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Enantioselective Analyses of Persistent and Modern Pesticides. A Step Toward Sustainable Agriculture

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Abstract. In the conflicting goals of sufficient food for a growing world population and conservation of natural resources, the safe use of environmentally friendly pesticides plays an important role. A general concept of sustainable agriculture and how modern, efficient pesticides comply with the basic ideas of a sustainable farming are given and discussed. Modern pesticides often are mixtures of stereoisomers with largely different biological properties on the target and non-target organisms. More and more of these pesticides are used in enantiopure forms, leading to clearly reduced risks for the environment. The assessment of the fate, environmental concentrations and risks related to the use of a specific compound relies mainly on modern environmental analytical techniques, such as enantioselective high-resolution gas chromatography with various mass spectrometric detection techniques. Several of these techniques are described and selected results presented.

Introduction

The last years have seen an increasing public awareness of limited resources in food production for a growing world population [1] and of risks related to current farming practices. The use of pesticides in agriculture is still indispensable to safeguard a sufficient quantity and quality of the crops. Therefore, considerable efforts have been spent to assess and reduce potential risks associated with the use of pesticides by national authorities and international bodies such as the OECD [2].

In this article, we describe some aspects of the current approach of the Swiss authority for pesticide registration to evaluate benefits and risks in the application of pesticides. In agreement with the agricultural policy for a more ecological agricultural production [3], we define the safe and ecological use of agrochemicals using the concept of sustainability. We are well aware that the use of pesticides is only a limited, but important aspect of this concept, which may briefly be defined as 'ecologically sound, economically viable,

socially just and humane' [4]. In this article, we focus on the ecochemical aspects of pesticide use and then describe the application of sophisticated analytical techniques to assess the fate of pesticides in the environment.

Sustainable Agriculture

The 'Rio Conference' has brought the concept of sustainability into broad acceptance [5]. The term sustainability has been coined for the effort of limiting the impact of human activities on the environment to such an extent, that no significant and long-term adverse effects should occur. Briefly, a sustainable economy can be described by the following four rules [6]: 1) the extent and the nature of the pollution of the environment should be limited to the amount, which can be eliminated in the respective environmental compartment, 2) harvesting of renewable resources should not exceed the rate of growth of these resources, 3) the use of non-renewable resources such as natural gas should be increasingly substituted by renewable ones, and 4) the market economy (prices of goods) should reflect the limited nature of non-renewable resources. We like to point out, that the first rule is in full agreement

with the Swiss ordinance on dangerous substances based on the Law on Environmental Protection [7], which requires sufficient degradability of organic substances intentionally deployed into the environment. Beside an evaluation of efficacy and the minimization of effects on non-target organisms, the assessment of the environmental behavior is of high priority in the registration of pesticides.

During the last 20 years, the phasing out of most of the persistent organochlorine pesticides was achieved. These 'old' compounds clearly did not fulfill the first rule of sustainability (see above). Nevertheless, it is still important to follow the decline of residues of such pesticides in the environment, as these compounds can serve as a benchmark to assess the behavior of more modern compounds.

The Need for Enantiopure Pesticides

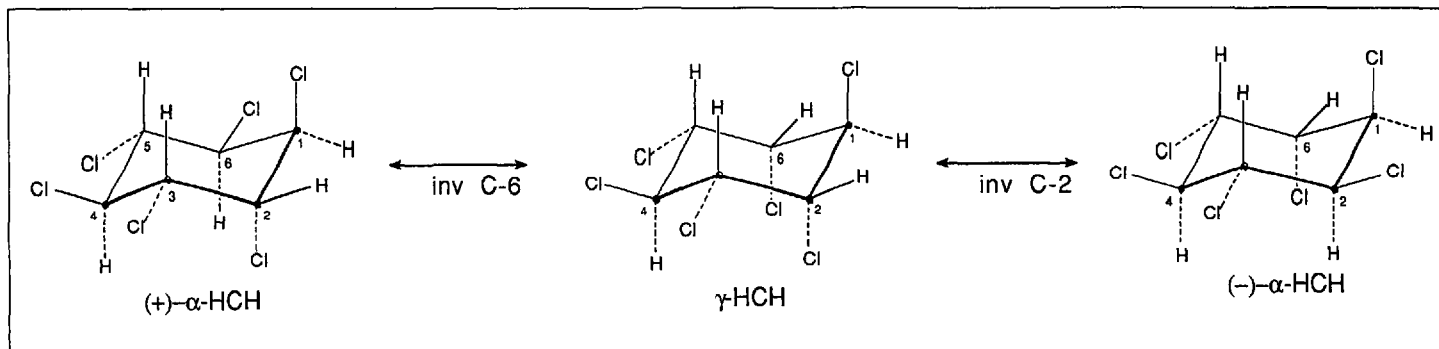
The last ten years have seen an increasing number of pesticides, initially marketed as mixtures of stereoisomers or enantiomers, being introduced as enantiopure compounds [8]. These developments do comply with the legal requirement that 'only the amount necessary for the desired purpose should be deployed into the environment' [7]. By using enantiopure pesticides, side effects and risks for the environment can be clearly reduced whereas the desired biological activity on the crop is still maintained. In our view, the use of enantiopure, environmentally 'friendly' pesticides is thus a key feature of implementation of the use of pesticides in a sustainable agriculture.

The substitution of racemic mixtures by enantiopure compounds, where most or all of the desired biological activity resides in one enantiomer, therefore, opens the possibility to significantly reduce the amount of pesticides deployed in the environment by omitting what is called 'isomeric ballast'. In this way, a considerable reduction of risks associated with the use of pesticides is achieved. However, a benefit-risk evaluation gets increasingly complex since the assessment of fate and side effects has to include additional considerations such as the potential racemization of the pure enantiomer.

The chemical and physicochemical properties of enantiomers (optical isomers) are identical, except that they rotate the plane of polarized light in opposite directions and that they react differently in a chiral environment. Their behavior (uptake, metabolism, excretion) in biological systems may thus be largely different.

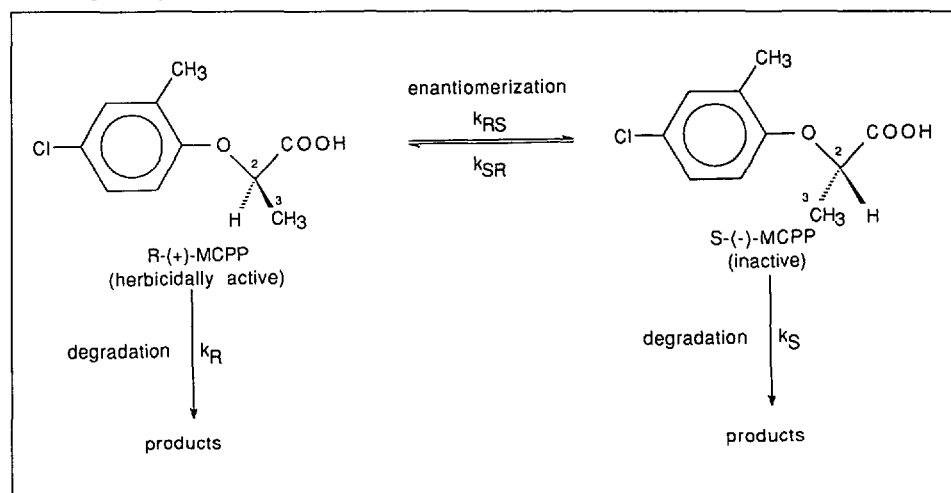
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Scheme 1. Structure and Relationship between the Enantiomers of α -HCH, and γ -HCH. The thermodynamically most stable conformers (chair forms, maximum number of chlorines in equatorial position) are shown. Inversion of a single Cl at C(2) (or C(6)) leads to the isomeric compounds.



Therefore, enantio-/stereoisomers of chiral pesticides may show largely different biological properties such as different herbicidal, fungicidal, or insecticidal activity [9]. Furthermore, one can assume that these isomers may also have different environmental fate as far as biological processes (e.g., microbial degradation) are involved, as we will show with some examples below. This is in contrast to abiotic processes (chemical processes, transport, distribution) where no enantioselectivity is expected. One of the prerequisites for the study of the environmental fate of enantio-/stereoisomers are adequate analytical techniques which are briefly outlined below.

Scheme 2. General Reaction Scheme for the Transformation of the Chiral 2-(4-Chloro-2-methylphenoxy)propionic Acid (MCP) via Enantiomerization and Degradation. The rates were used for modeling, as reported in [19].



Enantioselective Residue Analysis – The Key Element in the Assessment of the Environmental Fate of Chiral Pesticides

Enantioselective separations are carried out using high-resolution gas chromatography (HRGC) and high-performance liquid chromatography (HPLC). Enantiomer resolution is obtained by the presence of a chiral auxiliary reagent (chiral selector) in the columns. Enantioselective HRGC was carried out using columns based on mixtures of achiral polysiloxanes and various cyclodextrin (CD) derivatives (alkylated, acylated, silylated). Briefly, glass or fused silica capillary columns are statically coated with a mixture of an achiral polysiloxane (PS086, OV1701) and the desired CD derivative. The columns prepared show good separation efficiencies and inertness, and they tolerate temperatures up to 250°. In general, a careful selection of the columns was required as none of them showed sufficient enantio-/stereoselectivity for all compounds under investigation.

Mass spectrometric analyses were carried using a VG Tribrid double-focusing magnetic sector hybrid mass spectrometer

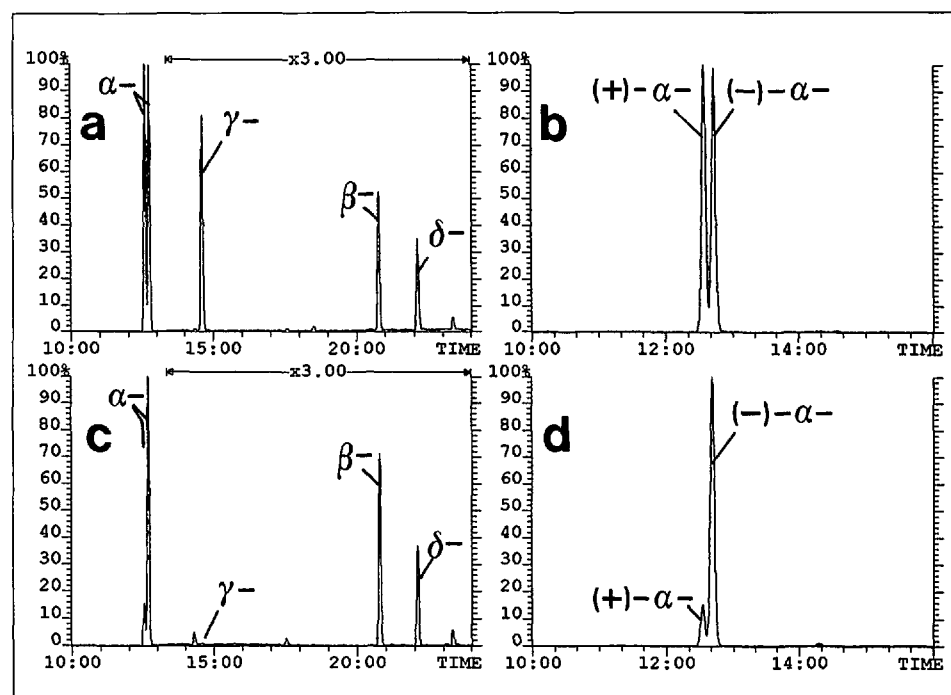


Fig. 1. EI SIM (m/z 219) Chromatograms showing the enantioselective degradation of the chiral α -HCH in sewage sludge from a communal sewage treatment plant (Zürich-Glatt). (a, c) Technical HCH after 0 and 172 h of incubation, respectively. (b, d) Racemic α -HCH after 0 and 172 h of incubation, respectively. Sample extracts were analyzed on an enantioselective PS086-PMCD HRGC column (PMCD = permethyl- β -CD) which eluted the (+)- α -HCH ahead of the (-)- α -HCH. Note also virtually complete degradation of γ -HCH from the technical HCH.

(VG Analytical Ltd., Manchester, England) with the ion source operated either in the electron ionization (EI, 70 eV, 180°) or electron-capture negative ion mode (ECNI, 50 eV, 140°, Ar as buffer gas). MS Analysis was done by recording full-scan spectra (resolution of $M/\Delta M$ of 500), or by using selected-ion-monitoring (SIM) for improved sensitivity. For selected analyses, the MS/MS capabilities of the instrument were used in the 'selected-reaction-monitoring' (SRM) mode with the quadrupole analyzer set at nominal resolution. In this mode, the formation of specific daughter ions generated through low-energy collisions from selected parent ions was monitored. In general, the samples are comparatively analyzed using columns with achiral and chiral stationary phases.

Enantioselective HPLC with native CDs, alkylated CDs or other chiral selectors in combination with UV, RI and polarimetric detection was primarily used to resolve and isolate small (μg - mg) amounts of enantio-/stereoisomers and for the assignment of the levo- and dextrorotating enantiomers *via* optical rotation. The enantiomerically enriched compounds were then used for an unambiguous assignment of the enantiomers in subsequent enantioselective HRGC-MS analyses. In general, the amounts isolated using this technique were sufficient not only for HRGC analyses but also for further chemical reactions. In this way, the absolute configurations of enantiomers of several other compounds could be assigned by chemical analogy (for an example, see below).

In the following sections we document the application of these techniques toward studies on the environmental fate and the behavior of persistent as well as of environmentally more 'friendly' pesticides. We selected results of our own studies on organochlorine (HCH, DDT) and on more degradable pesticides such as the phenoxyalkanoic acid and acetamide pesticides of which we have investigated specific chiral aspects. Although these examples are from pesticides that are known since a long-time, some for over 50 years, the chiral aspects of these compounds have only recently become of interest, mainly because enantioselective analytical techniques at trace level concentrations (parts-per-trillion) were previously not available.

Selected Results

Hexachlorocyclohexanes (HCHs)

HCH was among the most important insecticides for use in agriculture, forestry

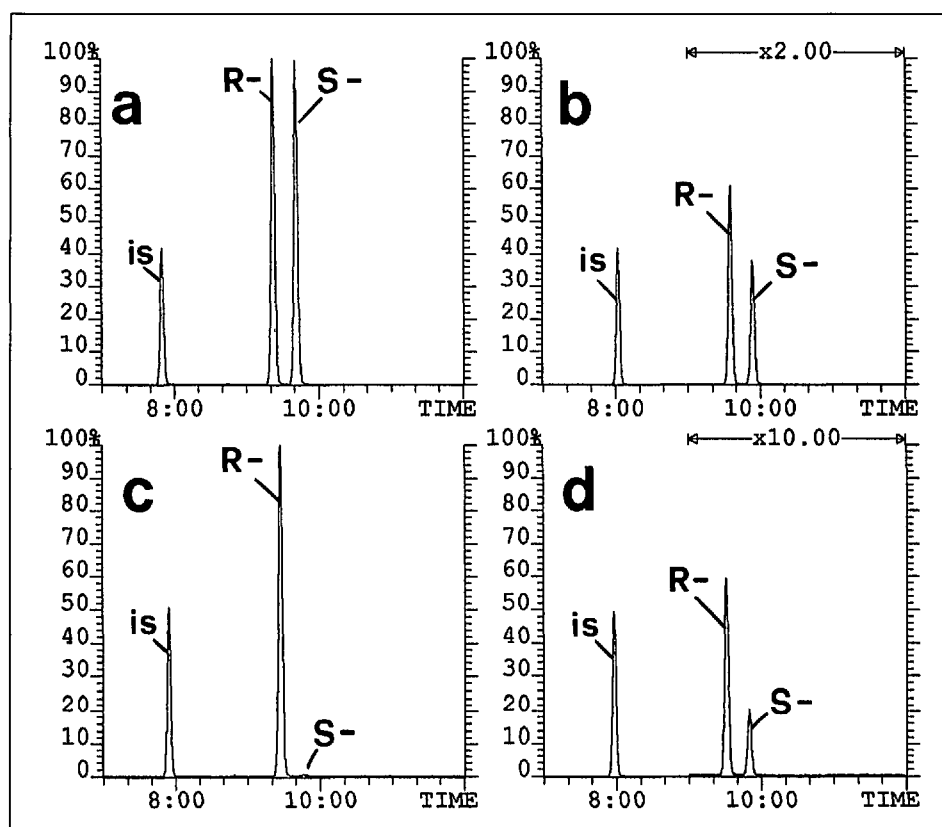


Fig. 2. EI SIM (m/z 228) Chromatograms showing enantioselective degradation and enantiomerization of the chiral MCPP in soil. (a, b) Racemic MCPP after 0 and 30 d of incubation, respectively. (c, d) Enantiopure (*R*)-MCPP after 0 and 30 d of incubation, respectively. Abbreviations: R- = (*R*)-MCPP, S- = (*S*)-MCPP, is = internal standard (clofibric acid, isomeric to MCPP). Note the enantiomer resolution of MCPP (analyzed as the methyl esters) achieved on the enantioselective OV1701-TBDM HRGC column (TBDM = heptakis(2,3-dimethyl)-6-*tert*-butyldimethylsilyl- β -CD). Note enantiomerization of the (*R*)- into the (*S*)-enantiomer as shown by chromatogram d.

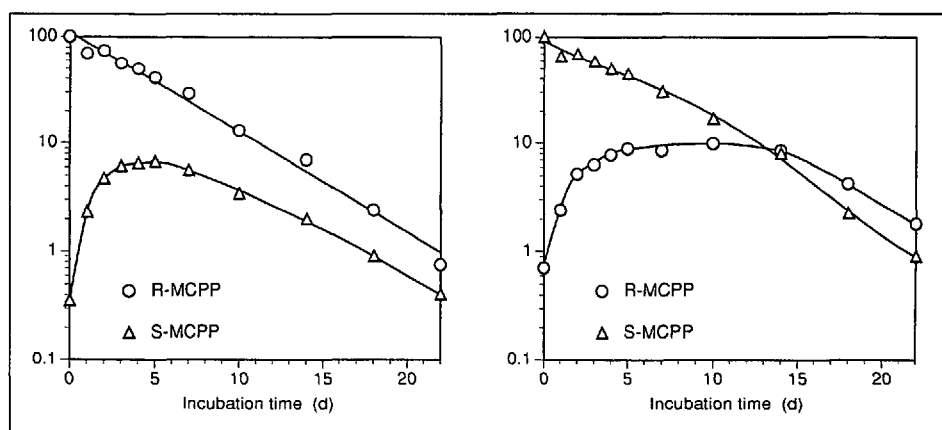


Fig. 3. Degradation of MCPP in soil under laboratory conditions. (a) Degradation of (*R*)-MCPP showing concurrent formation of (*S*)-MCPP, (b) degradation of (*S*)-MCPP with concurrent formation of (*R*)-MCPP. Normalized concentrations ($100 \times c/c_0$, logarithmic scale) are plotted vs. incubation time. Note that the curves for the (*S*)- and (*R*)-enantiomers intersect in panel b (racemic composition at 14 d), eventually indicating a 'reversed' enantiomeric composition ($R > S$). Note that the enantiomeric composition eventually is $R > S$ independent whether racemic or the enantiopure product was incubated.

and as a wood preservative [10]. It is produced by chlorination of benzene under UV light which leads to a mixture of various isomers [11]. Typically, the technical mixture consists of ~60–70% of α -HCH, 10–15% of γ -HCH, and other isomers. γ -HCH (lindane) reportedly is the only isomer with insecticidal properties. It

is isolated from the technical mixture by crystallization. Nowadays, the use of technical HCH has been discontinued in most industrialized countries, but it likely continues to be of some importance in developing countries [12]. HCH, in particular the α - and the γ -HCH isomers, continue to be major global pollutants and are readily

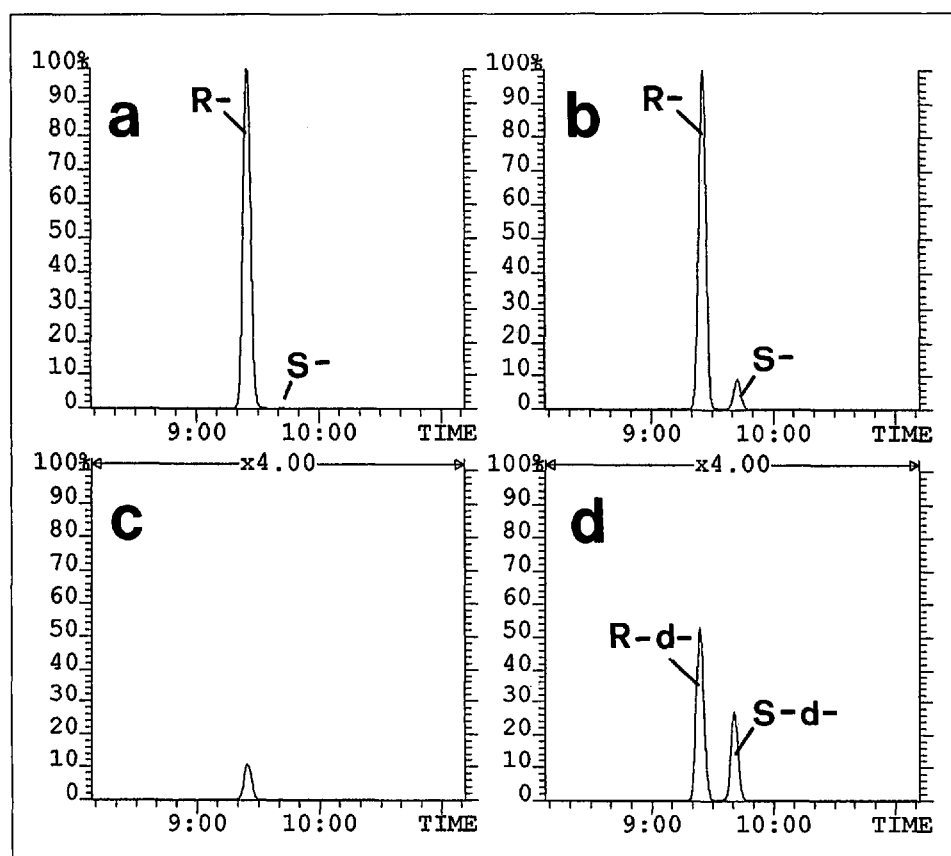


Fig. 4. SRM Chromatograms showing elution of (a,b) native MCPP (transition 169^+ to 125^+ , loss of CH_3CHO) and (c,d) deuterated analogs (transition 170^+ to 125^+ , loss of CH_3CDO) prior (panels a, c) and after (panels b, d) incubation of (R)-MCPP in $\text{D}_2\text{O}/\text{soil}$, analyzed as methyl esters on an enantioselective OV1701-TBDM HRGC column. Note enantiomerization of the native compound as shown by chromatogram b, and the formation of both deuterated analogs as indicated by chromatogram d. Intensities are normalized to that of the monoisotopic transition except for the vertical expansion as indicated. The small peak in chromatogram c is due to the ^{13}C isotopomer.

found in specimen from most environmental compartments. The major HCH isomer, α -HCH, is chiral and exists as two enantiomers (for structures, see *Scheme 1*; the absolute configurations of the α -HCH enantiomers are from analogy to those of the inositols [13]. Pure γ -HCH is still valuable in special, limited applications (seed dressing) and shows a more favorable environmental profile than certain modern insecticides. In the technical process α -HCH is formed as the racemate. Recent investigations [14] indicated α -HCH residues in biota to be non-racemic which can only be caused *via* biotic degradation.

Despite the extensive data on HCHs [15][16] the fate of these compounds in the environment is still not fully understood. In particular the distinction between biotic and abiotic processes is often difficult, and it is here that enantioselective analyses should come into consideration. In this context, we recently studied the anaerobic degradation of HCHs in sewage sludge as a model environment [17]. In *Fig. 1* we show EI SIM chromatograms of samples from the incubation of technical HCH and of α -HCH in sludge. The results show high enantioselectivity for α -HCH

with the (+)-enantiomer much faster degraded than the (–)-enantiomer. This and the fact that the degradation in sterilized sludge was significantly slower and non-enantioselective, indicated that the degradation in active sewage sludge is predominantly biotic, likely caused by anaerobic, methanogenic microorganisms. The results from the experiment with α -HCH showed little if any isomerization to γ -HCH. It is anticipated that enantiomerization (or racemization) is even less likely as it would require changing the position of not only one but of two Cl's (see *Scheme 1*).

Phenoxyalkanoic Acid Herbicides

This group of compounds includes a number of important herbicides. In particular the phenoxyacetic and the 2-phenoxypropionic acids such as MCPA, MCPP (mecoprop), 2,4-D, and others are very popular. Whereas the phenoxyacetic acids are achiral, the 2-phenoxypropionic acids (MCPA, others) are chiral. It was recognized some time ago that for these chiral compounds only the (R)-enantiomers show herbicidal activity [18], and since the 1980s the enantiopure products ((R)-enantiomers)

have replaced the earlier-used racemic products in Switzerland and other countries [8]. In *Scheme 2* we show the absolute configurations of the two enantiomers of MCPP.

The degradation of the chiral MCPP and related pesticides was studied by incubation of the racemic and the enantiopure compounds in soil under laboratory conditions [19]. The study showed the herbicidally active (R)-enantiomers to be slower degraded than the inactive (S)-enantiomers, as documented by the EI SIM chromatograms in *Fig. 2*. Unexpectedly the study also revealed significant enantiomerization with formation of the (S)- from the (R)-enantiomers, and *vice versa* (compare *Fig. 2, c* and *d*). This enantiomerization, which for the (R)-enantiomer eliminates part of the herbicidal activity, was found to be biologically mediated, as it was not observed in sterilized soil; the use of enantiopure (R)-MCPP still makes sense, as the compound is taken up by plants *via* the leaves. In *Fig. 3*, the degradation plots summarize the data from the experiments with enantiopure (R)- and (S)-MCPP. These plots document the significant enantiomerization and show that for (S)-MCPP the enantiomeric composition of the residues is eventually 'reversed'. It is anticipated that enantiomerization is an important process in the environmental fate and behavior of these compounds and that the residues in environmental samples (soil, water) will not necessarily reflect the enantiomeric composition of the products used.

The mechanism of enantiomerization was investigated in more detail from incubation experiments of MCPP in $\text{D}_2\text{O}/\text{soil}$, and following the formation of deuterated analogs using enantioselective HRGC and MS/MS [20]. Detection by MS/MS showed less interference from natural ^{13}C isotopomers than conventional MS and it allowed the localization of deuterium in the labeled compounds. The results indicated exclusive H/D exchange at C-2 (α -methin H). H/D Exchange proceeded with retention as well as inversion of configuration, thus forming both of the labeled enantiomers from each of the native ones (see *Fig. 4*) for (R)-MCPP in a process such as the one outlined in *Scheme 3*. The $\text{D}_2\text{O}/\text{soil}$ experiments thus gave a more detailed insight in the underlying mechanism of enantiomerization and revealed a considerable chiral instability of these compounds in soil.

Acetamide Pesticides

This group of compounds includes a considerable number of herbicides and fungicides for the control of weeds and

fungi in crops [21]. The stereoisomerism of these compounds is interesting since some of them show axial- and/or C-chirality. C-Chirality results from the presence of an asymmetrically substituted C-atom in the alkyl moiety, and axial-chirality results from the hindered rotation about the phenyl-nitrogen bond and a suitable asymmetric substitution of the phenyl ring. Metalaxyl is C-chiral and only the (*R*)-enantiomer shows fungicidal activity. Metolachlor is axial- and C-chiral and of the four possible stereoisomers, those with (*1'S*)-configuration (*aS,1'S*; *aR,1'S*) have the highest herbicidal activity (for structures see Chart 1) [22]. Whereas non-enantioselective HRGC analysis does not distinguish among these stereoisomers enantioselective HRGC analysis revealed two peaks for the enantiomers of metalaxyl and three peaks for the four stereo-

isomers of metolachlor (see Fig. 5, a and b) [23]. The chromatogram in Fig. 5, a also shows that the stereoisomeric composition of this particular sample of metolachlor cannot be 1:1:1:1 [23]. Further data revealed the following assignments: peak 1 = (*aS,1'S*), peak 2 = (*aR,1'S*) and (*aS,1'R*) and peak 3 = (*aR,1'R*). The two enantiomers in the second peak apparently are still unresolved by this technique. The analysis of different batches of metolachlor revealed a somewhat varying diastereoisomeric composition [23].

Incubation experiments in soil showed the degradation of these compounds to be enantioselective [24]. The data for metalaxyl show the fungicidally more active (*R*)-enantiomer to be much faster degraded and the residues to consist predominantly of the inactive (*S*)-enantiomer (see Fig. 5, b). For this compound the recent

introduction of the enantiopure product will not only lower the application rates (to ~60%), but also substantially improve the residue situation. The data for metolachlor show the herbicidally less active (*1'R*)-stereoisomers to be faster degraded (see Fig. 5, a). Our data also showed the degradation to be atropisomer selective which is the first reported case of this selectivity for this group of compounds. The degradation of these compounds in soil seems to have a preference for the (*R*)-enantiomers. The enantiopure (*S*)-metolachlor (*aS,1'S*, *aR,1'S*) has recently been registered and will replace the formerly used 'racemic' product. However, the chiral stability of these pesticides, in particular with respect to our data on the phenoxyalkanoic acid herbicides, will need further attention.

DDT

DDT is not only one of the most important pesticides ever used, it is also one of the most controversial. First introduced during the second world war, it was actually developed and first registered in Switzerland. It was obviously a valuable compound that helped avert millions of human deaths [25]. DDT is rather nontoxic to man but the compound itself or its metabolites, are highly accumulating and persistent in the environment. Eventually, DDT was banned in Switzerland (1971), the US (1972), and since then in most industrialized countries. Nevertheless, DDT continues to be an important vector-control product (malaria) in developing countries [12].

Technical DDT consists of ~70% of the 4,4'-isomer, of up to 25% of the 2,4'-

Scheme 3. General Reaction Scheme Showing Formation of the 2-Monodeuterio Analogs of MCPP, as Observed in the D_2O /Soil Incubation Experiments. H/D-Exchange in MCPP proceeded with retention (ret) as well as inversion (inv) of configuration, forming both of the labeled enantiomers from each of the native ones.

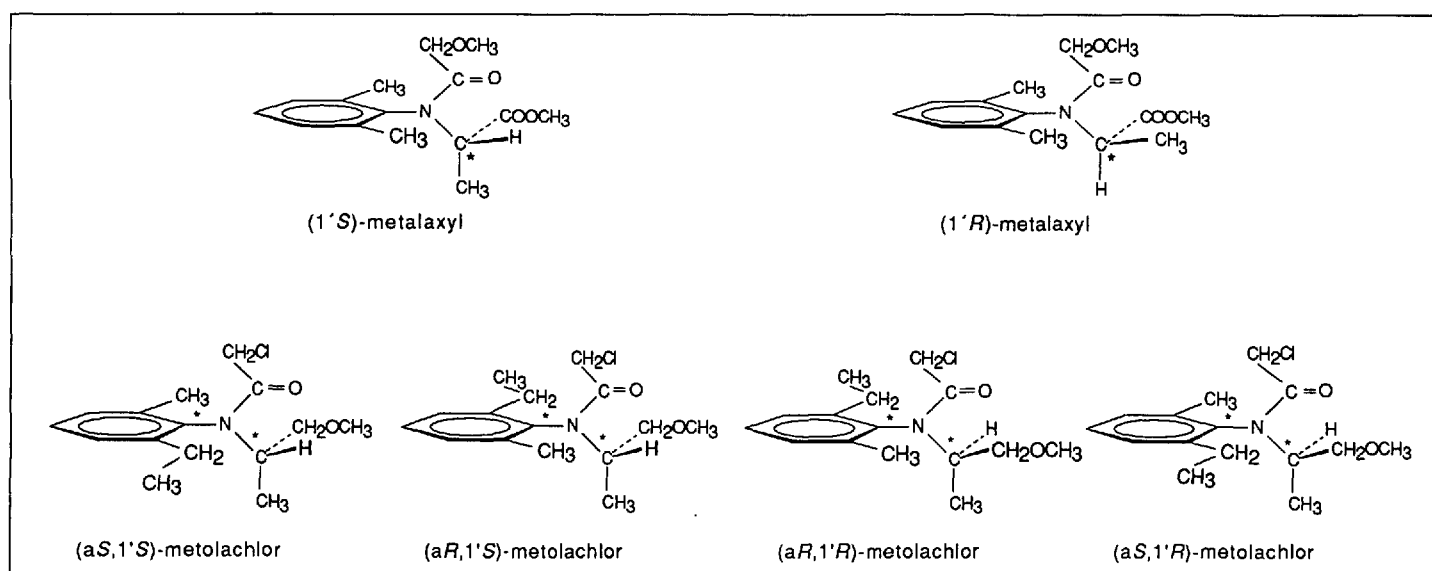
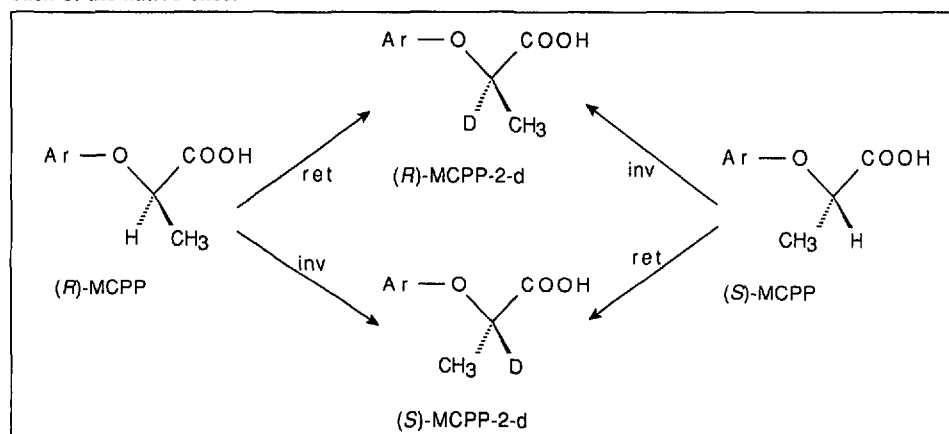


Chart 1. Structures (absolute configurations) of the two enantiomers of the fungicide metalaxyl (top row; the (*R*)-enantiomer is fungicidally active) and the four stereoisomers of the herbicide metolachlor (bottom row; the two (*1'S*)-stereoisomers are herbicidally active). Asterisks mark chiral axes and asymmetrically substituted C-atoms.

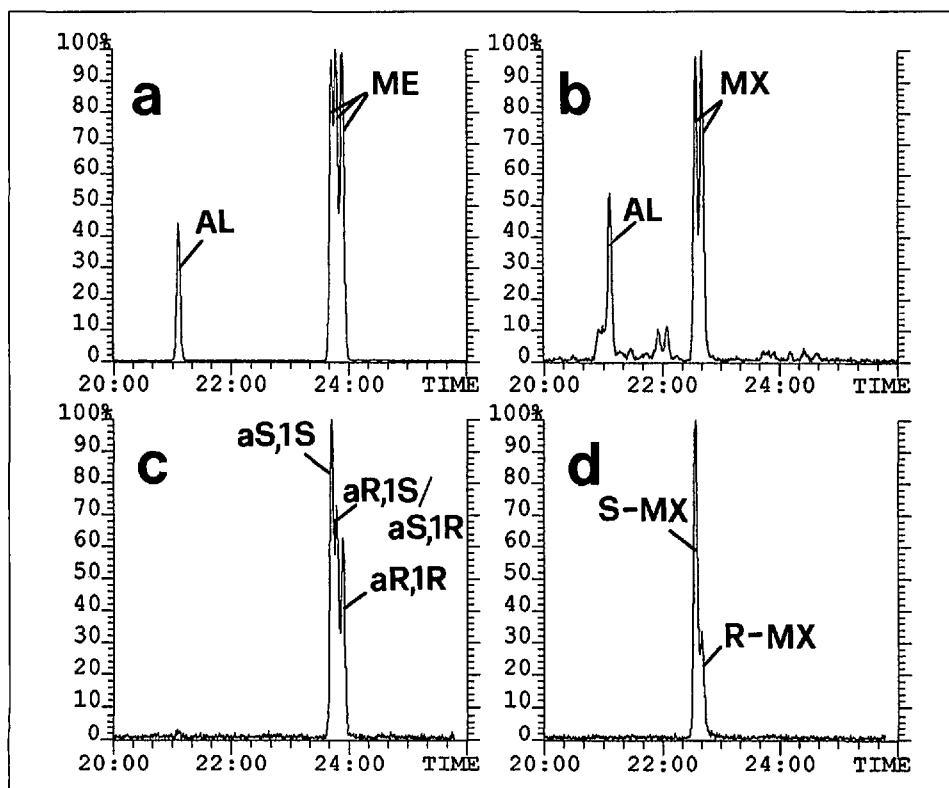


Fig. 5. EI SIM Chromatograms (m/z 238, left panels; m/z 206 right panels) showing elution of metolachlor (ME) and metalaxyl (MX) stereoisomers after (a,b) 0 and (c,d) 64 d incubation in soil. Note the enantio- and/or atropisomer selective degradation of both compounds with the (1*R*)- and (*R*)-enantiomers faster degraded. Note the presence of signals for alachlor (AL; faster degraded than the other compounds, see chromatograms a and c) which was also incubated in these experiments.

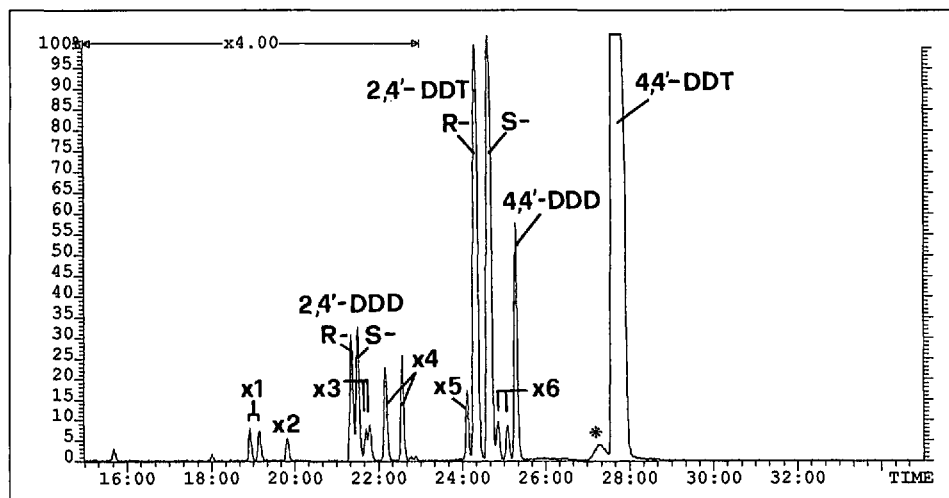


Fig. 6. EI SIM chromatogram (m/z 201, 235) showing elution of DDT-related compounds in technical DDT, analyzed using an enantioselective OV1701-BSCD HRGC column (BSCD = *tert*-butyldimethylsilyl- β -CD). Note the enantiomer resolution of 2,4'-DDT and 2,4'-DDD with the *R* enantiomers as earlier-eluting. Several other unknown chiral components are resolved; note also the racemic composition of the product. Artifact signal marked by asterisk.

isomer, and of other components. 4,4'-DDT is the only isomer with insecticidal properties. 2,4'-DDT, the second major component of technical DDT, can exert estrogenic effects [26] and it was likely the compound responsible for the eggshell thinning in predatory avian species. This isomer, in contrast to 4,4'-DDT, is chiral; the absolute configurations of the

(+)- and (-)-enantiomers are shown in Chart 2. In Fig. 6 we show a chromatogram of technical DDT analyzed using enantioselective HRGC-MS [27]. The particular sample was retained at our laboratory for over 40 years and presumably represents a DDT composition typical of that time. The chromatogram shows the enantiomer resolution of 2,4'-DDT, 2,4'-

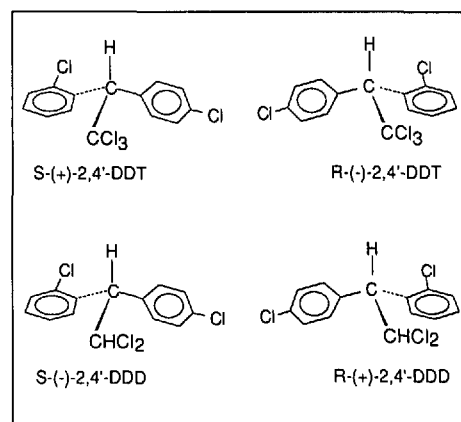


Chart 2. Structures (absolute configuration) of the two enantiomers of 2,4'-DDT (the second most abundant component in technical DDT) and the two enantiomers of 2,4'-DDD. The absolute configuration of the 2,4'-DDD enantiomers was assigned by chemical analogy, see text.

DDD and some other chiral components, clearly indicating a racemic composition of the technical material (enantiomeric ratios, ER \sim 1). In Chart 2 we also show the absolute configurations of (+)- and (-)-enantiomers of 2,4'-DDD which were assigned by chemical analogy from the NaBH_4 reduction of the 2,4'-DDT enantiomers [27].

The two enantiomers of 2,4'-DDT differ in estrogenic activity with the (-)-2,4'-DDT being far more estrogenically active [28]. In preliminary studies we observed an enantiomeric ratio of \sim 0.8 for 2,4'-DDT in a sample of human adipose tissue, indicating that the estrogenically more potent (-)-(*R*)-enantiomer (first-eluted) is less abundant. These results should have some impact on current research on environmental estrogens (endocrine disruptors) of which DDT compounds and metabolites (DDE) play an important role.

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Ozone LIDAR as an Analytical Tool in Effective Air Pollution Management: The Geneva 96 Campaign

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Abstract. The LIDAR (LIght Detection And Ranging) technique has developed into one of the practical high performance techniques for conducting air quality and meteorological measurements. Differential Absorption Lidar (DIAL) is used for measuring trace gases, including pollutants like ozone at low concentrations. Multiple wavelengths backscatter and depolarization measurements give information about particles in the atmosphere, and single wavelength lidar can be used for meteorological measurements like wind velocity and temperature. Range resolved *in situ* data obtained by lidar can play a significant role in our understanding of the air quality in the planetary boundary layer, particularly when applied in conjunction with air quality models. This is because DIAL can be used to measure concentrations in three dimensions in real time with a spatial resolution that corresponds well to that used in the model calculations. Thus one obtains an advantage when comparing with point measurements at or near ground level which are often perturbed by local emissions. A summary of the lidar principle is presented here, followed by different examples of vertical ozone profiles and time series obtained with a new optical layout of the EPFL-LPAS DIAL system using dual telescope detection. These data were obtained during the summer 96 field campaign in the Geneva area. Results are then compared with the mesoscale Eulerian model calculations performed in our laboratory. The overall results provide new insight into air pollution dynamics in the Geneva area and calculations are under way, using the model adjusted by the measurements, to optimize air pollution abatement strategies under certain atmospheric conditions in this part of Switzerland.

1. Introduction: Why do We Need a 3D Real-Time Measuring Technique for Air Quality Studies?

It is recognized that three-dimensional air quality models are one of the most powerful tools for identifying effective strategies to improve air quality. For example, the Eulerian mesoscale chemical transport model developed at the EPFL-LPAS is used to simulate pollutant dynamics over regions like Geneva, Athens Greece, canton Obwalden, and the Swiss Plateau to provide technical guidance to air quality management agencies. The domain covered typically ranges in the order of 100×100 km horizontally, and up to 6 km vertically. The grid resolution can range from below 1-5 km horizontally, with a vertical resolution of some tens of meters for the lowest layer of the model up to 500 m for the top layer. Before the results can be exploited with confidence, it is crucial to validate the model's ability to simulate the dynamics of air pollutants in an area.

Evaluation of air quality models is not as easy as it may seem. The traditional air

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