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Occurrence of high-tonnage anionic surfactants in Spanish sewage sludge

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ABSTRACT

Agricultural application has become the most widespread method of sewage sludge disposal, being the most economical outlet for sludge and also recycling beneficial plant nutrients and organic matter to soil for crop production. As a matter of fact, the European Sewage Sludge Directive 86/278/EEC seeks to encourage the disposal of sewage sludge in agriculture applications and regulate its use to prevent harmful effects on the soil environment. At the present time, the sewage sludge Directive is under revision and a possible cut-off limit for some organic chemicals may be implemented. Linear alkylbenzene sulphonate (LAS), the main synthetic anionic surfactant, has been included in the draft list of chemicals to be limited. The present research work deals with the monitoring of LAS and soap in Spanish sewage sludge. The average concentration of LAS found in anaerobic sewage sludge samples was 8.06 g/kg, higher than the average values for European sludge. Besides, it has been also found that more than 55% of Spanish anaerobic sludge would not fulfil the limit proposed by the 3rd European Working paper on sludge. As a consequence, the implementation of the limit for LAS would make the disposal of most Spanish biosolids for agricultural applications almost impossible. Regarding the mechanisms why anionic surfactants are found in sludge, two surfactants are compared: LAS and soap, both readily biodegraded in aerobic conditions. Irrespective of the anaerobic biodegradability of soap, its concentration found in sludge is higher than LAS (only anaerobically biodegradable under particular conditions). The relevance of anaerobic biodegradation to assure environmental protection is discussed for this case.

1. Introduction

The implementation of the Urban Waste Water Treatment Directive 91/271/EEC in all Member States is increasing the quantities of sewage sludge requiring disposal. The annual sewage production for the 25 countries of the European Union (EU) was estimated to be higher than 10 million tons of dry sludge (Laturnus et al., 2007) and this quantity is expected to increase in the future due to the strong demand of cleaner sewage water and the increasing population. Moreover, the Sewage Sludge Directive 86/278/EEC seeks to encourage the disposal of sewage sludge in agriculture applications and regulate its use to prevent harmful effects on the soil environment. As a matter of fact, the EU 3rd Working paper on sludge also suggested that sludge should be used when there is an agronomic interest for the crops or the quality of soil can be improved (EU Working paper on sludge, 2000). The treated sludge contains large quantities of organic matter (60–70% of dry matter during aerobic digestion, 40–50% during anaerobic digestion) and nutrients (around 3% of phosphorus and 1.5% nitrogen) (Laturnus et al., 2007). Hence, agricultural application has become the most widespread method of disposal (i.e. more than 55–60% in Spain or more than 65% in Denmark), being the most economical outlet for sludge and also recycling beneficial plant nutrients and organic matter to soil for crop production (Smith, 1996). Agricultural use of raw sludge is encouraged by national authorities as the best way for recycling (Bresters et al., 1997) and it is widely recognised that valorisation of sludge is desirable (Otero et al., 2003). Other disposal routes are incineration and land-filling. For both cases, the organic matter and nutrients are lost and the waste management problem is transformed but not solved (carbon dioxide and methane emissions, respectively). Considering the United States law framework, the EPA regulations for sewage sludge disposal and use (the Standards for the Use or Disposal of Sewage Sludge at Section 40 of the Code of Federal Regulations Part 503) establish numeric limits, management practises, and operational standards to protect public

Abbreviations: LAS, Linear alkylbenzene sodium sulphonate; HERA, Human and environmental risk assessment; EPA, US Environmental Protection Agency; WWTP, Waste water treatment plant; SS, Sum of squares; DF, Degrees of freedom; MSS, Mean squares.

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health and the environment from adverse effects of chemical and microbiological pollutants in sewage sludge. EPA has conducted three national surveys for purposes of identifying contaminants in sewage sludge coming from sewage facilities treating more than one million gallons of waste water per day. Although surfactants were not included in these surveys; the EPA is encouraged to review existing sewage sludge regulations at least every two years (Targeted National Sewage Sludge Survey, EPA. 2009). Moreover, Harrison et al. (2006) found more than 516 organic compounds in US sludge samples. Similarly, Cai et al., (2007) investigated the presence of organic compounds by GC–MS in sewage sludge during composting in China.

To our knowledge, no limit has been particularly proposed for LAS in these countries. Moreover, the EPA reports that about 50% out of the total treated sludge is being recycled to land and recommends its use as biosolids to fertilize fields for raising crops. Additionally, Fulazzaky et al. (2009) reviewed the problems of sludge pressure in Indonesia due to the potential increase in practises of legal and illegal logging as well as the increasing land and water demands. They concluded that application of sludge on the agricultural lands would promote sustainable development.

With respect to the current European legislation, the sewage sludge Directive established a maximum value for the amount of heavy metals in sludge and also the proper dose of sludge to avoid pollution of soils. At the present time, the sewage sludge Directive is under revision and a possible cut-off limit for some organic chemicals may be implemented even though whether they may provoke adverse effects on the environment via plant-uptake or soil leaching still remains a controversial discussion. Considering the case of LAS, which is the main synthetic anionic surfactant used in the formulation of laundry detergents and cleaning products, it is not clear whether a limit will be finally implemented (2.6 and 5 g/kg have been proposed in several drafts). In fact, there is profuse scientific literature dealing with its environmental fate, behaviour and risk assessment for many environmental compartments: water, sediments, soil or sewage treatment plants (HERA report, 2007). Regarding the fate of LAS in waste water treatment plants, LAS is a ready-biodegradable chemical and it is well-known that high removal of LAS is achieved in sewage treatment plants (Temmink and Klapwijk, 2004). Additionally, LAS tends to precipitate in the presence of calcium ions and to adsorb into solid matrices. As a result, the physical–chemical properties of most surfactants may result in a significant partitioning between aqueous and solid phase in the aquatic environment (Berna et al., 2007). Since sewage sludge is often anaerobically stabilised and considering that LAS is not degraded under anaerobic conditions in laboratory tests, LAS has been misleadingly seen as a potential risk for soil organisms. Besides, much research work has been done in order to monitor the presence of LAS in environmental solid matrices (Jensen and Jepsen, 2005; Schowanek et al., 2007) and to study the risk associated to the application of LAS-containing sludge to agricultural soil and terrestrial environments (De Wolf and Feijtel, 1998; Jensen et al., 2001, 2007; Krogh et al., 2007). According to the latter risk assessment literature, the predicted environmental concentration (PEC) for LAS is lower to the non-effect concentration (PNEC), giving a risk quotient (RQ) lower to 1. That means the concentration of LAS does not pose a risk for fauna and flora of environmental compartments. For instance, the risk quotient for LAS in sewage treatment plants is only 0.08. Considering the risk in soils (including sludge-amended soils), the RQ is 0.68. However, as the main mechanism for the presence of anionic surfactants in environmental solid matrices is the precipitation and adsorption in presence of salts (Berna et al., 2007) rather than the lack of anaerobic biodegradation, the environmental and legal consequences of the presence of surfactants in sewage sludge should be discussed. Therefore, the main assumption of this research paper is that the potential limit could render agricultural use of sludge almost unviable and that the inherent properties (water solubility, precipitation or adsorption) rule the presence of surfactants in solid compartments rather than the anaerobic biodegradability of the molecule. Thus, this paper is focused on the determination of high-tonnage anionic surfactants (LAS and metallic salts of long-chain fatty acids, i.e. soap) in Spanish sewage sludge samples.

2. Materials and methods

2.1. Sludge samples

Fifty one waste water treatment facilities were monitored during 2006–2007. The monitoring comprised four sampling periods and included several sludge treatment modes: aerobic, anaerobic, chemical, composting, drying, no treatment, etc. All WWTP were monitored in one of the sampling periods and only selected WWTP were monitored during the whole sampling periods. LAS was determined for all sludge samples while soap was analysed in a number of samples for comparison purposes.

2.2. Determination of LAS in sewage sludge samples

Commercial LAS (a complex mixture of homologues and isomers with alkyl chain length C10–C13) was used for calibration purposes. 2-phenyl C8 LAS was used as internal standard.

The analysis of LAS comprises the following stages: i) microwave-assisted extraction (MARS5, CEM Corp., New Jersey, USA) of LAS with 25 mL methanol (5 g of sludge, 1600 W at 70 bar, 15 min); and ii) RP-HPLC (Agilent 1100, Agilent Technologies, Santa Clara, USA) determination using C18 columns (RP-C18 Licrhospher 250 mm × 4.6 mm i.d. × 5 μm film thickness) as stationary phase and being water/acetonitrile (95:5) and acetonitrile the mobile phases (flow 1.0 mL/min, initial flow of acetonitrile 70%, then 50% at 20 min and 70% at 25 min). Triethylamine and acetic acid (both 5 mM) were used as buffer in the water mobile phase. The injection volume was 100 μL and a fluorescence detector (excitation 232 nm, emission 290 nm) was used. HPLC determination. It must be pointed out that no pre-concentration/purification stage was required, so the analysis time was reduced in comparison to previous analytical methods (López et al., 2003).

2.3. Determination of soap in sewage sludge samples

Fatty acids with alkyl chain length C8–C20 and tridecanoic acid (source of the internal standard) were obtained from Merck (Darmstadt, Germany). All other reagents and solvents were analytical grade: potassium carbonate, potassium chloride, ethylenediaminetetraacetic tripotassium salt (EDTA-3K), calcium chloride, acetone, 2-propanol, petroleum ether and methanol. The derivatization reagent 2,4-dibromoacetophenon (DAP) was also purchased from Merck. Solutions of calcium soap homologues from C8 to C20 (50 mg/mL in 2-propanol) and internal standard (potassium tridecanoate, 100 mg/mL in methanol) were prepared and stored at 4 °C. All the devices were similar to LAS determination (microwave solid-liquid extraction. However, The HPLC was equipped with RP-C8-Lichrospher columns (250 mm, 4 mm i.d., 5 μm film thickness; Agilent Technologies, Santa Clara, USA).

Due to their inherent physical–chemical properties, soap easily precipitates if calcium or magnesium ions are present in water. Consequently, the water-insoluble calcium soap is found in environmental solid matrices rather than soluble sodium or potassium salts. Therefore, the analytical methodology must be aimed at the determination of insoluble salts of fatty acids: calcium soap. A brief