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Fate of 4-nonylphenol in a biosolids amended soil

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ABSTRACT

The fate of the endocrine disrupting compound 4-nonylphenol (NP) in an agricultural soil amended with biosolids was assessed in a greenhouse study. A biosolids with a total NP concentration of 900 mg kg $^{-1}$ was incorporated into the 4 cm surface layer of soil columns at an agronomic rate equivalent to 1.7 kg m^2. Half of the columns were planted with *Triticum aestivum* L., red hardy winter wheat seeds, whereas the remaining columns were unplanted to evaluate the influence of plant growth on the fate of NP. The degradation of total NP and eight NP isomers was monitored over 45 d. The half-life of NP in this soil system ranged from 16 to 23 d depending on treatment. After 45 d from the start of the trail, 15% of the initial biosolids-NP remained in the planted columns, whereas ~30% remained in the unplanted columns, indicating enhanced degradation in the presence of plants. The eight NP isomers exhibited different degradation rates, but minimal amounts of all isomers persisted after 45 d. Movement of NP below the zone of incorporation was slight (<2% of total NP present at any sampling interval) and no NP was detected in column leachates or in wheat leaves.

1. Introduction

The detergent metabolite, 4-nonylphenol (NP), has been widely detected in aquatic and terrestrial systems (Kolpin et al., 2002; Vikelsøe et al., 2002; Uchiyama et al., 2008) and has been shown to have endocrine disrupting effects in a variety of species (Soto et al., 1991). For example, NP can bind to human estrogen receptors, inducing breast cancer cell growth (Inoue et al., 2000), and can stimulate the production of the female egg protein vitellogenin in male fish (Jobling et al., 1996; Loos et al., 2007; Viganò et al., 2008).

Many anthropogenically introduced endocrine disrupting chemicals (EDCs) leave wastewater treatment plants unaltered or incompletely degraded and are subsequently released into the environment through wastewater outflows or biosolids application (Kolpin et al., 2002; Pothitou and Voutsa, 2008). To date, EDC research has primarily focused on aquatic environments receiving wastewater discharge, with less attention focused on EDC release in terrestrial environments due to use of biosolids (Petersen et al., 2003; Hseu, 2006). Land application of biosolids (and associated EDCs) is common in the US, and the fate of biosolids-borne EDCs deserves study.

About 55% of the 6.5 × 10^6 Mg (dry wt.) of the biosolids produced annually in the US are land applied for agronomic, silvicultural, and/or land restoration purposes (NEBRA, 2007). Nonylphenol concentrations in biosolids can vary widely (from <5 to >1500 mg kg^{-1}). Kinney et al. (2006) reported median, minimum, and maximum NP concentrations of 261, 2.18, and 1520 mg kg^{-1}, respectively, for nine biosolids produced in the US that are typically land applied. The US EPA (1995) recommends applying biosolids at agronomic rates (typically ⩽2.0 kg m^2), which represents a median biosolids-NP application rate of about 5.2 kg NP ha^{-1}and a biosolids-amended soils NP concentration of about 2.6 mg kg^{-1} in the top 15 cm of soil. The fate of NP in biosolids-amended soils has been widely studied, but often under conditions intended to assess particular pathways (e.g. plant uptake, photolysis, toxicity to soil organisms), or to promote ease of analysis. Thus, studies have utilized unrealistically large application rates (Xia and Jeong, 2004), NP-spiked biosolids to attain loading rates (Topp and Starratt, 2000; Roberts et al., 2006), have not included growing plants (Marcomini et al., 1998), or grew the plants for short (14 d) periods (Roberts et al., 2006). Few studies considered possible differences in NP isomer fate (Das and Xia, 2008; Hayashi et al., 2005). Our purpose was to focus on the degradation of NP and Q2 eight NP isomers under typical biosolids application practices in the presence (and absence) of a typical northwestern US crop for 45 d under greenhouse conditions. We included periodic leaching events to evaluate NP mobility, and measured plant uptake of NP.

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2. Materials and methods

2.1. Soil, biosolids and plant characteristics

The soil used for the study was collected from an agricultural field in Prosser, WA and had no prior history of biosolids application. The Esquatzel silt loam is classified as a coarse, silty, mixed, superactive, mesic Torrifluventic Haploxerolls (Rasmussen, 1971). Biosolids were obtained from the West Point Wastewater treatment facility in King County, which produces about 12 000 Mg (dry wt.) of an anaerobically digested (Class B) biosolids per year. All of the biosolids produced are applied to agricultural soils for production of a variety of crops (King, personal communication), including *Triticum aestivum* L. (red hardy winter wheat grass) which was used in this study.

2.2. Experimental setup

The experiment was conducted at the University of Washington Arboretum greenhouse facility in Seattle, WA, USA during the summer of 2005. Temperature within the greenhouse ranged from 15 to 27 °C during the growth period from mid-June to the end of August (45 d). A 0.5 g aliquot of freeze dried biosolids were mixed with 16 g air-dry soil (equivalent to a 4 cm depth in the columns). Amended soil was placed on top of 41 g (~10 cm depth equivalent) of unamended soil in conical containers (22 cm long, 4.5 cm diameter) making the final total soil application rate equivalent to 1.7 kg m^2. Typical biosolids rates used in agronomic field applications based on the nitrogen requirements for a high yielding wheat are 0.8–2.0 kg m^2). Each container was initially plugged with glass wool, and the final soil arrangement mimicked a typical tilled agricultural settling following biosolids field application with minimal tillage. Wheat seeds (4) were planted in 50% of the containers, with the remainder unplanted to assess effects of plant growth on the fate of NP. Water was initially added to each container to bring the soil to field capacity and added periodically (every 4–5 d) thereafter to maintain optimal soil moisture. No supplemental fertilizer was added to either treatment.

The experiment was set up using a randomized complete design with three replicates of each treatment for each sampling time. Multiple soil sampling (Days 0, 3, 6, 9, 12, 15, 30 and 45) were conducted for biosolids alone treatments. Columns were harvested on day 0, 15, 30 and 45 from the biosolids + plant treatment. Three intact columns were harvested for each treatment for each sampling period. An unamended soil was also included in the experimental design as a soil only control.

2.3. Sample collection

On the day of crop harvest, all columns were over watered (50 mL) to generate drainage that was collected and analyzed for NP. The wheat foliage was collected by cutting the base of the plant approximately 50 mm above the soil surface using stainless steel scissors and placed in paper bags. Once the containers had drained and vegetation was removed, the containers and leachate sample cups were capped with foil. Plant tissue was washed in deionized water after harvest and air-dried. Soil was removed from containers and stored (along with water and plant samples) in a freezer at −4 °C to halt any degradation of NP until analysis. Soil columns were sampled by depth (0–4, 4–8 and 8–14 cm), and each sample analyzed separately for NP.

2.4. Sample analysis

The frozen soil and plant samples were freeze-dried and extracted using an Accelerated Solvent Extractor (model: Dionex ASE 200). An EDC surrogate (2,3,5,6 d_4 nonylphenol, Sigma Aldrich, CAT No. 614–343) was added to each sample immediately prior to extraction to determine extraction recoveries for NP. The cells were rinsed using an 80:20 solvent ratio of methylene chloride: acetone at 12 065 kPA and 100° C and the rinses were collected in 60 mL vials. The two rinses for each sample from the ASE were combined and concentrated using nitrogen blowdown on a turbovap (Zymark, Corporation, MA). Extracts were cleaned using silica gel fractionation on columns constructed from 10 mL serological pipettes plugged with glass wool and filled with 3 g of deactivated silica gel followed by 4 g of $NaSO_4$ crystals. The extract was added to the column followed by a 15 mL rinse of hexane that was discarded and a 30 mL 50/50 $MeCl_2$/ASE rinse, which was collected. The cleaned samples were concentrated again using the turbovap to a final volume of 1 mL prior to analysis by a gas chromatograph mass spectrophotometer (GC/MS).

The volume of each column leachate sample was measured. The samples were filtered (Whatman filter paper 40 cm) and placed into separatory funnels. Methylene chloride (55 mL) and EDC surrogate (50 μL) were added to the funnels and the mixture was shaken for 1 min to emulsify the $MeCl_2$ and water. The bottom $MeCl_2$ layer, containing the analytes of interest, was collected by releasing the stopcock and allowing the extraction solution to pour through a sodium sulfate funnel into a volatile organic analysis (VOA) septum vial. The solution was reduced to 1 mL (turbovap) before analysis by GC/MS.

Extracts of the soil, plant and water samples were analyzed using an Agilent 5972 GC/MS. Nonylphenol is a multi-responding compound due to the presence of multiple isomeric forms. A subset of eight isomers (peaks on a chromatogram) were monitored because of their high intensity and strong separation. The major ions included masses 121, 135, and 149. The secondary ions that were monitored included masses 107, 150, 136 and 177. The total NP value reported is the sum of the mean values for each.

Quality control and quality assurance procedures were as follows: prior to the experiment, the method was tested using freeze-dried and homogenized biosolids as well as the unamended soil. A deuterated NP (dNP) surrogate was used to test for extraction efficiency. This was added to the samples immediately prior to extraction. Recovery of the dNP ranged from 63% to 99% with an average extraction efficiency of 80%. Finally, an internal standard (D10 Phenanthrene, at 4 mg kg^{-1}) was used as a measure of instrument efficiency for the GC/MS (EPA, 2008). The method detection limits for NP were 5–10 μg L^{-1} for water and 33.3 μg kg^{-1} for soil, plant and biosolids samples.

2.5. Statistical analysis

Statistical analysis was conducted using SPSS 11.0.3. (SPSS Inc., 2004) Data were analyzed to determine the effects of plant presence and time on the degradation rate of total NP for each soil depth. The effects of time and plant presence were also tested in relation to the prevalence of specific isomers and changes in isomer prevalence over time for each treatment. One-way ANOVAs were used to compare changes in NP concentration in each treatment over time at $\alpha = 0.05$. A Duncan's post-hoc test was used for means separation once significant differences had been shown using the ANOVA procedure.

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3. Results and discussion

Q3 The concentration of NP in the biosolids was 900 mg kg^{-1}, a value similar to that reported in some studies (937 mg kg^{-1}, Xia and Jeong (2004) and 1000 mg kg^{-1}, Giger et al. (1984)), but greater than that reported in other studies (60 mg kg^{-1}, Petersen et al., 2003).

3.1. Degradation of NP across all treatments

Both time and treatment were significant factors in the degradation of NP, but there was no significant interaction between these two variables (Fig. 1). The concentration of NP decreased significantly ($p < .0001$) between each sampling period at the 0–4 cm depth in the biosolids + plant treatments. The same general trend was observed for the biosolids only treatment with one exception, where the concentration of NP did not decrease between Day 9 and Day 15. The general shape of each degradation curve was similar for the biosolids alone and biosolids + plant treatments. Both degradation curves were fitted using an exponential curve fitting function. The R^2 value for the biosolids alone curve was 0.95 and the value of the biosolids + plant curve was 0.99. The exponent for the biosolids + plant curve indicates a more rapid decay rate (0.043) than the biosolids alone curve (0.030). Half lives were calculated for both the biosolids alone and the biosolids + plant treatments using a first order decay model. The half-life of NP in the biosolids alone treatment was 23 and 16 d in the biosolids + plant treatment. The biosolids alone degradation data displayed a relatively steep slope from Day 0 to Day 30 that then tended to flatten out from Day 30 to 45. This may indicate two stages of degradation of NP in the absence of plants. Similar degradation curve shapes were reported by Das and Xia (2008) for decomposition of NP during composting and by Jacobsen et al. (2004) for NP decomposition in soils amended with biosolids. Roberts et al. (2006) also observed a similar pattern with ^{14}C-NP added to soil. Das and Xia (2008) reported half-lives of total NP ranging from 1.3 to 17.5 d during composting, depending on the ratio of biosolids to wood shavings used. The half-life found for NP by Jacobsen et al. (2004) study ranged from 31 to 46 d. Topp and Starratt (2000) reported half lives of NP from 4.5 to 16.7 d in biosolids amended soils. A recent study noted effects of biosolids conditioning and dewatering on NP degradation in spiked biosolids amended soils with degradation occurring most rapidly in liquid biosolids (Kouloumbos et al., 2008). Centrifuging and lime stabilization decreased rate of mineralization in comparison to the liquid biosolids. The half-lives were not reported, however, <7% of total NP applied in the liquid biosolids was mineralized in 80 d. This may be the result of the high rate of NP addition used in this study (2.5 g biosolids to 13 g soil). Differences in biosolids stabilization may account for some of the variation in degradation rates observed in the literature.

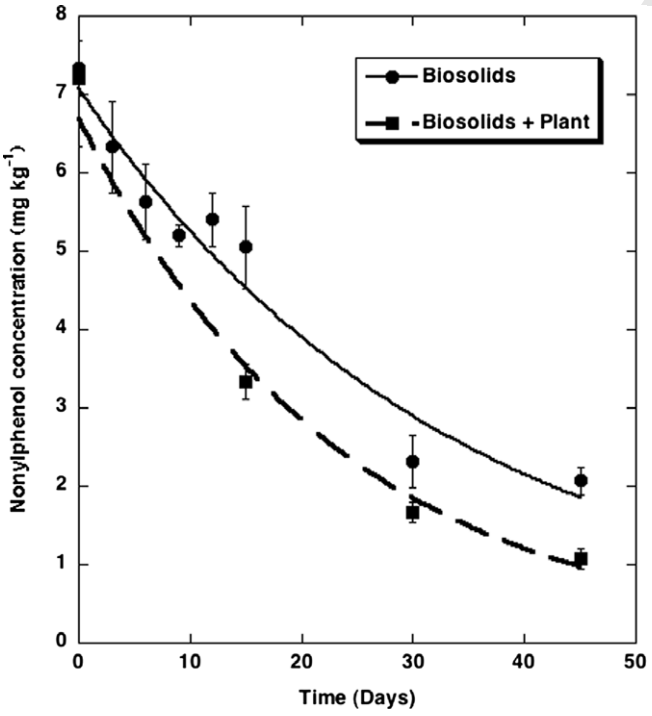

Fig. 1. Nonylphenol concentration in the biosolids + plant and biosolids alone treatments at the 0–4 cm depth of soils over the course of the study. Means and standard deviation are shown for each sampling interval. An exponential decay function was used to describe the lines. The equation for the decay of the biosolids alone treatment was $y = 7.07 * e^{(-0.03x)}$ with an R^2 value of 0.95. The equation for the biosolids + plant treatment was $y = 6.69 * e^{(-0.043x)}$ with an R^2 value of 0.99. The larger decay constant (0.043) for the biosolids + plant in comparison to the decay constant for the biosolids alone (0.03) treatments indicates that degradation of NP is enhanced in the presence of plants.

Plants significantly increased the rate of decomposition of NP (Fig. 1). Similar results were observed in a greenhouse study by Mortensen and Kure (2003) where NP, added to the soil as a component of biosolids, was degraded more rapidly in the presence of *Brassica napus* (rapeseed) than in the absence of the plant. After 30 d 13% of the added NP remained in the treatment with plants while 26% remained in the soil only treatment. Roberts et al. (2006) found plants either had no effect or hindered NP degradation depending on soil type. The plants in the Roberts et al. (2006) study grew for 14 d, and a plant effect may have had insufficient time to develop. At the end of the experimental period in this study, plant roots were distributed through the column depth. The shape of the columns may have encouraged vertical growth of the roots. The distribution of roots through the soil depth may have accelerated decomposition.

3.2. Preferential degradation of isomers

Nonylphenol is formed during wastewater treatment as the degradation product of nonylphenol ethoxylates (Thiele et al., 2004). Total NP is composed of a number of isomers. The different structural features of the isomers affect isomer behavior, including estrogenic activity and degradation rate (Routledge and Sumpter, 1997; During et al., 2002; Gabriel et al., 2008; Makino et al., 2008; Uchiyama et al., 2008). Thus, the prevalence of different isomers may have different environmental impacts. There is evidence that different isomers have different degradation rates. In one study, two recalcitrant isomers had greater estrogenic activity than isomers that degraded more rapidly (Gabriel et al., 2008). The disappearance of particular isomers may result from their transformation to other isomers rather than complete degradation.

The degradation of eight NP isomers was monitored over the course of the experiment in both treatments. To compare the behavior of each isomer in each treatment at each harvest date, the total concentration is shown as the composite of the individual isomers (Fig. 2). Both time ($p > 0.001$) and treatment ($p > 0.04$) significantly affected the degradation of individual isomers, but there was no interaction between the main effects.

The various isomers present in biosolids did not degrade equally with time. Isomer 1 was present at the greatest concentration of all isomers identified at Day 0, but was not detected at any other sampling period for either treatment. All other isomers de-

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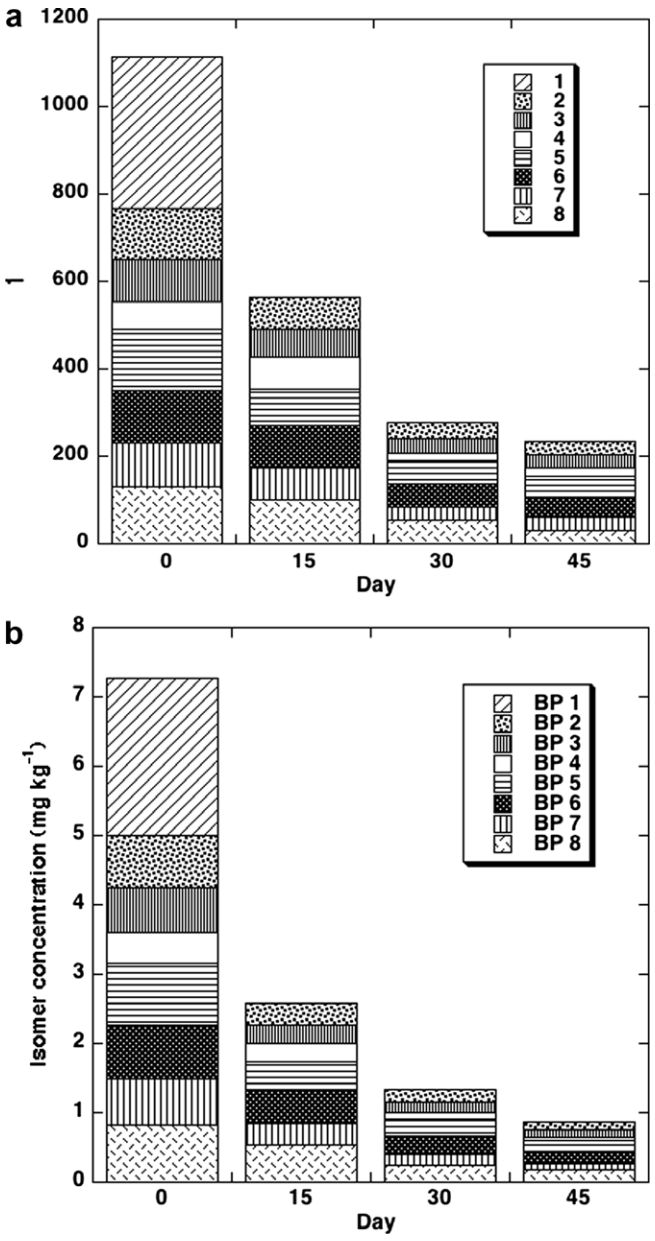

Fig. 2. Concentrations of eight nonylphenol isomers (mg kg^{-1}) for the biosolids alone (a) and biosolids + plant (b) treatments for each sampling period. Both treatment and time significantly affected the concentration of isomers in this study.

creased, albeit at different rates, over the course of the study. There was no indication of accumulation of particular isomers. While plant growth accelerated the rate of all isomer degradation, the relative abundance of individual isomers was unaffected. Hayashi et al. (2005) showed that NP isomers degrade at different rates depending on the length of the polyethoxylate chain. Degradation rates were greater for long-chain oligomers than for short-chain oligomers. Das and Xia (2008) also found that NP isomers exhibit different degradation rates based on structure during composting. Isomers with an α-methyl-α-propyl structure degraded significantly more slowly than isomers with less branched secondary α-carbon or tertiary α-carbon structures. In the study reported here, the exact structure of each of the eight isomers was not determined, but results generally agree with those reported elsewhere. NP isomers introduced into a soil system with biosolids exhibit different degradation patterns, but none of the isomers persist.

Table 1
Total NP concentrations at different sampling times and different soil depths. Nonylphenol concentration in the biosolids was 900 mg kg^{-1} with biosolids application rate of 1.7 kg m^{-2}. Means separation ($n = 3$) of NP concentrations in each treatment at different depths over time were carried out at $\alpha = 0.5$. Means within the same depth and time followed by the same letter are not significantly different ($p < 0.05$).

Time (d)	Total Nonylphenol (mg kg^{-1})	
	No plant	Plant
0–4 cm		
0	7.31 a	7.20 a
15	5.06 a	3.33 b
30	2.31 a	1.68 b
45	2.04 a	1.06 b
4–8 cm		
0	0.00 a	0.00 a
15	0.16 a	0.09 b
30	0.04 a	0.00 b
45	0.08 a	0.02 a
8–14 cm		
0	0.00 a	0.00 a
15	0.09 a	0.08 a
30	0.00 a	0.00 a
45	0.02 a	0.02 a

3.3. Mobility of NP in a soil system

The movement of NP through soil was monitored by analyzing NP in soil from three depths (0–4, 4–8, and 8–14 cm) within each column at each harvest (Table 1). Nonylphenol was detected at the 4–8 cm depth on Day 15, 30 and 45 in the biosolids alone treatment, and on Day 15 and 45 in the biosolids + plant treatment. The compound was also detected at the 8–14 cm depth at Day 15 and 45 for both treatments. The fraction of total NP detected at the 4–8 cm depth on Day 15 in both treatments was <2% of the total compound present in the entire soil column at that harvest. The quantity of NP at the 8–14 cm depth at Day 45 was approximately 1% of the compound present in the soil. At Day 45, the fraction of total compound present at both the 4–8 cm and 8–14 cm depths represented a similar portion of the total compound present in the soils for both treatments. The results suggest that movement of NP through the soil, although detectable, is minor.

Similar results have been observed in other NP mobility studies. In a field lysimeter study, Jacobsen et al. (2004) did not detect NP below the 15 cm depth of biosolids (1.0 kg m^2) incorporation at any time during an 110 day study. Vikelsoe et al. (2002) detected downward movement of NP in agricultural soils amended with biosolids (1.7 kg m^2 y^{-1} for 3 years) under conventional management practices, but NP was not detected below a soil depth of 50 cm. Roberts et al. (2006) detected NP in column leachates, but NP was initially homogenously distributed throughout the column.

3.4. Detection of NP in plant and water samples

Plant leaf tissues were analyzed for NP in plants harvested at Day 45. Nonlyphenol was not detected in any sampled plant tissue. The data suggest that plant roots did not take up NP and translocate it to above ground leaf tissue, or that the compound, if taken up, was degraded within the plant.

The plant uptake results conflict with the results of laboratory research conducted by Bokern and Harms (1997), who suggested that plants incorporate NP into cell walls as a mechanism to reduce the phytotoxicity of NP. A variety of plant cells, including soybeans, carrots, and quinoa, were exposed to NP concentrations ranging from 11 to 220 000 mg kg^{-1} (equivalent NP application rates: 24.6–493 240 kg ha^{-1}) in solution culture. Except for carrot cells,

4NP was toxic to all plant cells included in the study with the concentration causing 50% growth reduction ranging from 0.05 to >1 mM. Doucette et al. (2005) detected ^{14}C- from ^{14}C -NP in crested wheatgrass foliage grown in a hydroponic system containing NP at concentrations ranging from 0.007 to 0.07 mg kg^{-1} (equivalent application rate of 0.0156–0.156 kg ha^{-1}). However, no parent compound was detected in root or shoot tissue and 98% of the ^{14}C was detected in plant roots. Neither the cell culture nor the solution culture study is representative of plant/soil systems, and may not accurately reflect plant availability of NP in biosolids-amended soils.

Studies that mimic natural plant/soil conditions portray a different picture of the relationship of NP and plants. In field studies, Peterson et al. (2003) detected no NP in a third-year barley crop grown on biosolids amended soil. Mortensen and Kure (2003) detected no NP uptake by rape plants grown on soil amended with biosolids in a greenhouse pot study. Roberts et al. (2006) added ^{14}C-NP to assess the mobility of NP within the study system. Less than 5% of the total ^{14}C-NP added was detected in plant material, and the majority (approximately 80%) occurred in the plant roots rather than in the plant shoots (approximately 20%). However, the chemical form of the labeled carbon was not identified, and may have been transformation products (including $^{14}CO_2$). In general, results from studies that mimic soil systems agree with the results reported here that plant uptake of NP, and/or persistence of NP within the plant, is minimal.

Water samples were analyzed for NP at Day 15, 30 and 45, but NP was not detected in any sample. This study was not designed to quantitatively monitor leaching of NP through soils over time, and the results cannot be interpreted to mean that no NP left the system through leaching. However, the low concentrations of NP in the lower sections of the soil columns and the absence of NP in the water samples analyzed suggest that leaching did not occur. Similar results were reported in a field lysimeter study conducted by Jacobsen et al. (2004), who quantified NP in all water applied to plants grown on biosolids amended soil. The equivalent NP application rate was 1.26 kg ha^{-1}. No NP was detected in leachates from the lysimeters.

4. Conclusions

Applying biosolids containing 900 mg kg^{-1} NP at agronomic application rates of $\leqslant$1.7 kg m^2 in a terrestrial environment are unlikely to result in significant plant uptake or water quality degradation with nonylphenol. Once biosolids are incorporated into the top layer of soil, the majority of the NP remains in place and is subject to rapid degradation. The half-life of NP in this study ranged from 16–23 d and $\leqslant$ 30% of the added NP remained at Day 45 in the treatment that exhibited the slowest degradation rate. The presence of plants enhanced NP degradation so that $\leqslant$15% of added NP remained at Day 45. In contradiction to the findings of Roberts et al. (2006), no NP was detected in any of the leached water samples or in above ground plant tissue. Our data suggest that in practical field situations where typical biosolids (NP $\leqslant$ 1000 mg kg^{-1}) are applied at agronomic rates ($\leqslant$2.0 kg m^2), degradation of NP and its isomers will be accelerated so no NP will accumulate over time and plant uptake or water quality impairment will be minimal.

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