FATE AND DEGRADATION OF ORGANOCHLORINE COMPOUNDS IN TERRESTRIAL ECOSYSTEMS

I. Scheunert

GSF-Institut für Bodenökologie
Ingolstädter Landstr. 1
D-8042 Neuherberg, FRG

ABSTRACT:

In terrestrial ecosystems, organochlorine compounds are dechlorinated and converted to various transformation products. Mineralization rates and the formation of soil-bound residues depend on the degree of chlorination as well as on other substituents in the molecule.

INTRODUCTION:

Organochlorine compounds reach the soil both by intentional use and by unintentional processes, such as atmospheric deposition, waste disposal or spilling. Due to the xenobiotic C-Cl bond, most of them are persistent in the soil system, and residue decline is primarily by physical processes. Conversion reactions mostly concern other substituents present in the molecule besides the chlorine substituents. These reactions cause changes in the transport behaviour of chlorinated compounds in soil, as well as in volatilization into the air and in plant uptake rates. However, there exist also specific microorganism strains or other organisms in soil, which are able to cleave the foreign C-Cl bond by various reaction mechanisms. Similarly, abiotic dechlorination mechanisms exist in soil.

EXAMPLES OF BIOTIC DECHLORINATION MECHANISMS:

The following dechlorination mechanisms have been reported to occur in soil or in microorganisms isolated from soil or similar natural media:
1. Oxidative mechanism: Oxygenolysis of chlorinated aromatic compounds to 1,2-dihydroxy aromatics[1]
2. Reductive mechanism: Replacement of chlorine by hydrogen atoms (DDT → DDD[2]; lindane → tetrachlorocyclohexane[3]); elimination of chlorine bound to C-C-bonds, resulting in C=C bonds (lindane → benzene[4])
3. Hydrolytic mechanism: Replacement of chlorine by hydroxyl groups originating from water (2-haloalkanoic acids[5], chlorinated aromatic compounds[6], s-triazines[7])
4. Dehydrochlorination: Elimination of HCl (DDT → DDE[8]; lindane → pentachlorocyclohex-1-ene[9])
5. Dechlorination after conjugation: Replacement of chlorine by sulphur groups (pentachloronitrobenzene → 1,4-dithiomethyl-2,3,5,6-tetrachlorobenzene in earthworms[10])

In order to identify conversion products of lindane in soil, lindane-^{14}C was applied on various plants and soil (about 12 mg on a 60 · 60 cm area) in a lysimeter under outdoor conditions. At the end of the growth period, soil was extracted with methanol in a soxhlet. The extract was separated by various chromatographic methods, and conversion products were isolated and identified by gas chromatography/mass spectrometry[9].

In order to identify conversion products of lindane in compost, lindane-^{14}C was applied to a household and garden waste mixture (2 mg/kg dry weight) treated with a commercial composting inoculum, and incubated in a compost container (Ø 50 cm, height 91 cm) under outdoor conditions for 57 or 777 days, respectively. The compost was extracted and analysed for lindane metabolites as above.

For the determination of mass balance, biomineralization and bound residue formation of various ^{14}C-labeled organochlorine compounds in soil/plant systems, a closed aerated laboratory apparatus was used as described in [12,13]. [14]CO$_2$ was determined after trapping in a scintillation liquid containing an organic base. Soil-bound residues were determined, after soxhlet extraction of the soils with methanol, by combustion followed by liquid scintillation counting of [14]CO$_2$ formed.

## RESULTS AND DISCUSSION:

It was demonstrated that the chlorinated insecticide lindane-^{14}C undergoes, in soil, various dehydrogenation, dehydrochlorination, dechlorination, and oxidation steps resulting in pentachlorocyclohex-1-ene, chlorinated benzenes, and chlorinated phenols. Hexachlorobenzene was detected as a lindane metabolite only in trace amounts[9]. Upon composting household and garden wastes containing lindane-^{14}C, the parent compound could not be detected any longer after 55 days. After 55 or 777 days, respectively, all three isomeric trichlorobenzenes were isolated and identified, besides unidentified polar metabolites [11].

Biomineralization rates and soil-bound residues of various ^{14}C-labeled chlorinated compounds are shown in the following table. It shows that, in principle, chlorinated organic compounds can be mineralized to CO$_2$. Mineralization decreases with increasing chlorine content of the molecules; however, other substituents present in the molecules also play a role. Soil-bound residues greatly decrease mobility and plant bioavailability of organochlorine compounds. These residues also decrease with increasing chlorine content of the molecule; however, they are influenced also by other molecular substituents. Aromatic hydroxy or amino groups, for example, strongly favour the formation of soil-bound residues due to their chemical similarity to natural humic acid precursors in soil. Model experiments have demonstrated the formation of covalent bonds between chlorinated anilines and the humic acid precursor catechol [14].

Biomineralization and Soil-bound Residues of ^{14}C-labeled Organochlorine Compounds,
7 Days after Application to soil (in % of ^{14}C applied)

| ^{14}C-Chemical | [14]CO$_2$ | Soil-bound [14]C |
|---|---|---|
| 2,4,6-Trichlorophenol | 20.8 | 62.3 |
| Hexachlorocyclopentadiene | 19.4 | 51.5 |
| Trichloroethylene | 9.2 | 26.9 |
| Pentachlorophenol | 4.1 | 38.4 |
| Chloroalkylene-9 | 3.4 | 7.4 |
| 2,2'-Dichlorobiphenyl | 2.5 | 4.1 |
| Aldrin | 1.6 | 9.5 |
| 4-Chloroaniline | 1.1 | 70.0 |
| 2,5,4'-Trichlorobiphenyl | 0.7 | 1.9 |
| Atrazine | 0.5 | 4.0 |
| 1,2,4-Trichlorobenzene | 0.5 | 3.5 |
| 1,4-Dichlorobenzene | 0.4 | 0.8 |
| Hexachlorobenzene | 0.1 | 2.0 |
| Kepone | 0.1 | 1.6 |
| Kelevan | 0.1 | 1.2 |
| Dieldrin | 0.1 | 0.7 |
| 2,4,6,2',4'-Pentachlorobiphenyl | 0.1 | <0.1 |
| 1,2,3,5-Tetrachlorobenzene | <0.1 | 2.5 |
| Pentachlorobenzene | <0.1 | 1.1 |
| p,p'-DDT | <0.1 | 0.4 |

It may be concluded that in terrestrial ecosystems organochlorine compounds are transformed both by alterations of substituents other than chlorine and by dechlorination processes. Mineralization to $CO_2$ also occurs. By the interaction with soil humic substances, bound residues may be formed, which considerably decrease mobility in soil and plant availability. However, their role in the leaching of residues still needs more research.

REFERENCES:

1.  Reineke, W., Forum Mikrobiol. 12, 402 (1989)
2.  Golovleva, L.A., Skryabin, G. K., in: Microbial Degradation of Xenobiotic and Recalcitrant Compounds (eds.) Leisinger, H., Cook, A.M., Hutter, R., Nüesch, J., p. 287, London, Academic Press (1981)
3.  Haider, K., Jagnow, G., Arch. Microbiol. 104, 113 (1975)
4.  Fries, G.F., in: Fate of Organic Pesticides in the Aquatic Environment, Advan. Chem. Ser. 111, p. 256, Washington D.C., Amer. Chem. Soc. (1972)
5.  Motosugi, K., Soda, K., Experientia 39, 1214 (1983)
6.  Apajalahti, J.H.A., Salkinoja-Salonen, M.S., J. Bacteriol. 169, 675 (1987)
7.  Behki, R.M., Khan, S.U., J. Agric. Food Chem. 34, 746 (1986)
8.  Guenzi, W.D., Beard, W.E., J. Environ. Qual. 5, 391 (1976)
9.  Kohli, J., Weisgerber, I., Klein, W., Korte, F., J. Environ. Sci. Health B11, 23 (1976)
10. Khalil, A.M.: Aufnahme und Metabolismus von Hexachlorbenzol-$^{14}$C und Pentachlornitrobenzol-$^{14}$C in Regenwürmern. Doctoral Thesis, Technical University of Munich, FRG (1990)
11. Weber, B.: Verhalten von $^{14}$C-markierten Umweltchemikalien bei der Herstellung von Gartenkompost. Doctoral Thesis, Technical University of Munich, FRG (1989)
12. Kloskowski, R., Scheunert, I., Klein, W., Korte, F., Chemosphere 10, 1089 (1981)
13. Topp, E., Scheunert, I., Attar, A., Korte, F., Ecotoxicol. Environ. Saf. 11, 219 (1986)
14. Adrian, P., Lahaniatis, E.S., Andreux, F., Mansour, M., Scheunert, I., Korte, F., Chemosphere 18, 1599 (1989)