

Composition of Aldrin, Dieldrin, and Photodieldrin Enantiomers in Technical and Environmental Samples

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Aldrin and dieldrin belong to the group of polycyclic chlorinated insecticides that are banned under the Stockholm Convention (POP Convention). Despite the fact that the use of these compounds ceased many years ago, aldrin and, in particular, dieldrin are still present in the environment from former applications, leading occasionally to contamination of agricultural produce and food, particularly Cucurbitaceae. These prochiral compounds have a complex stereochemistry. In the environment, aldrin is rapidly converted to its epoxide, dieldrin. Photolysis is one of the environmental transformation processes reported to be important for the compounds, leading to photoproducts such as photoaldrin and photodieldrin. In contrast to the parent compounds, photoaldrin and photodieldrin are chiral and exist as pairs of enantiomers. Although dieldrin and its metabolites have been extensively reviewed, the chirality of many of its metabolites has so far not been considered. In this study, the composition of technical aldrin and dieldrin from the 1950s and their photoproducts was investigated using both non-enantioselective and enantioselective gas chromatography with detection by several mass spectrometric techniques. Full enantiomer resolution of photodieldrin was achieved using a column with a silylated γ -cyclodextrin as chiral selector. Photoaldrin, however, showed peak broadening, indicating some marginal resolution of the enantiomers. Whereas photodieldrin was formed as a racemate from both aldrin and dieldrin by natural sunlight, the analysis of environmental and biological samples (soil, biota) indicated its presence mostly with enantiomer compositions clearly differing from 1:1. The presence of photodieldrin in soil, treated more than 40 years ago with aldrin or dieldrin, documents that the photoreaction of dieldrin plays some role in the transformation of the compounds in the environment and that enantioselective biological processes are involved in its further transformation. The preliminary data also indicate that photodieldrin probably is not bioaccumulated more than dieldrin.

KEYWORDS: Photodieldrin; dieldrin; aldrin; enantioselectivity; chirality; soil degradation; environmental occurrence; photolysis

INTRODUCTION

Aldrin and dieldrin are structurally related polycyclic compounds with a rather complex stereochemistry (for structures, see **Figure 1**). The compounds were formerly used as insecticides, replacing even older products such as lead arsenate and pyrethrum. Dieldrin, probably the more important compound, was used as a broad spectrum insecticide in agriculture and for wood preservation in building construction. The insecticides were reported to act as antagonists of the γ -aminobutyric acid (GABA) receptor chloride channel complex (1). Dieldrin is very persistent in soil and, when released to the air, it may be transported to remote areas. It is now a global contaminant and listed under the Stockholm convention as a persistent organic pollutant (POP) (2). Eventually, the use of dieldrin and other chlorinated hydrocarbons was restricted or banned in the United States and in many countries throughout the world.

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In Switzerland, dieldrin was also responsible for a major food scandal in the late 1960s, when dieldrin was detected in dairy products from cows fed with hay or grass kept in barns treated with dieldrin (3, 4). In some soils, dieldrin still (2008) persists from applications several decades ago, and its presence occasionally leads to contamination of agricultural produce, particularly of Cucurbitaceae (cucumbers, zucchini, melons, pumpkins) (5–7).

Aldrin, a technical precursor of dieldrin, is also an insecticide on its own, formerly used against soil-dwelling insects in vegetable, fruit, and field crops. It is classified as moderately persistent (8). Aldrin is no longer produced or used in the United States or Europe, and environmental releases of the compound have probably resulted in its conversion to the epoxide, dieldrin.

Photolysis is one of the environmental transformation processes reported to be important for these compounds, leading to photoproducts such as photoaldrin and photodieldrin that have been reported to be more toxic than the parent compounds (8–10). The photoproducts are formed on soil and vegetation following application of aldrin or dieldrin (11). In contrast to the

parent chlorohydrocarbons, photoaldrin, photodieldrin, and other photoproducts are chiral and exist as enantiomers (Figure 1). Although dieldrin has been extensively reviewed and its global occurrence is well documented (8), surprisingly little is known about the environmental occurrence of the photoproducts, and in particular their chirality has so far hardly been considered.

Stereochemical aspects of persistent organic pollutants now receive wide attention (12–14). In particular, the enantiomerism of chiral environmental contaminants is important because enantiomers may often show different biological behaviors and properties (toxicity, uptake, metabolism, excretion by organisms) (15). Transformation reactions in biological systems and in the environment may thus be stereo- and enantioselective. In contrast, abiotic processes (chemical, photochemical, partitioning, and transport) will be the same for enantiomers, and enantiomer composition will thus remain unchanged. Information on enantiomer composition (enantiomer profiles) therefore is potentially important for a distinction of biotic versus abiotic environmental processes and may aid in distinguishing between residues from “old sources” and those from freshly applied pesticides (16).

In this study, we investigated the composition of technical aldrin and dieldrin from the 1950s and the formation of photoproducts upon exposure to natural sunlight. We then developed enantioselective techniques for the analysis of the chiral transformation products. We analyzed soil samples from areas formerly treated with the compounds, and we analyzed some samples (pumpkin seed oil, herring oil) from earlier studies retrospectively to gain insight into the environmental processes involved in the transformation of these two important compounds.

MATERIALS AND METHODS

Reference Compounds. Technical aldrin and dieldrin were obtained in the 1950s from Maag, Dielsdorf, Switzerland. The materials were originally produced by Shell, Pernis, The Netherlands. The purities of these materials were stated to be >90%. The materials have been archived (room temperature, darkness) at our institute in Wädenswil since the 1950s, and they were recently analyzed as part of this study. Photodieldrin, isodrin, endrin, endrin ketone, and endrin aldehyde, used for reference purposes, were of analytical grade (>99%) and obtained from Ehrenstorfer, Augsburg, Germany.

Sunlight Photolysis. Aldrin and dieldrin were exposed to natural sunlight in the presence of air. About 240 µg of each compound in 0.2 mL of ethyl acetate was placed in separate stoppered quartz glass tubes (16 mm i.d.; volume, 28 mL). The solvent was carefully evaporated in vacuo with gentle heating and axial rotation. This resulted in deposition of the substance as a thin film (covered area, ~5 cm²; calculated average film thickness, ~0.25 µm) on the bottom of a quartz tube. The tubes were then exposed to winter sunlight on February 5–10, 2008, for a total of 15 h at Wädenswil (temperature, 3–7 °C). After dissolution of the residues in ethyl acetate (1.0 mL), a small aliquot (1–2 µL) was analyzed.

Environmental and Biological Samples. Soil samples from an industrial site (17) and from horticultural fields from different locations in Switzerland were extracted and the extracts purified with a minimal cleanup so as not to discriminate among other POPs. Soil (50 g, sieved and air-dried) was mixed with distilled water (20 mL) and methanol (20 mL) and intensely shaken. The slurries were then extracted with a mixture of *n*-hexane (25 mL) and methylene chloride (7 mL). Emulsions were resolved by centrifugation (Sorvall RC5 centrifuge, 60 min at 1000 rpm), and the organic phase was removed. Extraction of the slurries was repeated twice with 30 mL of *n*-hexane/methylene chloride (2:1). The combined organic phases were evaporated at room temperature, and the residues, after dissolution in ethyl acetate (1 mL), were passed through a silica minicolumn (0.7 g of silica gel 60; Merck, Darmstadt, Germany; deactivated with 5% water; topped with 10 mm of anhydrous sodium sulfate; 5 mm i.d. Pasteur pipet) and eluted with 10 mL of ethyl acetate. The eluates were

reduced in volume to 200 µL, and 1 µL aliquots were then analyzed. The procedure gave acceptable recoveries for dieldrin, aldrin, and photodieldrin (>90%). Limits of detection (LODs) were estimated at 0.01 ng/g.

In addition, sample extracts from earlier studies on POPs were retrospectively analyzed, in particular an oil from Baltic herring (*Clupea harengus*, Gulf of Bothnia) (13). The sample went through an elaborate fractionating scheme for cleanup, whereby dieldrin and photodieldrin eluted into fraction 3 (18). Pumpkin seed oil extracts were provided by the State Chemist, Zurich, Switzerland (courtesy of A. Schürmann). These extracts were cleaned up for POPs using gel permeation chromatography (GPC) and were previously shown to contain dieldrin in the nanograms per gram range. Because of a smaller sample size (1 g) used in the extraction and cleanup of these oils, LODs were not as good as for the soil samples and estimated at 1 ng/g.

GC-MS Analysis. A Micromass QuattroMicro Triplequad mass spectrometer (Waters, Manchester, U.K.) was used for analyte detection and identification. The ion source was operated in either electron ionization (EI, 70 eV, 180 °C) or electron capture, negative ionization (ECNI, 70 eV, 120 °C) mode. In ECNI, neat argon was used as the buffer gas. ECNI is more sensitive for the detection of these compounds and was primarily used for the analysis of environmental and biological samples. Full-scan mass spectra (m/z 35–535, 1 s/scan, nominal resolution) were recorded for analyte identification. For quantitation and increased sensitivity, selected ion monitoring (SIM) with up to eight ions (0.5 s/scan) was used (in ECNI, m/z 327.85 and 329.85 for aldrin ($M^- - 34$ and satellites); m/z 342.85, 344.85, and 346.85 for photodieldrin ($M^- - 35$ and satellites); and m/z 377.85, 379.85, and 381.85 for dieldrin (M^- and satellites)). Concentrations of impurities in the technical materials and of photoproducts in photolysis samples were estimated from EI total ion chromatograms (TIC), assuming the same TIC sensitivity for the compounds. Concentrations of target compounds (aldrin, dieldrin, photodieldrin) in biological samples were determined from peak areas of SIM chromatograms in comparison to those of known quantities of reference compound. The data generated are semiquantitative, and quantitation was not of prime concern in this study.

Samples were comparatively analyzed using a non-enantioselective 30 m × 0.32 mm i.d., DB-5MS fused silica HRGC column (J&W Scientific, Folsom, CA) and a homemade chiral 16 m × 0.25 mm i.d., OV1701 with 25% bis-*tert*-butyldimethylsilyl- γ -cyclodextrin as chiral selector (OV1701/ γ -BSCD; 0.25 µm film thickness). Enantiomer ratios (ER values) of photodieldrin were defined as $ER = p_1/p_2$, where p_1 is the peak area of the earlier eluted enantiomer and p_2 is the peak area of the later eluted enantiomer. Split/splitless injection was used, and sample aliquots of 1–2 µL were injected (injection temperature, 250 °C). The temperature program using the DB-5MS column was as follows: 70 °C, 2 min isothermal, 25 °C/min to 120 °C, then 5 °C/min to 280 °C, followed by an isothermal hold at this temperature; for the enantioselective OV1701/ γ -BSCD column the conditions were similar except that the temperature rate was 3 °C/min and the maximum final hold temperature was 220 °C.

RESULTS AND DISCUSSION

Structural Considerations. Aldrin ([1*R*,4*S*,4*aS*,5*S*,8*R*,8*aR*]-1,2,3,4,10,10-hexachloro-1,4,4*a*,5,8,8*a*-hexahydro-1,4:5,8-dimethanonaphthalene; HHDN) and dieldrin ([1*R*,4*S*,4*aS*,5*R*,6*R*,7*S*,8*S*,8*aR*]-1,2,3,4,10,10-hexachloro-1,4,4*a*,5,6,7,8,8*a*-octahydro-6,7-epoxy-1,4:5,8-dimethanonaphthalene; HEOD) belong to a group of structurally related cyclodiene insecticides (Figure 1). Aldrin (1), the *endo-exo* isomer, is formed by the Diels–Alder (cycloaddition) condensation of 1,2,3,4,5,5-hexachlorocyclopentadiene (HEX) and norbornadiene. Dieldrin (2), the epoxide with the epoxy group in *exo* position, is technically produced by epoxidation of the parent chlorohydrocarbon aldrin or by condensation of HEX with the respective epoxide of norbornadiene. Of the further parent stereoisomers, only isodrin (3), the *endo-endo* stereoisomer and its epoxide, endrin (4), were of technical use, but are now also discontinued insecticides; the *exo-exo* (5) and the *exo-endo* isomers (6) had no technical significance. In soil, isodrin has likely been converted to endrin, similarly to aldrin to dieldrin. The

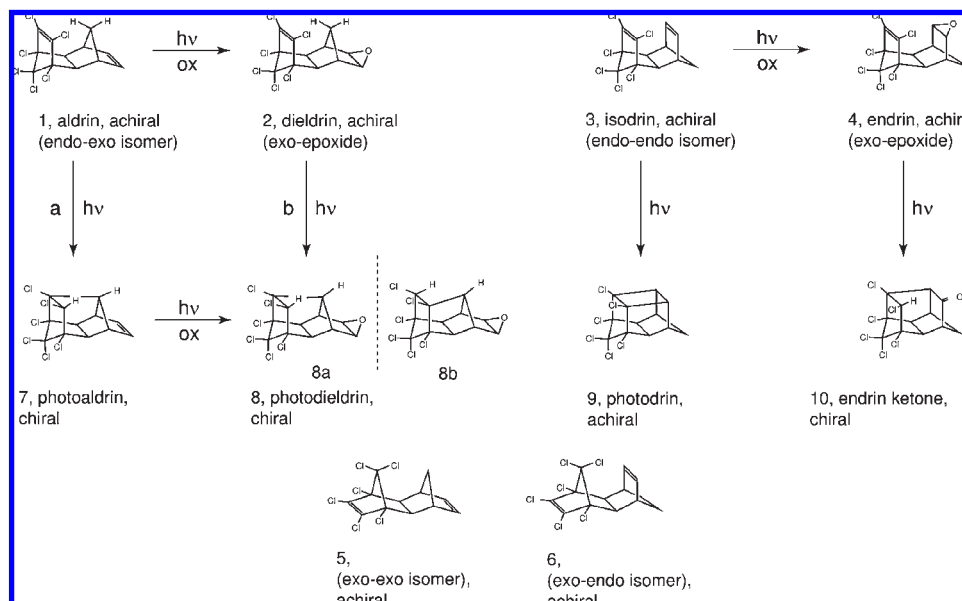


Figure 1. Chemical structures of aldrin, dieldrin, their stereoisomers, and some photoproducts. The structures of the two enantiomers of photodieldrin are shown (elution order unknown).

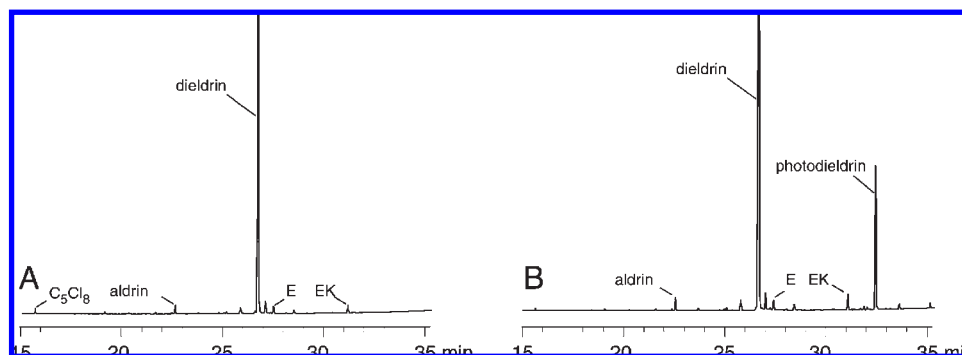


Figure 2. TIC chromatograms of technical dieldrin prior to (A) and following sunlight exposure (B), analyzed using a DB-5MS column and EI-MS conditions. Note the formation of photodieldrin upon photoexposure; note also the presence of some impurities (e.g., E, endrin; EK, endrin ketone). Vertical axes are suitably expanded.

epoxidation of aldrin and isodrin leads almost exclusively to the *exo* epoxides (19). All of these compounds are achiral (prochiral).

The photochemical transformation of the compounds is important. The major products photoaldrin (7) and photodieldrin (8) are formed from aldrin and dieldrin, respectively, via an internal isomerization with formation of new C–C bonds between the carbon of the methylene bridges and that of the Cl-bearing C–C double bonds (8). The resulting semicaged structures are shown in **Figure 1**. This formation is accompanied by a loss of symmetry: both compounds are chiral and exist as pairs of enantiomers. Photooxidation of aldrin also leads to dieldrin (epoxidation), and in a similar way, photoaldrin, which still contains a “nonhalo” C–C double bond, is photooxidized to photodieldrin. The final photoproduct thus expected from this reaction sequence is photodieldrin formed from aldrin via photoaldrin (route a) or via dieldrin (route b, **Figure 1**).

In this study we did not elaborate on other metabolites of dieldrin or on further degradation products of photodieldrin. Although many of these further metabolites are chiral (e.g., hydroxy and carboxy compounds), they are generally more polar and environmentally more mobile and judged to be less persistent and accumulative than dieldrin and photodieldrin themselves.

Although a microbial formation of photodieldrin from dieldrin or aldrin (20) cannot be ruled out completely, we presume that the photochemical pathway is more important because of the rapid kinetics observed and the racemic composition in one soil sample.

Composition of Technical Aldrin and Dieldrin. The actual stereochemical composition of technical aldrin and dieldrin formerly used in Switzerland was not exactly known because in the 1950s, when these compounds were produced, suitable analytical methods such as GC were only starting to develop. To assess the quality of the materials formerly used, we analyzed two samples of now over 50-year-old technical materials. In **Figures 2A** and **3A**, we show chromatograms of technical dieldrin and aldrin, analyzed using the nonenantioselective DB-5MS column and EI MS. The chromatograms indicate rather pure products with minor impurities present at a combined level of only a few percent. Technical dieldrin (**Figure 2A**) with dieldrin as the major component ($M^+ = 378$, Cl_6 ; base peak (bp), m/z 79; retention time (rt), 26.8 min) shows the presence of aldrin ($M^+ = 362$, Cl_6 ; bp, m/z 66; rt, 22.8 min), endrin ($M^+ = 378$, Cl_6 ; rt, 27.5 min), endrin ketone ($M^+ = 378$, Cl_6 ; rt, 31.2 min), octachlorocyclopentene ($M^+ = 340$, Cl_8 ; rt, 15.7 min), and a very late-eluted diadduct ($M^+ = 632$, Cl_{12} ; rt > 45 min), which was observed only when the column was kept at high temperature for an extended

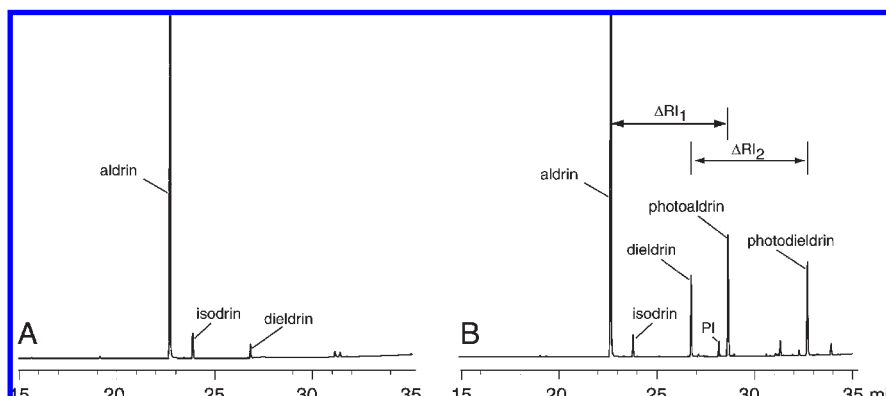


Figure 3. TIC chromatograms of technical aldrin prior to (A) and following sunlight exposure (B), analyzed using a DB-5MS column and EI-MS conditions. Note the formation of photoaldrin, dieldrin, and photodieldrin upon photoexposure. Note also the practically identical ΔRI values for photoaldrin/aldrin and photodieldrin/dieldrin. Vertical axes are suitably expanded. The minor photoproduct at 28.3 min is photodrin (photoisodrin, PI).

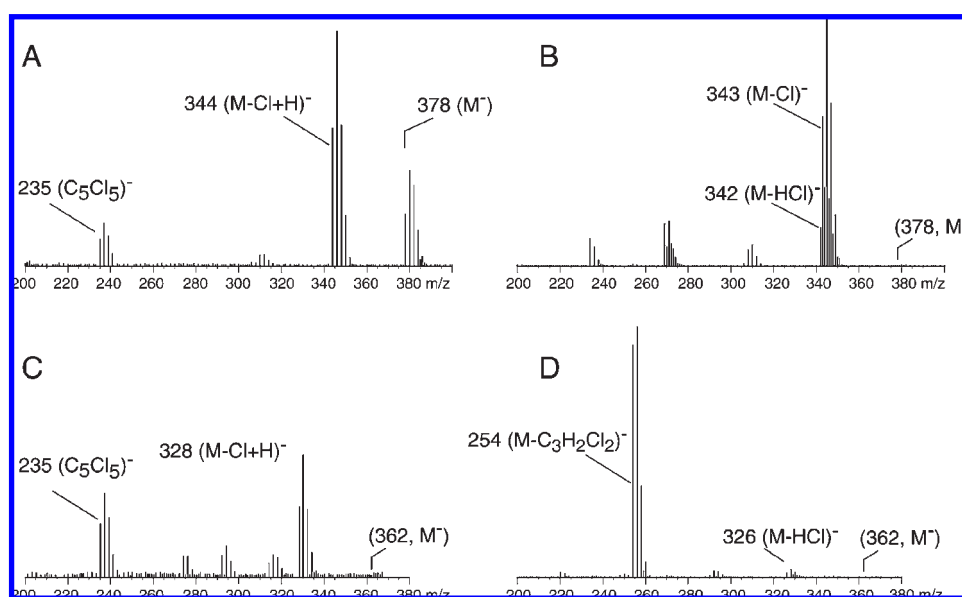


Figure 4. Partial ECNI mass spectra of (A) dieldrin ($M^+ = 378$, Cl_6), (B) photodieldrin ($M^+ = 378$, Cl_6), (C) aldrin ($M^+ = 362$, Cl_6), and (D) photoaldrin ($M^+ = 362$, Cl_6).

period of time (not shown in chromatogram). This diadduct was also contained in aldrin, the probable technical precursor; it is the product from condensation of two molecules of HEX with norbornadiene (19). Photodieldrin was not detected in technical dieldrin (<0.03%). Technical aldrin (Figure 3A) shows, besides aldrin as the major component (rt, 22.8 min), the presence of some impurities, mainly isodrin ($M^+ = 362$, Cl_6 ; bp, m/z 66; rt, 23.9 min) and dieldrin (rt, 26.9 min). Isodrin is the *endo* adduct in the synthesis of aldrin from HEX and norbornadiene and the source of endrin in technical dieldrin. The analyses indicate that technical aldrin and dieldrin consisted of materials with a relatively high stereochemical purity. This was also confirmed by nuclear magnetic resonance (NMR) spectroscopy (courtesy D. Rentsch, EMPA, Dübendorf, Switzerland; data not further detailed), which proved these materials to have structures as shown in Figure 1, in particular the *exo* isomerism of the epoxide.

Photochemical Transformation of Aldrin and Dieldrin. Solid-film photolysis of dieldrin and aldrin yielded photoproducts that were identified by MS and retention data, as illustrated next. Following the exposure of technical dieldrin to sunlight (Figure 2B), the formation (yield, ~15%) of a new, later-eluted compound is observed ($M^+ = 378$, Cl_6 ; bp, m/z 81; rt, 32.6 min),

identified as photodieldrin from comparison of its mass spectrum and retention time to that of authentic photodieldrin. The EI mass spectra of dieldrin and photodieldrin differ significantly and are listed in the NIST library of reference spectra (21); they are thus not presented here. However, ECNI mass spectra are shown in Figure 4A,B. When analyzed using the OV1701/ γ -BSCD column, photodieldrin was resolved into its enantiomers with an ER of 1.0 ± 0.01 ; the achiral dieldrin still eluted as a single peak. Photodieldrin apparently is formed as a racemate in our photoexperiment. The authentic reference compound also was racemic with an ER of 1.0 ± 0.01 when analyzed in the same way. Mass spectra of the two photodieldrin enantiomers were expectedly identical.

Following exposure of technical aldrin to sunlight (Figure 3B), the formation of dieldrin, photodieldrin, and a new hexachloro compound ($M^+ = 362$, Cl_6 ; bp, m/z 79; rt, 28.8 min) was observed. This new compound is isomeric to aldrin and identified as photoaldrin (7), the earlier reported major photoproduct of aldrin (9). Our identification is supported by the fact that the retention increase (RI) of the new compound to aldrin on the DB-5MS column (ΔRI_1) is practically identical to the retention increase of photodieldrin to dieldrin ($\Delta RI_2 \sim \Delta RI_1$), which is

Table 1. Concentrations and Enantiomer Ratios (ER) of Photodieldrin in Environmental and Technical Samples (Concentrations of Dieldrin and Aldrin for Comparison)

sample	date ^a	photodieldrin (PD)		dieldrin (D) concn (ng/g)	PD/D ratio	aldrin concn (ng/g)
		concn (ng/g)	ER ^b			
industrial soil	2004	1.8	1.0 ± 0.01	24.0	0.08	0.2
agricultural soil 1	2008	0.11	2.2 ± 0.3	2.0	0.06	~0.03
agricultural soil 2	2008	4.4	1.4 ± 0.03	23.0	0.19	0.16
agricultural soil 3	2008	1.0	2.2 ± 0.08	8.0	0.12	0.16
background soil, Wädenswil	2008	<0.01		<0.01		<0.01
pumpkin seed oil 1	2008	<1		80	<0.01	<1
pumpkin seed oil 2	2008	<1		3	<0.3	<1
pumpkin seed oil 3	2008	<1		4	<0.3	<1
Baltic herring oil	1990	~0.05	1.4 ± 0.05	~5.0	~0.01	<0.01
photodieldrin, reference compound			1.0 ± 0.01			
photodieldrin from the photolysis of aldrin			1.0 ± 0.01			
photodieldrin from the photolysis of dieldrin			1.0 ± 0.01			

^a Date sampled. ^b Average and range (SD, if applicable) from two or more measurements.

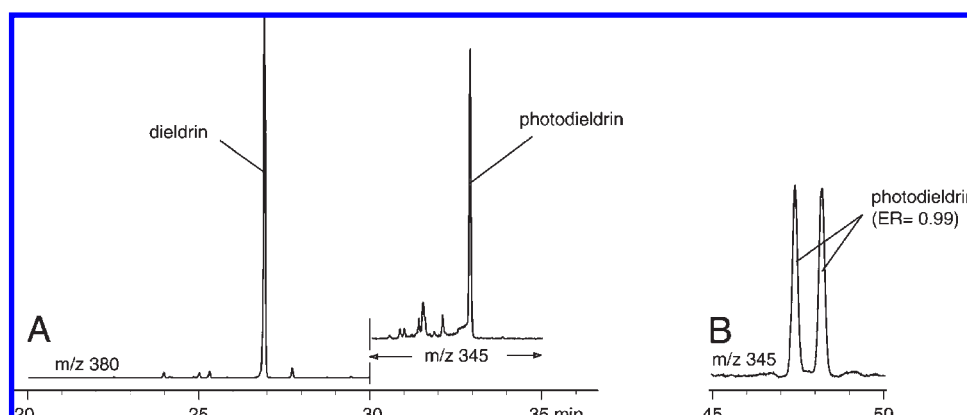


Figure 5. ECNI SIM chromatograms of soil from an industrial site showing (A) the presence of dieldrin (m/z 380) and photodieldrin (m/z 345, intensity $10\times$), when analyzed using the DB-5MS column and (B) resolution of photodieldrin (m/z 345) into its two enantiomers with a practically racemic composition when analyzed using the enantioselective OV1701/ γ -BSCD column.

expected for compounds differing in the same structural elements. The EI mass spectra of aldrin and photoaldrin are very different (data not shown), as were those of dieldrin and photodieldrin; similarly, the ECNI mass spectra of aldrin and photoaldrin are different as shown in **Figure 4C,D**. In contrast to photodieldrin, the chiral photoaldrin still eluted as a single peak when analyzed using the OV1701/ γ -BSCD column under normal conditions. However, when the programming rate was reduced from 3 to 0.8 °C/min, clear peak broadening was observed, indicating marginal resolution of the enantiomers, although retention times became excessively long (~130 min). The minor component at 28.3 min (M^+ = 362, Cl_6 ; bp, m/z 193, Cl_3) observed in sunlight-exposed aldrin is photodrin (= photoisodrin), the bird-cage compound **9** (**Figure 1**), a photoproduct of isodrin, the minor component observed in technical aldrin. Photodrin is achiral (prochiral); expectedly, it eluted as a single peak when using chiral HRGC even under slow temperature programming conditions.

The data indicate that the photooxidation of aldrin is highly stereoselective in that almost exclusively the *exo* epoxide, dieldrin, is formed. The situation is similar to another cyclic diene system: photoepoxidation of heptachlor also led almost exclusively to the *exo* epoxide (22). The experiments confirmed the facile photochemical conversion of both aldrin and dieldrin to photoproducts. Although we did not elaborate on other dieldrin metabolites, we point out that endrin ketone (**10**) and endrin aldehyde were enantiomerically resolved on the OV1701/ γ -BSCD column.

Presence of Photodieldrin in Soil from a Contaminated Industrial Site. Soil from a former industrial site near Zurich, Switzerland, was analyzed. At this particular site, technical hexachlorocyclohexane (HCH) was produced and other chlorinated pesticides (chlordane, toxaphene, aldrin, and dieldrin) were formulated in the 1950–1960s. Although extensive cleanup activities took place at the time, HCHs and other chlorinated pesticides remained detectable in soil and groundwater (17). Analyses of soil now also indicate the presence of dieldrin and photodieldrin as shown in **Figure 5A**. The concentrations of the two compounds in this particular sample are ~24 and ~1.8 ng/g of soil, respectively (**Table 1**); aldrin was detected only in trace amounts (0.2 ng/g of soil). In **Figure 5B** we show a partial chromatogram from the enantioselective analysis of photodieldrin, using the OV1701/ γ -BSCD column and ECNI SIM. The data indicate a racemic mixture (ER = 1.0 ± 0.01). Presumably racemic photodieldrin was initially formed on-site by photolytic transformation of spilled dieldrin, and then the two compounds were translocated to deeper layers in the soil. Assuming that biodegradation would have shown some enantioselectivity over a period of more than 40 years, the racemic composition suggests that photodieldrin underwent little if any biodegradation at this industrial site (see also below).

Presence of Dieldrin and Photodieldrin in Formerly Treated Agricultural Soils. Certain areas (pastures, farmland) in Switzerland were treated with aldrin and to a lesser degree with dieldrin in the 1950s–1970s for control of soilborne pests such as root

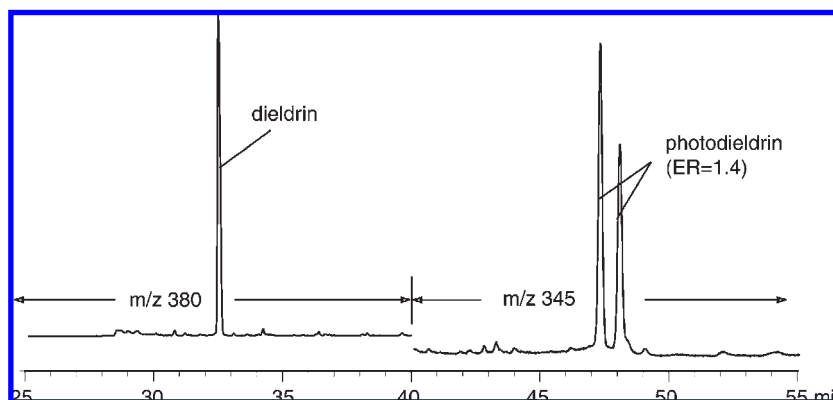


Figure 6. ECNI SIM chromatograms of agricultural soil 2 showing the presence of dieldrin (m/z 380) and photodieldrin (m/z 345, intensity $25\times$), analyzed using the chiral OV1701/ γ -BSCD column. Note the resolution of photodieldrin into its enantiomers and their presence as a nonracemic mixture.

worms (in potato and carrot fields) or cockchafer grubs (*Melontha melontha*, May beetle) (23). In 2008, dieldrin was still detectable at some of these sites. In **Table 1** we list data from three plots in northern Switzerland that were known to cause problems with residual dieldrin and from one plot presumably never having received dieldrin (background soil). In **Figure 6**, we show chromatograms of soil from the plot with the highest concentration of dieldrin (agricultural soil 2, 23 ng/g of soil). Photodieldrin was detected in this sample at a concentration of 4.4 ng/g of soil or about 19% relative to dieldrin; again, aldrin was detected only at a very low concentration (0.16 ng/g of soil). Field applications of aldrin or dieldrin are expected to have been on the order of 1 kg/ha and would lead to initial concentrations of ~ 1000 ng/g of soil or higher if we assume continued applications. Current soil concentrations of 20–25 ng/g would then point to time spans of >6 half-lives (assuming first-order kinetics) and thus to dissipation half-lives of <8 years for the 40–50 years since application. Actually, reported half-lives for dieldrin in soil are in the range of 2–15 years (8).

Enantioselective analysis of soil 2 interestingly now indicated a clear preference for the first-eluted enantiomer of photodieldrin ($ER = 1.4 \pm 0.03$); the same enantiomer preference is observed in soil from two other locations ($ER = 2.2$, **Table 1**). The background soil from Wädenswil, analyzed for control purposes, showed neither dieldrin nor photodieldrin present (<0.01 ng/g of soil). This indicates that potential atmospheric inputs did not lead to residues comparable to those from earlier direct applications.

In **Table 1** we also report the concentration ratios of photodieldrin to dieldrin (PD/D ratios) for these soils. The ratios of 0.06–0.19 were not so much different and similar to those from earlier studies (11, 24, 25). PD/D ratios result from the initial and possibly continued conversion of dieldrin to photodieldrin and the relative dissipation rates of the two compounds, whereby these rates may differ significantly. As an example, volatilization, a probably important translocation process for these POPs, is reported (11) to be 5 times lower for photodieldrin than for dieldrin itself. A significantly lower volatility of photodieldrin is also indicated by its markedly higher GC elution temperature (30 °C) (**Figure 2B**). Therefore, current soil PD/D ratios may not reflect initial ratios following application of dieldrin and/or aldrin and their photoconversion.

Assuming that photodieldrin is formed mainly photochemically, initially racemic compositions are expected ($ER = 1.0$). The nonracemic composition in the agricultural soils therefore is a clear sign of enantioselective microbial degradation that seems to proceed in the same sense in all of our agricultural soils

(second-eluted enantiomer more rapidly degraded, $ER > 1$). As mentioned above, the practically racemic composition of photodieldrin in an industrial soil may be explained by a low microbial activity of this particular soil. It also supports the assumption of a photochemical formation rather than a biological one.

The ER of a chiral compound subjected to enantioselective degradation is a function of exposure time and the individual dissipation rates of the enantiomers (e.g., k_1 and k_2 for enantiomers 1 and 2, respectively). Assuming that rate constants did not change over the total exposure time (t), an initially racemic composition ($ER_0 = 1$) of the contaminant, and no interconversion, the function is

$$\ln ER = -\Delta kt \quad (1)$$

where $\Delta k = k_1 - k_2$ (26). The larger the absolute value of Δk and the longer the exposure (t), the larger is the deviation of ER from that of a racemate. With $k_2 > k_1$ (second-eluted enantiomer more rapidly degraded), as with photodieldrin, ERs of >1 result. Interestingly, the ERs depend only on Δk and not on actual dissipation rates. The higher ERs of photodieldrin in soils 1 and 3 ($ER = 2.2$), as opposed to soil 2 ($ER = 1.4$) (**Table 1**), thus could result from a longer exposure (or earlier applications) or from a different (higher) microbial activity (larger Δk) in the former soils. Assuming that the last applications of aldrin/dieldrin to soil in Switzerland occurred about four decades ago and that the enantioselectivity of all agricultural soils is qualitatively similar ($k_2 > k_1$), then it is reasonable to assume that soil 2 (lower ER) was of lower biotic activity and that potentially other contaminants (e.g., dieldrin) are also less degraded. In fact, soil 2 showed a higher concentration of dieldrin than the other agricultural soils (**Table 1**). However, it should be pointed out that for chlordanes in global background soils correlations between concentration and enantiomer composition were not necessarily significant, although agricultural soils were reported to show enantioselectivity in the same sense (27). Certainly, considerations along these lines need more detailed attention and a much larger data set.

Presence of Dieldrin and Absence of Photodieldrin in Pumpkin Seed Oil. The presence of dieldrin and other POPs in agricultural soils occasionally led to contamination of certain crops, particularly of Cucurbitaceae. Cultivated plants of this family were shown to easily take up such residues from soil (6), and dieldrin and other POPs were accumulated in the edible parts of such plants and eventually, for example, in processed items such as pumpkin seed oil. Unfortunately, we were unable to obtain such produce from exactly the same plots we previously analyzed for residual dieldrin; producers of Cucurbitaceae usually avoid plots

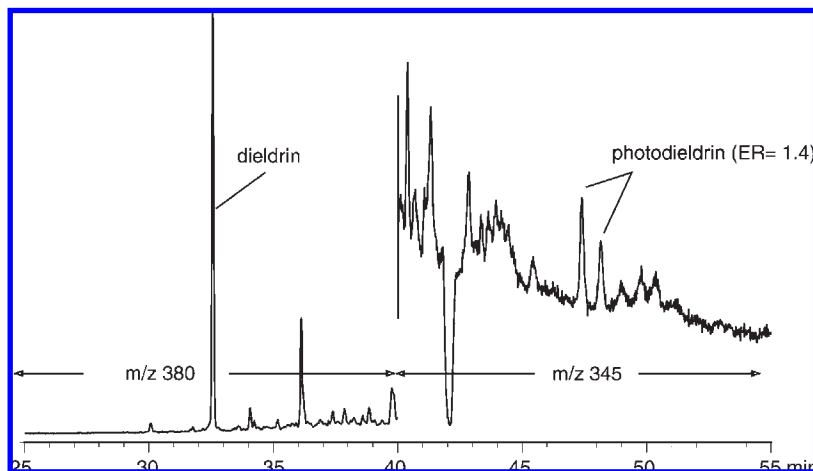


Figure 7. ECNI SIM chromatograms of Baltic herring showing the presence of dieldrin (m/z 380) and photodieldrin (m/z 345, intensity $50\times$), analyzed using the chiral OV1701/ γ -BSCD column. Note the resolution of photodieldrin into its enantiomers and its presence as a nonracemic mixture.

that are known to be contaminated with dieldrin or other chlorinated insecticides. Likewise, we were unable to trace oils that were available to particular sites. However, we were able to obtain samples from an official survey of commercial oils.

Three such oils were now confirmed to contain dieldrin at concentrations of 80, 3, and 4 ng/g of oil, respectively. However, none of the samples showed the presence of photodieldrin or aldrin at detectable concentrations (<1 ng/g of oil, **Table 1**). Nevertheless, the data confirm that these oils are from areas formerly treated with dieldrin. Furthermore, the data indicate that the concentrations of photodieldrin are clearly lower than those of dieldrin itself, and, taking the data from the sample with the highest concentration of dieldrin (80 ng/g of oil), probably even much lower (PD/D ratio < 0.01). With PD/D ratios of ~ 0.06 – 0.19 in our agricultural soils (**Table 1**), this would then suggest that photodieldrin is probably less accumulated in oil than dieldrin. In fact, an earlier study indicated a relatively lower uptake of photodieldrin by plants (25).

Presence of Dieldrin and Photodieldrin in a Herring Oil. To demonstrate further the feasibility of enantioselective analysis of photodieldrin in environmental biological samples, we include data of a sample (Baltic herring oil, 1988) from an earlier study on POPs (13). This particular oil previously showed the presence of photoproducts (heptachlorepoxide, photoheptachlor, photo-*cis*-chlordane) (13, 22, 28) of other, although structurally not very different, halogenated POPs at about $1/10$ of the total concentration of parent compound.

The retrospective analysis of this Baltic herring oil now clearly indicates the presence of dieldrin and, to a lesser degree, photodieldrin, when using the DB-5MS column. The concentrations of dieldrin and photodieldrin were estimated at 5 and 0.05 ng/g of oil, respectively (PD/D ratio ~ 0.01). Aldrin was not detected ($< 0.2\%$ relative to dieldrin). The data indicate that photodieldrin is detected but again suggest that its bioaccumulation is not greater than that of dieldrin itself, but likely much lower. The presence of both compounds was confirmed when analyses were repeated using the OV1701/ γ -BSCD column. As shown by the chromatograms in **Figure 7**, dieldrin eluted as a single peak, whereas photodieldrin is resolved into its two enantiomers. The peak areas indicate an ER of 1.4 ± 0.05 and thus a clearly nonracemic composition of photodieldrin. Such an ER is not unusual for POPs in aquatic species; the ERs of several chiral chlordane compounds were in the range of 1.2–2.4 in this same oil. It should be pointed out that the PD/D ratios possibly are changed in samples from retrospective studies but that ER changes are not anticipated

because chemical and physical processes would not affect enantiomer composition even during long sample storage.

Although the data are preliminary, and there is a large time span between samplings, the very similar enantiomer compositions of a fish oil from a remote area (Baltic) and agricultural soils, with a clear preference for the first-eluted enantiomer in all samples, suggest that photodieldrin likely originates from dieldrin-treated agricultural fields, although some additional photochemical formation of photodieldrin during atmospheric transport as well as further changes of enantiomer composition in the marine ecosystem cannot be ruled out. Any such “secondary” (atmospheric) formation of photodieldrin would change ERs from the “primary” (agricultural) source toward a more racemic composition and, in our case, would lower the observable ER of photodieldrin in an ecosystem.

In conclusion, the small number of data does not allow a very detailed analysis. Nevertheless, the fact that all analyses indicate the presence of photodieldrin in soil where dieldrin itself is present indicates that the photochemical conversion of this POP is of some environmental significance. The fact that the enantiomer composition of photodieldrin in an industrial soil is virtually racemic is a strong indication of a photochemical pathway leading to photodieldrin rather than a microbial one. Furthermore, the data clearly show that photodieldrin must have undergone some enantioselective microbial degradation. The data further document the importance of enantioselective analyses to determine the environmental fate of persistent organochlorine pesticides.

The hypothesis that the enantiomer composition of a chiral metabolite could be used as a marker or tracer for the continued degradation of parent contaminant is intriguing. ER measurements are possibly a more sensitive measure for continuing biodegradation than decreasing contaminant concentration. A potential application of such measurements could be to follow bioremediation actions of persistent contaminants in formerly treated soils, where concentrations are often highly variable (29).

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