Environ. Sci. Technol. **1998**, *32,* 626−633

Occurrence and Transformation Reactions of Chiral and Achiral Phenoxyalkanoic Acid Herbicides in Lakes and Rivers in Switzerland

HANS-RUDOLF BUSER* AND MARKUS D. MÜLLER

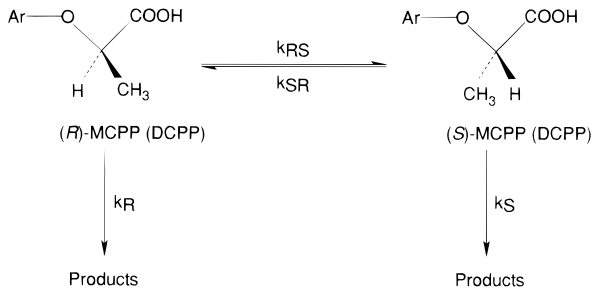
Swiss Federal Research Station, CH-8820 Wädenswil, Switzerland

The occurrence of chiral and achiral phenoxyalkanoic acid herbicides in lakes and rivers in Switzerland is reported. The compounds most frequently detected were the chiral 2-(4-chloro-2-methylphenoxy)propionic acid (mecoprop, MCPP) and the achiral 4-chloro-2-methylphenoxyacetic acid (MCPA), 2,4-dichlorophenoxyacetic acid (2,4-D), and dicamba, a benzoic acid derivative. The compounds were generally present at concentrations well below the ECE recommended drinking water tolerance level (100 ng/L), even in lakes situated in areas with intense agricultural activities. The chiral 2-(2,4-dichlorophenoxy)propionic acid (dichlorprop, DCPP) was hardly present, and none of the compounds was detected in mountain lakes. In case of MCPP, both enantiomers (*R* and *S*) were present, although only the technical material with the *R* enantiomer (mecoprop-P) is registered and used as a herbicide in Switzerland. Previous studies indicated significant enantiomerization of MCPP and DCPP in soil leading to residues enriched in *R* enantiomers independent of whether the racemic (*R*/*S*) or the enantiopure *R* compound was incubated. In some Swiss lakes now, the residues of MCPP showed compositions of $R > S$ as expected from the soil degradation data, but in other lakes, surprisingly, "reversed" compositions of $S > R$ were found. This suggested the occurrence of additional biotic processes in the aquatic environment and/or contamination with racemic MCPP from another source. Laboratory incubation of MCPP and DCPP in lake and river water confirmed significant enantiomerization. The enantiomerization is biologically mediated and leads to residues of MCPP and DCPP in these waters, which are eventually enriched in the *S* enantiomers.

Introduction

Phenoxyalkanoic acids are an important group of herbicides used in agriculture, industrial weed control, and forestry (*1*). Of particular importance are the phenoxyacetic and the 2-phenoxypropionic acids, which include such compounds as the 4-chloro-2-methylphenoxyacetic acid (MCPA), 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 2-(4-chloro-2-methylphenoxy)propionic acid (MCPP, mecoprop), and 2-(2,4-dichlorophenoxy)propionic acid (DCPP, dichlorprop) (see Chart 1, ref 2). The 2-phenoxypropionic acids (MCPP and DCPP) are chiral and exist as two enantiomers with *R* and *S* configuration. Only the *R* enantiomers are herbicidally active (*3*, *4*). Whereas formerly the racemic compounds were used, there are now efforts to produce and register only the enantiopure *R* compounds. For example, for about a decade only the *R* products (e.g., mecoprop-P) are registered in Switzerland for agricultural use (*5*). The racemic compounds, however, are still used in other European countries. The enantiopure *S* compounds have no commercial use.

CHART 1. Generalized Reaction Scheme with Enantiomerization (k_{RS}, k_{SR}) and Degradation Rates (K_R, K_S) for Chiral 2-Phenoxypropionic Acids, Used for Kinetic Considerations in the Study[a]



[a] Ar, 4-chloro-2-methylphenyl (MCPP) or 2,4-dichlorophenyl (DCPP).

In a previous study, the degradation of MCPP and DCPP in soil under laboratory conditions was shown to proceed enantioselectively (*2*). The enantioselectivity was the same for both compounds in that the *S* enantiomers dissipated faster than the *R* enantiomers. Furthermore, it was shown that both compounds are configurationally instable and enantiomerize in soil. The enantiomerization proceeded in both directions, resulting in the formation of the *S* enantiomers from the *R* enantiomers and vice-versa, and the reactions were found to be biologically mediated. Assuming these reactions to proceed under environmental conditions, the residues expected from the use of the racemic and the enantiopure *R* compounds should consist of both enantiomers but with an enantiomeric composition clearly favoring the *R* enantiomers ($R > S$).

When waters from various Swiss lakes were analyzed for the presence of these compounds, we observed that in some instances the enantiomeric composition of MCPP was $R > S$ as expected from the soil degradation data. However, in other instances the composition was reversed ($S > R$) with a predominance of the unexpected *S* enantiomer. This suggested that there are likely additional processes to those observed in soil that lead to changes in enantiomeric composition and/or there is contamination from another source, possibly with racemic MCPP. In this study, we show that there are in fact additional biologically mediated processes that can lead to further changes of the enantiomeric composition of MCPP and DCPP in the aquatic environment and that there are indications for additional sources of racemic MCPP.

Experimental Section

Description of Lakes Sampled. Surface water was collected from five lakes and two rivers situated in the central and eastern region of Switzerland (see Figure 1 for general situation and sampling locations). The lakes investigated were the Zürichsee (Lake Zurich) and Walensee (sampling near the centers) and the Greifensee, Sempachersee, and

* Corresponding author telephone: +41 1 783 6286; fax: +41 1 783 6439; e-mail: hans-rudolf.buser@mbox.faw.admin.ch.

S0013-936X(97)00652-4 CCC: $15.00
Published on Web 01/22/1998

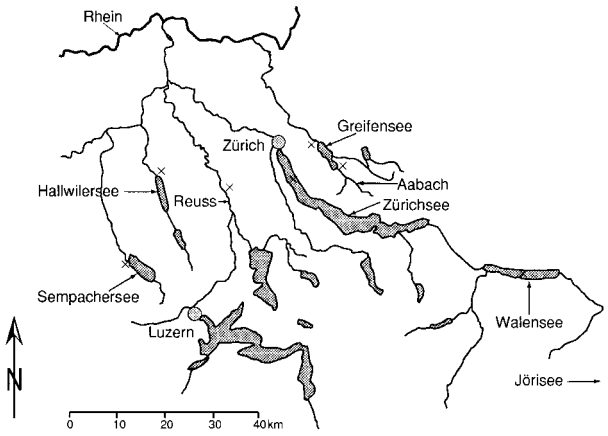


FIGURE 1. Map of eastern/central Switzerland with rivers, lakes, and sampling sites. Also indicated are the cities of Zürich and Luzern.

Hallwilersee (sampling at outlets). The rivers studied were the Aabach, one of the tributaries to Greifensee (sampling at the inlet to this lake), and the river Reuss (sampling at Ottenbach, ≈34 km from Luzern).

Zürichsee (406 m above sea level, msl; two basins, total surface area 88.4 km^2; mean water residence time, 1.2 yr) is situated in a more populated area, although there are still some agricultural activities nearby (catchment area, 1760 km^2; population, 315 000). It receives most of its water from Walensee (419 msl; surface area, 24.1 km^2; mean water residence time, 1.25 yr), which is situated in a more mountainous region. Greifensee is a smaller lake (435 msl; surface area, 8.4 km^2; mean water residence time, 1.1 yr) situated 10 km east of Zürich. There are agricultural activities in its catchment area (160 km^2), but the relatively high population (≈100 000 inhabitants) in this area cause an additional input of anthropogenic compounds. Sempachersee (504 msl; surface area, 14.4 km^2) is situated 40 km southwest of Zürich. This lake has a relatively long mean water residence time of 17 yr. In its relatively small catchment area (61 km^2) are intense agricultural activities, and there is a relatively small population of about 12 000 inhabitants. Finally, Hallwilersee (449 msl; surface area, 10.0 km^2; mean water residence time, 3.8 yr) is situated 25 km southwest of Zürich and has, as does Sempachersee, a predominant input from agricultural activities in its catchment area (138 km^2) (population, 23 000).

Typically, these lakes are stratified during the warmer season (April−November) with development of an epilimnion (thermocline at 8−15 m) and a hypolimnion. In late fall and winter, the waters are mixed down to significant depths. The residence times for water in the epilimnia during stratification are shorter (5−10×) than the mean water residence times indicated above (*6*). Lateral mixing in these lakes is fast (within days) as compared to other processes that influence the behavior of the compounds studied (*7*, *8*). In Sempachersee and Hallwilersee aeration programs are in progress, resulting in total vertical mixing in winter and increased hypolimnion mixing in summer (*9*, *10*). Additionally, a small mountain lake (Jörisee; 2519 msl; surface area, ≈0.05 km^2) with inputs only from snow, ice, and rain was analyzed.

Incubation of Natural and Fortified Lakewater. Lakewater for incubation was taken from Sempachersee on August 2, 1996, and the river Aabach on August 29, 1996. No fortifications were made to these waters. The water from Sempachersee was incubated in 1-L green glass bottles and incubated for up to 129 d at room temperature (rt, 20−23 °C). Periodically, one of the bottles was removed from storage, and the water was analyzed as described below. The water from the river Aabach was incubated in one batch in a 2.5-L clear glass bottle for up to 50 d at rt while being stirred with a Teflon bar. Periodically, 0.25-L subsamples were removed and analyzed as described below. From the amounts of oxygen dissolved and the relatively small amounts of dissolved organic matter, it can be assumed that the incubation conditions in both experiments were aerobic. There was some algal growth observed in the clear glass bottle.

Additionally, incubation experiments were carried out with fortified water, using water from Sempachersee and the river Aabach, collected on November 4, 1996. Two 2.5-L batches of each were fortified at 50−100 ng/L per compound with MCPA, 2,4-D, and clofibric acid and with (*R*)-MCPP and (*S*)-DCPP, or with (*S*)-MCPP and (*R*)-DCPP, respectively (sources of the compounds, see ref 2). There was thus one batch each fortified with one *R* and one *S* enantiomer of MCPP or DCPP, respectively. The waters were incubated at rt in amber bottles for up to 89 d. Periodically, 0.25-L subsamples were removed and analyzed as described below. The fortifications were made by adding 1.0 mL of a 250 ng/mL solution of the compounds in distilled water, prepared from stock solutions of the compounds in methanol.

Sampling and Analytical Procedures. Surface water (depth, 1 m) from the lakes was collected with standard equipment and filled on-site into methanol-rinsed 1-L glass bottles. A fossil groundwater (zero-contaminant water, ref 6) was also analyzed for control purposes. Water samples were fortified prior to analysis with 50 μL of a 0.4 ng/μL $^{13}C_6$-(*R*/*S*)-DCPP (Cambridge Isotope Laboratories, Cambridge, MA; courtesy C. Zipper, Swiss Federal Institute of Environmental Science and Technology, EAWAG, Dübendorf) in methanol (spike level, 20 ng/L). The samples were shaken vigorously and then kept at 4 °C until extracted, usually within a few days. The water samples were not filtered; however, course particles were removed by sedimentation. Therefore, the concentrations reported include the amounts dissolved and those adsorbed on fine, suspended particles. On the basis of partition coefficients (K_{OC}) of <100 (*11*) and with a maximum of 5 mg/L particulates in the water phase (*7*), the concentrations reported are >99% associated with the dissolved phase.

Extraction of the phenoxyalkanoic acids and dicamba from the acidified (pH ≈ 2) water was effected with a reusable small column containing a macroporous polystyrene adsorbent (Bio-Beads SM-2; Bio-Rad Laboratories, Hercules, CA), and the analytes were eluted and recovered as previously described (*12*). After methylation with diazomethane (see ref 13 and cautionary note therein), the extracts were concentrated (≈0.5 mL in diethyl ether) and passed through a small silica column (0.7 g of silica gel 60, Merck, Darmstadt, FRG; deactivated with 5% water; 5 mm i.d. Pasteur pipet) topped with 10 mm of sodium sulfate. The analytes (as methyl esters, ME) were eluted with 10 mL of *n*-hexane−methylene chloride (1:1). After careful concentration and dilution to 100−200 μL with *n*-hexane, 2-μL aliquots were used for analysis by high-resolution gas chromatography/mass spectrometry (HRGC/MS).

HRGC/MS analysis was carried out with a VG Tribrid mass spectrometer (VG Fisons, Manchester, England) under electron-impact ionization (EI, 70 eV, 180 °C) under full-scan (m/z 35−435, 1.16 s/scan; mass resolution $M/\Delta M$ = 500) or selected ion monitoring (SIM) conditions. SIM analyses were carried out for quantitation of the analytes using the molecular ($M^{\bullet+}$) ions m/z 214.040 (MCPA-ME), 228.055 (MCPP-ME), 233.985 (dicamba-ME, 2,4-D-ME), 248.001 (DCPP-ME), and 254.021 ($^{13}C_6$-DCPP-ME), and satellite $(M + 2)^{\bullet+}$ ions. The samples were analyzed using a homemade enantioselective 20-m OV1701-TBDM (TBDM, heptakis-(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin) fused silica (0.25 mm i.d.) column with 35% of

the chiral selector (amount relative to OV1701) (*2*). On-column injection was used. The column was temperature programmed as follows: 50 °C, 2-min isothermal, 20 °C/min to 120 °C, then at 2.5 °C/min to 240 °C, followed by an isothermal hold at this temperature. It enantiomerically resolved MCPP and DCPP with the *R* enantiomers as first-eluted and the *S* enantiomers as second-eluted (see ref 2). The amounts of an analyte were determined from peak area ratios relative to the internal standard ($^{13}C_6$-DCPP; summation of enantiomers) and in reference to suitable standard solutions. Enantiomeric ratios (ER) were defined as ER = p_R/p_S whereby p_R and p_S are the peak areas of the earlier-eluted *R* and the later-eluted *S* enantiomers, respectively. Enantiomeric compositions are indicated as $R > S$ and $S > R$ and indicate a predominance of the *R* and *S* enantiomers, respectively. A selection of samples were reanalyzed using an achiral 22-m SE54 HRGC column for the presence of 2,4,5-T and 2-(2,4,5-trichlorophenoxy)propionic acid (2,4,5-TP) (methyl esters, m/z 267.946 and 281.961, respectively).

Recoveries and Precision of Data. The solid-phase extraction procedure used for analysis allowed the detection of these compounds at concentrations of 0.2−1 ng/L per component when 1-L samples were used and 1 ng/L with 0.25-L samples. Separate experiments with the fossile groundwater, fortified with 10 ng/L of racemic and the enantiopure chiral compounds, revealed good accuracy and precision, no detectable racemization (MCPP, DCPP) during analysis, and acceptable recoveries (50−90%). Quality control included the determination of $^{13}C_6$-DCPP in each of the samples and the analysis of blanks and fortified samples. The concentrations reported are corrected for the recovery of the $^{13}C_6$-DCPP. The data are most precise for DCPP and are expected to be somewhat less accurate for the other compounds. The concentrations and the ER values for duplicate samples agreed to ±10% (10−50 ng/L level) and to ±2% (ERs), respectively.

Modeling of the Enantiomerization and Degradation Kinetic. The rate equation for the first-order degradation of an achiral compound is

$$d[C]/dt = -k[C] \quad (1)$$

whereby [C] is the concentration and k is the degradation rate of the compound. The rate equations for a chiral compound and the generalized reaction scheme as shown in Chart 1 and assuming first-order kinetics are

$$d[R]/dt = -k_R[R] - k_{RS}[R] + k_{SR}[S] \quad (2)$$

$$d[S]/dt = -k_S[S] - k_{SR}[S] + k_{RS}[R] \quad (3)$$

whereby [R] and [S] are the concentrations, k_R and k_S are the degradation rates, and k_{RS} (inversion of *R* to *S*) and k_{SR} (inversion of *S* to *R*) are the enantiomerization rates of the *R* and *S* enantiomers, respectively (see also ref 2). For modeling, the derivatives were replaced by finite differences, and a computer program was used to calculate the concentrations of *R* and *S* as a function of the rate constants and the time (initial concentrations of the *R* and *S* enantiomers were taken as known). The data sets from the incubation experiments were fitted to the above equations using this program and initial estimates of the rates. The rates were then varied in a way to minimize the sum of the squares of the errors. In the experiments where a lag phase was observed the rates were stepped from zero to the full rate at the end of the lag phase in an exponential way, and then varied for a reasonable fit by visual inspection (see data below). The model fitted curves are plotted along with some of the data.

Results and Discussion

Occurrence of Phenoxyalkanoic Acids and Dicamba in Swiss Lakes and Rivers. All lakes, with exception of those from the more mountainous areas, contained detectable concentrations of some phenoxyalkanoic acids and dicamba, as reported in Table 1. The concentrations in these lakes were at all times significantly below the ECE drinking water tolerance limit (100 ng/L). Also detected was clofibric acid, a pharmaceutical drug and a close analogue of MCPP (see ref 12). The most frequently detected compounds were MCPP, MCPA, 2,4-D, and dicamba. DCPP was detected only in very few of the samples at low concentrations. The presence of higher concentrations of MCPP than of DCPP is not unexpected since MCPP is a mixing partner in numerous herbicide formulations, whereas DCPP finds only limited application in Switzerland (*14*). 2,4,5-T and 2,4,5-TP were not detected (<1 ng/L) both compounds have been banned in Switzerland for more than a decade.

The data indicated some seasonal changes in concentrations for MCPP and the other compounds in the lakes. The most pronounced changes in concentration and the enantiomeric composition of MCPP, however, were observed in the small river Aabach, the inlet to lake Greifensee, with input maxima of MCPP in August 1996 (146 ng/L), of MCPA in August 1996 and May 1997 (107 and 75 ng/L, respectively), and of 2,4-D in April 1997 (45 ng/L) (see Table 1). It is expected that concentrations in this tributary change more drastically than in the lake itself (see also ref 15). In the case of MCPP (and DCPP, if present), both enantiomers were present, as illustrated in Figure 2 for samples of Greifensee and Sempachersee. At first sight, this finding is unexpected since only the *R* enantiomer of MCPP (mecoprop-P) is registered in Switzerland for agricultural use (*5*). There are some indications of a trend toward a higher contribution from (*S*)-MCPP (lower ERs) during the warmer season.

There are marked differences in the enantiomeric composition of MCPP in these lakes. Lakes Sempachersee and Hallwilersee showed compositions of $R > S$ (ERs up to 4.36) as expected from the soil degradation of MCPP (see above). However, Lakes Greifensee and Zürichsee (at particular times) and the rivers Aabach and Reuss unexpectedly showed reversed enantiomeric compositions of $S > R$ (ERs as low as 0.21). ERs < 1 cannot be explained by the soil degradation data and suggest the occurrence of additional, possibly aquatic, enantioselective processes or another route (source) of contamination (see below). Thus, the lakes with the highest contributions from agricultural practices (Sempachersee, Hallwilersee) showed an enantiomeric composition of $R > S$ as expected from the soil degradation data, but some other lakes and rivers did not.

Enantiomerization of MCPP in Natural Waters. A sample from Sempachersee, stored for over 2 yr and now analyzed also showed a reversed enantiomeric composition (ER = 0.29). Since it is unlikely that the actual MCPP composition in this lake should be reversed from that of 2 yr earlier, it was hypothesized that the enantiomeric composition of MCPP could have changed during storage in the laboratory. To test this hypothesis, incubation experiments with waters from Sempachersee (ER = 2.6; 14 ng/L) and the river Aabach (ER = 0.50; 30 ng/L) were carried out, thus using waters with a normal ($R > S$) and a reversed ($S > R$) enantiomeric composition of MCPP.

The concentrations of MCPP, MCPA, 2,4-D, and dicamba were reduced during the 50−129 d of incubation in both experiments. The data fitted approximate first-order kinetics without a lag phase. The overall degradation rate constants (k) for MCPP (summation of both enantiomers), MCPA, and 2,4-D thus estimated were 2.7×10^{-3}, 6.4×10^{-3}, and 3.5×10^{-3} d^{-1}, respectively, using the more precise data from

TABLE 1. Phenoxyalkanoic Acid Herbicides in Lakes and Rivers in Switzerland

		compound, concn (ng/L)							
		MCPP			DCPP				
lake, river	sampling date	(*R*)-	(*S*)-	(ER)	(*R*)-	(*S*)-	MCPA	2,4-D	dicamba
Jörisee	18 Jul 96	<0.2	<0.2		<0.2	<0.2	<0.2	<0.2	<0.2
Walensee	15 Jul 96	<0.2	<0.2		<0.2	<0.2	<0.2	<0.2	<0.2
Sempachersee	12 Jul 96	10.4	4.0	(2.64)	<1	<1	12.0	4.0	2.0
	2 Aug 96	9.8	3.8	(2.59)	<1	<1	7.5	4.2	3.8
	29 Aug 96	11.2	3.9	(2.86)	<1	<1	12.5	4.5	3.0
	18 Sep 96	8.6	2.2	(3.95)	<1	<1	1.2[a]	<1[a]	2.3
	23 Oct 96	9.1	2.3	(3.92)	<1	<1	6.2	3.2	2.4
	12 Dec 96	9.4	(5.1)[a]		<1	<1	5.7	3.2	2.0
	3 Mar 97	7.0	1.6	(4.35)	<1	<1	4.4	2.1	2.0
	15 Apr 97	4.2	1.0	(4.36)	<1	<1	2.3	1.6	<1
	6 May 97	6.3	1.5	(4.27)	<1	<1	5.0	3.0	<1
	2 Jul 97	5.9	1.9	(3.13)	<1	<1	4.4	1.7	1.4
Hallwilersee	12 Jul 96	10.6	6.4	(1.66)	1.2	1.5	20.0	5.5	3.3
	4 Nov 96	6.1	3.4	(1.81)	<1	<1	9.0	2.8	3.4
	15 Apr 97	7.0	2.1	(3.28)	<1	<1	7.2	4.1	2.3
	2 Jul 97	6.0	2.4	(2.50)	<1	<1	6.3	1.3	2.9
Zürichsee	14 Jun 96	4.8	5.2	(0.92)	<0.5	<0.5	3.0	2.0	1.0
	1 Jul 96	4.6	4.85	(0.95)	<0.2	<0.2	4.2	1.0	0.7
	1 Dec 96	3.7	4.2	(0.88)	<0.3	<0.3	1.8	1.0	0.9
	5 Mar 97	4.1	3.2	(1.27)	<0.5	<0.5	1.8	1.4	<0.5
	4 Apr 97	3.8	3.0	(1.25)	<0.5	<0.5	1.6	1.4	<0.5
	4 Jun 97	4.3	3.6	(1.20)	<0.5	<0.5	3.1	1.0	0.6
Greifensee	5 Jul 96	20.9	23.3	(0.90)	≈1	≈1	16.1	5.4	9.9
	2 Aug 96	19.7	25.0	(0.79)	<1	<1	15.0	5.5	14.7
	29 Aug 96	19.3	24.1	(0.80)	<1	<1	12.0	4.4	12.3
	18 Sep 96	16.3	18.6	(0.88)	<1	<1	3.0	<1	8.4
	23 Oct 96	16.1	20.7	(0.78)	<1	<1	8.3	4.7	8.3
	12 Dec96	15.2	19.2	(0.79)	<1	<1	7.5	4.2	6.6
	3 Mar 97	12.0	13.4	(0.90)	<1	<1	5.5	3.2	4.9
	15 Apr 97	15.4	15.1	(1.02)	<1	<1	6.9	3.9	4.8
	6 May97	5.9	5.8	(1.02)	<1	<1	5.8	3.4	<1
	2 Jul 97	14.5	18.0	(0.80)	<1	<1	6.0	2.2	6.0
Aabach	2 Aug 96	25	121	(0.21)	<1	<1	107	9.0	12.6
	29 Aug 96	10.0	20.2	(0.50)	<1	<1	9.2	1.1	5.4
	18 Sep 96	23	43	(0.54)	<1	<1	3.3	<1	10.5
	23 Oct 96	7.1	11.3	(0.63)	<1	<1	<1	<1	1.7
	12 Dec 96	7.2	9.7	(0.74)	<1	<1	<1	<1	<1
	3 Mar 97	6.7	7.6	(0.88)	<1	<1	<1	<1	3.5
	15 Apr 97	17.6	16.5	(1.05)	<1	<1	31	45	5.9
	6 May 97	7.8	8.5	(0.92)	<1	<1	75	3.1	1.5
	2 Jul 97	11.9	14.0	(0.85)	2.7	2.7	3.9	<1	5.8
Reuss	12 Jul 96	3.5	5.0	(0.70)	<0.2	<0.2	2.8	1.0	<1

[a] Values questionable due to low recovery or interference.

Sempachersee (1-L samples, longer incubation periods), indicating half-lives of 250, 100, and 200 d at 20−23 °C, respectively. The concentrations of DCPP were near the limit of detection and therefore not evaluated. The data indicate these compounds to be relatively stable in the aquatic environment whereas they degrade relatively quickly in soil (half-lives, 7−22 d, see ref 2).

In Figure 3a,b we show the data for MCPP from both experiments. The data from the incubation of water from Sempachersee (Figure 3a) clearly show enantiomerization of (*R*)-MCPP into (*S*)-MCPP. The enantiomeric composition is initially $R > S$ (ER = 2.6) and then gradually changes to a racemic and eventually a reversed composition *of* $S > R$ (ER = 0.4 after 129 d). In contrast, the data from the incubation of water from the river Aabach (Figure 3b) showed a relatively constant enantiomeric composition (ER ≈ 0.50). The enantiomeric composition of MCPP in both experiments thus was eventually $S > R$.

The data for MCPP indicated that the enantiomerization of *R* to *S* is several times faster than that of *S* to *R* and faster than actual degradation. The data showed relatively good fits to the first-order model using rate constants $k_R = 1 \times 10^{-3}$ d^{-1}, $k_{RS} = 13.5 \times 10^{-3}$ d^{-1}, $k_{SR} = 4.5 \times 10^{-3}$ d^{-1}, and $k_S = 4.5 \times 10^{-3}$ d^{-1}, as indicated by the model fitted curves in Figure 3a,b.

Enantiomerization of MCPP and DCPP in Fortified Waters. The data from the incubation experiments with the fortified waters confirmed that the enantiomerization of MCPP and DCPP is proceeding predominantly from *R* to *S*, as illustrated below. The data indicated some initial lag phase (duration 11−35 d) with smaller rates that were not observed in the previous experiments and may be due to the different (lower) biotic activity of the waters at this time.

In Figure 4a,b we plotted the data from an experiment with (*R*)-MCPP and (*S*)-DCPP. The data for MCPP (Figure 4a) show an approximately constant concentration of (*R*)-MCPP (55 ng/L; lag phase) up to 21 d, followed by a gradual decrease to ≈11 ng/L at 89 d, the largest decrease occurring between 21 and 63 d. During the latter period, the concentration of (*S*)-MCPP gradually increased from ≈3 to 44−48 ng/L and then also decreased. The curves for (*R*)- and (*S*)-MCPP thus intersect, leading eventually to a reversed enantiomeric composition ($S > R$), indicating significant conversion of the *R* into the *S* enantiomer. The data for DCPP (Figure 4b) show an approximately constant concentration of (*S*)-DCPP (≈62 ng/L) up to 21 d and then a gradual

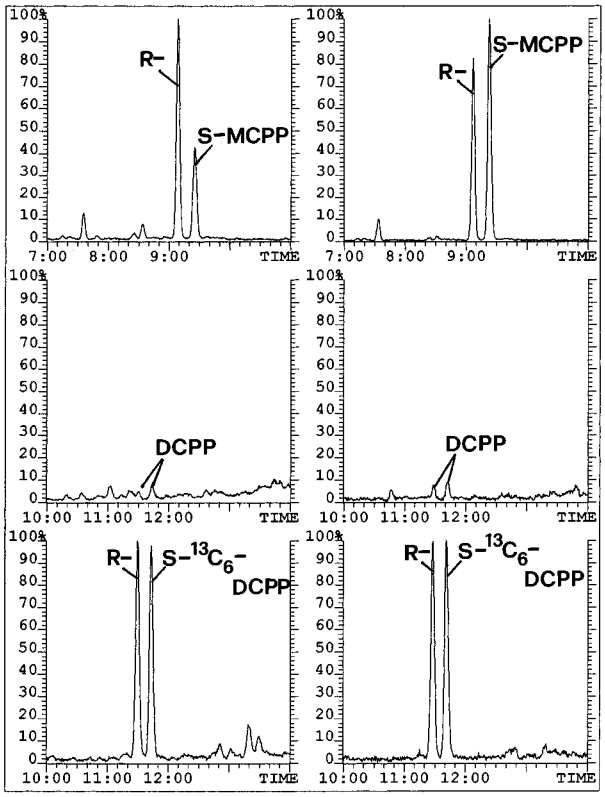


FIGURE 2. EI SIM chromatograms showing elution of (*R*)- and (*S*)-MCPP (*m/z* 228, top), (*R*)- and (*S*)-DCPP (*m/z* 248, middle), and (*R*)- and (*S*)-$^{13}C_6$-DCPP (*m/z* 254, bottom) as methyl esters in samples from Lakes Sempachersee (left-side panels) and Greifensee (right-side panels), respectively. Note the "normal" (*R* > *S*) composition in Sempachersee and the "reversed" composition (*S* > *R*) in Greifensee; racemic $^{13}C_6$-DCPP was used as the internal standard.

decrease to ≈38 ng/L at 89 d. During this time, the concentration of (*R*)-DCPP only marginally increased from <1 to ≈5 ng/L. The enantiomeric composition of DCPP thus remained *S* > *R*, indicating little conversion of the *S* into the *R* enantiomer.

In Figure 5a,b we plotted the data from an experiment with (*S*)-MCPP and (*R*)-DCPP. The data for MCPP (see Figure 5a) show a gradual decrease in the concentration of (*S*)-MCPP from ≈90 to 48 ng/L at 89 d. There is no increase but rather some decrease of (*R*)-MCPP from 16 to 12 ng/L during this time and hence little if any conversion of the *S* into the *R* enantiomer. The data for DCPP (Figure 5b) show a gradual decrease in the concentration of (*R*)-DCPP from ≈70 to ≈10 ng/L at 89 d and at the same time an increase in the concentration of (*S*)-DCPP to ≈50 ng/L. The curves for (*R*)- and (*S*)-DCPP thus intersect very much in the same way as for MCPP above (see Figure 4a) and hence clearly indicate conversion of the *R* into the *S* enantiomer. The results for MCPP and DCPP in all experiments thus indicate significant enantiomerization of the *R* into the *S* enantiomers, but little if any enantiomerization of the *S* into the *R* enantiomers.

In Figures 4 and 5, we also plotted model fitted data for MCPP and DCPP using estimates for the various rate constants. The estimates were initially based on the following considerations: (a) the experimental data indicate, after the lag phase, far higher values for k_{RS} than for k_{SR}; (b) at the period of highest change of concentration (21−62 d, see Figures 4a and 5b) about 80% of the decrease in an *R* enantiomer is converted into the respective *S* enantiomer, and hence the enantiomerization rates k_{RS} exceed the respective degradation rates k_R; (c) the degradation rates k_S (least affected by enantiomerization), estimated from the data in Figures 4b and 5a, are about 10×10^{-3} and 8×10^{-3} d^{-1} (half-lives, ≈60 and ≈80 d, respectively) for MCPP and DCPP, respectively, or less. From these considerations and taking an initial lag phase of 11−35 d into account, the rates that gave reasonable fits for the experimental data were $k_R = 1 \times 10^{-3}$ d^{-1}, $k_{RS} = 30 \times 10^{-3}$ d^{-1}, $k_{SR} = 3 \times 10^{-3}$ d^{-1}, and $k_S = 8 \times 10^{-3}$ d^{-1} for MCPP (see Figures 4a and 5a) and $k_R = 2.5 \times 10^{-3}$ d^{-1}, $k_{RS} = 34 \times 10^{-3}$ d^{-1}, $k_{SR} = 3 \times 10^{-3}$ d^{-1}, and $k_S = 6.5 \times 10^{-3}$ d^{-1} for DCPP (see Figures 4b and 5b). The rates for MCPP estimated in these experiments differed from those of the previous ones with the unfortified "natural" waters (see above), and the modeled data did not fit the experimental data as good. Nevertheless, all data show that k_{RS} and k_S dominate over k_{SR} and k_R.

Consequences for the Enantiomeric Composition of Environmental Residues of MCPP. The various incubation experiments suggest a preference for the *S* enantiomers in the aquatic environment. Enantiomerization seems to be a general phenomena as it was observed with waters from Lake Sempachersee and the river Aabach, and at two time periods

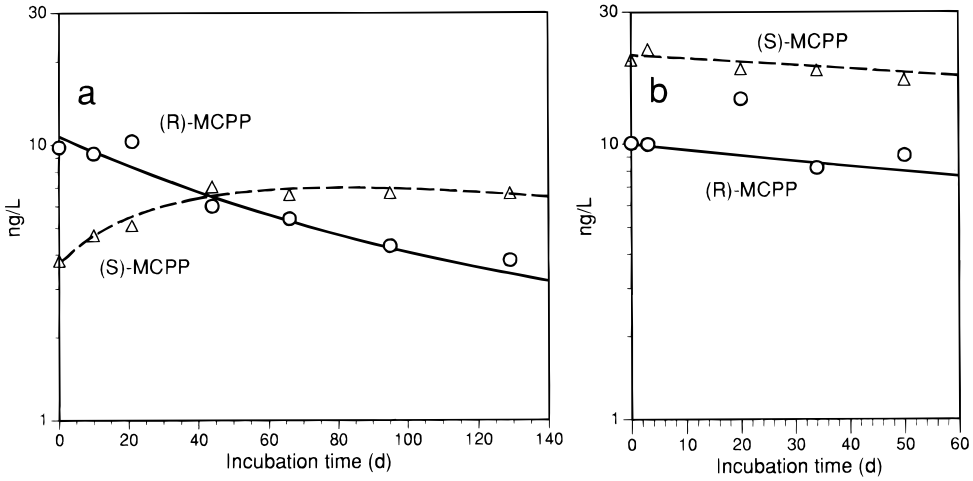


FIGURE 3. Degradation of MCPP in natural waters under laboratory conditions. (a) Degradation of (*R*)-MCPP in water from Sempachersee and concurrent formation of (*S*)-MCPP and (b) degradation of (*R*)- and (*S*)-MCPP in water from the river Aabach. The curves are from modeled values using the rates $k_R = 1 \times 10^{-3}$ d^{-1}, $k_{RS} = 13.5 \times 10^{-3}$ d^{-1}, $k_{SR} = 4.5 \times 10^{-3}$ d^{-1}, and $k_S = 4.5 \times 10^{-3}$ d^{-1}. Solid lines, circles: concentrations of the *R* enantiomers; dashed lines, triangles: concentrations of the *S* enantiomers. Note the eventual reversal of the enantiomeric composition in water from Sempachersee.

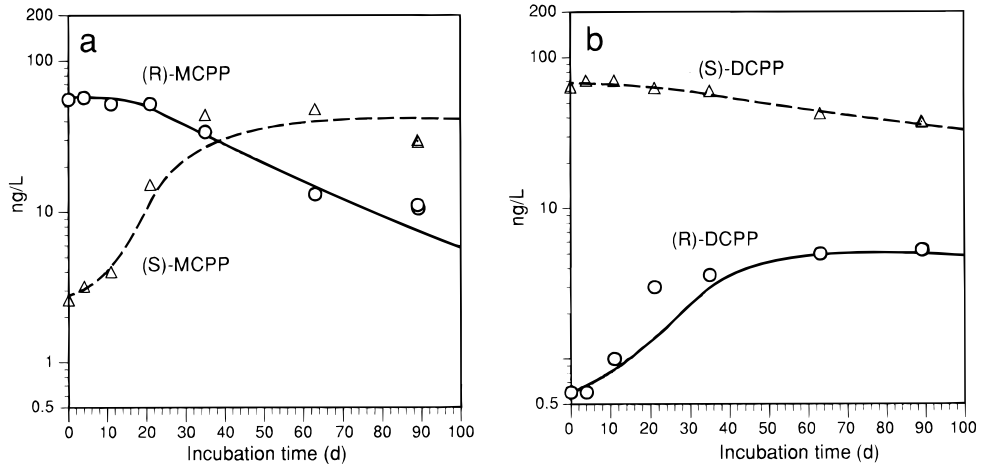


FIGURE 4. Degradation of MCPP and DCPP in waters fortified with (*R*)-MCPP and (*S*)-DCPP under laboratory conditions. (a) Degradation of (*R*)-MCPP and concurrent formation of (*S*)-MCPP with eventual reversal in enantiomeric composition and (b) degradation of (*R*)- and (*S*)-DCPP. The curves are from modeled values using the rates $k_R = 1 \times 10^{-3}$ d^{-1}, $k_{RS} = 30 \times 10^{-3}$ d^{-1}, $k_{SR} = 3 \times 10^{-3}$ d^{-1}, and $k_S = 8 \times 10^{-3}$ d^{-1} for MCPP; $k_R = 2.5 \times 10^{-3}$ d^{-1}, $k_{RS} = 34 \times 10^{-3}$ d^{-1}, $k_{SR} = 3 \times 10^{-3}$ d^{-1}, and $k_S = 6.5 \times 10^{-3}$ d^{-1} for DCPP; and assuming a lag time of 21 d (see text). Solid lines, circles: concentrations of the *R* enantiomers; dashed lines, triangles: concentrations of the *S* enantiomers.

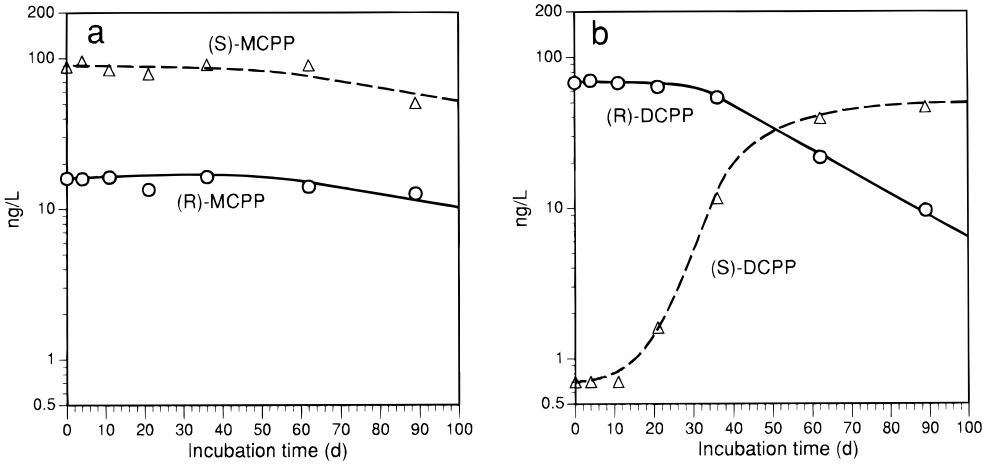


FIGURE 5. Degradation of MCPP and DCPP in waters fortified with (*S*)-MCPP and (*R*)-DCPP under laboratory conditions. (a) Degradation of (*S*)- and (*R*)-MCPP and (b) degradation of (*R*)-DCPP and concurrent formation of (*S*)-DCPP with eventual reversal in enantiomeric composition. Solid lines, circles: concentrations of the *R* enantiomers; dashed lines, triangles: concentrations of the *S* enantiomers. The curves are from modeled values using the same rates as in Figure 4.

(August and November 1996). The process is biologically mediated since the inversion of *R* to *S* was 3−10 × faster than the inversion of *S* to *R*. In chemically mediated reactions, the respective enantiomerization and degradation rates are identical ($k_R = k_S$; $k_{RS} = k_{SR}$), and the degradation curves for the enantiomers do not intersect (see below). The rates reported above should be considered as rough estimates as they likely depend on the actual microbial populations in the waters. The particular kinetic, with the enantiomerization rates exceeding the degradation rates, leads to a faster dissipation of the *R* than of the *S* enantiomer when in fact the degradation rate of the latter enantiomer (k_S) is larger ($k_S > k_R$). The degradation of MCPP (and DCPP) in these waters can best be described as an enantiomerization of the *R* into the *S* enantiomer, followed by degradation of the *S* enantiomer.

In Figure 6 we show modeled degradation curves for (*R*/*S*)- and (*R*)-MCPP assuming biological and chemical processes. The curves for (*R*/*S*)-MCPP in Figure 6a indicate that the enantiomeric composition remains racemic in case of chemically mediated reactions whereas it is changed to *S* > *R* in case of biologically mediated reactions. The curves for (*R*)- and (*S*)-MCPP in Figure 6b only intersect in case of biologically mediated reactions. It is interesting to note that Ludwig et al. (*16*) observed an enantiomeric composition *S* > *R* of DCPP (ER of 0.71 after 21 d, as calculated from their data) from the incubation of the racemate with a marine microbial culture and thus an enantioselectivity in the same sense as in our experiments. They attributed this result to a preferred degradation of (*R*)-DCPP. Assuming the same processes as observed in our study, their data could also be interpreted as enantiomerization of (*R*)-DCPP followed by degradation of (*S*)-DCPP (see Figure 6a).

The enantiomeric composition of MCPP and DCPP in soil from agricultural applications of the registered herbicides is expected to be *R* > *S* (*2*, *17*), but once the compounds are in the aquatic environment, via runoff or leaching from treated areas, and subjected to the processes described here, the composition can be somewhat changed toward the *S* enantiomer. Two of the lakes, Sempachersee and Hallwilersee, showed MCPP residues with a composition *R* > *S*, as expected from such applications; both lakes have relatively large agricultural activities in their catchment areas. We assume that most of the MCPP in these lakes is actually from

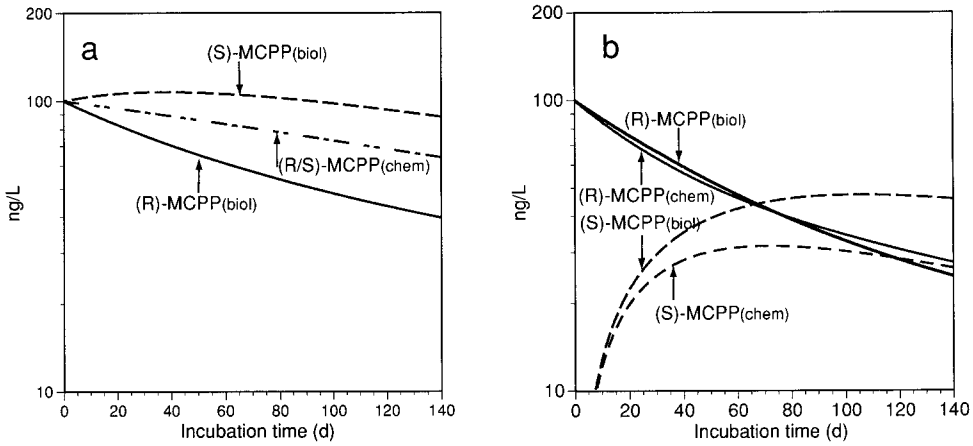


FIGURE 6. Modeled degradation curves for (a) racemic MCPP and (b) enantiopure (99%) (*R*)-MCPP assuming biological and chemical degradation. The rates assumed for the biological degradation [$k_R \neq k_S$; $k_{RS} \neq k_{SR}$; concentrations indicated as MCPP(biol)] were those from Figure 3; the rates assumed for the chemical degradation [$k_R = k_S$; $k_{RS} = k_{SR}$; concentrations indicated as MCPP(chem)] were 4.5 $\times$ 10^{-3} d^{-1} and 13.5 $\times$ 10^{-3} d^{-1}. Note intersection of the degradation curves of the *R* and *S* enantiomers in case of a biologically but not a chemically mediated degradation. Analogous results are obtained for DCPP.

such activities, but apparently the biotic activity and/or the residence time in the lakes are not large enough to fully revert the enantiomeric composition to $S > R$.

The two lakes Greifensee and Zürichsee, and in particular the river Aabach, showed MCPP residues with enantiomeric compositions of $S > R$ over extended periods of time. ER values as low as 0.21 are difficult to explain from initial compositions of $R > S$ followed by enantiomerization in the aquatic environment using the rate constants determined in this study. The time required to revert the enantiomeric composition for MCPP from $R > S$ to $S > R$ is estimated to be in the order of weeks. While residence times of this magnitude are reached in these lakes, even during stratification, the results from Lake Sempach with the longest residence time still indicate a composition $R > S$. Furthermore, the river Aabach (inlet to Greifensee) also showed an enantiomeric composition of $S > R$ over a period of several months although the residence time of MCPP in the river is expectedly short (hours to days).

The situation, however, may be different if one would assume inputs of (*R*/*S*)-MCPP, such as from illegal agricultural applications or from another source. The modeled degradation curves for (*R*/*S*)-MCPP (the same would apply for DCPP), with the rate estimates of this study, would lead much quicker to enantiomeric compositions of $S > R$, as shown by the modeled data in Figure 6a. Since enantiomeric compositions of $S > R$ are particularily observed in lakes with a higher contribution from nonagricultural activities (Greifensee, Zürichsee), such activities may thus be responsible for some of the MCPP in these lakes. It awaits further investigation whether the recently reported leaching of MCPP with runoff water from flat building roofs sealed with bitumenous materials containing (*R*/*S*)-MCPP−polyglycol diesters as a root protectant is such a source (*18*). However, because the water flowing out of Lake Greifensee showed a higher ER for MCPP than the water in one of the main tribuaries to this lake, there must still be other inputs enriched with the *R* enantiomer such as from agricultural MCPP applications. For the future, the enantiomeric composition of residues may thus aid in identifying the sources and pathways of contaminations.

Note Added to the Revised Manuscript. After this study, it was found that MCPP is present in this particular tributary of the Greifensee only at locations receiving water from wastewater treatment plants, thus pointing to major nonagricultural inputs of MCPP into this lake.

Acknowledgments

We thank our collegues Verena Buser and A. Zürcher for sample preparation and the sampling of the lakes, respectively. The samples from Zürichsee and Walensee were taken by S. Dunst (Water Works of Zürich). Many detailed discussions were held with the following persons and are kindly acknowledged: H. P. Kohler, S. Müller, and C. Zipper (EAWAG), R. Gächter (Lake Research Laboratory of ETH/EAWAG, Kastanienbaum), and J. Zeyer (Institute of Terrestrial Ecology, Swiss Federal Institute of Technology, ETH, Zürich). We also thank Brigitte Hinder and K. Hanselmann (Institute for Plant Biology, University of Zürich) for suggesting and sampling of Jörisee.

Literature Cited

(1) Humburg, N. E.; Colby, S. R.; Hill, E. R.; Kitchen, L. M.; Lym, R. G.; McAvoy, W. J.; Prasad, R. *Herbicide Handbook of the Weed Society of America*, 6th ed.; Weed Society of America: Champain, IL, 1989.

(2) Müller, M. D.; Buser, H. R. *Environ. Sci. Technol.* **1997**, *31*, 1953−1959.

(3) Loos, M. A. In *Herbicides: Chemistry, Degradation and Mode of Action*; Kearney, P. C., Kaufman, D. D., Eds.; Marcel Dekker: New York, 1975; Vol. 1, pp 2−101.

(4) Aberg, B. In *The Chemistry and Mode of Action of Plant Growth Substances*; Wain, R. L., Wightman, F., Eds.; Butterworth Scientific Publications: London, 1956; p 102.

(5) Williams, A. *Pestic. Sci.* **1996**, *46*, 3−9.

(6) Buser, H. R. *Environ. Sci. Technol.* **1990**, *24*, 1049−1058.

(7) Schwarzenbach, R. P.; Imboden, D. M. *Ecol. Modell.* **1983**, 22, 171−212.

(8) Schwarzenbach, R. P.; Molnar-Kubica, E.; Giger, W.; Wakeham, S. G. *Environ. Sci. Technol.* **1979**, *13*, 1367−1373.

(9) Stadelmann, P. *Wasser, Energie, Luft* **1988**, *80*, 81−96.

(10) Stadelmann, P. *Wasser, Energie, Luft* **1984**, *76*, 85−95.

(11) Montgomery, J. H. *Agrochemical Desk Reference, Environmental Data*; Lewis Publishers: Chelsea, MI, 1993.

(12) Buser, H. R.; Müller, M. D.; Theobald, N. *Environ. Sci. Technol.* **1998**, *32*, 188−192.

(13) Vogel, A. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman: London, 1978.

(14) Locher, N. Novartis Crop Protection, Dielsdorf, Switzerland, personal communication, 1997.

(15) Ulrich, M. M.; Müller, S. R.; Singer, H. P.; Imboden, D. M.; Schwarzenbach, R. R. *Environ. Sci. Technol.* **1994**, *28*, 1674−1685.

(16) Ludwig, P.; Gunkel, W.; Hühnerfuss, H. *Chemosphere* **1992**, *24*, 1423−1429.

(17) Garrison, A. W.; Schmitt, P.; Martens, D.; Kettrup, A. *Environ. Sci. Technol.* **1996**, *30*, 2449−2455.
(18) Voegelin, A. Master Thesis, Swiss Federal Institute of Technology, ETH, Zurich, Switzerland, 1997.

Received for review July 28, 1997. Revised manuscript received November 23, 1997. Accepted November 28, 1997.

ES970652W