

ANDREAS KREUZEDER

MODELLING PHOSPHORUS FLOWS IN SOILS

MASTERARBEIT

Master Thesis

zur Erlangung des akademischen Grades eines Magisters
an der Naturwissenschaftlichen Fakultät der Karl-Franzens-Universität Graz.

*to obtain the degree of a Master of Science
at the Department of Natural Sciences, Karl-Franzens-University Graz.*

Supervisors:

Univ.-Prof. Dr.rer.nat. Claudia R. Binder

Institute for Systems Science, Innovation & Sustainability Research (ISIS)
Karl-Franzens-University Graz

Ao.Univ.-Prof. Dr.phil. Anton Huber
Institute of Chemistry (IFC)
Karl-Franzens-University Graz

Graz, 2011

Bibliografische Information der Deutschen Bibliothek

Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über <http://dnb.ddb.de> abrufbar.

Kreuzeder, Andreas:

Modelling Phosphorus Flows In Soils

ISBN 978-3-941274-85-3

Alle Rechte vorbehalten

1. Auflage 2011, Göttingen

© Optimus Verlag

URL: www.optimus-verlag.de

Printed in Germany

Papier ist FSC zertifiziert (holzfrei, chlorfrei und säurefrei, sowie alterungsbeständig nach ANSI 3948 und ISO 9706)

Das Werk, einschließlich aller seiner Teile, ist urheberrechtlich geschützt. Jede Verwertung außerhalb der engen Grenzen des Urheberrechtsgesetzes in Deutschland ist ohne Zustimmung des Verlages unzulässig und strafbar. Dies gilt insbesondere für Vervielfältigungen, Übersetzungen, Mikroverfilmungen und die Einspeicherung und Verarbeitung in elektronischen Systemen.

Acknowledgements

Immeasurable gratitude goes to my family, my mother Margret and my father Johann, my brother Johannes and my sister Veronika who supported me in every imaginable way during my whole studies. This thesis would have been impossible without them.

A special thank is directed to Christine Zingl for her love and understanding support.

I want to thank my advisors Claudia Binder and Anton Huber for encouraging, guiding and supporting me during this thesis. My thanks also go to Shinichiro Nakamura for his highly valued input.

Furthermore, I want to thank Josef and Heidi Thalhamer for the enduring support, their unshakable trust and the example they have always set.

My thanks also go to my colleagues at the ISIS for their warm reception in their group, their support and constructive discussions. Especially, I want to thank Max Mrotzek for his input and critique in the fields of System Dynamics and his overall support.

Also, I want to thank Luis San Vicente Portes for his encouragement and support.

Thanks to all my friends, roommates and colleagues who have made studying in Graz joyful as well as for their friendship, support and encouragement.

Especially, I want to thank Hannes Draxler for the intensive and supportive exchange on the topic of phosphorus. Even more, thanks for the extra time in the laboratory spent to support this thesis.

Finally, I'd like to thank all the people who gave me advice or inputs and for their assistance.

Zusammenfassung

In allen lebenden Zellen kommt dem Phosphor (P) eine zentrale Rolle zu – speziell in der Energieumsetzung und im genetischen Code. Seine herausragende Wichtigkeit macht ihn zu einem essenziellen Nährstoff. Obwohl in der Natur in niedrigen Konzentrationen ubiquitär vorkommend, wird Phosphor als nicht-erneuerbare Ressource betrachtet. Die globalen Vorkommen sind limitiert und auf wenige Länder konzentriert.

Ungefähr 90% der globalen Phosphorproduktion finden als Dünger in der Landwirtschaft Verwendung, wo sie von enormer Wichtigkeit für die Produktion landwirtschaftlicher Güter sind. Durch diese nicht substituierbare Aufgabe als Dünger und die Begrenztheit als natürliche Ressource wird ein neues und historisches Kapitel eröffnet: Eine mögliche Versorgungskrise von Phosphor. Eine solche Krise kann durch die Minimierung von Verlusten und durch maximale Nutzungseffizienz vermieden werden. Zentral in einer solchen Strategie ist die schonende Verwendung von Phosphor als Dünger und die Berücksichtigung der Dynamik in Böden. Diese sind mittlerweile gut erforscht aber aufgrund der Komplexität besteht die Notwendigkeit dieses Verständnis an Praktiker, die für die Anwendung von Phosphor verantwortlich sind, weiter zu geben.

In dieser Masterarbeit wurden die Phosphorflüsse für Österreich durch Anwendung der Stoffflussanalyse (MFA) erhoben. Diese Analyse wurde für das Jahr 2008 durchgeführt und mit Daten von 2001 verglichen. Weiters wurde ein „System-Dynamics-P-Modell“ entwickelt, das auf die Charakteristiken von Phosphor im Boden eingeht. Es zeigt den Einfluss der Bodeneigenschaften, die Effekte von Düngeranwendung und Pflanzenaufnahme sowie deren dynamische Zusammenhänge. Entwickelt als Instrument zur praktischen Anwendung, fördert es speziell für Praktiker das Verständnis der Dynamik von Phosphor im Boden.

Die beiden zentralen Resultate dieser Masterarbeit sind:

1. Die Flüsse von Phosphor in der österreichischen Landwirtschaft sind signifikant höher als bisher angenommen. Weiters sind von 2001 bis 2008 die Importe von Phosphor durch Mineraldünger sowie der jährliche Aufbau des Bodenbestands um 5-10% gesunken.
2. Die Zusammenhänge von Anorganischem Phosphor, Phosphor in der Bodenlösung und organischem Phosphor lassen sich durch ein dynamisches Equilibrium von 500 : 1 : 250 beschreiben. Dieses Gleichgewicht wird hauptsächlich durch Parameter wie pH-Wert, Humusanteil, Tonanteil und Anteil von Mineralien die Phosphor komplexieren (Al, Fe, Ca) verschoben.

Abstract

In all living cells phosphorus (P) is a central component for the energy conversion system and in the genetic code. Its outstanding importance makes it an essential nutrient. Although ubiquitous in nature in low concentrations, it is considered a non-renewable resource. The global resources of phosphorus are limited and concentrated in only a few countries.

Around 90% of the global phosphorus production is used as fertilizer in agriculture where it is of great importance for the production of agricultural goods. This pivotal role as a fertilizer and the finiteness as a natural resource led to a new episode of historic importance: A possible upcoming phosphate crisis. Only by decreasing the losses and increasing the efficiency of phosphorus use such a crisis may be prevented. The nucleus of such a strategy is the use of phosphorus as fertilizer and its dynamics in soils. These dynamics are well investigated by now. Due to their complexity there is a need to provide additional means to facilitate the knowledge especially for practitioners, who are directly on the forefront of phosphorus use and thus sustainability.

This thesis shows the flows of phosphorus in Austria by using the method of material flow analysis (MFA). This analysis was performed for the year 2008 and compared to previously available data from 2001. Furthermore, a System Dynamics P-Model was developed outlining the characteristics of phosphorus and its use in soils. This model considers the complex interactions and processes in soils. It shows the influence of soil properties, the effects of fertilizer use and crop uptake, and their dynamic interrelations. Especially, designed as a hands-on tool it allows to foster the understanding for phosphorus dynamics in soils for practitioners.

The two main findings of this thesis are:

1. The flows of phosphorus in Austrian agriculture are significantly higher than previously expected. Also, the imports of phosphorus through mineral fertilizer as well as the build-up of the soil stock declined by 5-10% from 2001 to 2008.
2. The relationships of inorganic phosphorus, phosphorus in soil solution and organic phosphorus can be described by a dynamic equilibrium of 500 : 1 : 250. This equilibrium is influenced by other parameters, most notably: pH-value, organic matter content, clay content and content of minerals binding phosphorus in complexes (Al, Fe, Ca)

Glossary

Al:	Aluminium
Apoplasm:	In plants, especially roots, the apoplast or apoplasm is the free space outside the plasma membrane
ATP:	Adenosine triphosphate: energy carrier in the cells
Ca:	Calcium
CAL:	Citric Acetate Lactate-Method: is used to determine plant available phosphorus
Calibration:	Using empirical data sets, data from literature or general trends to estimate model factors or behaviour
DNA:	Deoxyribonucleic acid: a bio molecule that carries genetic information
Fe:	Iron (latin: Ferrum)
Flow (Material Flow):	Defines a mass transfer between two processes
Isotope:	Atoms with the same number of protons and a different number of neutrons. Isotopes are often used as radioactive markers
M:	Molarity or molar concentration (mol/l)
MFA:	Material Flow Analysis
Mineral Fertilizer:	Or synthetic fertilizer: composed of inorganic minerals or chemically synthesized
Mycorrhizal symbiosis:	Mutualistic association of fungus and roots of a vascular plant
nes / n.e.s.:	not else specified
Organic Fertilizer:	Fertilizer composed of enriched organic matter
Rhizosphere:	Upper layer of soil that is directly influenced by roots
SD:	System Dynamics
Stock:	Represents a quantity existing at a defined point in time
Symplast:	Is the inner side of the plasma-membrane
P:	Phosphorus
pH-Value:	pH is a measure of the acidity or basicity of an aqueous solution
P₂O₅:	Phosphorus oxide containing 44% phosphorus
Process:	Is a transformation, transport or storage of materials
White Phosphorus:	Very reactive phosphorus allotrope

Table of Contents

ZUSAMMENFASSUNG	I
ABSTRACT	III
GLOSSARY	V
TABLE OF CONTENTS	VII
LIST OF TABLES.....	XI
LIST OF ILLUSTRATIONS.....	XIII
1 INTRODUCTION.....	1
1.1 PHOSPHORUS IN NATURE.....	1
1.2 PHOSPHORUS IN SOCIETY.....	2
1.3 PHOSPHORUS IN THE ENVIRONMENT.....	3
1.3.1 <i>Phosphorus as a resource</i>	3
1.3.2 <i>Eutrophication</i>	10
1.4 PHOSPHORUS CHEMISTRY	11
1.4.1 <i>Phosphorus</i>	11
1.4.2 <i>Redox Effects</i>	11
1.4.3 <i>Inorganic Phosphorus</i>	11
1.4.4 <i>Soil Solution Phosphorus</i>	12
1.4.5 <i>Organic Phosphorus</i>	13
1.5 PHOSPHORUS AS A NUTRIENT	17
1.5.1 <i>Phosphorus in the soil plant system</i>	17
1.5.2 <i>Phosphorus Cycle and Phosphorus Movement</i>	21
1.6 PHOSPHORUS IN SOILS.....	23
1.6.1 <i>The Soil Phosphorus Cycle</i>	23
1.6.2 <i>Phosphorus Fractionation</i>	28

1.7	PHOSPHORUS AS FERTILIZER	29
1.8	GLOBAL FLUXES AND MATERIAL FLOW ANALYSIS FOR PHOSPHORUS.....	31
1.9	DYNAMIC MODELLING THE BEHAVIOUR OF PHOSPHORUS.....	34
1.9.1	<i>The Difficulty of Modelling Phosphorus in Soils</i>	34
1.9.2	<i>Existing Phosphorus Models.....</i>	34
1.10	QUESTIONS AND AIMS OF THE THESIS.....	36
1.11	METHODICAL APPROACH	37
1.12	CONTENT OF THE THESIS	38
2	METHODS	39
2.1	THE STUDY AREA.....	39
2.1.1	<i>Criteria for the Selection of the Study Area</i>	39
2.1.2	<i>Selection of the Study Area.....</i>	40
2.1.3	<i>Characterization of the Study Area</i>	40
2.2	MATERIAL FLOW ANALYSIS (MFA).....	44
2.3	MATERIAL FLOW ANALYSIS OF AUSTRIA	46
2.3.1	<i>System Analysis and Data Collection for the Material Flow Analysis</i>	46
2.3.2	<i>Data Quality</i>	47
2.4	SYSTEM DYNAMICS	48
2.5	THE SYSTEM DYNAMICS P-MODEL	49
2.5.1	<i>Data Collection for the System Dynamics P-Model.....</i>	49
2.5.2	<i>Validation and Testing.....</i>	49
3	RESULTS	51
3.1	MATERIAL FLOW ANALYSIS.....	51
3.1.1	<i>Phosphorus Flow Analysis for Austria</i>	51
3.1.2	<i>Comparison with older MFA-Data.....</i>	53
3.2	SYSTEM DYNAMICS P-MODEL.....	54
3.2.1	<i>Model Design.....</i>	54
3.2.2	<i>Input Data.....</i>	62

3.2.3	<i>Simulations for Austrian Soils</i>	66
4	DISCUSSION AND OUTLOOK	75
5	CONCLUSIONS	79
6	REFERENCES	81
7	APPENDIX	89
	A. DATA FOR MFA OF AUSTRIAN AGRICULTURE	89
	B. EQUATIONS FOR SYSTEM DYNAMICS P-MODEL	96

List of Tables

Table 1: Relative abundance of organic P compounds in soil	14
Table 2: Plant strategies and adaptations to low phosphorus levels in soils	19
Table 3: Selection of global phosphorus flows in the food production and consumption system.	32
Table 4: Characterization of Phosphorus Models.....	35
Table 5: Characterization of the three analyzed regions	40
Table 6: P Content Classes for Austrian Soils	43
Table 7: Phosphorus fertilization recommendations for crops in Austria	43
Table 8: Phosphorus fertilization recommendations according to P content class of soils in Austria.	44
Table 9: Data sources and assessment of data quality for the MFA of Austrian agriculture in 2008.....	47
Table 10: Minimum and maximum material flow values in Austrian agriculture in 2008.....	51
Table 11: Comparison of two Material Flow Analysis for 2001 and 2008	53
Table 12: IF THEN ELSE commands describing the soil processes.	59
Table 13: Determination of the Equilibrium.....	60
Table 14: Input parameters in the System Dynamics P-Model	63
Table 15: Initial Values for Pi, Po and Pss for the P Content Classes of soils	64
Table 16: Estimating the input ratio variables	65
Table 17: Shown simulations from the System Dynamics P-Model	66
Table 18: Data and calculation for the material flow Fodder.....	90
Table 19: Data and calculation for the material flow Organic Fertilizer.....	91
Table 20: Data and calculation for the material flow Mineral Fertilizer.....	92
Table 21: Data and calculation for the material flow Plant Growth.....	93
Table 22: Data and calculation for the material flow Soil Accumulation	95

List of Illustrations

Figure 1: Phosphorus availability bottlenecks (Unit is t P);.....	4
Figure 2: Historical global sources of phosphorus fertilizers from 1800 to 2000;.....	6
Figure 3: Structure of Inositol Hexakiphosphate (Phytic Acid);.....	14
Figure 4: General Structure of nucleotides and three examples of important mono- and triphosphates;.....	15
Figure 5: Structures of common orthophosphate diesters;	16
Figure 6: Structures of 2-Aminoethyl Phosphonic Acid and Fosfomycin;	16
Figure 7: Effects on phosphorus uptake by root hairs or mycorrhizal fungus hyphae;.....	20
Figure 8: The soil P-Cycle. An overview of the processes controlling the availability of phosphorus to plants and phosphorus transport;	24
Figure 9: Effect of pH on phosphate fixation reactions;.....	25
Figure 10: Decline curve of Olsen-P (form of plant available P);.....	26
Figure 11: Phosphorus fertilizers, their manufacture and relative availabilities;	30
Figure 12: Phosphorus Flows [kt P/a] of Austrian agriculture for 2001;	33
Figure 13: Methodical Approach;.....	37
Figure 14: Structure of MFA Systems;.....	45
Figure 15: Structure of the subsystem agriculture;.....	46
Figure 16: Stock and flow structure, feedbacks and time-delays in System Dynamics;	48
Figure 17: Phosphorus Flows [kt P/a] of Austrian agriculture for 2008;	52
Figure 18: Stock Flow Structure of the System Dynamics P-Model;	54
Figure 19: Schematic structure of the System Dynamics P-Model;.....	56
Figure 20: Main phosphorus stocks and flows in the System Dynamics P-Model; .	57
Figure 21: System structure of the System Dynamic P-Model;	58
Figure 22: The dynamic equilibrium ratio of Pi : Pss : Po Pools and the variables shifting this equilibrium;	60

Figure 23: Lookup Functions for the input variables – all axis are dimensionless [1];.....	61
Figure 24: P in soil solution in soils with the five P Soil Classes in a one year simulation;.....	67
Figure 25: Inorganic P content in soils with the five P Soil Classes in a one year simulation;.....	68
Figure 26: Organic P content in soils with the five P Soil Classes in a one year simulation;	68
Figure 27: P Effect in soils with the five P Soil Classes in a one year simulation;..	69
Figure 28: P-Effect: Development of three soils (P soil class: A, C, E) with mineral and organic fertilization in 10 years;	70
Figure 29: P Effect: Development of three soils (P soil class: A, C, E) with organic fertilization only in 10 years;	71
Figure 30: P Effect: Development of three soils (P soil class: A, C, E) with no fertilization in 10 years;.....	72
Figure 31: P-Effect: Effect of pH-values in a P class C soil in 10 years;.....	73
Figure 32: P in soil solution: Development of a highly fertilized soil (soil class E) over 100 years without fertilization;.....	74