Rapid Anaerobic Degradation of Toxaphene in Sewage Sludge

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Introduction

Technical toxaphene is a complex mixture of a multitude of components, including more than 600 chlorobornanes and related compounds. Chlorobornanes and other toxaphene components seem to be ubiquitous, and accumulate in biota and biomagnify in the food chain. Studies indicate a much less complex pattern in biota than in the technical mixture, suggesting degradation processes. However, currently the degradation processes are not fully understood. Fingerling, et al. (1) found significant degradation of toxaphene in soil, most likely via biotic pathways, using certain chlorobornane congeners and a technical mixture. Much less complex chlorobornane patterns also have been observed in sediments as compared with technical toxaphene mixtures (2, 3). Generally, reductive dechlorination is considered a major degradation pathway of the chlorobornanes, particularly under anaerobic conditions. HxSed and HpSed are common chlorobornanes that have been identified in sediments (2, 3). In an earlier publication, we recommended further research to determine whether these components were the result of a selective secondary degradation or a primary formation from another source (2). The results of another study presented at this conference exclude certain industrial activities as an additional source of these compounds (4). In this study, we report on the degradation and fate of a technical toxaphene mixture in sewage sludge as an anaerobic model system.

Experimental Section

The experimental conditions largely followed those used in a previous study on the degradation of hexachlorocyclohexanes (HCHs) in sewage sludge (5). Sludge from the anaerobic stabilizer from the municipal waste water treatment plant in Wädenswil, Switzerland, was used. Three 300-mL serum bottles were filled with ~ 250 g sludge each, to which 1 g of soluble starch and 2.5 g of bakers' yeast dissolved in 10 mL of water were added as nutrients. One bottle was autoclaved (2 h at 130°C) and then used as a sterile control. All bottles were then fortified with 750 µg of a technical toxaphene mixture (Hercules Corporation, Wilmington, DE, USA) and 100 µg of α-HCH, dissolved in 100 µL ethyl acetate, and then incubated at 25°C in the dark on a reciprocal shaker. α-HCH was added as a chiral marker for later analysis using enantioselective

determinations. Periodically (t = 0, 1, 2, 4, 7 and 16 d), 20-g samples were removed. Each sample was fortified with 100 ng $^{13}C_6$-γ-HCH as an internal standard, and was then extracted with 20 mL acetone/n-hexane (1/1, v/v) by vigorous shaking. After centrifugation, the supernatant was removed and partitioned with 10 mL of distilled water. Extraction was then repeated with a 10 mL portion of n-hexane. The organic phases were combined and concentrated to ~ 1 mL and then passed through silica in a Pasteur pipette with 10 mL of methylene chloride. After concentration, the residue was dissolved in 10 mL of toluene. A 1-μL aliquot was used for ECNI/MS analysis using a 25-m SE54 GC column under conditions previously described (6, 7) The amounts of hexa- to decachlorobornanes and related compounds in the samples were determined from peak area ratios relative to the internal standard ($^{13}C_6$-γ-HCH), monitored at m/z 259. The toxaphene components were monitored using the ions at m/z 307, 343, 377, 413, 445 and satellite ions previously listed (6, 7). The peak area ratios determined were then corrected for sample size, and the concentrations (C) were expressed in % relative to the initial concentration at t = 0 (C_0). Peak identifications were made in relation to individual congeners commercially available (Ehrenstorfer, Augsburg, Germany).

Results and Discussion

The chlorinated bornanes rapidly degraded under anaerobic conditions in sewage sludge. The degradation was much slower in the sterilized sludge, indicating that the degradation in active sewage sludge is predominately biotic -- likely caused by anaerobic, methanogenic micro-organisms.

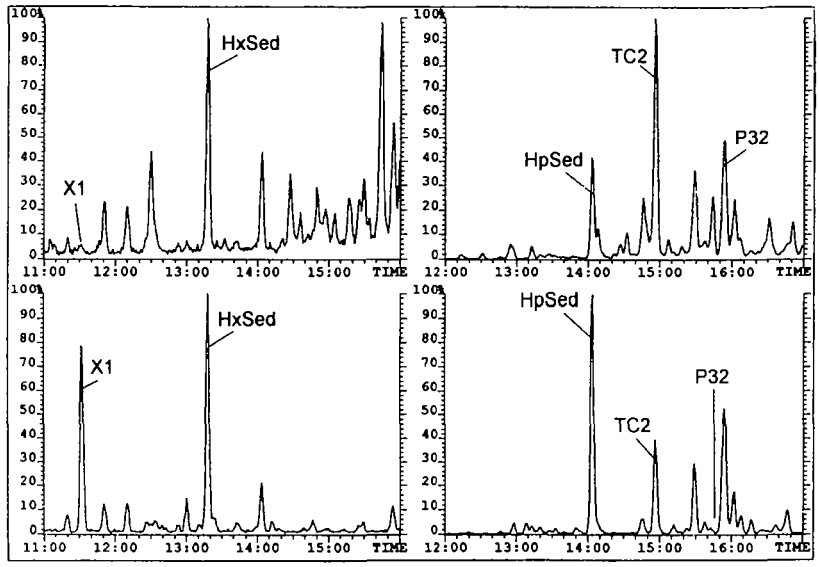

Figure 1: ECNI SIM chromatograms (m/z 307, left-side panels; m/z 343, right-side panels) showing elution of hexa- and heptachlorobornanes in active sewage sludge after 0 (upper panels) and 16 days of incubation (lower panels).

Figures 1 and 2 show the elution of hexa- through nonachloro homologues prior to (t=0) and after 7 days of incubation. As shown in the ECNI SIM chromatograms, the isomeric composition changed drastically after incubation. In the case of the hexachloro compounds, HxSed is the major component remaining after incubation. In addition, a not yet characterized (presumably) chlorobornene compound (X1) is present. In the case of the heptachloro compounds, P32 (toxicant B) is rapidly degraded, as is TC2 and others. The major heptachloro component remaining after incubation is HpSed. In the case of the octachloro compounds, several components are rapidly degraded, including P42 (toxicant A); the major components remaining after incubation are P41 and P44. In the case of the nonachloro compounds, all are degraded significantly, and the major component remaining after incubation is P63.

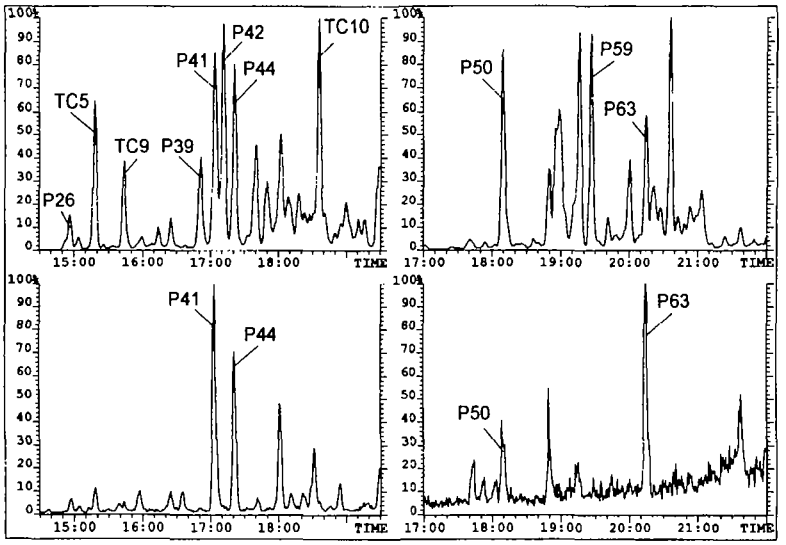

Figure 2: ECNI SIM chromatograms (m/z 377, left-side panels; m/z 413, right-side panels) showing elution of octa- and nonachlorobornanes in active sewage sludge after 0 (upper panels) and 16 days of incubation (lower panels).

Figure 3 shows the relative amounts of the hexa- through nonachloro homologues normalized to the initial (t=0) concentration plotted versus incubation time. The data show that the nonachloro compounds are most rapidly degraded, followed by the octa- and heptachloro compounds. The hexachloro compounds, on the other hand, particularly compounds X1 and HxSed, show an initial increase in concentrations, followed by a decrease.

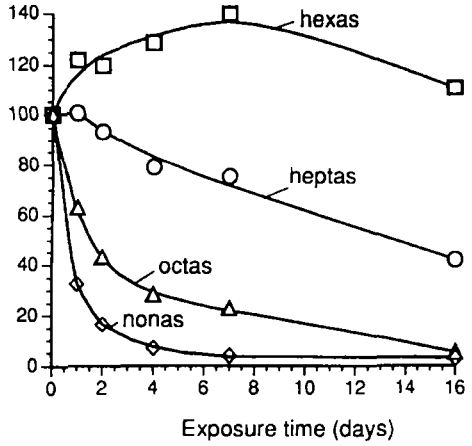

Figure 3: Degradation of hexa- through nonachlorobornanes in active sewage sludge. Relative amounts normalized to the initial (t=0) concentration plotted versus incubation time.

Our results follow the trend observed by Fingerling, et al. (1) for the anaerobic degradation of toxaphene in soil, but with significantly more rapid degradation in our case. In fact, we observed half-lives as low as one day. The predominant degradation pathway under these conditions appears to be reductive dechlorination as indicated by the increase in the hexa- and partially in the heptachloro congeners. This pathway was previously identified by Fingerling, et al. (1) for degradation in soil. Further, dehydrochlorination seems to be a possible additional degradation pathway, because of the formation of the unsaturated hexachloro component X1.

The data reveal that primarily congeners with *gem*-Cl_2 substitutions (*e.g.*, P32, P42, P59) are most rapidly degraded. The data further show that compounds previously considered quite resistant to degradation (*e.g.*, P26, P50, P63) are degraded significantly.

Acknowledgment

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References

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