University of Belgrade
Technical Faculty in Bor
28th International Conference Ecological Truth
& Environmental Research

# EcoTER'20

# PROCEEDINGS

EDITOR
Prof. Dr Snežana Šerbula

16 - 19 June 2020, Hotel Aquastar Danube, Kladovo, Serbia

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**ECOLOGICAL TRUTH AND ENVIRONMENTAL RESEARCH – EcoTER'20**

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**Publisher:** University of Belgrade, Technical Faculty in Bor

**For the Publisher:** Dean Prof. Dr Nada Štrbac

**Printed:** GRAFIK CENTAR, Beograd, 60 copies

**Year of publication:** 2020

ISBN 978-86-6305-104-1

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

502/504(082)(0.034.2)
574(082)(0.034.2)

**INTERNATIONAL Conference Ecological Truth & Environmental Research (28 ; 2020 ; Kladovo)**

Proceedings [Elektronski izvor] / 28th International Conference Ecological Truth and Environmental Research - EcoTER'20, 16-19 June 2019, Kladovo, Serbia ; [organized by University of Belgrade, Technical faculty in Bor (Serbia)] ; editor Snežana Šerbula. - Bor : University of Belgrade, Technical faculty, 2020 (Beogad : Grafik centar). - 1 USB fleš memorija : ilustr. ; 9 x 6 cm (u obliku kartice)

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 60. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-6305-104-1

а) Животна средина -- Зборници б) Екологија -- Зборници

COBISS.SR-ID 15372809

# 28th International Conference Ecological Truth and Environmental Research 2020

**is organized by:**

**UNIVERSITY OF BELGRADE, TECHNICAL FACULTY IN BOR (SERBIA)**

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## *PREFACE*

*The world today is faced with the rapid changes in technology. The excessive unsustainable consumption of fossil fuels and primary raw materials require a multidisciplinary approach in finding adequate sustainable solutions. That is why environmental research and ecological truth are at the focus of the 28th International Conference Ecological Truth & Environmental Research 2020 (EcoTER'20), which will be held at Kladovo, Serbia, 16-19 June 2020. On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the Conference.*

*We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.*

*The 28th International Conference Ecological Truth & Environmental Research 2020 is organized by the University of Belgrade, Technical faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, University of Zagreb, Faculty of Metallurgy – Sisak, University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.*

*These proceedings include 51 papers from the authors coming from the universities, research institutes and industries in 7 countries: Russia, Lithuania, Nigeria, Croatia, Bosnia and Herzegovina, Montenegro and Serbia.*

*As a part of this year's conference, the third student section is being held. We appreciate the research of the students and their mentors who have made a contribution to the conference. Abstracts of the students' papers have been included into the EcoTER'20 proceedings.*

*Financial assistance provided by the Ministry of Education, Science and Technological Development of the Republic of Serbia is gratefully acknowledged.*

*We appreciate the effort of all the authors who have contributed to these proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the Conference participants for their support to EcoTER'20. Sincere thanks go to all the people who have contributed to the successful organization of EcoTER'20.*

*On behalf of the 28th EcoTER Organizing Committee,*

*Snežana Šerbula, Professor*

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# TOXICITY SCREENING AFTER DEGRADATION OF ORGANOPHOSPHORUS PESTICIDES WITH CHLORINE DIOXIDE

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## Abstract

*Effectiveness, mineralization and toxicity of four organophosphorus pesticides (OPPs) azamethiphos (AZA), dimethoate (DM), fenitrothion (FEN) and malathion (MAL) in water with chlorine dioxide ($ClO_2$) as degradation agent were investigated. Analyses included toxicity tests of parent pesticides and their degradation products (DPs), using Daphnia magna test organisms, and total organic carbon (TOC) analysis. Toxicity tests showed that all four pesticide DPs were less toxic than parent pesticides, but DM had higher toxic DPs compared to parent AZA, FEN and MAL. All DPs were classified as category III (on a scale from I to V) of toxicity as acutely toxic. TOC analysis showed that AZA has lowest (only 18%) and MAL has highest mineralization (56%). Considering the obtained results, it could be concluded that $ClO_2$ efficiently degrades AZA, DM, FEN and MAL and represents good solution for a safer environment.*

**Keywords**: organophosphorus pesticides, chlorine dioxide, TOC, toxicity

## INTRODUCTION

According to US EPA estimates, organophosphorus pesticides (OPPs) represent about 40% of the world market value [1]. They are the most popular and most used pesticides because of their low cost, wide spectrum of application and multi-pest control capability. The widespread application of the OPPs represents a great potential risk to environment and human life [2]. They could easily reach and contaminate the underground and surface water by leaching or runoff [3].

It has been found that OPPs could be very toxic to human health [2]. They can cause minor and major disruptive disorders, such as allergies, nausea, pancreatitis, spontaneous abortions and death [2,4]. It was reported that OPPs are neurotoxic and high doses of them involve inhibition of acetylcholinesterase [4]. Many researchers have suggested association between post natal exposure of children with OPPs and caused health disorders. Attention deficit hyperactivity disorder was noticed [5], also poorer short-term memory and attention [6], slower motor speed [7], and developmental delay [8]. Because of this and many other health disorders, significant number of OPPs has been restricted by Environmental Protection Agency (EPA) and European Union (EU) [9].

Among the oxidants, chlorine dioxide ($ClO_2$) has been increasingly employed as disinfectant in water treatment systems due to its antibacterial and antiviral properties [10]. As a powerful oxidant, $ClO_2$ can remove many organic and inorganic pollutants [11,12]. Previous studies reported oxidative degradation using $ClO_2$ of some pesticides and pharmaceuticals [3,13,14].

The aim of this study was to investigate effectiveness, mineralization and toxicity of four OPPs (AZA, DM, FEN and MAL (Figure 1)) and their DPs, in water using $ClO_2$ as degradation agent. Toxicity screening was examined with the test organisms *D. magna*. Also, the mineralization degree was obtained by total organic carbon (TOC) analysis.

## MATERIALS AND METHODS

### Chemicals

In this research AZA, DM (Makhteshim Agan, 98%, obtained from the Institute for Plant Protection, Belgrade), FEN and MAL (Sigma Aldrich, 97%) were used. Concentrations of pesticides in experiments were 10 mg/L for AZA and DM and 20 mg/L for FEN and MAL. Reason why we used 20 mg/L AZA and DM, not 10 mg/L like FEN and MAL, was the quantification limit on high performance liquid chromatography (HPLC) for these two pesticides which becomes important for trace monitoring in the final steps of degradation. For toxicity test pesticides were diluted in medium, prepared according to standard procedure OECD Guideline 202, 2004 [15, 16]. $ClO_2$ was prepared by dissolving sodium chlorite (TwinOxide®) and sodium bisulphate (TwinOxide®) in 1 L of deionized water and standardized with 0.1000 mol/dm$^3$ standard solution of sodium thiosulphate according to the Standard Method SRPS EN 12671:2009 [17].

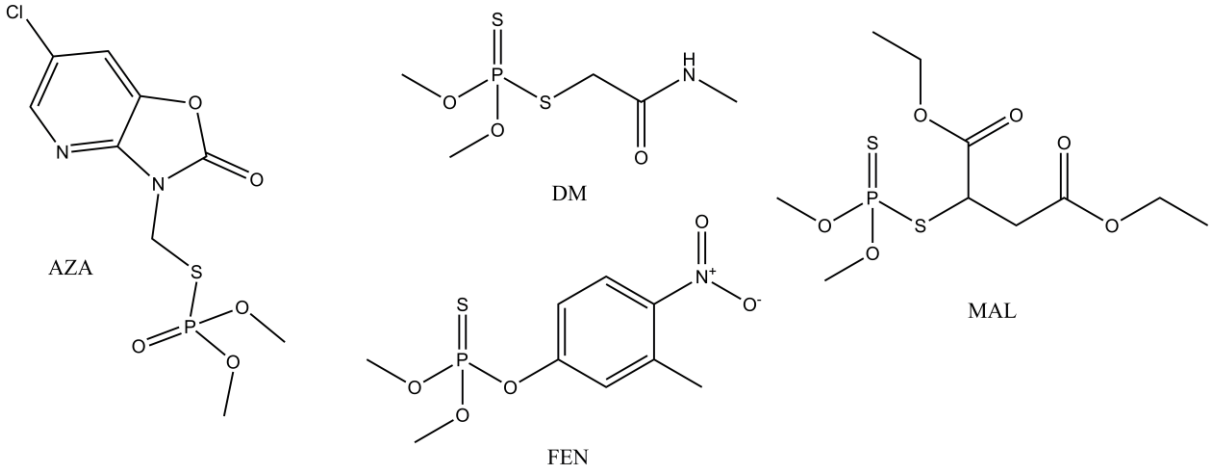


***Figure 1*** *Structures of organophosphorus pesticides*

### Experimental

*Optimization of pesticide degradation and preparation of samples for TOC analysis*

The optimal conditions for degradation of OPPs with $ClO_2$ in deionized water had to be determined. Degradation using different concentrations of $ClO_2$ (5 and 10 mg/L), degradation

time (0.5, 1, 2, 3, 6 and 24 h) and pH values (2, 3, 7, 9) was studied. The percentage of degradation was determined by HPLC analysis with photodiode array detection (DAD) as described previously by Pergal *et al.* [3]. Samples with the highest degree of degradation for each pesticide were analyzed by TOC analysis. TOC analysis was done on Zellweger LabTOC 2100 TOC Analyzer in accordance with method ISO 8245:2007 [3]. The optimal conditions for degradation of each pesticide were also applied to preparation of samples for toxicity tests.

*Sample preparation for toxicity tests*

All samples were diluted in medium prepared according to Klüttgen *et al.* [16]. One part of initial pesticide solution was taken for toxicity test and other part was set to optimal parameters and treated with optimal concentration of $ClO_2$ for obtaining of DPs. Test organisms *D. magna* were exposed to solution of pesticides and their DPs. A detailed examination using toxicity tests can be found in our paper Pergal *et al.* [3].

## RESULTS AND DISCUSSION

### Results of degradation efficiency

Optimization of OPPs degradation (AZA, DM, FEN and MAL) was performed in deionized water under sunlight conditions described previously by Pergal *et al.* [3]. In Table 1 are presented summarized optimal conditions for OPPs degradation (ranged from 81 to 100% in efficiency) and which were determined using HPLC-DAD analysis.

***Table 1*** *Optimized conditions for degradation of pesticides with* $ClO_2$

| Sample name | Concentration of sample (mg/L) | Concentration of $ClO_2$ (mg/L) | pH value | Duration of degradation (h) | Degree of degradation (%) |
|---|---|---|---|---|---|
| Azamethiphos | 10 | 10 | 9 | 0.5 | 100 |
| Dimethoate | 10 | 10 | 7 | 24 | 97 |
| Fenitrothion | 20 | 10 | 2 | 24 | 81 |
| Malathion | 20 | 5 | 7 | 24 | 98 |

### Toxicity test results

Toxicity tests of the pesticide solutions and their DPs were evaluated using test organisms *D. magna*.

After a 48 h of test period number of live and dead neonates was determined, and $LC_{50}$ (lethal concentration which causes 50% mortality in the daphnids) was calculated for each pesticide and its DP. Results of $LC_{50}$ for parent pesticides and DPs are shown in Table 2. Solution of parent AZA has the highest mortality of neonates and FEN has the lowest mortality as compared to other parent pesticides, but it was still high. For DPs of pesticides, AZA has higher $LC_{50}$ value, while DM has the lowest $LC_{50}$ value compared to other pesticides. DM has the highest and AZA has the lowest mortality. The pesticides degradation products were less toxic than parent pesticides. When compared the toxicity results of pesticide solutions with their DPs, it could be concluded that $ClO_2$ degradation of AZA was

successful. Also, there should be noted that in case of other tested pesticides toxicity of DPs was noticeable lower in comparison to starting pesticide solutions.

***Table 2*** *$LC_{50}$ values of pesticides and their degradation products (DPs) after 48 h of $ClO_2$ treatment*

| Sample name | $LC_{50}$ ( %, v/v) 48h | Sample name | $LC_{50}$ ( %, v/v) 48h |
|---|---|---|---|
| Azamethiphos | 2.5 | Fenitrothion | 23.2 |
| Azamethiphos DP | 61.3 | Fenitrothion DP | 45.8 |
| Dimethoate | 12.2 | Malathion | 12.9 |
| Dimethoate DP | 35.4 | Malathion DP | 42.6 |

A toxicity unit (TU) was calculated for each sample using the $LC_{50}$ results. On the scale from I to V [18] all DPs can be categorized in class III as acutely toxic.

**Results of mineralization analysis**

Mineralization percent was determined by TOC analysis for each pesticide and its DP. The results of mineralization are presented in Table 3. Results show that AZA and DM have low level of mineralization and MAL has the highest mineralization level as compared to other pesticides. But, low level of mineralization does not always mean that something is harmful or toxic. When all results have been compared (HPLC analysis, *D. magna* test and TOC analysis), we could see that AZA has a good degradation percent (100%) and its DP relatively high $LC_{50}$ (61%). It means that $ClO_2$ degrades AZA very efficiently, with significantly less toxic DPs but they are still of organic origin. FEN and MAL both have good degree of degradation (81 and 98%, respectively) and mineralization (45 and 55%) and less toxic DPs. In case of DM, even $ClO_2$ degrades this OPP with degradation efficiency of 97%, $ClO_2$ creates relatively toxic DPs and they are mostly of organic origin (mineralization of only 23%).

***Table 3*** *Mineralization degree of degradation products (DPs) of pesticides*

| Sample name | Degree of mineralization (%) |
|---|---|
| Azamethiphos DP | 17.7 |
| Dimethoate DP | 22.5 |
| Fenitrothion DP | 45.2 |
| Malathion DP | 55.8 |

## CONCLUSIONS

In this research, toxicity of AZA, DM, FEN and MAL pesticides and their DPs, after degradation with $ClO_2$ under optimal conditions for each pesticide, was studied. The toxicity test was done on *D. magna* neonates. Degree of mineralization was also obtained by TOC analysis for pesticides and DPs.

Results showed that AZA has a good degradation percent (100%) and relatively high $LC_{50}$ (61%). It means that $ClO_2$ degrades AZA very well, with significant less toxic DPs but they are still of organic origin (18% of mineralization). FEN and MAL both have good degree of

degradation (81 and 98% respectively) and mineralization (45 and 56%) and less toxic DP. In case of DM, $ClO_2$ degrades this OPP with degradation degree of 97%, $ClO_2$ creates relatively toxic DPs and they are mostly of organic origin (mineralisation of only 23%).

The results of toxicity tests showed that all DPs of pesticides belong to class III as acutely toxic. Further research should be directed towards obtaining less toxic products.

## ACKNOWLEDGEMENT

*This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, (Grant No. 451-03-68/2020-14/200026; 451-03-68/2020-14/200168). The authors would like to thank TwinOxide-RS d.o.o. for providing components for the preparation of $ClO_2$ (TWINS preparation).*

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