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Investigations of the determination and transformations of diazinon and malathion under environmental conditions using gas chromatography coupled with a flame ionisation detector

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Abstract

Degradation of two model insecticides, diazinon and malathion, and their degradation products 2-isopropyl-6-methyl-4-pyrimidinol—IMP (diazinon hydrolysis product) and malaoxon (malathion oxidation product) was compared and studied in the environment. The pesticides and their metabolites were extracted from samples (water, soil, chicory) with ethyl acetate and subsequently the extracts were analyzed by GC/FID. It was shown that hydrolysis is the major process in the degradation of these pesticides in water. In fact, 95% of diazinon was degraded, and only 10% of malathion was oxidised. In soil 30% of diazinon exposed to the sunlight was decomposed by photolysis, whereas in soil left in the darkness no degradation products were observed. In soil left under environmental conditions, 90% of diazinon was degraded and 40% from its initial concentration was transformed into IMP. The concentrations of the pesticides after 21 days on chicory were under maximal allowable concentration, which is 0.5 ppm for malathion and for diazinon. The concentration of malaoxon was more than twice as high as the allowable value, which is for the sum of malathion and malaoxon 3 ppm.

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Keywords: Pesticides; Organophosphorus; Hydrolysis; Oxidation products

1. Introduction

Organophosphorus compounds (OP) are mostly used in agriculture as pesticides. They have replaced organochlorine compounds because of the persistence and accumulation of the latter in the environment. Organophosphorus compounds do not accumulate in organisms and they degrade easily in the environment. They inhibit

acetylcholinesterase activity not only in insects but can also affect the nervous system of humans (Chambers, 1992; Racke, 1992).

Organophosphorus esters are very susceptible to hydrolysis, which is therefore the most common degradation pathway (Racke, 1992). Hydrolysis occurs at several reactive centres in a given organophosphorus pesticide molecule. It can occur by homogeneous mechanism, where H₂O and OH[−] (H⁺ catalysis is less common) act as nucleophiles. Alternatively, it can take place when dissolved metal ions enhance the rate of hydrolysis by catalysis (Pehkonen and Zhang, 2002). One of the important factors affecting hydrolysis is therefore the pH. Diazinon, for example, is rapidly hydrolyzed at

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low or high pH values since it is susceptible to both base- and acid-catalyzed hydrolysis (Freed et al., 1979). Malathion, on the other hand, is a classic example of complexities involved in the hydrolysis product study, where unexpected products, such as malaoxon, diethyl thiosuccinate, *O,O*-dimethyl phosphorothionic acid, and other product can be formed (Pehkonen and Zhang, 2002). The effect of dissolved matter and temperature on the hydrolysis of OP compounds was also studied (Noblet et al., 1996; Dannenberg and Pehkonen, 1998). In fact it was claimed that the presence of humic substances, metal oxides and the soil structure can affect the decomposition rate (Dowling and Lemley, 1995; Noblet et al., 1996; Dannenberg and Pehkonen, 1998). Heterogeneous surfaces such as Fe and Al oxides and different clays can enhance the rate of hydrolysis by providing surface sites at which nucleophile and OP can react (Pehkonen and Zhang, 2002). Thus, pesticide persistence in soil depends mostly on its catalytic capacity, on photodegradation processes, and precipitation (Freed et al., 1979; Chambers, 1992; Racke, 1992).

Light causes photolytic degradation of various organophosphorus compounds (Givens and Kueper, 1993; Durand et al., 1994; Mengyue et al., 1995; Doong and Chang, 1997). Degradation can occur by direct or indirect photolysis. In direct photolysis the pesticide absorbs UV light and afterwards reacts with substances in the environment or decomposes by itself. However, indirect photolysis is more common. This is caused by oxygen, and hydroxy or peroxy radicals, which are produced by photolysis in humic or inorganic compounds (Pehkonen and Zhang, 2002).

Some studies included simulation of the influence of water disinfection processes such as chlorination (Zhang and Pehkonen, 1999) and ozonization (Meijers et al., 1995; Roche and Prados, 1995) on the transformation of diazinon into its metabolites. However, it has to be stressed that laboratory experiments usually take place under specific conditions and cannot be applied to field researches. The degradation of OP under various conditions and in different matrices was investigated (Freed et al., 1979; Celik et al., 1995; Lacorte et al., 1995; Lartiges and Garrigues, 1995), but the comparison of metabolites formation among different matrices (water, soil, plant) could not be clearly deduced from the literature. Therefore the behaviour of OP in the environment remains of great interest.

Thus the aim of this study was to monitor the degradation of diazinon and malathion, two OP with different types of chemical structures, in the environment over a period of 21 days.

Both pesticides are registered and commercially accessible in Slovenia. We studied their behaviour in water, soil, and on chicory (*Cichorium intybus* L. var. *Cesere*), and the formation of their metabolites malaoxon (malathion oxidation product), and 2-isopropyl-6-methyl-4-pyrimidinol (IMP) (diazinon hydrolysis product). The chemical structures of studied compounds are presented in Fig. 1. The pesticides were chosen in order to observe two degradation processes—hydrolysis (IMP—irritant compound) and oxidation (malaoxon—toxic compound), and to establish which process is dominant. The optimal conditions for determination of the chosen compounds in different environmental samples were also determined.

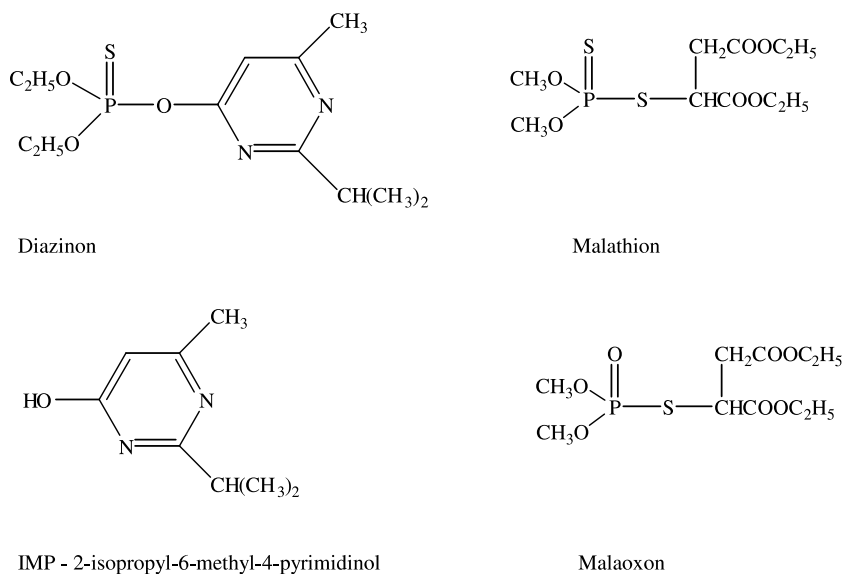


Fig. 1. The chemical structures of studied compounds.

2. Experimental section

2.1. Materials

The pesticides and metabolites used were at least 95% pure. Diazinon and malaoxon were provided from Pestanal and IMP from Aldrich. Malathion was kindly provided by the Agricultural Institute of Slovenia (Ljubljana, Slovenia).

Solvents were obtained from different suppliers: ethyl acetate and dichloromethane from RDH, hexane from J.T. Baker. Sodium sulphate—anhydrous was purchased from Merck, sodium chloride from Carlo Erba and potassium chloride from J.T. Baker.

3. Experimental set-up

Ethyl acetate extracts were analysed by a GC system (HP 6890) combined with a flame ionisation detector (FID). For separation a non-polar SPB-1 column (100% polydimethylsiloxane; 30 m × 0.53 mm; film thickness 3 µm) was used. The temperature programme was as follows: injector at 250 °C, oven (80–290 °C at 10 °C/min, maintained 5 min) and detector at 250 °C. Injection volumes of 4 µl were used in each analysis. Due to the time-consuming sample treatment (sampling, solvent extraction, drying, preconcentration, analysis), two (chicory and soil) or four (water) replicates were performed. Relative standard deviation in all experiments was 5–15%.

4. Optimisation of chromatographic conditions

Due to great differences in polarity of the pesticides and metabolites analysed selection of the proper column for their separation is essential. Preliminary analyses of standard solutions of pesticides and metabolites were performed on an HP-608 column. All phosphate esters were well separated, but the separation of IMP was not successful due to its high polarity. The chromatographic peak of IMP was non-symmetric, tailed and relatively broad. The same standard solution was also injected on weakly polar HP-5 and non-polar SPB-1 columns. We decided to perform all further analyses on the non-polar SPB-1 column.

In Fig. 2 the separation of the standard solution of two pesticides diazinon and malathion and their two metabolites on an SPB-1 column is shown.

4.1. Degradation experiments

A degradation study of two pesticides (diazinon, malathion) was carried out over 21 days in water, in soil and on chicory. In that period the weather conditions

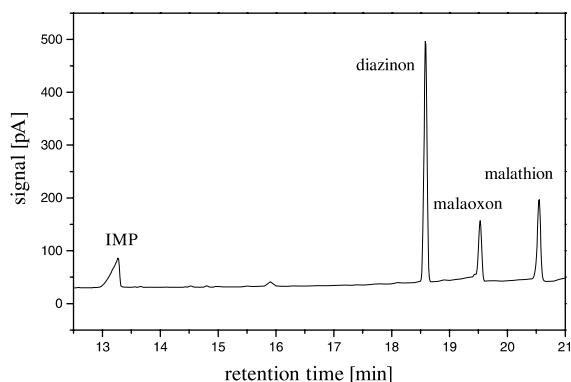


Fig. 2. A chromatogram of a standard solution of pesticides and metabolites on an SPB-1 column.

and number of sunny days were recorded. Pesticide and metabolite samples were prepared and treated as follows.

4.1.1. Water

Water samples were spiked in the following way: 1 l of pesticide mixture (diazinon—7.3 ppm; malathion—10.3 ppm) in MilliQ water was placed in the darkness and 1 l of the same spiked water was placed in sunlight. The temperatures during the natural degradation studies were from 10 °C to 25 °C.

Extraction with ethyl acetate was optimised using spiked tap water with preliminary experiments. Extraction yields were around 60% for three pesticides, but not for diazinon metabolite—IMP (30%). Successive extractions were used to improve extraction for last compound. Similar extraction yields were obtained with spiked MilliQ water, so we decided to proceed its using.

Aliquots of 10 ml were periodically taken from the samples, and extracted with three portions of ethyl acetate (25, 20 and 10 ml) with the addition of 50 ml Na₂SO₄ water solution (10 g Na₂SO₄/100 g H₂O). The organic phases were collected and evaporated to dryness, the residue was redissolved in 1 ml of ethyl acetate and analysed by GC/FID.

For quantification a calibration curve in the concentration range from 0.05 to 5 ppm was prepared. R^2 values calculated from trend lines were 0.9985 for diazinon, 0.9983 for IMP, 0.9962 for malathion, and 0.9987 for malaoxon.

4.1.2. Soil

All the experiments were performed on the soil from pesticide free field with pH 7.1 and 3.5% of organic matter. Soil samples were spiked in the following way: 2 kg of air-dried soil was spiked with pesticides (diazinon—6.9 ppm, malathion—10.0 ppm) in ethyl acetate. One half (1 kg) was placed in the darkness; the other half

(1 kg) was placed in sunlight protected from rain (absence of water, except from air humidity).

The third part of the soil experiment was carried out under environmental conditions. The pesticides (diazinon, malathion) were spread over a surface of 1 m² in the field (0.3 g of diazinon and 0.15 g of malathion/m²).

For the analyses all samples were treated in the same way. Aliquots of 10 g were periodically taken, 2.5 ml of water (to adjust for natural humidity) was added and then the mixture was extracted with three portions of ethyl acetate (15 ml and twice 10 ml). The organic phases were collected and evaporated and the residue was redissolved in 1 ml of ethyl acetate and analysed.

For quantification a calibration curve was prepared. Soil samples of 50 g were taken from a larger sample (1 kg—random sampling in a field area of 1 m²). An appropriate concentration of pesticides and metabolites in ethyl acetate was added (concentration range: 0.05–5 ppm) to the soil, and the solvent was evaporated in order to achieve a homogeneous dispersion of pesticides and metabolites throughout the soil. The next day pesticides and metabolites were extracted from soil and analysed by GC/FID. *R*² values calculated from trend lines were 0.9998 for diazinon, and 0.9998 for IMP. Unfortunately, malathion and malaoxon could not be determined due to interferences in the soil matrix.

4.1.3. Chicory

Chicory was grown in a pesticide free area. Pesticides (diazinon and malathion) were spread on grown chicory (0.08 g of diazinon and 0.15 g of malathion/m²) in an area of 30 m². Samples of 500 g of chicory were periodically taken from the field, and homogenised. For further analysis small samples (50 g) of homogenised chicory were extracted with 70 ml of ethyl acetate and 100 ml Na₂SO₄ water solution (10 g Na₂SO₄/100 ml water) was added. After shaking, the mixture was left in the hood for 4 h. The organic layer was then separated from water, the extracts were dried with anhydrous Na₂SO₄ and evaporated. The rest was redissolved in 1 ml of ethyl acetate, and analysed by GC/FID.

For quantification a calibration curve was prepared. Chicory samples (without pesticides) were spiked with pesticides and metabolites in ethyl acetate to reach the final concentration range of pesticides in vegetables from 0.05 to 10 ppm. The maximal allowable concentration for both malathion and diazinon according to Slovenian regulations should not exceed 0.5 ppm. *R*² values calculated from trend lines were 0.9992 for diazinon, 0.9948 for malathion, and 0.9999 for malaoxon. The IMP could not be determined by this procedure, due to its asymmetric, tailed and relatively broad peak, which was interfered by a matrix component.

5. Results

5.1. Degradation of diazinon and malathion in water

The concentrations of diazinon and its metabolite IMP in water samples kept in the darkness and in water samples exposed to sunlight during the 21 day experiment are presented in Fig. 3 and the concentrations of malathion and its metabolite malaoxon in Fig. 4.

5.2. Degradation of diazinon in the soil

Diazinon is a relatively non-polar organophosphate and also highly persistent in the soil. It undergoes hydrolysis under acidic conditions. In Fig. 5 concentrations of diazinon in soil under environmental conditions during the 21-day experiment are presented. For comparison in Fig. 6 concentrations of diazinon and IMP in sterile soil which was exposed to sunlight and kept in the darkness are presented. Unfortunately, we do

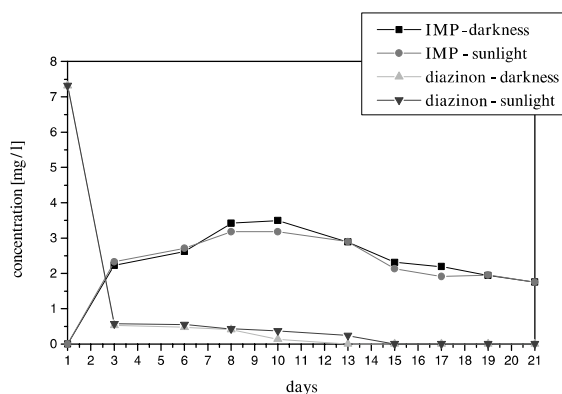


Fig. 3. Diazinon degradation and IMP formation in water.

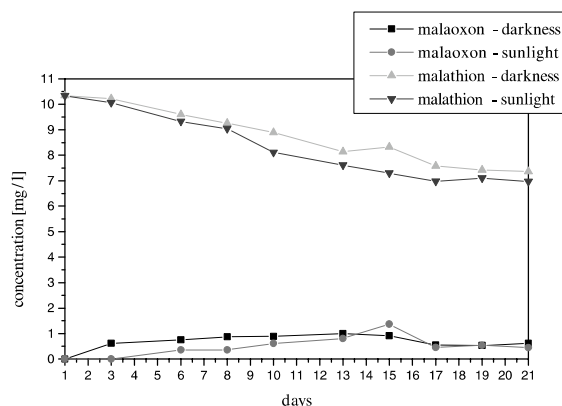


Fig. 4. Malathion degradation and malaoxon formation in water.

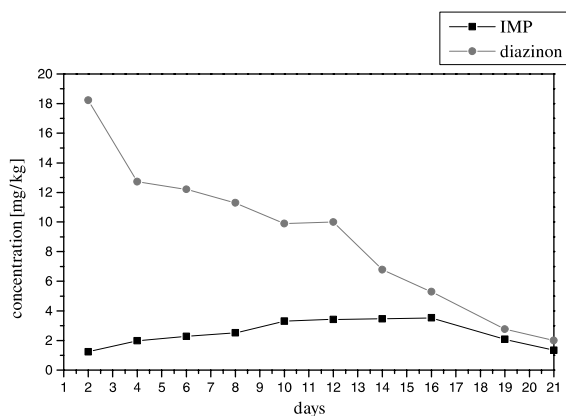


Fig. 5. Concentrations of diazinon and IMP in soil during the experiment under environmental conditions.

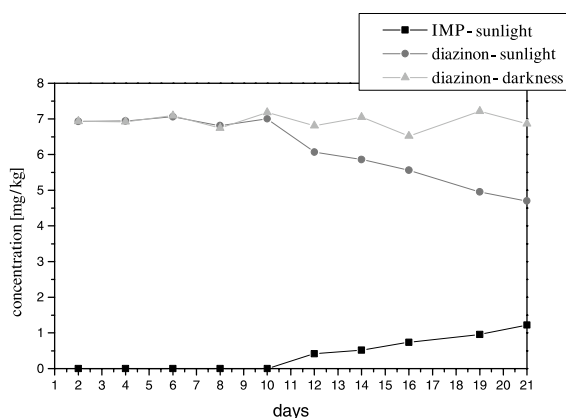


Fig. 6. The influence of sunlight on diazinon degradation.

not have any results regarding malathion in soil due to interferences present in soil.

5.3. Degradation of the diazinon and malathion on the chicory

The manufacturers declare in the OP user guideline for agricultural purposes that diazinon and malathion degrade to concentrations below the maximal allowable concentration in 21 days after application. In Slovenia this value for malathion and diazinon in food is 0.5 ppm and for the sum of malathion and malaoxon is 3 ppm (Official Gazette of the Republic of Slovenia, 13, 1999; Official Gazette of the Republic of Slovenia, 54, 1999). We performed our experiment to follow the degradation of both pesticides and malaoxon on the chicory during the 21 day period. The concentrations of diazinon, malathion and malaoxon on the chicory are presented in

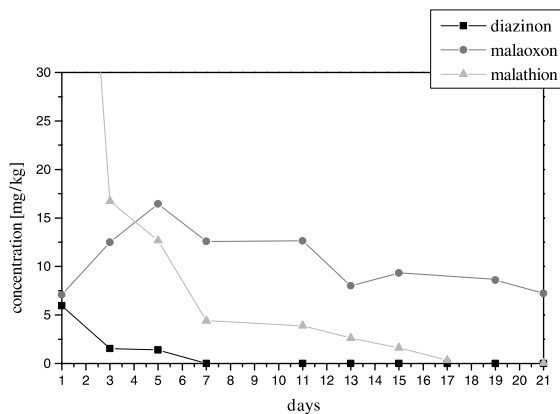


Fig. 7. The diazinon and malathion degradation on the chicory.

We were not able to determine the concentration of IMP on chicory due to rather complex matrix.

6. Discussion

Hydrolysis is the major process in degradation of diazinon and malathion. Our results showed that degradation of diazinon in water (Fig. 3) by hydrolysis into IMP is higher (95% from its initial concentration is degraded within 2 days) than malathion (Fig. 4) (30% from its initial concentrations is degraded within 14 days). About 10% of malathion is oxidized to malaoxon which seems to undergo further hydrolysis.

The influence of sunlight on the degradation (oxidation and hydrolysis) of diazinon and malathion (Figs. 3 and 4) and the formation of their metabolites were studied. The concentrations of pesticides determined in the water samples exposed to sunlight and those kept in the darkness were similar, what corresponded with the literature data (Chambers, 1992; Racke, 1992), that there is no effect of sunlight on the hydrolysis of the investigated pesticides in water.

Hydrolysis is the main degradation process also in soil. During the experiment under environmental conditions 90% of initial amount of diazinon was degraded and about 40% of IMP (maximum at 16th day) was formed (Fig. 5). The difference between the degraded amount of diazinon and the formed IMP is a result of natural effects such as “runoff”, soil humidity and microbiological and photochemical degradation. The concentration of diazinon decreases, due to its induced photodegradation in the sterile soil (without microorganisms) that was exposed to sunlight. The diazinon namely absorbs the light mostly in UV region ($\lambda_{\max} = 248 \text{ nm}$). The decomposition of diazinon in the sterile soli was 30% during 21 days and it was accompanied with the formation of IMP at 30% yield (Fig. 6).

On the contrary, the concentration of diazinon was stable, in the soil kept in darkness, the presence of IMP was not observed. This confirms our predictions about induced photodegradation of diazinon in soil.

Investigated pesticides degraded also on the chicory. The degradation of diazinon was almost complete in 5 days, whereas degradation of malathion was 95%. Malaoxon was present in the technical product used for spreading the pesticide, and was immediately found on the chicory. Its initial concentration was 7.09 mg/kg (fresh chicory). During the experiment, the concentration of malaoxon increased till the fifth day (Fig. 7), and after that it decomposed to about 40% of its maximum concentration. After the 21st day the concentration of malaoxon (7.23 mg/kg) exceeded more than twice the maximal allowable concentration prescribed in Slovenian legislation.

7. Conclusions

The persistence and transformation of the organophosphorus pesticides diazinon and malathion were investigated in environmental samples. Degradation of both pesticides was studied in water (in sunlight and in the darkness), in soil (in sunlight, in the darkness, and under environmental conditions) and on chicory over a period of 21 days. During the degradation of diazinon, its hydrolytic metabolite (IMP) is formed, while during the degradation of malathion its oxidation metabolite malaoxon is formed, respectively.

Degradation of diazinon and malathion in environmental samples depends upon the environmental conditions to which the samples are exposed. Within 2 days diazinon was 95% hydrolysed into IMP, malathion was degraded 30% and about 10% of its initial concentration is oxidised into malaoxon in water. No difference in the degradation of diazinon and malathion in water exposed to sunlight or kept in the darkness were observed.

The degradation of diazinon in sterile soil exposed to the sunlight was 30% and was accompanied with the formation of IMP. Degradation of diazinon in soil left in the darkness was not observed, which is the speculation for photoinduced degradation. In 21 days the degradation of diazinon in soil under environmental conditions was 90% and it was converted into 40% IMP (maximum at 16th day). Diazinon and malathion degradation on the chicory was nearly completed within 5 days, whereas the concentration of malaoxon (partially due to its presence in the technical product and its formation through oxidation) more than twice exceeded the maximal allowable value prescribed in Slovenian legislation. During this study some problems appeared, mostly connected with determination of the selected compounds (IMP in chicory, malathion in soil) at low

concentration level in environmental samples. Some interfering peaks were observed on GC/FID chromatograms, therefore further studies need to be carried out in order to identify all the peaks that can belong to the transformation products and to achieve a better understanding of the degradation pathways. It would be helpful to analyze samples' extracts by gas chromatography coupled with mass spectrometry (GC/MS).

Acknowledgements

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