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Degradation of Nonylphenol Ethoxylates (NPE) in Sewage Sludge and Source Separated Municipal Solid Waste Under Bench-Scale Composting Conditions

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There is a growing interest in recycling of sewage sludge and municipal solid waste to agriculture, but the occurrence of organic contaminants in the waste may prevent this. One such family of contaminants is nonylphenol ethoxylates (NPE) which enters the waste streams by the widespread use of non-ionic surfactants.

Generally, composting accelerates decomposition of organic material and should, therefore, be a useful technique to decrease the concentration of organic contaminants including NPE in waste products. That this indeed is the case, has been demonstrated by Jones and Westmoreland (1999) and Jones and Westmoreland (1998) who composted sludge from wool scour effluents resulting in a large reduction of the total concentration of NPE in the finished compost. As a result of the biodegradation process, the distribution of NPE oligomers changed and after 100 days of composting only the degradation products nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO) and 4-nonylphenol (4-NP) remained (Jones and Westmoreland, 1998). These degradation products are more toxic to the environment than the parent NPE surfactant itself (e.g. Bennie, 1999; Hawrelak et al., 1999). As a consequence, the Danish authorities has imposed a limit of 30 mg/kg dry weight of the sum of 4-NP, NP1EO and NP2EO in organic waste products used for agricultural purposes (Danish Ministry of Environment and Energy, 2000). This limit will be lowered to 10 mg/kg dry weight in 2002, which may prevent recycling of a substantial fraction of the sewage sludge produced in Denmark as concentrations ranging up to 370 mg/kg dry weight of these compounds have been found (Madsen et al., 1998). The concentration in municipal solid waste compost is generally lower, e.g. 0.8 mg/ kg dry weight has been reported (Kristensen et al., 1996), but as the present study demonstrates transitory concentrations approaching the limit value can be encountered during composting of municipal solid waste.

Accordingly, the aim of our investigation was to study the degradation of NP2EO, NP1EO and 4-NP in sewage sludge and MSW during composting with special emphasis on the influence of process temperature. The experiments were conducted in a laboratory scale composting system that makes it possible to keep

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the compost at a fixed temperature for extended periods of time and simultaneously ensures an adequate oxygen supply to the compost micro-organisms.

MATERIALS AND METHODS

Composting experiments were done using a lab-scale system consisting of six 10 l reactors insulated with polyurethane foam. The process-temperature in each reactor is controlled by heating (with an electrical heating element) or cooling (with a fan) the process-air that is re-circulated through the compost by a diaphragm air pump. Fresh air is pumped into the reactor by another diaphragm pump. This set-up makes it possible to control composting temperature and oxygen status in the reactors independently. The temperature of the compost is measured using temperature probes placed in the core of the reactors. The outlet air passes a gas-analyser measuring oxygen and carbon dioxide concentrations. A PC with process-control and data acquisition software (Genesis™ for Windows) controls composting temperature and oxygen concentration in the reactors.

Fresh municipal solid waste compost of source-separated organic household waste was obtained from a composting plant at Frederikssund, Denmark. The compost is pre-treated in a composting drum for approx. 24 hours. Then shredded garden and park waste is added and finally the waste mixture is placed in windrows. We collected samples of fresh municipal solid waste compost directly from the outlet of the drum. Sewage sludge compost was taken from the Odense Losseplads Nord composting plant that processes sewage sludge from a sewage treatment plant near the city of Odense. The sewage sludge is mixed 1:1:1 (vol.) with straw and garden and park waste before it is placed in windrows. We collected fresh sludge compost samples from windrows no more than one week old. The reactors were loaded with either 3 kg dry weight of fresh municipal solid waste compost with addition of 300 g of garden and park waste as structural material or 2 kg dry weight of fresh sewage sludge compost. At the beginning, the average moisture content (on wet-weight basis) of the experiments was 60 % in the municipal solid waste compost and 50 % in the sludge compost. Temperature control was initiated when the compost had self-heated to above 40°C (with 35°C set point at 34°C) and a fixed temperature (+-2°C) was held for the duration of the composting run. The oxygen concentration in the reactors was kept above 2 % as concentrations below this in previous experiments (data not shown) were determined to be limiting for the composting process.

At intervals compost samples were taken for chemical analysis: From each reactor five sub-samples of approx. 10 g of composting material were pooled and mixed. The concentration of pollutants in the pooled sample was regarded to represent the concentration in the entire reactor (in some experiments duplicate pooled samples were collected from each reactor). One half of the sample was used for determining dry matter content of the material by heating to 90°C for 24 hours before re-weighing. The rest of the sample, approx. 25 g, was used for chemical analysis for 4-NP, NP1EO, and NP2EO. The sample was placed in a 0.5 l

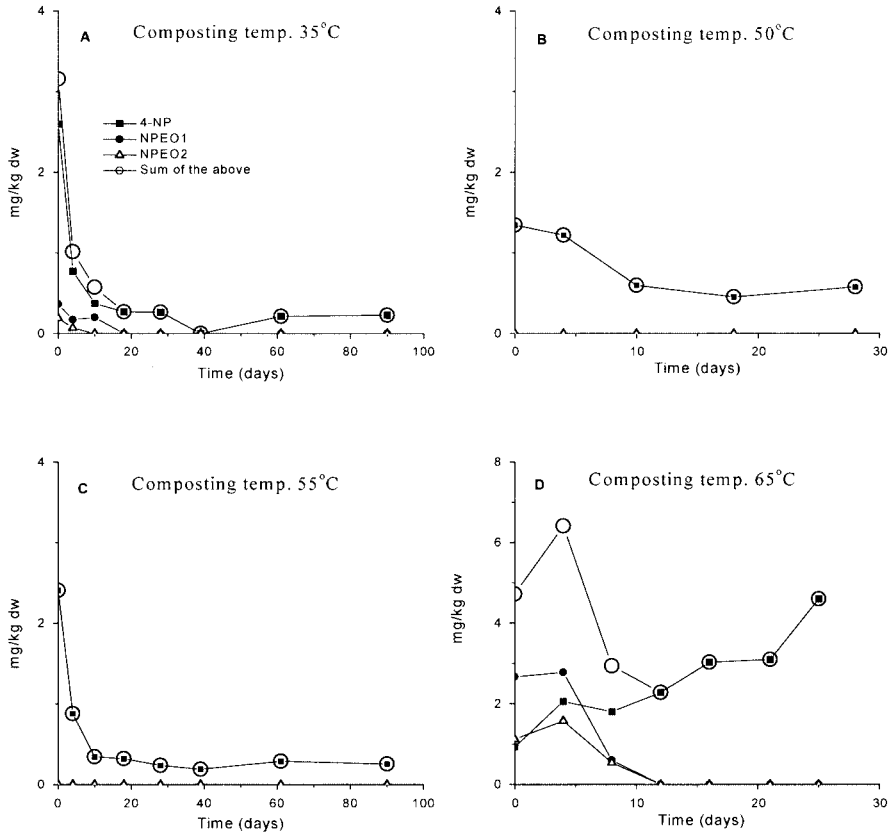

Figure 1. Degradation of nonylphenol ethoxylates during composting of sewage sludge. The sum of 4-NP, NPEO1 and NPEO2 is also shown as regulation in Denmark is based on this figure. In panel A and B each data point represents the concentration in one pooled compost sample. In panel C and D each data point represent the average of duplicate pooled compost samples.

blue-cap bottles (pre-heated to 500°C to prevent accidental contamination of the sample), the pH was adjusted to between 10 and 12 with sodium hydroxide and 150 ml of methylene chloride was added. After 5 min. of ultra-sonic extraction the mixture was placed on a wrist-action shaker (250 rev./min.) for two hours. The methylene chloride phase was concentrated approx. 15 times by placing it on a rotary evaporator.

The concentration of 4-NP, NP1EO and NP2EO in the extract was then determined by gas-chromatography/ mass spectrometry using selective ion monitoring (GC/MS-SIM). Using spiked samples a recovery of 90 % of the oligomeres was obtained by the extraction procedure.

RESULTS AND DISCUSSION

Figure 1 shows degradation of 4-NP, NPEO1 and NPEO2 during composting of sewage sludge. Identical patterns were seen during composting at fixed temperatures of 35, 50 and 55°C: At the beginning of the composting process 4-NP was present in concentrations around 2 mg/kg dw and NPEO1 as well as NPEO2 were practically absent. 4-NP was then degraded to concentrations below 1 mg/kg dw within 28 to 90 days of composting (fig. 1, panels A, B and C).

The initial concentrations of NPE in our experiments are much lower than the maximum concentrations in sewage sludge reported by Madsen et al. (1998). Several factors could influence that: There may be large differences between batches of sludge or an initial degradation process could have taken place in the windrows at the composting plant. Moreover, the fact that we measured the NPE concentrations in compost, i.e. in a mixture of sludge, wheat straw and garden waste should also be taken into consideration when comparing the levels in compost samples and sewage sludge alone.

In contrast to the other experiments, NPEO1 as well as NPEO2 were present at the beginning of the composting run held at 65°C (fig. 1, panel D). The different occurrence of the oligomers can be explained by the fact that the experiments were done using different batches of sludge. The pattern of degradation was also unique at 65°C as NPEO1 and NPEO2 rapidly disappeared while 4-NP accumulated resulting in a concentration of 5 mg/kg dw after 25 days of composting. It is also noteworthy that the sum of the three oligomers after four days of composting increased to 6.4 mg/kg dw even though the starting value was below 5 mg/kg dw.

We did not in the present study quantify the content in the waste products of NPEO oligomers with more than two ethoxylate groups, but others have shown that degradation of higher oligomers leads to formation of degradation products including 4-NP, NPEO1 and NPEO2. The reports differ, though, on the exact degradation pattern: Jones and Westmoreland (1998) saw accumulation of 4-NP, NPEO1 and NPEO2 following composting of wool scour containing high concentration of an NPE surfactant. In contrast, Potter et al. (1999) did not see any accumulation of 4-NP and only very small concentrations of NPEO1 during degradation of a NPE surfactant in estuarine water samples. Likewise, Manzano et al. (1998) reported transitory accumulation of NPEO2, but not of NPEO1, during degradation of a specific NPE surfactant. In our experiments with sewage sludge, composting at temperatures from 35°C to 55°C resulted in a net degradation of 4-NP and there were no sign of other degradation products. In contrast, composting at the extreme thermofilic temperature of 65°C resulted in a net accumulation of 4-NP with transitory elevated concentrations of the degradation products NPEO1 and NPEO2. As a consequence, it would be possible to start with a product that was in accordance with the regulation and as

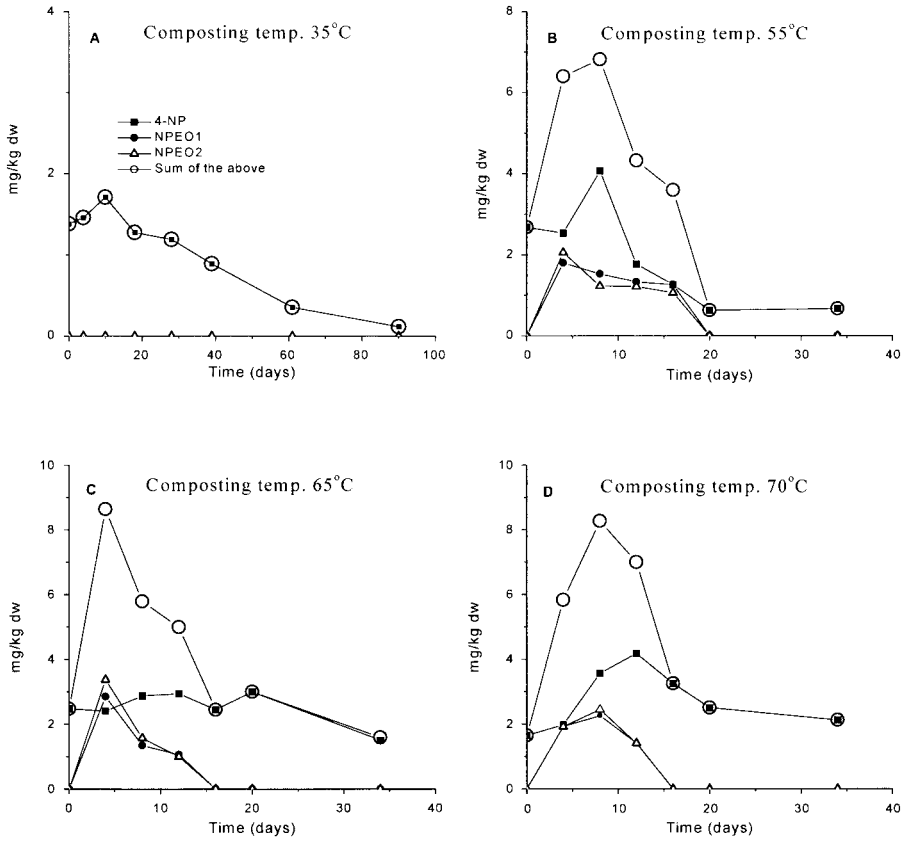

Figure 2. Degradation of nonylphenol ethoxylates during composting of municipal solid waste. In panel A and B each data point represents the concentration in one pooled compost sample. In panel C and D each data point represents the average of duplicate pooled compost samples.

a result of the composting process end up with an unsafe product (from the Danish authorities point of view) where the content of NPE exceeded the stipulated limit value.

Figure 2 shows degradation of 4-NP, NPEO1 and NPEO2 during composting of municipal solid waste. All four runs at 35, 55, 65 and 70°C had similar starting conditions with 4-NP concentrations around 2 mg/kg dw. NPEO1 and NPEO2 were not present. The three composting experiments at thermophilic temperatures (fig. 2, panel B, C and D) showed a transitory occurrence of NPEO1 and NPEO2 that was accompanied by an increased concentration of 4-NP after 8 days of composting. At this sampling date the sum of the three oligomers – with a maximum of 8.3 mg/kg dw at the 70°C composting run – approached the Danish 2002 limit value for NPE of 10 mg/kg dw allowing agricultural use of the

waste product. Following the disappearance of NPEO1 and NPEO2 the elevated 4-NP concentration slowly decreased except in the composting run at 70°C which showed a slight net increase in 4-NP after 39 days of composting. In contrast, there was no sign of the degradation products NPEO1 and NPEO2 during the composting experiment held at 35°C and there was a net degradation of 4-NP. This experiment was done with another batch of municipal solid waste compared to the other composting runs. The absence of NPEO1 and NPEO2 can, therefore, not solely be ascribed to the lower process temperature. It may be that the concentration of higher oligomers was different in the fresh waste, but the general pattern was that higher process temperatures resulted in decreased net degradation of 4-NP.

The reason for the decreased degradation rate of 4-NP at temperatures at 65°C and above is not obvious and has – to our knowledge – not previously been reported in the literature. One hypothesis is that degradation of 4-NP is done by micro-organisms that are unable to function at extreme thermophilic temperatures. This would indeed be the case if fungi were involved in 4-NP degradation as these organisms are known to stop growing above 65°C (Sharma and Johri, 1992). Another possibility is that 4-NP toxicity to micro-organisms increases at high temperatures – this mechanism has been demonstrated for a number of organic pollutants, e.g. polyaromatic hydrocarbons (Song et al., 1990).

To conclude, our study shows that NPEO1, NPEO2 and 4-NP are all degradable under aerobic composting conditions in sewage sludge as well as in municipal solid waste compost, but under extreme thermophilic conditions we observed accumulation of 4-NP in the waste. Our study, therefore, suggests that the composting process should proceed through an extended mesofilic stage in order to ensure maximum degradation of 4-NP. This is of special importance when – as in Denmark – it is the concentration of the contaminants in the untreated waste material that constitutes the basis of regulation of the use of the composted product in agriculture.

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