Identification of By-products Formed During the Oxidative Transformation of Phenylurea Pesticides

Gergő Simon[1,2]*, Virág Farkas[1,2], András Dombi[1], Klára Hernádi[1], Tünde Alapi[1,2]

[1]Research Group of Environmental Chemistry, University of Szeged, H-6720 Szeged, Rerrich Béla tér 1, Hungary
[2]Department of Inorganic and Analytical Chemistry, University of Szeged, H-6720 Szeged, Dóm tér 7, Hungary
e-mail: gsimon@chem.u-szeged.hu

Abstract

The goal of this study was to identify the by-products that form during the oxidative degradation of five phenylurea pesticides. Four advanced oxidation processes were used including photolysis, ozonation, heterogeneous photocatalysis, and the combination of photolysis with ozonation. After concentrating the by-products using solid phase extraction, our samples were analyzed by mass spectrometry. We have managed to identify the main products for each pesticide and process, from which we could determine that the main reactions during the application of AOPs were the dehalogenisation and hydroxylation of the aromatic ring, as well as the terminal demethylation and the oxidation of the methyl groups.

Introduction

Organic contaminants, such as pesticides, pharmaceuticals, etc. have become a major concern regarding the environment due to their persistence and low biodegradability that can lead to accumulation in soils and waters.[1] A large number of these contaminants have presumed or proven negative health effects (carcinogens, endocrine disruptors). Phenylurea herbicides are one such type of chemicals that are widely used for weed control, mostly in non-agricultural areas, and their high half-life in soils[2] causes them to wash into waters, even appearing in drinking water. Another problem is that regular water treatment methods often are ineffective in the removal of these contaminants. Therefore applicable methods are being developed based on advanced oxidation processes (AOPs) that are capable of the degradation of organic matter by forming highly reactive radicals. These methods include photolysis by ultraviolet light, ozonation, heterogeneous photocatalysis, Fenton-reaction, which can be effective themselves, but also can be further improved by their combination [3], resulting in higher radical concentrations or different reaction pathways. This also means that the various processes will result in different by-products that can be identified using mass spectrometry. This information is essential for the development of analytical processes for these compounds and their metabolites.

Materials and methods

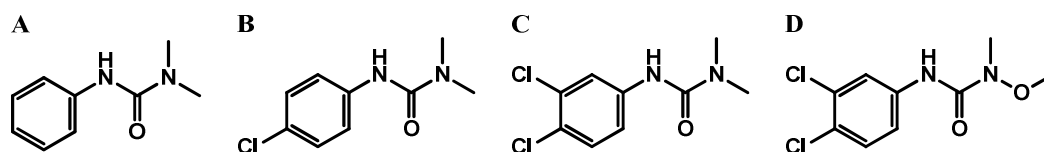Four phenylurea pesticides were used for our experiments, as presented on **Figure. 1**.

Figure 1. Molecularformulae of thepesticides: A: fenuron; B: monuron; C: diuron; D: linuron
During the experiments 500 cm^3 of aqueous pesticide solutions (c_0=3.7 $\times$ 10^{-5}mol dm^{-3}) were circulated with a peristaltic pump between the stirred reservoir and reactor tanks, both were thermostated at 25±0.1 °C. The solutions were bubbled with air (in case of photolysis and photocatalysis) or oxygen (in case of ozonation and the combined UV/ozone method) 10 minutes before and throughout the measurements.
Three low-pressure mercury vapour lamps with identical parameters (15 W, 227 mm arc length, 307 mm length and 20.5 mm external diameter) were used, emitting at differing wavelengths: standard UV (254 nm), UV/VUV (185 and 254 nm) and fluorescent lamp (with maximum emitted fhoton flux at 365 nm). Each process was executed by the selection of the light source and the material of the envelope (quartz or glass) covering it. The measurements were initiated by switching the lamp on.

Process	Lamp	Envelope
Photolysis	254 nm	quartz
Ozonation	185/254 nm	perforated glass
Photolysis and ozonation	185/254 nm	perforated quartz
Heterogeneous photocatalysis	365 nm	quartz

UV-vis spectrometry was performed using an Agilent 8453 spectrophotometer, while high-performance liquid chromatographic measurements were made utilizing an Agilent 1100 modular HPLC system equipped with a diode-array detector. The mobile phase consisted of acetonitrile and water (60:40 %V/V) for diuron and linuron, also methanol and water (60:40 %V/V) for fenuron and monuron. For isoproturon gradient elution was used according to Kovalczuk et al.[4]The separation of compounds was achieved on a LiChroCART® C-18 column (250 mm $\times$ 4 mm, 5 µm) at 25 °C temperature with an injection volume of 20 µL. The mass spectrometric measurements were performed on an Agilent G1956A quadrupole mass spectrometer.

Results
From the degradation curves of the target compounds, the initial rates of transformation can be obtained, which serves as the basis of the comparison of the processes. Furthermore, the time required to transform 50 % the parent compound can also be calculated, which is important in the identification of the by-products, the reason being that at this point most of them are present in the solutions.
Mass spectrometric measurements were made both with the original and the concentrated samples. The identified by-products are shown in the following tables (**Tables 1-4**).The tables contain the products' retention times, molecular weight, number of chlorine atoms, the suggested formulae, and the processes during which each of them were detected. The results indicate that during the oxidative transformation of these compounds the hydroxylation and dehalogenisation of the aromatic ring, the oxidation of the methyl groups, and terminal demethylation are the primary reactions in all cases.

Table 1. By-products formed during the oxidative transformation of diuron
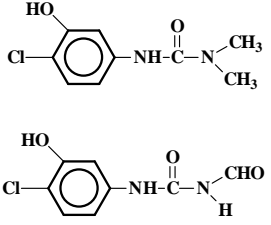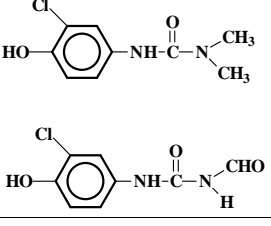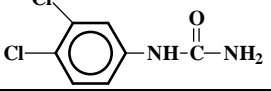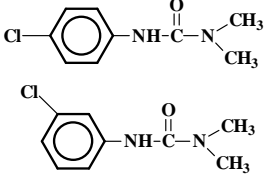(○: detected without enrichment by SPE, ●: detected after enrichment by SPE)

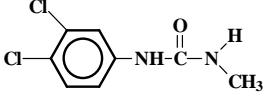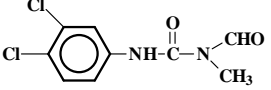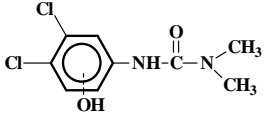| Retention time (min)	M	Cl	Suggested formula	UV photolysis (UV)	Ozona-tion (O₃)	Combined method (UV/O₃)	Het. Photocat. (TiO₂)
2.78	213	0		○			○
3.09	213	0		○		○	○
3.24	214	1		○●	●	●	●
3.39	214	1		●	●	●	●
4.06	204	2		○●	○●	○●	○●
4.51	198	1		●	○●	●	
5.06	218	2		○●	○●	○●	○●
5.58	203	2		○	●	○●	○●
8.22	246	2		○●	○	●	○●
9.08	248	2		●	●	●	●
9.38	232	2	possible diuron contamination	●	●	●	●

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Table 2. By-products formed during the oxidative transformation of linuron
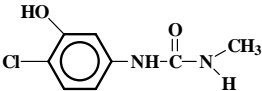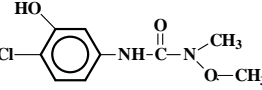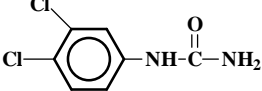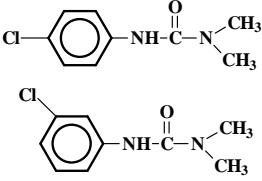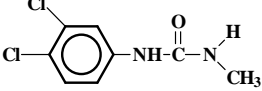(○: detected without enrichment by SPE, ●: detected after enrichment by SPE)

Retention time (min)	M	Cl	Suggested formula	UV photolysis (UV)	Ozonation (O₃)	Combined method (UV/O₃)	Het. Photocat. (TiO₂)
2.46	200	1	HO, Cl–C₆H₃–NH–C(=O)–N(CH₃)(H)	○●		○●	●
3.13	230	1	HO, Cl–C₆H₃–NH–C(=O)–N(CH₃)(O–CH₃)	●		●○	
3.22	204	2	Cl, Cl–C₆H₃–NH–C(=O)–NH₂	○●	○●	○●	○●
3.58	198	1	Cl–C₆H₄–NH–C(=O)–N(CH₃)₂ / Cl–C₆H₄–NH–C(=O)–N(CH₃)₂		●		●
4.04	218	2	Cl, Cl–C₆H₃–NH–C(=O)–N(H)(CH₃)	○●	●	○●	○●
4.55	234	2	Cl, Cl–C₆H₃–NH–C(=O)–N(CH₃)(OH)		●		●
4.64	203	2					●
4.86	232	2		●	●	●	●
5.90	203	2		●	●	●	●
11.20	280	2		●	●		

Table 3. By-products formed during the oxidative transformation of fenuron (○: detected without enrichment by SPE, ●: detected after enrichment by SPE)
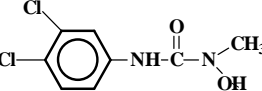
Retention time (min)	M	Suggested formula	UV photolysis (UV)	Ozonation (O₃)	Combined method (UV/O₃)	Het. Photocat. (TiO₂)
2.61	186		○●	○●	○●	○●
3.33	180	HO–C₆H₄–NH–C(=O)–N(CH₃)(CH₃)	○●	○●	○●	○●
4.00	186		○●	○	○●	○●
4.85	164			○●	●	●

Table 4. By-products formed during the oxidative transformation of monuron
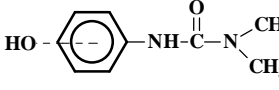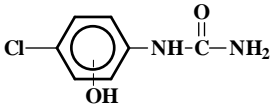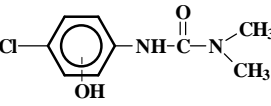(○: detected without enrichment by SPE, ●: detected after enrichment by SPE)

Retention time (min)	M	Cl	Suggested formula	UV photolysis (UV)	Ozona-tion (O₃)	Combined method (UV/O₃)	Het. Photocat. (TiO₂)
2.59	202	0		○●	○●	○●	○●
3.58	235	0		○●	○●	○●	○●
4.88	153	1		●		●	●
5.63	214	1				●	●
5.99	198	1	possible isomers of monuron				●
7.58	198	1				●	●
9.54	198	1			○●	○●	
11.09	220	1		●	●	●	

We have identified the most by-products for diuron, followed by linuron, while we could identify only 2 and 1 products for monuron and fenuron, respectively. In the case of monuron we have found several products with the same mass, which we consider to be contamination in the initial compound.

Conclusions
- We have successfully identified the main products of the oxidative transformation of four phenylurea herbicides
- The main reaction pathways have been found to be the dehalogenation and hydroxylation of the aromatic ring, and also the demethylation and oxidation of the methyl groups

References
[1] Barbash, J.E., Thelin, G. P., Kolpin, D. W., Gilliom, R. J., J. Environ. Qual., 2001. 30(3): p. 831-45.
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[3] Hoigne, J., The Handbook of Environmental Chemistry, 1998.
[4] Kovalczuk, T., J. Poustka, and J. Hajslova, Czech J. Food Sci., 2006. 26(2): p. 146-152.