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Degradation and Residues of Cyclohexyltin Compounds in Orchard Soil Following Field Application of Cyhexatin*

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The organotin based acaricides (cyhexatin (Plictran), azocyclotin (Peropal), fenbutatin oxide (Torque)) and the fungicide, fentin, are valuable in controlling phytophagous pests and fungal plant deseases. However, only limited data are available on the environmental behavior, degradation, and ecotoxicological relevance of residues of these compounds and their degradation products (Zuckermann et al. 1978). This may be due to the lack of comprehensive and sufficiently sensitive detection methods, as determination of organotin residues usually requires recovery of related, but with respect to their physico-chemical properties, widely differing compounds.

This paper describes the levels and environmental behavior of cyhexatin residues in soil of an orchard following an application of cyhexatin in the spring of 1985. Residues were monitored for a period of over 300 days by using a novel procedure for residue determination of organotin compounds in environmental samples (Müller 1984, 1986). Determination was based on extraction of the cyclohexyltin compounds as bromides and tropolon complexes in ethereal solution, ethylation with a Grignard reagent and analysis of the resulting tetrasubstituted cyclohexylethyltin compounds by high resolution gas chromatography with flame photometric detection (HRGC-FPD). The degradation of the parent compound (I, cf. Scheme 1) in soil was found to be slower than on apples (Getzendanner and Corbin 1972) and strawberries (Gauer et al. 1974). Dicyclohexylstannic oxide (II) and cyclohexylstannoic acid (III), the main environmental degradation products, were found to persist in soil for a much longer time than the

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parent compound. Repetitive applications of cyhexatin may therefore lead to high residue levels of cyclohexyltin compounds in soil.

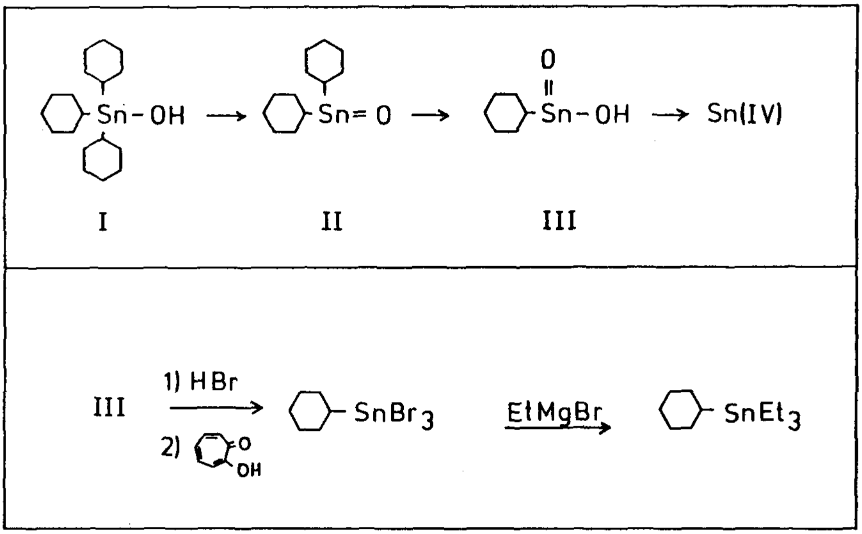
MATERIALS AND METHODS

The solvents used were of high purity and were obtained from Merck (Darmstadt, FRG) and Fluka (Buchs, Switzerland). The Grignard reagents were prepared from Mg turnings and ethylbromide or cyclohexylbromide, as appropriate. 2-Hydroxy-2,4,6-cycloheptatrien-1-on (tropolon) and HBr were obtained from Fluka.

Spraying was conducted at the end of May 1985 (2000 L spray solution /ha, 0.1 % of a formulation with 25 % active ingredient, corresponding to 0.5 kg cyhexatin/ha) using an air blast sprayer. Soil samples were collected one day before spraying and at various intervals after treatment. Each soil sample consisted of three replicate cores (6 cm inner diameter, 8 cm depth) taken under the semi-dwarf trees. At each sampling date, the new core samples were collected at locations closely adjacent to where previous samples were taken. The cores were homogenized and refrigerated at 2 °C in glass jars with aluminium foil-lined screw caps.

Details of the analytical method are given in Müller, (1986). It includes addition of an internal standard, tributyltin chloride, to the soil, treatment with about 1 N HBr, extraction of the cyclohexyltin compounds as bromides out of the aqueous slurry by using an ethereal tropolone solution and conversion of the mono-, di- and tricyclohexyltin bromides into the ethylated tetrasubstituted compounds (cf. Scheme 1, bottom) with a Grignard reagent (ethylmagnesiumbromide) for subsequent analysis by using HRGC- FPD and analyte confirmation by using HRGC/MS.

A Carlo Erba (Milan, Italy) 2101 gas chromatograph fitted with a split/splitless injector, a 15 m glass capillary column with a 0.15 µm film of SE 54 and a Carlo Erba type 250 SSD flame photometric detector without optical filter were used. Hydrogen (0.3 bar) served as the carrier gas. A temperature program (5 °C/min, starting at 80 °C) was used to elute the compounds of interest. For analyte confirmation, extracts and standard material were also analysed on a Finnigan 4000 GC/MS system, fitted with the same capillary column and using the same temperature program. Electron-impact (EI) mass spectra were recorded at 50 eV electron energy, by using a mass range of m/z 100 to 500.



Scheme 1: Degradation of Cyhexatin in the environment (top) and extraction and ethylation of cyclohexylstannoic acid (compound III) (bottom).

RESULTS AND DISCUSSION

Cyhexatin (I) is degraded according to Scheme 1 (Getzendanner and Corbin 1972) to successively yield dicyclohexyltin oxide (II) and cyclohexylstannoic acid (III). The parent compound is reported to have a half-life of about 20 days on fruits. Compound II reaches a concentration plateau after a short time, whereas III is reported to play a minor role, indicating a rapid mineralization yielding inorganic tin(IV).

In order to study the recovery of compounds I, II and III from soil, the two degradation products (II and III) were synthesized by reacting $SnCl_4$ with cyclohexylmagnesiumbromide. The reaction mixture contained I, II, III (as the respective chlorides) and tetracyclohexyltin, as determined by subsequent ethylation followed by a GC/MS analysis. The EI mass spectra for the three ethylated compounds are given in Figure 1. A weak molecular ion can be observed for all three compounds. Fragmentation is initiated by cleavage of either an ethyl- or a cyclohexyl-moiety (M^+-29 or -83), followed by a series of rearrangement reactions, where ethene (m/z 28) or cyclohexene (m/z 82) is cleaved off. This leads to a complex fragmentation pattern, where each ion cluster shows the typical isotope distribution for tin. The signal cluster around m/z 120 is due to SnH-compounds, the final breakdown product of the organotin molecule. The mass spectra for the ethylated compounds I and II are in good agreement with those described for the methylated ones (Stewart and Cannizzazaro 1980).

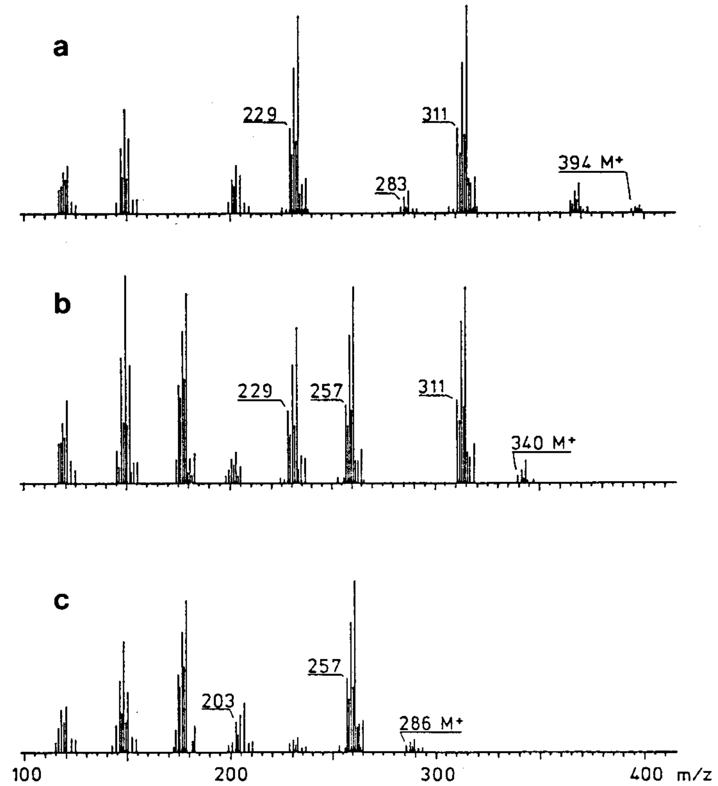


Figure 1: EI-mass spectra of ethylated compounds: I tricyclohexylethyltin (a), II dicyclohexyldiethyltin (b), III cyclohexyltriethyltin (c).

As pure reference standards of II and III were not available, calibration of the photometric response for the ethylated compounds II and III in the GC-FPD-analyses was conducted based on the response of tricyclohexylethyltin and corrected for the differing analyte response as described elsewhere (Müller 1986).

The known mixture containing compounds I, II, and III, as chlorides, was added at the low ppb-level to soil samples previously analysed and found to contain less than 0.1 ppb butyl- and cyclohexyltin compounds. Tributyltin chloride was added as an internal standard, and extraction was performed as described above. Recoveries for all compounds of interest were found to be in the range of 80 - 90 % . Inorganic tin(IV) is also recovered and may be quantitated as tetraethyltin after ethylation. As tin(IV) levels in the soil investigated were considerably higher (ppm level) than the contribution due to the degradation of organotin compounds (ppb level), inorganic tin was not determined.

The formulation used for spraying was analysed for degradation products and was found to contain less than

0.01 and 0.1 % of compounds II and III, respectively. Degradation of I under the extraction and derivatization conditions used was found to be negligible ($<$0.1 % for II and III).

Soil samples were collected at various intervals after application, homogenized, and analysed. Because the cyclohexyltin compounds appear to be strongly adsorbed on soil particles, the depth distribution for the three compounds of interest was investigated. More than 90 % of the cyclohexyltin compounds found was present in the uppermost 1-cm layer of the soil. Thus, the soil cores contained virtually all the organotin reaching the soil; also the homogenization of the total core sample diluted the compounds of interest. Cyhexatin transport into soil is assumed to occur as a result of
(a) direct input via spray fog,
(b) runoff from sprayed leaves and fruits, and
(c) secondary runoff with rainwater.

Routes (b) and (c) are believed to be the most important. Depending on spraying techniques, direct runoff is more or less pronounced; (c) is reported to be an effective route for removing cyclohexyltin residues from apples and pears (Getzendanner and Corbin 1972). Figure 2 shows the degradation of compounds I, II and III, given as relative concentrations (sum of I, II and III = 100 %) rather than absolute concentrations. One day before spraying, no cyclohexyltin compounds could be detected. After the treatment, compound I dissipated with a half-life of about 50 days. Residues of compound II were relatively constant over the time interval studied. The amount of compound III reached its maximum, when, after 300 days, the experiment was terminated as the soil of the orchard was ploughed and sampling was no longer possible. Due to the long and cold winter, sampling was not possible between late October 1985 and spring of 1986. Thus, no data are given in Figure 2 for the time interval between 80 and 300 d postapplication. Total residues in soil of compounds I, II and III for the 3- and 300-day samples were 72 and 68 ppb (dry weight), respectively. Thus, degradation of cyhexatin is more a conversion to cyclohexylstannoic acid rather than a mineralization process. These data indicate a clearly different situation than encountered for residues on fruits, where I and to a lesser extent II seem to be the predominating compounds (Getzendanner and Corbin 1972, Gauer et al. 1974, Möllhoff 1977, ten Broeke and Dornseiffen 1979), and III was either not determined or reported to play a negligible role. Cyhexatin residues are located on the surface of the fruit and therefore undergo photolytic degradation. In contrast,

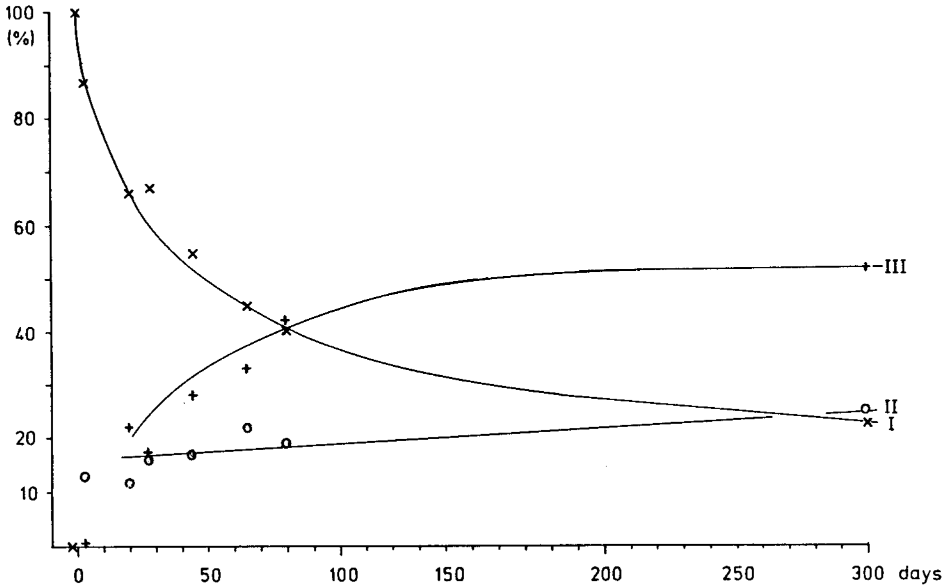


Figure 2: Relative amounts of cyclohexyltin compounds I, II and III (cf. scheme 1) in orchard soil after cyhexatin application t = 0 days. For details see text.

photochemical degradation in soil is limited to residues on the soil surface and there is a high potential for biotic and soil catalyzed degradation reactions. This may explain, together with analytical problems in the recovery of the highly polar compound III, the apparent difference in degradation behaviors. Cyclohexyltintribromide, a monoalkyltin compound, requires a complexing agent, tropolone, to render it sufficiently lipophilic for its extraction into an organic solvent (Meinema et al. 1978).

These data indicate a considerable persistence of the cyclohexyltin compounds in soil under field conditions. Low soil temperatures during winter prevent further degradation of cyclohexyltin residues. Repeated applications of cyhexatin and related products may therefore give rise to increasing residue levels of cyhexatin and its degradation products.

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