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MECHANISTIC AND KINETIC STUDIES TO REVEAL PHOTODEGRADATION BEHAVIOUR OF DISTINCTIVE PESTICIDES

ABSTRACT

Transformation of pesticides in the environment is a highly complex process affected by different factors. Both biological and physical-chemical factors may play a role in the degradation to variable extent. Our study is focused on revealing specific details of photolytic degradation of pesticides as photodecomposition might be regarded as one of the most crucial factors affecting the fate of pesticides. The toxicity of the examined pesticides is well known, however restricted information is available regarding their natural degradation processes. More detailed examinations are required in order to reveal the exact mechanism of the pesticide decomposition as well as the biological impacts of the degradates. Significance of this study is enhanced by the fact that decomposition of pesticides may result in the formation of toxic degradation products.

The photolytic degradation of frequently applied pesticides (acetochlor, simazine, chlorpyrifos, carbendazim, EPTC) with different chemical structure was investigated. A special, immerseable UV-light source was applied in order to induce photodegradation. The degradation processes were followed by TLC and GC/MS techniques. EI mass spectrometry was used to identify the degradation species. Detailed mechanism of photolytic transformation was established by identification of each degradate.

The photolytic degradation of pesticides of distinctive chemical character exhibited markedly different photodecomposition mechanisms. At least four degradation species were detected and identified in each case. Loss of alkyl, chloro and hydroxyl groups, as well as cleavage of alkyloxy, amide, amino-alkyl and ester bonds might be regarded as typical decomposition patterns. Deamination and ring opening might be observed at the very last stages of decomposition.

Key abbreviations: pesticide, photodecomposition, GC/MS technique, degradation kinetic, degradation mechanism

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INTRODUCTION

Investigating pesticide degradation occurring in the environment is of high interest as both parent compounds and decomposition products can be hazardous because of their toxicity. Photochemical degradation of pesticides is the breakdown of pesticides by light, particularly sunlight. Photochemical degradation of pesticides can be important in the decontamination of natural water or contaminated soils (Aaron et al., 2001; Coly et al., 1994).

Frequently applied pesticides of distinctive chemical structure and physical behaviour have been selected for our studies.

Simazine (6-chloro-N2,N4-diethyl-1,3,5-triazine-2,4-diamine), a wide-spread representative of s-triazine type pesticide, is a selective herbicide with photosynthetic inhibiting effect. It is used to control broad-leaved weeds and annual grasses. A comparative study between fragmentation processes taking place in mass spectrometry using an electron ionisation source and photodegradation processes has been carried out for atrazine, simazine and trietazine (Tremolada et al. 1993). The same kind of fragmentations were observed for the three compounds: C–N bond cleavage in the lateral chains, C–Cl bond scission and heteroatomic ring cleavage. The photochemical degradation and the kinetics of the degradation processes of s-triazine herbicides (atrazine, propazine, and prometryne) has been investigated in case of several types of natural waters and soils (Konstantinou et al. 2001). The photolytic behaviour of triazine herbicides (atrazine, simazine, trietazine, prometon, prometryn) in the presence of TiO_2 as a special photocatalyst has already been studied (Pelizzetti et al., 1990, Hequet et al., 2001). All the herbicides degraded rapidly, full mineralization was not observed. Cyanuric acid was found to be the common final photoproduct of all herbicides. The degradation pathway of the most frequently used triazine pesticide, atrazine, was investigated in aqueous phase by sonolysis, ozonation, photolysis at 254 nm and photocatalysis in the presence of TiO_2 (Bianchi et al., 2006). Dealkylation and dechlorination was induced by ozonation and photocatalysis, while direct photolysis at 254 nm promoted very efficient dechlorination. Triazine-derivatives are considered to be the representatives of pesticides of the most wide-spread practical application; therefore it is of crucial importance to evaluate their fate in the environment (Vidal et al. 1999). It was shown that some triazine herbicides undergo photodegradation to form deaminated derivatives (Mansour et al. 1993). The photodegradation products of some commonly used N-containing herbicides were detected however entire mechanisms have not been revealed (Lányi et al. 2005). (High-pressure mercury vapor lamp (254 nm, 125 W) and GC/MS technique were used during the examinations.) Decomposition products steming plausibly from loss of side-chains and substitution with OH-group were detected. Different metabolites formed having mixed side-chains, and the presence of dimer products could also be observed.

Acetochlor (2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl) acetamide), as a member of the chloroacetanilide class of broad leaf herbicides, is one of the most widely used herbicide. It is a growth inhibitor and applied as preemergence for control of annual grasses.

Chloracetanilide herbicides have been investigated the terms of revealing stability, water solubility and toxicity of degradates (Belfroid et al., 1998). Brekken and Brezonik (1998) studied the reaction between acetochlor and HO-, assuming that the primary source of HO is nitrate photolysis. According to their experimental data, the direct photolysis would be much slower than HO - mediated degradation. In case of acetochlor, serious efforts have been made in order to identify biodegradation products of the pesticide, however no specific reaction pathways have been mapped (Coleman et al., 2000; Thurman et al., 2002; Zheng et al., 2003).

Chlorpyrifos (O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate) is an organophosphate insecticide, acaricide and miticide used to control foliage and soil-borne insect pests on a variety of food and feed crops. The photodegradation of chlorpyrifos by simulated sunlight in water/methanol has been studied by Barcelo et al. (1993) and 3,5,6-trichloro-2-pyridinol was identified as the only degradation product. A method was developed to determine the rate of reaction of chlorpyrifos with HO radicals in the gas phase at high temperatures during photodecomposition (Hebert et al., 2000). Kamiya and Kameyama (1998) studied the effects of humic materials and metal ions on the photochemical degradation of various organophosphorus pesticides (including chlorpyrifos) (Kamiya et al., 2001).

Carbendazim (methyl benzimidazol-2-ylcarbamate) is a benzimidazole carbamate fungicide with systemic activity and broad effect spectrum. It inhibits fungal mitotic microtubule formation. The visible-light-promoted photodegradation of carbendazim was studied in water or water–methanol solution under various conditions (in the presence of air and a photosensitizer xanthene dye or pigment riboflavin, at various pH values (Escalada et al., 2006, Panades et al., 2000, Mazellier et al., 2002). It was established that the rate of photodegradation increased with pH and oxygen concentrations. The aqueous photodegradation of carbendazim was studied by Ibarz et al. (2000). The kinetics of the photodecomposition was determined using HPLC–DAD and the identification of photoproducts was carried out with HPLC–MS by Boudina et al., (2003). Three products were detected after the UV irradiation. One of them, 2,4-amino-benzimidazol has already been identified in a previous paper (Mallat et al, 1997, Tomlin, 1994). A plausible pathway for the photolytic degradation of carbendazim in pure water was proposed as well, however our studies pointed out marked differences when comparing the two different mechanisms.

EPTC (*S*-ethyl dipropylthiocarbamate) is a selective thiocarbamate herbicide used for control of annual grassy weeds, perennial weeds, and some broad-

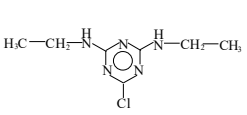
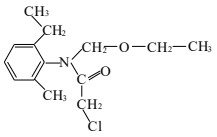
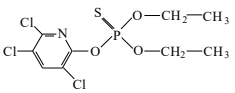
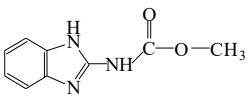
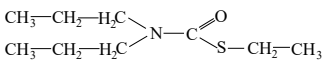
leaf weeds. It is a growth inhibitor pesticide usually applied preemergence. The photodegradation of EPTC by UV light supplied by a medium pressure mercury lamp in hexane has been studied by Marco et al. (1979) as well as Abu-Qare et al. (2002). Several photoproducts and cleavage of C-S and C-N bonds were observed but no reaction pathway was revealed. The kinetics of photodegradation of EPTC was studied by Dinya and Lányi (2005).

The abovementioned information shows that numerous photodegradation studies have been performed especially concerning s-triazines. However, with the exception of atrazine, detailed reaction mechanisms of the concerned pesticides have not been identified. In some cases, specific degradation products were detected without the aim of mapping the entire pathway of photodegradation. Thus our work contributes to a more extensive and comprehensive knowledge on pesticide photodecomposition with regard to both reaction mechanism and chemical characteristics of degradation products. The pathway of photolytic degradation of five pesticides having diverse chemical structure and practical application is mapped by GC/MS identification of degradation products.

MATERIALS AND METHODS

The five pesticides examined, which have diverse chemical structures and action mechanisms are acetochlor (acetanilide herbicide), simazine (triazine herbicide), chlorpyrifos (organophosphate insecticide), carbendazim (benzimidazole fungicide) and EPTC (thiocarbamate herbicide). The chemical structures of the pesticides are shown in table 1. The examined pesticides (higher than 99% HPLC purity) and other applied chemicals were purchased from Aldrich.

Table 1 Chemical structure and name of the studied pesticides.

Simazine	**Acetochlor**	**Chlorpyrifos**
		
Carbendazim	**EPTC**	
		

All aqueous and slightly acidic solutions were prepared from the pure pesticides in 500ppm concentrations. Into these solutions, the specific UV light source was immersed emitting constantly light of 254 nm wavelength being a component of natural sunlight, and resulting in faster and therefore more examinable degradation process. The light source was a low pressure mercury-vapour lamp of 15 W output manufactured by Millipore company. The degradation process was followed by TLC and GC. Thin layer chromatography was performed on precoated Merck 5554 Kieselgel 60 F254 foils using a chloroform - methanol developing system. Samples were taken in different times of UV-irradiation (in every 30 minutes until the completion of photodegradation) then extracted with chloroform and vacuum rotary evaporated. The pesticides and the obtained products were identified by using GC/MS technique. The structure identifications were based on the interpretation of the fragmentation pathways. The kinetic aspect of the photoinduced degradation of pesticides was estimated by assessing of the decreasing intensity of the peak of the parent compound as it is demonstrated in case of chlorpyrifos in table 7.

The pesticides and the obtained products were identified using GC/MS technique. The structure identifications were based on the interpretation of the fragmentation pathways. The GC separations and the mass spectrometric measurements were performed by using a GC-GC/MS QP-2010S Shimadzu under the conditions: column: HP-5MS (30m x 0.25mm x 0.25um), carrier gas: He (1 ml/min), detector: GC/MS QP-2010S, ionization mode: EI (70 eV), interface temperature: 230°C, ionsource temperature: 200°C, inject volume: 1 µl. The heating parameters were the follows: simazine: 110 ◦C (hold: 0 min) → 240 ◦C (15 ◦C/min) (hold: 0 min) → 290 ◦C (35 ◦C/min) (hold: 0,5 min); chlorpyrifos: 150 ◦C (hold: 0 min) → 290 ◦C (20 ◦C/min) (hold: 3 min); acetochlor: 80 ◦C (hold: 0 min) → 280 ◦C (15 ◦C/min) (hold: 0 min); carbendazim: 70 ◦C (hold: 1 min) → 180 ◦C (10 ◦C/min) (hold: 0 min) → 220 ◦C (20 ◦C/min) (hold: 0 min.); EPTC: 80 ◦C (hold: 0,5 min) → 280 ◦C (20 ◦C/min) (hold: 1 min).

RESULTS AND DISCUSSION

Photodegradation of acetochlor

In case of the photodegradation of acetochlor, there are alternative reaction pathways according to our findings. Several degradation products could be detected after some hours of irradiation, as it is demonstrated in figure 2 and 3. Major steps of photodecomposition are as follows: cleavage of ester-bond of N-ethoxy-methyl group, breaking off the chloro- and the hydroxyl-groups, resulting in the formation of [2-ethyl-6-methyl-N-methyl-aniline] (figure 1). This last degradation product might be formed from the parent compound in a direct way as well. Alternatively, the cleavage of chloro-, methyl- and ethoxy-groups of the

parent compound and the production of formanilid-derivatives (table 2) might also be observed. Cleavage of methyl-, ethyl and amino-groups produced toluene as the only end-product with confirmed impeding biological effects. Three main degradation products we detected were also determined by other studies aiming at modeling biodegradation of acetochlor (Coleman et al., 2000; Zheng et al., 2003), but the total degradation mechanism of acetochlor has not been revealed so far. The determination of all 9 degradation products and mapping the entire degradation pathway by our experiments contributes to the entire understanding of acetochlor's environmental behaviour.

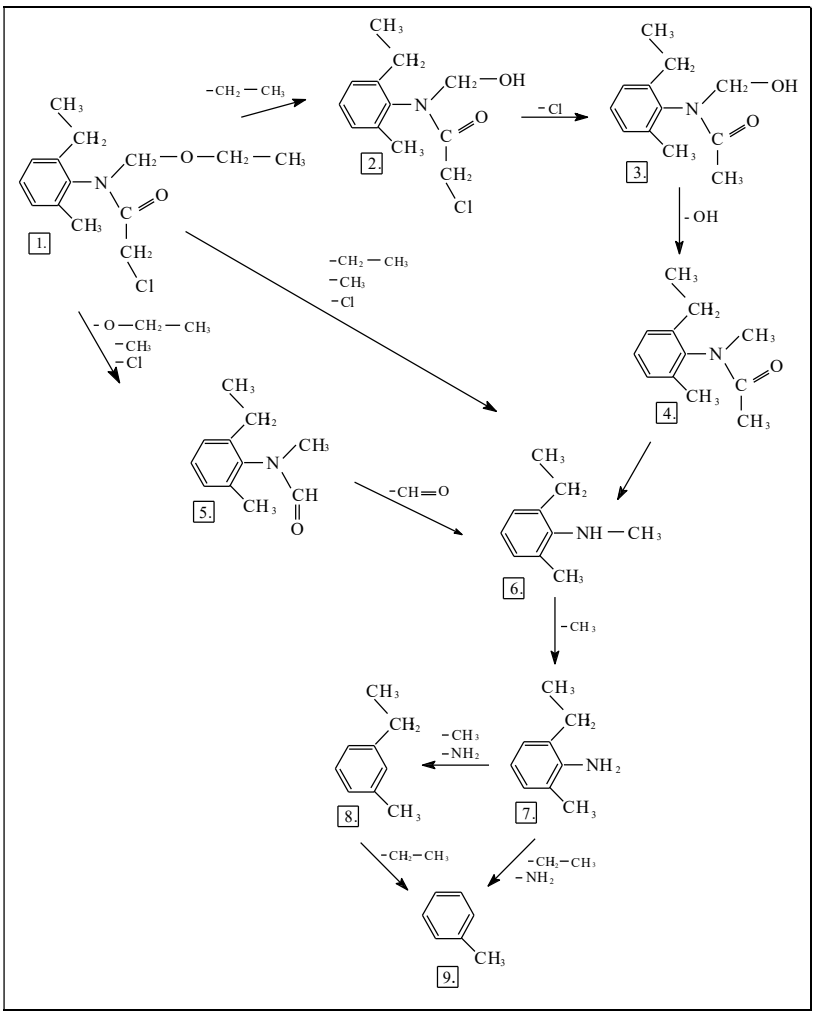


Figure 1. Proposed degradation mechanism of acetochlor.

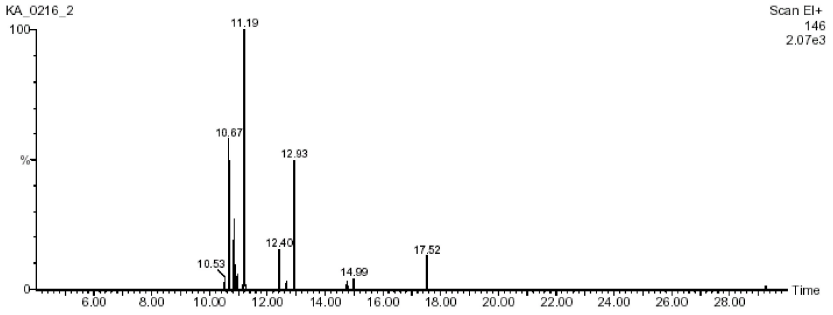


Figure 2. The GC-chromatogram of acetochlor and its degradation product after 3 hours of UV-irradiation.

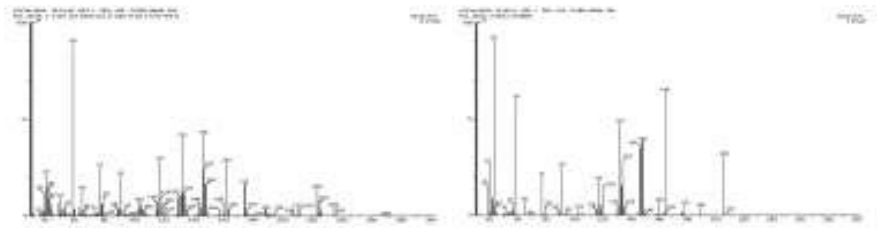


Figure 3. The mass-spectrums of the basic compound and the main degradation product of acetochlor.

Table 2 Products of photolytic degradation of acetochlor, their molecular mass and retention time in the GC-chromatogram.

	Name of compound	Molecular mass (g/mol)	Retention time
1.	2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide	269.5	12.950
2.	2-chloro-N-hydroximethyl-N-(2-ethyl-6-methylphenyl)acetamide	241.5	17.543
3.	N-hydroximethyl-N-(2-ethyl-6-methylphenyl)acetamide	207.0	10.668
4.	N-methyl-N-(2-ethyl-6-methylphenyl)acetamide	191.0	11.195
5.	N-methyl-N-(2-ethyl-6-methylphenyl)formamide	176.0	10.468
6.	2-ethyl-6-methyl-N-methyl-aniline	149.0	12.408
7.	2-ethyl-6-methyl-aniline	135.0	10.530
8.	3-ethyl-toluene	120.0	14.990
9.	toluene	92.0	10.855

Photodegradation of simazine

The degradation of simazine effected by UV-photons can take place via two parallel reaction pathways. Major steps of the photodecomposition were found to be as follows: cleavage of a chloro-group and its partial substitution to OH-group, loss of methyl and ethyl groups, and scissoring of OH-group. Symmetrical 2,4-diamino-1,3,5-triazine is obtained as the end-product of degradation (figure 4). A GC-chromatogram representing simazine and its most important degradation products, as well as the mass-spectrum of the most stabile product: [2,4-di(ethylamino)-1,3,5-triazine] are shown in figure 5 and 6. Efforts aiming at investigating the photolytic degradation of simazine have so far only demonstrated that degradation occurs and investigated the factors influencing it. Identification of the major degradation products (table 3) and revealing the complete decomposition pathway are significant new findings.

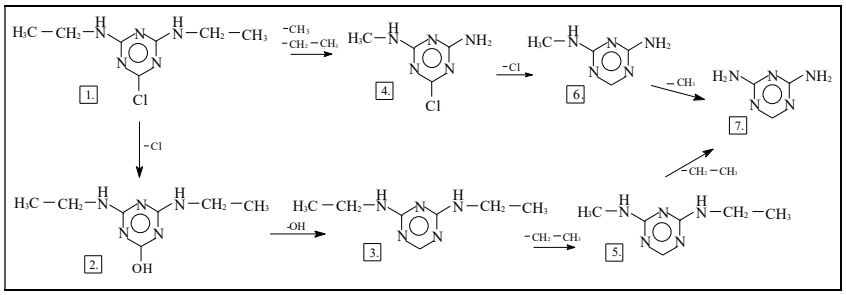


Figure 4. The degradation pathway of simazine.

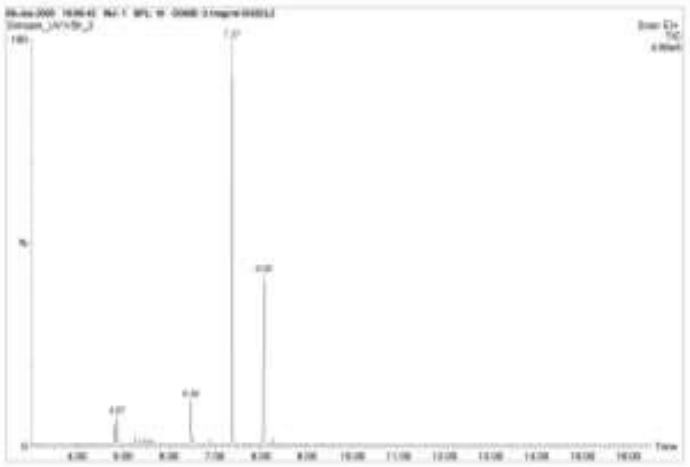


Figure 5. The GC-chromatogram of simazine and its degradation products after 1,5 hour UV-irradiation.

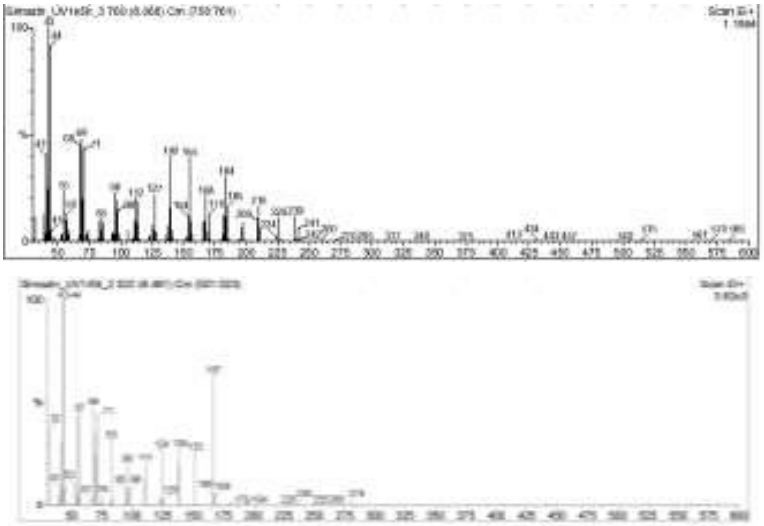


Figure 6. The mass-spectrums of the main degradation products of simazine.

Table 3 Products of photolytic degradation of simazine, their molecular mass and retention-time in the GC-chromatogram.

	Name of compound	**Molecular mass (g/mol)**	**Retention time**
1.	2,6-di(ethylamino)-4-chloro-1,3,5-triazine	201.7	7.374
2.	2,4-di(ethylamino)-hydroxy-1,3,5-triazine	183.2	8.061
3.	2,4-di(ethylamino)-1,3,5-triazine	167.2	6.481
4.	2-amino-4-chloro-6-methylamino-1,3,5-triazine	159.7	5.327
5.	2-ethylamino-4-methylamino-1,3,5-triazine	139.2	3.774
6.	2-amino-4-methylamino-1,3,5-triazine	125.2	5.321
7.	2,4-diamino-1,3,5-triazine	111.2	4.914

Photodegradation of chlorpyrifos

The photodegradation of chlorpyrifos may occur in two reaction patterns (figure 7). It might be initiated by the cleavage of either a chloro-group or an ethyl-group. Breaking away of another chloro-group leads to the formation of [O-ethyl-O-(5-chloro-2-pyridil)-hydrogene- phosphorothioate]. The existence of this degradation product is confirmed by the five-hour mass-spectrums (figure 8-9). The loss of the other ethyl-group results in the formation of [O-(5-chloro-2-

pyridil)-dihydrogene-phosphorothioate] as the end-product (table 4). Based on the GC-chromatograms it can be established that 16 hours of irradiation was needed for the total photodegradation of chlorpyrifos. The biological degradation of chlorpyrifos led to the formation of metabolites being not analogous to intermediers detected during our investigations (Coleman et al.).

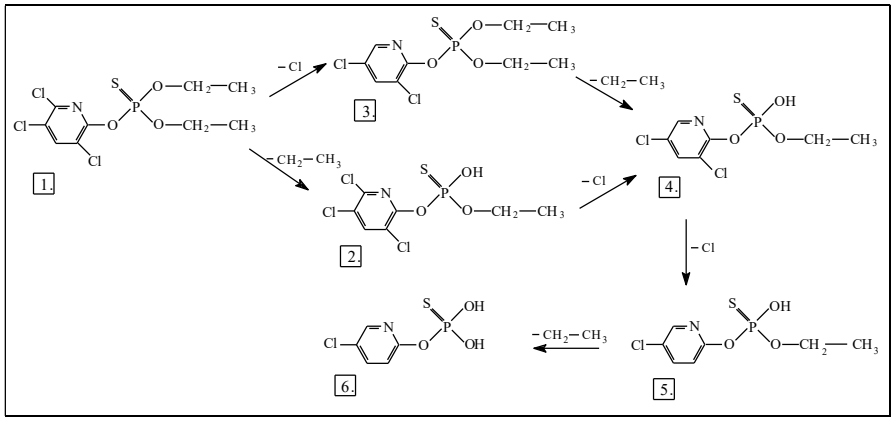


Figure 7. Proposed degradation mechanism of chlorpyrifos.

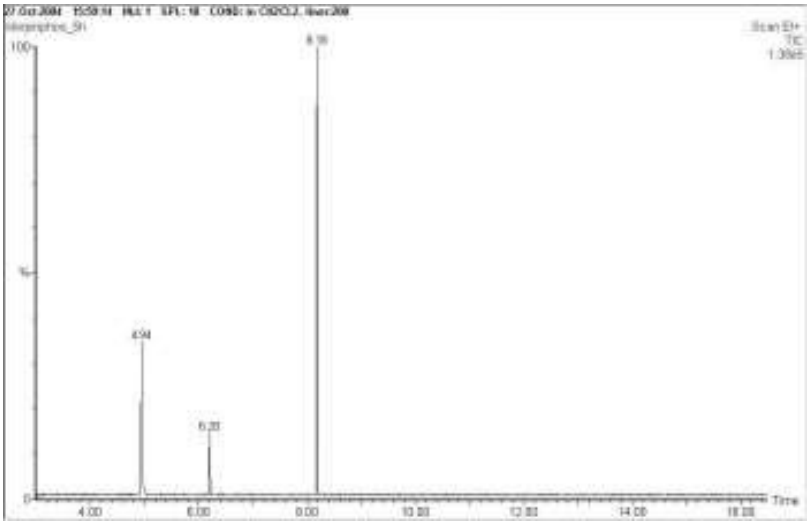


Figure 8. The GC-chromatogram of chlorpyrifos and its degradation products after 5 hour UV-irradiation.

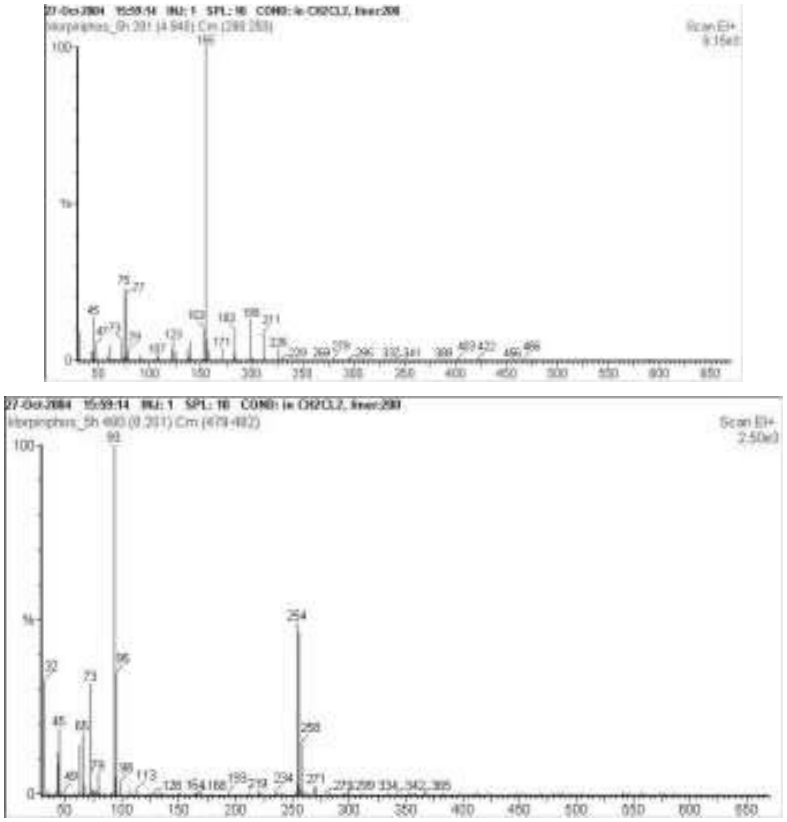


Figure 9. The mass-spectrums of the main degradation products of chlorpyrifos.

Table 4 Products of photolytic degradation of chlorpyrifos, their molecular mass and retention-time in the GC-chromatograms.

	Name of compound	**Molecular mass (g/mol)**	**Retention time**
1.	O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)phosphorothioate	350.6	8.180
2.	O-ethyl-O-(3,5,6-trichloro-2-pyridil)-hydrogene-phosphorothioate	323.0	5.861
3.	O,O-diethyl-O-(3,5-dichloro-2-pyridil)phosphorothioate	316.5	5.710
4.	O-ethyl-O-(3,5-dichloro-2-pyridil)-hydrogene-phosphorothioate	288.5	6.661
5.	O-ethyl-O-(5-chloro-2-pyridil)-hydrogene-phosphorothioate	254.0	6.201
6.	O-(5-chloro-2-pyridil)-dihydrogene-phosphorothioate	225.5	4.940

Photodegradation of carbendazim

The first step of the degradation of carbendazim was the loss of the methyl group and the formation of [benzimidazole-2-ylcarbamic-acide] (figure 10). This product showed small stability, and after the cleavage of a hydroxil- and a carbonyl group this product was transformed into [2-amino-benzimidazole]. This compound converted to benzimidazole, then after 6-hour-long UV-irradiation the imidazole-ring was opened and [2-methyl-amino-aniline] was formed. Subsequently, the cleavage of the N-methyl bond led to the end-product of the photodegradation: [1,2-diaminobenzene] (table 5). Degradation products identified by means of GC-chromatograms and mass-spectrums are demonstrated in table 5.

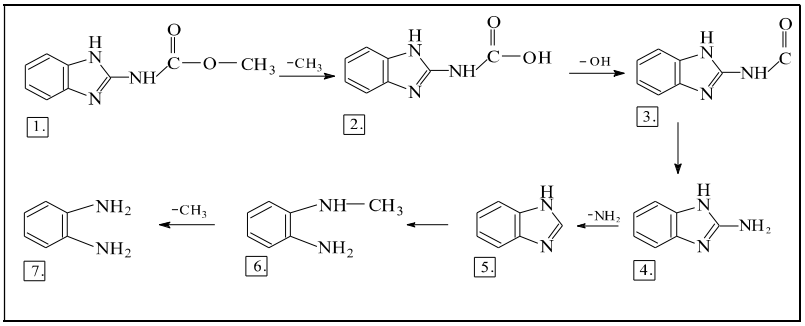


Figure 10. The degradation pathway of carbendazim.

Table 5 Degradation products of photolytic decomposition of carbendazim, their molecular mass and retention-time in the GC-chromatograms.

	Name of compound	Molecular mass (g/mol)	Retention time
1.	methyl-benzimidazole-2-ylcarbamate	191	7.530
2.	benzimidazole-2-ylcarbamic-acide	177	6.561
3.	benzimidazole-2-ylcarbamate	161	8.328
4.	2-amino-benzimidazole	133	8.280
5.	benzimidazole	118	7.662
6.	2-methyl-amino-aniline	122	8.003
7.	1,2-diaminobenzene	108	7.248

Photodegradation of EPTC

Photochemical decomposition of EPTC occurs rapidly as the appearance of the first degradation product was already to be detected after twenty minutes of UV-irradiation. During the photochemical decomposition of EPTC, [N,N-dipropyl-formamide] and [N,N-diethyl-propionamide] are formed at the first stage of degradation by the accomplishment of two alternative decomposition routes. Both the cleavage of S-ethyl-group and demethylation of N-propyl

groups are possible (figure 11). In accordance with the given reaction pathways it might be established that both the consecutive losses of alkyl-groups and the cleavage of the amide bond lead to the degradation end-product: [diethyl-amine] (table 6).

When comparing results of our studies with previous research on revealing products of biological degradation of EPTC (Abu-Qare et al., 2002) it might be established that photodecomposition and biological degradation do not lead to the formation of analogous products, as nor EPTC-sulfon or EPTC-sulphoxide were detected throughout our examinations.

The breaking off of S- and N-alkyl groups leads to the formation of the same degradates as identified during former studies, however derivatives of ketoformyl and ketocarbonyl might only be observed in TiO_2 catalytized photodegradation processes (Lányi and Dinya, 2005).

Table 6 Degradation products of photolytic decomposition of EPTC, their molecular mass and retention-time in the GC-chromatograms.

	Name of compound	**Molecular mass (g/mol)**	**Retention time**
1.	S-ethyl-dipropyl-tiocarbamate	189	5.833
2.	N,N-dipropyl-formamide	129	3.967
3.	tripropylamine	114	4.431
4.	dipropylamine	101	5.600
5.	dipropyl-ethyl-amine	85	5.334
6.	N,N-diethyl-propionamide	129	3.458
7.	diethyl-amine	73	8.912

Table 7 Decrease of the amount of the parent compound of chlorpyrifos as a function of UV irradiation time.

UV irradiation time	**Intensity**	**Rate of degradation**
0 h	5727	0 %
0.5 h	5667	1%
1h	5608	2%
2 h	4696	18%
3h	3780	34%
4h	2577	55%
5 h	1851	68%
6 h	1432	75%

7 h	973	83%
8 h	630	89%
9 h	458	92%
11 h	260	96%
13 h	149	97.4%
15 h	68.7	98.8%
16 h	0	100%

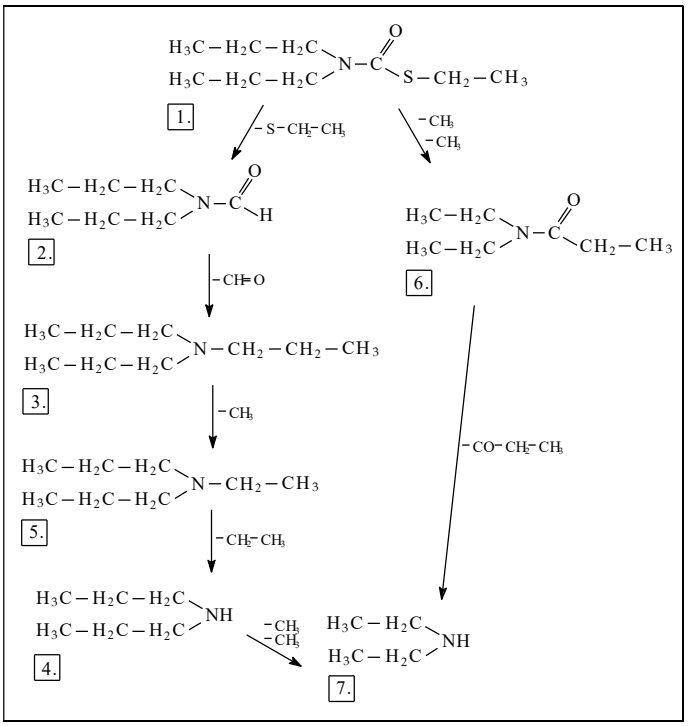


Figure 11. The degradation pathway of EPTC.

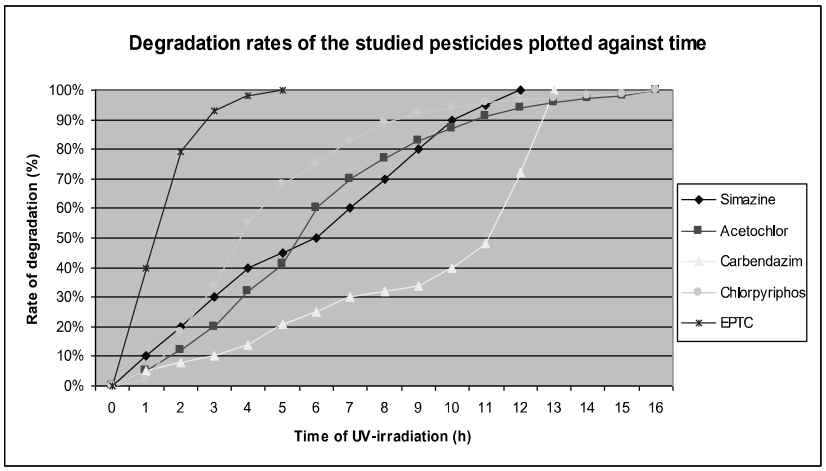


Figure 12. Degradation rates of the studied pesticides

The kinetic aspects of the photodegradation of the studied pesticides showed marked differences. The measured decrease of the amount of the parent compound served as the basis for estimating the extent of the photodecomposition of the tested pesticides. The degradation of EPTC was found to be the most intensive, as 2 hours of UV-irradiation resulted in 80% degradation. Carbendazim proved to be the most resistant against UV-light. To achieve 40% degradation, 10-hour-long UV-irradiation was needed. In case of acetochlor and chlorpyrifos, the last stage of degradation was particularly slow, since nearly 10 hours of UV-irradiation was required to convert the last 10% of pesticide residue.

CONCLUSIONS

Our study aims at revealing specific details of photolytic degradation of pesticides as important soil contaminants. Significance of these studies is enhanced by the fact that pesticide decomposition may contribute to soil degradation, and might have harmful biological effects by degrading to toxic products. The toxicity of the examined pesticides is well known, however scarce information is available regarding their natural degradation processes, the quality, structure and biological impact of the degradation products.

Phototransformation of pesticides has to be regarded as a key factor in their environmental behaviour. Each of the five different examined pesticides underwent photolytic decomposition, and the detailed mechanism of the photolytic decomposition was established. GC/MS technique proved to be a suitable method for detection and identification of the formed degradation products. At least

five distinctive degradation species were detected in each case, and parallel photodecomposition pathways could be observed for two pesticides.

Typical initial decomposition patterns were found to be cleavage of ester-bond, loss of alkyl-groups and chloro-groups. The photodegradation mechanisms comprised steps as follows: cleavage of ester-bonds, destruction of N-alkoxy, N-alkyl bonds, and loss of hydroxyl-groups. Deamination and ring opening occurred at the last stage of decomposition. Possibly toxic degradation products have been observed as well (Virág et al. 2007).

The research on revealing the exact reaction mechanisms of photolytic degradation of pesticides contributes not only to the proper understanding of environmental behaviour of pesticides, but also points out the possible environmental and biological risk factors by identifying possibly toxic degradation products.

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FIGURE CAPTIONS