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Application of liquid chromatography–electrospray-tandem mass spectrometry for the identification and characterisation of linear alkylbenzene sulfonates and sulfophenyl carboxylates in sludge-amended soils

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Abstract

A novel procedure was developed for the simultaneous determination of linear alkylbenzene sulfonates (LAS) and their major metabolites, sulfophenyl carboxylates (SPC), in sludge-amended soil. After pressurised liquid extraction with methanol/water (90:10) and a clean-up on C_{18} solid-phase extraction cartridges, final analysis was done by ion-pair liquid chromatography–electrospray–tandem mass spectrometry (LC–ESI–MS/MS). With this method, SPC with 5–13 carbon atoms in the aliphatic side chain were identified for the first time in agricultural soils treated with sewage sludge. Quantification of LAS and SPC in soil from 10 field sites, which differed in the history of sludge application, gave total concentrations of 120–2840 $\mu g\,kg^{-1}$ for LAS and of 4–220 $\mu g\,kg^{-1}$ for SPC. The data provided evidence for rapid biodegradation of LAS in the initial phase after sludge amendment with a transitory build-up of high concentrations of, mainly, short-chain SPC. Trace amounts of residual LAS and SPC were detected in soils having received the last sludge treatment 10 days to 4 years prior to sampling.

Keywords: Surfactants; Linear alkylbenzene sulfonates; Sludge-amended soil; Sulfophenyl carboxylates; Electrospray-tandem mass spectrometry

1. Introduction

In the Member States of the European Union the agricultural use of sewage sludge is, along with disposal to landfills, the most popular disposal route. Of the ca. 8 million tonnes (dry matter; dm) of sludge produced in European wastewater treatment plants every year, the percentage of reused sludge varies largely between the nations; for the year 2005 the reuse rates of sewage sludge for the most populated countries are predicted to reach levels as high as 50% in Germany, 54% in Spain, 65% in France and 71% in the United Kingdom [1]. Despite the valuable properties of sewage sludge, such as relatively high levels of organic matter and essential plant nutrients, the widespread application of sewage sludge in agriculture needs to be critically evaluated in view of the concomitant presence of a variety of inorganic and organic contaminants that may adversely affect crops and/or soil organisms [2]. Furthermore, the potential leaching of these contaminants into the subsoil may pose a threat to ground water supplies [3], which represent an important source of drinking water in Europe.

Against this background, the European Commission elaborated a draft of a "Working Document on Sludge" [4] to promote the use of sewage sludge in agriculture whilst improving the safety and harmonizing quality standards. This draft proposes cut-off limits for a series of organic micropollutants among which figure the anionic linear alkylbenzene sulfonate surfactants (LAS; Fig. 1). These surface-active substances are listed as a restricted compound in the draft document (cut-off value for agricultural use was set to 2600 $mg\,kg^{-1}$) due to their presence at high levels in sludge. In aerobic sludge concentrations have been reported to be in the range 100–500 $mg\,kg^{-1}$ [5–7], but in anaerobically digested sludge reported levels were between 1000 and 20,000 $mg\,kg^{-1}$ [6,8,9] with some exceptionally high values

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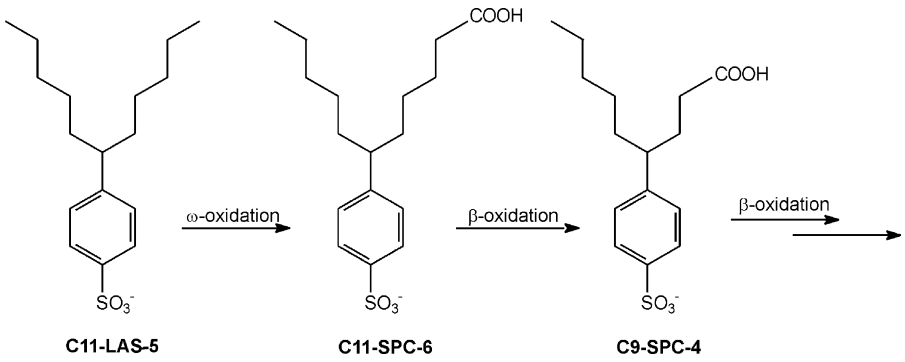

Fig. 1. Scheme illustrating microbial degradation of C11-LAS into C11-SPC and further to C9-SPC. Number after compound acronym indicates position of the sulfophenyl moiety on the carbon chain.

of up to 52,000 mg kg^{-1} [10]. In the latter sludge type, LAS concentrations are substantially higher compared with the aerobic sludge as the aromatic sulfonates do not biodegrade to a substantial extent under anaerobic conditions.

The first methods for the determination of LAS components—comprising the four alkyl homologues C10–C13, each of which with its positional phenyl isomers—in samples of sludge-amended soils date back to the late 1980s [5,11,12]. In these studies, Soxhlet or reflux extraction with methanol, clean-up on solid-phase extraction cartridges (reversed-phase (RP) or strong anion-exchange material) and analysis by high-performance liquid chromatography (HPLC) equipped with ultraviolet (UV) or fluorescence (FL) detectors were employed. By the mid-1990s, a series of methods had been published dealing with the occurrence, distribution and biodegradability of LAS in soils. These studies reported LAS levels in soil samples of about 50–150 mg kg^{-1} [5,13,14] directly after sludge application, which thereafter dropped rapidly within a few weeks to concentrations in the low mg kg^{-1}/high μg kg^{-1} range (limits of detection (LOD) achieved with UV or FL detectors typically between 0.2 and 1.0 mg kg^{-1}). Under field conditions, half-lives of LAS in soils were calculated to be 7–33 days [5,15]. This ready biodegradability and also the potential for ultimate mineralisation were corroborated by laboratory data gathered from studies on ^{14}C-LAS [16–18]. In the recent past, and in particular since the release of the EU "Working Document on Sludge" [4], the question on the whereabouts [2,19–21] and on possible risks [23–28] of LAS in soils has received further attention with studies performed by both industrial and academic researchers. Despite the large body of literature dealing with the fate and behaviour of LAS in sludge-amended soils—a comprehensive review on this subject is given in [29]—a gap of knowledge still exists with respect to the identity and occurrence of their degradation products in the terrestrial environment. It has been known for almost 40 years [30] that aquatic microbial communities biotransform LAS into sulfophenyl carboxyates (SPC; Fig. 1), via a mechanism initiated with an ω-oxidation of the alkyl side chain followed by a series of β-oxidations which result in the formation of a complex mixture of SPC homologues each of which with its positional phenyl isomers (Fig. 1) [30–32].

With the advent of sophisticated and robust mass spectrometric instruments equipped with atmospheric pressure ionisation interfaces the analysis of polar organic compounds became possible, and the identification of LAS degradation intermediates at trace amounts was accomplished in wastewaters [33], river waters [34,35], coastal waters [36] and even in drinking waters [37,38]. But as yet the presence of SPC in sludge-amended soils has not been confirmed, nor could other metabolites be determined in natural soils (though specific LAS-degrading soil bacteria cultured under laboratory conditions were identified [39,40]). This can be traced to the lack of sensitive and selective methods for identifying SPC in such complex matrices, while the lack of authentic standards has posed a further problem for a reliable quantitative analysis.

Thus, the objectives of the present work were: (i) to develop a sensitive analytical protocol for the simultaneous determination of LAS and SPC in sludge-amended soils employing pressurised liquid extraction (PLE); (ii) to unequivocally identify and characterise SPC by means of electrospray–tandem mass spectrometry (LC–ESI–MS/MS); (iii) to compare environmental concentrations of both sulfonated compound classes in soil samples from agricultural fields differing in the history of sewage sludge application.

2. Experimental

2.1. Standards and reagents

HPLC-grade 'Suprasolv' solvents water, acetonitrile and methanol were purchased from Merck (Darmstadt, Germany). Acetic acid (96%, puriss.) and hydrochloric acid (p.a.) were from Merck, triethylamine (>99.5%, puriss.) from Sigma–Aldrich (Madrid, Spain). Ethylenedinitrilo tetraacetic acid, di-sodium salt (EDTA–Na_2; p.a.) was obtained from Boehringer Mannheim (Mannheim, Germany). Commercial LAS with low dialkyl tetralinsulfonate content (<0.5%)