Environ. Sci. Technol. **1998**, *32,* 2623−2627

Degradation of Nonylphenol Ethoxylates during the Composting of Sludges from Wool Scour Effluents

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The aqueous scouring of raw wool produces an effluent that typically has a pollution load of at least 10 times that of domestic sewerage. The bulk of these pollutants may be removed by the SIROLAN-CF chemical flocculation process to produce a clear effluent and a sludge rich in wool wax. This sludge also contains practically all of the wool scouring detergent initially present in the untreated effluent. As the most commonly used detergents for this purpose, nonylphenol ethoxylates (NPE), are toxic to the environment, their fate must be carefully evaluated when disposal options for these sludges are considered. This paper examines the fate of NPE and the metabolites produced during the composting of a mixture of these sludges and municipal greenwaste. Over 14 weeks the NPE residues were decreased by >96%. The principal degradation pathway involved the oxidative hydrolytic shortening of the poly(ethylene oxide) chain of the hydrophile to produce low levels of the biorefractory metabolites nonylphenol (NP), nonylphenol monoethoxylate ($NPEO_1$), nonylphenol diethoxylate ($NPEO_2$), nonylphenoxy acetic acid (NPE_1C), and nonylphenoxyethoxy acetic acid (NPE_2C). Concomitant degradation of the nonylphenyl hydrophobe also occurred but at about half the rate of the degradation of the polyoxyethylene hydrophile. No metabolites of the breakdown of the hydrophobe were observed.

Introduction

Raw wool contains considerable quantities of wool wax, dirt, and suint that must be removed prior to the processing of the wool fiber into yarns and fabric. This is usually accomplished in an aqueous scour with the aid of a suitable nonionic detergent. After the scouring process, only a portion of the wax and dirt (≈30%) removed from the wool is recovered from the scour liquor in the recovery loops. The remaining contaminants are discharged from the scour as wastewater. Although this wastewater contains mainly natural contaminants, the organic effluent load from a typical scour line processing 1 ton of raw wool/h is equivalent to the sewerage produced by a town of 30 000 people (*1*).

Virtually every system for wastewater treatment has been tried for treating wool scour effluent ranging from relatively inexpensive lagooning systems to expensive evaporation/incineration plants, with many treatment plants using a combination of technologies. A recent development out of these laboratories has seen the commercialization of a simple in-line chemical flocculation process (*2*). This process removes virtually all the suspended solids, producing a relatively dry sludge that typically has the composition of 20% wool wax, 40% dirt, and 40% water. While a range of options are available for the disposal of this sludge, the most attractive are those that convert this waste product into a valuable reusable commodity. One such option is the use of this sludge to produce garden compost and/or potting mix.

Typically an aqueous scour uses between 5 and 10 kg of detergent/ton of raw wool. We have found that the bulk of this detergent partitions into the wool wax where it is distributed between the "cream-phase" wool wax that is recovered centrifugally and the more polar wool wax that remains suspended and/or emulsified in the scour liquor. It is this latter wax that is recovered in the form of a sludge by the chemical flocculation process. While there is a steady trend toward the use of the more readily biodegradable alcohol ethoxylates, one of the main classes of detergents still used in aqueous wool scours are the nonylphenol ethoxylates (NPE). These detergents and their metabolites are considered biorefractory (*3*, *4*) and toxic to aquatic organisms (*5*−*8*). The purpose of this study was to examine the extent of biodegradability of these detergents during the composting of the wool scour sludges produced by the SIROLAN-CF process (*2*).

Materials and Methods

Chemicals. Nonylphenol (NP) was obtained from Aldrich (Milwaukee, WI). Lissapol TN 450 (a nonylphenol ethoxylate with an average of 8.5 ethylene oxide units) and Teric N2 (a nonylphenol ethoxylate with an average of 2 ethylene oxide units) were obtained from ICI Australia (Melbourne, Victoria).

Nonylphenoxy acetic acid (NPE_1C) and nonylphenyl polyoxyethylene acetic acids (NPE_nC) were prepared by oxidation of Teric N2 and Lissapol TN 450 with acidic potassium dichromate as described by Reinhard and Goodman (*9*). (See Figure 1 for structures).

Compost. Strong flow wastewater from a commercial wool scour (Melbourne, Australia) using the NPE Lissapol TN 450 was chemically flocculated by the SIROLAN-CF process (*2*) to produce a clear effluent free of suspended or emulsified wool wax and dirt. The resulting sludge was dewatered by a commercial decanter centrifuge and had the average composition of 40% water, 17% wool wax, 42% mineral dirt, and 1.2% NPE. This sludge after blending with greenwaste (shredded municipal prunings) was placed on a concrete pad and allowed to compost for 14 weeks. During this time, the heap was turned and sampled every 3−4 days. At each sampling cycle 12 separate 100-cm^3 samples were collected from different regions within the heap and blended to make a single composite sample. This sample was freeze-dried, and the wax content of the compost was determined by extraction with dichloromethane for 4 h in a Buchi 810 Soxhlet apparatus (Buchi, Flawil, Switzerland). The total loss of material due to the composting process was estimated from the ratio of the weight of freeze-dried sample and the weight of its ash after ignition in a porcelain crucible at 600 °C and the weights measured at time zero.

Detergent Analysis. The total NPE present in the wax recovered as described above was determined by the two-phase titration of the potassium complex of NPE with sodium tetrakis(4-fluorophenyl) borate (*10*). The NPE oligomer distribution in the individual samples was determined by gas chromatography using flame ionization detection (GC-

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S0013-936X(98)00026-1 CCC: $15.00 Published 1998 by the Am. Chem. Soc.
Published on Web 07/28/1998

FID) after isolation from the wool wax by gel permeation chromatography (GPC) and normal-phase chromatography on silica gel.

Isolation of NP, $NPEO_n$, and NPE_nC (Where $n = 1-3$). About 1 g of recovered wax was accurately weighed and dissolved in dichloromethane (5 mL). An aliquot was loaded via a 2 mL sample loop onto a 250 mm × 22 mm i.d. column packed with Bio-Beads SX-3 resin (34 g, 200−400 mesh, Bio-Rad, Hercules, CA) swollen in hexane−dichloromethane (1:1). The eluting solvent, hexane−dichloromethane (1:1), was pumped at a rate of 4 mL/min by a model 2350 pump (ISCO, Lincoln NE). The fraction containing NPE and NPEC oligomers with 3 or less ethylene oxide units ($NPEO_n$ and NPE_nC where $n = 1-3$) was collected over the elution times of 10−18 min using an ISCO Foxy Jr fraction collector. This fraction was evaporated to dryness, and the residue was dissolved in ethyl acetate (1 mL) containing dodecanol (0.3 mg/mL) as an internal standard. This mixture was silyated with BSA (150 μL, Pierce) at 80 °C for 15 min.

Isolation of $NPEO_n$ (Where $n = 4-16$). A duplicate sample of wool wax was loaded onto the GPC column, and the fraction containing NPE oligomers with 4−16 ethylene oxide units was collected over the elution times of 5−11 min. After removal of the solvents, the residue was dissolved in a mixture of hexane and ethyl acetate (2:1, 5 mL) and quantitatively transferred to a SiO_2 extraction cartridge (Mega Bond Elut 6 cm^3/1 g, Varian, Harbor City, CA) that had been preconditioned with 5 mL of the loading solvent. The transfer of the wax was completed using a further 5 mL of the hexane−ethyl acetate mixture (2:1) and the bulk of the wool wax eluted with a mixture of hexane and ethyl acetate (1:1, 2 × 5 mL). This eluant was discarded. The higher NPE oligomers were then eluted from the silica cartridges with a mixture of ethyl acetate and methanol (1:2, 5 mL). After the solvents had been removed under N_2 at 80 °C, the residue was dissolved in ethyl acetate (1 mL) containing dodecanol (0.3 mg/mL) as an internal standard and silyated as described above.

Qualitative analysis of these silyated samples was performed by GC-FID on a Varian 3400 GC (Varian, Harbor City, CA) fitted with a 1093 septum-purge programmable injector and a BX-5 capillary column (6 m × 0.32 mm i.d., 0.25 μm film, SGE, Melbourne, Australia). The operating conditions were as follows: The injector was programmed from 60 to 360 °C at 100 °C/min and held at 360 °C for 20 min. The column oven was programmed from 80 to 390 °C at 15 °C/min and held at 390 °C for 5 min. The detector was set at 400 °C and used the gas flows for air, hydrogen, and nitrogen makeup as specified by the manufacturer. Helium was used as the carrier gas with a flow rate of 50 cm/s. The injection volume was 0.5 μL. The output data was collected and processed using DAPA software (DAPA Scientific, Kalamunda, WA, Australia). The individual oligomers were quantified by comparison with external standards using the effective carbon number concept (ECN) to calculate the appropriate response factors (*11*) from the formula: $ECN_n = 17.69 + 1.59n$, where n = the number of ethylene oxide units in the oligomer.

Confirmation of the NPE metabolites found was made using a Varian 3400 GC coupled to a Varian Saturn 2000 mass spectrometer (GC−MS) that was fitted with a DB5 capillary column (30 m × 0.252 mm i.d., 0.25 μm film, J&W Scientific, Folsom, CA). The operating conditions were as follows: The injector was set at 150 °C. The column oven was programmed from 80 to 350 °C at 15 °C/min and held at 350 °C for 5 min. The MS was operated in the EI mode using an ionization energy of 70 eV and an ion source temperature of 200 °C. Helium was used as the carrier gas with a flow rate of 50 cm/s. The injection volume was 0.5 μL. The output data was collected and processed using Star software (Varian, Harbor City, CA).

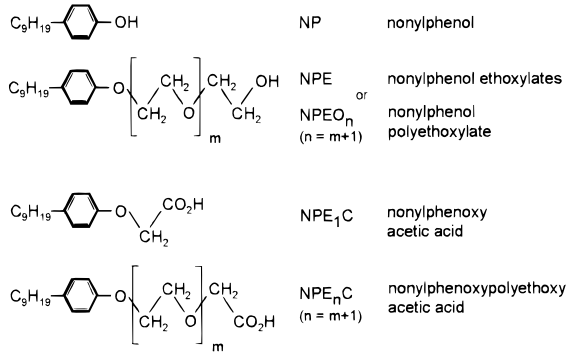

FIGURE 1. Structures, acronyms, and nomenclature of nonylphenol polyethoxylates and their metabolites.

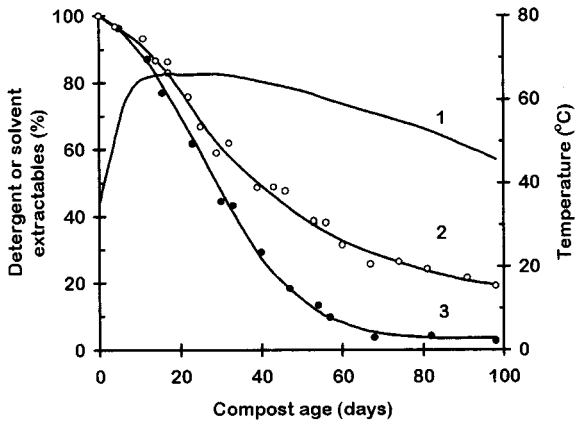

FIGURE 2. Decay of total solvent extractables (2) and NPE (3) measured by two-phase titration of the potassium complex against sodium tetrakis-(4-fluorophenyl) borate. (1) Average temperature of the compost heap.

Results and Discussion

Wool scour sludges, derived from the SIROLAN-CF process, when mixed with greenwaste formed a highly reactive mixture in which the composting process, as shown by the temperature profile of the heap, was observed to commence immediately. As shown in Figure 2, these biological processes substantially degraded both the wool wax and the detergent present during this thermophilic stage. On a dry weight of compost basis, this represents a reduction in the total NPE of 96%; however, if the net reduction in the mass of the heap due to the composting process is also taken into account, this reduction is of the order of 98%.

To evaluate the environmental risk, further information on the breakdown pathway and ultimate degradation was sought by examining the breakdown products by GC. The analysis of the individual detergent oligomers in the compost was complicated by the presence of the wool wax. Christoe and Evans (*12*) described a cleanup procedure involving normal-phase chromatography on silica, which was claimed to separate the detergent residues from the wax. This procedure worked well for centrifugally recovered wool wax and for detergent oligomers with 4 or more ethylene oxide units. However, the shorter oligomers as well as the parent nonylphenol coelute with the nonpolar wool wax esters and could not be isolated by this procedure. The wool wax emulsified in the wastewater from a wool scour differs markedly from the centrifugally recovered wool wax in that it contains significant quantities of autoxidized wool wax (*13*). This polar, oxidized fraction of wax is not readily separated from the detergent residues by chromatography on silica. Furthermore, a significant proportion of this oxidized wool wax has a much higher molecular weight than

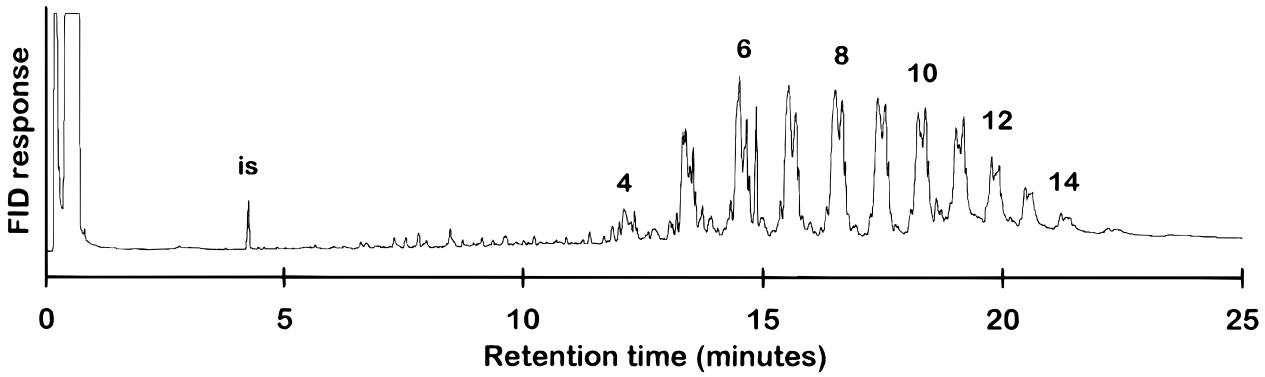

FIGURE 3. GC trace of NPE oligomers extracted from the compost mix on day 1. (is) dodecyltrimethylsilyl ether, (4−14) $NPEO_4$ TMS ether−$NPEO_{14}$ TMS ether.

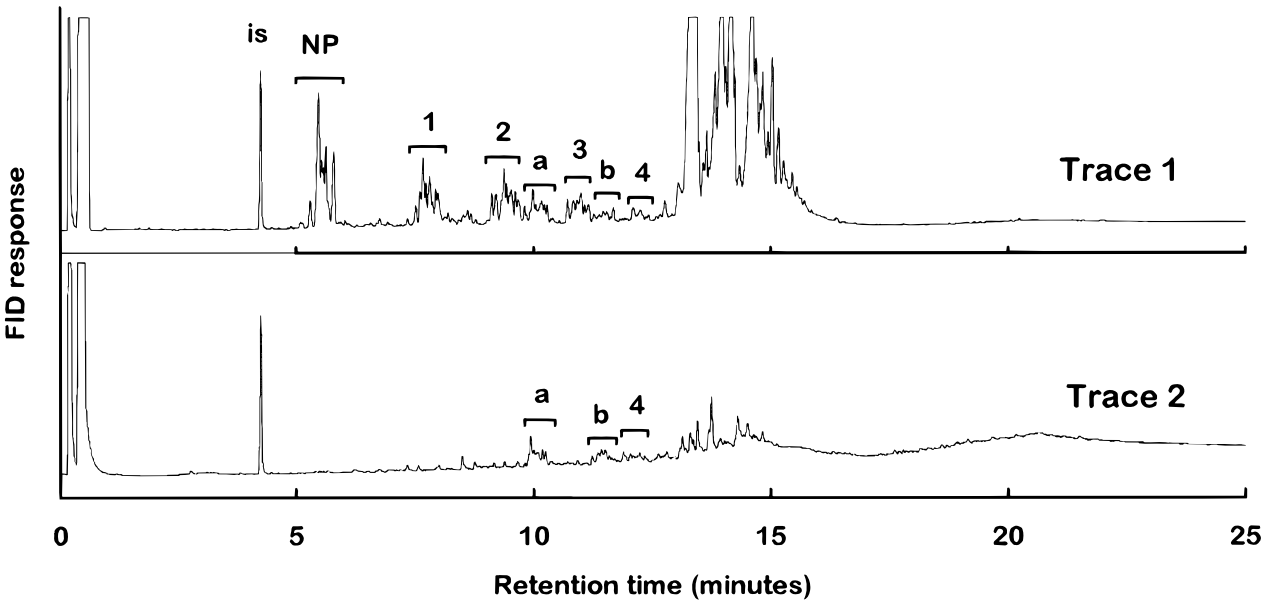

FIGURE 4. GC traces of detergent oligomers after 14 weeks of composting. Trace 1: GPC molecular weight fraction 100−500 amu. Trace 2: GPC molecular weight fraction 350−1000 amu after SiO_2 cleanup. (is), internal standard dodecyltrimethylsilyl ether; (NP), nonylphenyltrimethylsilyl ether; (1), $NPEO_1$ TMS ether; (2), $NPEO_2$ TMS ether; (3), $NPEO_3$ TMS ether; (4), $NPEO_4$ TMS ether; (a), NPE_2C TMS ester; (b), NPE_3C TMS ester.

the bulk of the wool wax esters and, as a result, does not elute from the GC column used without decomposition. To minimize these interferences, the solvent extractables from the compost were divided into two overlapping fractions by GPC. In this way the nonylphenol and lower ethoxylates ($NPEO_1$, $NPEO_2$, and $NPEO_3$) could be determined without further cleanup from the molecular weight fraction corresponding to 100−500 amu; whereas, the molecular weight fraction corresponding to 400−1000 amu containing the higher oligomers ($NPEO_4$−$NPEO_{16}$) required a secondary cleanup by chromatography on a short silica column prior to GC analysis.

A GC-FID trace of the oligomers initially present in the wax in the compost is shown in Figure 3, and GC-FID traces of the biological transformation products after 14 weeks of composting are shown in Figure 4. Despite the fractionation and cleanup procedures used, accurate quantification of trace levels of some oligomers was not always possible due to interference from residual wool wax components. Sufficient information, however, could be obtained to give a reliable overall picture of the breakdown pattern of the NPE shown in Figure 5.

In aqueous aerobic systems, the major pathway of biodegradation for NPE has been shown (*3*) to be the stepwise oxidation and cleavage of the polyoxyethylene chain either by hydrolysis or an oxidative hydrolytic mechanism. This pathway would also appear to be operative in the aerobic composting of the NPE in the wool scour sludge. The involvement of oxidation of the terminal hydroxyl groups to the corresponding carboxylic acids can be inferred from the small amounts of NPE_1C, NPE_2C and NPE_3C detected and confirmed by GC−MS in the samples collected toward the end of the composting process. These acids, as their trimethylsilyl (TMS) esters, eluted after the corresponding TMS ethers and except for the shorter oligomers listed above were not well resolved from the TMS ethers. It is therefore possible that the broadening of the isomer envelopes observed for the higher oligomers earlier in the composting process may also be due to trace amounts of the corresponding terminal carboxylic acids.

As with previous aerobic aqueous studies, no fission of the aromatic ether bond was observed. As a result, the accumulation of nonylphenol was only observed toward the end of the composting process after the sequential cleavage of the ethylene oxide units was complete.

Chain shortening was not the only pathway for the catabolism of these detergents. As shown in Figure 6, there was a rapid loss of the nonylphenyl moiety from the compost, albeit not as rapid as the loss of ethylene oxide units. This is probably not due to leaching as this detergent has a high

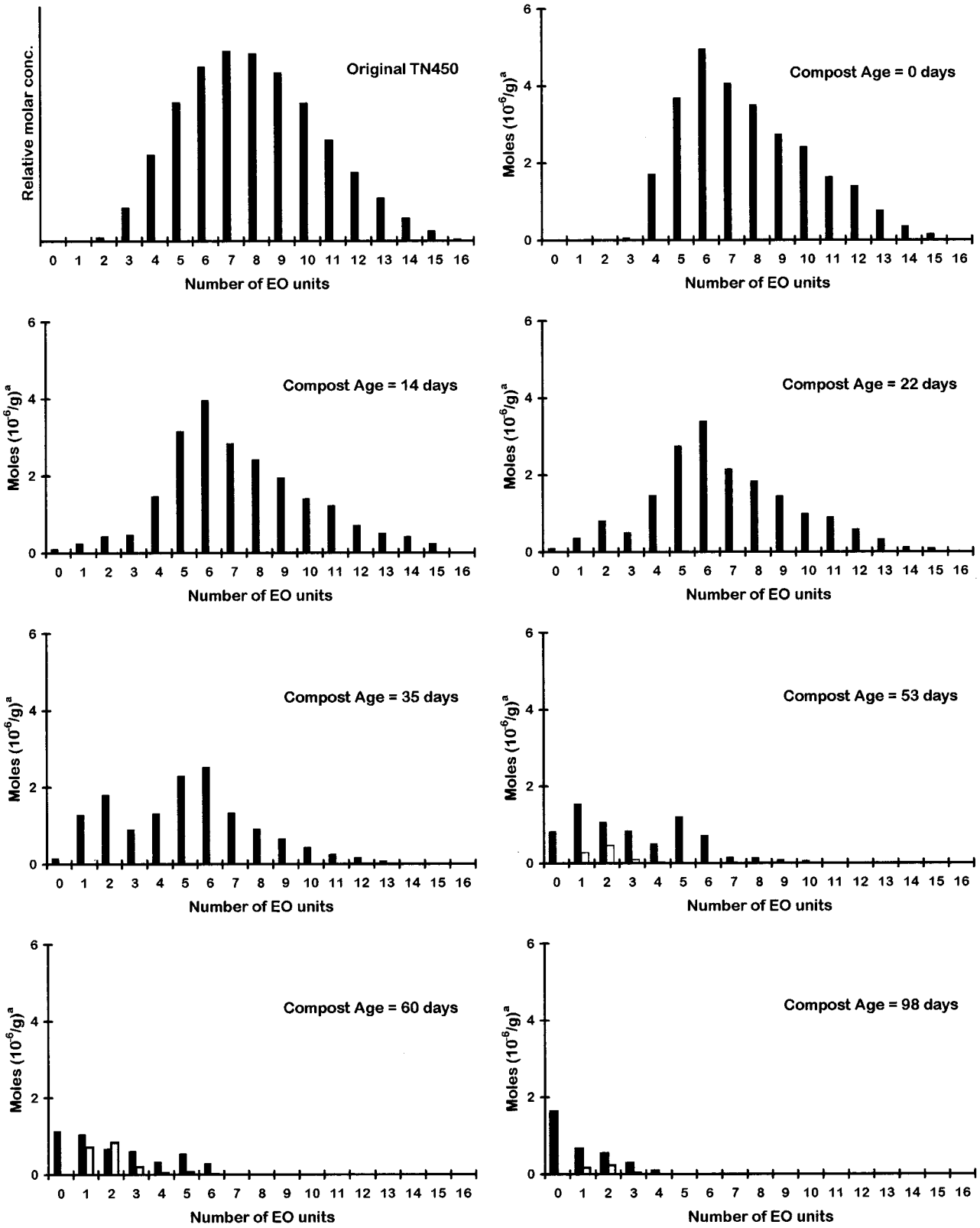

FIGURE 5. Changes in the concentration and distribution of the oligomers of TN_{450} during the composting of sludges derived from wool scour effluent. (■) $NPEO_n$; (□) NPE_nC.

affinity for the wool wax present. For example, the NPE present in this compost was initially recovered from aqueous wool scour effluent due to its partitioning into the wax recovered by chemical flocculation where the ratio of the wax to aqueous liquor was 1:200. Measurements of the concentration of the detergent in both the wax and treated wastewater indicate an average partition coefficient of 800–1000 for the NPE oligomers present. This affinity of the NPE for the wax would only be expected to increase as both the polarity of the residual wax increased with oxidation and the polyoxyethylene chain of the residual NPE oligomers were shortened during the composting process.

Little is currently known about the pathway of the biological degradation of the nonylphenyl hydrophobe in

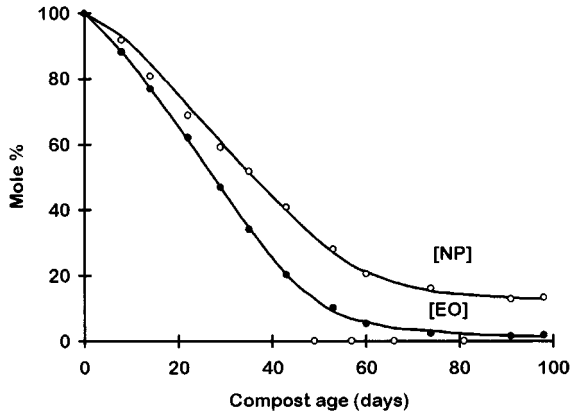

FIGURE 6. Residual mole percent of the nonylphenyl hydrophobe [NP] and total number of ethylene oxide units [EO].

NPE, although some early studies (*14*, *15*) have provided some evidence for the terminal oxidation of the alkyl group. Changes in the UV absorption characteristics of the aromatic ring during aerobic treatment on NPE have been observed (*16*), suggesting biodegradation in that region of the hydrophobe. However, to date no positive identification of the any metabolite involving the modification of the hydrophobe has been reported. Studies indicating the biorefractory nature of NP, $NPEO_1$, and $NPEO_2$ have generally been carried out on open systems such as sewerage works (*3, 4*) where mass balances could not be readily achieved. Kravetz et al. (*17*) using radiolabeled feed in a closed bench-scale biotreater demonstrated a steady-state condition in which 29% of the tritium label on the aromatic ring of the nonylphenyl hydrophobe had been converted to ^3H_2O as compared to the release of 58% of the ^{14}C as $^{14}CO_2$ from the labeled polyoxyethylene chain. They also found that the degree of degradation of the nonylphenyl hydrophobe was much more temperature dependent than the degradation of the polyoxyethylene chain with the degree of degradation falling to 10% and 50%, respectively, when the operating temperature of the bioreactor was decreased from 25 to 12 °C. These findings are consistent with the observations in the present study where the higher temperatures of the composting process produced a high degree of disappearance of the nonylphenyl hydrophobe. It is interesting that no metabolites that might be associated with the degradation of the hydrophobe were observed, suggesting that following the initial attack on this part of the molecule subsequent degradation was rapid.

After 14 weeks of composting, the total NPE and metabolites had been reduced from 14 to1.2 g/kg of compost on a dry weight basis. From the rate of degradation observed in this study, a further 14 weeks of composting would be required to degrade the recalcitrant nonylphenol, $NPEO_1$ and $NPEO_2$ oligomers to levels of less than 1 mg/kg. Alternatively, this degradation would substantially be completed by application of this material to soils. Marcomini et al. (*18*) examined the breakdown of NP, $NPEO_1$, and $NPEO_2$ in soils amended with contaminated sewage sludge and observed a very rapid disappearance of these contaminants with more than 80% being degraded within the first month. Complete degradation, however, was not observed with very little change in the concentrations occurring over the next 320 days. They postulated that this might be due to strong adsorption of the trace amounts of these molecules to the soil rendering them unavailable for further microbial degradation.

Results reported in this paper indicate that NPE detergents present in some sludges derived from the chemical flocculation of wool scour wastewaters are substantially degraded during composting with greenwaste producing only low levels of the recalcitrant nonylphenol and the lower ethoxylates. These products are expected to be further degraded during the subsequent horticultural use of the compost.

Acknowledgments

Financial assistance for this study was provided by the Australian Government and the Australian wool grower in the form of a research grant administered by the International Wool Secretariat. We also thank N. Milanovic for providing GC−MS analysis and assistance in interpretation; J. R. Christoe for helpful discussions; and D. E. Read, R. K. Martin, R. L. Elms, and G. Clifton for their technical assistance.

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Received for review January 13, 1998. Revised manuscript received June 5, 1998. Accepted June 10, 1998.

ES980026E