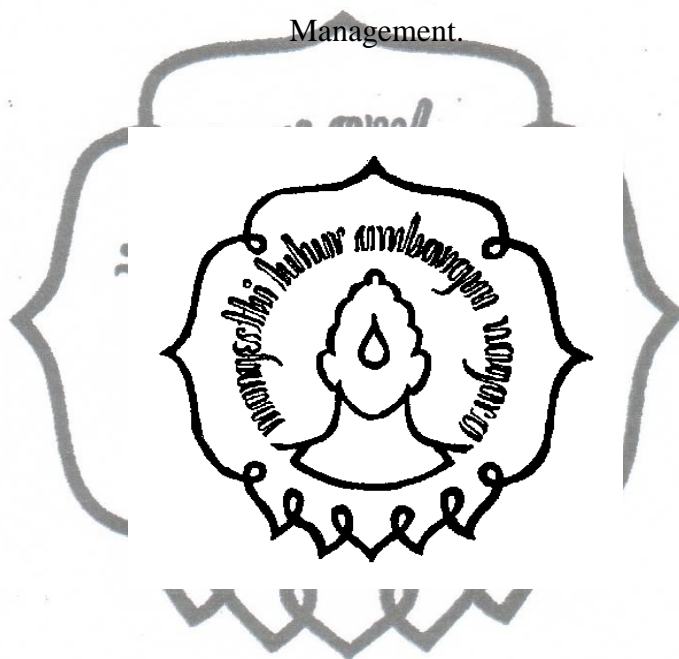


**RESIDUAL CADMIUM CONTENT IN SOIL ANDEMPON-EMPON AND
THE EFFICIENCY OF BINDING AGENTS ON IMMOBILIZATION OF
CADMIUM IN SOIL**

THESIS REPORT

Submitted in Partial Fulfillment for the Requirement of Master of Science Degree,
in Environmental Science Specialization in Natural Resources and Environmental
Management.



By

Arlindo Fernando Macie

A.131408019

ENVIRONMENTAL SCIENCE STUDY PROGRAM
SEBELAS MARET UNIVERSITY POSTGRADUATE PROGRAM
SURAKARTA


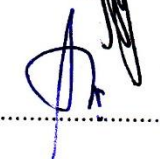
2016

commit to user

**RESIDUAL CADMIUM CONTENT IN SOIL AND *EMPON-EMPON* AND
THE EFFICIENCY OF BINDING AGENTS ON IMMOBILIZATION OF
CADMIUM IN SOIL**

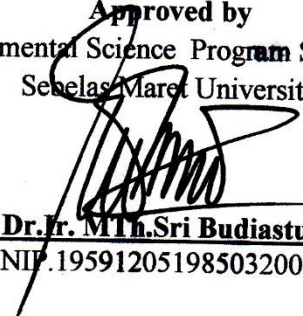
THESIS REPORT

Submitted by.
Arlindo Fernando Macie
A131408019

Supervisor committee	Name	Signature	Date
1st Supervisor	Dr. Prabang Setyono, M.Si. NIP.197205241999031		14-06-2016
2nd Supervisor	Dr. Ir. Widyatmani Sih Dewi, M.P NIP. 196311231987032002		6-6-2016

Been declared eligible and approved
on this date of 2016

Approved by
Environmental Science Program Study Head
Sebelas Maret University


Prof. Dr. Ir. MTh. Sri Budiastuti, M.Si
NIP.1959120519850320012

**RESIDUAL CADMIUM CONTENT IN SOIL ANDEMPON-EMPON AND
THE EFFICIENCY OF BINDING AGENTS ON IMMOBILIZATION OF
CADMIUM IN SOIL**

THESIS



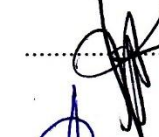
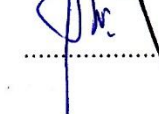
Submitted by.

Arlindo Fernando Macie

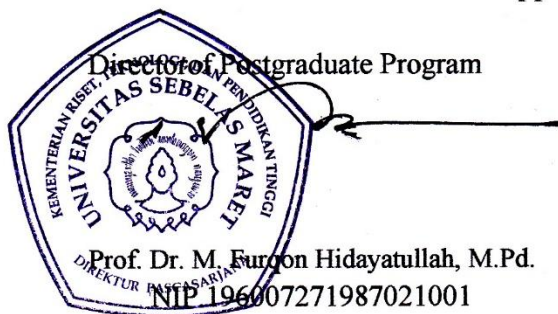
A131408019

Been declared eligible and approved
on this date of 2016

Examiner's committee:

Examiner's Charge	Name	Signature	Date
President	Prof. Dr.Ir.MTh.Sri Budiastuti, M.Si. NIP.195912051985032001		29/6 2016
Secretary	Komariah, STP., M.Sc., Ph.D. NIP.197805232008122001		28/6 2016
Examiner's Members	Dr. Prabang Setyono, M.Si. NIP.197205241999031		14-06-2016
	Dr. Ir. Widyatmani Sih Dewi, M.P. NIP. 196311231987032002		6/6 2016

Approved by



Head of Postgraduate Program
Master degree of Environmental
Science

Prof. Dr.Ir.MTh.Sri Budiastuti, M.Si.
NIP.195912051985032001

DECLARATION OF THESIS OWNERSHIP, ORIGINALITY AND PUBLICATION REQUIREMENTS

1. I, Arlindo Fernando Macie, certify that this thesis with the title "**Residual Cadmium Content in Soil and *Empon-Empon* and the Efficiency of Binding Agents on Immobilization of Cadmium in Soil**" comprises only my original research towards the Master degree and its content has not been submitted or presented in any form for another degree at any University or other academic forums, except where citations have been made in this thesis to acknowledge the respective authors. Therefore, I will be responsible of any sanction or penalty, if a part of the content of this thesis found previously published.
2. The partial or full publication of the content of this thesis in a journal or scientific forum *has to include the committee of Advisors as authors and the UNS Postgraduate program.* In case of violation of these rules of publication I will be responsible for any academic penalty resulting from such violation.

Surakarta, 6th June 2016



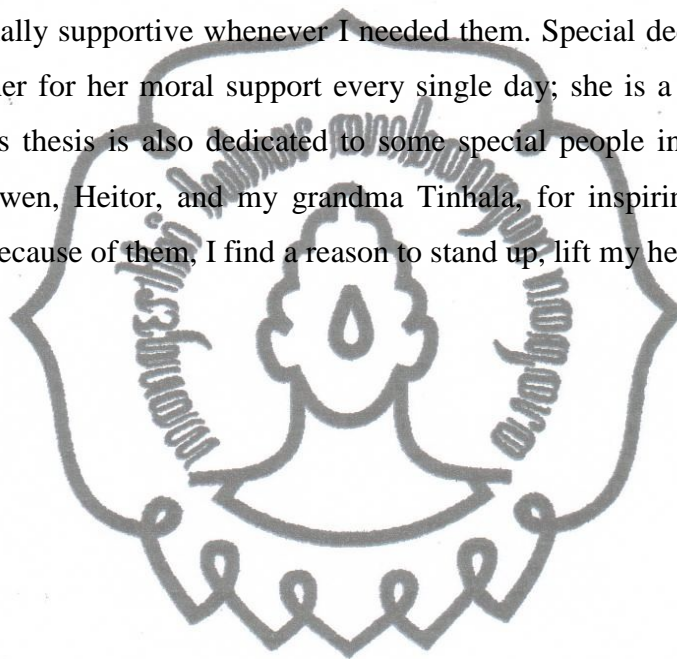
Arlindo Fernando Macie

A.131408019

DEDICATION

First of all I dedicate these outcomes to the Almighty God for His guidance and protection under the sun. I also thank God for boosting me with energy and wisdom, because without Him nothing of which I have achieved would be possible.

This thesis is dedicated to my Father, Fernando Macie and my mother Cecília Muchanga for having brought me to the light, and for being unconditionally supportive whenever I needed them. Special dedication I address to my mother for her moral support every single day; she is a real champion in person. This thesis is also dedicated to some special people in my life namely, Wahyu, Bowen, Heitor, and my grandma Tinhala, for inspiring me on a daily basis, and because of them, I find a reason to stand up, lift my head and fight.



ACKNOWLEDGEMENT

I am using this rare and grand opportunity to express my gratitude to everyone who has supported me throughout the course of this Master degree in environmental studies. I am very grateful for the inspiring guidance and invaluable constructive criticism during the research.

First of all, I would like to express my sincere gratitude to my advisors, Dr. Prabang Setyono, M.Si; Dr. Ir. Widyatmani Sih Dewi, MP, and my inspiring lecturer, Mrs. Komariah., STP., M.Sc., Ph.D for their patience, motivation, and immense knowledge. I really admire their professionalism and high commitment.

Besides my advisors, I would like to thank the Head of Environmental Science Department, Prof. Dr.Ir. Mth. Budiastuti, M.Si, Dr. Prabang Setyono, M.Si and Mrs. Dina Selvia, for their readiness to assist and guide whenever I needed their services. Honestly they will never leave my heart. I am also grateful for the direction of postgraduate and the Sebelas Maret University for the opportunity conceded in this magnificent university, as well as their hospitality. Mrs. Tika and Diana deserve a warm thank you for their services and professionalism, alongside the staff of the International office, which was my first door at Sebelas Maret University.

I owe thanks giving to my classmates Nur Aziza (from Suriname), Willie Suzuki (from PNG), Tommy Anderson (From Madagascar), and my loved Indonesian fellows, Mrs. (Ibu) Puji, Mr. Teguk, Mr. Hernowo, Mr. Puji, Beta Citra, Nabila (classleader), Sulvia Dessica (Honey), Mori, Rizky, Aldo, Ayu, Denny, Inksan, Mr. Eddy, Mr. Bardi (the humble man), Dewa, and Mrs. Naris. I am very proud of you. You all deserve the very best and are truly irreplaceable. Alongside you I fought a good battle.

I also thank my fellow laboratory mates, Arwa and Ahzar, for each opportunity of sharing and the togetherness which we have experienced during this restless time, and also the staff of the Soil Science Laboratory, for their humbleness and support. They have increased the spirit of teamwork in me, and in the meantime have helped me to more quickly adapt to the lab environment, which is quite demanding in terms of energy and time.

I would also wish to thank the Indonesian Government for having conceded the scholarship, and also the Gifu University for having provided needed funds for lab payments. I also would like to thank the *biofarmaka* farmers for their collaboration during the field survey.

Last but not least, I would like to thank my family, parents, my girlfriend, brothers and sisters, as well as my dear friend and Brother Benjamin Ellis for their support, and for being present in my life.

ABSTRACT

Arlindo Fernando Macie. A.131408019. 2016. Residual Cadmium Content in Soil and *Empon-Empon* and the Efficiency of Binding Agents on Immobilization of Cadmium in Soil. Thesis. 1st Advisor: Dr. Prabang Setyono, M.Si, Lecturer at Environmental Science Department, Postgraduate programme, Sebelas Maret University 2nd Advisor: Dr. Ir. Widyatmani Sih Dewi, MP, Lecturer at Faculty of Agriculture.

Medicinal and spice herbs have been of great importance since the ancient ages. People have relied much on them to fulfill their healthcare needs and as ingredients of diverse cuisines. Currently, the cultivation of medicinal plants based on agro-chemicals has posing lives because chemicals contain toxic elements, including Cadmium. This research determined the Cd concentrations oin soil and medicinal and spice plants, and determined the efficiency of three binding agents on immobilization of Cd in three soil types sampled in Karanganyar. Soil cores and rhizomes were sampled and analyzed for soil properties and Cd content. Three soil types were incubated in triplicate. Each soil (5 g) was treated with 0.2 g of dolomite, 1.0g of charcoal and organic fertilizer by adding 8 ml of distilled water in a 50 ml tube, and then incubated for 24 days after having been shaken for 16 h. were added 1ml of (HNO₃ and 3 ml KClO₄ to the mixture. The mixture was first heated at 80°C and then at 130°C till the orange smoke gets finished. Finally Cd was extracted with solution of 0.01 CaCl₂ (20 ml), and measured by AAS. The results showed that Cd in all the investigated villages still below the limits (1.0 mg Cd/kg). In soils Cd ranged from 0.224 to 0.354 mg Cd/kg, while in herbs ranged from 0.0285 to 0.0594 mg Cd/kg. Dolomite showed the highest efficiency (95.43%) followed by organic fertilizer (92.64%) and charcoal (91.53%) in Alfisols. In general dolomite wasthe better binding agent in each location, while the lowest efficiency was recorded with organic fertilizer (89.30%) in Mediterranean soils from Kemuning.

Keywords: *Immobilization; medicinal plants; Cadmium; binding agents; efficiency.*

ABSTRAK

Arlindo Fernando Macie. A.131408019. 2016. Kadar Residu Kadmium dalam Tanah dan Empom-Empon dan Effisiensi Bahan penyerap pada Imobilisasi Kadmium dalam Tanah. Tesis. Pembimbing I: Dr. Prabang Setyono, M.Si. Program Studi Ilmu Lingkungan, Program Pascasarjana. Pembimbing II: Dr. Ir. Widyatmani Sih Dewi, MP. Fakultas Pertanian, Universitas Sebelas Maret.

Obat herbal dan rempah-rempah sudah menjadi hal yang penting dari zaman dahulu kala. Orang-orang lebih mengandalkan obat herbal dan rempah-rempah untuk perawatan kesehatan ataupun untuk menambah cita rasa dalam masakan. Budidaya tanaman herbal berbasis pupuk kimia telah banyak dikembangkan, oleh karena itu, elemen-elemen toksik termasuk cadmium, memasuki rantai makanan. Penelitian ini bertujuan mengetahui konsentrasi Cd tanah dan tanaman herbal, serta menganalisis efisiensi yang mengikat tiga agen imobilisasi Cd dalam tiga jenis tanah di Karanganyar. Sampel tanah dan rimpang diteliti untuk unsur tanah dan Cd. Tiga diantaranya diinkubasi dalam rangkap tiga. Setiap tanah (5 g) diberi pelakuan 0.2 g dolomit, 1.0 g arang dan pupuk organik dengan menambahkan 8 ml air suling dalam tabung 50 ml, kemudian tanah tersebut diinkubasi selama 24 hari setelah diaduk selama 16 jam. Setelah itu tambahkan 1 ml HNO_3 dan 3 ml KClO_4 ke dalam campuran. Pertama panaskan tanah pada suhu 80°C sampai 130°C hingga asap berwarna oranye. Kemudian Cd diekstraksi dengan larutan 0,01 CaCl_2 (20 ml), lalu diukur dengan AAS. Dari hasil penelitian menunjukkan bahwa Cd dari semua desa yang diteliti masih dibawah batas ambang (1,0 mg Cd/kg). Cadmium di tanah berkisar antara 0,224-0,354 mg Cd/kg, sementara di jamu berkisar antara 0,0285 – 0,0594 mg Cd/kg. Dolomit menunjukkan efisiensi tertinggi (95.43%) diikuti oleh pupuk organik (92.64%) dan arang (91.53%) di Alfisols. Pada keseluruhan efisiensi dolomit lebih besar di semua tanah dan lokasi, sedangkan efisiensi terendah tercatat dengan pupuk organik (89.30%) di tanah Mediteran dari Kemuning.

Kata kunci: *Imobilisasi; tanaman herbal; Kadmium; Agen terkait; efisiensi.*

CONTENT LIST

DECLARATION OF THESIS OWNERSHIP, ORIGINALITY AND PUBLICATION REQUIREMENTS	Error! Bookmark not defined.
DEDICATION	iv
ACKNOWLEDGEMENT	v
ABSTRAK	viii
LIST OF TABLES	xii
TABLE OF FIGURES	xiv
LIST OF ABBREVIATIONS AND ACRONYMS	xvi
CHAPTER I	1
INTRODUCTION	1
A. Background	1
B. Statement of the problem	5
C. Objectives	6
D. Significance of the research	6
1. Medicinal herbs farmers in the Karanganyar district	6
2. Government of the Karanganyardistrict	7
3. Academics and society	7
CHAPTER II	8
THEORETICAL BASIS	8
A. Literature Review	8
1. Production of herbal plants	8
2. Production and uses of Ginger (<i>Zingiber officinale</i>)	8
3. Factors affecting the production of turmeric	11
4. Uses of Turmeric	12
5. Factors affecting the production of Javanese ginger	13
6. Characteristics of Cadmium and its occurrence in Soils	15
7. Geochemical occurrence of Cadmium	15
8. Origin of Cadmium in soils	16
9. The chemical behaviour of Cadmium in soils	18
10. Effects of pH on Cadmium adsorption in soils	20
11. Effects of competition from other metal ions	20

12.	Adsorption on Calcite	21
13.	Effects of organic ligands and Chloride ions on Cadmium adsorption.....	21
14.	Effect of Soil organic matter on Cadmium adsorption and availability.....	22
15.	Soil factors affecting the Uptake of Cadmium by plants	23
16.	Plant factors affecting the up taking of Cadmium from soils	26
17.	Negative effects of Cadmium on humans, animals, and plants	27
18.	Description of soil characteristics	29
a.	Characteristics of Andosols	29
B.	Relevant Studies	34
D.	Hypotheses	39
CHAPTER III.....		40
MATERIAL AND METHODS.....		40
A.	Location and research period	40
B.	Research design	42
1.	Research type	42
2.	Population and samples	42
3.	Variables of study	43
4.	Data collection and procedures	43
5.	Material	47
Table 1. Materials used in the field and laboratory		47
C.	Laboratory methods	47
1.	Atomic Absorption spectrometer (AAS)	47
2.	Determination of Soil pH	48
3.	Determination of Soil Organic Matter.	49
4.	Analysis of Soil Cation Exchange Capacity (CEC)	51
5.	Analysis of soil texture	53
6.	Analysis of Cadmium content in soil samples	57
7.	Analysis of Cadmium content in plant tissues.	58
8.	Lab experiment of immobilization of Cadmium in soils.	60
D.	Process of immobilization of Cd by organic materials and activated carbon	62
E.	Statistical Analysis	62
CHAPTER IV.....		64
RESULTS AND DISCUSSION		64
A.	Field Survey	64

1. Soil properties and precipitation patterns of the Study location	64
20. Analysis of Cadmium concentrations in soils from Karanganyar.....	67
21. Analysis of Cadmium content in rhizomes of medicinal and spice plants....	72
22. T-Test for comparison of means of soil Characteristics and Cd in soils and herbs	74
B. Results of Pearson correlation.....	81
C. Stepwise regression analysis.....	86
D. Laboratory Experiment on Immobilization of Cadmium	93
1. Effect of three binding agents on immobilization of cadmium in soils under medicinal plants cultivation	93
2. Analysis of pH of soil treated with binding agents	101
3. Outputs and outcomes of mitigation of Cadmium in soils.....	104
4. Adaptation strategies to Cd dynamics in plants and soil.....	108
E. Socio-economic analysis	110
CHAPTER V	119
CONCLUSION AND RECOMMENDATION	119
A. Conclusion.....	119
B. Recommendations	120
APPENDIX 1	127
APPENDIX 2.	132

LIST OF TABLES

Table 1. Materials used in the field and laboratory	47
Table 2. Soil Characteristics of the research sites	65
Table 3. Cadmium Concentration in Soil (mg Cd/kg) from Karanganyar	68
Table 4. Cadmium Concentration in Rhizomes	73
Table 5. Two Tailed t-Test of paired of pH Averages	75
Table 6. T-test for Averages of paired groups of Soil organic matter	76
Table 7. Two Tailed t-Test for Averages of paired groups in Soil	77
Table 8. t-Test for Averages of Paired groups of Cd in Rhizomes	78
Table 9. Table 9 t-Test for averages of paired groups of Cd averages in rhizomes of Turmeric	79
Table 10. T-test for Averages of paired groups of Cadmium in Rhizomes of Javanese ginger	79
Table 11. t-Test for paired means of Cd in three medicinal herbs.	80
Table 12. Pearson's correlation in Kemuning at 15 cm soil depth	82
Table 13. Pearson's correlation in Kemuning at 30 cm soil depth	82
Table 14. Pearson's correlation in Bakalan at 15 cm soil depth	83
Table 15. Pearson's correlation in Bakalan at 30 cm soil depth	83
Table 16. Pearson's correlations in Tamansari at 15 cm soil depth	84
Table 17. Pearson's correlations in Tamansari at 30 cm soil depth	85
Table 18. Pearson's correlations in Sambirejo at 15 cm soil depth	85
Table 19. Pearson's correlations in Sambirejo at 30 cm soil depth	86
Table 20. Soil properties and Cd concentration in the study location.	93
Table 21. ANOVA of Cadmium versus soil and adsorbents	94
Table 22. Advanced tukey's test for means of cadmium content in soil solution	95
Table 23. Advanced tukey's test for means of binding agents in the soil solution	96
Table 24. Advanced Tukey's test for Cd in soil solution versus combined factors	98
Table 25. ANOVA of pH versus soil and adsorbents	102
Table 26. Advanced tukey's test for soil pH average	102
Table 27. Educational background	111
Table 28. Use of chemical fertilizers	112

Table 29. Frequency and period of fertilization	112
Table 30. Types of organic fertilizers applied	113
Table 31. Effect of organic fertilizer on yields	114
Table 32. Perception of the farmers shifting to organic farming	115

APPENDIX LIST

APPENDIX 1	127
------------	-----

APPENDIX 2	132
------------	-----



TABLE OF FIGURES

Figure 1. Ginger Plant	9
Figure 2. Rhizomes of Ginger	9
Figure 3. Turmeric Plant	12
Figure 4. Rhizomes of Turmeric	12
Figure 5. Dried Rhizomes	13
Figure 6. Ground Rhizomes of Turmeric	13
Figure 7. Javanese Ginger Plant	14
Figure 8. Rhizomes of Javanese Ginger	14
Figure 9. Research Location	41
Figure 10. Soil Sampling Using an Auger	45
Figure 11. Sampling Scheme (Harrell, 2014)	46
Figure 12. pH meter	49
Figure 13. Air dried Rhizomes indoor	51
Figure 14. Shaker	51
Figure 15. Analytical weighing Scale	52
Figure 16. Filtration Process and Washing with alcohol	52
Figure 17. Distillation Chamber	53
Figure 18. Heating the Solution of HCl	55
Figure 19. Heating the Solution of H ₂ O ₂	55
Figure 20. Cooling of Solutions and H ₂ O ₂	55
Figure 21. Reaction of H ₂ O ₂ before the heating process	56
Figure 22. Filtration Process	56
Figure 23. Solution with Na ₄ P ₂ O ₇	56
Figure 24. Textural Triangle	57
Figure 25. Analysis of Cadmium using AAS	59
Figure 26. Extraction of Cadmium from soil and Rhizomes	59
Figure 27. Destruction process of the samples	60
Figure 28. Cattle as a source of manure	67
Figure 29. Collection of Cattle's manure	67

commit to user

Figure 30. Cadmium Concentration in Inceptisol from Kemuning	68
Figure 31. Cadmium Concentration in Alfisols from Bakalan	69
Figure 32. Cadmium Concentration in Ultisols from Tamansari	69
Figure 33. Cadmium Concentration in Ultisols from Sambirejo	70
Figure 34. Annual rainfall (Source: Department of Agriculture of Karanganyar District 71	
Figure 35. Agro-forestry System	72
Figure 36. Fruit Trees combined with medicinal plants	72
Figure 37. Effects of Sand Content on Cd in Rhizomes from Kemuning	87
Figure 38. Clay Content on Cadmium in Rhizomes from Kemuning	88
Figure 39. Effect of Soil pH on Cd in Rhizomes from Kemuning	89
Figure 40. Effect of Sand and Silt Content on Cd in Rhizomes from Bakalan	90
Figure 41. Effect of Clay Content on Cd in Rhizomes from Bakalan	90
Figure 42. Effect of Clay content on Cd in Soil from Tamansari	91
Figure 43. Effect of Soil Organic matter on Cd in Rhizomes from Sambirejo	92
Figure 44. Effect of Clay Content on Cd in Rhizomes from Sambirejo	92
Figure 45. Combination of Soil and Adsorbents versus Immobilized Cd	99
Figure 46. Mobile Cd in the Soil Solution versus percentage of Immobilized Cd	100
Figure 47. Cd Dynamics in Soil and plants before ammendment	107
Figure 49. Farmer's Annual Income upon the biofarmaka Clusters	117

LIST OF ABBREVIATIONS AND ACRONYMS

ANOVA	Analysis of Variance
ATP	Adenosine Triphosphate
Cd	Cadmium
CEC	Cation Exchange Capacity
DNA	Deoxyribonucleic Acid
EU	European Commission
EMPON-EMPON	Medicinal and spice plants
NPK	Inorganic fertilizer containing Nitrogen Phosphorus and Potassium
SCL	Sandy Clay Loam
SL	Sandy Loam
SNI	Indonesian National Standards
SOM	Soil Organic Matter
USA	United States of America
WHO	World Health Organization