

# A method for remediation of soil contaminated with simazine

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**Keywords:** simazine, remediation, soil, ozone.

**Abstract:** Although the utilization of pesticides accounted for the group of persistent organic pollutants was banned years ago, a count of pesticides are still directly or indirectly a source of contamination in Europe. One of them, simazine is still allowed for use in the United States. Aim of this experiment was development of soil remediation method which could be utilized for degradation triazine class pesticides – simazine was an example used. A method for soil remediation based on ozonation processes in fluidized bed was successfully utilized for removal of simazine from contaminated soil. For the study soil highly contaminated with simazine up to the concentration of 0.05% w/w was used. Determination of the pesticide levels in soil was performed using extraction and gas chromatography. The method allowed 80% reduction of pesticide concentration level. The degradation of pesticide was accompanied with changes of physicochemical parameters of soil, i.e., decrease of pH and a increase of nitrates concentration. Despite changes in physicochemical properties of the soil, the developed method proved to be highly effective and can be successfully applied on an industrial scale.

## Introduction

Since the Stockholm Convention on Persistent Organic Pollutants (POPs) (PAN 2009) and further international and internal legislative initiatives, e.g. Polish National Plan for Waste Management (KPGO) (KPGO 2010), the international community has been obliged to dispose banned plant protection agents. However, due to purely protected toxic waste disposals a count of incidents of soil contamination occurred. Up to date the most common approach to soil contamination problem is transporting of chemically contaminated soil on hazardous waste disposals. This results in additional economical costs of soil transport and the need for landfill leachate treatment. Verification of current law and state of the art (Balawejder 2012) lead to a conclusion that there is a need for scale effective soil remediation procedures that could be utilized in order to handle various toxic compounds such as pesticides.

A number of plant protection agents count for group of Persistent Organic Pollutants (POPs). One of them is simazine (6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine), which is a herbicide of the triazine class. Triazines are often used in crops, e.g., corn or potatoes cultivation. Compounds from this class and their degradation products are stable in soil (Barchańska et al. 2013).

Aside of the carbon-nitrogen aromatic ring simazine also contains chlorine atom and two ethyl amino groups connected to the ring. Aromatic properties and stabilization of carbon-nitrogen ring originates from delocalized charge of additional electrons between atoms of carbon and nitrogen (Gunasekara 2004). Simazine is thermally stable, colorless or white powder that is moderately soluble in water 5 mg/dm<sup>3</sup> (at room temperature). Solubility of simazine is in general low but highly dependent on temperature which is contributing to its mobility in the environment (Gunasekara 2004) mainly in the ground water (Camel and Bermond 1998).

Simazine is utilized for the control of broad-lived weeds and one year grass on farmland, fruits orchards, vinicultures, floricultures, bushes and forest trees. This active compound is a commercially available product and it can be found in various physical forms (powder, fluid, granular) (Gunasekara 2004). A number of maize and sugar cane strains are immune to simazine due to hydrolytic enzyme. Therefore, this compound can be effectively utilized for protection of those plantations.

In all countries of the EU utilization of simazine and other herbicides of the triazine class is banned. However, those compounds are in common use in the USA. One should consider the environmental risks of those compounds, such as high toxicity towards alga and a moderate toxicity towards fish and more complex organisms. Moreover, simazine can be absorbed by

plants where it is accumulated mainly in leaves and roots. This is related to a natural uptake of water and nutrition from soil. On the other hand, no accumulation was found in stalk and head.

Despite the low solubility in water, simazine can have an indirect impact on the environment due to the circulation of this herbicide. Toxicity of simazine towards water life is far higher than toxicity towards soil biota. This is a result of the natural processes occurring in soil. In particular, various toxic compounds show a high affinity towards soil organic matter, which reduces the bio availability of those compounds (Gunasekara 2004).

Simazine shows no acute toxicity, however, longer exposure may result in sub-acute toxicity.

It is relatively stable in soil and its half life time according to various data varies between 36 and 234 days. It has been reported that in laboratory condition this compound can undergo dechlorination if treated with high temperature and aggressive base. In nature, dechlorination can occur in acidic environment. As a result 2-hydroxy-4,6-bis(ethyloloamino)-simazine is generated which is lacking properties of the herbicide. Simazine can also be dealkalized and its metabolic product *N*-dealkylsimazine is formed. Photochemical degradation can lead to dealkalization of other alkyl group in *N*-dealkylsimazine. As a result its metabolic product diaminochlorotriazine is formed, which shows no herbicidal properties (Gunasekara 2004).

Half-life time values under aerobic and anaerobic condition show that simazine is highly persistent within the environment and it is rather resistant to degradation by microorganisms. However, there are microorganisms which can degrade simazine. They can utilize this compound as the only source of carbon and nitrogen (Kodama et al. 2011). Utilization of such microorganisms may potentially enable classic bioremediation methods for treatment of simazine contaminated soil (Zawierucha et al. 2014).

Simazine can be also degraded with Advanced Oxidation Process – (AOP). Fenton and photo-Fenton methods can be successfully utilized (Gunasekara 2004, Hudson and Pignatello 1999), however, a combination of photo chemical degradation with advanced oxidation method is more effective when homo or hetero photo catalysis is used (Gunasekara 2004).

Ozone is a promising oxidant that was already successfully utilized for removal of PAHs and other persistent organic pollutants. However, simazine is resistant to oxidation by O<sub>3</sub> molecules, therefore, a decomposition of this oxidant with the generation of other reactive oxygen species is indispensable. Oxidation of this herbicide in aqueous environment was achieved with the support of Mn(II) and Fe(II) based catalyst (Camel and Bermond 1998). Reaction rate of simazine degradation was found to be pH dependent. At higher pH the degradation rate increases, which can result from the presence of hydroxyl ions that can take part in a non-catalytic degradation of ozone to non-selective and highly reactive hydroxyl radicals (Gunasekara 2004, Camel and Bermond 1998, Balawejder et al. 2014). Remediation of soil is an issue due to limitation of mass transfer between oxidant and remediated matrix. A solution of this problem may be fluidization, which has already been successfully utilized for remediation of DDT contaminated soil (Balawejder et al. 2013, Balawejder et al. 2014).

In this study authors investigated the suitability of previously developed soil remediation method for degradation of triazine class pesticides on the example of simazine.

## Experimental

### Materials

Simazine CAS No. 122-34-9, was purchased from Yick-Vic Chemicals & Pharmaceuticals (H.K.) Ltd. (China). Acetone purity grade pure per analysis was purchased from (Honeywell, p.a.). Ag<sub>2</sub>SO<sub>4</sub> (p.a.), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (p.a.) solution of Mohr's salt and ortho-phenantroline were bought from POCH (Gliwice Poland).

A fluidized bed reactor (reactor cross-section of 5 cm, bed height of 20 cm) was fed with ozone by Korona 02/10 ozone generator (maximum ozone yield was 10 g/h) (C.S.I EKOTECH, Piotrków Trybunalski, Poland). Next to the reactor chamber a cyclone with absorber/ozone destructor was placed. Ozone concentration was analyzed with a medium range Ozone Analyzer UV – 106M (0–1000 ppm) (Ozone Solutions, Hull, IA, USA).

### Methods

#### Determination of TOC for remediated soil

During the analytical procedure 0.1 g of analyzed soil was weighed into a conical flask of 100 cm<sup>3</sup>. Then 10 cm<sup>3</sup> of 0.068 M solution of potassium dichromate in sulfuric acid and 0.05 g of the Ag<sub>2</sub>SO<sub>4</sub> catalyst were added. Subsequently the flask was heated, and later kept at gentle reflux for 5 minutes. After cooling the flask to room temperature (25°C) the remaining K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was titrated with 0.1 M solution of Mohr's salt. As an indicator ortho-phenanthroline was used. On the basis of differences in the volumes of Mohr's salt used to titrate the blank and the test organic carbon content and organic matter in soils analyzed were calculated. TOC values were determined for all three replies of the degradation experiments.

#### Determination of grain size distribution

Grain size distribution of the soil was determined using the granulometric method. Based on the analysis of grain composition, the soil was classified as sandy loam (loamy sand) (van Reeuwijk 2002). The results of this analysis were summarized in Table 1.

**Table 1.** Grain size distribution of the investigated soil

Fraction	Mass percentage [%]	Particle size [mm]
sand	76	2–0.1
	5	0.1–0.05
silt	4	0.05–0.02
	6	0.02–0.006
clay	6	0.006–0.002
	3	<0.002

#### Investigation on simazine desorption from soil surface in fluidized bed reactor

In order to determine the possible desorption of simazine due to exposition to the air stream in experimental conditions without ozone a 210 g of simazine contaminated soil (simazine concentration was 0.05% w/w (210 g) was placed into the

chamber of fluidized bed reactor. Then, this soil was exposed to the air stream with flow rate 18 dm<sup>3</sup>/min. To monitor changes of simazine concentration soil samples were taken in regular time intervals.

#### **Remediation of simazine contaminated soil using ozone in a laboratory scale fluidized bed reactor**

Simazine contaminated soil was prepared in the following manner: first the simazine was dissolved in acetone, than the solution was mixed with the soil. The soil was left for 24 hours so the solvent would evaporate. Than 210 g of simazine contaminated soil (simazine concentration was 0.05% w/w (210 g) was placed into the chamber of fluidized bed reactor. Then, the soil was exposed to ozone stream (ozone concentration was 8–10 ppm and the gas flow rate 18 dm<sup>3</sup>/min). Later another portion of clean soil was subjected to ozonation as a control. To monitor the course of the remediation process the soil samples were taken in regular time intervals and the simazine concentration was determined. The experiment was conducted for 144 hours until no further changes of simazine concentration in soil were observed.

#### **Extraction of Pesticides and GC-MS Analysis**

To extract simazine from the soil, 10g soil samples were treated with 10 cm<sup>3</sup> acetone for 1 h. The extract was separated by filtration through a filter of medium density (Chempur, Poland) and residues were extracted again with 5 cm<sup>3</sup> of acetone for 1 h. Extraction was conducted at room temperature (about 20°C) using magnetic stirrer. Then, after the second filtration both extracts were mixed together. The obtained extract was placed in a separator flask and, 50 cm<sup>3</sup> of distilled H<sub>2</sub>O, 3 cm<sup>3</sup> of saturated NaCl solution and 7 cm<sup>3</sup> of methylene chloride were added. The mixture was shaken for 5 min. After separation of phases, another 7 cm<sup>3</sup> portion of fresh methylene chloride was added to the aqueous layer, and the shaking process was repeated. The organic phases were combined and evaporated in a vacuum rotary evaporator at 60°C at pressure of 0.4 bar. The residue was dissolved in 2 cm<sup>3</sup> of acetone and dried over anhydrous sodium sulfate (VI). The resulting solution was injected for GC-MS analysis. The response of the detector was examined by the analysis of several standards with different concentration prepared as described earlier. The calibration curves from the peak areas were linear with high correlation coefficients of more than 0.98 at the range from 0,001–0.6 g/kg. Analytics was done with gas chromatograph Varian GC-450 coupled with mass spectrometer MS-240 (Santa Clara,

CA, USA). All analyses were carried out under the following conditions: Analytes were separated on a capillary column: 30 × 0.25 × 0.25 – L (m) × ID (mm) × OD (mm), stationary phase: VF-5 ms, film thickness 0.25 μm. Temperature of the column oven: 50–300°C, with 10°C/min temperature gradient (20-min isotherm at 300°C). Injector 1079 PTV (split ratio 1:5), temp. of injection 200°C, injection volume 1 μL. MS detector settings: scan mode 50–500 m/z. Gas flow rate (He) 1 cm<sup>3</sup>/min.

#### **Impact of ozonation on soil pH during the experiment**

During the ozonation process soil pH was determined. Analysis was conducted as follows. A soil suspension was prepared by mixing soil with demineralized water in a mass ratio 1:5 and another soil suspension was prepared by mixing soil with a solution of 1 M KCl in a mass ratio 1:5. The measurement of pH was conducted after 24 h leaching using a potentiometric method for three independent samples.

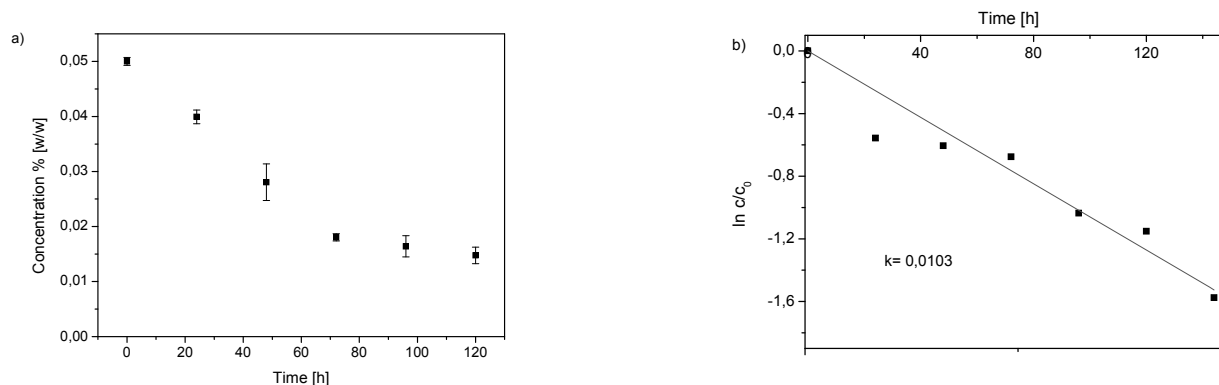
#### **Impact of ozonation procedure on the nitrates concentration in soil during the experiment**

Potential changes of pH of soil solution may result from the generation of nitric oxides during ozone generation when ozone is generated directly from the ambient air and as a result of mineralization of simazine. To verify this assumption the concentration of nitrate ions in soil was determined before and after the ozonation experiments for three independent samples. For this purpose soil solutions were prepared by mixing soil and deionized water in mass ratio 1:2. Then, the suspension was stirred for 12 hours and next filtered by a medium size paper filter. The filtrate was analyzed with ion chromatography. For this purpose ion chromatograph Dionex ICS-1000 with a conductometric detector and a suppressor ASRS 300 4 mm was used. Analytes were separated on the IonPack AS14A 4 × 250 column and IonPack AG14A 4 × 50 pre column. Phase: 8 mM sodium carbonate, 1 mM hydro carbonate, flow rate: 1 ml/min.

## **Results and discussion**

#### **Efficacy of soil remediation**

Three remediation experiments were conducted according to the procedure described above (see section 2.2). The course of simazine degradation was determined from three independent experiments and the results are presented as a mean (±SD) concentration of simazine in soil in Fig. 1.



**Fig. 1.** a) Course of simazine degradation during ozonation procedure. Obtained results are presented as a (mean ± SD) from three independent experiments, b) Determination of reaction rate constant.

To determine the efficacy of remediation method kinetic parameters of the process were quantified. A majority of reactions of organic compounds degradation in various environmental matrixes follows the first order kinetics. Therefore, to describe the kinetics of simazine degradation the equation describing the first order of kinetics was adapted.

$$-\frac{dc}{dt} = kc \Rightarrow t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

Where:

c – concentration,

t – time,

k – reaction rate constant

It was concluded that the course of  $\ln C/C_0$  is linear, which confirmed the assumption that the reaction follows the first order of kinetics (see Fig. 1).

On the basis of the results presented above the half life time of simazine during conducted experiments was determined to be around 67 h. However, the half-life time of simazine during degradation in nature is significantly longer. During fluidization process only a small portion of simazine was lost due to the desorption process. After 100 hours of exposition to the air stream simazine concentration in soil was reduced by less than 10%.

### Metabolic products of simazine degradation and the possible reaction pathway

Moreover, the reduction of simazine levels in soil was followed by generation of several metabolites that were detected after analysis of GC-MS chromatograms (see Fig. 2). One can observe that after the ozonation procedure a count of signals accounting to compounds which are probable metabolic products was detected.

One of the generated products i.e., *N*-dealkylosimazine, was also identified during simazine degradation conducted

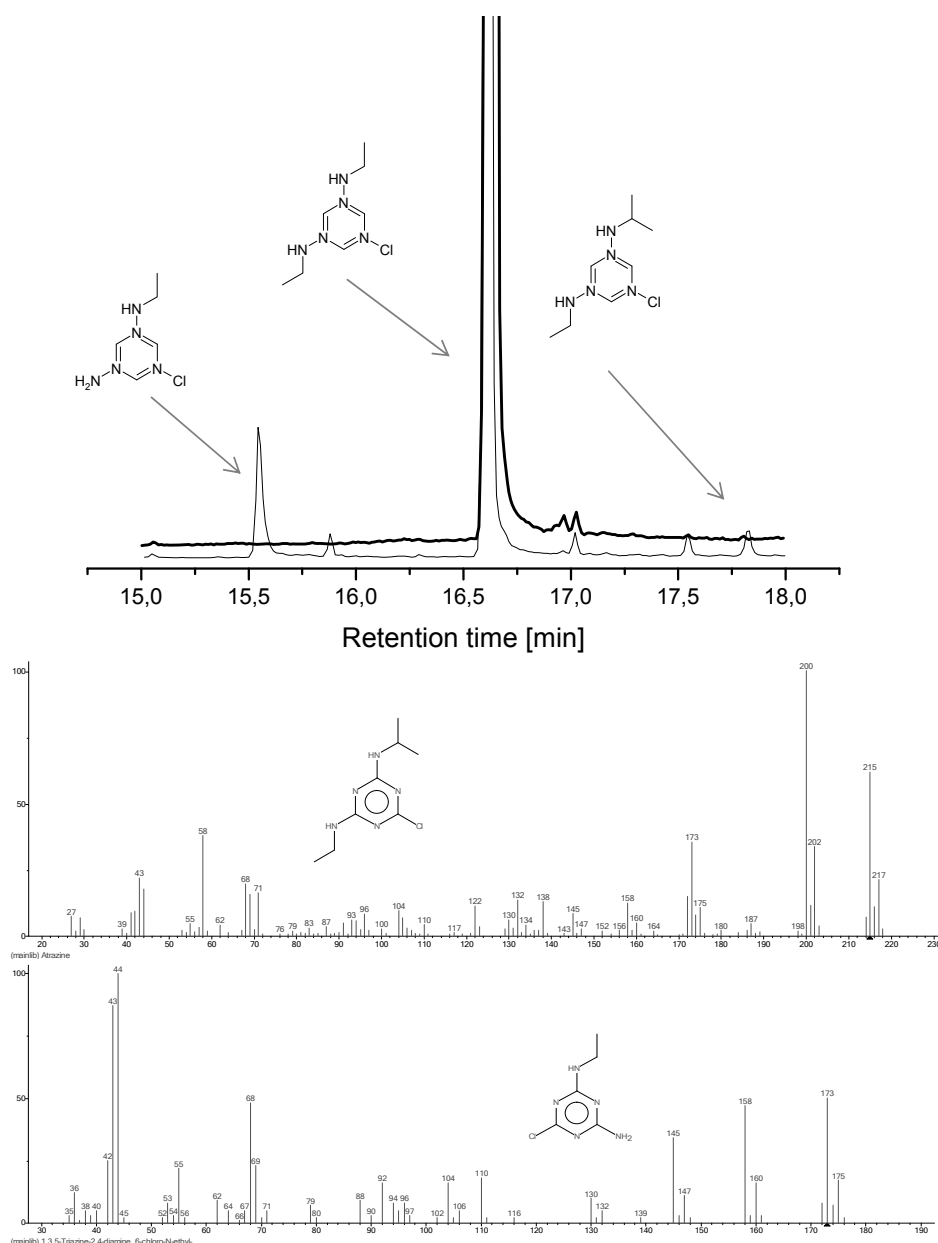


Fig. 2. Chromatograms and related mass spectra for simazine and its metabolites before and after 96 h of the exposition into the gaseous ozone

with other methods (Gunasekara 2004, Caracciolo et al. 2005, Meakins et al. 1995, Rivas et al. 2004). Second metabolite was atrazine, which was not detected in simazine standard or uncontaminated soil. Based on the analysis of concentration profiles of the generated products (see Fig. 3.) it was concluded that these metabolites are products of consecutive reactions during simazine degradation experiments.

After analysis of the course of simazine degradation and the course of its metabolites generation followed by their degradation, a pathway of simazine degradation during reaction with ozone and other reactive species, e.g., hydroxyl radicals, was suggested (see Fig. 4). Probably this process has a radical mediated or mixed mechanism. It is suggested that in the first stage a hydrogen atom is abstracted from the ethylic group with the generation of secondary radical, then, the C-N bond breaks which leads to dealkylation product and generation of alkyl radicals. These radicals can take part in

consecutive radical alkylation of the reactive radical species generated from simazine, which leads to generation of atrazine as a product. However, the described reactions are of negligible importance since the concentration of detected metabolites is relatively low comparing to the initial concentration of simazine (see Fig. 2). It is expected that the main pathway of its degradation is direct mineralization to inorganic products such as  $\text{CO}_2$ ,  $\text{NO}_x$ ,  $\text{H}_2\text{O}$  and  $\text{HCl}$ .

#### Impact of the procedure on the soil properties

Based on the analysis of pH and the nitrate concentration it was concluded that the remediation procedure had an impact on soil characteristics. During 144 hours of soil exposition both parameters changed significantly which was analyzed with a test-t of the significance of the differences between two populations means at significance level  $\alpha=0.01$ . as presented in Table 2.

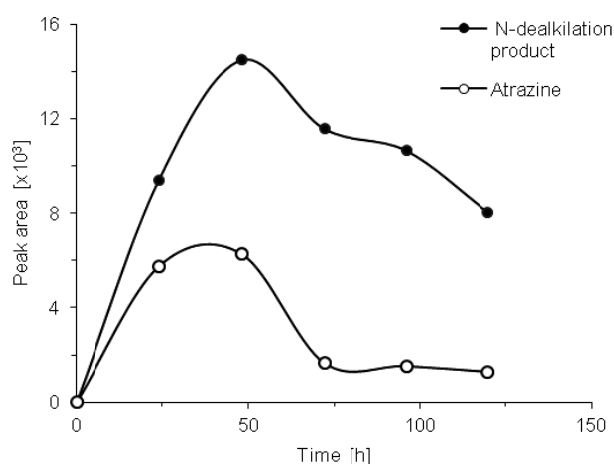


Fig. 3. Course of generation of simazine degradation products and their further degradation

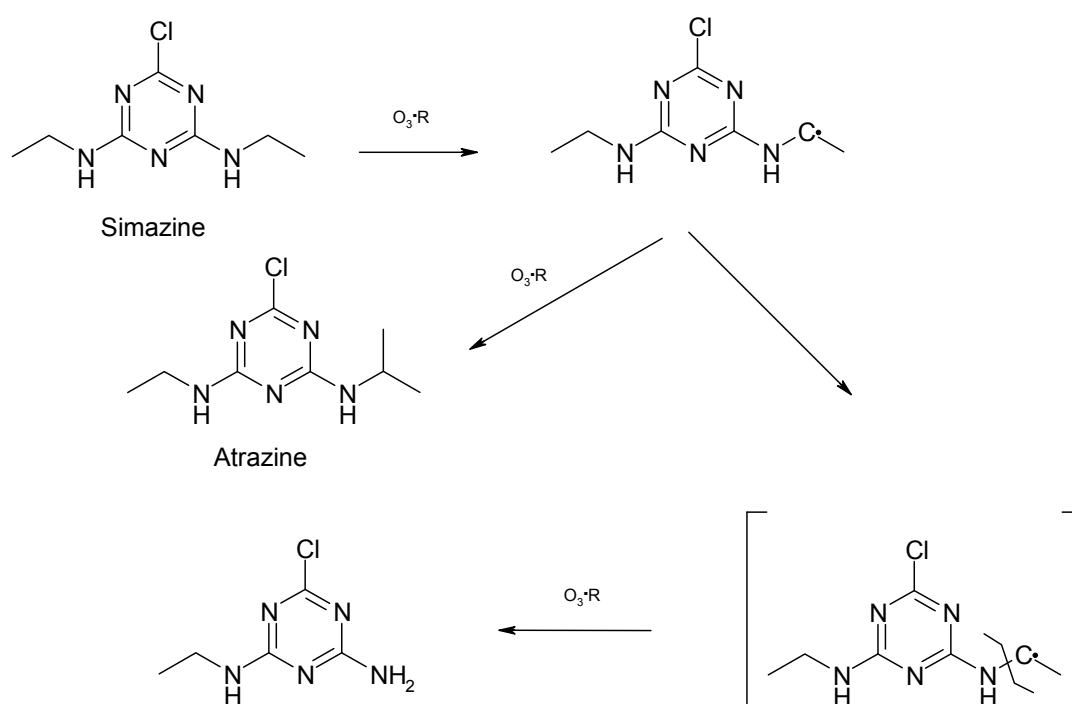


Fig. 4. A suggested pathway of simazine degradation during exposition to the mixture of air and ozone



**Table 2.** Values of pH and concentration of the nitrates during the remediation procedure

	pH in H <sub>2</sub> O	pH in KCl	Nitrates concentration [mg/kg]	TOC
Uncontaminated soil before ozonation	6.91±0.32	6.43±0.36	36.3±1.4	5%±0.5%
Uncontaminated soil after ozonation	4.42±0.21	4.47±0.22	488.6±4.2	5%±0.5%
Contaminated soil before ozonation	6.91±0.34	6.43±0.29	36.3±0.34	5%±0.5%
Contaminated soil after ozonation	4.37±0.27	4.45±0.31	529.3±0.27	5%±0.5%

As presented, the detoxication process had an impact on the characteristics of the investigated soil. Lowering of the soil pH is not a desired effect, since at lower pH the mobility of heavy metals in soil is increased. However, the soil pH can be easily compensated by standard agrochemical procedures. There is a clear correlation between the decreased pH and the elevated concentration of NO<sub>3</sub><sup>-</sup> ions. Those ions can be generated during oxidation of simazine, but more probable, they are generated during ozone generation in electric arc from ambient air and later absorbed by the soil. This issue could be possibly eliminated if ozone would be generated from pure oxygen. As presented in Table 2 the TOC values remained on constant levels before and after the experiment. However, it cannot be excluded that some conversion of organic matter form occurred.

## Conclusion

In this study a procedure for detoxication of pesticide contaminated soil was utilized for remediation of soil contaminated with a compound from triazine herbicide class (simazine).

Soil detoxication procedure was proven to be successful. After 144 hours of exposition on the stream of gaseous ozone the concentration of simazine was reduced by over 80%. This is a satisfactory result since simazine half-life time in soil under natural condition reaches up to 234 days. Based on the identified products a pathway of simazine degradation was suggested. What is important *N*-dealkylosimazine that was the main metabolite of Simazine degradation shows no herbicide properties. Other metabolites such as atrazine were detected only as a trace (see Fig. 2). Atrazine was not yet identified as a metabolic product of simazine degradation. The research presented can be exploited for scaling-up in order to design a technical scale process for the removal of simazine from solid materials such as soil.

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