



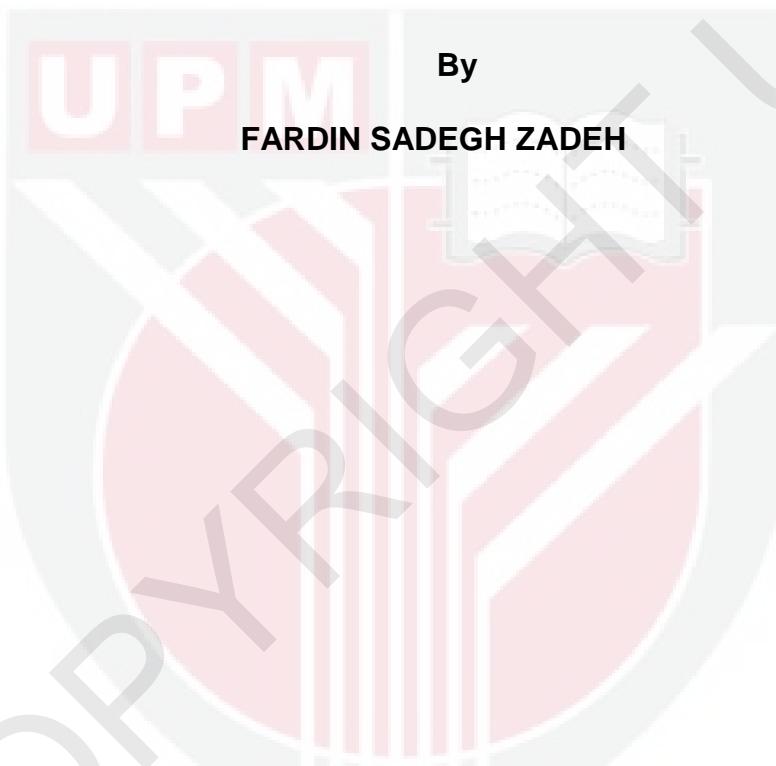
UNIVERSITI PUTRA MALAYSIA

**SORPTION-DESORPTION, DEGRADATION AND LEACHING OF
NAPROPAMIDE IN SELECTED MALAYSIAN SOILS**

FARDIN SADEGH ZADEH

FP 2010 30

**SORPTION-DESORPTION, DEGRADATION AND LEACHING
OF NAPROPAMIDE IN SELECTED MALAYSIAN SOILS**



By
FARDIN SADEGH ZADEH

Thesis submitted to the School of Graduate Studies,
Universiti Putra Malaysia, in Fulfilment of the Requirements for
the Degree of Doctor of Philosophy



September 2010

DEDICATION

Dedicated to my wife and family.

Their patience, encouragement, and support have allowed me to achieve
my goals.



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

SORPTION-DESORPTION, DEGRADATION AND LEACHING OF NAPROPAMIDE IN SELECTED MALAYSIAN SOILS

By

FARDIN SADEGH ZADEH

September 2010

Chairman: Samsuri Abd Wahid, PhD

Faculty: Agriculture

Sorption, degradation and leaching are the important processes affecting fates of pesticides in the soil environment. Sorption influences the magnitude of the other processes and is considered to be one of the major processes affecting the interactions occurring between pesticides and the solid phase in the soil environment. Dissipation of pesticides can occur by degradation and leaching. There is no reported study on napropamide fates in Malaysian soils or even in tropical soils. Napropamide is one of the pre-emergence herbicides used to control several grasses and broadleaf weeds in tobacco and kenaf fields in Malaysia. Sorption-desorption, degradation and leaching of napropamide were studied in selected Malaysian soils and Baging soil amended with chicken dung (CD) and palm oil mill effluent (POME). The ability of a UV-spectrophotometry to determine napropamide concentration in soil sorption study was studied as well. Results showed that UV-spectrophotometry method was as reliable as the HPLC in determining

napropamide concentration in the supernatant of batch equilibrium sorption study. Interference by dissolved organic carbon in the napropamide determination by the spectrophotometer method could be easily corrected using a dual beam spectrophotometer. Baging soil has very low affinity for napropamide. The sorption capacity (K_f) of Baging soil and Baging soil amended with 80 Mg ha⁻¹ CD and POME were 0.22, 41.6 and 3.96, respectively. Dissolved organic carbon (DOC) derived from CD or POME did not affect sorption capacity of amended Baging soil. The sorption capacities of the selected Malaysian soils for napropamide were in the following order: Linau (K_f = 66.2) > Teringkap (K_f = 56) > Gunung Berinchang (K_f = 43) > Jambu (K_f = 26) > Rudua (K_f = 8) > Baging soil (K_f = 0.22). The results indicated that sorption increased with increasing clay and organic carbon content (OC) of the soils. Among the BRIS soils studied, the Baging which has the lowest organic matter and clay content, also has the lowest K_f . Napropamide half-life was lowest in the Baging soil (43 d) and its half-life was increased to 69 (d) and 49.5 (d) with the addition of 20 Mg ha⁻¹ CD and POME, respectively. Degradation of napropamide decreased in Baging soil receiving DOC derived from CD and POME. The shortest and longest half-lives among the selected Malaysian soils were observed in Baging (43 d) and Linau soil (100 d), respectively. The results indicated that napropamide degradation decreased with the increasing soil sorption capacity. Napropamide was leached out earlier in the Baging soil as compared to the other soils. The results showed that soils which have low sorption capacities for napropamide leached napropamide earlier from the soil column. On the

other hand, for Linau soil which had the highest sorption capacity for napropamide ($K_f = 66.2$), no napropamide was detected in the leachate even after seven pore volumes of effluent water. The results also suggested that DOC did not affect the leaching of napropamide. Overall, application of napropamide in the selected Malaysian soils would not pose a threat to the environment especially the groundwater except in soil with low organic matter and clay content, and high hydraulic conductivity such as the Baging soil.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk mendapat ijazah Doktor Falsafah

**JERAPAN- NYAHJERAPAN, DEGRADASI DAN LARUTLESAP
NAPROPAMIDE DI TANAH MALAYSIA TERPILIH**

Oleh

FARDIN SADEGH ZADEH

September 2010

Pengerusi: Samsuri Abd Wahid, PhD

Fakulti: Pertanian

Jerapan, degradasi dan larutlesap adalah proses penting yang boleh mempengaruhi nasib racun perosak dalam persekitaran tanah. Jerapan mempengaruhi besarnya proses yang lain dan dianggap sebagai salah satu proses utama yang mempengaruhi interaksi yang terjadi antara racun perosak dan fasa pepejal di persekitaran tanah. Disipasi racun perosak boleh berlaku oleh degradasi dan larutlesap. Tidak ada kajian dilaporkan pada nasib napropamide di tanah Malaysia atau bahkan di tanah tropika sekalipun. Napropamide adalah salah satu racun rumpai pra-muncul yang digunakan untuk mengawal beberapa rumput dan rumpai berdaun lebar di ladang tembakau dan kenaf di Malaysia. Jerapan-nyahjerapan, degradasi dan larutlesap adalah proses utama yang mempengaruhi nasib pestisida di persekitaran tanah. Jerapan mempengaruhi napropamide telah dikaji pada tanah Malaysia yang terpilih dan tanah Baging yang telah diperbaiki dengan tahi ayam (TA) dan

eluen kilang kelapa sawit (EKKS). Kebolehan spectrofometer Ultra Lembayung (UL) untuk penentuan kepekatan napropamide dalam kajian jerapan tanah juga dikaji. Keputusan menunjukkan yang spectrophotometer-UL adalah boleh diharap sama seperti Kromatografi Cecair Prestasi Tinggi (KCPT) dalam penentuan napropamide di dalam supernatant kajian jerapan kumpulan keseimbangan. Gangguan dari karbon organik terlarut dalam penentuan napropamide menggunakan spektrofotometer boleh dibetulkan dengan mudah menggunakan spektrofotometer dua jalur. Tanah Baging mempunyai tarikan yang lemah kepada napropamide. Kapasiti penjerapan (K_f) dari Baging tanah dan tanah Baging yang ditambah dengan 80 Mg ha⁻¹ CD dan POME adalah 0.22, 41.6 dan 3.96, masing-masing. Karbon organik terlarut (KOL) yang datang dari CD atau POME tidak mempengaruhi kapasiti penjerapan tanah Baging yang diperbaiki. Kapasiti penjerapan tanah Malaysia yang terpilih untuk napropamida berada di urutan menurun sebagai berikut: Linau ($K_f = 66.2$)> Teringkap ($K_f = 56$)> Gunung Berinchang ($K_f = 43$)> Jambu ($K_f = 26$)> Rudua ($K_f = 8$)> Baging ($K_f = 0.22$). Hasil penelitian menunjukkan bahawa jerapan meningkat dengan meningkatnya kandungan lempung liat dan kandungan karbon organik (KO) pada tanah. Di antara tanah BRIS yang diteliti, Baging yang memiliki bahan organik dan kandungan lempung terendah, juga memiliki K_f terendah. Separuh-hayat napropamida adalah terendah dalam tanah Baging (43 d) dan setengah-hayat meningkat menjadi 69 (d) dan 49.5 (d) dengan penambahan 20 Mg ha⁻¹ CD dan POME, masing-masing. Meskipun penambahan bahan organik menurunkan degradasi napropamida,

mereka mampu meningkatkan daya pegang napropamida di tanah Baging. Degradasi napropamida menurun di tanah Baging yang menerima KOL yang berasal dari CD dan POME. Oleh karena itu, adalah lebih baik untuk menggunakan napropamida di tanah Baging yang diperbaiki setelah hujan yang akan membuang KOL. Separuh-hayat paling cepat dan paling lama di antara tanah Malaysia yang terpilih adalah pada Baging (43 d) dan tanah Linau (100 d), masing-masing. Hasil penelitian menunjukkan bahwa degradasi napropamida menurun dengan peningkatan kapasiti penjerapan tanah. Napropamida telah terlarutlesap terlebih dahulu dari tanah Baging dibandingkan dengan tanah lainnya. Hasil penelitian menunjukkan bahwa tanah yang memiliki kapasiti penjerapan rendah untuk napropamida akan kehilangan napropamide terlebih dahulu dari kolom tanah. Di sisi lain, untuk tanah Linau yang memiliki kapasiti jerapan tertinggi untuk napropamida ($K_f = 66.2$), tiada napropamide yang dapat dikesan walaupun setelah setelah tujuh isipadu liang air yang telah dilarutlesap. Hasil penelitian juga menyarankan bahwa KOL tidak mempengaruhi larutlesap napropamide. Secara keseluruhan, penggunaan napropamida di tanah Malaysia yang terpilih tidak akan menimbulkan ancaman bagi alam sekitar terutama pada air bawah tanah kecuali pada tanah yang mempunyai kandungan bahan organik lempung yang rendah, dan konduktiviti hidraulik yang tinggi seperti tanah Baging.

ACKNOWLEDGEMENTS

First and foremost I am especially grateful to my supervisor Dr. Samsuri Abd Wahid, not only for the invaluable opportunity to conduct this research but also for his constant encouragement and unconditional friendship. My most sincere gratitude to my committee members, Assoc. Prof. Dr. Radziah Othman and Prof. Dr. Dzolkhifli Omar for their guidance through all these years in conducting this research. I am thankful to the members of the Land Management Department especially to Mr. Alias and Mr. Aziz for providing me the equipments to conduct the research. I am thankful to Universiti Putra Malaysia for financial support (Graduate Research Fellowship) throughout this study period. This research was supported by Research University Grant Scheme from Universiti Putra Malaysia under Grant No. 01/01/0010RU.

I certify that a Thesis Examination Committee has met on 27 September 2010 to conduct the final examination of Fardin Sadegh Zadeh on his Doctor of Philosophy thesis entitled "Sorption-desorption, degradation and leaching of napropamide in selected Malaysian soils" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15th March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Zaharah Abdul Rahman

Professor

Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

Rosli Mohamad

Professor

Faculty of Agriculture
Universiti Putra Malaysia
(Internal Examiner)

Mohamed Hanafi Musa

Professor

Institute of Tropical Agriculture
Universiti Putra Malaysia
(Internal Examiner)

Dar-Yuan Lee

Professor.

Department of Agricultural Chemistry
National Taiwan University
(External Examiner)

BUJANG KIM HUAT, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Samsuri Abd Wahid, PhD

Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

Dzolkhifli Omar, PhD

Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

Radziah Othman, PhD

Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

HASANAH MOHD GHAZALI, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 11 April 2011

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or other institutions.

Fardin Sadegh Zadeh

Date: 27 September 2010

TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSTRAK	vi
ACKNOWLEDGEMENTS	ix
APPROVAL	x
DECLARATION	xii
LIST OF TABLES	xvii
LIST OF FIGURES	xix
LIST OF ABBREVIATIONS	xxi
CHAPTER	
1 INTRODUCTION	
1.1 Pesticides	1
1.2 Fates of pesticides in soils	2
1.4 Justification of the study	2
1.4 Objectives of the study	3
2 LITERATURE REVIEW	
2.1 Environmental impacts of pesticides	6
2.2 Environment fates of pesticides	7
2.3 Major factors affect fates of pesticides in soils	9
2.4 Definition of sorption phenomena	9
2.5 Factor affecting sorption of pesticides in soils	9
2.5.1 Characteristics of pesticides	9
2.5.2 Characteristics of soils	12
2.5.3 Mechanisms of sorption	17
2.5.4 Sorption isotherms	21
2.6 Napropamide	24
2.6.1 Sorption of napropamide as affected by dissolved organic matter, organic matter and clay minerals	27
2.6.2 Determination of pesticides concentration in sorption experiment	28
2.7 Degradation of pesticides	30
2.7.1 Kinetics of pesticides degradation in soil	30
2.7.2 Microbial degradation of pesticides	32
2.7.3 Effects of organic matter amendments on pesticides degradation in soil	33
2.7.4 Chemical conversion and degradation	34
2.7.5 Photodegradation	35
2.8 Degradation of napropamide in soil	37
2.9 Leaching of pesticides in soil	37
2.9.1 Leaching of pesticides in organic amended soil	40
2.9.2 Leaching of napropamide	41

2.9.3	Effect of dissolved organic matter on leaching of napropamide in soil	42
2.10	Malaysian soils	43
2.11	Kenaf plantation in BRIS soil	46
3	MATERIALS AND METHODS	
3.1	Study 1 – Comparison between UV-spectrophotometry and HPLC methods for determine concentration in sorption study	48
3.1.1	Soil sample collection	48
3.1.2	Determination of soil properties	48
3.1.3	Chemicals	51
3.1.4	Napropamide determination using the UV-spectrophotometry method	51
3.1.5	Napropamide determination using HPLC	53
3.1.6	Linearity of absorbance against concentration of napropamide	53
3.1.7	Recovery, inter and intra-day precision	53
3.1.8	Recovery in spiked soil samples	55
3.1.9	The effects of DOC on the napropamide absorbance using UV-spectrophotometer	57
3.1.10	Soil samples and napropamide sorption study	58
3.1.11	Mass balance determination	58
3.2	Study 2 – Sorption and desorption of napropamide in selected Malaysian soil series and Baging soil amended with chicken dung and palm oil mill effluent	59
3.2.1	Incorporation of CD and POME to Baging soil series	59
3.2.2	Extraction of dissolved organic carbon for sorption study	59
3.2.3	Recovery study	60
3.2.4	Sorption and desorption of napropamide	60
3.2.5	Napropamide sorption on DOC	61
3.2.6	Napropamide sorption on the soil in the presence of DOC	62
3.2.7	FT-IR analysis of POME and CD before and after Sorption of napropamide	62
3.2.8	Data analysis	64
3.3	Study 3 – Degradation of napropamide in selected Malaysian soil series and Baging soil amended with chicken dung and palm oil mill effluent	64
3.3.1	Degradation studies	64
3.3.2	The effect of adding DOC derived from CD And POME to the Baging soil samples on napropamide degradation	66
3.3.3	Effect of DOC on napropamide degradation in Baging soil	67
3.3.4	Enumeration of bacterial population	67
3.4	Study 4 – Leaching of napropamide in selected Malaysian soil series and Baging soil amended with chicken dung and palm oil mill effluent	68
3.4.1	Leaching experiment	68
3.4.2	Extraction of napropamide from leachate	70
3.4.3	Extraction of napropamide from soil column	71
3.4.4	Correlation coefficient between K_f and other	

parameters such as napropamide half-life, napropamide leaching, and clay and organic matter content of soils	71
--	----

4 RESULTS AND DISCUSSION	
4.1 Study 1 – Comparison between UV-spectrophotometry and HPLC methods for determine concentration in sorption study	72
4.2 Study 2 – Sorption and desorption of napropamide in selected Malaysian soil series and Baging soil amended with chicken dung and palm oil mill effluent	86
4.2.1 Properties of Baging soil and Baging soil amended with CD and POME	86
4.2.2 Sorption and desorption of napropamide non-amended and amended Baging soil	86
4.2.3 Napropamide association with DOC extracted from Baging soil and Baging soil amended with CD and POME	95
4.2.4 Competition between DOC and napropamide for sorption sites in non-amended Baging soil and amended Baging soil with CD and POME	97
4.2.5 Sorption of napropamide in selected Malaysian soils	100
4.3 Study 3 – Degradation of napropamide in selected Malaysian soil series and Baging soil amended with chicken dung and palm oil mill effluent	104
4.3.1 Properties of Baging soil amended with CD and POME	104
4.3.2 Effects of organic matter amendments and DOC derived from CD and POME on napropamide degradation in Baging soil	104
4.3.3 Bacterial population in Baging soil amended with CD and POME over time in the degradation study	116
4.3.4 Napropamide degradation in selected Malaysian soils	121
4.3.5 Bacterial population in selected Malaysian soil over time in the degradation study	124
4.4 Study 4 – Leaching of napropamide in selected Malaysian soil series and Baging soil amended with chicken dung and palm oil mill effluent	126
4.4.1 Leaching of napropamide in non-amended and amended Baging soil with CD and POME	126
4.4.2 Leaching of napropamide in selected Malaysian soils	131
5 SUMMARY, GENERAL CONCLUSIONS AND RECOMMENDAT FOR FUTURE RESEARCH	
5.1 Summary	136
5.2 General conclusions	140
5.3 Recommendation for future research	142

REFERENCES	143
APPENDICES	158
BIODATA OF STUDENT	160
LIST OF PUBLICATIONS	161

