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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 lg 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

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.

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 deter- mine 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.

Materials and methods

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 Gaz- eran, 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 high- est 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.

Chemicals and reagents

All chemicals and solvents were of analytical grade. N-phosphonomethylglycine (glyphosate), 3-(3,4-dichloro- phenyl)-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).

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.

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.

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 Na2SO4. Nonylphenol was eluted with 10 ml dichloromethane and 10 ml dicloromethane:methanol (1:1, v:v). A third elution with 5 ml pure methanol constituted a control. The two-first fractions were combined, supplemented with 5 ml isopropanol, and the mixture was concentrated to 2–3 ml for analysis. Nonylphenol was analysed by HPLC with fluorescence detection (HP 1050 series and 1046 A detector). Samples (10 ll) were analysed using an analytical C18 column (Vydac 201TP54, 250 x 4.5 mm, 5 lm particles). The solvent system was acetonitrile and water at a flow-rate of 1 ml min^{-1}, beginning with 50% acetonitrile, followed

by a linear increase to 100% acetonitrile over 25 min, a stationary phase of 10 min, before a return to the initial conditions. The HPLC column was maintained at 30°C. Both the fluorescence emitted at 310 nm after excitation at 229 nm and the UV absorption (200-400 nm) were monitored. In addition, peak identity was checked by GC–MS (EI) analysis in several samples.

Analytical features

The method for glyphosate and AMPA analysis showed mean recoveries of 70% (RSD < 9%) for glyphosate and 63% (RSD < 5%) for AMPA, using centrifuged sludge samples collected before liming, composting or drying. Limits of quantifications (LOQs, S/N of 5) were 35 and 50 $\mu g\ kg^{-1}$ d.m. (dry matter) for glyphosate and AMPA, respectively (Ghanem et al., 2007). The multi-residue method, developed for the other herbicides exhibiting more common physico-chemical properties, showed higher recoveries of 79%, 84%, 85%, 91% and 96% as mean values for atrazine, deisopropylatrazine, deethylatrazine, diuron and 3-(3,4-dichlorophenyl)-1-methylurea, respectively (Ghanem et al., submitted for publication). LOQs always ranged from 0.4 to 2 $\mu g\ kg^{-1}$ d.m. in sludge for the five compounds. Low RSD (< 3%) demonstrated good repeatability for the method developed and applied for monitoring. These results were not significantly modified by the type of sludge analyzed (centrifuged, limed, com- posted or dried). For nonylphenol, the method described above gave 98% recovery (RSD < 2%), whatever the type of sludge. The LOQ was 2.1 $mg\ kg^{-1}$ d.m. Methods involving LC-ESI-MS/MS analysis fulfilled the European Union requirements (EU, 2002).

Determination of specific loads for chemicals in sewage sludge

The release of a substance into a wastewater might be misinterpreted if only concentrations in sewage sludge are considered. By contrast, the specific load in sewage sludge per inhabitant connected per year is a more reliable para- meter (Kupper et al., 2004). The specific load for a chemical is defined as follows:

$L_{sp} = C_{ss} \times P_{ss} \times cap^{-1}$

where L_{sp} is a load of a specific chemical in the sewage sludge per inhabitant connected per year ($mg\ cap^{-1}\ y^{-1}$), C_{ss} the concentration of the chemical ($mg\ kg^{-1}$ d.m.), P_{ss} the production of aerobically or anaerobically centrifuged sewage sludge ($kg\ d.m.\ y^{-1}$) and cap the number of inhabitants connected to the WWTP.

Results and discussion

Concentrations of herbicides and nonylphenol in sewage sludge

Glyphosate, AMPA, diuron and nonylphenol were quantified in all the samples (Table 1). Concentrations of glyphosate and AMPA were found at the mg kg^{-1} (d.m.) level in the sludge. The highest mean values for glyphosate were detected in the samples from Plaisir and Elancourt (1.1 and 1.4 mg kg^{-1} d.m.), whereas sludge from Saint-Cyr was less contaminated (0.4 mg kg^{-1} d.m.). Accordingly, mean values of 20.3 (Plaisir), 11.5 (Elancourt) and 2.8 (Saint-Cyr) mg kg^{-1} d.m. were calculated in the sludge. The concentrations of AMPA should be attributed to glyphosate degradation. Nevertheless, aminophosphonates (EDTMP and DTPMP) contained in household cleaning products can be converted to AMPA in wastewaters and WWTPs (Nowack, 2003). That urban source could explain the high amounts of AMPA measured in our study. In contrast, only low concentrations of the herbicide, diuron, were detected. Samples from Saint-Cyr were the most contaminated (46.6 lg kg^{-1} d.m.) as compared to these of Plaisir and Elancourt (11.2 and 20.0 μg kg^{-1} d.m.) Sludge contamination by diuron was comparable to that reported in Switzerland (Plagellat et al., 2004). DCPMU, the metabolite of diuron, was never detected. As observed in studies published previously (Abad et al., 2005), concentrations of nonylphenol were high in all the samples. The highest mean concentration was found in the sludge from Saint-Cyr (161.4 mg kg^{-1} d.m.) and the lowest in samples from Plaisir and Elancourt (61.7 and 90.0 mg kg^{-1} d.m.). In all samples, concentrations of nonylphenol were equal or above the limit proposed in the draft for the future European sewage sludge directive (50 mg kg^{-1} d.m.).

Despite incomplete sampling, the data for Gazeran revealed a contamination level similar to that observed for Plaisir and Elancourt for glyphosate, AMPA and diuron. Although these compounds are widely used in urban areas as herbicides, it was difficult to define a clear relation- ship between sludge contamination and periods of weed treatment.

Finally, we were unable to quantify triazine compounds in all the samples analyzed. The use of atrazine for weed control was forbidden in 2003 in France. Our results indicate that these compounds are no longer released in the wastewaters entering the investigated WWTPs, or they are present at concentrations lower than the limits of quantification of our analytical method.

Effect of sludge treatment on the concentrations of nonylphenol

Because the recovery rates of our analytical method did not depend on the type of sludge analyzed for nonylphenol, we assumed that sludge treatment had an influence on its concentration in the final product (Table 2). The highest decreases (significant at $P < 0.001$) were 72% after drying and 31% after liming sludge from plants in Plaisir and Elancourt. Drying the sludge may modify the structure of the organic matter, and then increase the sequestration of the nonylphenol within the matrix. Heating the sludge (one min at 120 C) could contribute to partial volatilization of nonylphenol with the stream of water. Additional experiments are in progress to determine the effect of drying on sludge chemical content. Concerning the limed samples, the apparent decrease may be related to the addition of lime (ca. 30% by weight). In samples from Gazeran or Saint-Cyr, the decreases in nonylphenol contents were not significant.

Specific loads for chemicals in sewage sludge

The specific loads for diuron, glyphosate, AMPA and nonylphenol were calculated in the sludge samples from Plaisir, Elancourt and Saint-Cyr (Table 3). The lowest mean values were obtained for diuron in the range of 0.26–0.74 mg cap^{-1} y^{-1}. A similar calculation for glyphosate alone gave values between 5.43 and 30.10 mg cap^{-1} y^{-1}, and between 166 and 494 mg cap^{-1} y^{-1} when AMPA was considered. The loads calculated for nonylphenol ranged from 1424 to 2578 mg cap^{-1} y^{-1}.

It was expected that the loads for herbicides would be lower in sludge samples provided by WWTPs connected to separate sewer systems, as compared to these obtained in combined systems receiving runoff waters. The loads for glyphosate and AMPA did not follow that postulate, and they were the highest in sludge samples originating from Plaisir and Elancourt, two WWTPs treating mainly domestic wastewaters. These results are in agreement with a domestic origin of the aminophosphonates, which could be diluted in the WWTPs by runoff waters entering through the combined systems.

Conclusions

The present study demonstrates for the first time the presence of substantial amounts of herbicides (glyphosate and its metabolite AMPA, diuron) in sewage sludge originating from urban areas in France. The occurrence of nonylphenol in sludge was also confirmed. It

can be concluded that an important part of the herbicides detected comes from domestic households. Research should now focus on the identification of the main sources of these compounds. In that context, it should be of interest to determine the real contribution of phosphonic acids from cleaning products in the overall contamination of sludge by glyphosate and AMPA.

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Table 1. Concentration of herbicides and nonylphenol in centrifuged sludge samples

	Plaisir (SS-MI)	Gazeran (CS-AI)	Elancourt (SS-MI)	Saint-Cyr (CS-MI)
Glyphosate/AMPA (mg kg^{-1})				
July 2004	1.2/32.0	nm	2.3/15.6	0.3/2.1
August 2004	1.2/23.0	nm	2.1/20.9	0.3/2.4
September 2004	1.3/26.0	nm	2.9/19.6	0.1/1.5
October 2004	nm	nm	1.4/13.6	0.1/1.8
November 2004	0.6/13.4	0.8/15.2	1.4/14.5	0.1/2.0
December 2004	0.6/24.3	1.4/12.7	1.2/11.8	1.7/11.5
January 2005	1.8/33.3	nm	0.8/8.6	nm
February 2005	0.5/16.6	nm	0.2/2.3	nm
March 2005	0.8/9.6	0.9/11.8	0.8/6.5	0.3/2.1
April 2005	1.3/21.8	0.7/7.1	1.6/9.5	0.2/1.2
May 2005	1.4/10.8	1.2/15.3	1.0/8.4	0.2/1.7
June 2005	1.0/12.7	nm	0.4/6.1	0.1/1.7
Mean	1.1/20.3	1.0/12.4	1.4/11.5	0.4/2.8
Median	1.2/21.8	0.9/12.7	1.3/10.7	0.2/1.9
Minimum	0.5/9.6	0.7/7.1	0.2/2.3	0.1/1.2
Maximum	1.8/33.3	1.4/15.3	2.9/20.9	1.7/11.5
Diuron (µg kg^{-1})				
July 2004	9.8	nm	20.6	84.0
August 2004	16.4	nm	18.6	64.0
September 2004	13.0	nm	14.4	24.0
October 2004	nm	nm	11.2	33.0
November 2004	14.4	10.4	15.0	27.0
December 2004	8.2	9.9	37.8	47.2
January 2005	8.6	nm	36.4	nm
February 2005	8.0	nm	22.0	nm
March 2005	6.6	28.0	11.4	11.6
April 2005	8.8	30.0	27.0	61.0
May 2005	18.6	54.0	10.6	76.8
June 2005	11.2	nm	15.4	37.0
Mean	11.2	26.5	20.0	46.6
Median	9.8	28.0	17.0	42.1
Minimum	6.6	9.9	10.6	11.6
Maximum	18.6	54.0	37.8	84.0
Nonyphenol (mg kg^{-1})				
July 2004	38.7	nm	49.6	215.1
August 2004	16.5	nm	51.6	216.5
September 2004	25.8	nm	51.5	204.9
October 2004	nm	nm	96.6	152.6
November 2004	58.6	75.6	104.4	144.9
December 2004	104.3	150.7	81.1	183.3
January 2005	78.9	nm	94.0	nm
February 2005	71.6	nm	81.6	nm
March 2005	62.7	173.2	102.5	89.8
April 2005	124.9	111.2	124.5	nm
May 2005	21.6	153.4	135.5	129.2
June 2005	75.2	nm	117.4	116.1
Mean	61.7	132.8	90.9	161.4
Median	62.7	150.7	95.3	152.6
Minimum	16.5	75.6	49.6	89.8
Maximum	124.9	173.2	135.5	216.5

Results are given as mg or µg per kg dry matter.
nm: not measured (not considered for the calculation of the mean and the median).
SS: separate sewer system; CS: combined sewer system; MI: moderate industrial activity; AI: agricultural and industrial activities.

Table 2. Effect of sludge treatments on the concentrations of nonylphenol

WWTP and treatment	Samples analyzed	Mean concentrations		Decrease (%)
		Before treatment	After treatment	
Plaisir – drying	11	61.7 ± 34.4	17.3 ± 6.2	72***
Gazeran – composting	3	145.9 ± 31.7	119.9 ± 14.4	18 n.s.
Elancourt – liming	12	90.9 ± 28.9	62.5 ± 14.1	31*
Saint-Cyr – liming	9	161.4 ± 45.9	130.0 ± 35.8	19 n.s.

Mean concentrations are given as mg per kg dry matter.
n.s. Not significant.
* Significant at $P < 0.05$ using the non parametric Wilcoxon–Mann–Whitney test.
*** Significant at $P < 0.001$.

Table 3. Specific loads (mg/connected inhabitant per year) of herbicides and nonylphenol (maximum/mean/minimum) in sludge samples from 3 WWTPs

	WWTP		
	Plaisir (SS-MI)	Elancourt (SS-MI)	Saint-Cyr (CS-MI)
Diuron	0.43/0.26/0.15	0.85/0.45/0.25	1.34/0.74/0.38
Glyphosate	41.55/24.55/11.54	64.99/30.10/4.48	27.15/5.43/1.60
Glyphosate + AMPA	810/494/233	533/289/56	211/166/21
Nonylphenol	2883/1424/381	3037/2027/1112	3458/2578/1434

SS: separate sewer system; CS: combined sewer system; MI: moderate industrial activity.