The role of sludge conditioning and dewatering in the fate of nonylphenol in sludge-amended soils

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Abstract: One of the main concerns associated with the recycling of biosolids to arable land is their contamination by organic pollutants, like endocrine disruptors. Conditioning and dewatering are usually the last steps of the sewage sludge treatment, before its further utilization. The choice of the specific conditioning/dewatering method may have an effect, not only on the amount of residues in the biosolids, but also on the fate of these compounds in amended soils. Anaerobically digested wastewater sludge was conditioned at lab-scale by means of physical and chemical methods and subsequently dewatered by centrifugation. The produced biosolids plus non-conditioned and non-dewatered sludges were amended separately to soil and spiked with 14C radiolabelled single isomer of nonylphenol. The persistence and leaching potential of nonylphenol after an incubation period of three months were correlated to the sludge treatment method. In comparison to non-conditioned sludge, 54% and 72% higher amount of pollutant residues were extractable when freeze-thawed and limed sludge, respectively, were used. Conditioning of sludge with cationic polymer decreased the leaching potential of nonylphenol in sludge-amended soils, while liming increased it. Fractions of the model compound recovered as extractable and bound residues were analyzed in order to interpret nonylphenol fate.

Keywords: Bioavailability; Fate of nonylphenol; Leaching; Sludge conditioning and dewatering

INTRODUCTION
In the perspective of regulations concerning municipal water treatment, the global amount of sewage sludge production is expected to increase in the future. Since disposal routes such as sea or landfill disposal are already banned or will be prohibited in many countries, agricultural use and incineration are the main remaining sustainable options. Recycling in agriculture can be regarded as the more sustainable one. Nevertheless, the amendment with sludges polluted with xenobiotics presents a potential risk for ecosystems (Harrison et al., 2006). Persistent chemicals with toxic or endocrine disrupting activity may be taken up by organisms and have adverse effects and/or they can leach to groundwater.

Sludge treatment before agricultural use is a bounden practice. The steps of the processes, e.g. thickening, stabilizing, conditioning, dewatering vary from one wastewater treatment plants (WWTPs) to another. Sludge treatment was identified as a critical factor for the elimination rates of organic pollutants in treated solids. For instance, the timing of sludge was reported to favour the desorption of alklyphenols from sludge matrix through the deprotonation of the phenolic group, thus leading to biosolids with lower amounts of these compounds (Ivashechkin et al., 2004). Nonetheless, sludge treatment is expected to have an influence on the physico-chemical properties of the biosolids. Sorption and sequestration of contaminants to soil organic matter are determinant for the bioavailability of pollutants, i.e. the amount available to soil microorganisms for catabolism and anabolism and also for the overall toxicity to organisms. Additionally, sorption and bioavailability influence the leaching to groundwater. Moreover, sludge treatment may affect the microbial populations of sludge-amended soil, thus affecting xenobiotics degradation rates and pathways. This can occur either through effects on the microorganisms, which are contained in biosolids, or through indirect effects to the soil population due to the pH value, nutrients content, and chemical composition of the sludge.
Nonylphenol (NP) is one of the major toxicants in excess sludge (la Farré et al., 2001) and is the breakdown product of the widely used non-ionic surfactants nonylphenol polyethoxylates. NP is toxic to living forms and can affect biodiversity of ecosystems through its effects on the endocrine system of many organisms. The influence of sludge stabilization on the fate of NP on sludge-amended soils has been recently reported, as Hesselsoe et al. (2001) observed 10% less mineralization and 2-8% more residues of 4-NP after 38 days of incubation in soil amended with aerobically digested sludge instead of anaerobically digested sludge. La Guardia et al. (2001) compared the leaching potential of NP contained in two composted and one limed sewage sludges. The NP amount in the leachate derived from a leaching-simulation extraction was lower for the limed sample (1.2%) than for the composted ones (1.8–2.3%). Mortensen and Kure (2003) found higher residues of NP in composted biosolids than in soil amended with aerobically/anaerobically stabilized sludge. No significant differences were detected between a dewatered- and a mixture of dewatered and composted sludge (Xia and Jenong, 2004).

One common characteristic of all the above studies is that treated biosolids have been sampled from separate sources. Thus, the differently treated sludges vary in origin, properties and composition. In the present study, liquid sewage sludge was sampled from a local WWTP and aliquots were treated further at lab-scale according to different conditioning and dewatering methods. The aim of the study was to investigate the correlation between the sludge conditioning/dewatering treatment and the risk (persistence, leaching) concerning xenobiotics residues in sludge-fertilized soil. Indications about the mechanisms responsible for this correlation were also examined.

MATERIALS AND METHODS

Sludge sampling and treatment

Liquid mesophilic-anaerobically digested sludge (2.4% dry matter, DM) was sampled from Soers WWTP (Aachen, Germany). Sludge was conditioned using four various treatments, i.e. freeze-thawing (freezing at -21 °C overnight), addition of FeCl₃ (15% / DM), addition of Ca(OH)₂ and FeCl₃ (50% and 15% / DM), and addition of cationic polymer (Nerolan Wassertechnik GmbH Krefeld, Germany) (1.0% / DM), respectively. The conditioning chemicals were added in the form of aqueous solutions and correspond to maximal doses applied in practice (Ivashchekin et al., 2004). The aliquots were homogenized by shaking for 30 min at 180 rpm. The four conditioned sludges plus one non-conditioned were dewatered by centrifugation (3,500 g, 60 min).

Soil amendment and spiking

Three 1.5 g (wet mass, WM) aliquots of each dewatered sludge and non-dewatered sludge (as control) were amended to 13 g air-dried standard soil samples (loamy sand, organic C: 2.3%, pH: 5.7, LUFAS Speyer, Speyer, Germany). The eighteen sludge-soil systems were spiked with a single isomer of nonylphenol, i.e. the ¹⁴C-radiolabelled 4-[1-ethyl-1,3-dimethylpentyl]phenol (0.16 MBq, corresponding to 15 mg/kg of amended soil, DM). This isomer of NP was synthesized according to the method of Vinken et al. (2002) and it was uniformly labeled at the aromatic ring. This isomer was preferred to the commercially available technical mixture in order to circumvent analytical problems. p353-NP is one of the most relevant isomers of the technical mixture of NP in terms of abundance and effect (Russ et al., 2005; Preuss et al., 2006). Spiking of sludge-amended soil was performed by adding 4 mL aqueous solution spiked with 150 µL of ethanolic NP solution. Spiking corresponded to an irrigation of the soil until 90% WHC (100% WHC for the liquid sludge). The spiked soil-sludge mixture was homogenized by stirring before incubation.

Incubation of sludge-amended soils

The sludge-amended soils were incubated over a period of 95 days at 20 °C in flow-through systems in triplicate series (Telscher et al., 2005). During the incubation, the mineralization of labeled NP was determined by trapping the ¹⁴CO₂ in flasks containing 2M NaOH. 0.5 mL aliquots from the NaOH solution were sampled regularly for radioactivity measurement using Liquid Scintillation Counting (LSC, see below). Volatilized compounds were trapped in ethylene glycol traps.
**Soil extraction and fractionation**

After homogenization, 5 g aliquots from the incubated sludge-amended soils were extracted by a sequential extraction and shaking (180 rpm). The solutions used for liquid-liquid extraction were acetone (25 mL, 5 min), n-hexane (25 mL, 40 min), methanol (25 mL, 40 min) and NaOH 0.1 M (twice, 25 mL, 40 min). After each extraction step the slurries were centrifuged (3,500 g, 10 min) and the radioactivity was determined in 1 mL from the supernatants using LSC before pooling the organic extracts and alkali solutions separately. The NaOH extracts were later extracted by n-hexane to obtain the physically bound NP residues. The remaining NaOH phase was further fractionated by acidifying to pH<1 with HCl 3 M to humic acids (HA, precipitated) and fulvic acids (FA, dissolved). The radioactivity of the supernatant containing the fulvic acids fraction was measured by LSC. The extracted soils after sequential extraction were dried before taking samples for determining the radioactive residues bound to humin and minerals. On this stage the soil consisted of two fractions, i.e. a dark brown elastic layer which was considered to contain mostly the humin fraction and a light colored sandy material which was considered as the minerals fraction. The two fractions were separated manually and sampling (0.2-0.3 g) was performed respectively. Catalytic combustion and subsequent LSC measurement were carried out as reported elsewhere (Corvini et al., 2004).

Another 2 g aliquot from the incubated systems was subjected to a modified method of the U.S. Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP, SW-846, EPA Method 1311). Extraction was performed using an aqueous solution (40 mL) containing NaOH (0.13 M) and acetic acid (0.19 M) (pH~5) under gentle shaking (80 rpm) for 10 h. The radioactivity contained in 1 mL sample of the extract (after centrifugation, 3,500 g, 10 min) was measured by LSC. The leachate extract was later extracted by n-hexane for further analysis.

**LSC, HPLC**

Liquid scintillation counting was carried out using a Beckmann device (Corvini et al., 2004). The extracts from soil samples were filtered through Na₂SO₄, concentrated by a Rotary Evaporator and analyzed by HPLC coupled to radiodetection (Cirja et al., 2006).

**RESULTS AND DISCUSSION**

**Risk Assessment Indicators**

*Mineralization and volatilization.* The evolution of ^14^CO₂ produced by the mineralization of NP phenolic ring is presented in Figure 1A for the soils amended with six sludges. In general the mineralization was low, not exceeding 6% after 95 days of incubation (Figure 1B). FeCl₃ conditioning did not influence the process. Liming and freeze-thawing of the sludge amended to the soil led to a relative decrease of about 40% in the CO₂ produced from the mineralization of NP, in comparison to non-conditioned sludge amendment. Conditioning with the cationic polymer led also to low rates, especially towards the end of the incubation period. Concerning NP mineralization, amendment with non-dewatered sludge led practically to the same result as when equal wet mass of centrifuged sludge was applied. The variation in the mineralization rates for soils amended with the same type of sludge was not much lower than the deviation among the different types of sludge. The radioactivity in the ethylene glycol traps was very low (0.1-0.4% of applied radioactivity). No significant differences in the occurrence of volatilized compounds were observed among systems amended with the various sludges (data not shown).
Figure 1 Mineralization of the NP radiolabelled phenolic ring in soil amended with non-conditioned (CE), freeze-thawed (FT), FeCl₃ conditioned (FE), lime and FeCl₃ conditioned (LM), polymer conditioned (PO) and non-dewatered (LQ) sludge. A: evolution during incubation (average of triplicate series) B: mineralized NP after 95 days of incubation (average of triplicates, error bars indicate minimum and maximum values obtained).

Extractable NP and degradation products. The radioactivity, which was recovered by extracting the incubated soil-sludge mixtures with organic solvents, was characterized by HPLC analysis. The amounts of NP and its degradation products were determined. After incubation of the eighteen systems 44-87% of the spiked radioactivity was extractable by organic solvents. Depending on the system considered, 73-96% of this radioactivity corresponded to the parent compound. NP was considerably persistent, since extractable NP ranged between 33% and 83% (Figure 2A). A comparison with mineralization data shows that the amendments, which led to relatively diminished mineralization (freeze-thawed and limed sludge), were also characterized by a high amount of unaltered parent compound at the end of the incubation period. Although the data were subject to high variation, a correlation between the high mineralization rates with increased amounts of degradation products was observed (Figure 2B), except for polymer conditioned sludge. For the latter, despite a decreased mineralization rate, the amount of NP available to organic solvents was as low as in soils amended with non-conditioned sludge (Figure 2A).

Figure 2 Extractable residues of NP (A) and rest of extractable radioactivity (B) after 95 days of incubation, expressed in% of applied NP, in soil amended with non-conditioned (CE), freeze-thawed (FT), FeCl₃ conditioned (FE), lime and FeCl₃ conditioned (LM), polymer conditioned (PO) and non-dewatered (LQ) sludge.
Figure 3 NP (A) and rest of radioactivity (B) amount extracted through leaching-simulation extraction after 95 days of incubation, expressed as % of applied NP, in soil amended with non-conditioned (CE), freeze-thawed (FT), FeCl₃ conditioned (FE), lime and FeCl₃ conditioned (LM), polymer conditioned (PO) and non-dewatered (LQ) sludge.

Leaching potential. TCLP is used by the U.S. EPA to determine the mobility of contaminants present in wastes. The method simulates leaching from a landfill under a mismanagement scenario (unlined landfill). By following a similar protocol, the leaching potential was evaluated by investigating the extractability of NP and degradation products in the present study. At the end of the incubation, the leachate extract contained 3-5% of the radioactivity spiked. In contrast with the organic solvents extract, further HPLC analysis showed that only 47-66% of the radioactivity was attributed to NP. In most of the cases an average of 2.5% of the parent compound spiked was available to the aqueous phase after three months (Figure 3A). However, it was observed that NP leaching potential from soil amended with limed sludge was higher than for other treatments. On the contrary, less NP could be mobilized from the systems where polymer conditioned sludge was used. For the latter, the amount of radioactivity corresponding to NP metabolites in the leachate-extract was also the lowest (Figure 3B).

Discussion - Interpretation of NP fate data

General fate. NP was very persistent, being degraded only partially after three months of incubation. In the literature much higher degradation and mineralization rates are often reported. The difference can be attributed to the use, in the current study, of a single branched isomer of NP. When linear 4-NP was spiked at comparable levels to soil-sludge mixtures at similar ratio and water content, about 50% mineralization was observed after two months (Gejlsbjerg et al., 2001). Linear NP spiked was completely degraded after one month, while significant portion of the naturally occurring branched NP was detectable under the same conditions (Mortensen and Kure, 2003). Concerning leaching, the results are in agreement with literature data (La Guardia et al., 2001) and characteristic of the hydrophobicity of NP (log Kᵣₛ = 3.3-4.5, Ivashechkin et al., 2004).

Variation in parallel incubations. Considering the parallels conducted with the same type of sludge, the variation in fate, although not very high, was comparable to the deviations among the sludges. One possible explanation is the heterogeneity of distribution of spiked NP between soil and sludge organic matter. The sludge aggregates size, which was not constant due to the low dewaterability of sludge under the experimental conditions (12-21% DM for the obtained biosolids) may have played a role as well.

Effect of freeze-thawing. Soils amended with freeze-thawed sludge were characterized by low mineralization rates and high extractable residues of NP. This observation can be theoretically attributed either to a lower bioavailability of NP or to an influence of freezing on the endogenous microbial population of sludge. Bioavailability is linked to physico-chemical properties of sludge. The ratio between “leached” and extractable (not bound) residues served as evidence concerning the sorption of NP to the organic matter of the soil-sludge mixtures. By calculating this ratio separately for NP and degradation products (Table 1), interesting conclusions...
could be derived. The NP leaching potential for soil amended with freeze-thawed sludge was similar to that observed when soil was amended with non-conditioned sludge, although NP residues were lower in the latter case. A possible reason for the lower availability of NP in freeze-thawed sludge could be the better dewaterability (19% instead of 14% DM), leading to a more condensed organic matter.

**Effect of FeCl₃ and lime addition.** The slightly lower extractability of NP in the aqueous phase from limed sludge relatively to non-conditioned sludge (Table 1, Indicator A), cannot explain as high NP residues as for the freeze-thawed one. This indicates an effect of lime to the microorganisms of sludge or of soil after amendment. The pH during sludge liming was 8.5 and that of limed sludge amended soil was 6.5. Concerning leaching, the high potential observed for NP in limed sludge is attributed mostly to the high amount of NP residues. Less degradation products were present, but they remained more available in limed sludge (Table 1, Indicator B). Finally, this resulted in an equal amount of potentially leached products as for the single centrifuged sludge.

Table 1 Indicators used for the interpretation of NP fate: A: leached NP / extractable NP; B: leached degradation products / extractable products (range: minimum-maximum); C: FA residues: HA residues: humin residues (average). First row: sludge amendments: non-conditioned (CE), freeze-thawed (FT), FeCl₃ conditioned (FE), lime and FeCl₃ conditioned (LM), polymer conditioned (PO) and non-dewatered (LQ).

**Effect of cationic polymer addition.** The treatment of sludge with cationic polymer had a considerable effect on the mineralization of NP, although the extractable amount of the latter was the same as for centrifuged sludge after incubation. By comparing systems with similar mineralization rates from the two series (that was possible due to the high variation in replicates), the amount of bound residues was significantly higher in the first. Fractionation of them showed an accumulation of radioactivity in the humin. Except this, a lower bioavailability of the extractable residues was observed in the case of polymer containing sludge (Table 1). Thus, the reason for the low amount of NP extractable residues when polymer was used seems to have been a faster binding of NP rather than fast degradation, as observed in systems containing non-conditioned sludge. Mineralization rates were decreasing over prolonged incubation times, indicating that decomposition process was possibly hindered by the binding of the intermediate degradation products. The low NP leaching was attributed to the reduced extractability in water of the NP residues (equal amount of) due to polymer properties. Low leaching of degradation products was mainly due to the low amount of extractable products.

**Effect of dewatering.** Fractionation of the bound residues in the soils amended with liquid sludge suggested that the type of binding was different than in the case of centrifuged sludge. Although the radioactivity of bound residues was the same in the case of liquid sludge, the radioactivity in FA and HA was significantly higher (and lower in the humin). This effect is not necessarily connected to the properties of sludge organic matter, but it can result from a different distribution of spiked NP between the organic matter of soil and sludge (dewatered sludges were amended in aggregates).

**CONCLUSIONS**

The branched isomer of NP, which was used as a model compound, was significantly persistent when spiked in sludge-amended soil. Its leaching potential was low, although the mobility of degradation products was higher. For the first time the effect of various sludge treatments on the fate of a major organic pollutant was studied by applying the treatments on the same precursor sludge. A range of conditioning methods was tested. The results indicated tendencies, which need to be investigated further. Liming of sludge may have an effect on the degrading microorganisms and could be connected to higher risk concerning the contamination of groundwater. Freeze-thawing may decrease the bioavailability of NP-like compounds. Conditioning with cationic polymer tended to enhance the bound residues formation process, thus limiting mineralization, but also
When sludge treatment has significant effect on the fate of the pollutants, the determination of tolerance values should take the type of sludge treatment in consideration (Schowanek et al., 2004). Treatments with the perspective to reduce environmental risks should be preferred.

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