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ScienceDirect
Chemosphere 69 (2007) 1368–1373
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Concentrations and specific loads of glyphosate, diuron, atrazine, nonylphenol and metabolites thereof in French urban sewage sludge

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Received 27 February 2007; received in revised form 6 May 2007; accepted 8 May 2007
Available online 22 June 2007

Abstract

Indirect soil pollution by heavy metals and organics may occur when sewage sludge is used as fertilizer. It is essential to define the nature and amounts of pollutants contained in sewage sludge in order to assess environmental risk. Here, we present results from a one-year monitoring of herbicides (glyphosate, diuron and atrazine) and their major degradates in sewage sludge sampled from three wastewater treatment plants and one composting unit in the vicinity of Versailles, France. The concentrations of these compounds were determined, as well as these of the surfactant nonylphenol. We demonstrated the presence of glyphosate and aminomethylphosphonic acid at the mg kg^{-1} (dry matter) level in all samples. Diuron was detected at the μg kg^{-1} (d.m.) level, whereas its degradate and triazine compounds were below the limits of quantification. Nonylphenol amounts were higher than the future European limit value of 50 mg kg^{-1} (d.m.).

Keywords: Sludge treatment; Herbicide; Surfactant; Monitoring; Pollution; Specific loads

1. Introduction

Application of sewage sludge to cultivated soils is nowadays a political decision and an economic need in France. The fertilizer properties of this waste material, rich in organic matter, macro and micronutrients, are well documented. It has been assumed for many decades that the application of organic amendments improves the biological properties, the functioning and the structure of the soil (Tyler, 1982; Fliessbach et al., 1994). However, the benefits of sewage sludge spreading onto agricultural soils can be mitigated by the risks of indirect soil contamination. As sludge is the by-product of wastewater treatment plants (WWTPs), it contains numerous pollutants able to induce adverse effects on biological life, inside and outside the soil ecosystem, including heavy metals, persistent organic pollutants or possible pathogens (Mena et al., 2003; Fjällborg and Dave, 2004; Helaleh et al., 2005). The European Union for requires many years the control of sludge to avoid environmental contamination (EU, 1986). More recently, a review concerning priority organic pollutants was published by the European Union (EU, 2001). Furthermore, a draft for a future directive is intended to improve sewage sludge management with respect to human, animal and plant health, quality of ground and surface waters and long-term quality of the soil (Abad et al., 2005). But the regulation concerning sludge takes only into account classical persistent organic pollutants, phthalates and alkylphenols.

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0045-6535/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2007.05.022

Kolpin et al. (2006) demonstrated the urban contribution of glyphosate and its metabolite, AMPA, to wastewaters in the United States. Nevertheless, the occurrence of herbicides in sewage sludge is poorly documented. In Europe, only Plagellat et al. (2004) reported the contamination of sludge by diuron in Switzerland. Because herbicides are widely used in urban areas for weed control or biocidal applications, they may enter wastewaters, thus allowing postulating a wider contamination of sludge samples by herbicides. In the present study, our first aim was to determine the concentrations of glyphosate, diuron and atrazine and their main metabolites in sludge samples from three WWTPs and one composting unit near Versailles (France) over 1 year. The widespread contaminant nonylphenol, the main biodegradation product of the surfactant nonylphenol polyethoxylates in WWTPs, also used as formulating agent for pesticides, was taken into account. All the selected chemicals are recognized as endocrine disrupters exhibiting either estrogenic or anti-androgenic activities (Thibaut and Porte, 2004; Richard et al., 2005). We next studied the effect of sludge treatment on the concentrations of nonylphenol. Finally, we calculated the specific loads of all the chemicals quantified in the sludge samples.

2. Materials and methods

2.1. Characterization of sampling sites and sampling

Sewage sludge was sampled from three urban wastewater treatment plants and one composting unit in the vicinity of Versailles (France). In all cases, the treatment process included screening, grit removal, primary sedimentation with use of chemical coagulants (except the plant of St-Cyr), phosphorus and nitrogen elimination and conventional activated sludge treatment. The plants of Plaisir and Elancourt were each connected to a separate sewer system (SS) and an urban catchment area with moderate industrial activity (MI). The plant of Saint-Cyr has a similar catchment area, but it is connected to a combined sewer system (CS). The WWTP of Plaisir provided dried (pelleted) sludge, whereas sludge treatment was obtained by liming in Elancourt and Saint-Cyr. In the unit of Gazeran, sludge was composted with wood chips as a bulking material. Sludge also originated from several WWTPs, located in a rural area with a mixture of agricultural (breeding of cattle) and industrial activities (AI). Wastewaters were collected by several sewer systems, mainly of the combined type (CS). The concentrations of glyphosate, diuron, atrazine, nonylphenol and their main metabolites have been monitored monthly from July 2004 to June 2005 in sludge samples obtained from the WWTPs. Centrifuged samples were used for all analyses, because the highest extraction yields concerning the herbicides were obtained in these samples. Other samples were then collected after drying, composting or liming to show an effect of sludge treatment on chemical content. Unfortunately, some technical problems in the composting plant of Gazeran prevented a complete campaign of sampling. Sludge samples (1 kg wet weight) were collected in aluminium cans, frozen within 1 h after sampling and stored at −20 °C until analysis.

2.2. Chemicals and reagents

All chemicals and solvents were of analytical grade. *N*-phosphonomethylglycine (glyphosate), 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron) and 6-chloro-N^2-ethyl-N^4-isopropyl-chloro-1,3,5-triazine-2,4-diamine (atrazine) (99.5%, 99.0% and 99.0% purity, respectively), and their respective metabolites were purchased from Dr. Ehrenstorfer (GmbH, Germany). (2-^{13}C, 99%; ^{15}N, 98%)-glyphosate and ^{13}C, 99%; ^{15}N, 98%; Methylene-D_2, 98%)-AMPA in water at 100 μg ml^{-1} were provided by LGC Promochem, Teddington, UK. Atrazine-D_5 and diuron-D_6 in acetone solutions at 100 μg ml^{-1} were provided by Dr. Ehrenstorfer (GmbH, Germany). 4-Nonylphenol and 4-*n*-nonylphenol (purity >98.0%) was obtained from Lancaster (France) and Riedel de Haën (Germany). Other chemicals were from Sigma (France).

2.3. Analysis of glyphosate and aminomethyl phosphonic acid (AMPA)

The concentrations of glyphosate and AMPA in sludge samples were determined according to Ghanem et al. (2007). Briefly, the extracts obtained from alkaline extraction were purified on a strong anion-exchanger resin before FMOC-Cl derivatization on the same solid support. Samples were concentrated by reversed-phase SPE before analysis by LC-ESI-MS/MS in the MRM (Multiple Reaction Monitoring) mode.

2.4. Analysis of phenylurea and triazine compounds

Diuron and 1-methyl-3-(3,4-dichlorophenyl)urea (DCPMU), atrazine, deethylatrazine and deisopropylatrazine were analyzed according to Ghanem et al. (submitted for publication) using a multi-residue method. It consists of liquid–liquid extraction, a Florisil clean-up, and LC-ESI-MS/MS analysis in the MRM mode.

2.5. Analysis of nonylphenol

4-Nonylphenol in sewage sludge was determined using the following protocol. Fresh samples were dried at 40 °C and homogenized with a paddle stirrer. Then, 2-g dry aliquots were layered onto anhydrous Na_2SO_4 in an extraction thimble, spiked with internal standard (4-*n*-nonylphenol), and covered with Na_2SO_4. Nonylphenol was then Soxhlet-extracted with 150 ml methanol during 16 h. After cooling, the extract were dried onto Na_2SO_4 and reduced under vacuum to 2–3 ml. The concentrates were cleaned-up on a 8-g activated alumina column supplemented with 2 g Na_2SO_4. Nonylphenol was eluted with