Enantioselective degradation of Bromocyclene in sewage plants

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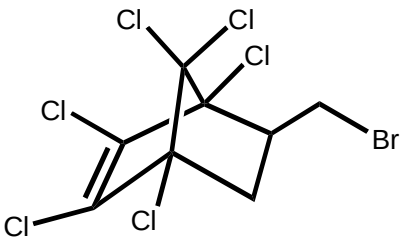
Introduction

Bromocyclene (structural formula in fig. 1) has been utilised as insecticide against ectoparasites, however the production in Germany was stopped around 1995. Until that time it was used in pet care as well as in sheep farming. Due to its high bioaccumulation it was detected not only in sewage systems and sewage treatment plants[1)], but also in fresh water fish [2,3)]. Enatioselective determination at that time was used to obtain results on the biodegradation of Bromocyclene in fish. Considering the long time period since the phase out of Bromocyclene it was surprising it was easily identified in sludge samples from 2002 (compare fig. 2).

Fig. 1: Structural formula of Bromocyclene



Methods and Materials

Sewage sludge was sampled from 20 sewage treatment plants in Northrhine-Westphalia (Germany). The respective sludge samples were lyophilised and homogenised. Subsamples of these were Soxhlet-extracted (6 h ethylacetate). The extracts were concentrated afterwards and successively cleaned up by means of size exclusion and silica (The procedure is described in detail in Bester 2003 [4]). The samples were quantified by means of GC-MS in electron impact (70 eV) mode using a "Trace" GC-MS (Thermo-Finnigan, Dreieich, Germany) equipped with a DB-5 column. The following temperature programme was utilised: 90 ^{o}C [2 min] -> 10 ^{o}C/min -> 280 ^{o}C [15 min].

After an additional Silica gel clean-up (eluent *n*-hexane 5 % MTBE) the samples were analysed by GC-MS utilising a 25 m 0.25 mm ID, heptakis-(2,3-di-O-methyl-6-*O*-*t*-butyldimethyl-silyl)-ß-cyclodextrin column (Macherey und Nagel, Düren, Germany) utilising a temperature programme of: 110 ^{o}C [1 min] -> 5 ^{o}C/min -> 152 ^{o}C [40 min] -> 5 ^{o}C/min -> 230 ^{o}C [20 min] in a "Trace Plus" GC-MS system in electron impact (70 eV) mode (Thermo-Finnigan, Dreieich, Germany).

Baseline separation of the enantiomers was achieved and three mass fragments, i.e., 357, 359 and 361 were used for enatioselective determination (compare fig. 3).

Results and Discussion

Bromocyclene was identified by GC-MS in German sewage sludge samples from 2002 (Fig. 2). In these samples the concentrations varied from < 1 ng/g to 240 ng/g (Fig. 4). This variation is much higher than those determined for Triclosan, the polycyclic musks (HHCB, AHTN) or other compounds which were determined in the same samples. On the other hand the concentrations of Bromocyclene was significantly lower than those for Triclosan. This leads to the assumption that either diverse processes are relevant in the diverse sewage treatment plants (STPs) or the sources are diverse and possibly not continuous in time.

Enantioselective analysis was applied to study whether or not biodegradation may take place in the respective sewage treatment plants, possibly the digesters..

The enantiomeric ratios that were determined ranged from 0.75 to 1 (+/-0.02). This may be indicating that Bromocyclene is not processed the same way in all sewage treatment plants, but there are different ecosystems in the diverse digesters due to differing sludge retention, different dominant carbon sources, different temperatures etc. These differences may result in different degradation pathways or kinetics.

Anyway, the degradation process is in none of the sampled sewage treatment plants fast enough to eliminate Bromocyclene totally from the sludge, though. As 30 % of the sewage is currently added to agricultural land this may lead to increased concentrations of this biocide in soils.

Fig.2: EI-Mass spectrum of Bromocyclene from a sludge sample

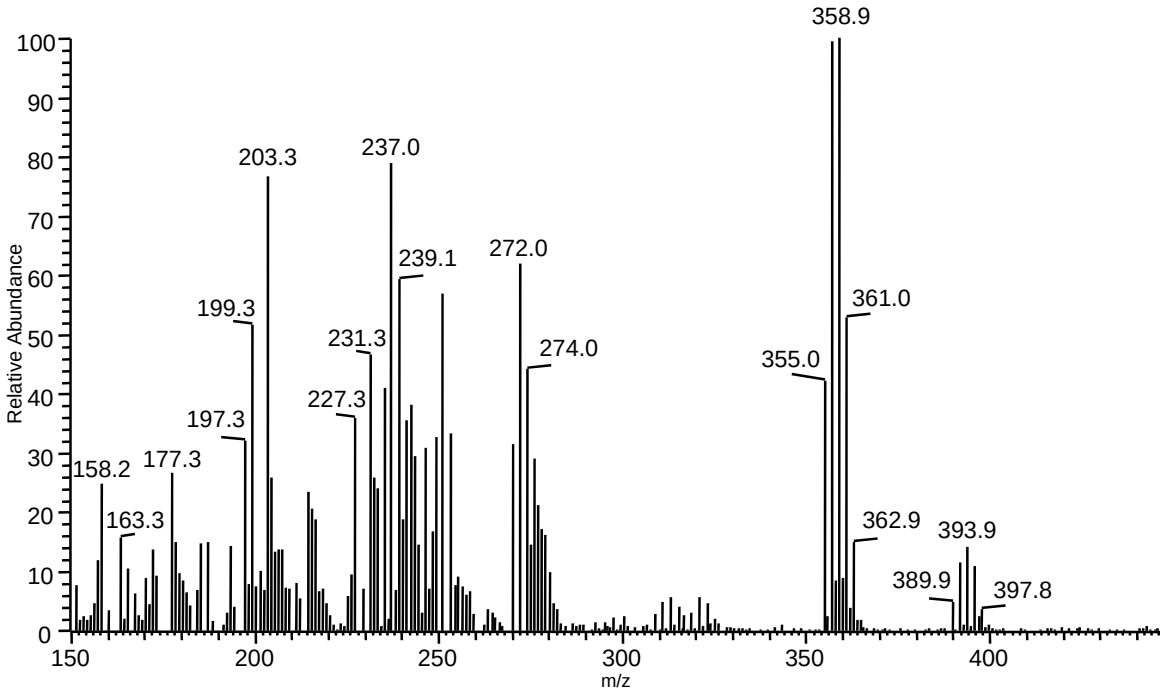


Fig. 3: Enantioselective determination of Bromocyclene in a sewage sludge sample elution order following Bethan et al. [1].

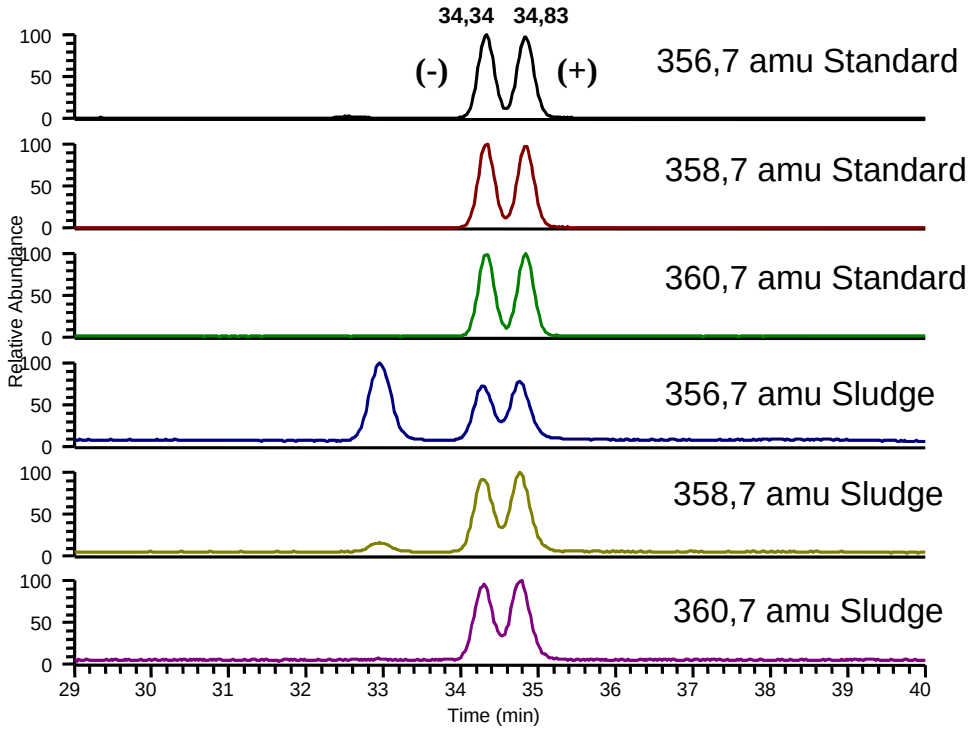


Fig. 4: Concentrations of Bromocyclene in sewage sludge samples (15a and 20a are from the same plant).

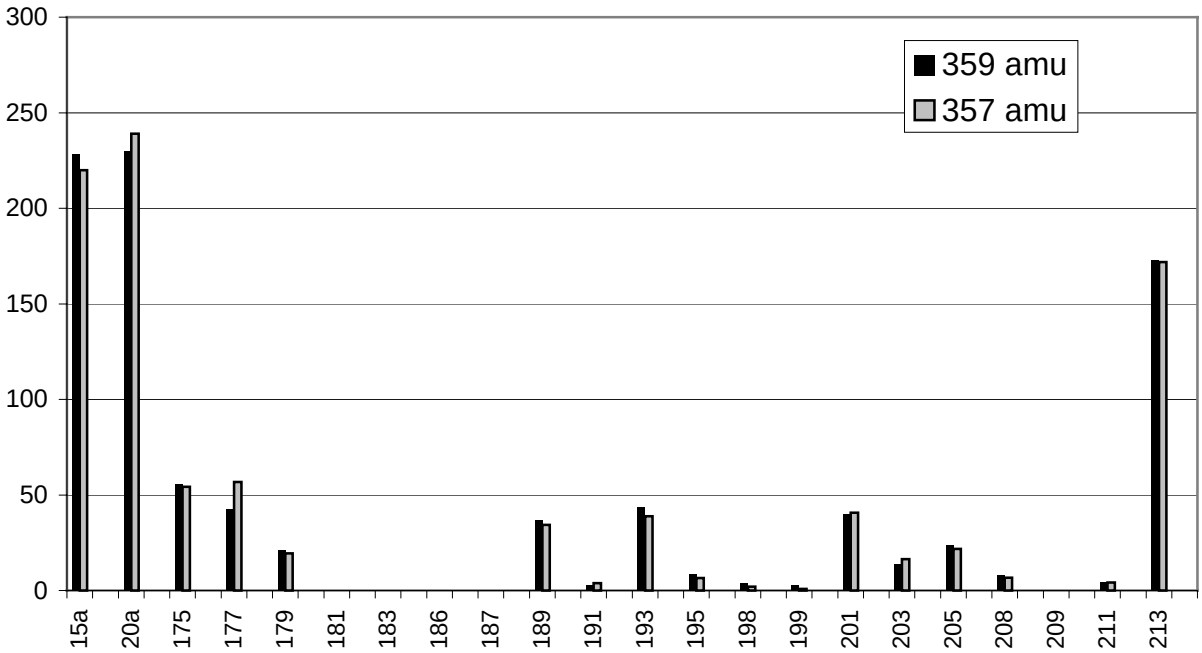
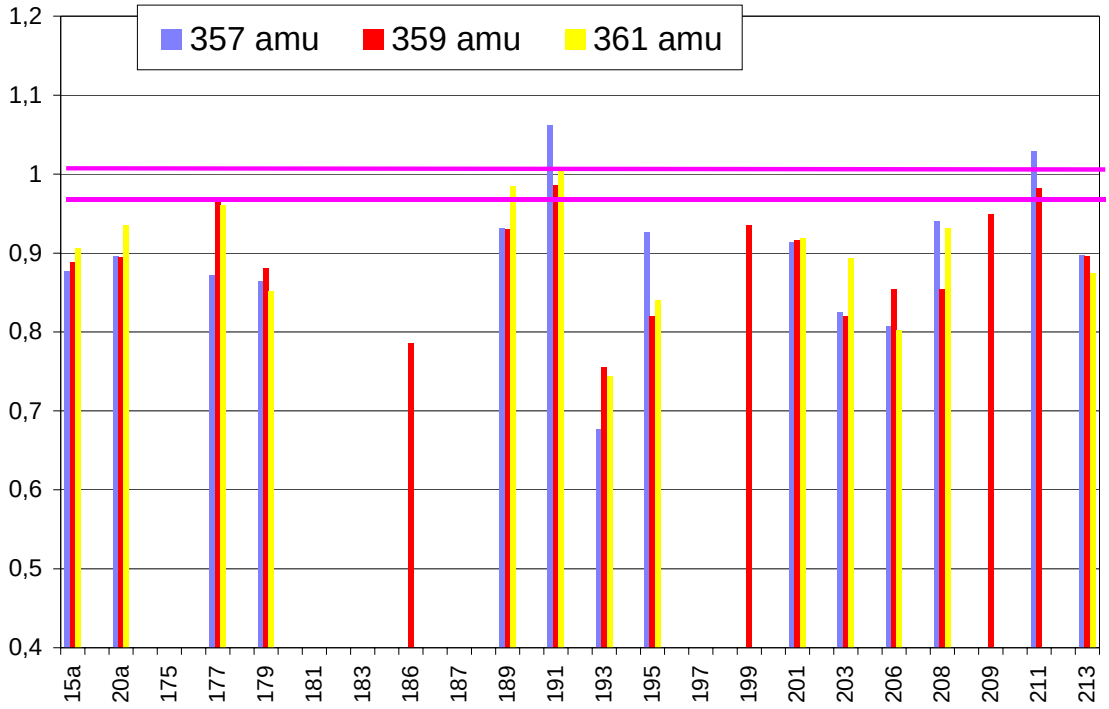


Fig. 5: Enantiomeric ratios of Bromocyclene in sewage sludge samples. The standard deviation of the measurements are indicated by a bar.



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