Scientific paper

Stability of Pesticides' Residues Under Ultraviolet Germicidal Irradiation

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Abstract

Legislation for food safety is limited mostly to pesticides monitoring and no attention is paid to the presence and toxicity of by-products formed after pesticide application. Stability studies of three selected transformation products: IMP – 2-isopropyl-6-methyl-4-pyrimidinol (diazinon hydrolysis product), TCP – 3,5,6-trichloro-2-pyridinol (chlorpyrifos transformation product), and 6CNA – 6-chloronicotinic acid (imidacloprid and acetamiprid transformation product) were performed under exposure to sunlight at room temperature (22 °C) and in the dark at 4 °C over 90 days. The results showed slight change in concentration with samples under refrigeration in darkness.Alternatively, an aqueous solution of TCP exposed to sunlight resulted in a high decrease of initial concentration within time. The toxicity assessment was performed using luminescent bacteria *Vibrio fischeri* and the results expressed low toxicity in the case of IMP and 6CNA. However, for TCP the calculated EC_{50} value after 30 minutes of exposure equated to roughly 15.1 mg L^{-1}. Stability of the selected transformation products upon 245 nm irradiation indicated little decrease in concentration for IMP and 6CNA in deoxygenated and oxygenated aqueous solutions. In the case of TCP, the photochemical behaviour appeared to depend on oxygen concentration in the medium. For more detailed comparison, the degradation quantum yields were calculated.

Keywords: Pesticides transformation products, quantum yield, toxicity, *Vibrio fischeri*

1. Introduction

One of the most important goals of the food scientists is to make food as safe as possible whether it is consumed fresh or processed. Several techniques are applied for food preservation, mostly heating, preservation by low water activity, low pH and organic acid, and by the addition of specific chemicals such as carbon dioxide, sulphite, nitrite and nitrate.[1] Recently, ultraviolet irradiation as a food preservation tool has gained application interest.[2–3] The most effective and widely used is an UVC germicidal lamp with emission at wavelengths around 254 nm. The wavelength of 253.7 nm is most efficient in terms of germicidal effect since photons are mostly absorbed by the micro-organisms' DNA.[4]

Through food processing and consumption, it is possible to ingest pesticides as well as their transformation products (TP) in the food chain. According to food safety legislation only residues of insecticides in vegetables and fruits are required to be monitored.Alternatively, there is no control for the presence of transformation products which can be formed after the application of insecticides. In the literature there is a wealth of publications regarding the identification of transformation products of different insecticides in different food matrices,[5–6] as well as in water samples.[7] In addition, metabolic pathways of some insecticides were studied and major degradation products were identified.[6,8,9] Much information is available on the adverse effects of parent chemicals (pesticides) and almost none about the possible adverse effects

of transformation products. However, transformation products may possess greater toxicity as in case of organophosphorus insecticides; they can be more persistent and more mobile than their parent compounds.[10] Toxicity tests of selected pesticides and their transformation products on aquatic organisms (daphnids) were performed as well as on terrestrial organisms (earthworms)[11] and it has been clearly demonstrated that on the basis of earthworms ecotoxicologocal data, the transformation product 3,5,6-trichloropyridinol can be classified in a higher risk category than its parental compound chlorpyrifos.

In general, we may say with assurance that few studies have been published on transformation products regarding their chemical properties, stability and toxicity. For this reason we decided to explore the properties of three selected transformation products, studing their persistence, toxicity and stability under various conditions: presence and absence of oxygen, temperature and sunlight with the emphasis on their degradation under UV irradiation as a tool for food preservation, since all those conditional changes might occur during food processing.

This research focused on three transformation products from two different groups of insecticides. From the group of organophosphorous pesticides, the transformation product of diazinon: 2-isopropyl-6-methyl-4-pyrimidinol (IMP) and the transformation product of chlorpyrifos: 3,5,6-trichloro-2-pyridinol (TCP) were chosen.[5,12] From the group of neonicotinoid insecticides the common transformation product of acetamiprid and imidacloprid: 6-chloronicotinic acid (6CNA) were chosen.[13] The chemical structures of selected chemicals are shown on Figure 1.

It has been reported that 2-isopropyl-6-methyl-4-pyrimidinol (IMP) can be formed by diazinon hydrolysis within a few days.[6] Possible toxic effects of IMP on cultivated human blood cells and skin fibroblasts were investigated and the results showed that IMP possesses stronger genotoxic potential than diazinon alone.[14] As mentioned above, the primary transformation product of chlorpyrifos, by both hydrolysis and photolysis, is 3,5,6-trichloro-2-pyridinol (TCP).[14–15] Investigations on selected food were performed and the results indicated the presence of TCP in several agricultural crops such as spinach, cauliflower and potato.[5] Moreover, TCP has been found also in human urine in the United States.[16] The acute toxicity of TCP was studied on *Daphnia carinata* and it has been suggested that it is more toxic to *D. carinata* than its parent chemical compound chlorpyrifos.[17] Since neonicotinoid insecticides are a quite new group of insecticides, little data on their environmental fate is available in comparison with organophosphorous insecticides. The presence of 6-chloronicotinic acid was confirmed in soil and toxicity was tested on the honeybee *Apis mellifera*, however, no adverse effects were observed.[18–19]

2. Experimental

2. 1. Materials

The transformation product IMP (2-isopropyl-6-methyl-4-pyrimidinol), 99% pure was provided by the Aldrich Chemical Company Inc., TCP (3,5,6-trichloro-2-pyridinol) analytical standard was provided by Fluka and 6CNA (6-chloronicotinic acid), 97.0% pure was also provided by Fluka. Solvents for the HPLC mobile phase were obtained from different suppliers: acetic acid glacial 100% p.a. from Merck and acetonitrile, CHROMASOLV for HPLC grade from Sigma Aldrich Company Ltd. Chemicals used in toxicity tests were supplied from different producers, sodium hydroxide p.a. from AppliChem, sodium chloride from Carlo Erba Reagenti and hydrochloric acid 37% puriss. p.a. from Sigma Aldrich Company Ltd. Deionised water (< 18 MΩ/cm) was prepared through the NANOpure water system (Barnstead, USA).

2. 2. Analytical Procedures

HPLC-DAD: Aqueous solution of 2-isopropyl-6-methyl-4-pyrimidinol, 3,5,6-trichloro-2-pyridinol and 6-chloronicotinic acid were analyzed by HPLC-DAD (UV-Vis) consisting of a Hewlett Packard 1100 Series chromatograph, coupled with DAD detector. The separation was achieved using C8 column with stationary phase Chromasil 100 (5 μm) produced by BIA Separations d.o.o., kept at 25 °C. The injection volume was 75 μL. The eluents consisted of acetonitrile (A) and acetic acid 1.5 vol. % (B); flow rate was 1 mL min^{-1} and the wavelength 242 nm. The gradient elution was as follows: 0 min to 16 min 15% A; 16 min to 20 min 70% A. The retention time for 2-isopropyl-6-methyl-4-pyrimidinol was 6.6 min, for 6-chloronicotinic acid 12.5 min and for 3,5,6-trichloro-2-pyridinol 18.4 min. For quantification purposes calibration curves for all three transformation products from 0.1 ppm to 100 ppm were prepared. The r^2 value of the regres-

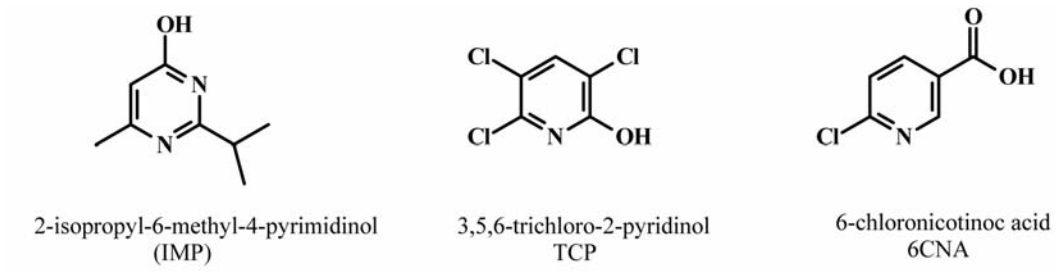

Figure 1: The chemical structures of the studied compounds.

sion line for 2-isopropyl-6-methyl-4-pyrimidinol was 0.9998, for 6-chloronicotinic acid was 0.9985 and for 3,5,6-trichloro-2-pyridinol was 0.9998.

UV-Vis spectra were recorded on a Cary 300 scan spectrophotometer produced by Varian.

2. 3. Stability Tests

Stability of 2-isopropyl-6-methyl-4-pyrimidinol, 3,5,6-trichloro-2-pyridinol and 6-chloronicotinic acid was assessed by exposing water samples to different temperatures, different pHs (4,7,10), presence of sunlight and absence of oxygen. Samples containing selected transformation products were dissolved in double deionised water and stored under different laboratory conditions in 100 mL SCHOTT DURAN flasks. One set of flasks was kept on the laboratory desktop at direct sunlight at room temperature 22 °C and the second set of flasks was kept in a refrigerator in the dark, at 4 °C. The selected pH was achieved by adding hydrochloric acid or sodium hydroxide. During the period of 90 days, the concentration of solutions were monitored with the HPLC-DAD system and the pH was monitored with a pH meter, Hanna Instruments HI 8417.

2. 4. Ultraviolet Irradiation of Samples

Quartz cells (10 × 10 × 40 mm) were filled with aqueous solution of each chemical and placed in front of the monochromatic low pressure mercury germicidal lamp emitting at 254 nm. The photon flux was evaluated by actionometry using potassium ferrioxalate and the value obtained was 4.86×10^{14} photons s^{-1} cm^{-2}. The solutions were stirred and irradiated for a given period of time (0, 5, 10, 20 and 30 min) then analysed by the HPLC-DAD (UV-Vis) as well as by an UV-Vis spectrophotometer. After each sample collection, a fresh sample was irradiated in order to retain the same sample volume. All the samples were irradiated in deaerated oxygen free solutions. In the latter case, prior to irradiation, the samples were purged for 10 minutes with argon. In order to obtain a better insight into possible degradation behaviour, the additional experiments were performed in order to estimate the degradation quantum yields under various conditions. Adequate values were calculated by employing the following expression;

$$\Phi = \frac{\left(-\frac{dC}{dt}\right)(N\, l\, 10^{-3})}{[I_0(1-10^{A0})]} \quad (1)$$

dC/dt: the slope of the initial linear part of the kinetic curve (concentration as a function of irradiation time) [mol L^{-1} s^{-1}]

N: Avogadro number [molecules mol^{-1}]

l: optical path length [cm]

I_o: photonic flux evaluated to 4.68×10^{14} [photons s^{-1} cm^{-2}]

A_0: the initial absorbance of the studied solution at the excitation wavelength 254 nm.

2. 5. Toxicity Experiments

Toxicity of 2-isopropyl-6-methyl-4-pyrimidinol, 3,5,6-trichloro-2-pyridinol and 6-chloronicotinic acid was assessed using luminescence bacteria *Vibrio fischeri* with system LUMIStox, Dr.LANGE. The toxicity endpoint was determined as reduced luminescence emittion after incubating with presence of the selected chemical or mixture. The crucial experimental step was sample preparation in order to avoid possible adverse effects due to an incorrect pH value or inappropriate sodium chloride concentration. Before analyzing the samples, adjusting the pH to 7 ± 0.2 with hydrochloric acid or sodium hydroxide was performed as well as adding the correct amount of sodium chloride salt i.e. 2% w/v. Bacteria were incubated for 15 min in reactivation solution, meanwhile the samples were mixed with 2% sodium chloride solution (1:1 v/v) and temperature controlled at 15 °C in a thermoblock. Luminescence of each cuvette with bacteria was measured; afterwards the sample was added and thermostated to 15 °C for 30 minutes. After 30 minutes the luminescence of bacteria with sample was measured again and the inhibition of luminescence according to ISO 11348-2 was calculated. Luminescence was measured with a photomultiplier also temperature controlled at 15 °C. The blank test was performed with 2% sodium chloride. All the measurements were carried out in two aliquots. As an appropriate endpoint for toxicity assessment, the EC_{50} value was calculated.

3. Results and Discussion

The results of stability tests for 2-isopropyl-6-methyl-4-pyrimidinol (IMP), 3,5,6-trichloro-2-pyridinol (TCP) and 6-chloronicotinic acid (6CNA) in double deionised water was performed at room temperature (22 °C) under exposure to sunlight and in the dark (in the refrigerator at 4 °C) are shown in Table 1.

The experiments performed at 4 °C in the darkness clearly indicate that the thermal degradation or transformation is very low in case of all three substances over the 90 days of experiment. Moreover, the concentration of IMP and 6 CNA samples exposed to sunlight decreased for 2% and 9% and can be compared with the samples kept in the refrigerator, where the observed decrease was very similar, i.e. 3% and 8%. However, experiments with TCP performed at room temperature (22 °C) with exposure to sunlight led to an important transformation. Within 90 days of experiment, 70% conversion was observed, compared to the sample kept in the dark which resulted in only 2% conversion. It should be noted, that this result clearly shows the transformation of TCP into another compound(s), which were not recorded and monitored at that time.

Toxicity assessment of aqueous solutions for all three substances were performed and the results revealed

Table 1: Concentration of IMP, TCP and 6CNA within time in refrigerator and exposed to sunlight.

time [days]	refrigerator T = 4 °C C/C$_0$ [%]			sunlight T = 22 °C C/C$_0$ [%]		
	IMP	TCP	6CNA	IMP	TCP	6CNA
0	100	100	100	100	100	100
7	99.6	99.6	96.8	99.8	81.8	97.2
17	100	99.6	96.8	99.8	68.7	98.9
28	100	98.3	100	100	59.5	96.9
45	99.1	97.8	93.8	99.2	51.2	93.9
62	99.0	96.7	95.0	98.3	40.0	94.7
90	97.8	98.2	91.6	98.1	28.9	91.1

relatively high toxicity in case of 3,5,6-trichloro-2-pyridinol (TCP), while for 2-isopropyl-6-methyl-4-pyrimidinol (IMP) and 6-chloronicotinic acid (6CNA) solutions did not cause significant inhibition in luminescence of *Vibrio fischeri* bacteria. The results are presented in Table 2.

Table 2: Inhibition of luminescence in *Vibrio fischeri* bacteria for IMP, 6CNA and TCP aqueous solution.

concentration [mg L^{-1}]	inhibition of the luminescence [%]		
	IMP	6CNA	TCP
54	7.6 ± 0.7	21.4 ± 1.1	80.1 ± 0.1
27	6.6 ± 0.0	14.8 ± 1.3	65.6 ± 0.4
13.5	7.3 ± 0.1	8.3 ± 0.9	45.3 ± 1.1
6.8	3.6 ± 2.2	8.7 ± 2.7	25.1 ± 1.9
3.4	3.2 ± 0.5	5.0 ± 1.6	10.0 ± 0.2

On the basis of results listed above, the dose response curve for TCP was derived and the 30 min EC$_{50}$ value of 15.1 mg L^{-1} was calculated. The dose response curves for 6CNA and IMP could not be derived due to the very low toxicity of samples and consequently, the 30 min EC$_{50}$ values for these solutions were not calculated. Nevertheless, the used concentrations were still very high from the environmental point of view.

The influence of the germicidal lamp emitting at 254 nm on the stability of 2-isopropyl-6-methyl-4-pyrimidinol (IMP), 3,5,6-trichloro-2-pyridinol (TCP) and 6-chloronicotinic acid (6CNA) was assessed as possible change in concentration within irradiation time. Experiments were performed in aerated as well as in deaerated by bubbling with argon for roughly 10 minutes. Under both experimental conditions, similar results were obtained. In Table 3, the percentages of initial concentrations still remained in the solution for each sample after given times of irradiation are presented. Within 30 minutes of irradiation, the highest disappearance rate was achieved by the TCP aqueous solution – it retained just 54% of its initial concentration, but for the 6CNA and IMP the remaining concentrations in the solution were still relatively high (around 84%).

The disappearance of all three studied products in aqueous solutions was also monitored by UV-Vis spectroscopy within 200–400 nm. On Figures 2, 3 and 4 the

Table 3: Concentration of IMP, TCP and 6CNA within irradiation time with low pressure mercury lamp (254 nm) in the presence and in the absence of oxygen.

oxygenated aqueous solutions						
time [min]	IMP		TCP		6CNA	
	C/C$_0$ [%]	C [mol L^{-1}]	C/C$_0$ [%]	C [mol L^{-1}]	C/C$_0$ [%]	C [mol L^{-1}]
5	96.2	1.13×10^{-4}	83.9	9.15×10^{-5}	98.2	1.33×10^{-4}
10	93.7	1.11×10^{-4}	74.0	8.06×10^{-5}	96.6	1.30×10^{-4}
15	89.7	1.06×10^{-4}	61.7	6.73×10^{-5}	98.5	1.25×10^{-4}
20	84.6	9.98×10^{-5}	54.4	5.93×10^{-5}	89.8	1.21×10^{-4}
deoxygenated aqueous solutions						
time [min]	IMP		TCP		6CNA	
	C/C$_0$ [%]	C [mol L^{-1}]	C/C$_0$ [%]	C [mol L^{-1}]	C/C$_0$ [%]	C [mol L^{-1}]
5	97.1	1.15×10^{-4}	84.7	9.23×10^{-5}	95.2	1.28×10^{-4}
10	95.2	1.12×10^{-4}	73.5	8.01×10^{-5}	90.6	1.22×10^{-4}
15	90.2	1.06×10^{-4}	62.2	6.78×10^{-5}	84.5	1.14×10^{-5}
20	/	/	/	/	/	/

absorption spectra of IMP, TCP and 6CNA are given as a function of irradiation time.

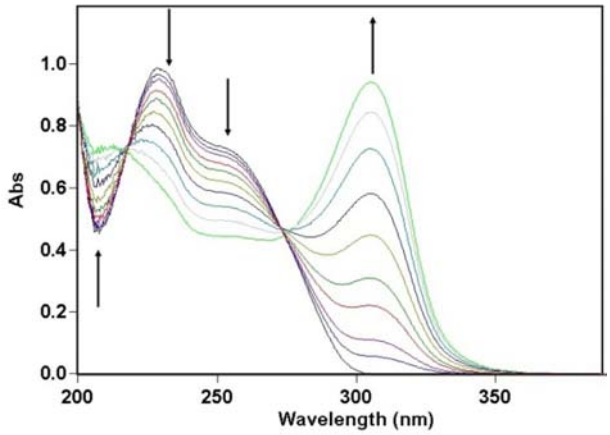

Figure 2: Absorption spectra for the oxygenated solution of IMP upon excitation at 254 nm for 30 minutes.

Note: The (↑) indicates increase of absorbance in comparison to stationary spectra and (↓) indicates decrease of absorbance.

As shown in Figure 2, the 254 nm irradiation of an oxygenated solution of IMP, led to important changes in the absorption spectrum. The absorbance decreased within the wavelength range 225–375 nm which clearly reflects the photodegradation of IMP, whereas the absorbance significantly increased at wavelength range 275–340 owing to the formation of by-product(s). The presence of an isobestic points are observed at 275 nm and 220 nm, that lead to the conclusion that a clean photochemical reaction was occurring.

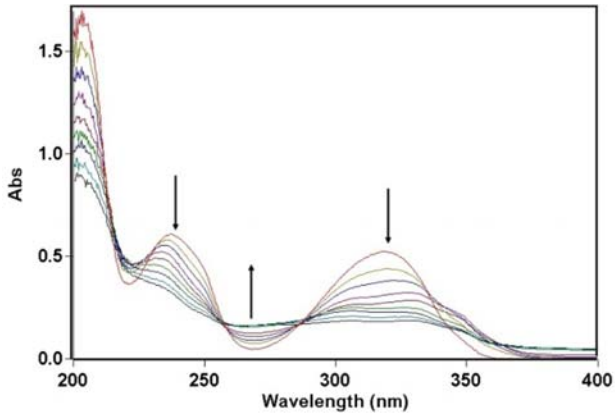

Figure 3: Absorption spectra for the oxygenated solution of TCP upon excitation at 254 nm for 30 minutes. Note: The (↑) indicates increase of absorbance in comparison to stationary spectra and (↓) indicates decrease of absorbance.

A similar trend has been observed in case of TCP irradiation at 254 nm. The absorbance decreased within the wavelength range 225–255 nm and 290–340 nm which again demonstrates the transformation of TCP. However, the absorbance slightly increased within the wavelength range 255–290 nm and this was again attributed to no newly formed by-product occurring.

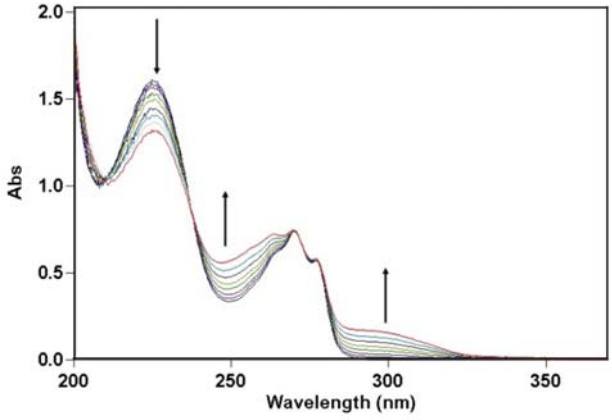

Figure 4: Absorption spectra for the oxygenated solution of 6CNA upon excitation at 254 nm for 30 minutes. Note: The (↑) indicates increase of absorbance in comparison to stationary spectra and (↓) indicates decrease of absorbance.

The smallest change in evolution absorbance spectra upon excitation at 254 nm was recorded in the case of 6CNA aqueous solution. There a decrease in absorbance at wavelength range 210–235 nm was indicated and an increase at wavelength ranges 235–270 nm and 275–325 nm. The presences of at least three isobestic points are demonstrating a clean photochemical process. It is worth nothing that no change in the absorption spectra occurred with deoxygenated conditions in comparison with oxygenated conditions; therefore the figures are not presented. All the results are in compliance with HPLC-DAD data, where the highest photo degradation was recorded for the TCP aqueous solution and the lowest in the case of 6CNA aqueous solution.

In order to better estimate the effect of aerated or deoxygenated conditions to transformation products photodegradation, the quantum yields were calculated for each compound within specific conditions. The calculated parameters for degradation quantum yields are detailed and presented in the Table 4.

In case of the IMP aqueous solution, the quantum yields, as calculated from data obtained from both conditions, are very similar and low. However, the results are in compliance with degradation quantum yields for pesticides, calculated in similar research recently published.[20] The quantum yield is the number of destroyed molecules divided by the number of photons absorbed by the system. This, therefore, means that only small part of molecules for IMP were actually degraded by absorbed photons. A slightly different situation appears with the quantum yields

Table 4: Parameters for photodegradation quantum yields for oxygenated and deoxygenated samples of IMP, TCP and 6CNA.

	oxygenated aqueous solutions		
	IMP	**TCP**	**6CNA**
***A* [254 nm]**	0.725	0.291	0.372
–dC/dt [mol L^{-1} s^{-1}]	9.662×10^{-9}	2.620×10^{-8}	8.476×10^{-9}
Φ [molecules $photons^{-1}$]	0.015	0.069	0.019
	deoxygenated aqueous solutions		
	IMP	**TCP**	**6CNA**
A [254 nm]	0.725	0.291	0.372
–dC/dt [mol L^{-1} s^{-1}]	1.000×10^{-8}	3.330×10^{-8}	1.724×10^{-8}
Φ [molecules $photons^{-1}$]	0.016	0.088	0.039

calculated from the experiment with the aqueous solution of TCP. Degradation quantum yield was slightly higher in the case of deoxygenated conditions. We can thus propose that oxygen could have an inhibitory impact on the photo degradation of TCP. Obvious changes in degradation quantum yields for oxygenated and deoxygenated conditions were observed for the aqueous solution of 6CNA. When performing irradiation experiments in presence of argon, the degradation quantum yield increased.

4. Conclusions

This work constitutes the first attempt to understand pesticides' residues behaviour under an ultraviolet germicidal lamp (254 nm). Our investigations involved analysis of three selected pesticides' transformation products under diverse conditions, such as presence of natural sun light, as well as UVC light radiation. Samples of 6-chloronicotinic acid and 2-isopropyl-6-methyl-4-pyrimidinol exposed to the natural sun light showed persistency, in the same conditions the 3,5,6-trichloro-2-pyridinol showed high susceptibility to natural sunlight, therefore, within 90 days of our experiment the concentration decreased by 70%. Exposure of three transformation products to the 254 nm germicidal light resulted in degradation of just 3,5,6-trichloro-2-pyridinol. Quantum yields have been determined for all three compounds within oxygenated and deoxygenated conditions. The obtained values were in the range 0.088 to 0.15. As it was demonstrated through the research, the application of an ultraviolet germicidal lamp does not degrade transformation products completely, so it is critical and necessary to extend the quality of toxicity testing for food and water. The toxicity testing clearly pointed out the fact, that 3,5,6-trichloro-2-pyridinol posses toxicity towards bacteria *Vibrio fischeri*, while the other two transformation products showed negative effects. In this work it was demonstrated that additional attention needs to be paid to the chemicals formed after pesticide application. The persistence under various natural conditions within the environment as well in the different food matrices should be thoroughly investigated and monitored. However, additional analyses of possible by-products formation with GC-MS or LC-MS techniques will be part of our future research. It needs to be stressed that attention must be paid also to further investigations of possible adverse effects to several organisms or even biomarkers.

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Povzetek

Zakonodaja glede varnosti hrane je pretežno omejena na sledenje pesticidov, zelo malo pozornosti pa je namenjeno ugotavljanju prisotnosti in ocenjevanju strupenosti razgradnih produktov, ki nastanejo pri razgradnji pesticidov. Študije stabilnosti treh izbranih razgradnih produktov pesticidov: IMP – 2-izopropil-6-metil-4-pirimidinol (hidrolizni produkt diazinona), TCP – 3,5,6-trikloro-2-piridinol (razgradni produkt klorpirifosa), in 6CNA – 6-kloronikotinska kislina (razgradni produkt imidakloprida in acetamiprida), so bile izvedene na podlagi izpostavljenosti s pesticidi onesnaženih vodnih vzorcev sončni svetlobi pri sobni temperaturi (22 °C) in v temnem prostoru pri 4 °C tekom 90 dni. Rezultati so pokazali majhno spremembo koncentracije vzorcev, hranjenih v hladilniku v temi, kar nam nakazuje da so IMP, TCP in 6CNA v vodi dokaj stabilne spojine. Po drugi strani, je bilo v vodni raztopini TCP, ki je bila izpostavljena soncu, zaznati veliko znižanje začetne koncentracije v izbranem času. Oceno strupenosti izbranih razgradnih produktov smo izvedli z luminiscenčnimi bakterijami *Vibrio fischeri* in rezultati so pokazali majhno strupenost za IMP in 6CNA. V primeru TCP pa smo EC50 po 30 minutni izpostavljenosti ocenili na približno 15,1 mg L^{-1}. Stabilnost izbranih razgradnih produktov smo raziskali tudi med obsevanjem z germicidno sijalko z valovno dolžino 245 nm in rezultati so pokazali majhno zmanjšanje koncentracije za IMP in 6CNA tako v prisotnosti kisika kot tudi v prisotnosti argona. Nasprotno pa se je koncentracija TCP pod vplivom svetlobe in v prisotnosti kisika spreminjala skladno s spreminjanjem koncentracije kisika. Za podrobnejšo primerjavo stabilnosti in razumevanje procesov vseh izbranih razgradnih produktov pri različnih pogojih smo izračunali tudi kvantne izkoristke pri procesu razgradnje.