EO	0.001	94	14	0.001-0.1	0.999	0.3

The different compounds were identified by the presence of the adduct with ammonium $[M+NH_3]^+$ or the deprotonated molecule $[M-H]^-$. Figure 2, shows the chromatograms obtained injecting extracts of a soil that does not contain surfactants and this soil spiked at 0.1 mg/ kg with the different surfactants. Soil extracts are clean without interfering substances. In the same figure, the mass spectrum corresponding to the studied nonylphenol ethoxylates (n=1-15) is inserted. The method was applied to the determination of nonylphenol, octylphenol, AEOs and APEOs in soil treated with sludges from six WWSTP of the Valencian Community. Results presented in Table 2 demonstrate that these compounds are incorporated to the treated soils. In three of them, the presence of octylphenol was detected in significant amounts, as well as nonylphenol and its ethoxylates (until $n > 5$). The presence of AEOs is scarce although it is also detected in some samples.

Figure 2. Chromatograms (A) soil in which surfactants presence was not detected and (C) fortified soil at 0.1 mg/kg with the different compounds. The spectrum corresponding to the nonylphenol ethoxylates is shown as an insert.

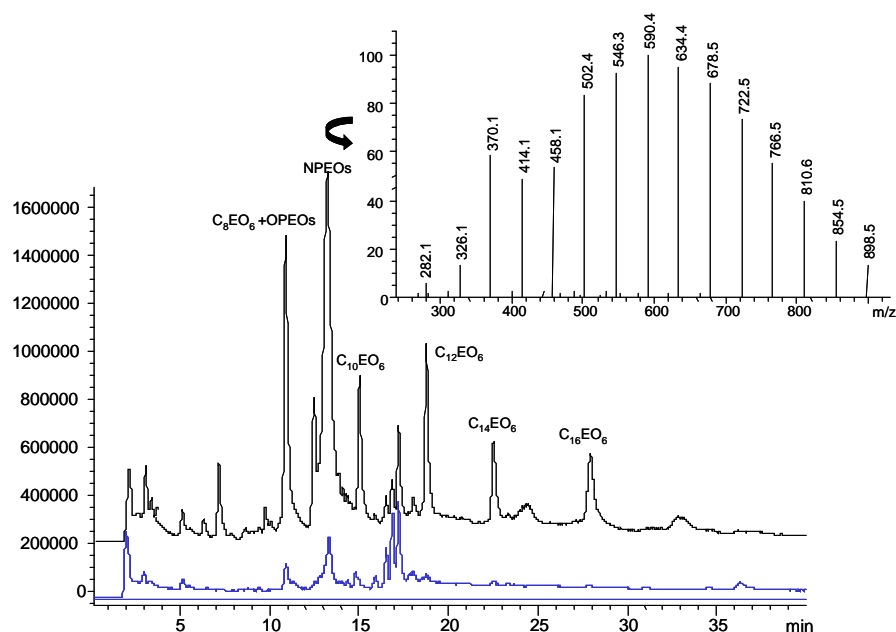


Table 2. Concentration (mg/kg) of the different compounds in soil.

Coming from sludge	OP	NP	OPEOs	NPEOs	AEOs
T0	0.5	0.5	0.8	0.9	--
T1	1	2	5	4	1
T2	1	3	0.2	0.4	0.1

Conclusion

The determination of neutral surfactants by PLE, SPE and LC-MS is a sensitive, selective and reliable analytical method. The application to soil treated with organic amendments demonstrates the presence of these compounds that are a risk to control especially in agricultural soils.

References

- European Union EU (2000). Working Document on Sludge, 3rd Draft-Brussels, April 27, pp. 1-19.
 Krogh, K.A., Mogensen, B.B.; Halling-Sorensen, B.; Cortés, A.; Vejrup, K.V.; Barceló, D. (2003). Analysis of alcohol ethoxylates and alkylamine ethoxylates in agricultural soils using pressurized liquid extraction and liquid chromatography-mass spectrometry. *Anal. Bioanal. Chem.* (2003) 376: 1089-1097.

La Guardia, M.J.; Hale, R.C.; Harvey, E.; Mainor, T.M. (2001) Alkylphenol ethoxylate degradation products in land-applied sewage sludge (Biosolids). *Environ. Sci. Technol.* 35, 4798-4804.

Magoarou, P (2000). En: *Proceedings of Workshop on Problems around sludge* (Langenkamp, H., Marmo, L., ed), EUR 19657 EN, p.8