



Interpretation and modelling of environmental behaviour of diverse pesticides by revealing photodecomposition mechanisms

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ABSTRACT

Pesticides are commonly applied agrochemicals, however their long-term chemical behaviour and environmental fate involving degradation processes have not been studied thoroughly and extensively yet. As photolytic decomposition might be regarded as one of the key factor in determining environmental behaviour of pesticides, it is of high relevance to have comprehensive knowledge on characteristics of pesticide degradates having potential harmful biological effects. Toxicity of the examined pesticides is well known, however scarce information is available on their natural degradation processes, as well as the quality, structure and biological impact of the decomposition products.

Our study is focused on revealing specific details of photolytic degradation behaviour of 3 frequently applied pesticides and mapping the entire decomposition mechanisms.

Special, immerseable, low pressure mercury-vapour lamp was applied to induce photolytic transformation, which was followed by TLC and GC. 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.

All the pesticide studied proved to be photosensitive and major stages of the UV-degradation pathway were found to be the loss of alky-groups, cleavage of the chloro-group and the hydroxylation, scission of N-alkyl groups and decarbonylation.

In contrast to previous studies, different and specific degradates and end-products have been established, and the existence of alternative conversion pathways was revealed.

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1. Introduction

Photodecomposition of several organic contaminants involving distinctive pesticides is a topic of high interest for researchers in recent years. Several efforts have recently been made aiming at reduction of potential risks attributed to pesticides, however comprehensive assessment of potential hazards, including characterisation of photodegradates, has not been performed yet [1,2].

In order to clarify the photolytic decomposition behaviour of 3 selected pesticides and to be capable of right interpretation of the complete mechanisms, our major goal was to isolate and identify the degradation products by applying HPLC-MS technique. Subsequently the most plausible degradation pathways were established, and the kinetic aspect of photodecomposition was also revealed. Such an arborescent research study presenting the total mechanisms of the photoinduced degradation of various pesticides was performed by Kiss and Virág [3] in case of acetochlor, simazine, chlorpyrifos, carbendazim.

Essence of previous studies concerning the examined pesticide is presented as follows.

Atrazine (2-chloro-4-ethylamine-6-isopropylamino-S-triazine) was one of the most popular selective triazine herbicide until it has been classified as a Restricted Use Pesticide (RUP) due to its potential for groundwater contamination [4]. It is a photosynthetic inhibitor and used to control broadleaf and grassy weeds.

Photolytic degradation of some frequently applied s-triazine type pesticides was investigated by Kiss et al. [5]. Determination of products obtained by photolysis of atrazine in soil samples was performed by Durand and Barcelo [6,7]. Hydroxy, 2-H and 2-methoxy derivatives of the parent compound were identified. TiO₂ catalysed mineralization of atrazine was also studied along with other triazines [8–11]. Products formed by oxidation, ring opening, decarboxylation, isomerization, hydroxylation and cyclization were found to be the main degradates. By the loss all of the side chains formation of cyanuric acid and 2-amino-4,6-dihydroxy-1,3,5-s-triazine were observed. The structure of each photolytic degradates (in the presence of porphyrin and phthalocyanine complexes as catalysts) was given by Hequet et al. [12,13].

Diuron (N-(3,4-dichlorophenyl)-N,N-dimethyl urea) is a substituted urea type non-selective herbicide with photosynthesis inhibition effect [14].

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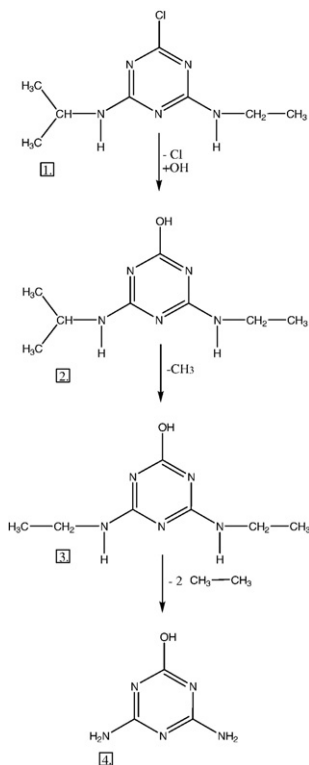


Fig. 1. Proposed degradation mechanism of atrazine.

Its principal breakdown product 3,4-dichloroaniline is more toxic than diuron itself. It is persistent and contaminates marine waters, groundwater, sediment and soil [15]. It is considered as a Priority Hazardous Substance by the European Commission [16].

EPTC (*S*-ethyl dipropylthiocarbamate) is a selective, growth inhibitor herbicide of thiocarbamate-type. The UV-photodegradation of EPTC in hexane has been studied by Marco et al. [17] as well as Abu-Qare et al. [18]. Formation of several photoproducts and the 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 [10].

In summary it might be stated that huge efforts have been made to characterise both the chemical and environmental behaviour of

pesticides, however the precise reaction mechanisms of photodegradation have not been revealed, and in some cases controversial results have been obtained. Hence identification of major degradates might be considered as a major task in order to gain insight into the photodegradation and environmental behaviour of the selected and investigated pesticides.

2. Materials and methods

The three pesticides examined, having diverse chemical structures and action mechanisms are diuron (substituted urea herbicide), atrazine (triazine herbicide) and EPTC (thiocarbamate herbicide). The examined pesticides (higher than 99% HPLC purity) and other applied chemicals were purchased from Sigma Aldrich (Germany).

Slightly acidic, aqueous, pesticide solutions of 500 ppm concentrations were treated with a special UV light source (254 nm wavelength, 15 W, low pressure mercury-vapour lamp, manufactured by Millipore company, Hungary). The degradation process was followed by TLC and GC. Thin layer chromatography was performed on precoated Merck 5554 Kieselgel 60 F254 foils using chloroform–methanol (9:1) developing system. Samples were taken at different times of the UV-irradiation (in every 30 min 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 GC separations and the mass spectrometric measurements were performed by using GC-GC/MS QP-2010S Shimadzu (Shimadzu Corporation, Kyoto, Japan) device under the following conditions: column: HP-5MS (30 m×0.25 mm×0.25 μm), carrier gas: He (1 ml/min), detector: GC/MS QP-2010S, ionization mode: EI (70 eV), interface temperature: 230 °C, ion source temperature: 200 °C, inject volume: 1 μl. The heating parameters were the follows: EPTC: 80 °C (hold: 0.5 min) → 280 °C (20 °C/min) (hold: 1 min); diuron: 70 °C (hold: 1 min) → 180 °C (10 °C/min) (hold: 0 min) → 220 °C (20 °C/min) (hold: 0 min); atrazine: 90 °C (hold: 0 min) → 250 °C (20 °C/min) (hold: 3 min).

3. Results and discussion

3.1. Photodegradation of ATRAZINE

The five-hour-long UV-irradiation of atrazine [2-chloro-4-ethylamine-6-isopropylamino-S-triazine] (1.) resulted in the cleavage of the

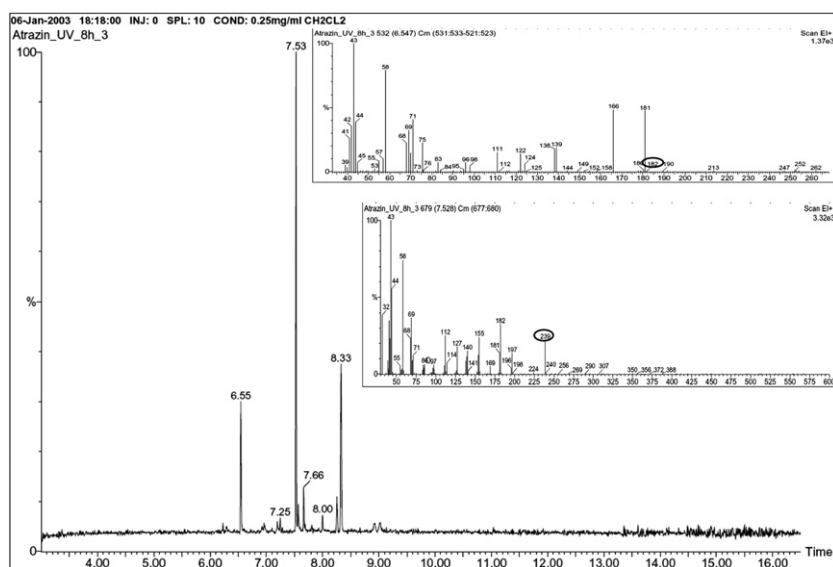


Fig. 2. The GC-chromatogram and the mass-spectrums of the main degradation products of atrazine after 8 hours UV-irradiation.

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