

**FATE AND TRANSPORT OF GLYPHOSATE AND
DEGRADATION BYPRODUCTS: IMPLICATIONS FOR
REMEDICATION AT CKD_u ENDEMIC AREAS IN SRI
LANKA**

Abesinghe Arachchige Shankani Uthpala Gunarathna

(158008R)

Degree of Master of Engineering

Department of Civil Engineering

University of Moratuwa
Sri Lanka

February 2018

**FATE AND TRANSPORT OF GLYPHOSATE AND
DEGRADATION BYPRODUCTS: IMPLICATIONS FOR
REMEDICATION AT CKD_u ENDEMIC AREAS IN SRI
LANKA**

Abesinghe Arachchige Shankani Uthpala Gunarathna

(158008R)

Thesis submitted in partial fulfillment of the requirements for the
degree Master of Engineering in Civil Engineering

Department of Civil Engineering

University of Moratuwa
Sri Lanka

February 2018

DECLARATION

“I declare that this is my own work and this thesis does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

Also, I hereby grant to University of Moratuwa the non-exclusive right to reproduce and distribute my thesis, in whole or in part in print, electronic or other medium. I retain the right to use this content in whole or part in future works (such as articles or books).”

Signature:

Date:

The above candidate has carried out research for the Masters thesis under my supervision.

Name of the supervisor: Dr. (Ms.) W. B. Gunawardana

Signature of the supervisor:

Date:

The above candidate has carried out research for the Masters thesis under my supervision.

Name of the co-supervisor: Prof. J. M. A. Manatunge

Signature of the supervisor:

Date:

Abstract

Glyphosate, which is commercially available as Roundup®, was the widely used herbicide in Sri Lanka until 2015 and is suspected to be one of the causal factors for Chronic Kidney Disease of unknown etiology (CKDu). This research, therefore, focuses on investigation of glyphosate and Aminomethylphosphonic acid (AMPA), the major degradation product of glyphosate, immobilization in top soil and subsequent mobilization to water and their effective and efficient removal. A field study and a series of mesocosm studies were performed to investigate the immobilization of glyphosate in the top soil and the mobilization of glyphosate and AMPA to water. Further, a long term batch experimental study was carried out to study the degradation of glyphosate in water in the absence and presence of hardness, for 240 days. Finally, the applicability of Ozonation process for glyphosate removal from water was studied using batch experiments. Glyphosate and AMPA were analyzed using LC/MS and GC/MS. It was evident that glyphosate persistence in the environment was high, especially due to the sorption of glyphosate to soil. Mobilization of glyphosate to water was minimal and it was catalyzed by the event of first precipitation after the application of glyphosate and application of Triple Super Phosphate (TSP) to the soil. Furthermore, glyphosate degradation was hindered and its persistence was increased due to the presence of hardness in water and surfactants in commercial grade glyphosate. Ozonation process rapidly degraded the glyphosate present in water both in the absence and presence of hardness to levels less than 700 µg/L which is the USEPA Maximum Contaminant Level for drinking water. In conclusion, this study provides the insight that the dominant mechanism of glyphosate in the environment is adsorption of glyphosate to the topsoil and mobilization to water is minimal. Further, Ozonation is an effective and efficient method to remove glyphosate in water in CKDu prevalent areas despite the presence of hardness and surfactants.

Key words: Adsorption, AMPA, Desorption, Hardness, Ozonation.

ACKNOWLEDGEMENT

First of all, I would like to extend my heartfelt gratitude to my supervisor Dr. Buddhika Gunawardana, for giving me the opportunity to complete the research. Your guidance and encouragement given at every step of the way in the research helped me to achieve the goals. Your support was immense and I am very fortunate to have you as my supervisor. I extremely appreciate the advice given in experiments, writings and moral assistance given to complete this research.

I am very grateful to my co-supervisor Prof. Jagath Manatunge, for providing his guidance and support for the research project. Your advice and assistance given is very much appreciated. Furthermore, I would like to extend my gratitude to Prof. Mahesh Jayaweera for guiding me to conduct a fruitful and successful research. Your feedback on my experiments, writing, helped me to complete a very productive study.

I wish to express my sincere thanks to the laboratory staff of Environmental Engineering Laboratory, Department of Civil of Engineering, University of Moratuwa; Ms. Nilanthi Gunathilake and Mr. Justin for the assistance received to conduct my research experiments successfully in the Environmental engineering laboratory. Additionally, I wish to thank Mr. Kasun Zoysa, analytical chemist, for providing his expertise and knowledge for the research, especially with the development of the GC/MS method for glyphosate and AMPA analysis. Moreover, I would like to extend my thanks to Mr. Pradeep Herath, former analytical chemist, for giving his insight at the design phase of the research.

Furthermore, I wish to acknowledge the financial assistance given by the National Research Council (NRC), Sri Lanka (Grant Nos. 15-056 and 12-086) and the Senate Research Committee (SRC) Grant of the University of Moratuwa (Grant No. SRC/LT/2015/03) for the successful completion of this study.

I would like to thank head and the staff of the Department of Civil of Engineering, University of Moratuwa for assisting me in various ways to complete the research study. Additionally, I am grateful to the staff of the Soil Mechanics Laboratory, Department of Civil of Engineering, University of Moratuwa for the assistance provided to conduct my experimental work. Moreover, I would like to extend my

gratitude to the staff, Analytical Laboratory, Department of Materials Science and Engineering, University of Moratuwa for allowing me to use laboratory equipment.

Further, my sincere thanks are extended to Mr. Rohitha Gunarathna, Mr. Imesh and staff of Bureau Veritas Consumer Product Services Lanka (Pvt) Ltd. for providing laboratory services to conduct the LC/MS analysis for the research project. Additionally, I would like to thank Mr. Gunapala and his family for helping me with collecting samples in CKDu prevalent areas.

I would like to thank Ayomi, Thilini and Gimhani for their friendship, guidance, strength and assistance given in the period of the research study. Thank you, Madhusa for being my research partner and helping me in various ways to complete the research and giving me the moral support for the completion. My special thanks go to Nipuni for helping me with the experimental work, when I am going through a difficult phase of my life.

I am grateful to my family for being there for me, giving their unconditional love and support to fulfill my aims. Finally, I would like to thank my husband, Chamod for supporting, encouraging and understanding me in my quest.

TABLE OF CONTENTS

DECLARATION	i
Abstract	ii
ACKNOWLEDGEMENT	iii
TABLE OF CONTENTS	v
LIST OF FIGURES	viii
LIST OF TABLES	x
LIST OF ABBREVIATIONS	xi
1. INTRODUCTION	1
1.1. Introduction.....	1
1.2. Approach.....	3
2. LITERATURE REVIEW	5
2.1. Glyphosate	5
2.2. Commercial use of glyphosate	6
2.2.1. Course of action of glyphosate in plants	6
2.2.2. Effect of surfactants present in Roundup®	7
2.3. Degradation of glyphosate	8
2.3.1. Possible degradation mechanisms	8
2.3.2. Microbial degradation of glyphosate	9
2.3.3. Photodegradation of glyphosate	10
2.4. Glyphosate interaction with soil	11
2.4.1. Factors affecting adsorption of glyphosate onto soil particles	12
2.4.2. Impact of application of phosphate fertilizer on glyphosate sorption to soil	14
2.5. Mobilization of glyphosate to surface water and groundwater	14
2.6. Effect of glyphosate on human health.....	16
2.6.1. CKDu	16
2.7. Removal of glyphosate from water.....	19
2.7.1. Possible methods of glyphosate removal from water	19

2.7.2. Ozonation.....	19
3. MATERIALS AND METHODS.....	21
3.1. Experimental Procedures and setups.....	21
3.1.1. Persistence of glyphosate in different environmental matrices in areas where CKDu is prevalent – Field studies	21
3.1.2. Glyphosate and AMPA immobilization in top soil and mobilization of glyphosate and AMPA to water – Mesocosm studies	26
3.1.3. Glyphosate (high purity and commercial grade) degradation pattern in deionized water and hard water	31
3.1.4. Applicability of Ozonation process as an effective and efficient removal method of glyphosate and AMPA from water	32
3.2. Extraction and detection of glyphosate and AMPA in all samples.....	33
3.2.1. Extraction and detection of glyphosate and AMPA in soil samples	33
3.2.3. Detection of glyphosate and AMPA in deionized water.....	33
4. RESULTS AND DISCUSSION	35
4.1. Persistence of glyphosate in different environmental matrices in areas where CKDu is prevalent – Field studies	35
4.1.1. Glyphosate and AMPA levels in topsoil.....	35
4.1.2. Glyphosate and AMPA levels in surface water	42
4.1.3. Glyphosate and AMPA levels in shallow groundwater	45
4.1.4. Glyphosate and AMPA Levels in Sediment	47
4.1.5. Summary	48
4.2. Glyphosate and AMPA immobilization in top soil and mobilization of glyphosate and AMPA to water – Mesocosm studies.....	50
4.2.1. Immobilization of glyphosate in soil prior to precipitation events	50
4.2.2. Mobilization of glyphosate subsequent to multiple precipitation events	54
4.2.3. Mobilization of glyphosate subsequent to TSP application followed by multiple precipitation events	56
4.2.4. Non-detection of AMPA in soil and water samples.....	57
4.2.5. Summary	58

4.3. Glyphosate (high purity and commercial grade) degradation pattern in deionized water and hard water.....	59
4.3.1. Glyphosate degradation in water.....	59
4.3.2. Effect of hardness on glyphosate degradation	59
4.3.3. Effect of presence of surfactants on degradation of glyphosate.....	60
4.3.4. Summary	60
4.4. Applicability of Ozonation process as an effective and efficient removal method of glyphosate and AMPA from water	62
4.4.1. Glyphosate degradation by Ozonation	62
4.4.2. Effect of hardness on glyphosate degradation by Ozonation.....	63
4.4.3. Effect of presence of surfactants on degradation of glyphosate by Ozonation	63
4.4.4. Summary	64
5. CONCLUSIONS	65
5.1. Contributions from the study	65
5.2. Recommendations.....	66
REFERENCE LIST	68

LIST OF FIGURES

Figure 2.1 Chemical Structure of glyphosate.....	5
Figure 2.2 Bjerrum diagram of glyphosate. Acid dissociation constants of glyphosate: pKa1 = 2.22, pKa2 = 5.44 and pKa3 = 10.13	5
Figure 2.3 Shikimate pathway and mode of action of glyphosate	7
Figure 2.4 Chemical Structure of Aminomethylphosphonic acid (AMPA)	8
Figure 2.5 Production of Sarcosine and inorganic phosphate by direct cleavage of C-P bond	9
Figure 2.6 Production of AMPA and glyoxylate by direct cleavage of C-P bond and further degradation of AMPA (1) cleavage of C-P bond and (2) transamination of AMPA	10
Figure 2.7 Glyphosate sorption by an iron oxide	12
Figure 2.8 Spread of CKDu in Sri Lanka.....	18
Figure 2.9 Ozonation mechanism	20
Figure 3.1 Study area; Thambalagollawa, Rembewa	22
Figure 3.2 Collection of top soil from agricultural fields	23
Figure 3.3 Sample collection from surface water bodies and preservation	23
Figure 3.4 Schematic diagram of the experimental setup	26
Figure 3.5 Experimental Setup for the plot study	27
Figure 3.6 Experimental Sequence; (a) Plot 01 - the control plot where neither glyphosate nor TSP were applied, (b) Plot 02 – the plot where only glyphosate was applied initially, (c) Plot 03 – the plot where glyphosate was applied initially and TSP was applied after 14 days and 28 days of application of glyphosate	29
Figure 3.7 Experimental setup for investigation of glyphosate degradation in water	31

Figure 3.8 Experimental Setup for Ozonation	32
Figure 4.1 Glyphosate/ AMPA concentration vs. Time.....	61
Figure 4.2 Degradation of glyphosate (high purity) using Ozonation(i) in the absence of hardness (◆) (ii) in the presence of hardness (■).....	62
Figure 4.3 Degradation of Roundup® using Ozonation (i) in the absence of hardness (◆) (ii) in the presence of hardness (■).....	62

LIST OF TABLES

Table 4.1 Glyphosate and AMPA levels of topsoil of agricultural fields selected for the study with other information related to agricultural practices	36
Table 4.2 Physical characteristics of topsoil samples	37
Table 4.3 Chemical characteristics of the topsoil samples	38
Table 4.4 Water quality characterization of surface water samples.....	43
Table 4.5 Water quality characterization of groundwater samples.....	45
Table 4.6 Organic matter content in the sediment samples	48
Table 4.7 Plot 02 – Only glyphosate application and effect of subsequent multiple precipitation.....	51
Table 4.8 Plot 03- Effect of TSP application and subsequent multiple precipitation	52
Table 4.9 Physical and chemical characteristics of the soil	53

LIST OF ABBREVIATIONS

Abbreviation	Description
AMPA	Aminomethylphosphonic acid
CKDu	Chronic Kidney Disease of unknown etiology
EPSP	5_enolpyruvylshikimate_3_phosphate synthase
EPSPS	Enolpyruvyl shikimate-3-phosphate synthase
GC/MS	Gas Chromatography/Mass Spectrometry
GFR	Glomerular filtration rate
LC/MS	Liquid chromatography/Mass Spectrometer
PEP	Phosphoenolpyruvate
POEA	Polyethoxylated tallowamine
S3P	5-hydroxyl of shikimate 3-phosphate
TFAA	Trifluoro-acetic anhydride
TFE	Trifluoroethanol
TSP	Triple Super Phosphate
UCSC	Unified Soil Classification System
USEPA	United States Environmental Protection Agency