Impact of soils and metals on the photodegradation of diverse pesticides

Attila, Kiss* – *Diána Virág

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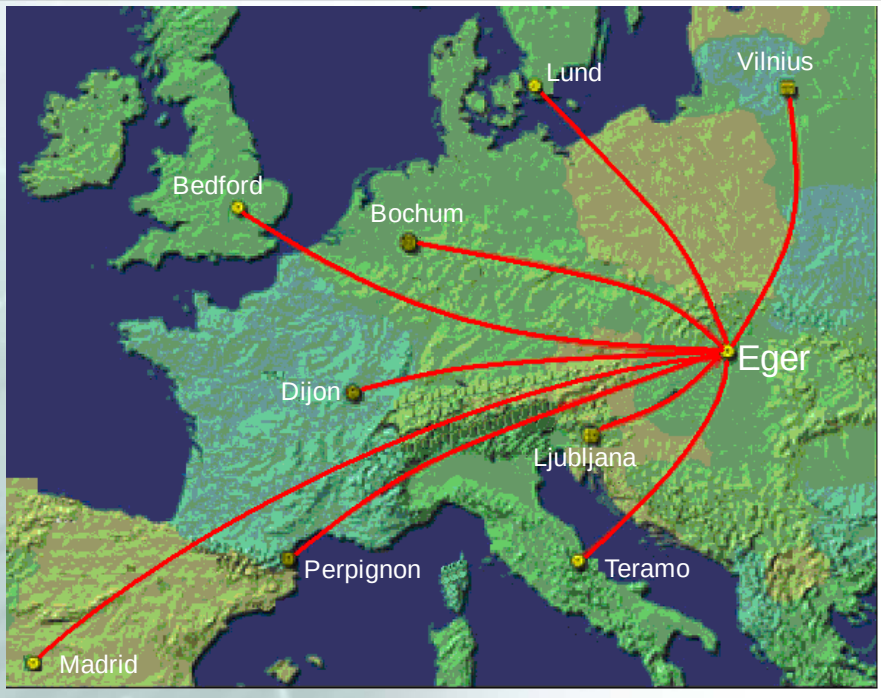

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Relevant developments of EGERFOOD Regional Knowledge Centre

- Elaboration of improved methodology for the precise analytical studies.
- Testing the improved methods on real samples.
- Development of new functional products and new nourishment supplements with enhanced antioxidant impact.
- Comparative studies of the composition of distinctive real samples.
- Identification of specific natural compounds and contaminants.
- Study on speciation of microcontaminants in natural samples.

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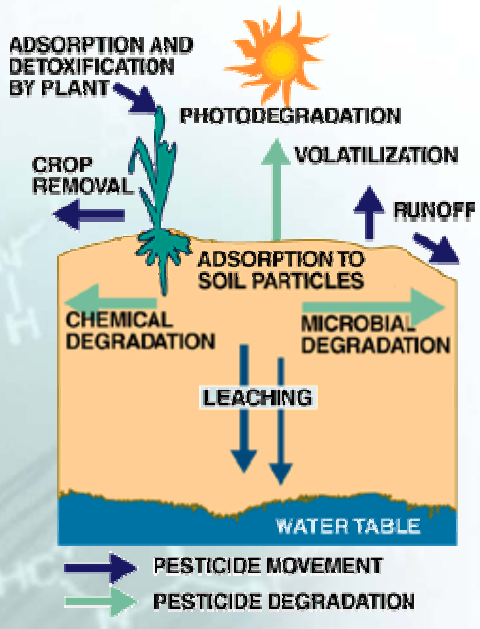
Factors affecting pesticide fate after application



Previous studies on pesticides

- Analytical improvements

(detection and quantitative determination of pesticide-residues in food)

- Studies on biodegradation and physiological effect of pesticides
- Leaching studies of parent compounds

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Objectives

• Justification of validity of model studies under natural circumstances.

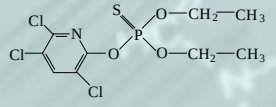
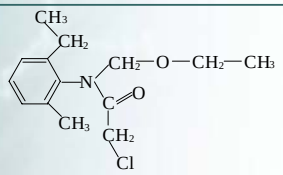
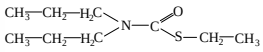
• To reveal the interactions between transformation products of pesticides and major soil components.

• Persistence of pesticides in different type of soils.

• Examination on influence of soil parameters on photodegradation of pesticides.

• Implementation of comparative studies of pesticide transformations in distinctive soil types.

Studied pesticides

	Chlorpyrifos	Acetochlor	EPTC
Chemical name	diethoxy-sulfanylidene-(3,5,6-trichloropyridin-2-yl)oxyhosphorane	2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methyl-phenyl)acetamide	S-ethyl dipropylthio-carbamate
Chemical type	organophosphate	acetanilide	tiocarbamate
Mode of action	cholinesterase inhibitor	root inhibitor	growth and protein synthesis disruptor
Application	insecticide	herbicide	herbicide
Chemical structure			

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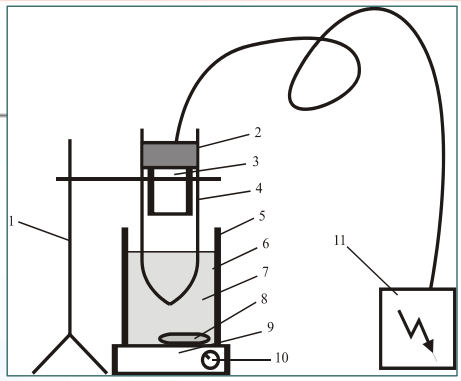
Studied soils

Soil type	Sand (m%)	Coarse silt (m%)	Silt (m%)	Clay (m%)	pH (H_2O)	Spec. conductivity (µs/cm)	OM (%)
Sandy	94.8	5.2	*u.d.l.*	*u.d.l.*	6.53	64.2	2.06
Brown forest	6.0	41.0	31.0	22.0	6.60	82.0	5.94

u.d.l. – under detection limit

Applied apparatuses



- **Immerseable UV-source** (Millipore Co.)
  254 nm wavelenght, constans inensity

- **GC-MS** (Shimadzu, QP-2010S)
  Quantitative and qualitative analysis of pesticides and degradates.

- **AAS** (Varian Spectraa 50B)
  Mesuring the metal content of soil samples.

- **UV-spectrophotometer** (Jasco V-650)
  Pesticide-metal complex generating ability.

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Sample preparation I.

	Acetochlor	EPTC	Chlorpyrifos	Motivation / Prospective conclusions
Dark controll (14 days)				Persistence of pesticides in dry conditions.
Concentration	200ppm	50ppm	250 ppm	Feasibility of detection of minor degradates.
Time of irradiation	1h	45 min	3.5 h	Effection of significant degradation.
Pure pesticide solution	300ml of pesticide solution			Rate of photodegradation.

Sample preparation II.

	Acetochlor	EPTC	Chlorpyrifos	Motivation / Prospective conclusions
Pure pesticide solution	300ml of pesticide solution			Rate of photodegradation
Pesticide solution with normal soil	10g soil sample + 300ml of pesticide solution			Effect of soil types on the rate of photodegradation and formation of degradates.
Pesticide solution with demetalized soil	10g soil sample (previously extracted with EDTA solution) + 300ml of pesticide solution			Effect of the metal content of soil on the process of photodegradation.
Pesticide solution with decreased organic matter content soil	10g soil sample (previously destroyed the organic matter content with acidic and alkaline treatment) + 300ml of pesticide solution			Effect of the organic matter content of soil on photodegradation processes.
Pesticide solution with metal salts	300ml of pesticide solution + Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}			Effect of the metals on the photodecomposition processes.

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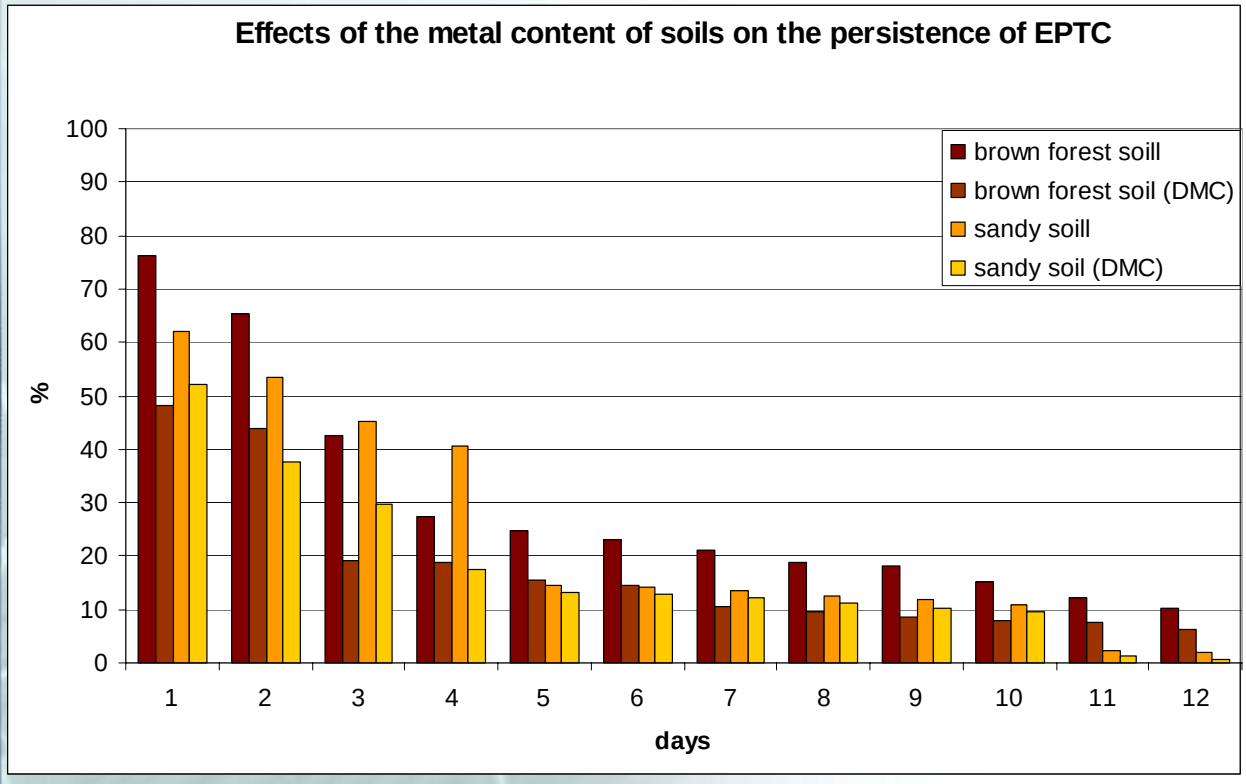

DMC – soil sample with Decreased Metal Content

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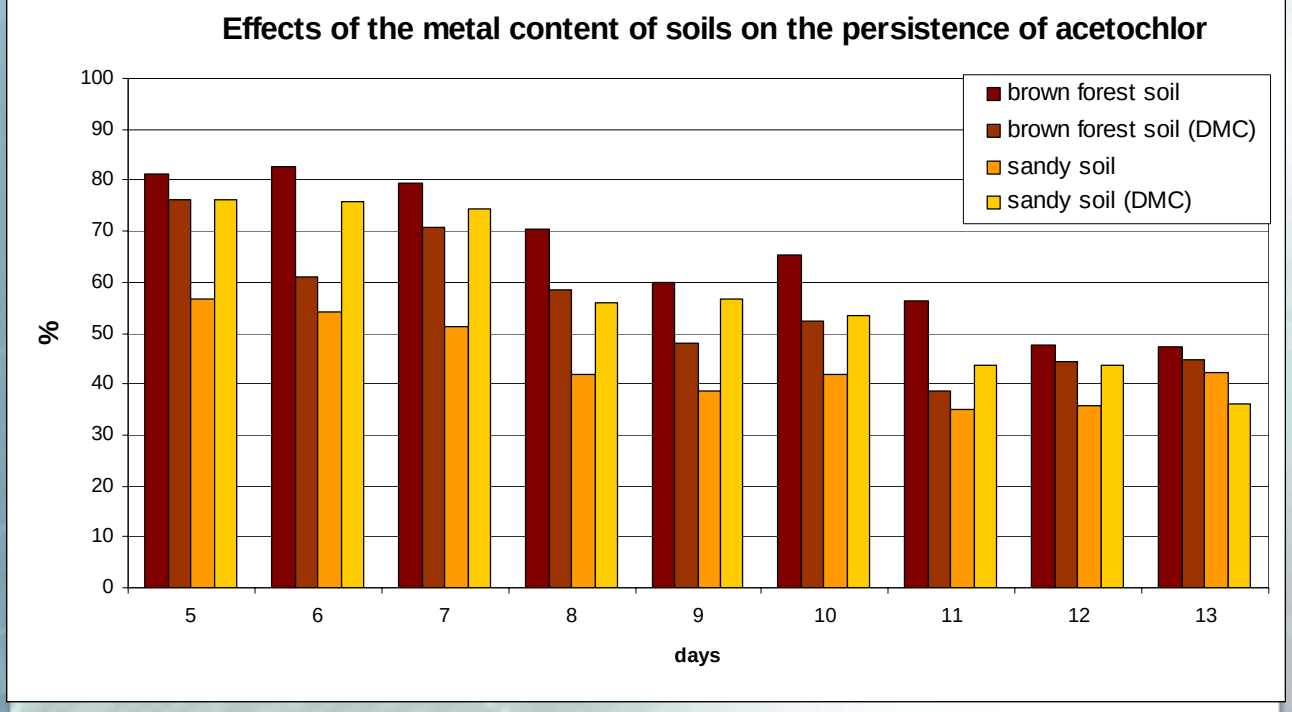

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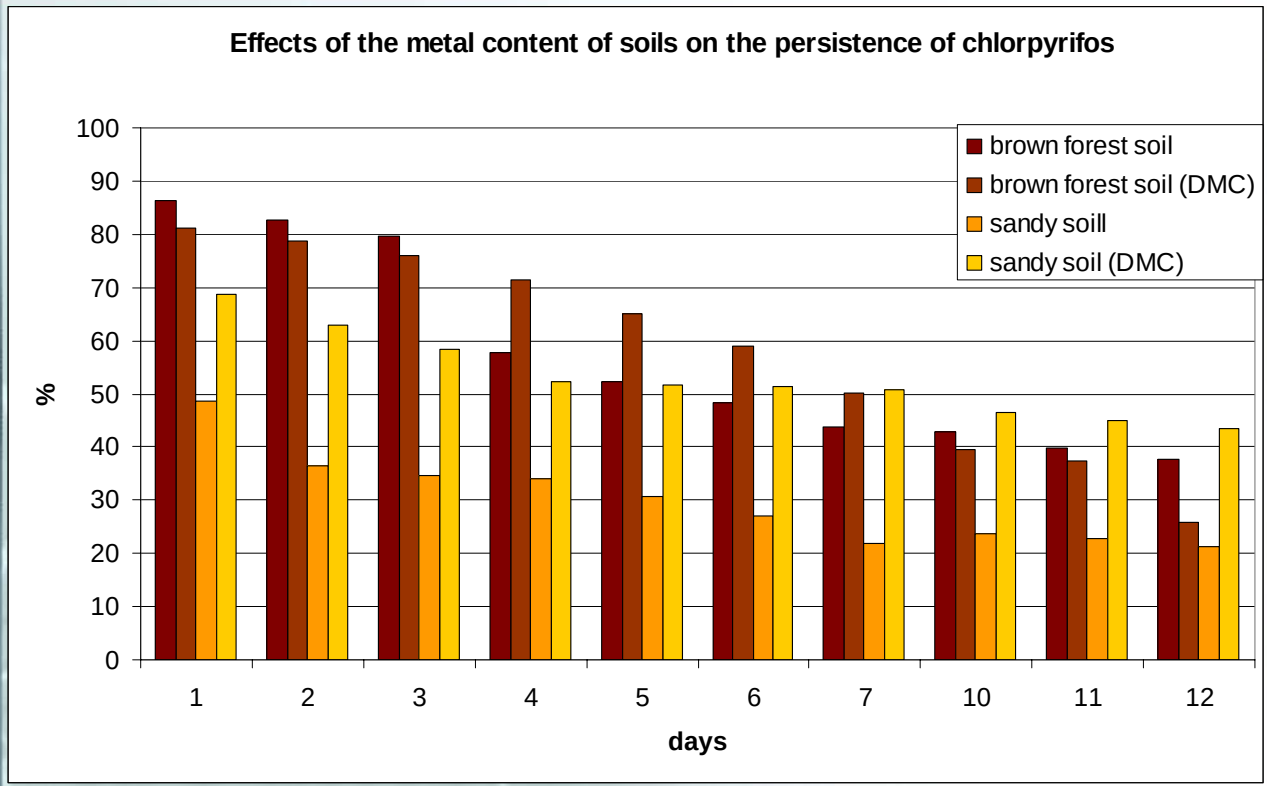
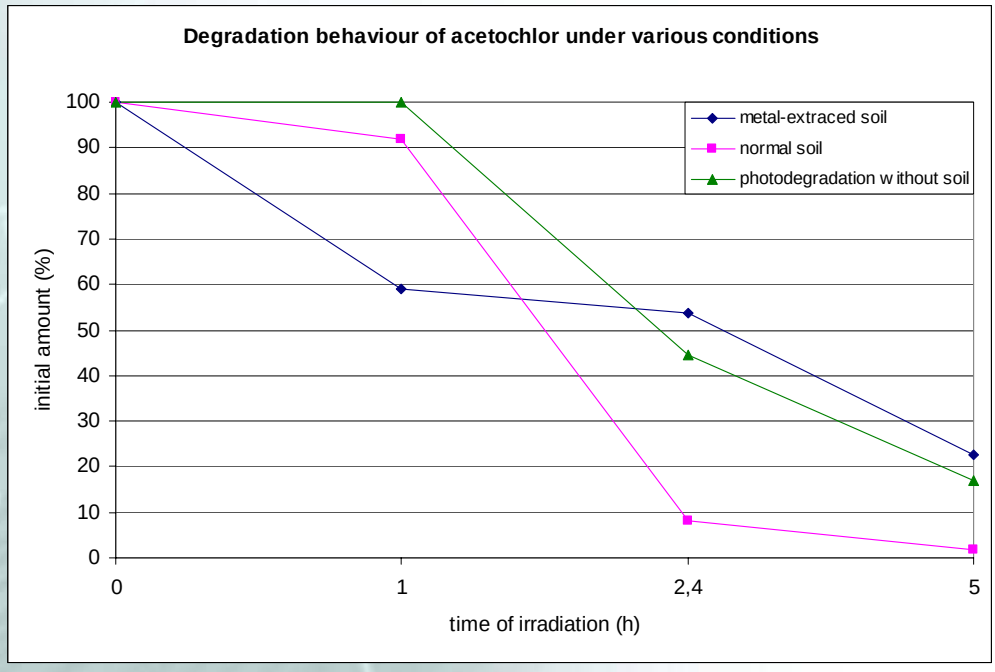


DMC – soil sample with Decreased Metal Content

Degradation of acetochlor in case of various irradiation conditions.



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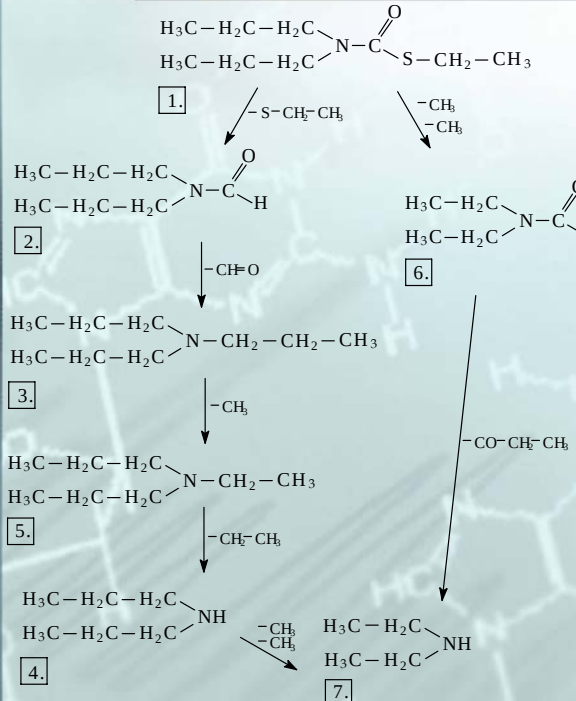
Proposed degradation mechanism of EPTC.

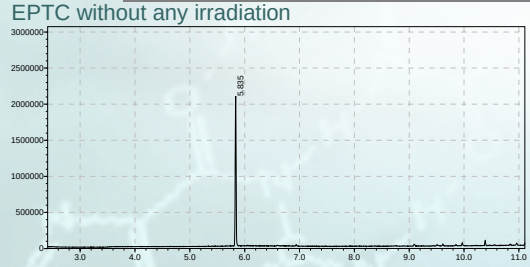


	Name of compound	Molecular mass (g/mol)	Retention time
1.	S-ethyl-dipropyl-tiocarbamate	189	5.833
2.	N,N-dipropyl-formamide	129	3.967
3.	tripropylamine	114	4.431
4.	dipropylamine	101	5.600
5.	dipropyl-ethyl-amine	85	5.334
6.	N,N-diethyl-propionamide	129	3.458
7.	diethyl-amine	73	8.912

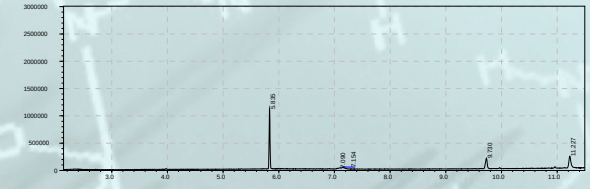
Degradation products of photolytic decomposition of EPTC, their molecular mass and retention-time in the GC-chromatograms.

GC-chromatograms and MS spectrums of EPTC and degradates formed by UV-irradiation

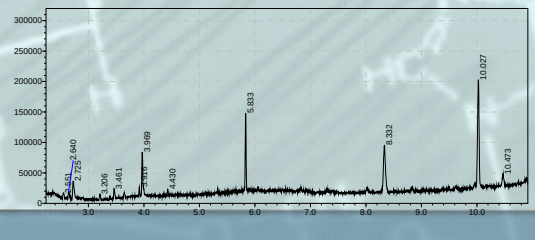
EPTC without any irradiation

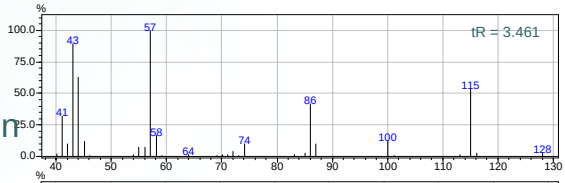


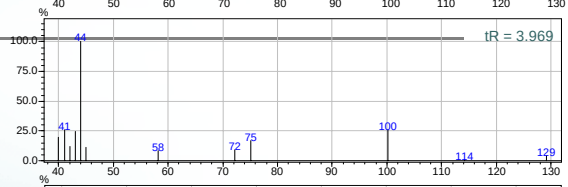
EPTC after 30 minutes of irradiation

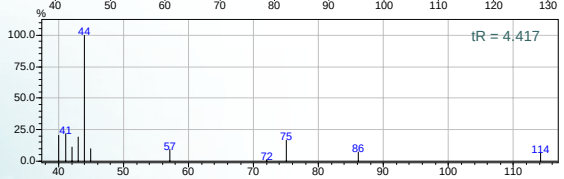


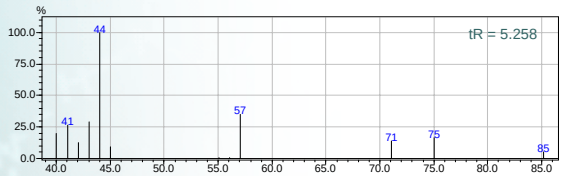
EPTC after 3 hours of irradiation

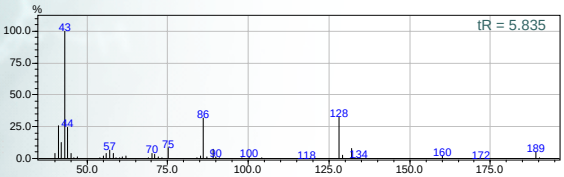












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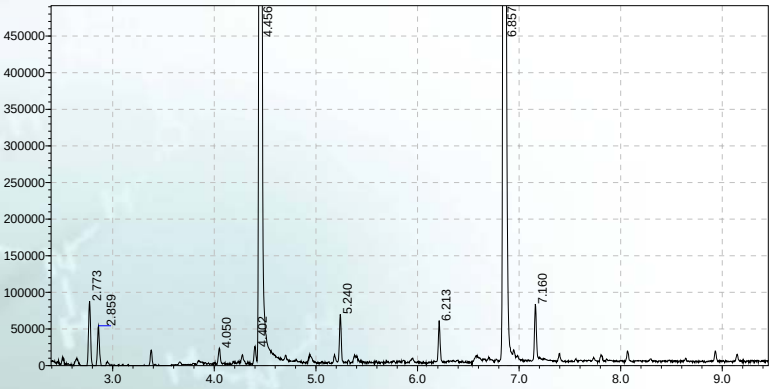
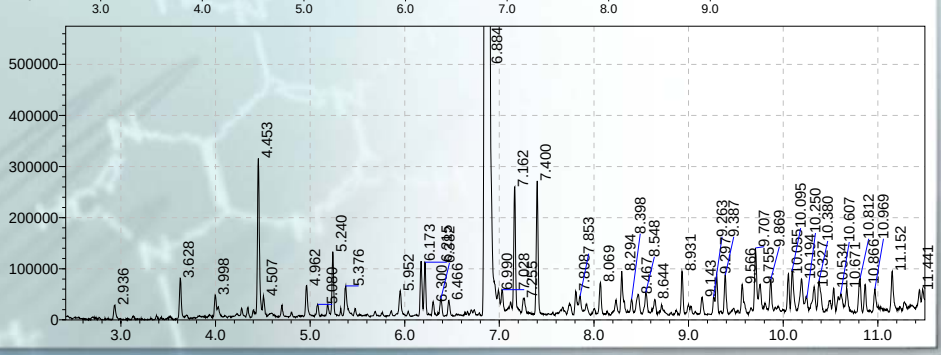
GC-chromatogram of EPTC and degradates formed in brown forest soil

Controll (EPTC solution)



Brown forest soil



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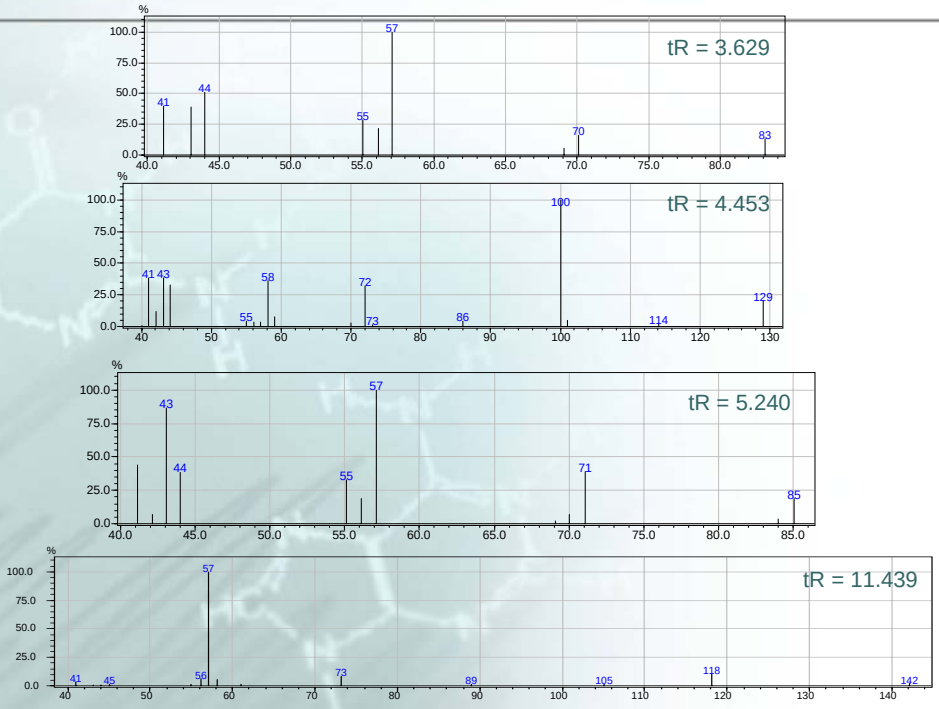
MS spectrums of EPTC and degradates formed in brown forest soil



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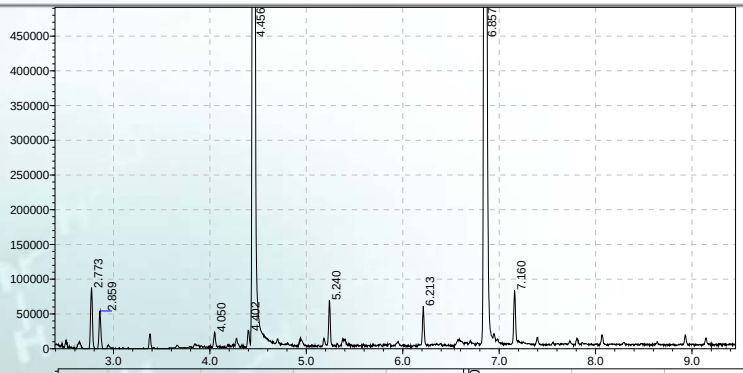
EPTC and degradates formed in brown forest soil

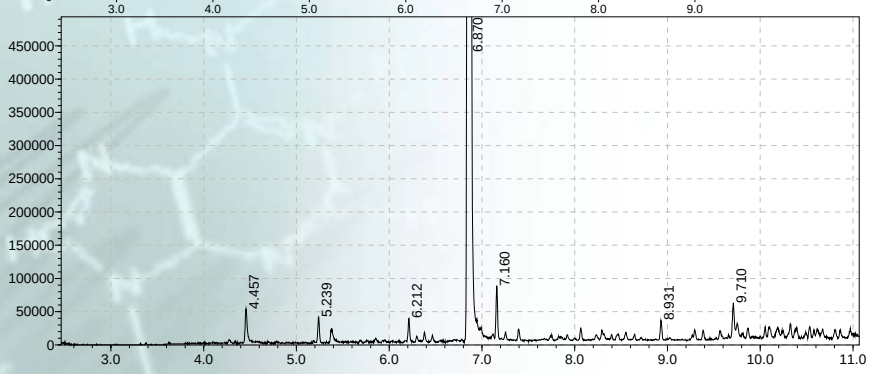
t_R	ref. ion	area	MW		%
2.936	45	11162	122	$C_4H_{10}S_2$	0.07
3.629	57	36291	83	$C_8H_{18}O$	0.24
4.453	100	135923	129	$C_7H_{15}NO$	0.91
4.965	**56**	**18086**	**98**	**C_6H_9OH**	**0.12**
5.240	57	63171	85	C_4H_7NO	0.42
6.173	**43**	**40903**	**175**	**$C_8H_{17}NOS$**	**0.27**
6.214	57	34772	85	$C_5H_{10}N$	0.23
6.884	43	1421466	189	$C_9H_{19}NOS$	94.4
7.030	71	10886	129	$C_7H_{15}NO$	0.07
7.162	**57**	**76268**	**99**	**C_5H_9NO**	**0.51**
7.256	**57**	**10379**	**175**	**$C_8H_{17}NOS$**	**0.07**
7.401	**57**	**215309**	**203**	**$C_{10}H_{21}NOS$**	**1.44**
8.069	57	20879	113	$C_7H_{15}N$	0.14
8.468	**91**	**16112**	**161**	**$C_7H_{15}NOS$**	**0.11**
8.932	**57**	**27821**	**127**	**$C_7H_{13}NO$**	**0.19**
9.708	55	45587	113	$C_7H_{15}N$	0.30
11.439	**105**	**25275**	**143**	**$C_7H_{13}NS$**	**0.17**

EPTC and degradates formed in the presence of brown forest soil (DOMC).

Controll (EPTC solution)



Brown forest soil (DOMC)



DOMC – soil sample with Decreased Organic Matter Content

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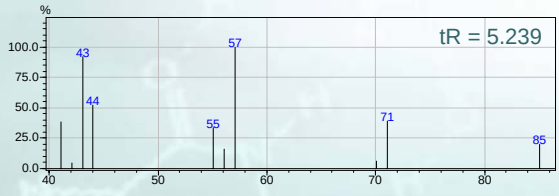
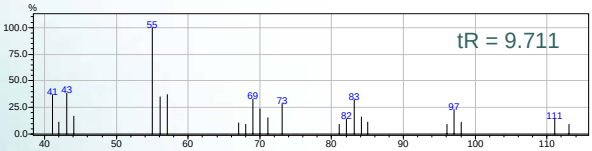
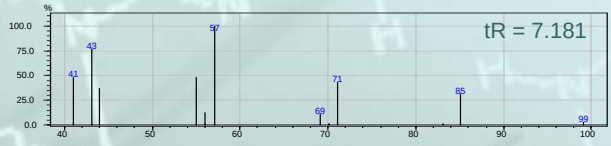
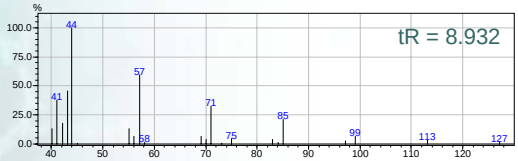
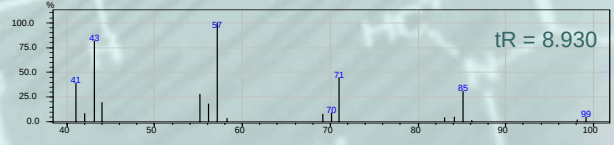
MS spectrums of EPTC and degradates formed in brown forest soil (DOMC)











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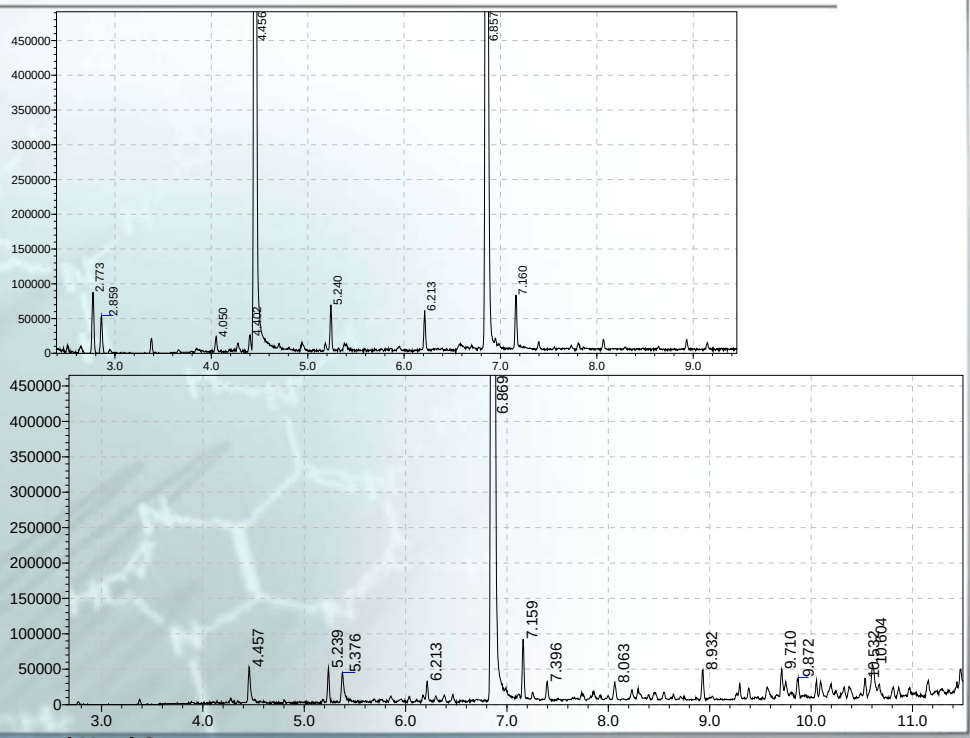
EPTC and degradates formed in the presence of brown forest soil (DMC).

Controll (EPTC solution)

Brown forest soil (DMC)



DMC – soil sample with Decreased Metal Content

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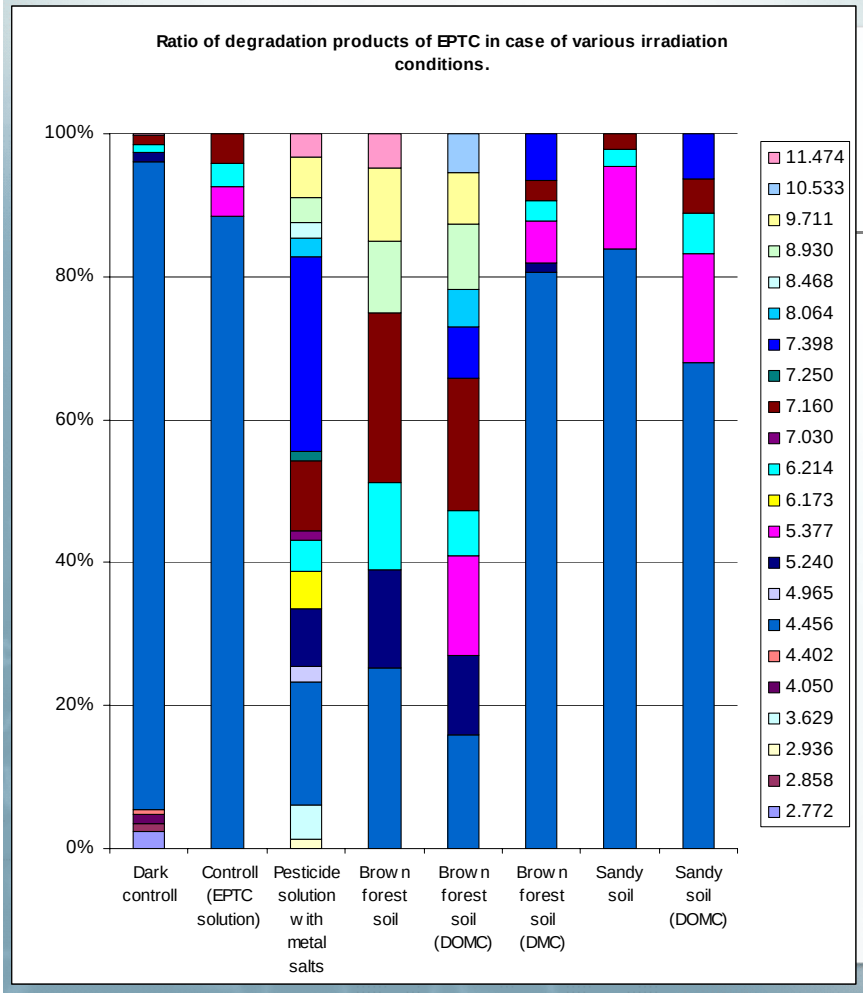
Ratio of degradation products of EPTC in case of various irradiation conditions.

Retention time [min]	Controll (EPTC solution)	Pesticide solution with metal salts	Brown forest soil	Brown forest soil (DOM)	Brown forest soil (ME)	Sandy soil	Sandy soil (DOM)	Sandy soil (ME)
2.772	1.23	-	-	-	-	-	-	-
2.858	0.53	-	-	-	-	-	-	
4.456	**44.56**	**9.68**	**0.91**	**0.38**	**0.39**	**8.94**	**6.16**	**2.79**
4.721	-	-	-	-	-	0.28	-	-
4.825	-	-	-	-	-	-	0.19	-
4.965	-	-	**0.12**	-	-	-	-	-
5.240	**0.63**	**-**	**0.42**	**0.21**	**0.27**	**0.15**	**-**	**-**
5.377	-	0.46	-	-	0.34	0.64	0.84	0.63
6.173	-	-	0.27	-	-	-	-	-
6.214	0.58	0.36	0.23	0.19	0.15	0.32	0.17	0.24
6.857	**50.82**	**88.29**	**94.65**	**98.50**	**97.57**	**88.25**	**92.07**	**95.90**
7.03	-	-	0.07	-	-	-	-	-
7.160	**0.63**	**0.45**	**0.51**	**0.36**	**0.45**	**0.32**	**0.17**	**0.20**
7.250	-	-	**0.07**	-	-	-	0.17	
7.398	-	**0.45**	**1.43**	**-**	**0.17**	**0.72**	**0.23**	**0.26**
8.064	-	-	0.14	-	0.13	-	-	-
8.468	-	-	**0.11**	-	-	-	-	-
8.930	-	-	**0.19**	**0.15**	**0.22**	-	-	-
9.711	-	-	0.30	0.15	0.18	-	-	-
10.304	-	-	**0.17**	**0.07**	-	-	-	

DOM – soil sample with Decreased Organic Matter content
ME – Metal Extracted soil sample



- **6 new compounds** than previously identified.
- Their ratio depending on the various soil parameters.
- Large influence on the reaction pathways and the ratio of the intermediates.
- Highest number of degradates was detected in case of pesticide solution with metal salts.
- Significantly different composition and product ratios.

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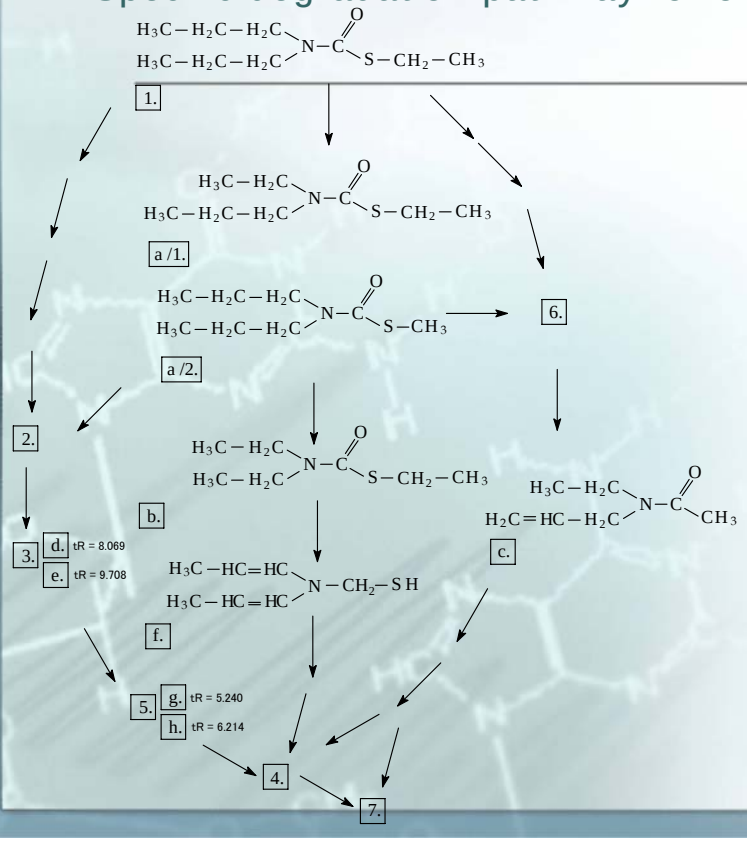
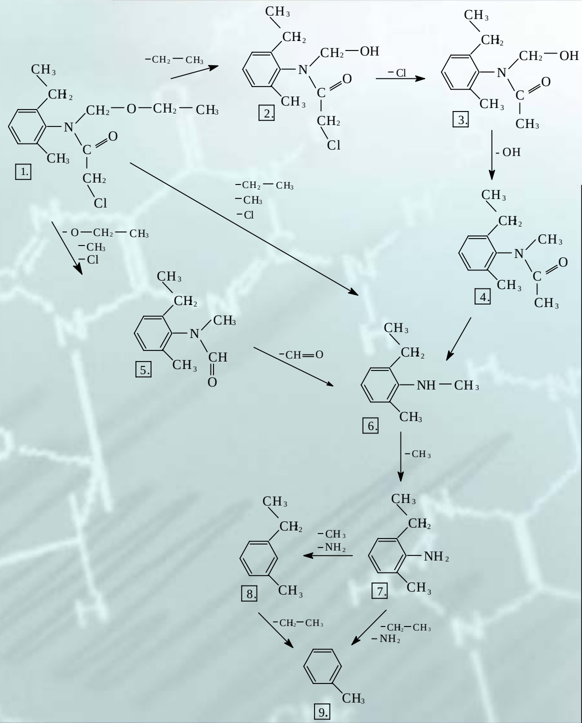
Specific degradation pathway for environmental conditions



	Molecular mass (g/mol)	Retention time (min)
a/1.	175	6.173
a/2.	175	7.256
b.	161	8.468
c.	127	8.932
d.	114	8.063
e.	114	9.708
f.	143	11.439
g.	85	5.240
h.	85	6.214

Proposed degradation mechanism of acetochlor.



Products of photolytic degradation of acetochlor, their molecular mass and retention time at 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

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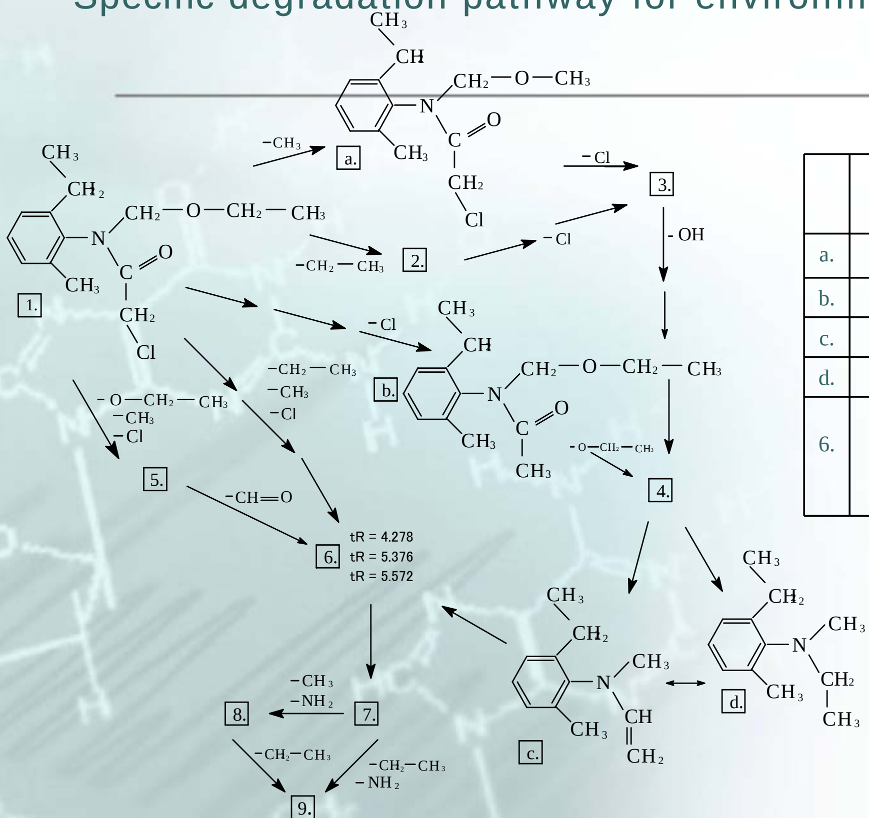
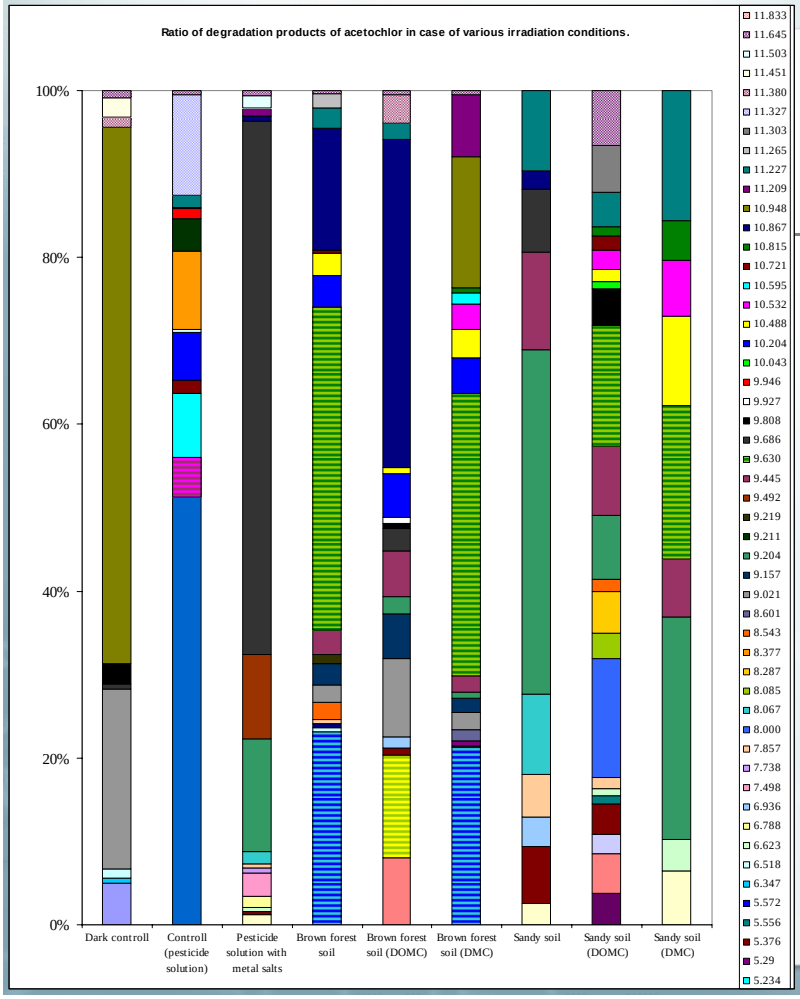
Specific degradation pathway for environmental conditions



	Molecular mass (g/mol)	Retention time (min)
a.	255	11.227
b.	234	9.204
c.	175	9.492
d.	177	8.118
6.	149	4.278
		5.376
		5.572



- **More products** than in case of EPTC and chlorpyrifos.
- Different structural characteristics of the three pesticides.
- Highest number of acetochlor's degradates was detected in case of DOMC sandy soil.
- Lowest number of products was formed in case of DMC sandy soil**.**
- Role of OMC of soils in the photodegradation of pesticides.
- Significantly different composition and product ratios.

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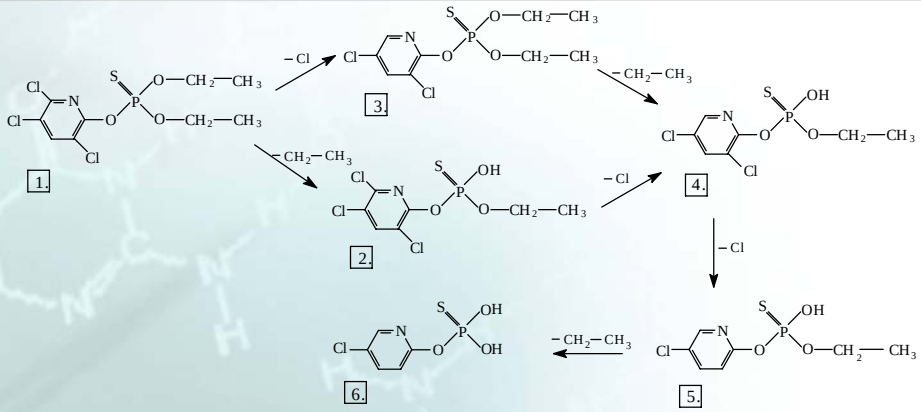
Proposed degradation mechanism of chlorpyrifos.



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 (min)
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

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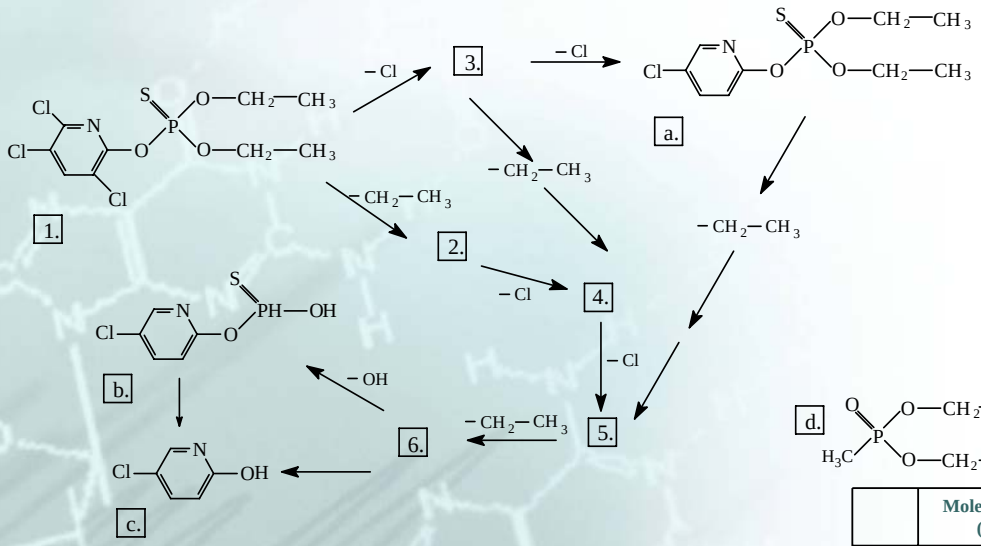
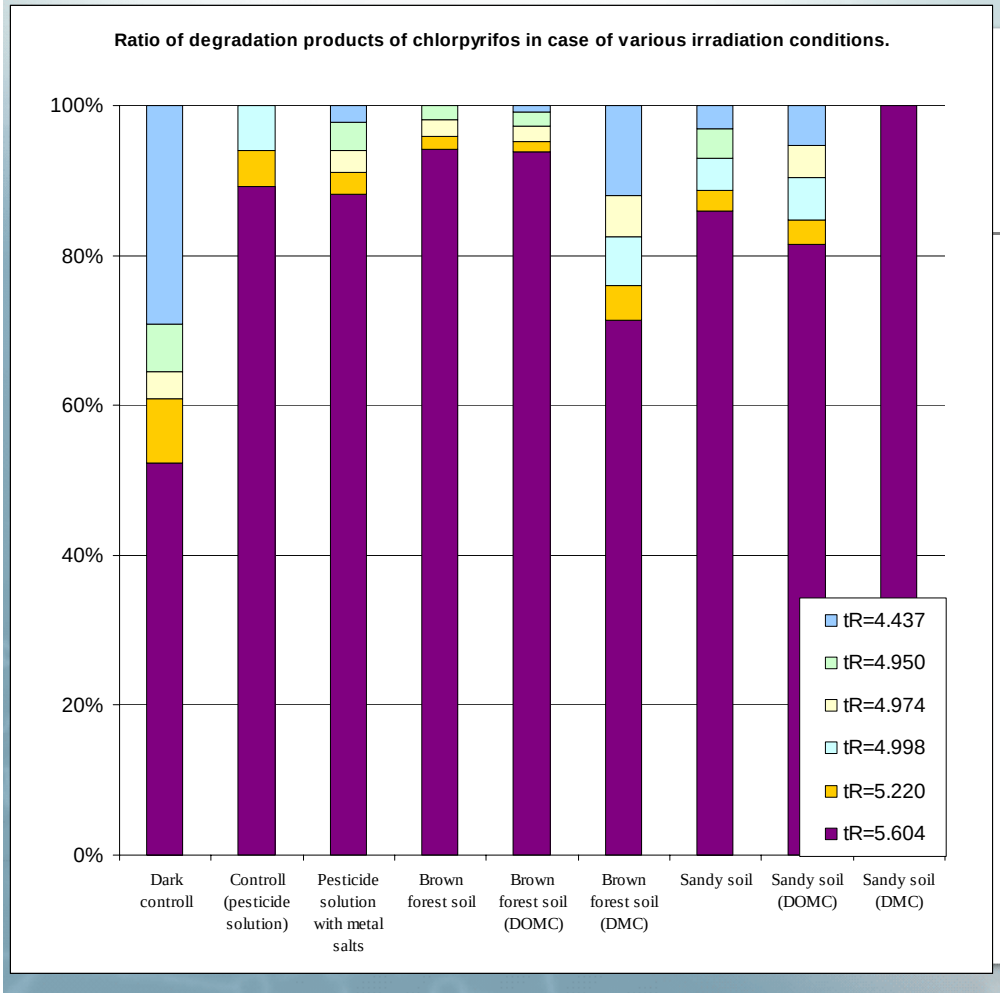
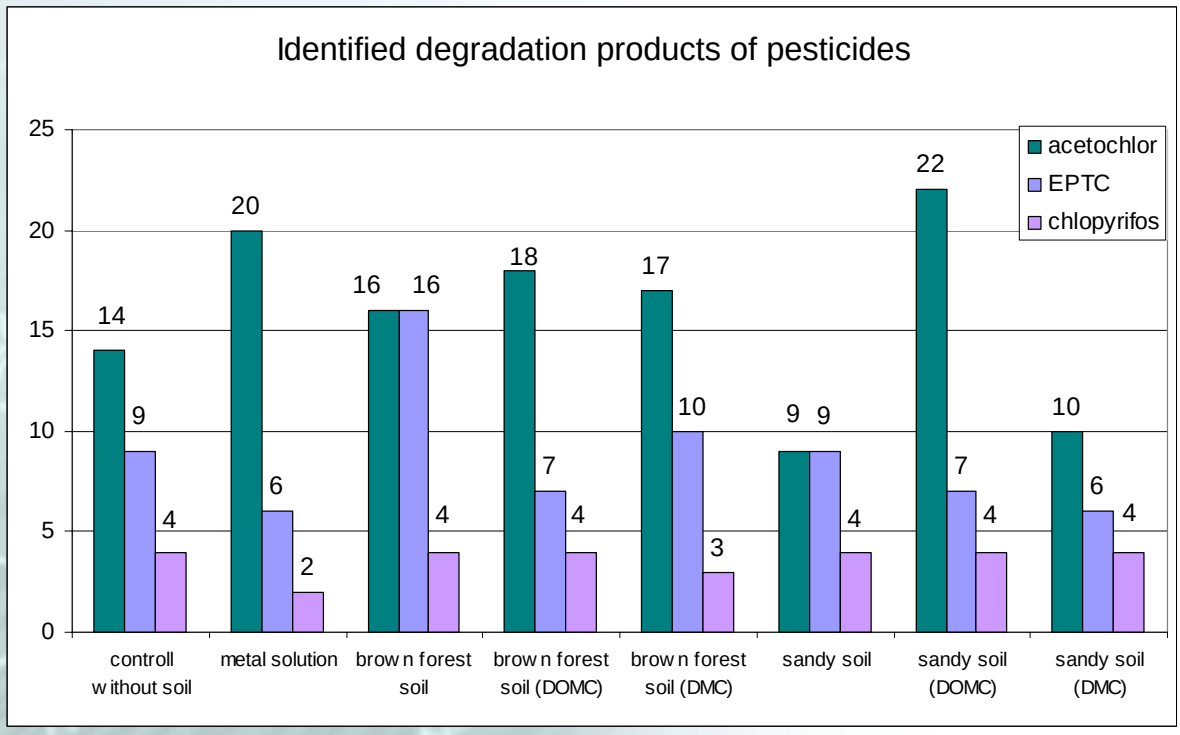
Specific degradation pathway for environmental conditions



	Molecular mass (g/mol)	Retention time (min)
a.	281	4.993
b.	210	5.237
c.	129	4.454
d.	152	4.974



- **4 new** degradates.
- Influence of soil parameters.
- Amount of one new product reaced the 15% of the total degradation products.
- Significantly different composition and product ratios.



DOMC – soil sample with Decreased Organic Matter Content
DMC – soil sample with Decreased Metal Content

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Conclusions

The studied soil parameters (soil type, organic matter content, metal content) have effect on the:

- rate of the degradation of the studied pesticides
- the generation of specific degradation products
- the ratio of the distinctive degradates.

Application perspectivites:

- enhance the food safety
- promote the production of safe food basic materials
- optimalization of agrotechnological applications.

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