

Phosphorus 2020 – Challenges for Synthesis, Agriculture, and Ecosystems

8th International Phosphorus Workshop IPW8



Foto: L. Tiepolt

September 12–16, 2016

Rostock, Germany

International Phosphorus Workshops (IPW)

IPW1	September 27–29, 1995	Wexford, Ireland	Teagasc, Agriculture and Food Development Authority
IPW2	June 16–19, 1998	Antrim, Northern Ireland	Greenmount College of Agriculture and Horticulture
IPW3	August 28–September 1, 2001	Plymouth, United Kingdom	Robbins Centre, Plymouth University
IPW4	September 16–19, 2004	Wageningen, The Netherlands	Alterra, Wageningen UR
IPW5	September 3–7, 2007	Silkeborg, Denmark	Faculty of Agricultural Sciences, Aarhus University
IPW6	September 21–October 1, 2010	Seville, Spain	University of Seville
IPW7	September 9–13, 2013	Uppsala, Sweden	Swedish University of Agricultural Sciences (SLU)
IPW8	September 12–16, 2016	Rostock, Germany	Leibniz ScienceCampus Phosphorus Research Rostock

8th International Phosphorus Workshop IPW8

Rostock, Germany, September 12–16, 2016

Program and
Book of Abstracts

Published by

The Organizing Committee of the 8th International Phosphorus Workshop (IPW8)
Leibniz ScienceCampus Phosphorus Research Rostock, Germany

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Seestraße 15
18119 Rostock
Germany

The Leibniz ScienceCampus Phosphorus Research Rostock is pleased to host the

8th International Phosphorus Workshop (IPW8) in Rostock (Germany), September 12–16, 2016

PHOSPHORUS 2020 – CHALLENGES FOR SYNTHESIS, AGRICULTURE, AND ECOSYSTEMS

Phosphorus (P) is of vital importance for all life on Earth. It is a major component in animal feed and plant fertilizers but, when present in excess, also a disruptive element in freshwater and marine water bodies. Today, limitations in global mineral P resources have strengthened the demand for efficient alternative P sources and for P-recycling technologies. The International Phosphorus Workshops (IPWs) are well-known for presenting the latest results of research into agricultural and environmental P cycles as well as new methods of P analysis. Recently, environmental problems arising from P surplus but also the implications for food production posed by P deficiencies have made fair and sustainable P distribution a societal challenge. Therefore, at the IPW8, P governance will be an important focus. In addition, given the research interests of the hosting Leibniz-ScienceCampus Phosphorus Research Rostock, the role of P in catalytic reactions and technical applications will debut as a workshop topic. Other topics, addressing subjects ranging from the atomic/molecular to the societal, are guaranteed to stimulate interesting and productive transdisciplinary discussions during the workshop. The themes of IPW8 are:

- Phosphorus cycles and fluxes in the environment
- Sufficiency and efficiency of phosphorus utilization
- Phosphorus recycling: technologies and product applications
- Syntheses of and with phosphorus-containing compounds
- The development of advanced phosphorus analysis methods
- From knowledge to action: phosphorus-related issues in politics and society
- Phosphorus characterization and use efficiency

Supporters



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Introduction

The northern German city of Rostock hosts the 8th International Phosphorus Workshop (IPW8) September 12–16, 2016. The workshop has been conducted regularly in the autumn every 3 years since 1995, convening at different locations. During this time, it has established itself as one of the most significant scientific events focusing on phosphorus. The workshops examine different aspects of phosphorus research and attract scientists, experts, managers, policy-makers, and administrators from around the world who are interested in scientifically sound, sustainable phosphorus management. The first IPW took place in Wexford, Ireland (1995), meeting thereafter and with different emphases in Antrim, Northern Ireland (1998); Plymouth, England (2001); Wageningen, The Netherlands (2004); Silkeborg, Denmark (2007); Sevilla, Spain (2010); and Uppsala, Sweden (2013).

The IPW8 is organized by the Leibniz ScienceCampus Phosphorus Research Rostock, where more than 70 scientists from the University of Rostock and from 5 Leibniz Institutes perform comprehensive research on phosphorus, its numerous chemical compounds, and their effects. Its aims are to promote long-term research cooperation in order to establish the scientific foundations for various P-related processes in the terrestrial, agricultural, limnic and marine environment; to search for new approaches to sustainable phosphorus management; and to develop advanced technologies for the use of phosphorus. Thus, the scope of IPW8 has been extended, as reflected in its thematic sessions covering the topics of P flux in the environment, the sufficiency and efficiency of P utilization, P recycling, P synthesis, P-analytical methods, and a session entitled "From knowledge to action: P-related issues in politics and society."

For IPW8, more than 230 registrations have been received, with participants coming from more than 30 countries. Despite the overwhelming number of Abstracts submitted for oral presentations and posters, we decided to organize the workshop in not more than two parallel sessions. On the first and the last day, there will be single sessions with overarching themes. Sufficient place has been set aside to allow posters to be shown for more than one day and to devote sufficient time and attention to the poster presentations. The program schedule and the Abstracts are provided in this booklet. The venue is located in the heart of the University of Rostock and near Rostock city center, as shown on the map at the back of this booklet. The scheduled activities and half-day excursions to interesting P-research sites will allow IPW8 participants of IPW8 to exchange their knowledge and ideas on P research and applications, and hopefully to establish new cooperations.

The organizers thank the University of Rostock and all participating Leibniz Institutes, the workshop's sponsors, and all those who enthusiastically contributed their help and support in the realization of IPW8.

On behalf of the organizing team, we wish you an interesting, rewarding, and enjoyable conference,

Ulrich Bathmann and Peter Leinweber

Leibniz ScienceCampus Phosphorus Research Rostock (P-Campus)

The overarching goal of interdisciplinary cooperation within the Leibniz ScienceCampus Phosphorus Research Rostock is, through a thematically oriented integrated network, to explore options for the more sustainable management of phosphorus (P). The center seeks to establish the scientific basis for making economic cycles largely independent of mineral phosphate supplies. This will rely on the efficient use, recycling, and recovery of phosphorus. It also studies phosphorus cycles and fluxes in the environment along with the environmental problems, especially in aquatic systems, arising from inefficient phosphorus use or a lack of phosphorus recycling.

The Leibniz ScienceCampus P-Research grew out of a long-standing initiative to integrate phosphorus research in Mecklenburg-Vorpommern, Germany. Officially, the ScienceCampus was launched in 2014, with the signing of a cooperation agreement. The ScienceCampus' partners are the University of Rostock, the Leibniz Institute for Baltic Sea Research Warnemünde (IOW), the Leibniz Institute for Catalysis (LIKAT), the Leibniz Institute for Farm Animal Biology (FBN), the Leibniz Institute of Plant Genetics and Crop Plant Research (IPK, Satellite Collections North), and the Leibniz Institute for Plasma Research and Technology (INP).

The P-Campus conducts strategic research and encourages interdisciplinarity in its topics, projects, and methods. Its efforts include bringing together the expertise of its members to provide the basis for a comprehensive investigation of the essential element P, its diverse chemical compounds, and its modes of action in agriculture and the environment as well as in technical and industrial processes. Along with basic and applied research, the P-Campus seeks to develop new technologies for phosphorus use and to subsequently transfer them to the economy.

Research foci of the Leibniz ScienceCampus Phosphorus Research are phosphorus cycles and fluxes in the environment, sufficiency and efficiency of phosphorus use and phosphorus recycling, and phosphorus as an element in and out of catalytic processes. Additionally, the development of advanced analytical methods in phosphorus research has been defined as a cross-sectional task to serve and stimulate the above-mentioned research clusters.

In 2016, members of the Leibniz ScienceCampus Phosphorus Research included more than 70 scientists and doctoral students belonging to 45 working groups. In addition to around 30 thematically assigned, externally funded projects, new research projects are being developed continuously. To support networking among scientists of the P-Campus and other institutions, numerous internal as well as public events are organized each year, such as the lecture series "Phosphorus Research," colloquia with guest lectures, annual symposia, doctoral student meetings, events for young scientists and international events.

The graduate program of the Leibniz ScienceCampus Phosphorus Research offers excellent, structured training of young scientists in innovative phosphorus

research topics. It supports students with phosphorus-related theses, doctoral students, and postdocs carrying out phosphorus research. The core of the program is the Graduate School of Phosphorus Research, currently with 11 PhD students and funded by the Leibniz Association. The topics of the interdisciplinary supervised projects range from the study of different phosphorus forms in the aquatic environment, phosphorus cycles in aquaculture, P uptake in crop production and by livestock, phosphorus in catalytic processes, and the political and legal aspects of phosphorus management.

In addition, the Leibniz ScienceCampus Phosphorus Research is linked to political and economic networks through its membership in the Deutsche Phosphor-Plattform e.V. (DPP) and the European Sustainable Phosphorus Platform (ESPP). The Leibniz ScienceCampus Phosphorus Research is funded by the Leibniz Association and the Ministry of Agriculture, Environment and Consumer Protection Mecklenburg-Vorpommern, Germany.

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More information can be found at: www.sciencecampus-rostock.de

Partners:



LEIBNIZ INSTITUTE
FOR FARM ANIMAL BIOLOGY



Local Organizing Committee

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Prof. Dr. Peter Leinweber, University of Rostock

Coordination office

Dr. Inga Krämer, Leibniz ScienceCampus Phosphorus Research Rostock
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Prof. Dr. Felix Ekardt, University of Rostock and Research Unit Sustainability and
Climate Policy
Prof. Dr. Marko Hapke, Leibniz Institute for Catalysis
Dr. Gerald Jandl, University of Rostock
Dr. Monika Nausch, Leibniz-Institute for Baltic Sea Research Warnemünde
Prof. Dr. Detlef Schulz-Bull, Leibniz-Institute for Baltic Sea Research
Warnemünde
Prof. Dr. Jens Tränckner, University of Rostock
Dr. Thomas Werner, Leibniz Institute for Catalysis
Prof. Dr. Klaus Wimmers, Leibniz-Institute for Farm Animal Biology
Dr. Dana Zimmer, University of Rostock

International Scientific Advisory Board

Theme 1: Phosphorus cycles and fluxes in the environment (Prof. Dr. U. Bathmann, Dr. M. Nausch)

Prof. Dr. Philip Haygarth, Lancaster Environment Centre/UK

Prof. Dr. Ellery D. Ingall, Georgia Institute of Technology

Prof. Dr. Heide Schulz-Vogt, Leibniz Institute for Baltic Sea Research
Warnemünde (IOW)

Prof. Dr. Paul Withers, Prifysgol, Bangor University/UK

Theme 2: Sufficiency and efficiency of phosphorus utilization (Prof. Dr. B. Eichler-Löbermann, Prof. Dr. P. Leinweber, Prof. Dr. K. Wimmers)

Prof. Dr. Emmanuel Frossard, Swiss Federal Institute of Technology in Zurich
(ETH Zurich)

Dr. Philippe Hinsinger, French National Institute for Agricultural Research
(INRA)/France

Dr. Alan Richardson, Commonwealth Scientific and Industrial Research
Organisation (CSIRO)/Australia

Prof. Dr. Markus Rodehutschord, University of Hohenheim

Theme 3: Phosphorus recycling: technologies and product applications (Prof. Dr. J. Tränckner)

Prof. Dr. Heribert Insam, University of Innsbruck

Dr. Christian Kabbe, Berlin Centre of Competence for Water

Dr. Kornél Kovács, University of Szeged

Prof. Dr. Hisao Ohtake, Osaka University Japan

Theme 4: Syntheses of and with phosphorus- containing compounds (Prof. Dr. M. Hapke, Dr. T. Werner)

Prof. Dr. Matthias Beller, Leibniz Institute for Catalysis (LIKAT)

Prof. Dr. Christian Müller, Freie Universität Berlin

Prof. Dr. Manfred Scheer, Universität Regensburg

Prof. Dr. Klaus-Dieter Weltmann, Leibniz Institute for Plasma Science and
Technology (INP)

Theme 5: The development of advanced phosphorus analysis methods (Prof. Dr. P. Leinweber, Prof. Dr. D. Schulz-Bull)

Dr. Barbara Cade-Menun, Semiarid Prairie Agricultural Research Centre, Canada

Prof. Dr. Axel Schulz, University of Rostock

Prof. Dr. Albert Sickmann, Leibniz-Institut für Analytische Wissenschaften (ISAS)

Prof. Dr. Donald Sparks, University of Delaware

Theme 6: From knowledge to action: P-related issues in politics and society (Prof. Dr. F. Ekardt)

Arnoud Passenier, president ESPP, Dutch Ministry of Infrastructure and the
Environment

Michael Spitznagel, Deutsche Phosphor-Plattform DPP e.V.

Prof. Dr. Susanne Stoll-Kleemann, University of Greifswald

General Information

Conference venue

The workshop will take place at the Ulmencampus, Ulmenstraße 69, University of Rostock (see the city map on the back cover). The presentations will be held in the Audimax and in two lecture halls within the Arno-Esch-Building (Hörsäle HS1 and HS2). The poster exhibition will take place in Haus 1 (see Overview Ulmencampus, page 16/17).

Registration and Information Desk

Registration will start in the entrance area of the Audimax at 2 pm on Monday September 12. From Tuesday to Thursday, the Registration and Information Desk can be found in the Arno-Esch-Building, and on Friday again at the Audimax.

We recommend that you wear your name tag during the workshop so that you can easily pass access the conference rooms.

Homepage of IPW8

www.sciencecampus-rostock.de/ipw8-home.html

Presentations

All lecture halls have projectors and there will be a person responsible for them in every hall. Please bring your presentation file on a usb flash drive to the Registration and Information Desk not later than 30 minutes before your presentation session starts, but preferably during your registration, to transfer it to a local computer. To guarantee the visual quality of your presentation, the format should be in PowerPoint 2003 to 2010 or OpenOffice 3.4.

Posters

Posters will be presented in the rooms 124 and 126 of Haus 1 on Tuesday and Thursday afternoon. The posters should be mounted with pins (available at the Registration and Information Desk). At the beginning of the poster sessions, each poster (in pdf format as one slide) can be shown in a 3-minute presentation (Poster Slam). The best presentations of young researchers will be recognized with an award.

Internet access

Throughout the workshop, internet access via WLAN will be available, most easily by using eduroam. There is a computer pool in room 224 (Haus 1, 2nd floor) where you can also get a guest account if you are unable to use eduroam.

Coffee and lunch

Coffee and lunch will be served in the tent in front of the Audimax. Lunch will be available on a self-payment basis. Additionally, there are several restaurants and snack bars near the venue.

Welcome reception, Monday, September 12, starting at 6 pm in the tent in front of the Audimax.

Guided city walk, Tuesday, September 13, starting at 5:30 pm.

A city walk to see Rostock and its historical attractions.

Starting point: Doberaner Platz, which can be reached on foot or by tram (see map on the back cover).

On foot: From Ulmenstraße you will reach the Saarplatz, turn left into the Wismarsche Straße, Doberaner Platz is located at the end of this street.

By tram: Take tram no. 6 (direction Mensa) from Parkstraße to Doberaner Platz, which will be the second stop.

Excursions, Wednesday, September 14

Participants who have registered for an excursion are asked to meet in front of Haus 3 (see map on page 16) at the given time:

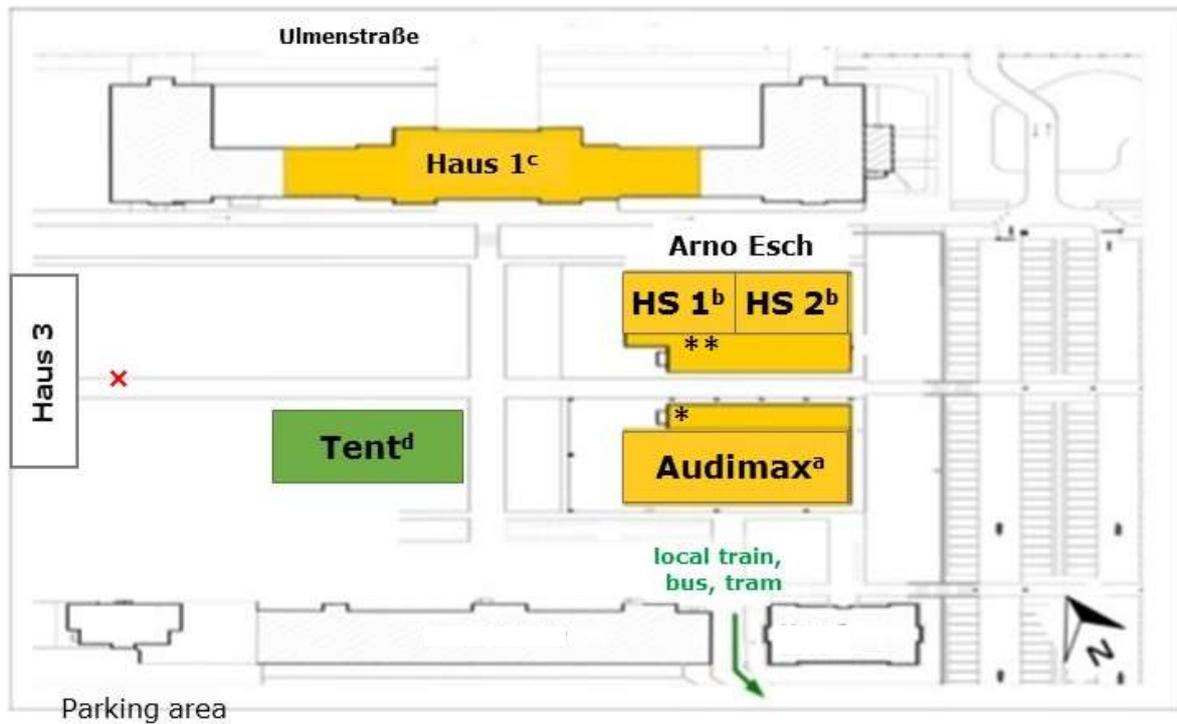
Excursion	Starting time	Appr. return time
1 <i>A trip to the coast: The Leibniz Institute for Baltic Sea Research and the Hütelmoor fen</i>	1:00 pm	6:30/7 pm
2 <i>Energy from biomass: Visit experimental and industrial energy-production plants</i>	1:15 pm	5:30 pm
3 <i>Experimental Animal Facilities at the Leibniz Institute for Farm Animal Biology</i>	-	
4 <i>Extremely fertile soils in the Baltic coast region: natural phenomena or anthropo-/pedogenesis?</i>	1:00 pm	8:00 pm
5 <i>Full scale P-recycling from dairy-industry wastewater</i>	12:40 pm	6:30/7 pm
6 <i>Phosphorus analytics</i>	1:30 pm	

Conference dinner (Warnemünde), Thursday, September 15, starting at 6.30 pm

The conference dinner will take place in a former train-engine shed ("Lokschuppen"), located at the mouth of the Warnow River and near the harbor entrance, close to the beautiful seaside resort of Warnemünde and its large beach. From here, you can watch the arrival and departure of many different types of ships, including large cruise lines. There may even be fireworks, as a send-off for three cruise lines departing that evening. You can reach the Lokschuppen via the local train (S-Bahn) from the Parkstraße station, near the Ulmencampus (direction Warnemünde). Get off at the final destination, which is Warnemünde and follow the signs (about 250 m walking distance). Please wear your name tag.

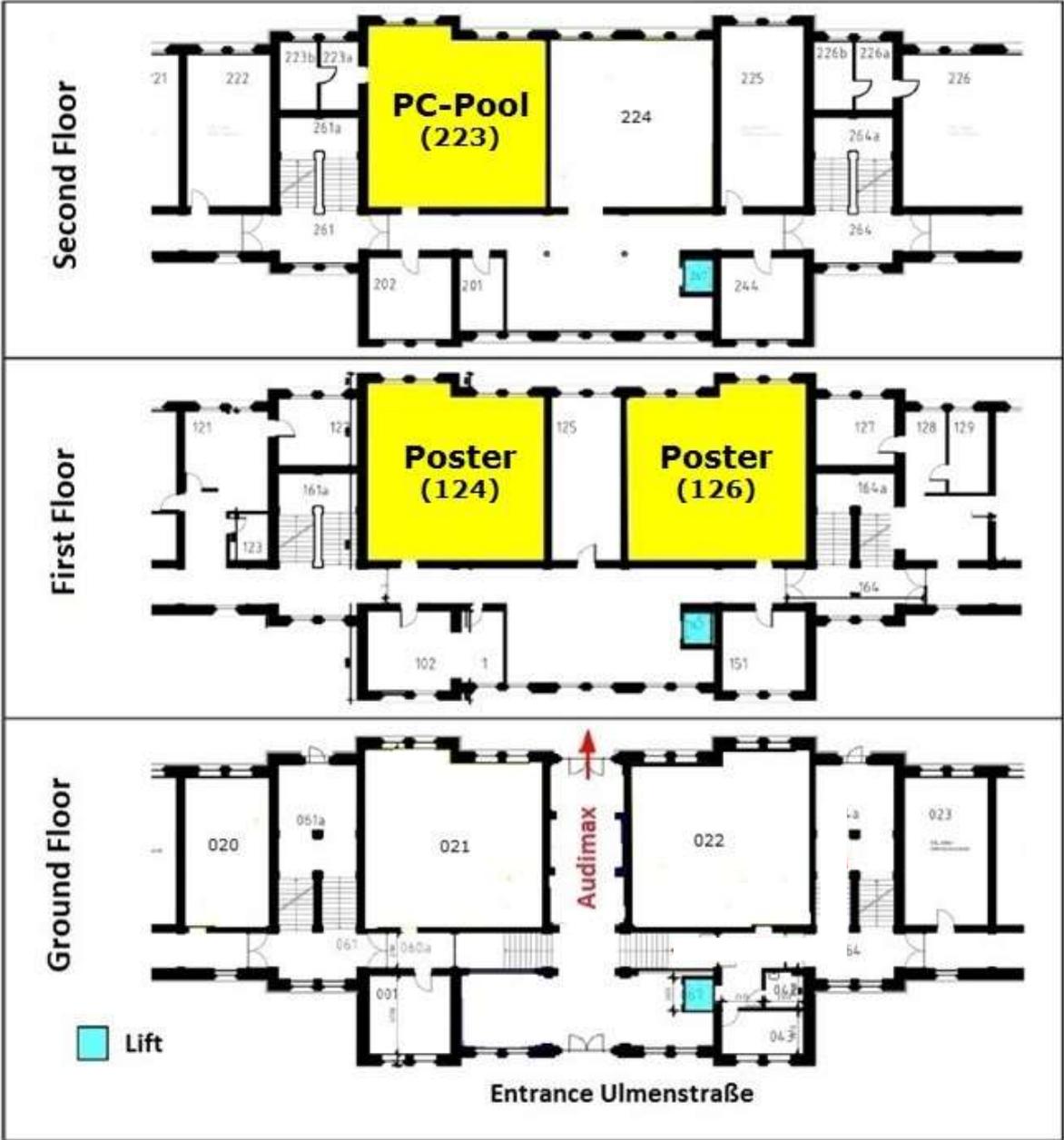
Members of the organizing committee of the IPW8 can be identified by their red T-shirts bearing the green "P" logo of the Leibniz Science-Campus Phosphorus Research.

Overview Ulmencampus (Workshop Venue)



- ^a Audimax: Oral presentations Monday & Friday
- ^b Arno-Esch: Oral presentations Tuesday–Thursday
- ^c Haus 1: Poster presentation Tuesday & Thursday (detailed overview of the building on p. 17)
- ^d Tent: Catering (Welcome reception, coffee & lunch breaks)
- * Registration & Information Desk Monday & Friday (Audimax)
- ** Registration & Information Desk Tuesday–Thursday (Arno-Esch)
- × Starting point for excursions

Overview „Haus 1“



Practical Information

Electricity

The electrical voltage used throughout Germany is 220/230 V.

Emergency calls

Please dial 112 if the services of an ambulance, the police, or the fire department are needed. 112 is a special emergency number that provides access regardless of whether you are calling from a fixed or a mobile telephone.

The emergency number to reach the police is 110.

International calls

Dial 00+country code+area code+phone number. For example, the country code for China is 0086, and for the US/Canada 001.

Medical services

The University Hospital is located in the Südstadt district of Rostock.

Telephone: 0381 44010. The emergency room in German is the Notaufnahme.

Money exchange, currency

The Euro is the official currency in Germany. There is a currency exchange agency (ReiseBank) in the Warnemünde train station (Am Bahnhof 10A, 18119 Rostock). Opening hours are Monday to Friday 9 am to 6 pm and Saturday & Sunday 9 am to 12 noon.

Money can be also exchanged at local banks. Many restaurants and shops in Warnemünde and Rostock accept US dollars as well as credit cards.

Shopping

Most stores in Rostock are open from 9 am to 8 pm. Some stores, especially in Warnemünde, are open on Sundays as well. Grocery stores usually have longer opening hours.

Pharmacy

There are many pharmacies (in German, Apotheke) in Rostock. Look for the red "A".

Smoking

Smoking is not allowed in the conference venues or indoor establishments such as restaurants and bars.

Tourist information

The local tourism office provides information on services such as car rental, bicycle rental, boat rental, etc.

Addresses:

- Universitätsplatz 6, 18055 Rostock
- Am Strom 59, 18119 Rostock-Warnemünde

Homepage: www.rostock.de

E-Mail: touristinfo@rostock.de

Program Overview

Program overview

Monday, Sept. 12		Tuesday, Sept. 13		Wednesday, Sept. 14	
		09:00-12:30	Oral presentations T2 + T3	09:00-12:30	Oral presentations T1 + T7
14:00	Registration	13:30-15:00	Poster presentations ('Slam') T2 + T3	13.30	Excursions
16:00-18:00	Opening session	15:30-17:00	Poster presentations		
18:00	Welcome reception	17:30-19:00	Guided city walk		

Thursday, Sept. 15		Friday, Sept. 16		
09:00-12:30	Oral presentations T4 + T5	08:30-11:10	Oral presentations T6	Audimax
13:30-15:00	Poster presentations ('Slam') T1, T4, T5, T6	11:10-13:00	Panel discussion	Arno-Esch-Building
15:30-17:00	Poster presentations			„Haus 1“
18:30	Conference dinner			Tent

T1 Theme 1: Phosphorus Cycles and Fluxes in the Environment

T2 Theme 2: Sufficiency and Efficiency of Phosphorus Utilization

T3 Theme 3: Phosphorus Recycling: Technologies and Product Applications

T4 Theme 4: Syntheses of and with Phosphorus-Containing Compounds

T5 Theme 5: The Development of Advanced Phosphorus Analysis Methods

T6 Theme 6: From Knowledge to Action: P-Related Issues in Politics and Society

T7 Theme 7: Phosphorus Characterization and Use Efficiency (oral presentations only)

Panel discussion & synthesis "Handling the phosphorus paradox in agriculture and natural ecosystems: the scarcity, necessity, and burden of P".

Panelists: Prof. Dr. U. Bathmann, Prof. Dr. F. Ekardt, Prof. Dr. Philip Haygarth, Dr. Christian Kabbe, Prof. M. Rodehutschord, Prof. Dr. S. Stoll-Kleemann

Moderator: Sonja van Renssen

Monday, September 12, 2016

14:00	Registration
16:00 - 16:40	Opening remarks
16:40 - 17:20	Keynote talk: Jarvie: Back to the future: Historical phosphorus fluxes, legacies, and water-quality management
17:20	Keynote talk: Kaasinen: Towards sustainable phosphorus management in the Baltic Sea region
18:00 - 22:00	Welcome reception

Tuesday, September 13, 2016

Theme 2 Sufficiency and Efficiency of Phosphorus Utilization	Theme 3 Phosphorus Recycling - Technologies and Product Applications
09:00 - KEYNOTE Frossard: How much phosphorus do our agro-ecosystems really need?	09:00 - KEYNOTE Kabbe: Circular economy - challenges and opportunities for phosphorus recycling
09:40 - Eichler-Löbermann, Busch, Brand, Stahn, Miegel, Uptmoor: Phosphorus utilization in mixed cropping systems	09:40 - Folberth, Binder: Global flows of nitrogen and phosphorus embedded in agricultural products and recycling potential
10:00 - McLaren, Simpson, McLaughlin, McBeath, Smernik, Guppy, Richardson: The fertilizer phosphorus use efficiency of leguminous-based pastures under different management in the high rainfall zone of south eastern Australia	10:00 - Bünemann, Symanczik, Koller, Menold, Oelmann, Stemann: Evaluation of pyrolysis chars from sewage sludge as phosphorus fertilizers
10:20 - Meyer, Bünemann, Frossard, Maurhofer, Mäder, Oberson: Can inoculation with <i>Pseudomonas protegens</i> CHA0 enhance the mobilization of scarcely soluble phosphorus from soil and uptake by <i>Lolium multiflorum</i> ?	10:20 - Herzel, Adam, Stemann, Hermann: A thermochemical process for P-fertilizer production from sewage sludge ashes investigated from lab to industrial scale
10:40 – 11:10 Coffee Break	
11:10 - Bruun, Harmer, Bekiaris, Christel, Zuin, Hu, Jensen, Lombi: The effect of P speciation on soil availability of P in biochar produced from solid fraction of manure at different pyrolysis temperatures	11:10 - Amann, Egle, Zoboli, Rechberger, Zessner: Impact of co-incineration of refuse derived fuels (RDF) on sewage sludge ash quality with focus on P-recovery
11:30 - Rodehutschord: Possibilities and perspectives to improve P efficiency in livestock feeding	11:30 - Herr, Mocker, Mayer: Phosphorus recycling in the mineral fertilizer industry - co-processing of sewage sludge ash during chemical wet phosphoric acid production
11:50 - Oster, Just, Büsing, Muráni, Polley, Vollmar, Wolf, Ponsuksili, Wimmers: Elucidating the biodiversity of P homeostasis towards improved P efficiency in pigs	11:50 - Ohtake, Okano, Kunisada, Takano, Masuda: Innovatively simple technology for phosphate recovery using a bifunctional adsorption- aggregation agent
12:10 - Zhang, Hao, Tan, Welacky, Wang, Hao, Hong: Long-term cumulative contribution of phosphorus-based swine manure application to soil test phosphorus under corn-soybean rotation	12:10 - Tränckner, Beetz, Koegst, Cramer: Cost-efficient phosphorus removal in rural waste water treatment plants (WWTP)
12:30 – 13:30 Lunch Break	
13:30 – 15:00 Poster Presentations („Slam“) Theme 2, 3	
15:00 – 15:30 Coffee Break	
15:30 – 17:00 Poster Presentations	
17:30 – 19:00 Guided City Walk	

Wednesday, September 14, 2016

Theme 1 Phosphorus Cycles and Fluxes in the Environment	Theme 7 Phosphorus: Characterization and Use Efficiency
09:00 - KEYNOTE Ingall: Nature and dynamics of marine dissolved organic phosphorus	09:00 - Rydin, Sjöberg, Kumblad, Ek: Organic phosphorus forms in Baltic Sea sediments
09:40 - Mellander, Jordan, Bechmann, Shore, McDonald, Fovet, Gacuel-Odoux: Weather amplifications as overriding drivers of P loss in Western Europe	09:20 - Hupfer, Herzog, Jordan, Rothe, Kleeberg: The long-term storage of phosphorus via vivianite formation in iron rich surface sediments is prevented by nitrate
10:00 - Zilla, Angulo-Schipper, Carlos Méndez, Dippold, Kuzyakov, Spielvogel: Effects of spatial P heterogeneity on microbial P uptake and community structure in forest soils	09:40 - Richardson, McLaren, McBeath, McLaughlin, Smernik, Guppy, Moore, Simpson: Inefficiencies associated with phosphorus fertilization of a grazed pasture system
10:20 - Ulén, Stenberg, Wesström: Using a waterflow flashiness index as predictor for phosphorus losses from subsurface drains on a Swedish farm with clay soils	10:00 - Duboc, Santner, Golestani Fard, Tacconi, Zehetner, Wenzel: A complementary set of methods to characterize P availability from fertilizers of varying origin and solubility
10:40 – 11:10 Coffee Break	
11:10 - Shore, Melland, Mellander, Jordan: The relative and combined impacts of storm and low-flow phosphorus pressures on stream ecology in agricultural catchments: a five year study	11:10 - Nkebiwe, Weinmann, Bar-Tal, Müller: Placement of P and N to improve crop nutrient acquisition and yield: a meta-analysis
11:30 - Gruau, Gu, Dupas, Gascuel-Odoux, Rumpel: Complex inter-play of soil characteristics, groundwater dynamics and biogeochemical processes on the release of dissolved phosphorus from riparian vegetated buffer strips	11:30 - Buczko, van Laak: Re-evaluation of Phosphorus fertilizer recommendations based on meta-analyses of long-term field experiments
11:50 - Berthold, Schumann: How the catchment area prevents the “good ecological state” of a shallow estuary. A case study in the coastal water bodies of the southern Baltic Sea	11:50 - Gu, Gruau, Dupas, Gascuel-Odoux, Rivard, Marcel: Distribution of Phosphorus-containing colloids in shallow groundwater from a small agricultural catchment as revealed by the combination of ultrafiltration, ultracentrifugation, ICP-MS and XANES data
12:10 - Nausch, Nausch, Leipe, Neumann: Phosphorus in the Baltic Sea – measured since decades, but really understood?	12:10 - Polain, Guppy, Knox, Wilson, Siebers: Delta18O-P as a marker for depth resolved microbial turnover of phosphorus in native and cropped Australian Vertisols
12:30 – 13:30 Lunch Break	
Excursions (starting times see p. 15)	

Thursday, September 15, 2016

Theme 4 Syntheses of and with Phosphorus- Containing Compounds	Theme 5 The Development of Advanced Phosphorus Analysis Methods
09:00 - KEYNOTE Müller: Recent 09:40 Developments in the chemistry of low-coordinate phosphorus heterocycles	09:00 - KEYNOTE Cade-Menun: Phosphorus 09:40 research and ³¹ P-NMR spectroscopy: Current knowledge and future directions
09:40 - Zhang, Jiao, Michalik, Selent, 10:00 Franke, Börner: Hydrolysis stability of bidentate phosphites utilized as modifying ligands in the Rh-catalyzed n-regioselective hydroformylation of internal olefins	09:40 - Gros, Ahmed, Kühn, Leinweber: 10:00 Glyphosate binding in soil as revealed by sorption experiments, mass spectrometry and quantum-chemical modeling
10:00 - Holz, Rumpel, Börner: A new 10:20 strategy for the synthesis of P-chiral ligands for asymmetric catalysis	10:00 - Gamble, Northrup, Sparks: Novel 10:20 spectroscopic techniques to examine soil phosphorous speciation
10:20 - König, Heller: Rhodium diphosphine 10:40 complexes in homogeneous catalysis – How to use the catalysts more efficiently?	10:20 - Kubis, König, Selent, Ludwig, 10:40 Franke, Börner: In situ-IR- spectroscopy for the study of kinetic and mechanistic aspects of alkene hydroformylation with metal catalysts modified by phosphorus(III) ligands
10:40 – 11:10 Coffee Break	
11:10 - Steinbauer, Büttner, Werner: CO ₂ 11:30 valorization utilizing new P-based catalysts	11:10 - Oelmann, Sorkau: Quantification of 11:30 enzyme-mediated hydrolysis by means of the oxygen isotope ratio of phosphate in grassland and forest soils
11:30 - Grandane, Schirmer, Suna, 11:50 Werner: Phosphorus-based organocatalysts for base free catalytic Wittig reaction	11:30 - Sjöberg, Thelin, Rydin: Separation 11:50 of inositol phosphate isomers in environmental samples by ion- exchange chromatography coupled with electrospray ionization tandem mass spectrometry
11:50 - Täufer, Hapke, Schulz: P-N- 12:10 Compounds as synthons in cyclisation reactions	11:50 - McIntyre, Evershed, Johnes, 12:10 Arthur, Lloyd: Application of high resolution mass spectrometry to high the characterisation of organic phosphorus in environmental matrices
12:10 - Rabeah, Brückner: Highly tunable 12:30 organic-inorganic hybrid materials based on the utility of vanadium organophosphonate clusters	12:10 - von Sperber, Lewandowski, 12:30 Tamburini, Bernasconi, Frossard, Amelung: Real-time monitoring of oxygen isotope exchange between phosphate and water using Raman spectrometry
12:30 – 13:30 Lunch Break	
13:30 – 15:00 Poster Presentations (,Slam`) Theme 1, 4, 5, 6	
15:00 – 15:30 Coffee Break	
15:30 – 17:00 Poster Presentations	
18:30 Conference Dinner	

Friday, September 16, 2016

Theme 6	
From Knowledge to Action: P-Related Issues in Politics and Society	
08:30 - 09:10	KEYNOTE Stoll-Kleemann: Meat consumption, human behaviour and phosphorus
09:10 - 09:30	Douhaire, Stubenrauch: EU regulatory and policy objectives relevant to sustainable agricultural land and phosphorus use
09:30 - 09:50	Garske, Wieding: Changing animal food consumption as part of phosphorus regulation?
09:50 - 10:10	Buckley, McDonald, Leach: What influences the achievement of optimal soil P status at farm level?
10:10 – 10:30 Coffee Break	
10:30 - 10:50	Klages, Osterburg: German fertiliser legislation: current and future rules on phosphorus
10:50 - 11:10	Wang: Strategies for mitigating China's phosphorus resource crisis
11:10 - 13:00	PANEL DISCUSSION "Handling the phosphorus paradox in agriculture and natural ecosystems: scarcity, necessity and burden of P" Moderation: Sonja van Rensen
13:00 End	

Overview Poster Presentations

Theme 1 Phosphorus Cycles and Fluxes in the Environment (Poster numbers P1.1-P1.43 in the given order)

Translocation of P-carrying natural nanoparticles and colloids in forest soil mesocosm effluents

Missong, A., Holzmann, S., Bol, R., Nischwitz, V., Puhlmann, H., Siemens, J., von Wilpert, K., Klumpp, E.

Quality, quantity and transformation of P losses from diffuse sources to the Baltic Sea

Jahn, S., Kahle, P., Schulz-Vogt, H., Lennartz, B., Nausch, M.

Cellular structures of filamentous cyanobacteria affected by phosphate availability

Braun, P., Schulz-Vogt, H., Siebers, M., Dörmann, P., Nausch, M.

Phosphorus storage and mobilization in coastal Phragmites wetlands: Influence of local-scale hydrodynamics

Karstens, S., Buczko, U., Jurasinski, G., Glatzel, S.

Phosphorus dynamics in agricultural used lowland catchments in NE-Germany

Koch, S., Kahle, P., Lennartz, B.

Visualization of colloid transport pathways in mineral soils

Koch, S., Kahle, P., Lennartz, B.

Determination of Inositol Phosphates in Aquatic Systems of the German Baltic Coastal Area

Recknagel, C., Sjöberg, P., Abraham, M., Schulz-Bull, D.

The characterization of colloid-bound and dissolved phosphorus in topsoil water extracts along a grassland transect from Cambisol to Stagnosol

Jiang, X., Bol, R., Nischwitz, V., Willbold, S., Bauke, S., Vereecken, H., Amelung, W., Klumpp, E.

Impact of phosphate saturation degree and other edaphic factors on groundwater P concentration, in acid sandy soils and on a regional scale

Mabilde, L., De Neve, S., Sleutel, S.

Soil organic matter reduces the sorption of arsenate and phosphate: a soil profile study and geochemical modelling

Verbeeck, M., Nicolas Soenens, N., Smolders, E.

Drying-rewetting cycles release phosphorus from forest soils

Dinh, M.-V., Schramm, T., Spohn, M., Matzner, E.

Mechanisms of adsorption and desorption of phosphorus on crystalline iron, aluminum, manganese (hydr)oxides as well as iron and calcium phosphates in comparison to amorphous iron-aluminum compounds

Gypser, S., Freese, D.

Iron coated sand/glaucanite filters for phosphorus removal from artificially drained agricultural fields

Vandermoere, S., De Neve, S.

Vivianite - the disregarded phosphorus sink in aquatic sediments

Rothe, M., Kleeberg, A., Hupfer, M.

Heterogeneity of the phosphorus sorption kinetics in soils: from compartment models to a continuous distribution model

Warrinnier, R., Braun, S., Gustafsson, J. P., Smolders, E.

Effect of land-use management on phosphorus budgets in German grassland

Sorkau, E., Traub, K., Oelmann, Y.

Phosphorus budgets of the land-water transitional zones in a cold temperate lagoon

Berthold, M., Karstens, S., Buczek, U., Schumann, R.

Phosphorus demand in phytoplankton communities - alkaline phosphatase activity as a proxy?

Schaub, I., Schumann, R., Karsten, U.

Organic phosphorus changes by tillage systems and cover crops to sustainable soybean/cotton succession in Brazilian Cerrado

Rodrigues, M., Pavinato, P. S.

Soluble vs. Particulate Phosphorus in Stormwater

River, M., Richardson, C.

A complementary set of methods to characterize P availability from fertilizers of varying origin and solubility

Duboc, O., Santner, J., Golestani Fard, A., Tacconi, J., Zehetner, F., Wenzel, W.

Elemental composition of particulate inorganic phosphorus in discharges from an artificially drained lowland catchment

Nausch, M., Woelk, J., Kahl, P., Nausch, G., Leipe, T., Lennartz, B.

Phosphorus cycling within a low productive plankton community in the Gulf of Finland (Northern Baltic Sea)

Nausch, M., Achterberg, E., Bach, L., Goldstein, J., Hellemann, D., Czerny, J., Schulz, K., Riebesell, U.

Molecular Level Investigation of P-related Reaction Mechanisms at Soil Mineral Surfaces

Ahmed, A.A., Leinweber, P., Kühn, O.

The role of biological soil crusts in P-cycling

Baumann, K., Glaser, K., Karsten, U., Leinweber, P.

Reducing Phosphorus Leaching and Runoff from Poultry Litter with Alum: Twenty Year Small Plot and Paired-Watershed Studies

Moore, P.A. Jr., Huang, L., Kleinman, P.J.A., Elkin, K.R., Savin, M.C., Pote, D.H., Edwards, D.R.

Biodiversity of biological soil crusts from sand dunes and their functional role in the P and C biogeochemistry (CRUSTFUNCTION)

Glaser, K., Schulz, K., Mikhailiyuk, T., Leinweber, P., Karsten, U.

The role of the organic layer for phosphorus nutrition of young beech trees (*Fagus sylvatica* L.) at two sites differing in soil Phosphorus availability

Hauenstein, S., Pütz, T., Oemann, Y.

Development of soil phosphorus and phosphatase activities under different management in an organic farm over 12 years from conversion

Ohm, M., Paulsen, H. M., Moos, J. H., Schüler, M., Fystro, G., Eichler-Löbermann, B.

Nanoparticulate and colloidal Phosphorus in forested headwater catchments

Gottselig, N., Bol, R., Nischwitz, V., Amelung, W, Siemens, J, Klumpp, E.

Which soil P test reflects best the phosphorus availability for leaching?

Amery, F., Vandecasteele, B., Ruyschaert, G., Odeurs, W., Warrinier, R., Nawara, S., Smolders, E.

Phosphorus from source to sea – Integrated phosphorus and water resources management for sustainable water protection (PhosWaM)

Krämer, I., Nausch, G., Börner, R., Mehl, D., Lennartz, B.

Relating soil chemistry to phosphorus (P) mobilisation along the P transfer continuum at catchment scale

McDonald, N.T., Wall, D.P, Mellander, P-E., Shore, M., Daly, K.

Phosphorus Loss with Phosphorus-Based Cattle Manure Application from a Clay Loam Soil

Zhang, T.Q., Tan, C.S., Wang, Y.T., Welacky, T.

Effects of long-term fertilisation management on microbial P mobilisation and community structure in the crop rhizosphere

Goers, M., Baum, C., Grafe, M., Schulz, S., Schloter, M., Leinweber, P.

Drivers and constraints for Polish farmer´s implementation of measures to remediate phosphorus and nitrogen leaching to waters

Ulén, B., Tonderski, K.S., Pietrzak, S., Kielbasa, B., Drangert, J.-O., Fila, J., Radtke, K., Krystoforsky, M., Wojcieszak, L.

Background soil phosphorus levels in marine sediments in Norway

Bechmann, M.

The role of clay minerals in phosphorus sorption in sandy acid soil

Debicka, M., Woźniczka, P.

Modeling Phosphorus Capture by Grasses Growing in a Midwestern Riparian Buffer

Kovar, J.L., Rahutomo, S., Thompson, M.L.

Phosphorus solubilization by microorganisms at different stages of soil development

Brucker, E., Spohn, M.

The storage of P in riparian Buffer Zone soils related to the Shape of the buffer zone and the adjacent Landscape

Hille, S., Holton Rubæk, G., Heckrath, G.J.

Modelling natural phosphorus export from lake catchments

Tammelin, M., Kauppila, T.

Organic phosphorus as affected by soil properties and fertilization in Mediterranean environments

Recena, R., Cade-Menun, B., Delgado, A.

Theme 2 Sufficiency and Efficiency of Phosphorus Utilization
(Poster numbers P2.1-P2.49)

Phosphorus stocks and speciation in top- and subsoils of a long-term fertilization experiment: evidence from sequential fractionation, ³¹P-NMR, and P K-edge XANES spectroscopy

Koch, M., Kruse, J., Eichler-Löbermann, B., Zimmer, D., Willbold, S., Leinweber, P., Siebers, N.

Effect of soil phosphorus availability on legume distribution and phytodiversity

Mahnke, B., Müller, J., Wrage-Mönnig, N.

Plant uptake of phosphorus recycled from urban waste on calcareous soil

Meyer, G., Frossard, E., Nanzer, S., Udert, K., Mäder, P., Oberson A.

Cattle slurry distribution and acidification influence the initial P availability for maize

Pedersen, I., Rubæk, G. & Sørensen, P.

Influence of different recycled digestate fertilizers on P-uptake of maize plants and soil biological processes in different soils

Bach, I.-M., Müller, T.

Synthetic minerals to increase P availability in soils

Everaert, M., Degryse, F., De Vos, D., Smolders, E.

The effect of soil pH on phosphorus fertiliser efficiency as measured by soil test P, herbage growth and herbage P concentration at contrasting grassland sites.

Fox, I., Bailey, J.S., Watson, C.J., Wall, D.P.

Long-term P and K fertilisation can partially alleviate yield losses in response to environmental stress and increase N use efficiency.

van der Bom, F., Magid, J., Stoumann Jensen, L.

The equivalence of the CAL and DL extraction method to assess the amount of plant available phosphorus in soils

van Laak, M., Buczko, U.

Mechanisms of carbon-phosphorus trading in arbuscular mycorrhizal symbioses and consequences for carbon sequestration in soils

Andrino, A., Boy, J., Sneider, C., Winkelmann, T., Guggenberger, G.

Interactive effects of phosphate-solubilizing *Penicillium* spp., arbuscular mycorrhizal fungi and biochar on growth of wheat

Efthymiou, A., Grønlund, M., Jensen, B., Müller-Stöver, D.S, Jakobsen, I.

Phosphate solubilising bacteria: A key to efficient phosphorus utilization

Seth, K., Moot, D.J., O'Callaghan, M., Ridgway, H.J.

Genetic regulation of phosphatase production and activity to increase P uptake from deficient soils

Wacker, K., Dehmer, K. J., Eichler-Löbermann, B., Uptmoor, R.

Mechanisms of P mobilization in the rhizosphere involving weeds and crop plants

Zacher, A., Baum, C., Gerowitt, B., de Mol, F., Dehmer, K. J.

Impact of dietary phosphorus on hormone balance and gene expression in kidney and its implications on immune status of weaned piglets

Just, F., Oster, M., Büsing, K., Muráni, E., Ponsuksili, S., Polley, C., Vollmar, B., Wolf, P., Wimmers, K.

Agronomic effectiveness of P resources

Gropp, T., Uptmoor, R., Eichler-Löbermann, B.

Phosphorus flows in Berlin-Brandenburg

Theobald, T.F.H., Schipper, M., Kern, J.

Unravelling Plant-Availability of Recycling Phosphorus-Fertilizers by Pot Experiments using Phosphorus XANES Spectroscopy

Vogel, C., Rivard, C., Wilken, V., Muskolus, A., Adam, C.

Nanoparticles of silicate minerals enhance phosphorus availability in soil

Zaimenko, N., Bedernichek, T., Slyusarenko, O.

Changes in Grassland Soil P Forms with Fertilizer Application and Withdrawal

Cade-Menun, B.J., Doody, D.G., Liu, C.W., Watson, C.J.

Phosphorus in deep soil layers: an inventory of Belgian soils

Odeurs, W., Nawara, S., Amery, F., Merckx, R., Smolders, E., Vandendriessche, H., Elsen, A.

Use of alternative P fertilisers and cover crops for enhancing P availability to wheat and maize

Weissengruber, L., Halasgo, A., Humer, M., Möller, K., Friedel, J.K.

Plant availability of phosphorus in biomass gasification biochars

Li, X., Rubæk, G.H., Müller-Stöver, D.S., Sørensen, P.

Some relevant aspects of maize phosphorus deficiency on acid soils in the North-West of Romania

Moldovan, A.

Legacy phosphorus in a tropical soil influenced by phosphate sources and cover crops

Pavinato, P.S., Teles, A.P.B, Rodrigues, M., Herrera, W.F.B, Sartor, L.R., Withers, P.J.A.

Phosphorus availability in sugarcane as affected by phosphate fertilizer sources in a tropical acid soil

Soltangheisi, A., Pavinato, P.S.

Long-term effect of varying P fertilizer and lime applications on yield and P uptake of winter wheat, winter barley and sugar beet

von Tucher, S., Hörndl, D., Schmidhalter, U.

Phosphorus fertilization to only wheat in a rice-wheat rotation in China: Soil P pools and microorganisms

Wang, Y., Wang, S.Q, Zhao, X.

Phosphorus fertilisation and – leaching: new insights from long-term lysimeter studies

Meissner, R., Leinweber, P.

InnoSoilPhos – a new long-term research program in Germany

Leinweber, P.

Intraspecific diversity of the rhizodeposition of *Lupinus angustifolius* L. regarding the phosphorus mobilization in the soil

Baum, C., Prüfer, D., Eickmeyer, F.

Fungal soil bioinoculants and their skills to improve phosphorus slow solubilisation and release

Ceci, A., Pinzari, F., Fabiana, R., Maggi, O., Persiani, A.M.

Activity of enzymes in the rhizosphere and in the leaves of agricultural crops as affected by water supply in combination with phosphorus deficiency

Caus, M., Eichler-Löbermann, B.

The effect of *Penicillium bilaii* inoculation on plant and root growth, root architecture and P uptake of oil seed rape in a low P soil

Hansen, V., Bonnicksen, L., Jensen, L.S.

Rhizobacterial impact on plant P acquisition

Ruppel, S., Berger, B., Becker, M., Patz, S., Hasan, S., Eichler-Löbermann, B.

Measuring P in soil microbial biomass: the use of soil- and treatment-specific extraction efficiency k_P determined by ³³P labeling

Yevdokimov, I., Larionova, A., Blagodatskaya, E.

Sustainable agriculture and phosphorus management practices in the Everglades Agricultural Area

Bhadha, J.

Industry perspectives on agricultural phosphorus use efficiency

Bruulsema, T.

Phosphorus fertilization: Phosphate reuse as part of circular economy

Horta, C.

Future Sustainable Phosphorus Management: Optimum P-Supplies of agricultural Soils to meet Efficiency, Consistency and Sufficiency

Isermann, K., Isermann, R.

Agronomic efficiency of P recycling products from waste water treatment and rendering by-products

Kratz, S., Bloem, E., Harborth, P., Leinweber, P., Panten, K., Schick, J., Schnug, E.

Benchmarking P and N use efficiency in Irish farm systems to motivate practice change

Murphy, P., Hennessy, T., Buckley, C.

Management of phosphorus in agriculture in Poland - production and environmental aspects

Kopiński, J., Jurga, B.

Mitigation of phosphorus losses from agriculture -synthesis of a Swedish phosphorus research programme

Aronsson, H., Geranmayeh, P.

Measures to reduce phosphorus losses from agricultural land in Sweden

Malgeryd, J., Olofsson, S.

Influence of phosphorous fertilization on copper phytoextraction and antioxidant enzymes in castor bean (*Ricinus Communis* L.)

Hongqing, H.

Genetic analysis of phosphorus utilization in Japanese quail

Stratz, P., Beck, P., Preuß, S., Rodehutschord, M., Bennewitz, J. U.

Zinc and phosphorus accumulation in wheat as affected by organic matter amendment and *Bacillus subtilis* inoculation

Moreno, A., Recena, R., del Campillo, M.C., Torrent, J., Delgado, A.

Estimation of total available P to plants in representative by using different P extraction methods

Recena, R., Díaz, I., del Campillo, M.C., Torrent, J., Delgado, A.

Theme 3 Phosphorus Recycling - Technologies and Product Applications (Poster numbers P3.1-P3.29)

Adsorptive phosphate recovery in decentralized wastewater treatment - From adsorbent screening to phosphorus recovery in pilot test

Kunaschk, M., Dittmar, T., Schmalz, V., Bahr, C., Worch, E.

Lanthanum and Magnetic Nanoparticles Composites for Phosphorus Recovery

Belfon, R.

Screw pyrolysis for phosphorous recovery - The example of chicken manure

Tomasi Morgano, M., Bergfeldt, B., Leibold, H., Richter, F., Stapf, D., Seifert, H.

Investigating residual products from thermal conversion of sewage sludge as potential inoculation carriers for phosphorus-solubilizing *Penicillium bilaiae*

Raymond, N., Müller-Stöver, D., Bukh, C., Stoumann Jensen, L.

Enhancing P-solubilisation by *Penicillium bilaiae* from sewage sludge ash through addition of different carbon and nitrogen sources

Raymond, N., Müller-Stöver, D., Stoumann Jensen, L.

Mobilization and leaching of phosphorus and cadmium in soils amended with different bone-/activated chars

Morshedizad, M., Leinweber, P.

Plant availability of phosphorus in sewage sludge compost

Knorre, S., Bernsdorf, S., Meissner, R.

Phosphate solubilizing microorganisms as fertility tools for nutrient deficient soils of Cameroon

TchuisseuTchakounté, G.V., Fankem, H., Silke, R.

Phosphorus limited aquaponics – causes and consequences

Strauch, S., Knaus, U., Bischoff, A.A., Palm, H.W.

Sugarcane bagasse ash as alternative nutrient sources for plant nutrition

Dombinov, V., Schrey, S., Poorter, H., Watt, M., Jablonowski, N.D.

PARFORCE – An innovative technology for phosphate recovery from secondary raw materials

Lohmeier, R., Martin, G., Bertau, M., Fröhlich, P.

Tailored calcium silicate hydrates as adsorbents for the phosphorus recovery from wastewater

Zeggel, L., Fritzsche M., Gellermann, C., Stauber, R.

Phosphate recovery from aqueous wastes by hydrotalcite-type clay materials

Seftel, E.M., Michielsen, B., Pype, J., Meynen, V., Mullens, S., Cool, P.

Porous filter material for trapping phosphate from agricultural drainage water

Hansen, H.C.B., Heiberg, L., Lyngsie, G., Kjærgaard, C., Holm, P.E., Borggaard, O.K.

Urine – An efficient fertilizer product in closed nutrient cycle

Viskari, E.-L., Vilpas, R., Lehtoranta, S., Kallio, J., Pakula, S., Tuukkanen, K.

Low-cost recyclable filter media for phosphate elimination

Koegst, T., Lennartz, B.

Phosphorus Transformations in Agro-Industrial By-Products Induced by Pyrolysis

Robinson, J.S., Hu, Y., Kebelmann, L., Leinweber, P.

Phosphorus recovery from anaerobic digested sludge as struvite

Ochi, S., Nakata, Y., Matsushita, T., Nakamura, T.

Sewage sludge ash (SSA) from incineration plants as a potential source of phosphorus

Smol, M., Kulczycka, J.

Development of a technology for recovering resources from livestock waste

Ueda, K., Sakamoto, R., Kabaya, J., Nagano, Y., Suzuki, T., Sano, S., Sekito, T., Dote, Y.

Decision tool for predicting P fertilisation effects of secondary resources

Brod, E., Øgaard, A.F.

Fertilizer replacement value of digestate, processed animal manure, compost, biochar and struvite as renewable P sources

Vanden Nest, T., Fryda, L., Vandaele, E., Boogaerts, C., Bilbao, J., Vandecasteele, B.

Bone char as novel alternative phosphorus fertilizer: from submicroscopic characterization to fertilization experiments

Zimmer, D., Panten, K., Leinweber, P.

Plant phosphorus availability in biochar and ashes from sewage sludge processed by different thermal conversion technologies

Thompson, R., Thomsen, T., Müller-Stöver, D.

Application of sugar cane ashes and mycorrhiza fungi to different Cuban soils

Fundora, O., Torrecilla, Y., Rodríguez, K., Gálvez, G., Eichler-Löbermann, B.

Can P extractions of waste products predict their P fertiliser value?

Christiansen, N.H., Sørensen, P., Rubæk, G.H.

Phosphorous in raw and hydrothermally carbonized sewage sludges

Clemens, A., Görsch, K., Brade, E., Klemm, M.

The Influence of the Composting Process on Plant Availability of Phosphorus in a Green Waste Compost and in a Mixture of Green Waste Compost and Ash from a Biomass Power Plant

Stölzer, S., Eichler-Löbermann, B.

A more efficient and sustainable fertilization through recycling phosphorus as struvite

Robles Aguilar, A.A., Bodewein, T., Schrey, S., Postma, J., Blossfeld, S., Temperton, V.M., Jablonowski, N. D.

Theme 4 Syntheses of and with Phosphorus-Containing Compounds (Poster numbers P4.1-P4.6)

In situ infrared-spectroscopic investigations on heterogeneous catalysts for the hydroformylation of alkenes

König, M., Kubis, C., Selent, D., Börner, A., Franke, R.

Synthesis of annular PNP containing ligands

Höhne, M., Müller, B.H., Rosenthal, U.

Synthesis of new bidentate tertiary P-stereogenic triaryl phosphines

Rumpel, K., Holz, J., Börner, A.

Synthesis and properties of cobalt-phosphite complexes

Pientka, T., Hapke, M.

Synthesis of carbonate-bearing hydroxyl apatite (CHAP) via calcite transformation: Calibration of stable isotope (C, O) and monovalent cation partitioning

Böttcher, M.E., Schmiedinger, I., Wacker, U., Conrad, A.C., Grathoff, G., Schmidt, B., Bahlo, R., Gehlken, P.-L., Fiebig, J.

Chromium catalysts with phosphorus-based ligands for the selective ethylene oligomerization

Müller, B.H., Rosenthal, U., Peulecke, N., Müller, W., Wöhl, A., Al-Hazmi, M., Alqahtani, A.M.

Theme 5 The Development of Advanced Phosphorus Analysis Methods (Poster numbers P5.1-P5.13)

Can Laser-Induced Breakdown Spectroscopy be used as an accurate and fast method for determining Total Phosphorus in soils?

Sánchez-Esteve, S., Knadel, M., Rubæk, G., Heckrath G.

Quantification of inorganic polyphosphates in activated sludge by ³¹P NMR spectroscopy

Staal, L.B., Jørgensen, C.A., Nielsen, P.H., Nielsen, U.G., Reitzel, K.

Carbonate effect on phosphate crystallization from Polyphosphate

Omelon, S.

Development and Validation of an Analytical Method for the Determination of Glyphosate, Glufosinate, AMPA and 2-AEP in Seawaters

Skeff, W., Recknagel, C., Schulz-Bull, D.

A Microextraction Method for the Simultaneous Determination of 20 Organo Phosphorous Pesticides from Marine Water Samples

Habedank, F., Abraham, M., Schulz-Bull, D.

Investigation of Soil Legacy Phosphorus Transformation in Long-term Agricultural Fields Using Sequential Fractionation, P K-edge XANES and Solution P-NMR Spectroscopy

Liu, J., Hi, Y.F., Yang, J.J., Abdi, D., Cade-Menun, B.J.

Characterizing Phosphorus in Snowmelt Runoff from Cattle Winter Bale-Grazing Sites in Saskatchewan Canada

Cade-Menun, B.J., McConkey, B.G., Iwaasa, A.D., Lardner, H.A.

Suitability of methods for analyzing plant available P-fractions in digestates of biogas plants

Lehmann, L., Bloem, E., Schick, J., Schnug E.

Predicting plant available phosphorus – Is DGT better than classical soil analyses?

Øgaard, A.F., Kristoffersen, A.Ø., Almås, Å.R.

Microdialysis of soil P: A means to mimick root uptake?

Schack-Kirchner, H., Demand, D., Lang, F.

Phosphate-bound Oxygen Isotope Ratio Analysis: A New Tool for the Characterization of Phosphorus Cycling in Anoxic Groundwater

Neidhardt, H., Schleinitz, A., Taubald, H., Schöckle, D., Trang, P.T.K., Lan, V.M., Viet, P.H., Berg, M., Oelmann, Y.

Phosphorus extraction from various environmental and biological materials

Schumann, R., Berthold, M., Zimmer, D.

Using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy at the phosphorus (P) K-edge to determine the local atomic environment of P in bonechar

Dela Piccolla, C., Novotny, E.H., Abdala D.B.

Theme 6 From Knowledge to Action: P-Related Issues in Politics and Society (Poster numbers P6.1-P6.3)

Phosphate Rock – The chance and need for zero waste activity

Yajie, S.

On the potential of mussel farms as nutrient retention measure in a eutrophied lagoon

Friedland, R., Buer, A.-L., Dahlke, S., Grov, M., Meyers, L., Schernewski, G., Schulze-Böttcher, K., Stybel, N.

Phosphorus-related Services of Sediments in German Coastal Seas - Aspects of the SECOS Project

Kunz, F., Hiller, A., Lipka, M., Böttcher, M. E., Schernewski, G., Bathmann, U.

Excursions

Wednesday, 14th September

1# A trip to the coast: The Leibniz Institute for Baltic Sea Research and the `Hütelmoor fen`

Participants will visit the Leibniz Institute for Baltic Sea Research Warnemünde (IOW) and its departments. They will also have the opportunity to view the drawings and sculptures by Günter Grass, which are on loan to the Institute. Two of the IOW's laboratories that conduct phosphorus research will be presented as well. This will be followed by a hike over the dunes, bordered on one side by the Hütelmoor fen and on the other by the Baltic Sea. The area is the site of IOW studies on the interaction (nutrient fluxes) between land and sea, conducted in collaboration with the University of Rostock.

Responsible scientist: Monika Nausch (Leibniz Institute for Baltic Sea Research)

2# Energy from biomass: Visit experimental and industrial energy-production plants

Participants will tour the experimental short-rotation plantation of the State Research Institute for Agriculture and Fishing Mecklenburg-Western Pomerania. Here, poplar trees and willows are grown for energy production. Additionally, an industrial-scale biogas plant, by far the largest facility of its kind in the world, will be visited.

Responsible scientist: Bettina Eichler-Löbermann (University of Rostock)

3# Experimental Animal Facilities at the Leibniz Institute for Farm Animal Biology

After a short introduction to the Institute, participants will visit the Experimental Animals Facilities for swine, cattle, and poultry as well as the "Tiertechnikum," with respiratory chambers for large farm animals. Current experiments related to animal welfare and resource efficiency will be presented. We will also visit the biogas plant of the state-owned farm "Gut Dummerstorf."

Responsible scientist: Klaus Wimmers (Leibniz Institute for Farm Animal Biology)

4# Extremely fertile soils in the Baltic coast region: natural phenomena or anthro-/pedogenesis?

Participants will become acquainted with examples of the black, deep, humus-rich soils that occur regionally along the Baltic Sea coast, including on the islands of Poel (Wismar Bay: excursion site), Fehmarn, and in some places in Denmark. Morphologically, these soils can be classified as chernozems (WRB) and mollisols (USDA). Thus far, the geological and climatological contexts that gave rise to their genesis have yet to be elucidated.

Responsible scientist: Peter Leinweber (University of Rostock)

5# Full scale P-recycling from dairy-industry wastewater

Phosphate and ammonia are present in high concentrations in dairy-industry wastewater. Both are effectively removed by the Rephos technology, in which the end product is struvite. Tour participants will be able to view the entire wastewater treatment plant and the embedded Rephos technology. Additional information on the agricultural use of the struvite will be provided.

Responsible scientist: Jens Tränckner (University of Rostock)

6# Phosphorus analytics

Analytical methods for characterization and quantification of phosphorus and its compounds: Focus will be on mass spectrometry and nuclear magnetic resonance methods. We will show the required instruments, as they are installed in the Leibniz-Institute for Catalysis and in the University of Rostock's Department "Life, Light and Matter," together with some examples of application.

Responsible scientist: Wolfgang Baumann (Leibniz-Institute for Catalysis e.V.)

Abstracts

Keynote Presentations

Opening Session

Back to the Future: Historical phosphorus fluxes, legacies, and water-quality management.

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Society's future food, water and bio-energy security will become increasingly dependent on our ability to manage phosphorus (P) more sustainably. Long-term historical P flux datasets provide a key to understanding the impacts of societal efficiencies in P use, and the effects of conservation and remediation measures, on water-quality. Long-term and large-scale accumulation of P within watersheds and water bodies has led to the build-up of "legacy P", in pools with varying residence times. Chronic release of P from legacy stores can mask the effects of nutrient management and conservation programmes. And, today's water quality can, in part, reflect land management from a decade or more ago. To improve our understanding of legacy phosphorus and recovery timescales, we need new information on how landscape P pools evolve through time.

Historical P fluxes will be examined for key UK and US basins: the Thames (UK) and the Western Lake Erie Basin (US). A seventy-five year dataset from the Thames catchment will be used to show how changes in human population and agricultural practices have resulted in shifting patterns in watershed P flux inputs and outputs, and large scale changes in the accumulation and depletion of legacy P stores. In the last decade, Lake Erie has entered a marked phase of re-eutrophication, after dramatic improvements in water quality during the 1980s and 1990s. Forty-year datasets for rivers entering the Western Lake Erie Basin (WLEB), will be used to explore the drivers of change in P fluxes. The early 2000s marked the start of large-scale and widespread increases in riverine soluble reactive P (SRP) fluxes entering the western basin of Lake Erie. These elevated SRP fluxes have been sustained over the last 12 years. Empirical regression models are used to quantify the contributions of increasing runoff from changing weather and rainfall patterns to the increased SRP fluxes. On average, c. 30-40 % of the increase in SRP loads since the early 2000s can be attributed to higher runoff volumes, with c. 60-70 % arising from enhanced SRP delivery. These increases in SRP delivery have occurred during a time of steady declines in watershed P budgets, with net reductions in total P availability the WLEB watersheds since the mid-1990s. This suggests that a broad change in watershed functioning may have occurred in the Lake Erie watersheds since the early 2000s, with selective increases in the availability and transmission of the labile P fractions, relative to particulate P fractions. These increases in SRP delivery have also occurred against a backdrop of long-term, large-scale changes in land management designed to reduce erosion and particulate P losses from surface runoff, through conservation tillage and tile drainage. However, these practices can also result in a build-up of labile P fractions at the soil surface, and increased transmission of soluble P fractions via sub-surface drainage. The results indicate that the changes in river SRP delivery may reflect converging

cumulative impacts of gradual increases in SRP source availability, and increased hydrological connectivity over the decades, which may have contributed to a threshold in enhanced SRP delivery to Lake Erie around 2002. If so, this presents an “inconvenient truth” that well-intentioned conservation measures, which began in the 1980s to reduce PP losses to Lake Erie, and have gradually increased in extent over the following 30 years, may have unintentionally contributed to the marked rise in ecologically-damaging SRP fluxes entering the WLEB since the early 2000s. The Thames and Lake Erie watershed case studies highlight the need to go “back to the future” in water quality management, and that historical P fluxes can provide a basis for learning from the past, when planning for the future.

Towards sustainable phosphorus management in the Baltic Sea region

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The Baltic Sea is a small sea on a global scale, yet it is one of the world's largest semi-enclosed bodies of brackish water. The Baltic Sea is almost entirely land-locked and the water exchange is very limited. Its special geographical, oceanographic, and climatological characteristics render the Baltic eco-system highly susceptible to the environmental impacts of human activities at sea and in its catchment area, which is home to over 85 million people.

The Baltic Marine Environment Protection Commission (HELCOM) is an intergovernmental organization of the nine Baltic Sea coastal countries (Denmark, Estonia, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden) and the European Union. It works to protect the marine environment of the Baltic Sea from all sources of pollution and to ensure safety of navigation in the region. Since 1974, HELCOM has been the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" more commonly known as the Helsinki Convention.

The HELCOM Initial Holistic Assessment provided the first ecosystem health assessment of the entire Baltic Sea, also providing information on the associated benefits and costs to society. The assessment, based on data for the years 2003 – 2007, showed that none of the open-water basins are in a good environmental state. Most sub-basins are negatively affected by eutrophication, hazardous substances and the conservation of species is unfavorable. The human communities linked to the sea have been negatively affected by the deteriorated state of the Baltic Sea. Given the current impaired status of ecosystem health, the pressures from agriculture, fisheries, industries, the maritime sector as well as from communities need to be effectively managed.

Eutrophication is one of the most serious threats to the Baltic Sea. According to the Updated Fifth Baltic Sea Pollution Load Compilation, the total normalized waterborne and airborne nitrogen and phosphorus inputs in 2010 were 802,000 tonnes and 32,200 tonnes respectively. The main sources for the waterborne load of both nutrients are diffuse sources, point sources and natural background load. The largest contributor to the diffuse load is agriculture while municipalities are the main point sources.

HELCOM Baltic Sea Action Plan (BSAP) adopted in 2007 is an ambitious programme to restore the good ecological status of the Baltic marine environment by 2021. It is regularly updated in Ministerial Meetings. BSAP included HELCOM Nutrient Reduction Scheme which was updated in the Copenhagen Ministerial Meeting in 2013. According to the scheme, Maximum Allowable Inputs (MAI) of nutrients, indicating the maximal level of inputs of water- and airborne nitrogen and phosphorus to Baltic Sea sub-basins that can

be allowed to fulfill the targets for non-eutrophied sea, are 792,209 tonnes of nitrogen and 21,716 tonnes of phosphorus.

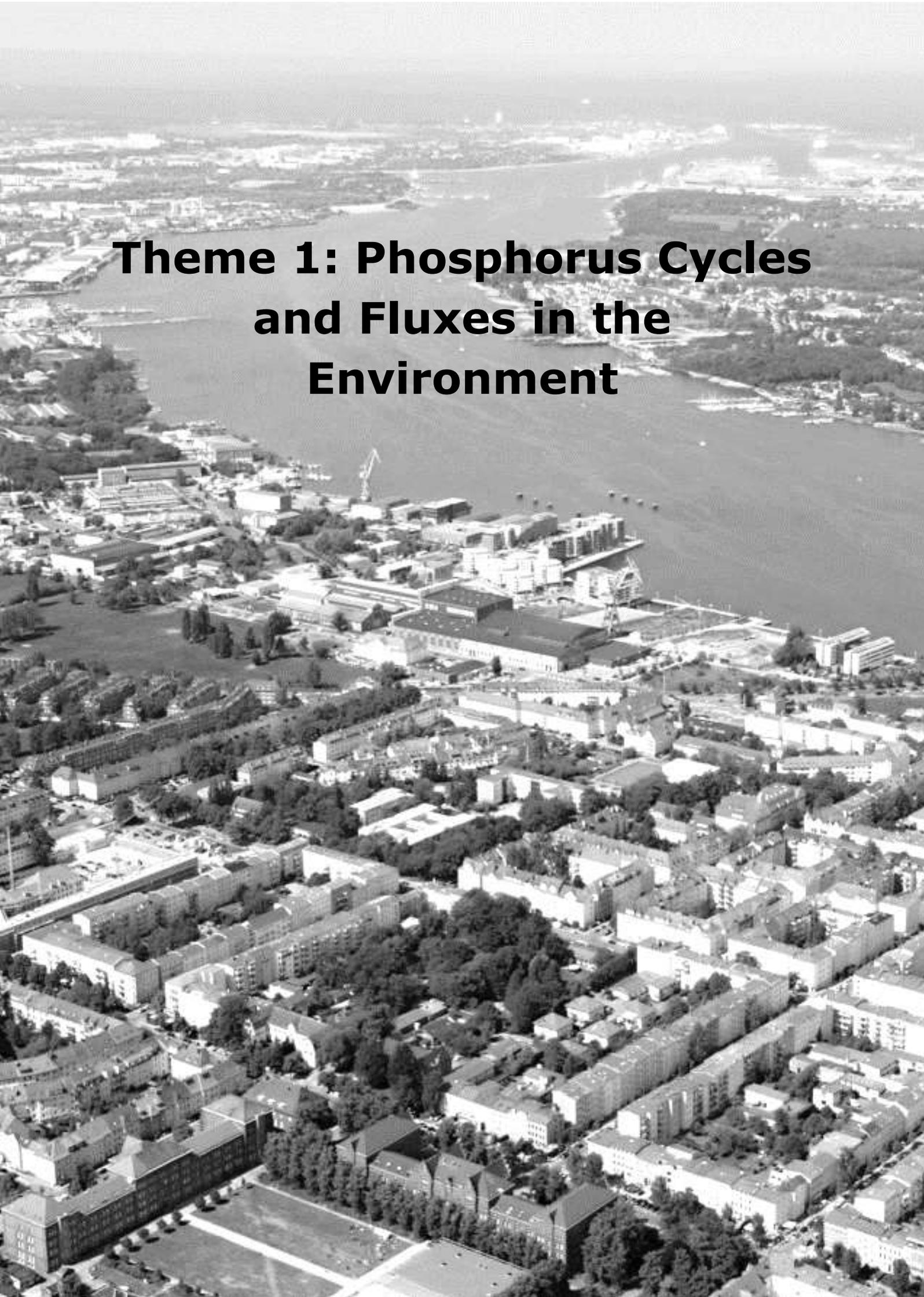
For those HELCOM Contracting Parties being also EU Member States the EU Marine Strategy Framework Directive establishes a framework within which the Member States shall take the necessary measures to achieve or maintain good environmental status of the marine environment by the year 2020 at the latest.

In addition to nutrient reductions, nutrient recycling is also being addressed within the HELCOM framework. The HELCOM Contracting Parties agreed in the Ministerial Meeting in 2013 to enhance the recycling of phosphorus (especially in agriculture and waste water treatment) and to promote development of appropriate methodology.

Efficient manure management is the key to nutrient recycling and reducing nutrient loading to the Baltic Sea. Treating manure not as a waste but as a resource requires taking manure nutrients fully into account when fertilizing the crops. The work of the HELCOM Group on Sustainable Agricultural Practices to develop advanced manure standards and to apply nutrient accounting on farm level in the Baltic Sea region are important steps towards nutrient recycling.

HELCOM Pressure group is working on a recommendation on sewage sludge handling. The objective of the recommendation is to assure maximum utilization of the valuable component contained by the sludge and contemporary minimize possible negative environmental impact. The draft recommendation considers application of treated sewage sludge and its products in agriculture, forestry, landscaping and land reclamation and other spheres.

Sustainable practices aimed at minimizing nutrient inputs to the environment are considered also in the newly adopted HELCOM Recommendation on sustainable aquaculture. The document inter alia implies recommendations aimed at prevention of additional nutrient discharges by optimizing nutritive requirements and encourages the use of regionally sourced products as fish feed ingredients.

An aerial, black and white photograph of a city, likely Stockholm, Sweden, showing a dense urban area with numerous buildings and a large body of water (the bay) in the background. The text is overlaid on the upper portion of the image.

Theme 1: Phosphorus Cycles and Fluxes in the Environment

Theme 1

Phosphorus Cycles and Fluxes in the Environment

Oral Presentations

Responsible scientists: Ulrich Bathmann, Monika Nausch (both from the Leibniz Institute for Baltic Sea Research Warnemünde, Rostock, Germany)

Keynote Speaker: Ellery D. Ingall (Georgia Institute of Technology, Atlanta, USA)

Much of the phosphorus (P) applied as fertilizer on agricultural fields enters inland waters, estuaries, and the sea. This session deals with the transport of P along freshwater and marine systems, including leaching from arable land or other sources and the impact on the respective ecosystem. Phosphorus enters aquatic systems as a nutrient for plants and as a component of herbicides and insecticides. In all ecosystems (terrestrial, freshwater, and marine), it undergoes constant transformation and thereby intervenes in nearly all biogeochemical processes. The scale of influence of P ranges from the cellular, as a regulator of growth and cell function, to the ecosystem, in the form of element cycling. Accordingly, P studies range from microscopic measurements to ecosystem modeling. The aim of environmental P investigations is to better understand P fluxes and cycles and to establish effective protection and rehabilitation measures.

Key concepts:

- P loads in marine and freshwater systems (e.g., leaching of P from arable land)
- P in aquatic environments: sources, impact, transport, and fate
- Phosphatase (activity) in soil and water
- P in the regulation of growth and cell functions
- P in biogeochemical processes (freshwater, marine, and terrestrial ecosystems)
- Natural and anthropogenic organic P compounds in the environment
- Exchange processes between solid and liquid phases
- Modeling

Keynote abstract:

Nature and dynamics of marine dissolved organic phosphorus

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Marine dissolved organic matter (DOM) is a key source of the nutrient phosphorus to microbial life in the oceans. DOM from diverse ocean regions and depths contains surprisingly consistent proportions of three P compound classes, P esters, ~83%; polyphosphates, ~10%; and phosphonates, ~7%. This uniform dissolved organic phosphorus (DOP) composition is distinct from the P-ester dominated composition of particulates derived from marine organisms. Marine DOP composition has been interpreted as resulting from selective microbial utilization and decomposition processes. One major unknown in the marine P system is the composition of DOP initially produced by microorganisms. DOP is produced via degradation of non-living organic matter and is also actively produced by living organisms including phytoplankton, which are considered a source of labile DOP. Labile DOP is preferentially utilized, predominantly by marine heterotrophs, over timescales of minutes to weeks. However, ambient pools of marine dissolved organic matter, which are typically characterized in compositional studies, have radiocarbon ages in the range of thousands of years and, thus, may not reflect freshly produced, labile DOM.

Complexities associated with DOP isolation from seawater have hampered its compositional characterization. Recently developed electro dialysis (ED) techniques have improved DOP recoveries from seawater by approximately three times compared to previous methods. Higher recovery yields a final sample much more representative of bulk DOP in comparison to other recovery methods, which have selection biases for high molecular weight or surface reactive organic fractions. ED techniques were used to extract DOM produced under nutrient replete, N stressed, and P stressed conditions in triplicate, axenic cultures of the marine diatom, *Thalassiosira pseudonana*, in order to provide insight into the composition of freshly produced, potentially bioavailable DOM supplied to marine systems. N and P stress resulted in greater cell-normalized production of dissolved organic carbon (DOC) relative to nutrient replete cultures at the same growth phase. Despite the different nutrient conditions, DOC composition and molar ratios of carbon to nitrogen (C:N) were similar in all cultures. In contrast, P stress influenced DOM molar carbon to phosphorus (C:P) ratios and dissolved organic phosphorus (DOP) composition. Under nutrient replete, N stressed, and P stressed conditions, DOM C:P ratios were 130 (± 22), 81 (± 4), and 2446 (± 519), respectively. ^{31}P Nuclear Magnetic Resonance (NMR) spectroscopy identified P esters (>90% of DOP) as the dominant P species in DOM produced under nutrient replete and N stressed conditions, with small or negligible contributions from phosphonates, and polyphosphates. However, based on direct fluorometric analysis, DOP from P stressed cultures was greater than 8 times enriched in dissolved polyphosphate compared to DOP from replete and N stressed cultures.

Nutrient ratios, dissolved organic carbon (DOC), and DOP composition of freshly produced, potentially bioavailable phytoplankton-derived DOM is compositionally distinct from ambient surface ocean DOM. Preferential utilization of N and P relative C during decomposition may lead to observed ambient surface ocean DOM C:N and C:P ratios. Furthermore, DOC and DOP compositional differences suggest preferential utilization of amino acids and P esters relative to other C and P containing compounds. DOM production by *T. pseudonana* is strongly altered by P stress resulting in increases in the ratio of dissolved polyphosphate to DOP. This increase is consistent with growing observations of polyphosphate enrichment in marine particulates and increased polyphosphate gene abundance in P stressed ocean regions. Forecasted shifts towards P stress in some ocean regions may lead to higher dissolved C:P ratios and dissolved polyphosphate content, which may ultimately alter the species-specific bioavailability of DOP and microbial species composition.

Weather amplifications as overriding drivers of P loss in Western Europe

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The effects of agricultural pressures on water quality and the efficacy of mitigation measures for reducing phosphorus (P) loss, can be challenged by the influence of weather. The temporal variability influences P loss and may vary depending on site-specific mobilisation and transfer, together with flow controls, time lags and hydrological connectivity. In Europe weather patterns are influenced by the North Atlantic Oscillation (NAO). In northwestern Europe a positive phase in the NAO index (NAOi) over the winter period is associated with more frequent large rain events in autumn/winter than normal. The objective of this study was to investigate the catchment-scale influences and relationships of naturally altered hydro-meteorological processes on diffuse P loss across the Western seaboard of Europe (Ireland, Norway and France). Regional weather amplification was investigated by comparing long-term frequency of average daily rainfall (1961-1990) with recent data (2009-2015). Six hydrological years of monthly average reactive P concentrations in stream water (aggregated from high frequency monitoring) were correlated to the NAOi for 13 catchments. The degree of correlation was analysed in terms of P mobilisation, transfer pathway, hydrological connectivity, and weather amplification. There was an increase in wintertime NAOi during the monitoring period, resulting in more frequent large rain events in winter. This was amplified in some areas. In catchments with poorly drained soils, where P was likely lost via surface runoff, annual average reactive P concentrations were positively correlated to NAOi (R^2 up to 0.96) and in other catchments there were negative correlations, poor or no correlation. In catchments where reactive P concentrations were negatively correlated to NAOi it was likely that P was either not mobilised and/or not hydrologically connected to the streams. Some catchments with well-drained soils also appeared sensitive to weather shifts for reactive P loss due to leaching to groundwater. Amplified weather patterns may override positive benefits of mitigation measures for reducing P loss in some years or indicate greater benefits in other years, and this will be catchment specific due to dominating mobilisation and transfer processes and hydrological connectivity. A consideration of these processes should be included in policy reviews of diffuse P management.

Effects of spatial P heterogeneity on microbial P uptake and community structure in forest soils

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Phosphorus (P) is the most important growth limiting nutrient in soils beside nitrogen. Yet, only little information is available about the spatial heterogeneity of P content in forest soils. Even more, no information at all is available concerning the effects of a homogenous vs. heterogeneous soil P distribution on microbial P acquisition and community structure. Thus, a rhizotron experiment based on a P-deficient forest soil was conducted to investigate competitive P uptake strategies of microbes. *F. sylvatica*-bearing rhizoboxes were labeled with $\text{Fe}^{33}\text{PO}_4$, a P source which is hard to mobilize and native in that soil. Homogenous and heterogeneous P patterns were created to study the effects of spatial P heterogeneity on plant and microbial P acquisition. P mobilization by microorganisms was tracked by an improved ^{33}P -PLFA method, linking ^{33}P incorporation in microbes with changes in microbial community structure and activity in soils in situ.

The microbial P uptake was enhanced in rhizotrons with high P availability and strongly increased with a more patchy P distribution. Characteristic PLFA indicate a massing of ectomycorrhizal fungi associated with beech in P-rich patches. These ectomycorrhizal fungi are likely to strongly increase P mobilization from the used $\text{Fe}^{33}\text{PO}_4$ in high P habitats. In contrast, habitats with low P availability require a more complex microbial community structure without a dominant group to mobilize this hardly accessible P species. Therefore, hotspots of P are likely to promote the efforts of fungal hyphae for P mobilization – an effect which decreases with lower P content. Additionally, gram positive and negative bacteria exhibit a vastly higher P uptake under increasingly patchy P distributions. Yet, they form a smaller portion of the microbial community than in a homogeneously P enriched rhizotron, suggesting filamentous organisms to benefit from the patchy P distribution. Thus, only a heterogeneous P distribution promotes P acquisition of forest microbial communities from low-bioavailable mineral P sources.

These first advances into the previously unknown territory of spatial P distributions in forest soils will hopefully shed further light on microbial P cycling and thereby help to tackle the oncoming global P crisis.

Using a waterflow flashiness index as predictor for phosphorus losses from subsurface drains on a Swedish farm with clay soils

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Risk assessment for enhanced phosphorus (P) losses by water from agricultural land is commonly based on indices since these are highly episodic and hard to predict. Seventy percent of Swedish arable land has drainage systems commonly placed at a depth of 1 m. Here a flashiness index (FI), representing daily water flow alteration from drainage systems was estimated from measured discharge (agro-hydrological years 2004-2013) after reconstructing all drain tile systems of 16 fields at a former pig farm. The fields were monitored for topsoil ammonium lactate-extractable soil P (P-AL), clay, carbon and other soil parameters in 2004. Transport of total P (TP), dissolved reactive P (DRP) and unreactive P (UP) was estimated from concentrations in composite water samples taken flow-proportional up to 20 times per year. As a mean 2.20 kg TP ha⁻¹ yr⁻¹ was leached with 27% in DRP form from the entire farm. The FI factor was negative and significant correlated (Pearson correlation coefficient $p < 0.05$) to mean yearly discharge from each field. Stepwise regression demonstrated FI index as the most important single explanatory parameter for flow-proportional yearly-mean concentration of unreactive P (UP) from each field with 0.67 as coefficient of determination (r^2). The corresponding concentrations of dissolved reactive P (DRP) was positively and significant correlated ($p = 0.015$) to soil PAL and to FI. A regression model for TP leaching losses based on FI, P-AL and yearly discharge (Q) from 11 of the fields over 9 years ($r^2 = 0.67$, $p = 0.002$) was validated against TP leaching from remaining 5 fields (32% of the farm area). Root mean square error (RMSE) was 0.43 equal to 20% of measured leaching (mean 2.14 kg TP ha⁻¹ yr⁻¹). For individual years RMSE between all 16 fields was 37-80% of measured TP leaching (0.8-3.7 kg TP ha⁻¹ yr⁻¹). According to historical records on soil P status, P leaching losses from different fields, crop- and soil management may persist for many years. However, any changes in soil physical status, such as changes in soil structure after a long period of farming with reduced tillage, need to be monitored. Phosphorus losses and FI index are specifically discussed for winter conditions with snow accumulation and frozen soil. Additionally, FI index on hourly basis is used demonstrating spatial variation of both phosphorus and pesticide leaching from experimental plots in a flat area.

The relative and combined impacts of storm and low-flow phosphorus pressures on stream ecology in agricultural catchments: a five year study

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The majority of phosphorus (P) losses from agricultural land generally occur during winter storms. However, summer low-flow P concentrations can have a greater impact on riverine ecology. Nevertheless, the magnitude, sources and ecological impacts of low-flow P pressures in agricultural catchments are not well known. Therefore, the aim of this study was to investigate the relative and combined impacts of storm and low-flow P pressures on stream ecology in rivers draining agricultural catchments.

High-resolution (sub-hourly) data-sets of stream discharge and total reactive P (TRP) concentrations from six agricultural catchments (3-30 km²) were analysed over five years (2010–2014) to characterise; (i) the magnitude of storm and low-flow P pressures in these catchments and (ii) potential ecological effects of these seasonal P pressures. The former (i), was characterised by the duration of time the riverine P standard of 0.035 mg/L was exceeded during high (i.e. storm pressures) and low flows. Subsequent impacts on stream ecology (ii) were investigated using macroinvertebrate and diatom surveys taken every May and September in each catchment.

Low-flow P pressures (likely from rural point sources) were present in five of the study catchments (i.e. TRP concentrations >0.035 mg/L during low and/or very low flows). Storm P pressures were also high in four of these catchments (i.e. TRP concentrations >0.035 mg/L during high and/or very low high), but tended to be similar or lower than the low-flow P pressures. Seasonally, P concentrations tended to be highest in summer due to the high magnitude and long duration of low-flow P pressures during this time. Diatom quality declined between May and September in four of the catchments and corresponded with elevated P concentrations during the intervening summer period. Seasonal variations were less apparent in the macroinvertebrate indices; however there was a good relationship between antecedent P concentrations and macroinvertebrate quality ($R^2 = 0.55$) across sites and years (data not shown).

Low-flow P pressures, caused elevated stream P concentrations during 'sensitive' summer seasons in five of the study catchments and appeared to be having an impact on the stream ecology. This poses a challenge for linking ecological signals to changes in diffuse winter storm P pressures, e.g. reductions in soil P levels. These temporal patterns in P pressures and ecological response will need to be considered in source apportionment tools.

Complex interplay of soil characteristics, groundwater dynamics and biogeochemical processes on the release of dissolved phosphorus from riparian vegetated buffer strips

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Riparian vegetated buffer strips (RVBS) have been promoted worldwide as a tool to reduce diffused phosphorus (P) emission from agriculture lands, mainly through their ability to retain particulate P. However, moisture conditions may temporarily fluctuate in RVBS due to changes in water table depth, a situation which can increase the solubility of soil P and ultimately favor the transfer of P from soils to watercourses.

In this study, we evaluated how soil characteristics (P concentrations and P speciation), groundwater dynamics and biogeochemical processes interact together to control the release dynamic of dissolved P in RVBS, by monitoring over two years molybdate reactive dissolved P and total dissolved P concentrations in soil solutions from two RVBS (Gueriniec and Kerroland) set in an agricultural catchment located in Western France (Kervidy-Naizin catchment). Two main mechanisms were evidenced that released dissolved P, each under the control of groundwater dynamics: i) soil rewetting during water table rise after dry periods; ii) reductive dissolution of soil Fe-(hydr)oxides during prolonged water saturation periods. This second mechanism was, however, shown to be strongly temporarily and spatially variable, being dependent on i) the local topographic slope and ii) the amount and frequency of rainfall. In fact, the second monitored year which was characterized by numerous dry episodes during the winter season resulted in the almost total inhibition of this second mechanism in Gueriniec RVBS, the steeper of the two monitored RVBS. Comparison of sites also revealed strong differences in the size of the mobile P pools as well as in the speciation of the released P, the latter being mainly composed of organic P in the Kerroland RVBS, while being dominantly composed of inorganic P in the Gueriniec one, a difference which was found to correlate with differences in the status and speciation of P in the soils of these two RVBS. Overall, results from this study show that RVBS are effective risk areas with regards to P transfer in agricultural landscapes, due to their ability to biogeochemically transform particulate P into more mobile, and more bioavailable dissolved P species. However, results also show that the risk may strongly vary in space and time, due to the complex interplay of soil characteristics, groundwater dynamics and biogeochemical processes. Clearly, this variability should be taken into account when installing RVBS in agricultural landscapes.

How the catchment area prevents the “good ecological state” of a shallow estuary. A case study in the coastal water bodies of the southern Baltic Sea

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Anthropogenic induced rapid eutrophication is one major threat for aquatic systems. The eutrophication process was accelerated by the increased availability of limiting nutrients, like phosphorus (P). Countermeasures, like the EU-water framework directive, were introduced, which reduced the P loading by point sources, like rivers. However, not all systems regenerated after the nutrient reduction. One of those aquatic systems is the Darß-Zingst Bodden chain, a shallow estuary in the southern Baltic Sea. P inputs were lowered 25 years ago, but the system remained eutrophicated. Effective countermeasures need a clear knowledge about the systems autochthonous and allochthonous P sources. This work analysed both the influence of autochthonous and allochthonous P sources in the estuary.

A 15 year-data set of the Biological Station Zingst was analysed to determine allochthonous effects on the estuary and the estuary was influenced by the P potential in the catchment area. There was a 3-times higher total P concentration in years with high precipitation, compared to years with average precipitation. Simultaneously, the seston concentrations were 3-times lower, whereas the Chlorophylla concentration was doubled. Total P in sediments (mg m^{-2}) was highest close to the land-water transitional zone. The phytoplankton growth close to the freshwater inflow was in 90% of all cases higher with P addition, compared to 40% in the middle part of the estuary. The growth experiments showed that the P loading in the estuary is still high enough to sustain permanent growth close to freshwater inflows. Phytoplankton at more distant sites was probably co-limited by other nutrients or light. The long-term development showed that stochastic events, like high precipitation, mobilise the P potential in soils of the catchment area. These periodic events become important for ecosystem recovery. There will be no ecosystem recovery, as long as the P potential by diffuse sources remains high.

Phosphorus in the Baltic Sea – measured since decades, but really understood?

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On the first glance, the phosphorus (P) cycle seems to be relatively simple compared to the cycles of nitrogen or carbon. It comprises dissolved inorganic phosphorus (DIP or PO_4), dissolved organic phosphorus (DOP) and the particulate inorganic and organic fractions (PIP and POP) which however interact with each other in numerous ways. DOP and the particulate fractions are quite heterogeneous in composition. Moreover, only DIP and total phosphorus (TP) are measured in most cases whereas the database of the other fractions is sparse. I will give here an overview about different investigations performed by IOW in the Baltic Sea over the last decades.

1) Eutrophication is the most serious problem in the Baltic Sea still, despite numerous measures were undertaken to reduce N- and P-loads. Thus, DIP concentrations in the winter surface layer, were doubled since the 1950/60s. A decrease in the open sea cannot be seen. But there are huge interannually variations which cannot be explained easily. These long-term data series can also be used when the deviation from target values for DIP are defined. The data are needed for the fulfillment of the aims of the Baltic Sea Action Plan and the Marine Strategy Framework Directive.

2) Phosphorus is the key factor in triggering cyanobacteria blooms which occur regularly in summer. Modes of DIP supply as well as first steps in the regulation of the blooms can be described. Thus, upwelling plays an important role in fostering blooms when DIP is depleted in the surface.

3) DOP becomes the dominant source in the surface layer in summer when DIP is exhausted. Under these circumstances DOP can partly be used for primary production. DOP and its bioavailable part show clear regional differences.

4) P reservoirs in the sediments are substantial and can play a major role as internal P source. New results of sediment geochemical mappings in the German Baltic Sea reveal that even shallow water sandy areas (e.g. Pomeranian Bight) can store remarkable amounts of mobile P in the fine sediment fraction (<63 μm).

5) In the deep waters of the central basins which are anoxic over more or less longer times DIP is enriched to a huge extent. A central question is how can this DIP be transported through the permanent halocline into the surface layer and influence there phytoplankton growth and eutrophication. Modelling approaches are used here beside measurements.

All these investigations deliver interesting parts of the whole phosphorus cycle in the Baltic, but they have to be unified and supplemented by further studies to a general picture.

Theme 1
Phosphorus Cycles and Fluxes in the Environment
Poster Presentations

P1.1

Translocation of P-carrying natural nanoparticles and colloids in forest soil mesocosm effluents

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Soil nanoparticles ($d < 100\text{nm}$) and colloids ($d < 1\mu\text{m}$) exert a decisive control on the mobilisation of strongly sorbing compounds such as phosphorus (P), due to their surface charge and high specific surface area. We investigated the nanoparticles and colloids (NPC) present in forest soil leachates examining their role in the translocation of P in soils. Mesocosm experiments with three German forest soils (upper 20 cm) were conducted. The mesocosms were planted with young beech trees and three different treatments were imposed: i) Ambient: irrigation with artificial rain, ii) Acidification: irrigated after treatment with ammonium-nitrate and iii) Liming: irrigation after application of carbonate. Soil leachates from three soil depths (below the organic layer, the upper mineral soil, and mineral soil) were collected. The leachates were analysed concerning their vertically translocated NPC-associated P content.

The field flow fractionation (FFF) technique coupled online to UV- and DLS-detectors and inductively coupled plasma mass spectrometry (ICP-MS) or to an organic carbon detector (OCD) enabled a size resolved characterization and quantification of the nanoparticulate and colloidal fractions and their elemental composition (P, Corg, Fe, A, Si, Ca, Mn). To visualise and better characterise the particles present in the leachates, transmission electron microscopy with energy-dispersive x-ray spectroscopy (TEM-EDX) measurements were performed.

The leachates from the various soil depths showed distinct compositions pointing interactions of translocated NPC with the soil matrix. The translocated particles exhibited sizes up to 350 nm with up to 90% (on average $\sim 30\%$) of the leached P being associated with these NPC. The acidification treatment enhanced the mobilisation of NPC especially NPC carrying P and Corg. The higher NPC-P output was probably linked to the higher NPC-Corg output indicating that a higher percentage of NPC-Porg was mobilised by acidification. Furthermore, the liming enhanced the NPC mobilisation of both P and calcium. Our qualitative and quantitative analysis of the soil leachates showed that NPC-P is a crucial vector controlling the P fluxes in forest ecosystems and could be a significant, but as yet still poorly quantified P loss factor.

Quality, quantity and transformation of P losses from diffuse sources to the Baltic Sea

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Phosphorus (P) as an essential and limiting factor for primary production is a major contributor to eutrophication of rivers, lakes and seas, such as the Baltic Sea. Most of this P is coming from diffuse sources of agricultural origin. Studies and surveys often focus on total phosphorus (TP) and/or orthophosphate for risk assessments, however, the particulate phosphorus (PP) makes out a big part of the TP entering surface water bodies. To reconstruct the quantity and composition of the phosphorus reaching the Baltic Sea one needs to look at the sources and the transport path. The Warnow, the second biggest German river draining into the Baltic Sea, is situated in an agriculturally dominated catchment representative of northern Germany. Our study was conducted in the Zarnow sub-catchment. Weekly water samples were taken from a tile drain, drainage ditch, surface close groundwater (3-4 m), four stations along the river Zarnow and two along the river Warnow, starting with the discharge period in November 2015. The samples were analysed for DIP (dissolved inorganic P), DOP (dissolved organic P), PIP (particulate inorganic P), and POP (particulate organic P). Spatial and temporal changes and variations were made visible. Based on present data, tile drain water contained the lowest TP concentrations of $0,88 \pm 0,4 \mu\text{mol l}^{-1}$ and was dominated by DIP (>80%). TP concentration in the drainage ditch was $2,08 \pm 1,1 \mu\text{mol l}^{-1}$ and had a higher contribution of PP. In sharp contrast to this are the results from the groundwater with TP values of $5,05 \pm 2,6 \mu\text{mol l}^{-1}$, exceeding those in ditch water by factor 2 and predominately (>90%) resulting from PP. Following down the Zarnow, TP is increasing on the way to the Zarnow river mouth: from $2,00 \pm 1,2 \mu\text{mol l}^{-1}$ at the innermost station to $3,33 \pm 1,3 \mu\text{mol l}^{-1}$ at the Zarnow mouth to the Warnow. PP amounted between 32% and 49% of TP. Overall, TP concentrations related to water discharge in the Zarnow catchment. In the river Warnow TP concentrations ($3,00 \pm 0,9 \mu\text{mol l}^{-1}$) remained on the same level like in the Zarnow, but, with lower variations, and the contribution of PP (58%) increased slightly. At the end of the catchment area at a tranquillized area of the Warnow, TP values slightly decrease again, possibly due to sedimentation processes. Nevertheless, TP frequently reaches the threshold values set in accordance with the EU WFD. A closer look at the causes and composition of P will help to further reduce its input to surface water bodies.

P1.3

Cellular structures of filamentous cyanobacteria affected by phosphate availability

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Phosphorus (P) is an essential nutrient and plays a major role in the metabolism of all living organisms. In surface water of marine ecosystems phosphate is only available in a small amount and is a limiting factor for phytoplankton growth. Filamentous cyanobacteria are limited by P due to their ability to fix nitrogen from the air. However, they can still grow when phosphorus is depleted in the water. The two cyanobacteria species *Nodularia spumigena* and *Aphanizomenon spec.* occur in the Baltic Sea where they form regularly huge blooms during the summer month. These cyanobacteria can accumulate phosphorus intracellularly if it is available and use those storages under deficiency (P-depleted) conditions. This change in the phosphorus content is reflected in the carbon to phosphorus (C:P) ratio. Until now it is still unknown how and where P is incorporated or degraded in the cell and which cellular structures are involved. In the present study, experiments with a natural cyanobacteria community were conducted onboard of the research vessel "Meteor" (M-117) in July and August 2015 in the Baltic Sea to answer this question. As phosphate was detected at very low concentrations ($<0,025 \mu\text{M/l}$) in the water we assumed the population to be P-limited. Therefore phosphate in form of PO_4 was added at the beginning of the experiments to induce P incorporation into the cells. At defined times, subsamples were taken to follow the phosphate depletion in water and the associated changes within the cells. Therefore, cellular components having a high phosphorus content and elementary functions in the cell metabolism like polyphosphates, phospholipids and ATP were measured besides the total carbon and phosphorus content. First results showed that immediately after PO_4 addition phosphate was decreasing in the water while the amount of cellular polyphosphate was increasing. When PO_4 was completely depleted in the water after some days, the amount of polyphosphates decreased while the ATP concentration increased. The present study shows that cellular polyphosphates and ATP were influenced by phosphate availability in water. It seems that cyanobacteria incorporated phosphate into the polyphosphate pool at first and later under P-depleted conditions this phosphate is transferred to ATP possibly for energy generation and to other cell structures to sustain the metabolism.

Phosphorus storage and mobilization in coastal Phragmites wetlands: Influence of local-scale hydrodynamics

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Coastal Phragmites wetlands are at the interface between terrestrial and aquatic ecosystems and are of paramount importance for nutrient regulation. They can act both as sinks and sources for phosphorus, depending on environmental conditions, sediment properties as well as on antecedent nutrient loading and sorption capacity of the sediments. The Darss-Zingst Bodden Chain is a shallow lagoon system at the German Baltic Sea coast with a long eutrophication history. It is lined almost at its entire length by reed wetlands. In order to elucidate under which conditions these wetlands act as sources or sinks for phosphorus, in-situ data of chemo-physical characteristics of water and sediment samples were combined with hydrodynamic measurements and laboratory experiments. Small-scale basin structures within the wetland serve as sinks for fine-grained particles rich in phosphorus, iron, manganese and organic matter. Without turbulent mixing the bottom water and the sediment surface lack replenishment of oxygen. During stagnant periods with low water level, low turbulence and thus low-oxygen conditions phosphorus from the sediments is released. But the sediments are capable of becoming sinks again once oxygen is resupplied. A thin oxic sediment surface layer rich in iron and manganese adsorbs phosphorus quickly. We demonstrate that sediments in coastal Phragmites wetlands can serve both as sources and sinks of soluble reactive phosphorus on a very short time-scale, depending on local-scale hydrodynamics and the state of the oxic-anoxic sediment interface.

P1.5

Phosphorus dynamics in agricultural used lowland catchments in NE-Germany

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Eutrophication of fresh and coastal waters following leaching of phosphorus (P) from agricultural land is still a major environmental threat. We analyzed an extensive data set of dissolved (DP) and total phosphorus (TP) concentrations originating from nine sub-basins of the agricultural used Warnow River basin in north-eastern Germany for the years 1990-2010. The objective of the study was to relate P dynamics to discharge and watershed characteristics.

P concentrations did not vary considerably among the investigated sub-basins and ranged from 0.054 to 0.151 mg/l DP and 0.114 to 0.184 mg/l TP. The P concentrations decreased significantly at all monitoring stations in the eleven-year period from 1990 to 2000 and are invariable ever since. The concentrations of DP and TP follow a marked seasonal pattern with concentration maxima in summer and minima in winter and spring although this pattern seems attenuated for TP. A simple non-linear regression model showed strongly decreasing DP and TP concentrations with increasing discharge in all sub-basins.

The loads of DP and TP varied strongly across all sub-basins and added up to mean annual DP and TP loads of 25459 kg and 63200 kg which equals 8.38 kg/km² PO₄³⁻ and 20.87 kg/km² PO₄³⁻ at the outlet of the entire watershed. We modelled annual P loads using simple multiple linear regression (period 1990–2000 (trended) and 2000–2010 (not trended)) with streamflow characteristics (runoff, baseflow, peakflow, Richards-Baker flashiness) and precipitation data and achieved coefficients of determination of higher than 0.5 with the exception of one sub-basin for the 2000–2010 data set. Model quality increased significantly as we applied the models to not-trended data. The model quality and driving parameters varied across the sub-basins and are conditional to watershed properties, such as size, land use type and, particularly morphology. The absolute number of sewage plants is as well significantly negatively correlated to DP and TP loads for both investigation time periods.

Although the concentrations of DP and TP are low as compared to concentrations reported elsewhere, the annual loads are still relevant for freshwater quality and impact algae dynamics in the Baltic Sea. Long-term monitoring of DP and TP has to consider event based sampling strategies as well to certainly circumvent underestimation of annual loads.

Visualization of colloid transport pathways in mineral soils

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There is increasing evidence that the transport of strong adsorbing compounds such as phosphorus and pesticides through soils is facilitated by colloids. The quantification and an according risk assessment of hot spots of colloidal transport in soils are difficult mainly because of experimental constraints. The objective of this study was to visualize colloid transport pathways in soils and their separation from mobile water regions operational for solutes. Comparative dye tracing studies employing the well-known Brilliant Blue (BB; real solution) and the newly introduced Titanium Dioxide Tiona AT-1 (TiO_2 ; micro-sized dispersion with an average particle size of $0.3 \mu\text{m}$) were conducted on soils with contrasting clay contents (1 to 15%) and soil structure. 50 mm of the tracer solution/dispersion were applied under ponding conditions over separated areas of 70 by 70 cm each. A first analysis of the stained soil profiles revealed that the infiltrating BB homogeneously penetrated the A-horizon, which is regularly subjected to agricultural soil treatment. In deeper horizons BB followed the secondary pore system as formed by the soil peds. The lateral spreading of the solute from the inter-aggregate pore space into aggregates indicated the importance of diffusional processes. In comparison to the BB images, the area stained by TiO_2 was much smaller (less than 10%). TiO_2 marked singular macro-pores in the A- and B-horizon only, whereas the appearance of BB was area-filling in the A- and patchy-like in the B-horizon. Irrespective of the differences in the images both dye tracers produced, penetration depth was equal and greater than 70 cm. From a qualitative interpretation of the images it can be concluded that BB basically marks the structure related pore space while the TiO_2 suspension tends to follow biologically induced (larger) macro-pores especially earthworm holes. The clay gradient had seemingly no impact on the transport behavior of both compounds. Dye tracing with TiO_2 provides an interesting option to investigate colloid transport mechanisms in soils; future studies should concentrate on a systematic variation of experimental boundary and soil conditions.

P1.7

Determination of inositol phosphates in aquatic systems of the German Baltic Coastal Area

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Inositol phosphates are a group of organophosphorus compounds derived from the six-fold alcohol inositol. They exist in different isomeric forms and with different states of phosphorylation in which myo-Inositol hexakisphosphate is the most common one in terrestrial soils.^[1] It is used e.g., by plants to store phosphorus in seeds. In aquatic systems they make up a substantial fraction of the total organic phosphorus pool and there is evidence that they can be a phosphorus source for some aquatic organisms such as cyanobacteria. Therefore, they may play an important role during eutrophication of aquatic systems.^[2] The main source of inositol phosphates in aquatic systems remains unclear as there is terrestrial input as well as production by some aquatic plants.

Regarding the German Baltic coast area there is a lack of information about the occurrence and the role of inositol phosphates in the different compartments. In this study different sediments from the Baltic Sea, the Darss-Zingst-Bodden chain and some rivers in the Baltic Sea catchment area are investigated. The samples were analyzed by a new ion chromatographic electrospray mass spectrometric method similar to a recently published method at Uppsala University.^[3]

The presented data will provide first information on the occurrence of inositol phosphates and their significance for the different systems. Furthermore, those data may open prospects on the fate of inositol phosphates after entering the marine environment and their possible role during eutrophication.

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The characterization of colloid-bound and dissolved phosphorus in topsoil water extracts along a grassland transect from Cambisol to Stagnosol

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The availability and transport of phosphorus (P) in soil solution is related to both its speciation and concentration. In our study, the total P of soil water extracts <450 nm was divided into three procedurally (filtration and centrifugation) defined fractions: (i) nano-sized colloidal P (d=1-20 nm), (ii) small-sized colloidal P (d=20-450 nm) and (iii) dissolved P (non-colloidal fraction, d=<1nm). The total P of soil water extracts increased significantly along the grassland Cambisol to Stagnosol soil transect (Rollesbroich, Germany), mainly due to the increasing contribution from the dissolved P fraction. Furthermore, field flow fractionation (AF4-OCD-UV-ICP/MS) results did reveal that more organic carbon (OC) and the OC-Fe/Al-P associations appeared in the nano-sized colloidal fraction of the Stagnosol than in the Cambisol. ³¹P-NMR results did highlight that the proportions of organic phosphorus (mainly orthophosphate monoesters) in the colloidal P fraction significantly decreased along the Cambisol to Stagnosol transect in this German grazed grassland system. Orthophosphate and pyrophosphate appeared to be more important in the Stagnosol, both colloidal and dissolved forms, when compared to other P species. Finally, the orthophosphate diesters and phosphonate were found mainly to exist in the dissolved P fraction. Overall, the P distribution and speciation of the soil water extracts of grassland transect was clearly dependent on the soil type underlying the grassland.

P1.9

Impact of phosphate saturation degree and other edaphic factors on groundwater P concentration, in acid sandy soils and on a regional scale

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Possible factors affecting the leaching of P to the groundwater in the Belgian sandy area are examined via regression analysis. The main objective is to investigate the dependency of phreatic groundwater (GW) phosphate (PO_4^{3-}) concentrations on soil phosphate saturation degree (PSD) ($n=1032$). Additionally explored parameters include: depth distributions of Fe- and Al-(hydr)oxides, sorbed P and phosphate sorption capacity and soil pH. Interpolated data of these soil parameters in 3 depth layers were generated by Ordinary Kriging. Secondly, we assessed the significance of other edaphic factors potentially controlling the GW PO_4^{3-} : topsoil OC %, soil clay content and fluctuation of the groundwater table. Overall, the mean PSD halved with each 30 cm depth layer. The statistical significance of the correlation with GW PO_4^{3-} concentrations increased with depth layer. The poor correlation ($R^2=0.01$) between PSD and GW PO_4^{3-} concentration indicates that many factors, other than soil P status, control the transport of P from soil solution to the groundwater in Belgian sandy soils. A significant positive non-linear relationship was found between GW PO_4^{3-} concentration and pHKCl in all three studied depth layers. Within the studied pH range (4.0-5.7), PO_4^{3-} solubility should increase with pH. Elevated soil OC % surprisingly co-occurred with low GW PO_4^{3-} concentrations. Groundwater PO_4^{3-} was significantly and positively correlated to clay % in both the 0-15 cm and 60-90 cm depth increments. These positive correlations were unexpected and could be indirect through mutual relations with groundwater level. Indeed, a shallower groundwater level corresponded with higher PO_4^{3-} concentrations. The shortened distance between 0-90 cm soil PO_4^{3-} and the GW logically explains this positive relation. In sum, factors other than soil P status more strongly determine GW PO_4^{3-} concentrations but extensive observational datasets are much needed to unravel such indirect mediating effects of edaphic parameters. Structural equation modeling (SEM) or path analysis was used to understand the complex interactions involved in the leaching of P to the groundwater.

The exploratory analysis showed an important direct effect of sorbed P, Al-(hydr)oxides and groundwater level on GW PO_4^{3-} . pH[-]KCl indirectly affects GW PO_4^{3-} , either via Al-(hydr)oxides or sorbed P. The role of clay % is somewhat equivocal, because it correlated negatively with Al-(hydr)oxides. Moreover, clay % covariates with GW level and pH.

Soil organic matter reduces the sorption of arsenate and phosphate: a soil profile study and geochemical modelling

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Arsenate (AsO_4) and phosphate (PO_4) share almost identical sorption properties in aerobic soils, i.e. sorption on iron (Fe) and aluminium (Al) oxyhydroxides. Adsorption KD values of As are required to predict the migration of this contaminant and its fate cannot be described without describing P sorption. In this study, the effect of soil organic carbon (SOC) on the adsorption of AsO_4 in soils is evaluated, by measuring carrier-free $^{73}\text{AsO}_4$ adsorption KD values in 1) two soil profiles with natural SOC gradient (<0.1 below-ground – 4.1% at surface) and 2) in experimentally modified samples (addition and depletion of natural organic matter). Geochemical modelling with the three plane surface complexation CD-MUSIC model was used to explain the results.

The natural AsO_4 adsorption KD values increased strongly with depth in the soil profile, with KD values ranging 1,600–73,000 L/kg in profile 1 and 550–83,000 L/kg in profile 2. The soil organic carbon (SOC) exhibited the strongest correlation with As KD among most conventional soil properties and was negative ($r=-0.65$ in log-log). Soil oxalate-extractable phosphorus (Pox) concentrations also declined with soil depth but did not largely explain the AsO_4 adsorption KD values. Adding natural organic matter (NOM) to samples with low SOC (0.19–0.25%) decreased adsorption KD values up to factor 15, with low effect (factor 2) in samples with high SOC (2.4–3.9%). By depleting the SOC content by oxidation with NaOCl, the adsorption of AsO_4 increased by factor 2 in a sample with high initial SOC (5.1%), while no effect was observed in samples with intermediate to low SOC (0.1 and 1.3%). Geochemical modelling shows the importance of phosphate, silicic acid and organic matter as competitive anions for AsO_4 adsorption. The ligand “reactive organic carbon” (RO), added as adjustable parameter to fit As data, increased with increasing SOC. However, in samples with low degree of phosphate saturation (DPS<10%), the RO/SOC was factor 5 larger than that in samples with DPS>10%, suggesting more efficient binding of organic matter on oxyhydroxides at low P loading, a feature requiring further model improvement. This study highlights the cardinal role of SOC on P and As sorption in soils.

P1.11

Drying-rewetting cycles release phosphorus from forest soils

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Drying-rewetting cycles (D/W) occur frequently in topsoils and may mobilize phosphorus (P). We investigated the effect of repeated D/W on the release of dissolved inorganic (DIP) and organic P (DOP) from forest floors and A horizons. Samples were taken from 3 European beech sites and from 3 Norway spruce sites. Soils were desiccated up to pF 6 (-100 MPa) in three D/W cycles in the laboratory, while the controls were kept permanently at 50% water holding capacity. After each drying, P was extracted from the soils by water. D/W caused the release of DIP and DOP especially from O layers. There was no general difference in response to D/W between samples from beech and spruce. The net release of DIP after D/W was largest from the Oe horizons (average 50-60 mg P kg⁻¹) for both beech and spruce forest soils. The net release of DIP from Oi layers was on average 7.8 and from spruce Oa layers 21.1 mg P kg⁻¹. In the A horizons, net DIP release was similar in beech and spruce soils with 0.4 mg P kg⁻¹. The release of DOP was less than the release of DIP except for the A horizons. Repeated cycles did not increase the release of DIP and DOP. The release of DIP and DOP was positively correlated to the microbial biomass in Oe and Oa layers but not in Oi layers. Our results suggest that D/W may significantly influence the short term availability of dissolved P in both beech and spruce forest soils. Furthermore, it can be speculated that fungi that dominate the microbial community in the Oi layer are more resistant to D/W than bacteria that are more abundant in the Oe and Oa layer. Currently, we are investigating the response of fungi and of bacteria to D/W in terms of P release in another set of incubation studies.

Mechanisms of adsorption and desorption of phosphorus on crystalline iron, aluminum, manganese (hydr)oxides as well as iron and calcium phosphates in comparison to amorphous iron-aluminum compounds

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Inorganic phosphorus (P) plays an important role as plant nutrient in fertilizers, but also as a major pollutant to aquatic ecosystems by leaching from arable land. The mobility and bioavailability of P depends on adsorption, desorption and precipitation processes at soil mineral surfaces. In the soil matrix, P can be found in the forms of iron, aluminum or calcium complexes, adsorbed on mineral surfaces. P reactions in soil, especially the fixation on iron and aluminum (hydr) oxides, have been thoroughly studied. But the much slower process of P release has to be attended as well regarding the prospective supply of fertilizers and the use of plant available P pools in arable soils. The P adsorption ability of pedogenic oxides depends on their crystallinity, while soils contain both crystalline minerals such as goethite or ferrihydrite, as well as amorphous iron and aluminum compounds. In this study, long-term adsorption and desorption experiments were carried out to investigate the P binding mechanism during the sorption processes at certain time steps. For adsorption experiments, various experimental conditions such as pH, P ionic strength, competitive ions such as SO_4^{2-} and Ca^{2+} as well as time will be considered. For desorption experiments, a Flow-Through-Reactor-Technique will be applied to investigate desorption kinetics and processes under nearly natural conditions without disturbance of the mineral-solution interface. Additionally, the release of P from the iron and calcium phosphates vivianite and hydroxyapatite, a main supplier of inorganic P and model substance for bone char, will be investigated. By using Fourier-Transformation-Infrared-Spectroscopy, changes of P binding mechanisms during ad- and desorption processes and easily as well heavily purgeable P can be detected. Aim is to identify fundamental processes of P fixation and mobilization as well as to specify similarities and differences of P binding on crystalline and amorphous reactive surfaces of pedogenic oxides.

P1.13

Iron coated sand/glaucanite filters for phosphorus removal from artificially drained agricultural fields

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In Flanders (Belgium) reactive phosphorus concentrations in streams and lakes are three to four times higher than the 0.1 ppm P limit set by the Water Framework Directive. Much of the excessive P input in surface waters is derived from agriculture. Direct P input from artificially drained fields (short-circuiting the buffering capacity of the subsoil) is suspected to be one of the major sources. We aim to develop simple and cheap filters that can be directly installed in the field to reduce the P concentration of the drain water. Here we report on the development and performance of such filters tested at lab and field scale. As starting materials for the P filter, iron coated sand and acid pre-treated glauconite were used. These materials, both rich in Fe, were mixed in ratios of 100/0, 90/10, 80/20, 70/30, 50/50 and 0/100 (iron coated sand/glaucanite ratio, based on weight basis) and filled in plastic tubes. A screening experiment using the constant head method with a 0.01 M CaCl₂ solution containing 0.5 ppm P showed that all types of mixtures reduced the P concentration in the outflowing water to almost zero, but that only the 100/0, 90/10 and the 80/20 mixtures had a sufficiently large hydraulic conductivity of 5 to 20 cm/min. In a second experiment the iron coated sand and acid pre-treated glauconite were mixed in ratios of 100/0, 90/10 and 80/20 and filled in the same plastic tubes as in the first experiment. Subsequently a 0.01 M CaCl₂ solution containing 0.5 ppm P was passed through the filters during several days, to check P removal efficiency and durability of the filter. This experiment showed that in all cases the hydraulic conductivity was fluctuating and slowly decreasing. Also it showed that the pure mixtures of iron coated sand removed P the most efficiently. Therefore two filters with only iron coated sand were tested at field level. One at a site with discontinuous flows and high P concentrations (0.4 ppm P/L) and one at a site with continuous flows and rather low P concentrations (0.1 ppm P/L). Both filters were capable of handling large amounts of water per day (>6000 L/day) and caused a mean P reduction of 59 to 66% in the drainage water entering the ditch.

Vivianite - the disregarded phosphorus sink in aquatic sediments

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The binding of phosphorus in aquatic sediments and the processes involved in its early diagenetic transformation have been studied for decades. Despite iron-oxy-hydroxides are known for their scavenging capacity and their exceptional relevance in binding phosphate at oxic/anoxic boundaries, iron has so far been disregarded in its function to sequester phosphorus in the long-term. Here, we give an overview on recent advancements made in the identification, occurrence and environmental significance of vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) - the most common reduced iron(II) phosphate mineral forming in waterlogged soils and aquatic sediments. The development of a novel analytical approach was key to demonstrating the presence of vivianite in various surface freshwater sediments, providing evidence for the quantitative importance of vivianite in phosphorus sequestration. Our investigation revealed that pore water equilibrium calculations, commonly used to predict the occurrence of vivianite in sediments, are not appropriate because they are not able to accurately reproduce the small-scale chemical conditions within this complex reaction matrix. Vivianite forms in oligotrophic as well as in eutrophic systems. Depending on the iron inventory, the production, supply and degradation of organic matter determine the extent of iron sulphide formation relative to that of the iron pool and thus the concentration of inorganic phosphate and Fe^{2+} in pore waters. Only if there is enough iron available, vivianite forms. This finding allows to stimulate vivianite formation by using iron supplements aimed at restoring eutrophied lakes. Recent results from coastal marine sediments suggest that vivianite authigenesis is of significance for phosphorus sequestration also in the marine realm. Vivianite authigenesis is likely important at the global scale, but has so far largely been ignored.

P1.15

Heterogeneity of the phosphorus sorption kinetics in soils: from compartment models to a continuous distribution model

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The sorption of phosphorus (P) in soils controls leaching of P and the availability for plant uptake. Both adsorption and desorption of P in soil have distinct kinetics that, in turn, affect the fate of P in soil. The reaction rates are commonly described as fast and slow reactions. The first ends within hours-days while the second takes years to complete. A discrete two compartment model is a common description for this. The fast reaction does however not obey first order kinetics when focusing on the min-hour timescale, and may further be split in two additional compartments. Alternatively, empirical models have been proposed to describe such data. The compartmental models (CM) disregard the heterogeneity of sorption reactions in soil. Here we postulate that the heterogeneity of sorption kinetics is better described with a continuous distribution (CD) function of rate constants. This conceptually agrees with a continuum of different sorption sites and solid-state diffusion depths. Practically, the CD offers the benefits that it requires fewer adjustable parameters (2: a mean and a variance) in comparison to CMs.

The model was applied to data of ^{33}P sorption kinetics, measured after reaction times ranging from 3 min to 3 months. The sorbents included goethite-nanoparticles, ferrihydrite, goethite, hematite and a series of contrasting soils, including soil samples from a Swedish long term fertility experiment, soils with or without previous P removal of a P mining trial and soils from a toposequence sampled in Da Loan (Vietnam) representing different weathering stages of iron rich soils. Our model was calibrated to the data by nonlinear least-squares regression and rate constant distributions were obtained. Fewer parameters in our CD model versus CM offered superior fits.

Effect of land-use management on phosphorus budgets in German grassland

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Phosphorus (P) is an essential macronutrient for all living organisms and cannot be substituted by any other element. Thus, agricultural systems, which provide humans' food security, depend strongly on P as their productivity is often (co-)limited by this element. Besides cropland, grassland is important for our food production. Around 35% of the total agricultural area in Germany is used as permanent grassland, whereof more than half (57%) is managed as pastures (including mown pastures) and 39% as meadows. P is removed from these systems mainly through hay harvesting and grazing. In order to maintain P soil fertility and P plant nutrition these nutrient amounts have to be replenished. It is important to gain knowledge on the P budgets in order to evaluate the effectiveness of different management measures as they are actually carried out in Germany and to achieve a sustainable and efficient use of P. The overall research question is: Which implications for a sustainable P management can be derived from long-term P budgets of grassland ecosystems under different land-use management in Germany? The P budget is calculated by subtracting all P outputs (harvesting, erosion, leaching, animal uptake) from all P inputs (atmospheric deposition, seed, fertilizer, animal excretion) for each grassland plot per year. The collection of raw data for grassland plots has already been completed. For example (all values in kg P ha⁻¹ yr⁻¹), P in excrements added as manure was 5.5±standard error 0.8 (order SCH>HAI, ALB), mineral fertilizer addition yielded 6.4±2.1 (order ALB>SCH, HAI) and output by grassland harvest removed 6.7±0.9 (order ALB, HAI>SCH). Given the low P fertilizer application rates, we expect that the increased productivity of high-intensity/low-diversity grasslands will be associated with an increased removal of P with the harvest, so that high-intensity/low-diversity grasslands will be characterized by more negative P budgets than grasslands of low management intensity and high plant diversity.

P1.17

Phosphorus budgets of the land-water transitional zones in a cold temperate lagoon

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The main pathways for phosphorus from land to water are erosion, groundwater and drainages. Phosphorus supports primary production in the water column and can elevate phytoplankton and macrophyte growth. These pathways can act as diffuse sources for aquatic systems and support primary producers, even though phosphorus transport by rivers is reduced. However, Phragmites wetlands and submerged macrophytes (e.g. *Chara sp.*) can influence phosphorus fluxes in the land-water transitional zone. The macrophytes can possibly act as a buffer for phosphorus run-off. This buffer capacity is important in agricultural used land to prevent further phosphorus input into water bodies. The Darß-Zingst Bodden chain as typical shallow lagoon of the southern Baltic Sea is such a eutrophic aquatic system. Therefore, an evaluation of phosphorus budgets is an important tool for determining the retention potential of macrophytes. This interdisciplinary approach determined the phosphorus budgets in the transitional zone of a cold temperate lagoon at the southern Baltic Sea.

Phragmites sp., submerged macrophytes, water and sediment samples were taken along a transect. Also, phytoplankton growth was determined close and apart from the wetland. The phosphorus budgets in the terrestrial part of the Phragmites wetland were highest with up to 9000 mg P m⁻² and 70% higher than Phragmites near the water. The submerged macrophytes stored only 300 mg P m⁻² close to the wetland. The sediment phosphorus was highest close to the wetland (10000 mg m⁻²) and reduced by 40% to the deeper lagoon parts.

However, phosphorus in the water column showed no trend and was around 47 to 77 µg l⁻¹. Phytoplankton could always grow close to the wetland, but not further away. This study indicates that macrophytes can act as phosphorus sinks in the transitional zone. The sediment phosphorus values show that there is a possible phosphorus accumulation on a longer time-scale. However, short-term release of phosphate within the Phragmites wetland supports phytoplankton. Phytoplankton can use this nutrient pulses immediately or later and support high biomass and turbidity within the system.

Phosphorus demand in phytoplankton communities - alkaline phosphatase activity as a proxy?

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Phosphorus (P) is required in all living organisms for the synthesis of nucleic acids, membrane phospholipids and for the energy transfer by ATP. P can only be used by plants and microorganisms in the form of dissolved inorganic phosphorus (DIP). However, only a small fraction of the total phosphorus in aquatic habitats is in the form of DIP and is, therefore, directly bioavailable. Under DIP limiting conditions, organisms can use a second phosphorus pool, the dissolved organic phosphorus (DOP), which occurs often in higher concentrations than DIP in the environment. The enzymatical cleavage of phosphorus from this organic matter is catalyzed by phosphatases. The alkaline phosphatase activity (APA) is often used to indicate phosphorus limitation conditions in phytoplankton communities, since the APA is often inversely proportional to DIP. However, DIP availability and APA do not correlate inversely in all aquatic ecosystems. Low as well as high phosphatase activities have been observed in different aquatic habitats at low phosphate levels.

We evaluated the phosphatase activity as a proxy for the phosphorus demand in phytoplankton communities of different aquatic habitats along the coast of the Baltic Sea. For this purpose, we determined the relationship of APA to different abiotic and biotic parameters, like DIP, DOP, C:N:P ratio, chlorophyll a, bacterial abundance, seston and POM. To characterize the APA, we measured the maximal reaction velocity (V_{max}) at substrate saturation and the substrate affinity (KM). With the KM value and DOP concentration, we determined the actual DOP turnover rates for the first time.

P1.19

Organic phosphorus changes by tillage systems and cover crops to sustainable soybean/cotton succession in Brazilian Cerrado

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Organic phosphorus (Po) can be an important source for plants, reducing P fixation and increasing phosphate availability, mainly in undisturbed soils. Moreover, the evaluation of Po forms in soil can be helpful to explain the dynamic of this nutrient in tropical systems. The aim of this study was to evaluate the long term changes in soil Po forms in Brazilian Oxisol, under two tillage systems and cover crops. The study consisted in evaluation of a soil management trial established in Costa Rica-MS (Central region, in Cerrado biome), since 1994 (18°15'10"S and 53°12'41"W), consisted in a long-term tillage systems trial (No Tillage, NT and Conventional Tillage, CT), in successive cultivation of soybean/cotton. These summer crops were rotated with cover crops, which were: pasture (*Brachiaria ruziziensis* syn. *Urochloa*), millet (*Pennisetum glaucum*), and additional treatments, maize (second grain crop) and control (fallow). The soil is classified as clayey (65%) Typic Hapludox. The experiment was randomized in blocks scheme, in a 2x4 factorial, with three replicates. The factors consisted in the tillages, NT and CT, and the cover crops (previously mentioned). The soil depths layers of 0-10 and 10-20 cm were sampled in august/2015, after the cover crops cultivation. The Hedley P fractionation (modified by Condron et al., 1985) procedure was used to identify organic P fractions in soil, using the following extractors: NaHCO_3 0.5 mol L⁻¹ (PoBIC), NaOH 0.1 mol L⁻¹ (PoHID01) and NaOH 0.5 mol L⁻¹ (PoHID05). The Pototal were calculated by the sum of all Po fractions. The data were statistically analyzed to homoscedasticity. The results were evaluated by ANOVA and means were compared by LSD test (5% of significance). The NT cultivation resulted in increment of 34% in Pototal of soil, compared with CT (in topsoil, 0-10 cm). Labile Po (PoBIC) not differed with the tillage, but with cover crop species adoption, with increments around 17% (maize) to 40% (pasture and millet), compared with the fallow. The maintenance of same labile Po levels in NT and CT tillage systems is related to nutrient depletion of more recalcitrant forms, with reduction of the moderately labile (PoHID01) and non-labile (PoHID05) P. The labile Po is not determined in routine P analysis, but we recommend your evaluation, mainly to determine the phosphorus bioavailability in tropical soils.

Soluble vs. particulate phosphorus in stormwater

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Accurate measurement of dissolved versus particulate phosphorus is critical in designing stormwater BMP's to remove phosphorus. Particulate phosphorus (PP) is often the largest component of the total phosphorus load in stormwater. Fine-resolution measurement of particle sizes allows us to investigate the mechanisms behind the removal of this PP, since the diameter of these particles determines both their settling velocity (via Stokes' Law) and the amount of phosphorus adsorbed to them (via their surface area).

In this presentation, we will present data on continuous particle size distributions of particles in stormwater, along with SEM/TEM images to show the particles in detail and XRD/FTIR data to quantify the mineralogy of the particles. We will also present data on laboratory settling experiments of stormwater in which we investigate settling mechanisms and the relationship between PP and particle surface area.

P1.21

A complementary set of methods to characterize P availability from fertilizers of varying origin and solubility

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Due to the limitation of global phosphorus (P) reserves, recycling fertilizers produced from heterogeneous P-rich biowastes such as sewage sludge, slaughterhouse waste or animal manures will become increasingly relevant. Various waste treatment processes further increase the diversity of products. Standard extractions to predict P bioavailability in fertilizers and soils have often been developed and calibrated for a limited range of substrates. It is therefore needed to assess the accuracy and predictive power of P tests on a wider range of P-rich substrates, including conventional and recycling fertilizers.

We investigated a set of complementary approaches to characterize fertilizer P availability. Using standard methods of fertilizer analysis (H_2O , 2% formic acid, 2% citric acid and neutral ammonium citrate extractions) in combination with comparatively new approaches (diffusive gradient in thin films (DGT), depletion-induced desorption of P from fertilizer, and imaging of P diffusion in soil from granulated fertilizer), more information about the characteristics of P fertilizers is expected to be gained than with standard extracts alone. The method evaluation was conducted on 13 P fertilizers of contrasting origins and solubility, with a 6-week pot trial (*Secale cereale*) in a carbonate-free soil ($pH_{H_2O} = 6.8$) as reference.

The range of P availability in the fertilizer test set was wide and homogeneously distributed. While the sewage sludge biochars performed worst, chicken manure and struvite (magnesium ammonium phosphate) were as efficient as conventional superphosphate. The DGT method explained nearly 90% of variance in plant growth (Mitscherlich equation fitting) while the coefficients of correlation between plant growth and P extracted by standard extracts were much lower. Implemented in combination with chemical imaging, these extracts could nevertheless help understand and predict the P release dynamics from granulated fertilizer.

Overall, our results indicate the potential of a selected set of complementary methods to characterize highly contrasting P fertilizers and to help optimize their use in agriculture.

Elemental composition of particulate inorganic phosphorus in discharges from an artificially drained lowland catchment

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Actually, agricultural diffuse sources constitute the major part of phosphorus fluxes to the Baltic Sea. Aiming at better understanding the phosphorus load composition, its eutrophication potential and opportunities for reduction measures, the phosphorus (P) speciation and the elemental composition of particulate matter were studied in water samples from a tile drained sub-catchment of the Warnow river basin from November 2013 until the end of April 2014.

With, in mean 30%, particulate inorganic phosphorus (PIP) formed a large part of the total phosphorus load in most of the measurements. Element analysis of the suspended matter (SPM) using the total reflection x-ray fluorescence spectrometer (PICOFOX) and a scanning electron microscope showed that silicon (Si) $\sim 500 \mu\text{g l}^{-1}$, iron (Fe) $\sim 182 \mu\text{g l}^{-1}$ and calcium (Ca) $\sim 224 \mu\text{g l}^{-1}$ were the dominating elements.

P accounted only for 1 % of the suspended matter. While concentrations of SPM were similar along the flow path, PIP concentrations showed an increasing trend. Single particle analysis showed that the P content of single particles became higher. The mean P content of the particles varied from 0.23 to 2.28 mass%. Apatite, Fe(hydr)oxides, vivianite, clay minerals, and polyphosphates were identified as the P bearing minerals. Clay minerals and Fe(hydr)oxides had a low P content. Thus, binding capacity of P with iron and clay seemed to be limited, but the number of these particles was very high. Inversely observations were made for Ca-containing particles which had a high P content but were low in abundances. There are indications that the mineral binding of P varies along the flow path and with the seasons. Our study demonstrates that suspended matter plays an important role in the P-fluxes through an artificial drainage system. The quality of the particles in sense of their chemical composition plays a prime role in the overall exported P-load.

P1.23

Phosphorus cycling within a low productive plankton community in the Gulf of Finland (Northern Baltic Sea)

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Within a pelagic plankton community, phosphorus (P) circulates between the fractions (phosphate (PO₄), particulate organic P (POP) and dissolved organic P (DOP)). Despite the phosphorus cycling looks relative simple, the quantity and quality of the flow between these fractions is not well understood. The use of mesocosms is a useful tool for such studies because influence from external sources can be excluded. In summer 2012, mesocosm experiments were performed in the Storfjärden (western Gulf of Finland) to study the impact of fCO₂ elevation on the plankton community. In addition, the P cycling between the fractions could be investigated in the period from day 1 to day 17 of the experiments by measuring P-pool sizes and [³³P] PO₄ and [³³P]ATP uptake rates. Turnover times of 4d for PO₄ and 1d for ATP indicated that these P pools are converted several times within this period. Thus the transformed quantity was higher than the pools sizes: about 619 nmol l⁻¹ PO₄ were converted, 85-90% of that was very fast in recirculation so that it couldn't be seen in any of the other fractions. Only about 8 nmol l⁻¹ were fixed in POP and is exported via sedimentation. Circa 185 nmol l⁻¹ PO₄ have to be transformed into DOP to increase this pool by 26.5 nmol l⁻¹ whereas the remaining 157.5 nmol l⁻¹ seemed to be converted back to PO₄. Elevated fCO₂ did affect the P cycling only on the level of POP-formation when its formation was coupled with increasing phytoplankton biomass.

Molecular level investigation of P-related reaction mechanisms at soil mineral surfaces

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The future of universal supply with phosphorus (P) fertilizer has got critical attention that alarmed the public research platforms and also initiated novel ones. The improvement of our understanding to the soil P cycle needs advances in analytical and theoretical methods. In this contribution, P-related reaction mechanisms at mineral surfaces are investigated using computational chemistry. Since P exhibits a great diversity of inorganic and organic P species, different binding motifs, i.e. including mono-, bi-, and tri-dentate, and energies of these species at different mineral surfaces are explored using density functional theory. Particular attention is paid to unravel the competition between P and organic compounds for mineral surface sites in the presence of water. The importance of proton transfer from P-containing compounds to surfaces and bond dissociation followed by bond formation with the surfaces are unraveled. Furthermore, effect of pH is investigated and PO_4^{3-} and HPO_4^{2-} is found to bind stronger to the mineral surfaces than H_2PO_4^- & H_3PO_4 . Finally, adding more phosphates led to a decrease in the average binding energy per P-species.

References:

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P1.25

The role of biological soil crusts in P-cycling

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Biological soil crusts (BSCs) are the community of organisms living at the surface of soils. Major components are cyanobacteria, green algae, microfungi, mosses, liverworts and lichens. BSCs play an important role in the biogeochemical, often interlinked cycles of C, N and P. To elucidate the ecological role of BSCs in the P-cycle and disclose land use intensity effects, we examined BSCs collected from the German Biodiversity Exploratory Schorfheide. Total P of the compartments crust, adhering soil underneath and crust-free soil was quantified and inorganic and organic P content in five different P fractions of the different compartments was determined. In addition, P species were characterized using P-XANES (x-ray absorbance near edge structure) and ³¹P-NMR (nuclear magnetic resonance) spectroscopy. BSC biodiversity of green algae was morphologically determined using enrichment cultivation. Results showed an accumulation of total P in the crust as well as a distinct pattern of P fractions in this compartment. We further observed a different P-species composition characterized by high percentages of Asolectin and Adenosin-Tri-Phosphate in crust compared with crust-free soil. Certain inorganic P fractions as well as the number of green algae were positively affected by land use intensity. Thereby, P fraction characteristics were possibly affected via BSC biodiversity. We conclude that BSCs are particularly involved in the transformation of mineral to organic P fractions and thus play an important role in P mineralization and weathering of soils.

Reducing phosphorus leaching and runoff from poultry litter with alum: Twenty year small plot and paired-watershed studies

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Aluminum sulfate (alum) additions to poultry litter have been shown to reduce ammonia (NH₃) emissions and phosphorus (P) runoff losses. Two 20-year studies were conducted to determine the long-term effects of treating poultry litter with alum on P availability, leaching and runoff. Poultry litter was applied annually from 1995 to 2015 in a paired watershed study comparing alum-treated and untreated litter, and in a small plot study that utilized 13 treatments (unfertilized control, four rates of alum-treated litter, four rates of untreated litter and four rates of NH₄NO₃). In the paired watershed study, total P loads in runoff were 231% higher from the watershed receiving untreated litter (1.96 kg P ha⁻¹) than from that receiving alum-treated litter (0.85 kg P ha⁻¹). In both studies, alum-treated litter applications resulted in significantly higher Mehlich III P (M3-P) and lower water extractable P (WEP) near the soil surface, indicating better retention of applied P and reduced availability of that P to runoff or leaching. Mehlich III P was much lower when analyzed by colorimetry than by inductively coupled argon plasma emission spectrometry (ICP) in soils fertilized with alum-treated litter, possibly due to the formation of an organic P mineral phase, such as aluminum phytate. Far less P was leached from alum-treated litter than untreated litter: M 3 P at 10-50 cm was 266% greater in plots fertilized with untreated litter (331 kg M3-P ha⁻¹) than with alum-treated litter (124 kg M3-P ha⁻¹). These studies provide strong evidence that treating poultry litter with alum provides not only short-term, but also long-term benefits to P conservation and water quality.

P1.27

Biodiversity of biological soil crusts from sand dunes and their functional role in the P and C biogeochemistry (CRUSTFUNCTION)

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Biological soil crusts (BSC) are a consortium of different microorganisms; together with their by-products they create a micro-ecosystem bound together by organic materials. They can be characterized as “ecosystem-engineers” forming water-stable, aggregated surface layers that have important multi-functional ecological roles in primary production, mineralization, bioweathering, and the stabilization of soils. Although BSCs are known to have crucial ecological functions in terrestrial ecosystems they are only poorly investigated in coastal sand dunes in temperate zones. We collected BSCs in five sand dunes along the Baltic Sea coast on the islands Rügen and Usedom and characterized their biogeochemical and community composition for the first time.

The species composition of dune BSCs revealed a high diversity of cyanobacteria and eukaryotic algae, higher diversity than reported for BSCs originating from other habitats. Compared to crust-free sand the BSCs had a higher amount of labile and a lower amount of stable organic matter compounds. Further, we observed a clear trend of nutrient (C, N and P) accumulation in BSCs. The concentration of total P in sand was the only factor, besides a site-specificity, that significantly influenced the community composition of algae in biological soil crust. The investigation of biological soil crusts from coastal sand dunes highlights their heterogeneity and complexity in terms of community structure, function in nutrient accumulation and the ability to withstand high frequency of disturbance.

The role of the organic layer for phosphorus nutrition of young beech trees (*Fagus sylvatica* L.) at two sites differing in soil phosphorus availability

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The accumulation of an organic layer in forests is linked to the ratio between litterfall- and decomposition rates with decomposition rates being decelerated due to acidification and associated nutrient depletion with proceeding ecosystem development. Nevertheless, the nutrient pool in the organic layer might still represent an important source for Phosphorus (P) nutrition of forests on nutrient-poor soils. Our objective was to assess the importance of the organic layer to P nutrition of young beech trees at two sites differing in soil P availability. We established a mesocosm experiment including plants and soil from a Phosphorus depleted forest site on a Haplic Podzol in Lüss and a Phosphorus rich forest site on a Eutric Cambisol in Bad Brückenau either with or without the organic layer. After 1 year, we applied ^{33}P to the pots. After 0 h, 24 h, 48 h, 96 h, 192 h, 528 h we destructively harvested the young beech trees (separated into leaves, branches, stems) and sampled the organic layer and mineral soil of the pots. In each soil horizon we measured concentrations of resin-extractable P, plant available P fractions and total P. We extracted the xylem sap of the whole 2-year-old trees by means of scholander pressure bomb. ^{33}P activity was measured for every compartment in soil and plant. The applied ^{33}P was recovered mainly in the organic layer in Lüss, whereas it was evenly distributed among organic and mineral horizons in pots of Bad Brückenau soil. Comparing pots with and without an organic layer, the specific ^{33}P activity differed by 323% between pots with and without an organic layer present in the Lüss soil. For both sites, the presence of the organic layer increased ^{33}P activity in xylem sap compared to the treatment without by 104% in Bad Brückenau and 700% in Lüss. Whereas the existence of an organic layer did not influence the total ^{33}P activity in plant tissue in pots from the site Bad Brückenau over 528 h, a strong increase of 155 kBq/g DM was recorded for the site Lüss. Therefore, the key role of the organic layer for plant P nutrition on a P depleted site like Lüss was reflected in the increased P uptake rates (xylem sap) and increased accumulation of P in plant tissue comparing the presence and absence of an organic layer. In conclusion, our results prove the more efficient cycling of P in the organic layers in Lüss as opposed to Bad Brückenau corroborating the hypothesized P recycling and P acquiring strategy in Lüss and Bad Brückenau, respectively.

P1.29

Development of soil phosphorus and phosphatase activities under different management in an organic farm over 12 years from conversion

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In the organic research farm Trenthorst in North Germany on glacial loamy soils two farm types – DAIRY (62 ha) and STOCKLESS (30 ha) – were compared over two crop rotations in terms of plant available P contents, mineral P fractions and phosphatase activities. Except minor P-input by mineral feed additions in DAIRY, no P was imported since conversion to organic farming in 2001. Top-soil samples from long term monitoring points were compared. Additionally development of these values in permanent grassland of the DAIRY farm (54 ha) were assessed. The farm types had 6-field crop rotations with different percentages of fodder legumes (33%, 16% red clover grass). In arable land of DAIRY livestock manure from farm own feed production was applied, whereas in STOCKLESS clover-grass was recycled by mulching. In DAIRY average yearly soil P-balances were negative in grassland and arable land (-7.9 , -10.9 kg ha⁻¹ a⁻¹ P). A farm internal P transfer from grassland to arable land of 1 kg ha⁻¹ a⁻¹ P was found. Plant available P-CAL in soils was sufficient in all years according to common fertilising recommendations. But contents in arable land and grassland decreased slightly. In an initial comparison of samples from the years 2001 and 2013 easily soluble mineral P-fractions in topsoil samples (P-H₂O, P-Resin, P-NaHCO₃, P-NaOH) were found to be significantly lower in grassland after 12 years. In arable land of both farm types these values were more variable but also lowest in 2013. Total P was significantly lower in grassland soils in 2013 (2001: 1366 ± 116 , 2013: 951 ± 28 mg kg⁻¹ soil), whereas development in arable land of DAIRY and STOCKLESS showed no clear trend in the years 2001, 2009, 2013 (Range: 444-544 mg kg⁻¹ soil). Alkaline and acid phosphatase activities in soils of grassland were not different in 2001 and 2013. In arable land phosphatase activities were higher in 2013 (ranges, 0-30 cm topsoil layer: grassland: alkaline phos.: 173-174, acid phos.: 176-184, arable land: alkaline phos.: 139-156, acid phos.: 133-160 [μ g p-Nitrophenol g⁻¹ soil]).

Nanoparticulate and colloidal phosphorus in forested headwater catchments

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Headwater catchments reflect the natural load of nutrients and minerals cycled or released from ecosystems; yet, little is known about natural colloids (1-1000 nm) and especially nanoparticles (NNP, 1-100 nm) as nutrient carriers in forested headwater streams. We hypothesized that the majority of P is bound to NNP in forest streams but that their size and composition varies for different forested headwater systems.

Four forested sites in Germany and one in Norway, which differ in total P content, were sampled for stream water during base flow conditions and analyzed for NNP and colloidal fractions. P, Al, Si, Mn and Fe were determined in the fractions via ICP-MS and the organic carbon content was derived online via OCD.

Through the refined Asymmetric Flow Field Flow Fractionation (AF4) method, the results showed that the NNP and colloids of all sites could be distinguished into three distinct fractions (approx. 1 nm-20 nm, >20 nm-60 nm, >60 nm-300 nm), yet the elemental concentrations in the fractions were not homogeneously distributed. Exploratory data analysis showed that each fraction had unique elemental signatures with different preferential P binding partners. P was preferentially associated to Fe in the smallest size fraction, with increasing contribution of organic C associated P as the hydrodynamic diameter of the fractions increased. The largest fraction was dominated by clay minerals. The relative contribution of the NNP and colloidal fractions for ecosystem nutrient supply can be expected to rise as total P concentrations decline.

P1.31

Which soil P test reflects best the phosphorus availability for leaching?

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Soil phosphorus (P) tests are important for estimating the P status in soil. A variety of soil P tests is used worldwide, ranging from mild to relatively harsh soil extraction methods. The historical development of most tests is based on the need for fertilisation advice, i.e. the result of the test should reflect the P availability in the soil for the crops. Nowadays, P fertilisation is restricted in order to reduce P losses to ground and surface water to diminish eutrophication. In some NW European countries or regions the maximum allowed P fertilisation dose depends upon the soil P availability measured with a certain soil P test. It is however unclear if the soil P availability, measured with a method developed for crops, is also a good measure for the availability for P losses.

In Flanders (Belgium) the suitability of the standard soil P test (ammonium lactate extraction) for measuring the P availability for leaching, is compared to other soil P tests. Twenty-one soils, with textures ranging from sand over sandy loam to loam, were tested for their P leaching risk in a soil column experiment. Disturbed soil columns were irrigated with artificial rainwater with a flow rate representative for Flemish net rainfall conditions. A vacuum pump created an underpressure of 10 kPa to mimic field capacity. During one month, filtrate was sampled twice a week. In the filtrate, Fe, Al, Ca and P concentrations were measured. The P concentration in the leachate stabilized mostly two weeks after the start of the experiment.

Soil P availability was measured in the 21 soils by different methods: (1) extraction with ammonium lactate and acetate at pH 3.75 (Egnér et al. 1960); (2) extraction with 0.5 M NaHCO₃ (Olsen et al. 1954); (3) extraction with 0.01 M CaCl₂ (Houba et al. 2000); (4) extraction with ammonium oxalate (Schwertmann 1964), with possibility to calculate the phosphate saturation degree; (5) diffusive gradient in thin film technique (DGT) (Degryse et al. 2009). For each method, the stabilized P concentrations in the leachate was plotted versus the measured soil P availability. A curve was fitted on the data. The method for which the uncertainty on the "critical soil P availability", i.e. the soil P availability related to unacceptable P concentrations for surface waters, is the smallest among the tested availability methods, is selected as the best method for measuring the soil P availability for leaching. Results will be presented at the conference.

Phosphorus from source to sea – Integrated phosphorus and water resources management for sustainable water protection (PhosWaM)

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Despite depletion of phosphorus (P) rock reserves, undesired amounts of P are still 'wasted' causing environmental problems, especially in aquatic systems. The goal of the researchers and practice partners involved in the project PhosWaM is to enlarge the knowledge base with regard to the sources, transport routes, and transformation processes of P compounds in waterways. Process and modelling studies are supplemented by studies of measures such as controlled drainage, filter systems for small sewage treatment plants, and the opening of piped watercourses. Proposals are to be drawn up for optimising the monitoring plans and action programmes regarding P to fulfil the requirements of the EC Water Framework Directive (WFD), the EC Marine Strategy Framework Directive (MSFD), and the Baltic Action Plan. The focus of the investigations is on the Warnow River Basin, the brackish Unterwarnow estuary, and the adjacent coastal waters of the Baltic Sea. At 3,324 km², the Warnow and Unterwarnow are the second largest German catchment area that drains into the Baltic Sea. The region is mainly agricultural, and its hydrologic balance has been strongly altered by anthropogenic influences. The entire flow path from the source to the sea is considered, because management decisions in the river basins affect the P-loads into the sea.

Project aims are:

- Quantify emission sources such as drainage-, groundwater- and erosion paths as well as small sewage treatment plants with the help of modelling
- Model the impact of measures and altered hydrological conditions on phosphorus losses
- For various arable crops, assess the risk of agricultural phosphorus losses into water bodies by means of field trials and by using a phosphorus index
- Examine how various phosphorus fractions contribute to water pollution and how they change along the course of a waterway
- Develop and test measures to reduce phosphorus inputs and/or control phosphorus retention
- Develop an overall concept for improving phosphorus retention
- Develop recommendations for regional and national planning authorities

P1.33

Relating soil chemistry to phosphorus (P) mobilisation along the P transfer continuum at catchment scale

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Soil phosphorus (P) testing in Ireland uses Morgan's extractable P, arranged in bands of indices, to identify an agronomic optimum for crop production and more recently potential risk of P loss to water. However, soil P tests alone don't provide information on ancillary soil attributes that could account for variations in soil P solubility and subsequent transfer to hydrologically active pathways at catchment scale. The objectives of this study were to demonstrate the role and relevance of laboratory scale soil chemistry data in risk assessment at catchment scale. In this study, soils samples covering a range of mineral soil types and parent material were taken from six agricultural catchments in Ireland. Samples were dried (40°C), sieved (<2 mm) and subsequently analysed for a range of soil chemical properties including available and total amounts of P and related metals, aluminium (Al) and iron (Fe). Concentrations of extractable P varied within and between catchments, ranging from 1.2-29.5 mg/l Morgan's P and from 16 to 204 mg/kg for Mehlich-3 P. Total P (TP) across the catchments ranged from 350 to 2660 mg/kg, reflective of large reserves of P in soils which are not captured in agronomic P testing. Within the agronomic range of Morgan's P, TP did not vary significantly between indices, which is also reflected by the non-significant correlation between these P variables. Total P was more significantly correlated with total Al and total Fe in soils, reflecting the parent material types underlying the catchments. Extractable forms of P related metals such as Al and Fe may prove more relevant for assessing differences in P solubility between soil types and recent Irish and international research has shown that Al in soil provides sorption sites for P, characterised by strong binding energies helping to retain P within the soil matrix. Across the six catchments, laboratory scale, water soluble P (WSP) was negatively correlated ($r=-0.50$, $p < 0.05$) with extractable Al in soil, demonstrating the low P solubility associated with high Al in soil. This concurs with recent research on Irish soils, correlating high Al with low P availability and supply. Although factors such as management and drainage are influential on P losses from soil to water, in this present study, we demonstrate that integrating laboratory soil data with other catchment variables can provide an indicator of P mobilisation from soil along the P transfer continuum at catchment scale.

Phosphorus loss with phosphorus-based cattle manure application from a clay loam soil

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Changes in manure application from nitrogen-based to phosphorus (P)-based approach can alter P dynamics in soil and its fate from soil to surface water, and the later has to be quantified to improve P management efficiency and to program long-term nutriment management planning. We investigated the effects of P-based application of liquid (LCM) and solid cattle manure (SCM), in comparison with chemical fertilizer (CF), on soil P loss in both surface runoff and tile drainage in a clay loam soil under corn-soybean rotation over a four-year period. Each of the three sources of P was applied at 50 kg P ha⁻¹ to the corn phase of the rotation. Both surface and sub-surface flows were continuously monitored and sampled on a year-round base using the state-of-art auto-systems. Water samples were analyzed for dissolved reactive P (DRP) and particulate P (PP). Concentration of DRP with SCM was generally higher than with CF and LCM addition in surface runoff, while in tile drainage it was largely identical amongst the three P sources. Concentrations of PP in both surface runoff and tile drainage water followed the order of SCM>CF>LCM. As a result, total soil P loss (TPL) in both surface runoff and tile drainage with LCM remained unchanged, although the DRP loss was 16% less, relative to CF. In contrast, addition of SCM decreased the TPL by 19% through the reduction in PP loss, although it increased the DRP loss by 54%, compared with CF. The calculated values for manure P source coefficients (PSC) were 0.84 and 1.54 based on DRP loss, and 0.99 and 0.81 based on TPL, for LCM and SCM, respectively. The PSC values can be applied to improve the prediction efficiency of site P index for risk assessment of soil P loss and to develop manure application BMPs.

P1.35

Effects of long-term fertilisation management on microbial P mobilisation and community structure in the crop rhizosphere

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The efficiency of the arable P use can be fundamentally increased by improving arable management strategies. We aim to disclose soil microbial fundamentals to optimise P storage, P mobilisation and P turnover in agricultural systems for better plant growth and higher crop yields. We investigated treatments from two long-term fertilization experiments in Freising (Bavaria) and Rostock (Mecklenburg-Western Pomerania). Soil sampling was conducted in spring and autumn of 2015 and 2016. Microbial P storage, enzymatic P mobilization and the community structure of bacteria and arbuscular mycorrhizal fungi (AMF) as key players of the P mobilisation and transfer were analysed at 4 fertilisation treatments (no fertilisation, triple super phosphate (TSP), compost, TSP+compost).

Microbial P (P_{mic}) was significantly site- and fertilisation-affected and higher at the Freising than at the Rostock experimental site. P_{mic} was larger by factor two to three in fertilised treatments than in the control. The microbial P storage did not differ significantly between mineral (TSP) and organic (compost) fertilisation treatments. The activities of acidic and alkaline phosphomonoesterases, phosphodiesterase and beta-glucosidase were significantly higher in treatments with organic fertilisation compared to those with no or mineral fertilisation, independent on season. The community structure of bacteria and AMF from the 4 treatments differed slightly from each other. Additionally, rhizosphere bacteria from maize were isolated and screened for their P mobilisation ability. Highly capable strains were identified and physiologically characterised.

The present findings contribute to one of the overarching objective of the BonaRes-project (BMBF) InnoSoilPhos to improve the P use efficiency of arable crops by selection of suitable management strategies in the agricultural practice.

Drivers and constraints for Polish farmer´s implementation of measures to remediate phosphorus and nitrogen leaching to waters

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This 3-year study, addressed two challenges, exemplified for 50 farmers in two Polish regions (Pomerania and NW Mazovia): (1) the agricultural sector´s contribution to eutrophication of the Baltic Sea, and (2) reduced yields arising from non-optimal phosphorus (P) and nitrogen (N) management in farming and animal husbandry. Sixty advisors were educated and four new approaches were introduced to change agriculture management and reduce P and N leaching to water; soil mapping of all fields, nutrient farm-gate balances, an excel-sheet for estimating N leaching and a 'farm-walk' with the adviser aimed for discussing possibilities to reduced nutrient losses from any hot-spots. 28 of the farmers were interviewed with open questions before and after the project end. Results demonstrated highly varied level of farmers' perception of nutrient flows on their farms and of possibilities to improve the fertiliser and soil management. In Pomerania 28% of the farmers introduced one or two measures directly aimed to reduce P and leaching; improved manure storage, use of fertiliser plans, to avoid soil tillage on steep slopes and to incorporate catch crop in the crop rotation. In Mazovia nutrient analyses of the farmers own manure was encourage by the regional advisors and, together with the soil maps, used for planning fertilisation. In this region, with a dry climate no farmer was interested in free-of charge catch-crop seed since they were afraid of water-competition with the main crop. All farmers found soil mapping valuable, and many the farm-gate balances useful but some considered the latter too academic and detailed. On many farms, acid soils are common which, apart from reducing yields may trigger P leaching. All of the most acid fields and grassland, except some which were leased, were limed in accordance with advises. In Pomerania 600 ha of liming was subsidised by 26%, and in Mazovia (with less farms with acid problems) to 50% of the total costs. This study clearly demonstrated the need for farmer to become familiar with P and N flows on their farms, especially in a changing world with the need to be better prepared for flexibility in their production.

P1.37

Background soil phosphorus levels in marine sediments in Norway

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According to the Water Framework Directive, European water bodies should achieve good ecological status by 2021. Phosphorus is a key element in achieving this goal, since it is the limiting nutrient for eutrophication in many water bodies. There are significant challenges in achieving good ecological status where agricultural land affects the water quality greatly and when defining the goal, it is therefore necessary to relate the losses to the reference conditions and the natural background phosphorus losses.

The natural background losses of phosphorus may in some areas be high due to natural conditions, for example high natural concentrations of phosphorus in the soils. In Norway, some of the main agricultural areas are located on marine clays with a high content of apatite contributing to the phosphorus loss from these areas.

The aim of this study was to quantify the contribution of phosphorus from natural marine clays to the total phosphorus losses from these agricultural landscapes and to define the background level of phosphorus losses from these areas.

In this study, soil and water samples were taken in a forested area with marine clay soils. 90 soil samples were taken from the 0-10 cm upper soil layer and analysed among others for concentrations of total phosphorus, soil phosphorus status (P-AL), watersoluble phosphorus, iron and aluminium. Furthermore, soil water samples and water samples from the two small streams draining this area was taken.

Preliminary results from this study showed that the soil phosphorus status of the natural marine clays was up to 234 mg P-AL/kg. The total phosphorus concentration of the soils varied from 0.15 to 1.5 mg/kg. The total phosphorus concentration measured in soil water was up to 99 ug/L.

The final results from this study will be presented in the poster.

The role of clay minerals in phosphorus sorption in sandy acid soil

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In the paper we present the results of the research whose aim was to determine the influence of the selected clay minerals on the course of phosphorus sorption in acid sandy soil. The research was conducted on the Brunic Arenosol (Dystric) (FAO-WRB 2014) soil profile localised in Bytom Odrzańskim (The Dalkowskie Hills, Poland). Sorption experiments were carried out by means of standard clay minerals of different structure and properties: kaolinite (KGa), illite (IMt), montmorillonite (STX), bentonite (ZwBen). Clay minerals were mixed with the soil material in the proportion 1:10 and subject to the phosphorus sorption process. The phosphorus concentration left in the solution after the reaction of sorption was measured in each sample by means of the ICP-EAS method. The phosphorus quantity sorbed by the sample was calculated from the difference between the doses introduced and P concentration in solution after the reaction. The results obtained showed significant influence of the clay minerals on phosphorus sorption in all genetic horizons of the soil under examination. The clay minerals' biggest influence was observed in the surface horizon (Ap) with this effect dropping down in the Bv and C horizons. The weakest influence on the soil's sorptive capacity was observed with kaolinite and illite. Attention is drawn by minimal soil's reaction to addition of kaolinite, especially on the Ap and Bv horizons. Clay minerals' impact was strictly connected with the size of their specific surface as well as with the mechanisms of P binding, typical of particular minerals. Bentonite had by no means the biggest influence on the phosphorus sorption capacities in soils. The growing influence of the materials on phosphorus sorption in all horizons can be ranged as follows: kaolinite<illite<montmorillonite<bentonite.

P1.39

Modeling phosphorus capture by grasses growing in a Midwestern Riparian buffer

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The loss of phosphorus (P) from agricultural lands has been a subject of growing interest in the environmental community for more than two decades. Recent research suggests that P flux to receiving waters can be reduced by maintenance of adequate riparian and stream bank vegetation and other site-specific management of soils and sediments with the greatest risks of P release in a watershed. Various types of riparian vegetative buffers have been developed and implemented with the intention of retarding the movement of P to surface waters. Buffers can significantly reduce particulate P entering surface waters, but control of dissolved P inputs is more challenging. Soluble P may enter a stream by overland flow or through flow from lands adjacent to the stream or from groundwater and natural seeps. Given that plant roots remove P from soil solution, it follows that plant uptake (phyto-extraction) can reduce losses of dissolved P to some extent. Using data from a current field study in central Iowa, as well as unpublished data from a controlled-climate study, the first objective of this study was to use a mechanistic nutrient uptake model (e.g., NST 3.0) to explore P uptake from the soil profile during an entire growing season in simulated buffer communities composed of mixtures of reed canarygrass (*Phalaris arundinacea* L.) and switchgrass (*Panicum virgatum* L.), two plant species commonly found in riparian buffers in the Midwestern U.S. The second objective was to use the model to explore the impacts of changes in key soil supply and plant parameters, as determined by sensitivity analysis, on estimates of P uptake by the two test species. A third objective was to use the model to explore potential P capture from both surface (A horizon) and subsoil (B horizon, buried A horizon) during a growing season. The buffer species tend to be deep-rooted, so we hypothesized that P uptake from subsoil could be significant. Preliminary results suggest that a simulation model such as NST 3.0 can provide both useful insights into the ability of various plant cover types to capture solution P and a means to explore which soil and plant factors are the most influential in predicting plant P uptake.

Phosphorus solubilization by microorganisms at different stages of soil development

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An important process of phosphorus (P) mobilization is solubilization of P from minerals such as apatite. It is widely accepted that the release of protons and organic acids by plants and microorganisms is a key mechanism by which P is solubilized. Despite its relevance, little is known about the changes in P solubilization processes at different stages of soil formation. We wanted to test the hypothesis that rates and mechanisms of P solubilization change during soil development. For this purpose, we studied soils in four different areas along a climate gradient in Chile. All soils developed on granitic bedrock. We expected the different P fractions to follow the dynamics proposed by Walker and Syers (1976), i.e., increasing amounts of Fe/Al-P and decreasing amounts of primary P-minerals with soil development. To determine the rates and mechanisms of P solubilization, we conducted incubation experiments with soil extracts and different P sources, and in some experiments with an additional C and N source: i.) apatite; ii.) apatite + minimal growth medium (C and N source); iii.) parent material of each soil. Soil samples were shaken with water (wt/vol 1:10), filtered through cellulose filters, and the extracts were incubated for one to three months at 15°C in serum flasks. Sterile controls as well as soil extracts without apatite were added to test for abiotic P solubilization and the influence of organic P mineralization, respectively. Inorganic P concentrations, pH-value, and optical density (absorption at 600 nm) were measured weekly. Additionally, the concentrations of several organic acids were determined via HPLC-MS every 3 weeks. Moreover, we determined different P fractions such as apatite-P, occluded P and P sorbed to iron- (Fe) and aluminum (Al)-hydroxides by the Hedley method. This is one of the first studies that relates soil P fractions that form during pedogenesis to rates and mechanisms of P solubilization.

References:

Walker, T.W. & Syers, J.K. (1976): The fate of phosphorus during pedogenesis. *Geoderma* 15 (1), 1-19.

P1.41

The storage of P in riparian buffer zone soils related to the shape of the buffer zone and the adjacent landscape

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Permanently vegetated buffer zones (BZs) between the agricultural land and the water course are often established to reduce losses of P and sediments arising from erosion or surface runoff at agricultural fields. The effectiveness of such BZs increases significantly if BZ width is adapted to the steepness and risk of erosion from the area behind the BZ, and BZs below such areas can be enriched with sediments and P from the fields above. What is less well known is to which extent storage of P can be related to the relief of the actual BZ area, how much P is already stored in the soils near the surface waters and to which extent the vegetation type of the well-established parts of the BZ is related to soil P storage.

We conducted a study on P storage and distribution along paired transects from stream towards field with sampling points at increasing distance from the stream in three landscape types (chosen based on prevailing vegetation type) at two different locations in Denmark. At each site there was an old (early 1990s), well-established BZ between 0-2 m from the stream and an additional zone approx. 3-10 year old zone at 2-10 m. We sampled soil cores to 50 cm depth in 25 cm intervals and measured elevation of each sampling point and total P and bulk density of each soil layer.

For sites with a depression in the 2-10 m buffer zone, a sloping landscape behind and a slight elevation in the 0-2 m zone, more P was stored in the newer 2-10 m than in either the older 0-2 m BZ or the area from the adjacent fields. When such a depression was missing less P was stored in the BZ than in the adjacent fields.

We therefore conclude that for the BZ to be effective in retaining P, a depression within the BZ is required, where runoff water can be retained, allowing sediments and nutrients to settle. The relief of the BZ area seemed to be more important than the age of the buffer zone for the amount of P stored in the more recently established 2-10 m BZ area and this zone most probably also retained P before BZ establishment, if the depression already existed before BZ establishment. For management purposes is therefore important to take into account not only the landscape shape of the area behind the BZ, but also the local relief of the BZ area when planning the placement of buffer zones alongside water bodies.

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Modelling natural phosphorus export from lake catchments

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Diffuse phosphorus (P) loading is a persistent challenge in lake water management. The source of this loading is often anthropogenic (e.g. agriculture), but a notable portion of P export from catchment to lake may also be natural. Therefore, to effectively manage lake waters, it is crucial to know the baseline, i.e. the natural level of P export.

In order to determine the amount and spatial variation of natural P export in an area with a steep local P gradient (4-122 $\mu\text{g l}^{-1}$), we used palaeolimnological methods combined with P mass balance modelling for 50 boreal lakes (53 sampling sites). The palaeolimnological approach comprised of reconstructing past lake water total P (TP) for pre-human disturbance sediment samples with a diatom-TP transfer function developed specifically for these lakes. Our study area, located in central-eastern Finland, is exceptional because of its naturally eutrophic lakes surrounded by less nutrient-rich ones. Current anthropogenic P export sources in the area include livestock breeding and grass cultivation-based agriculture, forestry, and scattered settlements. We compared the natural P export to modern P export to quantify the amount of anthropogenic P loading in the study area and to the Quaternary deposits (e.g. till, clay, sand and peat) of the subcatchments to see if there is a connection between certain deposits and high natural P export.

Natural P export ranges from 3 to 23 $\text{kg a}^{-1} \text{km}^{-2}$ in the study area and, in general, is highest along the Iisalmi lake route near the municipalities of Kiuruvesi and Iisalmi. This is in accordance with previous studies that have reported natural P export values ranging 2-15 $\text{kg a}^{-1} \text{km}^{-2}$ (Finér et al. 2010) and 2-18 $\text{kg a}^{-1} \text{km}^{-2}$ (Mattsson et al. 2003). However, the effects of lake infilling and artificial water level lowering to lake morphology have not yet been taken into account in the P retention calculations. Anthropogenic P loading (0-45 $\text{kg a}^{-1} \text{km}^{-2}$) has increased P export to most lakes, up to fivefold in some cases. The high values of natural P export seem related to high clay and fine-grained till percentages in the subcatchment. Therefore, it is important to consider the geology of the catchment in addition to anthropogenic loading when making lake water management decisions.

P1.43

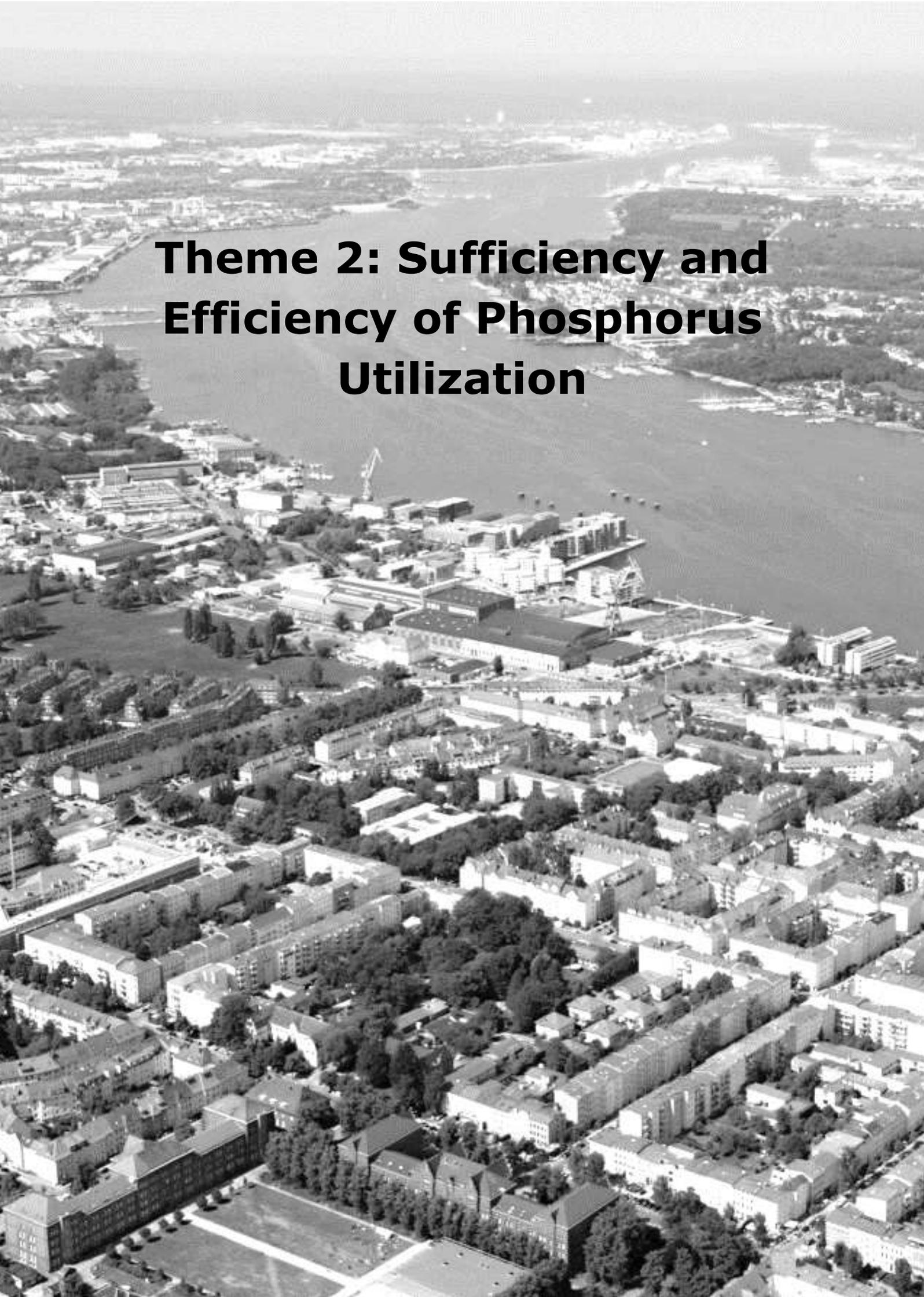
Organic phosphorus as affected by soil properties and fertilization in Mediterranean environments

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The knowledge of organic P (OP) compounds is necessary to fully understand P dynamics in soils. This study was aimed at evaluating the effect of P status, uses, and properties of soils on OP compounds in representative Mediterranean soils. To this end, 8 soils were selected. Solution ^{31}P NMR spectroscopy was used to characterize P in NaOH-EDTA extracts from soils, using two samples per soil with very different P status ("low" and "high" P samples).

Orthophosphates monoesters (Mono) dominated OP, accounting for around 50% of total OP in low- and high-P samples. Differences in Mono concentration between high- and low-P samples increased with increased differences in Olsen P between both types of samples ($R^2=0.61$, $P<0.05$). In addition, Mono to diesters ratio increased with increased Olsen P in soil ($R^2=0.49$; $P<0.01$). These results suggest an increased Mono degradation under P limitation conditions in soils. Therefore, in the long term, potential contribution of Mono to P uptake by crops can be expected when the P availability to plants is low in soil. Myo- and chiro-inositol-6-phosphate (IP6) were the dominant IP6 stereoisomers and contributed almost equally to total extracted P. These both isomers were more abundant than Scy-IP6. This shows that soils from Mediterranean area may have a different pattern of stabilization of IP6 than soils from other geographical areas. The contribution of monoesters and most of the IP6 isomers to OP increased with increased Olsen P in soil, but only where the crop residue accumulation was scarce (vineyards and olive orchards). This result supports the hypothesis of a degradation of monoesters including IP6, under limited P conditions may be supposed, allowing one to expect some contribution of these OP forms to plant P supply. Myo-IP6 concentration increased with the enrichment in Fe oxides of the clay fraction and decreased with increasing pH. This suggests that adsorption on Fe oxides stabilized myo-IP6 in these soils. None of the other IP6 stereoisomers was significantly related to the ratio of Fe oxides to clay or to pH in soils. The relevance of the precipitation of IP6 different from myo- can explain the different proportion of IP6 stereoisomers found in our soils when compared with soils from other geographical areas.

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An aerial, black and white photograph of a city, likely Stockholm, Sweden. The city is built on islands and connected by bridges. A large body of water, the Baltic Sea, is visible in the background. In the foreground, there is a dense residential area with many multi-story apartment buildings and trees. In the middle ground, there is a large industrial or commercial area with several large buildings and a crane. The text "Theme 2: Sufficiency and Efficiency of Phosphorus Utilization" is overlaid in the upper center of the image.

Theme 2: Sufficiency and Efficiency of Phosphorus Utilization

Theme 2

Sufficiency and Efficiency of Phosphorus Utilization

Oral Presentations

Responsible scientists: Peter Leinweber, Bettina Eichler-Löbermann (both from the University of Rostock, Germany), Klaus Wimmers (Leibniz Institute for Farm Animal Biology, Dummerstorf, Germany)

Keynote Speaker: Emmanuel Frossard, Swiss Federal Institute of Technology Zürich (ETHZ), Switzerland

Animal and plant systems, both terrestrial and aquatic, account for a large proportion of the P cycle. P leaving this cyclic P flux is mostly in the form of undesired losses from agricultural systems into natural terrestrial and aquatic environments, leading to eutrophication and other ecological challenges. While previous fertilization practices were directed at building-up P reserves in soil, current concerns are related to environmental P pollution and the rising price of P on the world market. Together, they strongly call for new recommendations regarding the agricultural use of P and the more sustainable use of this scarce resource. Accordingly, this conference session addresses the availability of P compounds in soils, the efficiency of intrinsic P utilization by plants and animals, the optimization of recycling processes of excreted P, and the minimization of P losses from agricultural production systems.

Keywords: plant, animal, soil, aquaculture, feeding, manuring, fertilization, rhizosphere

Keynote Abstract:

How much phosphorus do our agrosystems really need?

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Phosphorus (P) fertilizers (either mineral or organic) are rarely applied in appropriate amounts to crops and grasslands. Excessive P inputs can be due to the presence of high animal density leading to slurry and/or manure inputs in excess to plant needs, or to fertilization practices including a margin of security to ensure that crops will not suffer from P deficiency. In other cases, especially in Sub Saharan Africa, the lack of financial resources of subsistence farmers leads to situations where P inputs are either very low or inexistent, resulting in the exhaustion of soil P resources. These practices have to be modified as they lead to water quality degradation in the case of excessive P inputs, to low yields and food insecurity when soil P resources are exhausted and no P is added, and as the use efficiency of natural resources must increase. This presentation reviews approaches that have been or could be taken from the farm to the field levels to adjust P inputs for an optimal plant production. The first approach that will be presented is the "needs/inputs" budget measured at farm level. This accounts for the total estimated needs of crops and grasslands and the total inputs by mineral and organic fertilizers. This approach has been implemented in Switzerland in the 1990s as part of the direct payment scheme and resulted in a significant decrease of P inputs in agrosystems without decreasing plant productivity. However, this approach is based on estimated plant needs and inputs for manure derived from references values, it does not consider soil P availability and it does not consider the field level. An approach that can be used at the field level is the soil system P budget. It takes into account the P exported by crops/grasslands, the P added by fertilizers and the P losses from the soil profile. This approach allows seeing whether the system studied is in balance for P, and how inputs are used for agricultural production even at rotation level. But it does not take into account soil P availability and it does not inform on the plant P nutritional status. Soil analyses have been used for decades to predict the needs of P fertilizers for plant biomass production. A popular way to study this relationship is to carry out long-term field experiments with varying doses of P and to compare the soil P status estimated by a given chemical extraction to crop yields. This type of approach allowed the establishment of fertilizers inputs recommendations as a function of plant type and soil extractable P and other soil properties. However these recommendations are derived from estimated plant needs, ignoring the variability of plant nutritional composition, and from relatively few long term field experiments as these are extremely expensive to maintain. Furthermore, as the currently used soil chemical extractions only provide a rough estimation of soil P

availability, progress still needs to be done for a more mechanistic estimation of soil P availability that can be implemented in the practice. A further possibility is to include a diagnostic on plant nutritional status in the fertilization strategy. This is relevant as biomass production is a function of N uptake which itself controls P uptake. The phosphate nutrition index (PNI) can be used as a diagnostic tool to estimate whether a plant has a sufficient level of P compared to its N concentration. Plant biomass production, grasses PNI, and soil P extractability have been measured in different types of grasslands. These data allowed estimating the amount of soil extractable P needed to reach a sufficient P nutritional status and biomass production in these grasslands. The limit for the implementation of this approach is to have rapid and reliable measurements of plant biomass and N and P concentrations in plants. Furthermore, this approach does not quantify the amount of P to be added to the plant stand, it only states whether the plant P status is sufficient or not. Whereas remote sensing approaches provide reliable estimations of biomass, leaf surface and N concentration in plants, measurement of P concentration in plant tissue is much more difficult because only indirect spectral features are related to P status of a plant (for example anthocyanin contents). A generic tool allowing estimating P needs and fertilization for different type of crops, growing in different climates and soils and submitted to different management practices, is still needed. Mechanistic models taking into account both the soil and the plant can help to achieve this. The FUSSIM-P-maize model is an example of this approach. It is composed of three modules: one that calculates P needs based on the plant growth as allowed by climatic conditions, one that calculates soil P availability based on the diffusion of P from the soil phase of the soil to the solution, and one that calculates the uptake of P by the root system from the soil solution. If sufficient P is available, the plant will reach maximal growth. But if soil available P is limited then P uptake will be limited, this will reduce carbon fixation, modify C allocation in the plant, affect root growth and morphology and this will decrease P uptake on the long term. The principles of the model are applicable for other plants species (*Festuca*, *Pinus*). The model needs to be tested in the presence of multiple stresses (N or water limitation, soil compaction) and other agricultural plants. It has the potential to quantify the effect of "rhizospheric processes" on P uptake, which will probably become more significant as soil available P will decrease. And it can be used to predict the critical level of soil available P under which plant biomass production could be negatively affected.

Phosphorus utilization in mixed cropping systems

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The cultivation of crops in mixed cropping systems can lead to a complementary utilization of growing factors whereby the interactions among crops are context dependent and shift from facilitation to competition as environmental stress decreases (stress-gradient-hypothesis). The performances of different crops in sole and mixed cropping regarding phosphorus (P) utilization were thoroughly investigated in a four years research project. Monocots + legume combinations with maize (*Zea mays*) or sorghum (*Sorghum bicolor*) combined with runner bean (*Phaseolus coccineus*), blue lupin (*Lupinus angustifolius*), Andean lupin (*Lupinus mutabilis*), or soybean (*Glycine max*) were tested in I) an experiment with rhizotrones, II) pot experiments in greenhouse, III) a field experiment with a rainout-shelter and an irrigation system, and IV) a long-term field experiment with different P management treatments. Mixtures of monocots with legumes received only 50 % of the nitrogen (N) supply compared to the monocots alone. Plant growth, shoot biomass yields and nutrient uptake were analyzed as well as a broad spectrum of chemical and biological soil characteristics. Advantages of mixed cropping were rather found under unfavorable growing conditions, and under P deficiency the yields of the mixtures were comparable or even higher than maize or sorghum cultivated alone. At optimal P supply however, the single cultivated maize showed the highest yields of all crop treatments in all experiments. The mixtures had a higher yield stability and were less affected by fertilizer or water supply. Accordingly, in the field experiment the maize-runner bean combination had the same yield in the control plots without any P supply during the last 17 years as in the plots which have received about 600 kg during this period. Usually higher activities of enzymes in soil were found in the mixed cropping treatments. Mainly the activity of the acid phosphatase was raised when monocots were cultivated together with legumes which points to a higher P utilization from organic P compounds in soil by the mixtures. This effect was measurable in field directly after the harvests and even in the next spring. The results of this study underline a higher mobilization of less available P sources when different crop species are cultivated together and point to a direct facilitation of the monocots by the legumes. Legumes as partners for monocots are also useful because of the lower N fertilizer demand in the mixtures.

The fertilizer phosphorus use efficiency of leguminous-based pastures under different management in the high rainfall zone of south eastern Australia

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The pressure to improve the productivity of grasslands for animal production, is a pertinent issue as global food demand for meat is predicted to rise over the coming decades. Animal production will have to increase to meet these challenges. However, concomitant with this will be a four-fold increase in the use of phosphorus (P) fertilizer: P being a major nutrient limitation of grasslands. Better knowledge of the fertilizer P use efficiency of grasslands and the effect of agronomic management is an essential requirement for improved grassland productivity.

The efficiency of P fertilizer use on clover-based (*Trifolium subterraneum*) pastures was investigated in two field experiments in 2013 (Naracoorte, SA and Ginninderra, ACT) and in two field experiments in 2014 (Inman Valley, SA; and again at Ginninderra). Briefly, in 2013, this involved the addition of ³³P-labelled single superphosphate (SSP) to the soil surface at mid-season (late winter) of a clover pasture to supply ~12 kg P/ha, whereas in 2014, this involved the addition of ³³P-labelled SSP to supply ~20 kg P/ha but under different management: (i) to the soil surface at early-season (ii) to the soil surface at mid-season, and (iii) at 6 cm below the soil surface at early-season. In addition, at the Ginninderra field experiment in 2014, ³³P-labelled SSP was added early-season to the soil surface of pastures maintained at three levels of soil P fertility: (i) P0, non-fertilized, (ii) P1, fertilized to agronomic optimum, and (iii) P2, fertilized above the agronomic optimum (based on Olsen soil P tests).

Clover growth and recovery of fertilizer P by clover was generally highest when fertilizer P was added at early-season, on the soil surface, and in soils maintained at the P1 level of soil P fertility. Up to 50% of the added fertilizer P was recovered by clover plants (shoots and roots), less than 15% remained in the fertilizer granule, and ~30% was retained in the 0–4 cm soil layer (largely as inorganic P) in the year of application. We demonstrate that clover pastures were able to recover nearly half of the added fertilizer P, which was achieved through surface application of SSP granules, which is a cost-effective strategy for pasture management. Furthermore, our findings suggest that the inefficiency of phosphatic fertilization in grasslands (export of P as products relative to inputs of fertilizer P) is not wholly caused by the rapid accumulation of P in fertilized soils on a single season timeframe.

Can inoculation with *Pseudomonas protegens* CHA0 enhance the mobilization of scarcely soluble phosphorus from soil and uptake by *Lolium multiflorum*?

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Phosphorus (P) availability to plants in calcareous soil is often limited due to strong sorption of P onto calcium carbonate containing solid phases in the soil. Fostering microbial activity via the addition of P mobilizing microorganisms holds promise to increase P availability to plants from scarcely soluble P forms in soil by mineralization of organic P and/or solubilization of inorganic P. However, most results of P solubilization are variable and direct and indirect effects, e.g. plant pathogen suppression, of P mobilizing microorganisms on plant P uptake cannot be separated. Therefore, we propose ^{33}P isotopic dilution approach to assess microbial P mobilization in soil-plant systems. We studied the effect of the P solubilizing bacterial strain *Pseudomonas protegens* CHA0 on the availability of P from soil and thermo-chemically treated sewage sludge ash (SSA) in an incubation and plant growth study with *Lolium multiflorum* using the ^{33}P isotopic dilution technique. We expected that the inoculant would increase the availability of P from otherwise non soluble P forms thus increase the P uptake by *L. multiflorum* from soil and SSA P. The strain CHA0 was able to solubilize P from SSA under controlled conditions in liquid media (without soil), but did not enhance P mobilization from soil or SSA in soil. In the presence of CHA0, soil organic P mineralization and soil respiration were decreased suggesting inhibition of the soil inherent microbial activity. Thus, any inorganic P solubilized by the inoculant might have been offset by less basal organic P mineralization. When inoculated with CHA0, *L. multiflorum* took up more P until the first harvest. We attributed this increased P uptake to reduced pathogenic pressure in the rhizosphere rather than to increased P availability from soil or SSA, as the isotopic composition of P ($^{33}\text{P}/^{31}\text{P}$) in the shoots was not affected compared to non-inoculated control. Cumulative P uptake of *L. multiflorum* of three harvests was not affected by the inoculant CHA0. Low survival rate of the inoculant was indicated by the absence of culturable CHA0 cells on roots of *L. multiflorum* after the third harvest and in the incubated soil 69 days after inoculation. With the isotopic dilution approach we were able to show that inoculating a microbially active calcareous soil with the P solubilizing bacterium CHA0 did not increase P availability to *L. multiflorum*. In another experiment we are currently elucidating constraints for P solubilizing activity of CHA0.

The effect of P speciation on soil availability of P in biochar produced from solid fraction of manure at different pyrolysis temperatures

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One of the mechanisms by which biochar has been proposed to improve the fertility of soil is through by improving phosphorus (P) availability. However, very little information is available regarding P speciation in biochar and what effects this may have on the subsequent P availability in the soil. The purpose of the current study is to use a range of different analytical techniques to understand how the pyrolysis temperature affects P speciation and how this may affect the availability of P in the biochar and in soils to which the biochar is applied. Therefore P speciation of biochar samples produced at different temperatures from manure-based digestate solids was analyzed by X-ray absorption near edge spectroscopy (XANES) at the K and L-edges as well as by X-ray Photoelectron Spectroscopy (XPS) and elemental mapping, using scanning electron microscopy with an energy dispersive x-ray detector (SEM-EDX) was used to analyze spatial co-occurrence of elements. In addition, soil incubations where the effect of the biochar application on P availability from the amended soils was assessed by the diffusive gradients in thin films (DGT) technique were conducted. The XANES spectra indicated that the primary species of P in digestate solids were simple calcium (Ca) phosphates, such as calcium phosphate dibasic. However, a high co-occurrence of magnesium (Mg) and P as observed by SEM-EDX indicated that struvite or other Mg phosphates may also be important species. When biochar is produced at low temperature, the XANES spectra indicated that rather small changes in the speciation, but as the temperature increased above 600°C, the phosphorus species are gradually becoming more thermodynamically stable and crystalline in species such as apatite. At very high temperatures, above 1000°C, there were indications that reduced forms of P, like phosphines was forming. Biochar production decreased the immediate availability of P in comparison with the original digestate solids. However, for biochar produced at low temperature, the availability quickly increased to the same levels as in the digestate solids. For biochar produced at higher temperatures, the availability remained depressed for much longer, resulting in P availability in the soil at the same level as the unamended control soil or even lower. The low availability of P in the biochar produced at high temperatures is likely explained by the formation of less soluble P species in the biochar.

Possibilities and perspectives to improve P efficiency in livestock feeding

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Feed phosphates produced from rock phosphate are used as feed supplements in order to fulfil the phosphorus (P) requirement of the animal. The need for supplementation of feed phosphates depends on the plant feed ingredients that are used. The P concentration in feed ingredients of plant origin is highly variable. The availability of different P sources for the animal also is variable. A professional formulation of complete diets and rations for livestock takes this variation into account and adjusts the inclusion of feed phosphates – if necessary at all – to the animal's requirement. This contribution will address the situation in different animal species as well as perspectives we have to reduce the amount of feed phosphates used.

Cattle and other ruminants have a high potential for utilisation of plant P sources because microbes in the rumen release phosphate from phytate. Cattle rations that contain high amounts of maize products may require some feed phosphate addition; however, most rations fulfil the P requirements of cattle without any feed phosphate supplementation. Feeding of non-ruminant animals such as pigs, broiler chickens and turkeys has to consider a lower digestibility of P from plant sources and feed phosphates are often used. During the growth period, feed phosphate supplementation can be continuously reduced with increase in the body weight of the animal, often referred to as phase feeding. Phase feeding is of particular relevance in areas with high livestock density. P concentration in diets for pigs and poultry also can be reduced when enzymes are supplemented to the feed. Specific enzymes can increase the digestibility of phytate-P in the digestive tract. However, to date application of such enzymes does not make feed phosphate supplementation totally superfluous.

Current research involves approaches that might increase the efficacy of the enzymes and better understand interactions with other feed constituents. Recent research also indicated some genetic background of P digestibility in poultry. This suggests that breeding for high P digestibility might get on the agenda of breeding programs in the future. With a combination of tools both on the feed and the animal side it will be become possible to feed livestock with less (or even without) feed phosphates. However, the most effective approach to improve sustainable P handling would be the re-approval of meat and bone meal in the feeding of pigs and poultry.

Elucidating the biodiversity of P homeostasis towards improved P efficiency in pigs

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Phosphorus (P) is an irreplaceable component of life and is used in all agricultural production systems. In monogastric organisms, P homeostasis is maintained via a number of known and yet to be elucidated regulators, transporters, hormones, and paracrine signals. Specifically, P utilisation is basically mediated by calcitriol (1,25(OH)₂D₃), fibroblast growth factor 23 (FGF23), and parathyroid hormone (PTH). Furthermore, bone resorption is controlled by a system composed of soluble RANKL (receptor-activator of nuclear factor kappa beta ligand) and its decoy receptor osteoprotegerin (OPG). The biodiversity of pigs regarding their serum P levels (mean±SD: 8.4±1.0 mg/dl; min: 6.0 mg/dl; max: 12.7 mg/dl in German Landrace) provides a huge potential for selective breeding towards improved P efficiency. In order to elucidate the genetics of P utilisation in pigs, candidate gene approach (including VDR, FGF1R, PTH1R, RANK, and OPG) and genome-wide association studies (GWAS) were employed to identify genomic regions building the molecular foundation of P homeostasis. Analyses were conducted based on a German Landrace population of >500 pigs which were genotyped using 60K-SNP arrays. Most promising quantitative trait loci were detected on chromosomes 4 and 14 ($p < 10^{-6}$) covering each a 2 Mb region. Positional candidates are involved in osteogenic differentiation and osteoclast activity, respectively. For a single nucleotide polymorphism (SNP) located in TRAFD1 (TRAF-Type Zinc Finger Domain Containing 1) we have found significant association with serum P level. At this locus, homozygous carriers of the alternative allele show an increased serum P level. As a complementary approach we also consider functional candidates by identifying transcripts whose abundance is modulated due to high vs. low dietary P supply. The identification of genetic variation in functional and positional candidate genes relevant for P efficiency will contribute to establish novel approaches of P management to balance economic and environmental sustainability. Consequently, associated positional and functional candidate genes will be further investigated.

Long-term cumulative contribution of phosphorus-based swine manure application to soil test phosphorus under corn-soybean rotation

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Bioavailability of phosphorus (P) in manure varies and can be temporally cumulative depending on the types and forms. Determination of long-term trends of manure form-specific effects on soil P is essential to nutrient management and planning. A study was conducted to quantify the long-term changes of soil test P (STP, Olsen-P) with application of three forms of swine manure (liquid, LM; solid, SM; and liquid manure compost, MC), in comparison with chemical fertilizer (CF), and to determine the values of manure P source coefficient (PSC) in a clay loam soil under corn-soybean rotation from 2004 to 2011. Phosphorus addition at $100 \text{ kg ha}^{-1} \text{ year}^{-1}$ to the corn phase of the crop rotation over the eight-year period increased STP levels in both 0-15 and 15-30 cm depths, regardless of the sources. Increases in STP were related linearly to the cumulative rates of net P addition, but the incremental rates varied, depending on the P source applied and the depth of soil sampled. The effect of P addition on STP followed the order of $\text{LM} > \text{CF} \sim \text{MC} > \text{SM}$ in the 0-15 cm layer, whereas at 15-30 cm depth, it followed the order of $\text{MC} \sim \text{CF} > \text{SM} \sim \text{LM}$. Clearly, P added in MC behaved similarly to CF, while the effect of LM on STP occurred mainly in the surface soil layer. When taking crop P removal and the changes in STP in both 0-15 and 15-30 cm depths into account, it required 12.2, 9.8, 16.1 and 10.7 kg ha^{-1} net P addition for CF, LM, SM, and MC, respectively, to increase STP by 1 mg kg^{-1} soil. As a result, similar values of PSC were observed with 1.10, 1.07 and 1.02 for LM, SM, and MC, respectively, in the 0-30 cm soil profile. Long-term effects of swine manure addition on STP were similar to that of CF, regardless of the forms.

Theme 2
**Sufficiency and Efficiency of Phosphorus
Utilization**
Poster Presentations

P2.1

Phosphorus stocks and speciation in top- and subsoils of a long-term fertilization experiment: evidence from sequential fractionation, ^{31}P -NMR, and P K-edge XANES spectroscopy

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The world's agricultural productivity highly depends on the use of phosphorus (P) for which worldwide shortages were prognosticated. Current estimates indicate that not only the topsoil, but also the subsoil can hold immense P stocks. Accessing also these mainly unused stocks for plant nutrition might help to reduce external P inputs. Thus, in order to estimate the P utilization potential by plants exact knowledge about the P speciation and its bioavailability is essential. In our study we compared the P status of topsoils (0 to 30 cm) and subsoils (30 to 60 cm, 60 to 90 cm) of a Stagnic Cambisol with various P fertilization treatments (control, compost, triple superphosphate (TSP), compost+TSP). To identify different chemical forms and P availabilities we used wet chemical extraction procedures (Hedley fractionation) and liquid ^{31}P nuclear magnetic resonance (NMR) in combination with P K-edge X-ray absorption near edge structure (XANES) spectroscopy. Results indicated that P fertilization increased soil P not only in the top- but also in the subsoil. Total P stocks in both subsoil layers averaged between 45% and 52% compared to the topsoil. Compared to the control we measured a 1.3 fold higher P stock in the compost and TSP treatments and 1.5 fold higher stock in the compost+TSP treatment in the subsoil. The Hedley fractionation showed equal concentrations of Resin-P and $\text{NaHCO}_3\text{-P}$ in the top- and subsoils but higher concentrations of residual P in the topsoils. Yet an increase of NaOH-Pi and $\text{H}_2\text{SO}_4\text{-P}$ in the subsoils suggested the dominance of predominantly inorganic, stable P forms. The ^{31}P -NMR analyses supported these findings by 2 fold higher concentrations of orthophosphate monoesters in the topsoil than in the subsoil. The extracts were dominated by orthophosphate monoesters in several stereoisomeric configurations of the sugar inositol and inorganic orthophosphate and no orthophosphate diesters were present. Further, P XANES revealed mainly the presence of inorganic P species such as stable Fe- and Ca-P compounds besides organic P. First estimations revealed that Ca-P proportions increased with depth and that there was a shift in proportions depending on the fertilization treatment. Our findings proofed that the subsoil holds comparable or even higher P stocks compared to the topsoil, which have an equal or even better P availability holding the potential for agricultural use. Further studies have to focus on the accessibility of these stocks by plants.

Effect of soil phosphorus availability on legume distribution and phytodiversity

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In semi-natural grasslands, productivity often conflicts with biodiversity. N fixing legumes play an important role in providing N and achieving high forage quality, especially in organically managed grasslands. Many farmers observe both temporal and spatial variation of the legume distribution on their grassland sites. Legumes have high P requirements, so that legume and total yield can be increased by P fertilisation. However, large concentrations of soil P negatively impact phytodiversity. The objective of this study was to investigate if there is a relation between a) soil P fractions and the presence of legumes and b) between soil P and biodiversity.

The study was conducted on different semi-natural grassland sites under organic management in north-eastern Germany. Here, several plots were investigated with a clear spatial differentiation between the functional groups 'legumes' and 'non-legumes'. The species richness of each plot was recorded. Vegetation and soil samples were taken and analysed separately for legumes and non-legumes. Soil P contents of the different fractions and thus P availability could not explain the spatial distribution of legumes and no relation between soil P and biodiversity was found.

P2.3

Plant uptake of phosphorus recycled from urban waste on calcareous soil

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The growing human population and urbanization result in greater phosphorus (P) fluxes from agro-ecosystems to consumers and finally into urban waste, such as municipal organic waste and sewage sludge. While the P contained in municipal organic wastes can be recovered by anaerobic fermentation, direct application of sewage sludge to agricultural land is increasingly debated and alternatives to recycle P from waste water are needed. Options are the precipitation of P either from waste water or from separately collected human urine or the recycling of P from sewage sludge incineration ash. In either way the recycling of P back to crop land requires that the plant availability of P in the recycling product is known. The P availability of most fertilizers on calcareous soils is low due to strong sorption and slow dissolution processes. Thus, we studied the availability of P contained in fertilizers recovered from waste water as magnesium ammonium P (MAP) and as calcium P (CaP-SS), from urine (CaP-U), from sewage sludge ash (SSA) and from digested municipal organic waste (DMOW) to *Lolium multiflorum* grown on a calcareous soil. We used ³³P radioisotope dilution technique to determine the amount of P in *L. multiflorum* taken up from the fertilizer in the greenhouse. The relative fertilizer use efficiency (RUE) is expressed as P uptake from the fertilizer relative to water soluble mineral P. The RUE of recycling P fertilizers increased in the following order: SSA, CaP-SS, DMOW, MAP and CaP-U. In conclusion, only DMOW, MAP and CaP-U are suitable as P fertilizers on calcareous soils. Currently we are studying whether cover crops with P mobilization mechanisms can enhance the RUE of P contained in SSA and DMOW on a calcareous soil.

Cattle slurry distribution and acidification influence the initial P availability for maize

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To ensure sufficient phosphorus (P) supply in the early growing stages of maize, positioned starter mineral P is routinely applied in addition to manure. However, maize is typically grown in livestock farms with excess of P in the supplied manure. The aim of this study was to test whether cattle slurry P can replace starter mineral P.

The study was conducted in climate-controlled chambers. Maize (*Zea Mays* L.) was established in oblong pots with three plants in a row using two typical Danish top soils: A loamy sand and a coarse sandy soil. The experiment had three factors: Acidification level of slurry (pH=3.8, pH=5.5 or untreated slurry), slurry application time (32 or 2 days before sowing) and slurry application technique (slurry injection in a narrow band (4 cm) or broad band (13 cm)). The application rate was equivalent to 20 kg P/ha except a reference with no P application. Dry matter (DM) yield, P concentration in the maize plants ([P]) and total P-uptake (PU) were measured 45, 60 and 75 days after sowing (DAS).

Total dissolved P was two times greater ($P < 0.05$) in acidified slurry than in untreated slurry. DM yield 75 DAS was at the same level or higher ($P < 0.05$), when the slurry was injected in a broad band compared to DM yield in the treatment with mineral positioned P (20 P/ha). This observation was valid for both soils irrespective of acidification level. In contrast to this, injection of untreated slurry in a narrow band 32 days before sowing at the loamy sand, which is normal practice, showed no effect on DM yield compared to 0 P/ha. Moreover, treatments with strongly acidified slurry (pH=3.8) had a higher DM yield ($P < 0.05$) than the treatment with mineral positioned P (20 P/ha) on the coarse sandy soil. A positive response to P was reflected in [P] 45 DAS on both soils. On the coarse sandy soil, treatments with strongly acidified slurry (pH=3.8) had a 49% higher PU ($P < 0.05$) 75 DAS compared to untreated slurry. Contrastingly, no effect of slurry acidification on PU was observed on the loamy sand, whereas an effect of application technique on PU ($P < 0.05$) was found at 45 and 60 DAS with highest PU after injection in a broad band.

Results of the study demonstrate that strongly acidified slurry improved initial P uptake on a coarse sandy soil, and a higher DM yield was obtained on both soil types, if the slurry was injected in a broad band, indicating that initial maize yields are able to benefit from cattle slurry P.

P2.5

Influence of different recycled digestate fertilizers on P-uptake of maize plants and soil biological processes in different soils

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Digestates of biogas fermentation are nutrient-rich particularly for Phosphor (P). Limited P-rockphosphate stocks call for a recycling of digestate as alternative P-fertilizers. The project "General optimization of biogas processes" aims on the production of a customized design fertilizer from recycled digestates by chemical and thermal processing. The influences of recycled P-fertilizers resulting from differing digestate treatments on plants and soil microbial functions in comparison to common Triplesuperphosphate (TSP) fertilization is crucial for the assessment of their fertilizer value. We hypothesize higher P-availability of the recycled P-Salt and a positive fertilization effect when combining P-Salts with separated solid matter (SM) compared to TSP. Furthermore the different drying process of air dried and steam dried SM (Air SM and Steam SM resp.) may show differences in their influence on soil microbial functions. A seven week pot greenhouse experiment with different recycled digestate products (P-Salt, separated solid matter dried at 40°C (Air SM) or 120°C (Steam SM) were investigated in a fully randomized block design with different soils (silty loam (loess), clayey loam, sand) on maize in four repetitions. The recycled digestate products were applied separately and combined (Air SM + P-Salt/Steam SM + P-Salt) in different ratios (1:1/1:2). Combined application was performed with and without mixing of the two components before addition to the soil. All recycled digestate products were applied in amounts equivalent to 150 mg P/kg soil. Soil samples were taken simultaneously from each pot after fertilisation and after harvest to analyse phosphatase activity and plant available P (CAL-P). Plant dry matter and P content in shoots were measured. In conclusion this study showed that recycled P-Salt and even combination of SM and P-Salt from digestates were equally effective to TSP. They have a high potential to reduce the dependency of agricultural P fertilizers derived from rockphosphate.

Synthetic minerals to increase P availability in soils

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The global phosphorus crisis in recent years highlights the importance of efficient phosphate use. In strong P fixing soils, such as acid weathered soils and calcareous soils, current commercial P fertilisers have low efficiencies due to fast and irreversible P sorption/precipitation. Here, layered double hydroxides (LDHs) are tested as a new slow release P fertiliser, to provide plants with available P for a longer period, thereby bypassing P fixation reactions. The LDHs are layered inorganic anion exchangers consisting of layered divalent (e.g. Mg^{2+}) and trivalent (e.g. Al^{3+}) hydroxides and intercalated anions such as HPO_4^{2-} . Depending on soil conditions, release of HPO_4^{2-} ions from LDH fertilisers will be driven by different mechanisms. In a calcareous soil, the intercalated HPO_4^{2-} can be exchanged with CO_3^{2-} , while in acid soils the main release mechanism depends on acid dissolution of the material.

The aim of this study is to (i) synthesise P exchanged LDHs, (ii) determine their P desorption characteristics, and finally (iii) compare their fertilisation efficiency with current soluble fertilisers. Using cheap and readily available Mg and Al nitrate salts, Mg/Al LDHs were successfully synthesised and their layered structure was confirmed by X-ray diffraction (XRD). The nitrate LDHs were treated in PO_4 solutions, yielding an uptake of up to 6 wt% P, confirming the theoretical anion exchange capacity of the LDHs. The desorption kinetics from P loaded LDH powder material were examined in a carbonate solution, which proved the slow release characteristics of the LDH material. XRD-analysis confirmed the uptake and removal of P in the interlayer of the material after adsorption and desorption, which proves P is bound electrostatically and reversible in the LDHs. Taking it one step closer towards fertiliser application, slow P release from the P-LDH was also confirmed in an experiment visualising the P diffusion from granules of different P fertilisers in soils. Finally the P exchanged LDHs and soluble P were used as P fertilisers in an acid and calcareous soil in a pot trial, whereby plant yield and P uptake were compared. The P use efficiency of the P LDH in the acid soil was up to 4.5 times higher than that of the soluble P, while in the calcareous soil, the P use efficiency at low doses was factor 1.2 higher than that of soluble P but lower at high doses. It can be concluded that LDHs can be a promising new class of P fertilisers to overcome current P fertilisation problems.

P2.7

The effect of soil pH on phosphorus fertiliser efficiency as measured by soil test P, herbage growth and herbage P concentration at contrasting grassland sites.

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Phosphorus (P) is an essential element for grassland production but P availability to the grass plant is strongly related to the soils pH status. Previous research has shown that through regulation of soil pH, soil P availability was greatly increased leading to increased P assimilation and yield of grasslands. The objectives of this experiment were to investigate the relationship between soil pH, P fertiliser and soil P availability, and to quantify the interaction effects of lime and P fertiliser applications on herbage P concentration and production across a range of soil pH and soil test P levels under an intensive grassland production scenario.

A P fertiliser and lime study was established on two existing field sites with contrasting soil types (free and moderately drained soils) each with legacy gradients in initial soil test P (STP) (Morgan's extractable P) and soil pH levels (low <5.8 and optimum 6.3-6.5). In this experiment four P fertiliser treatment rates (0, 20, 40 & 60 kg ha⁻¹ P) were applied while the low and optimum soil pH areas were sub-divided (half receiving no lime (0 t/ha) and half receiving lime (5 t/ha). This gave a 4x4 factorial experimental design (i.e. P fertiliser rate X lime treatment). Phosphorus was applied as Triple Super Phosphate (16% P) in the spring of each growing season, and lime was applied as ground lime stone at the start of the experiment. Annually, 300 kg ha⁻¹ nitrogen fertiliser was applied to all the experimental treatments. A herbage harvesting regime (i.e. 4-5 week intervals) to a cutting height of 4 cm to simulate grazed grassland was employed. To date two years of experimental data have been generated and the results are presented as follows

There was a significant increase in soil P with increasing P application rates regardless of lime application (P<0.0001) at both sites. While there was no significant interaction effect between background soil pH and lime applications for soil P and crop P concentration, the addition of lime significantly increased STP and crop P (P<0.0001). Fertilizer P rate had a significant effect on herbage yield up to 20 kg ha⁻¹. These results indicate that maintenance of soil pH for efficient soil and fertiliser P efficiency is an essential element of nutrient management planning. On acid soils, liming in addition to P fertiliser application was the most effective and efficient method to optimise soil P supply for grass growth and achieving optimum crop P concentration for grazing animals.

Long-term P and K fertilisation can partially alleviate yield losses in response to environmental stress and increase N use efficiency.

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The challenges of population growth, global warming and perturbation of nutrient cycles urgently require strategies for better use of moderately fertile land and higher and stable yields in low input systems.

A long-term field experiment with mineral and organic inputs was established on a sandy loam soil, which had received only mineral nitrogen (N) in the preceding 30 years, and hence had become rather depleted of phosphorus (P) and potassium (K). The effects of fertilisation on P and K availability, crop productivity and yield stability were studied for a 13-year period (1996-2008).

Differential yield responses were observed immediately from the first year of cropping. Changes of Olsen-P and exch. K were closely associated to partial P and K balances (inputs–offtake). Depending on the year, spring barley yields under unfertilised management (U) were between 21-85% of reference $N^{1/2}P^{1/2}K^{1/2}$ (60-10-60); and 100-194% under $N1P1K1$ (120-20-120). No temporal yield trends were found, as year-to-year variability probably concealed any effects of fertility changes.

Inclusion of weather variability into a multiple regression model revealed a significant effect of temperature sums: larger yields were attained in the most nutrient deficient treatments when temperatures were higher during crop emergence; and lower during grain-filling. This agrees with common theories about the temperature dependency of crop physiological development. Lower spring temperatures therefore lead to larger relative depressions for U, but at the same time larger relative gains for the fertilised crop. The differential response demonstrates how increased P and K availability can partially alleviate the negative effects of early cold stress.

After 13 years of fertilisation treatments, the residual effects of these were evaluated in a follow-up experiment. Annual P and K inputs were withheld. Instead, levels of mineral fertiliser N were applied in each of the plots. Yields and fertiliser N use efficiency (NUE) increased according to the previous long term inputs, demonstrating the important role of P and K supply for overall resource efficiency of the cropping system. The highest yields were attained under the long term addition of animal slurry, suggesting a superior residual value of organic over mineral inputs.

Overall, the results signpost how P and K fertilisation can play vital role in maintaining high and stable yields, while minimizing environmental impacts through high N use efficiency.

P2.9

The equivalence of the CAL and DL extraction method to assess the amount of plant available phosphorus in soils

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Phosphorus fertilizer recommendation in most European countries are based on a very similar procedure which entails three steps: 1.) Extraction of plant available soil P; 2.) calibration of those soil test results; 3.) deducing the recommended amount of P fertilizer. However, the term "plant available" is not defined unambiguously and there is a large variety of extraction methods in use, worldwide and in Europe.

In Germany there are two established extraction methods to assess plant available soil phosphorus. The Calcium-Acetate-Lactate (CAL) method which is used in the majority of the German states and the Double-Lactate (DL) extraction method.

Based on data sets from fertilizer trials and the use of simple and multiple regression we aim to derive equations which might be used for practical transformation between P(DL) and P(CAL) values. Furthermore, by applying novel statistical approaches such as Classification and Regression Tree (CART) analysis we hope to identify the main soil parameters which influence the comparability between P(DL) and P (CAL) values.

Currently, it is often assumed that the two extraction methods yield largely equivalent results. However, most comparative studies have found only very poor correlations between P-CAL and P-DL. Moreover, the comparability of both methods seems to depend on several soil parameters, most notably the soil pH-value, but presumably also soil texture and humus content, which are often not considered in comparative studies.

In order to allow a better comparison of soil P status and effectiveness of P-fertilization in Germany, we aim to derive a precise procedure to transform both extraction methods into each other.

In contrast to results reported in other studies, we found for 319 data sets from fertilizer field trials in Halle, Bad Lauchstädt and Rostock a strong correlation between P-CAL and P-DL with $R^2=0.93$. However, the pH value of the samples did not have a significant impact on this relationship. In 84% of the samples, higher amounts of P were extracted with the DL compared with the CAL method, and in about half of the samples, the DL method yielded at least 30% more P. However, despite this substantial difference, the nutrient classifications in the states that use DL or CAL do not differ very much.

Mechanisms of carbon-phosphorus trading in arbuscular mycorrhizal symbioses and consequences for carbon sequestration in soils

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The present work focuses on the trading mechanisms that *Solanum lycopersicum* L. establishes on its photosynthetic carbon transfer to *Rizophagus irregularis*, an arbuscular mycorrhizal fungi, under different accessible phosphorous sources. We hypothesize that plant carbon investment to its fungal symbiont depends on the availability of the P source.

We performed a time course experiment with a mesocosm under controlled conditions. The mesocosm consisted of a central compartment which contained the mycorrhizal plant and was connected to an outer compartment, where only the mycelium was able to develop and access the different P sources, orthophosphate as soluble P, apatite as P mineral P and phytate as organic P source. During 112 days, we determined photosynthetic gas exchange, the plant nutrient content, CO₂ efflux rates from the fungal compartment as a proxy of its metabolic activity, total C content from the fungal compartment and the PLFA/NLFA composition for monitoring the different C consumers.

The amount of C invested into hyphal infrastructure to explore the soil differs with the accessibility of the sources. High amounts of freely available P initiated a fast development of large amounts of mycelium, while more stable P sources triggered more C investment for metabolic purposes. In those AM plants which had access to a P source, the photosynthetic rates were significantly increased. The amount of C invested thereby differed largely in the order apatite > phytate > phosphate.

Our results point towards AM plant performing different P uptake pathways. Different energy levels of nutrient acquisition might be important in the steering of nutrient self-sustainability on the ecosystem level. These preliminary results should help us to understand how the performance of nutrient acquisition by the AM plant controls the C flux belowground.

P2.11

Interactive effects of phosphate-solubilizing *Penicillium spp.*, arbuscular mycorrhizal fungi and biochar on growth of wheat

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In order to maintain food production under future scenarios with declining supplies of phosphate fertilizer there is a need to efficiently utilize phosphorus (P)-rich waste products in plant production. Pyrolysis of organic wastes such as sewage sludge ensures energy recovery, improved hygiene, volume reduction and a biochar product that is a potentially valuable phosphorus fertilizer. Phosphate-solubilizing microorganisms (PSM) represent a promising biotechnological resource for managing the soil P resources and there is a need to investigate their ability to solubilize phosphorus from recycling products.

In this study 15 PSM strains were screened for their in vitro capacity to solubilize inorganic phosphate from sludge biochar and two *Penicillium spp.* (*P. bilaiae* and *Penicillium sp.*) having the highest biochar-P solubilisation and citrate production were selected for further study.

Both *Penicillium spp.* were screened for their ability to utilize biochar as a P source in a pot experiment with wheat grown under controlled conditions. Both *Penicillium spp.* increased wheat biomass when grown in soils amended with biochar. The abundance of PSM in soil was determined by quantitative PCR and PSMs persisted until the time of harvest.

In conclusion our data suggest that two *Penicillium* species identified by their in vitro ability to solubilize inorganic P can increase wheat biomass when inoculated in biochar sludge-amended soils and that the PSMs may promoted the use of P-rich wastes in crop production.

Phosphate solubilising bacteria: A key to efficient phosphorus utilization

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Only about 5-30% of phosphorous (P) fertilizer input is utilized by plants. The remainder complexes with metal ions and accumulates as unusable deposits. Soils can accumulate P at 5-15 kg ha⁻¹ yr⁻¹ and many agricultural soils have sufficient deposited P to last 100 years.

Rhizosphere bacteria can make this large P reserve available by phosphate solubilisation (PS). Bacteria are known to release organic acids and phosphatases to release bound P for plant uptake. Many studies have screened phosphate solubilising bacteria (PSB) in vitro, but few have been proven in planta. This means there are currently no large scale bacterial commercial products for PS. The objective of this study was to screen nodule clover inhabitants for PS and to study the efficacy of PSB on legume growth.

A total of 2220 nodule inhabiting bacteria were collected from four sites with contrasting long term P fertilizer histories, using white (*Trifolium repens*) and subterranean (*T. subterraneum*) clovers as bait plants. Isolates were screened for in vitro PS using media containing highly insoluble hydroxyapatite (HA) as the sole P source. Only 79 (3.6%) of bacteria were found to solubilise P. More ($p < 0.05$) isolates that originated from subterranean than white clover nodules could solubilise P, which suggests active host recruitment of PSB. A higher ($p > 0.05$) proportion of PSB was also recovered from plants grown in high P soils, which implies an adaptation of bacteria to solubilise P.

Out of the 79 PSB, only 25 were *Rhizobium* spp., while *Enterobacter* spp. (23) and *Pseudomonas* spp. (15) were also found within clover nodules. Genera specific differences in PS activity were also observed, which indicates that some genera are more effective than others. Only 11 isolates (*R. leguminosarum* bv. *trifolii*), were able to fix nitrogen (N). When white clover plants were supplemented with HA as the only P source and minimum N, all 11 isolates increased plant growth in comparison with the uninoculated control. The most effective isolates produced a 73% increase in dry weight compared with our standard commercial inoculant *R. leguminosarum* bv. *trifolii* TA1. It seems likely that increase in plant growth was the result of bacteria solubilising P, which was then available as an energy source to increase the amount of nitrogen fixation.

A steady release of bound P by bacteria could be used to reduce P fertilizer requirements and indirectly address the problems associated with P runoff and eutrophication.

P2.13

Genetic regulation of phosphatase production and activity to increase P uptake from deficient soils

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The genetic regulatory network resulting in an enhanced expression of genes encoding phosphatases in response to phosphorus (P) starvation is to date not completely understood.

In order to identify genes, which are involved in the signaling and activation cascade to improve P efficiency of crop plants by improved inorganic phosphate remobilization and acquisition, state of the art molecular and phenotyping methods will be used. This includes methods like quantitative rt-PCR assays of candidate genes and root exudate (phosphatase) measurements as well as the extraction and analysis of different P compounds in potato leaves, stems and roots.

Based on a preliminary study with 36 potato genebank accessions screened for their phosphorus use (PUE) and acquisition efficiency (PAE), four genotypes with contrasting PUE and PAE were selected for further experiments. The genotypes were grown for eight weeks in sand filled pots. The experiment had two different treatments: low amount of anorganic P (Pi) and low amount of organic P (Po). Root architecture of the four genotypes was characterized, root exudates (phosphatases) and P contents were quantified, and expression of three purple acid phosphatases genes (PAP) was measured. First results showed that the genotypes varied for some traits in their responsiveness to different P fertilization strategies.

More genotypes of the potato diversity set will be tested in further experiments to analyze morphological and physiological adaptation mechanisms to cope with P starvation.

Mechanisms of P mobilization in the rhizosphere involving weeds and crop plants

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In the present agricultural management, the impact of crop-weed species interactions on P-mobilization is not under consideration, although it might offer crop promoting combinations by increasing the diversity of P mobilization strategies in the rhizosphere. Therefore, the present study aims to select highly P efficient combinations of plant species in arable crop production systems for a decreased need for P-fertilization. For this reason, interactive P mobilization in crop-weed combinations was investigated in a pot trial using a P-deficient soil. Maize was used as a mycorrhizal host crop in combination with six mycorrhizal and non-mycorrhizal weeds. Increased competition for nutrients was represented by very similar strategies for P mobilization between maize and the associated weed species under different combinations. Interactions in joint rhizosphere of mycorrhizal and non-mycorrhizal species were investigated. On one hand, soil phosphatase activity, microbial biomass P, plant available P, and root colonization of arbuscular mycorrhizal fungi were taken into consideration for soil analyses, whereas on the other hand maize yield and the total P content of maize were determined. In conclusion, the presentation will provide a description of plant species-specific mechanisms of P mobilization and a selection of promising combinations of plant species to increase P-use efficiency in crop production.

P2.15

Impact of dietary phosphorus on hormone balance and gene expression in kidney and its implications on immune status of weaned piglets

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In animals phosphorus (P) is of vital importance for many aspects of the metabolism. Blood P homeostasis is maintained by strict regulation of intestinal absorption, osseous mobilization, and renal excretion. In order to identify measures to increase the efficiency of P utilization, we investigated the physiological and transcriptional responses to modulated dietary P supply in growing pigs. After weaning (28 days post-natum; dpn), German Landrace piglets were randomly assigned to one of three groups fed diets varying in digestible P content [low (L) 0.3, medium (M) 0.5 and high (H) 0.7% P on dry matter basis (DMB)] for 5 weeks (until 64 dpn). Blood samples were collected at four time points followed by analyses of physiological parameters and hormones as well as bone characteristics. Genome-wide expression profiles were analyzed by Affymetrix microarrays in kidney.

The modulated dietary P supply was reflected by serum parameters relevant for P homeostasis. A restriction of P intake revealed lowered inorganic phosphate and parathyroid hormone (PTH) levels and increased calcium and vitamin D, respectively. The circulating vitamin D is known to have negative effects on both PTH synthesis and secretion, resulting in enhanced renal calcium excretion, but inhibited renal P excretion. Furthermore, the reduced PTH level indicates a limited bone resorption, as suggested by the unaffected bone mineral density and bone volume in the low P group.

In kidney the gene expression was affected due to decreased P intake, but not due to H diet. The statistical evaluation with Ingenuity Pathway Analysis (IPA) revealed a number of calcium dependent signaling pathways. Specifically, the increased phospholipase C- β (PLCB4) signaling triggered by G protein-coupled receptor CASR (calcium sensing receptor) may mediate dietary effects to maintain mineral homeostasis. The resulting intracellular release of calcium and subsequently, the presumable activation of protein kinase C (PRKCB) have multiple effects, e.g. the activation of NFATc2 (nuclear factor of activated T cells 2). According to IPA the transcription factor NFATc2 and other transcripts (e.g. CD3D, CD3E, LCP2 and FCGR3B) were associated with the regulation of the immune response mediated by T cells and CD3 complex, suggesting a link between dietary phosphorus and adaptive immune system.

In conclusion, L animals were able to maintain the P homeostasis via systemic and local mechanisms resulting in improved P efficiency.

Agronomic effectiveness of P resources

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Due to the scarcity of mineable phosphorus (P), an efficient use of traditional and novel P fertilizers are indispensable. Furthermore, recycling of organic residues as compost and manure in agriculture is an important practice to replenish soil P pools and to save mineral fertilizer. Long-term field experiments are an important tool to evaluate the agronomic impact of P fertilizer strategies.

In order to evaluate the effects of organic (cattle manure, biowaste compost) and mineral (TSP, biomass ash) amendments in single and combined application in comparison to a control without any P input, a long-term field trial was established in 1998 in Rostock. Since 1998 soil samples were collected in spring and autumn and analyzed regarding their P pools, further chemical and physical soil parameters. Microbiological indicators were also investigated to describe the active mobilization of mineral P sources by microorganisms as an elemental factor to counteract the loss of P plant availability. State of the art molecular methods like 16S rDNA DGGE analysis are used to investigate the soil bacterial community under the different P management treatments.

Two years after the start of the experiment relatively small alterations of the bioavailable P contents in soil were measured and between the control and the compost treatments significant differences were detected. After 14 years, however, the control showed a clear reduction of the bioavailable P of about 10 mg per kg soil, which was significantly less than all the other treatments. The highest value of bioavailable P was found in Compost+TSP treatment. Despite the differences in the soil P concentrations, the P management only partly affected the crop yields and in 2015 no fertilizer effect on the sorghum yields was detected. For maize only two out of nine fertilizer treatments showed yield increasing effects. The low yield differences imply that plants are able to adapt to low P input strategies to a certain extent by active mobilization of soil P resources.

P2.17

Phosphorus flows in Berlin-Brandenburg

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Even though global P supplies are limited much of it is wasted in today's societies, also having negative consequences for the environment. Hence, in order to ensure an adequate future supply a better knowledge of P flows is needed. For the German region of Berlin-Brandenburg a substance flow analysis for P was conducted for the year 2011. The aim of this analysis was to create a starting point to improve P management in various sectors such as forestry, agriculture, human consumption and waste, wastewater management and urban soils. Within the system boundary under study, agricultural soils showed the largest negative balance (-3,617 t P), which was connected to low P fertilizer application and low livestock densities. Forest soils followed (-424 t P) possibly as compensating inputs by weathering and atmospheric deposition cannot clearly be defined. According to the recent literature it can be concluded that atmospheric deposition to soil pools has often been overestimated in P substance flow analyses and that forest productivity may become more P limited due to imbalances in nutrition. The greatest P accumulation was found in landfills (3,492 t P) and urban soils (664 t P). The largest flows were associated to agriculture, followed by human consumption. The efficiency of agricultural soils was high (127%), as reflected by a negative soil balance due to the low livestock density and input of mineral P. Agricultural soils are the largest contributor of P emissions (1,051 t P) to water bodies. For the region under study, weather variations are the major driver for P-removal by the main crops (50% range) influencing the overall P removal by about 46% during the years 2005 to 2011. The recovery efficiency of P from wastewater was very high (91.5%). Among the recovered phosphorus however, the agricultural reuse of the large potential of P in the wastewater was still very low (11%). Also, the recycling of P in organic municipal wastes has not been considered sufficiently, as most organic wastes are not collected separately today. Based on climate change projections for the region, possible future implications for P flows of the region may be discussed.

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Unravelling plant-availability of recycling phosphorus-fertilizers by pot experiments using phosphorus XANES spectroscopy

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Pot experiments are often performed to analyze the plant-availability of phosphorus (P) in P-fertilizers. However, these experiments do not determine the P compounds present in the soil which are responsible for the yield increase. In order to better understand the results of pot experiments we analyzed the soils by P K-edge X-ray absorption near-edge structure (XANES) spectroscopy to determine the P species and unravel transformation processes. We carried out pot experiments with maize testing different waste water derived recycling P-fertilizers on an acidic and a neutral soil. Soils samples before sowing and after harvest were collected and prepared for analysis. A combination of macro- and μ -XANES spectroscopy was used to determine the chemical state of the overall soil P and to identify P compounds in P-rich spots localized by micro-X-ray fluorescence (μ -XRF). P K-edge macro-XANES spectroscopy detected organic P and/or P sorbed onto organic matter or other substrates in the unfertilized and fertilized soils. In addition, μ -XRF mapping in combination with P K-edge μ -XANES spectroscopy evidenced that some P phases present in recycling P-fertilizers (magnesium phosphate and calcium sodium phosphate) react with co-fertilized ammonium nitrate and form highly plant-available ammonium phosphates in the soil. In opposite, apatites were not affected by the presence of ammonium. Thus, for a boost of the plant-availability of P in recycling P-fertilizers these fertilizers should be directly co-fertilized with nitrogen (N) sources that contain a high amount of ammonium instead of nitrate. Possibly, a specific preparation of NP-fertilizers by granulation of recycling P-fertilizers with ammonium compounds and a nitrification inhibitor could enhance the plant-availability of the produced fertilizer whereby they become more competitive to commercially available NP-fertilizers based on phosphate rock.

P2.19

Nanoparticles of silicate minerals enhance phosphorus availability in soil

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The most important source of phosphorous, phosphate rock is becoming increasingly expensive and scarce. On the global scale, the availability of phosphate rock becomes the subject of not only agricultural and environmental, but also geopolitical processes.

However, the problem of phosphorous deficiency may be solved in alternative way. Total phosphorus content in soil is often relatively high, but only several percents of total P have nutritional value and are available to the plants. Most of P in soil is located in insoluble inorganic or organic compounds resistant to microbial mineralization. Therefore, the increase of phosphorous solubility in soil is a matter of a very high importance.

Most of the recent studies in this field are focused on soil microorganisms as mediators of P availability and often include application of different inoculants to enhance microbial ability to mobilize P from different soil fractions. In this study we investigated the possibility of indirect influence on soil microorganisms by improving soil agrophysical properties and providing readily-decomposable substrates.

Soil of the experimental plots was Gleyic Phaeozem under continuous monoculture of corn and sugar beet. The mixture of nanoparticles of analcime and rotten stone (3:7) was applied (300 kg ha^{-1}).

It was found that application of nanoparticles of silicate minerals did not affect the total P content in soil, but caused a notable increase of water-extractable P content – by 20% under corn and by 18% under sugar beet. These changes were attended by significant increase of acid phosphatase activity in topsoil by 44% under corn and by 35% under sugar beet. Green mass productivity of corn after the application of the studied soil amendment was increased by 44% and productivity of sugar beet by 28%.

Application of silica nanoparticles led to synthesis of polysilicic acids $n\text{SiO}_2 \cdot m\text{H}_2\text{O}$ in soil. Most of these acids are unstable and poorly soluble in water. In soil they form different colloidal suspensions, which significantly improve agrophysical soil properties and led to gradual increase of labile organic matter content. We consider these indirect impacts on P availability in soil to be as important as direct inoculation with phosphatase producing bacteria. There are many such microorganisms in soil and it looks to be more beneficial to create optimal conditions for them rather than enrich soil with effective, but non-native microorganisms.

Changes in grassland soil P forms with fertilizer application and withdrawal

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Long-term phosphorus (P) applications can increase soil P concentrations in excess of agronomic optima, posing a risk to water quality. However, once fertilization stops, there may be a time lag in the decline in soil P concentrations. And while P fertilization adds orthophosphate, little is known about the changes in other soil P forms during P build-up and drawdown. This study examined the changes in P pools (total P, Olsen P, Mehlich P, water extractable P) and P forms determined by ^{31}P -nuclear magnetic resonance spectroscopy (P-NMR) in grassland plots from Northern Ireland. Between 1994 and 2000 all plots received 10 kg P ha⁻¹ with variable rates of N (ranging from 100-500 kg N ha⁻¹). From 2000 to 2005, these plots received 0, 20, 40, or 80 kg P ha⁻¹; from 2005 to 2010, all plots received no P fertilizer. In 2005, soil P pool concentrations in the soils fertilized at the highest rates were significantly higher compared to concentrations in 2000, but these concentrations had dropped back to 2000 levels by 2010. In the soils receiving no P, soil P pool concentrations were not significantly different in 1994, 2000 and 2005, but were significantly lower in 2010. There were few changes in P forms determined by P-NMR. Orthophosphate followed the same trend observed for the soil P pools; total organic P, total inositol phosphates and total orthophosphate monoesters and diesters were highest in samples receiving the lowest fertilization in 2010.

P2.21

Phosphorus in deep soil layers: an inventory of Belgian soils

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In Belgium the optimal concentration of soil phosphorus (P) in the ploughing layer is based on P analysis of the ploughing layer. Recent data indicate that more than 78% of the sampled arable parcels have a P pool larger than optimal. The large P pool in the ploughing layer impacts significantly the surface water quality, both by run-off and leaching. As a consequence, P fertilization standards are nowadays directly linked to the P pool present in the ploughing layer.

In the present study an inventory was made of the P pools present below the ploughing layer. The high P stock in the ploughing layer assumes the P enrichment of deeper soil layers due to P leaching. For this purpose 200 arable parcels were selected, representing the different soil textures present in Belgium. Soil samples were taken in 3 layers, 0-30 cm, 30-60 cm and 60-90 cm. Soil P availability was measured by different methods: (1) extraction with ammonium lactate and acetate at pH 3.75 (Egnér et al. 1960); (2) extraction with ammonium oxalate (Schwertmann 1964); (3) extraction with 0.01 M CaCl₂ (Houba et al. 2000).

In the deep soil layers a significant P pool is present in all soil textures. On average, the P pool extracted with ammonium lactate decreased from 304 mg/kg in the 0-30 cm soil layer to 153 mg/kg in the 30-60 cm soil layer and finally to 76 mg/kg in the 60-90 cm soil layer. Although the amount of P extracted differed among the different methods, all extraction methods confirmed the importance of the P pool in the deep soil layers.

In view of the regulatory restrictions on P fertilization, the P pool in the deep soil layers has an important potential to increase the efficiency of phosphorus utilization for deep rooting crops like wheats.

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Use of alternative P fertilisers and cover crops for enhancing P availability to wheat and maize

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In this study, the effect of alternative phosphorous (P) fertiliser (APF) application combined with cover crops (CC) used for green manuring on P uptake and growth of two following main crops, i.e. winter wheat and maize, was tested. A pot experiment in a randomised complete block design with two low-P soils, one calcareous and one carbonate-free, two APF (sewage sludge ash and digestate), three cover crops (buckwheat, phacelia and red clover), and control treatments (no APF, rock phosphate; no CC) was conducted. Soil properties like pH and plant available nutrients (mineral N, CAL-extractable K and P) were tested before growing season started. Plant biomass, P, C and N concentrations of CC were assessed. For the main crops wheat and maize, above-ground plant biomass, grain weight (wheat only), P, C and N concentrations were measured.

Soils had a strong effect on performance of the main crops winter wheat and maize which was generally better in the carbonate-free soil than in the calcareous soil. Wheat grain weight was increased following red clover and phacelia CC, mainly in the calcareous soil and also in combination of these CC with sewage sludge ash and rock phosphate application. P concentrations in wheat grain varied only little between soils and treatments. Variability in maize shoot biomass was high. It was generally reduced following buckwheat and, in the calcareous soils only, slightly increased following red clover. APFs had no clear effect on maize shoot biomass. Also for maize shoots, P concentrations varied only little between soils and treatments.

P2.23

Plant availability of phosphorus in biomass gasification biochars

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Thermal gasification of biomass can be a flexible and efficient renewable energy production system. It also produces a residue material, mixed ash and char (i.e. gasification biochar (GB)). The nutrients embedded in GB, particularly phosphorus (P), have to be recycled, e.g. in agriculture as a substitute for mineral fertiliser P (MP), to enhance sustainability. In this study, we investigated the P availability in GBs from different biomass feedstocks applied to three soils (i.e. acid clayey [pH 5.8, 17% clay], acid sandy [pH 5.8, 3% clay] and alkaline sandy [pH 7.8, 3% clay]) in an incubation experiment, as well as to a loamy sand soil of low P status (pH 5.4, 8.6% clay, 24 mg Olsen-P kg⁻¹ soil) in a field mini-plot experiment with spring barley as the test plant. The biomass was gasified at 700–750 °C. The GB was mixed with the soils at 139 mg P kg⁻¹ for a 16-week incubation, and at 30 and 60 kg P ha⁻¹ in the mini-plots (0–15 cm topsoil). Mineral P fertiliser and a control without any amendment were included for comparison.

Gasification biochars from straw (Str) and shea nut (Nut) increased pH markedly in all three soils during incubation, while GBs from poultry manure (Poul) and two sewage sludges mixed with straw (SSa and SSb) only increased pH in the two acid soils. A recovery of 21–29% as resin-extractable P (available P) from applied Str, Nut and Poul was seen in the two acid soils, while the recovery from Str in the alkaline soil almost matched that from the MP (49 vs. 52%) after 16 weeks. There was an increasing trend of resin-P in the Str treatment, especially in the alkaline sandy soil. Contrarily, the Poul showed an initial rapid decline in the resin-P recovery in all soils, which was similar to the MP. The recovery from SSa and SSb was similar and constantly low (<11%) across the three soils. The temporal trend of resin-P recovery from amendments was confirmed by the Olsen P and water-extractable P data. The resin-P content clearly increased with pH in soils amended with GBs with low P concentrations (Str, Nut, SSa and SSb). In the mini-plot experiment, the soil pH, available P, barley yield and P uptake in all GB and MP treatments did not differ significantly from the control treatment. In conclusion, the P availability of gasification biochars varied among biomass feedstocks and soil types and biochars may be used to supplement MP. In the high pH soil resin-extractable P surprisingly increased to a high level after application of some biochars.

Some relevant aspects of maize phosphorus deficiency on acid soils in the North-West of Romania

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Acidic soils in the N-W of Romania are in general poorly supplied with phosphorus (P).

The setup of long-term fertilization and amendment experiments in the fall of 1961 respectively 1968 at the Agricultural Research and Development Station Livada paved the way for identifying the incriminated causes of phosphorus deficiency in maize plants.

The presented results were obtained on the basis of determinations made in long-term experimental fields in the phase of 2-3 leaves of young corn plants.

Phosphorus deficiency is one of the nutritional imbalances quite common on acid soils and it is intensified by cold and rainy weather conditions. The purple coloring of young corn plants is caused by the accumulation of anthocyanins. This accumulation is a plant defense reaction against adverse conditions and it is also considerably influenced by the genetic variety of the cultivated maize hybrid.

Studying the influence of systematic fertilization with increased doses of N (nitrogen) and P, obvious P deficiency symptoms were revealed for the plots unfertilized with P or for the plots that were fertilized with a low P dose (up to 40 kg P₂O₅/ha). In these circumstances, the increased dose of N clearly intensified the P deficiency symptoms.

Analyzing the evolution of the same phenomena experienced with increasing doses of farmyard manure applied once every five years on four different funds of N and P, it is found that the effect of increased doses in the first year of manure application reduces the intensity of the P deficiency event. In the absence of fertilization with P, P deficiency symptoms are visible only up to 40 tones/ha.

Fluorescence measurements conducted in the second part of the growing season of maize under exacerbated drought and heat conditions in the previous summer proved that in fertilized plots where the treatment was done by following the principles of agrochemical optimization corn plants tolerated significantly better the stress induced in their photochemical system.

P2.25

Legacy phosphorus in a tropical soil influenced by phosphate sources and cover crops

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Plants can develop different mechanisms to absorb and solubilize phosphorus (P) from the soil, especially in soils under low P availability. This study aimed to evaluate the legacy P pools in a clayey tropical soil under winter cover crops associated to the residual effects of soluble and rock phosphates applied in the summer crop. The experiment has been carried out for six consecutive agricultural years (2009-2015) in a clayey Hapludox soil in Paraná State, Brazil (25°44'05" S; 53°03'31" W). It was set in a randomized split-plot block design with three replicates, using the phosphate sources (105 kg soluble P₂O₅/ha/year): Rock Phosphate (RP), Single Superphosphate (SSP) and without P (no P); and cover crop species: common vetch (*Vicia sativa*), white lupin (*Lupinus albus*), fodder radish (*Raphanus sativus*), ryegrass (*Lolium multiflorum*), black oat (*Avena strigosa*), white clover (*Trifolium repens*) and fallow. Soil samples were taken after the sixth year of cover crop cultivation for P pool analysis by fractionation. According to the results of P fractionation, cover crops were not effectively able to change the levels of labile P in the soil over six years of evaluation. Phosphate fertilizers have promoted increase of both labile and moderately labile P pools in soil in the near surface layer (0-5 cm), especially under rock phosphate, with small increase in the 5-10 cm layer and no effect in deeper layer, emphasizing that Brazilian clayey soils are a sink of P from fertilizer and its mobility is almost null. This accumulation of P in near surface layers has the potential to be a great legacy P for the next crop cycles.

Phosphorus availability in sugarcane as affected by phosphate fertilizer sources in a tropical acid soil

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Phosphorus (P) recovery in crops, in general, is only 10-15% in the year it is applied and P fertilizers cost a lot for farmers. This recovery can be increased by proper management of P fertilization, selecting both type of fertilizer and application method. With this goal, a field experiment was conducted in Macatuba, Sao Paulo, Brazil, at latitude 22°29'39"S, longitude 48°41'14"W and altitude of 515 m in a clayey soil, to evaluate the effect of two sources (Bayovar rock phosphate and triple superphosphate) and three placement ways (broadcast, furrow and half broadcast/half furrow) of phosphate fertilizers (180 mg P₂O₅ ha⁻¹ based on NAC+water extractor) on P availability in the soil in a sugarcane field. The experiment was conducted with three blocks in a split plot design considering the source as main plot and placement as subplot. A control without P fertilizer was also considered. Soil samples were collected to a depth of 10 cm immediately after harvest (1 year after P application). Different fertilizers affected soil P content significantly, with Bayovar presenting the highest available P in the soil. Placement of P fertilizer also had a significant effect on soil P availability, in the order of broadcast>Half/Half>furrow. The interaction of P source × placement was significant ($P \leq 0.01$) which shows that the impact of different sources of P on available soil P depended on their application method. Both fertilizers resulted in the highest available soil P when they were broadcasted. When TSP applied in the planting furrows, it was not able to increase P in soil significantly ($P \leq 0.05$) as compared to control. Bayovar, when applied broadcast, is the most effective source and can increase the availability of soil P up to 4.5 times higher than the control and 2.5 times higher than TSP when applied with the same method.

P2.27

Long-term effect of varying P fertilizer and lime applications on yield and P uptake of winter wheat, winter barley and sugar beet

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Most of the agricultural soils in Germany are sufficiently or even highly supplied with P, in particular in regions with intensive livestock husbandry, the latter posing a high risk for P losses to water bodies. However, in soils where P application was decreased or even omitted in the last decades, the P availability may have become too low for a sufficient crop production. For such situations it still remains to be answered which soil P concentrations are adequate. Due to the different strategies to mobilize sparingly soluble soil P, plant species differ in their susceptibility to low soil P values. In addition, soil P binding and release behavior is dependent on soil pH and may therefore be affected by liming.

The effects of different P application and liming doses on the yield and P uptake of winter wheat, winter barley and sugar or forage beet were therefore analyzed using data from a long-term factorial P and liming experiment started in 1978 and located in the Bavarian tertiary hills (790 mm annual precipitation, 8.4°C average temperature). The silty loam contains 1.1% Corg and 0.12% Nt. Soil pH differs according to the liming treatments between about 5.0 (no liming), 6.2 (lime level 1) and 6.6 (lime level 2). Besides the control treatment receiving no P water soluble P fertilizer was annually applied with 22 or 44 kg P ha⁻¹. The application of N, K, Mg and S was kept at adequate levels.

The analysis of the results from the long-term trials indicates that compared to the limed and P fertilized treatments the reduction of yield and P uptake by omitted P application was more pronounced with beet than with barley. Winter wheat yield and P uptake over time were neither affected by a low soil pH nor by the reduced soil P level.

In the most recent crop rotation cycle from 2012 to 2014 the yields and P uptake of all three crops were significantly reduced by both the omitted liming and omitted P application, but no yield difference between the two levels of either liming or P fertilization was observed. The relationship between soil P content as obtained by CAL extraction and crop yield showed that very low soil P levels decreased yields especially at low, suboptimal soil pH values. But it is also evident that in the investigated soil P levels lower than currently recommended will be sufficient to achieve adequate yields if soil pH is kept at a site-specific optimal level. Crop specific requirements should be included into future P fertilizer recommendations.

Phosphorus fertilization to only wheat in a rice-wheat rotation in China: Soil P pools and microorganisms

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Crop production in the Taihu Lake Region (TLR) of China has been greatly improved by increasing phosphorus (P) fertilizer input, but overuse of P has led to a dramatic spike in P accumulation, low P use efficiency, and increased environmental risk. We investigated the effects of four P fertilization regimes, including P fertilization only during the wheat-growing season (PW), P fertilization only during the rice-growing season (PR), P fertilization during both the rice- and wheat-growing seasons (PR+W), and no P fertilization during either season (Pzero; control) in pot and field experiments with four years of rice-wheat cropping. The results showed that skipping P fertilizer application during the rice season in the rice-based cropping paddy field in TLR is entirely feasible and efficient for reducing environmental impacts relating to soil P over accumulation without compromising rice yield. We found that P fertilization only during the wheat-growing season produced grain yields as well as the current farmer practice of P fertilization regime, P fertilization during both the rice- and wheat-growing seasons, while it maintained soil Olsen-P accumulation and phosphate utilization efficiency. Moreover, under P fertilization only during the wheat-growing season, the soil supplied adequate levels of labile P and moderately labile P and no significant change on microbial composition for crop growth.

P2.29

Phosphorus fertilisation and – leaching: new insights from long-term lysimeter studies

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It is generally accepted that the yield effects of P fertilizers decrease with increasing contents of plant available P in soil and this can be described by the classical yield-response-curves. At the same time, the risk of P leaching increases, following two combined linear functions that are connected by a “change point” or an exponential curve. Detailed knowledge of these causal relationships could help to recommend P fertilizer applications or levels of plant available P in soil that meet the plant requirements and avoid the risk of P leaching. However, such data are scarce and causal relationships have not yet been described by mathematical functions for major soil types in Germany. We present data evaluations from long-term fertilizer experiments in which the effects of land use (grassland vs. arable), soil texture (sandy vs. loamy), crop rotation and P-fertilizer application on the soil P-status (total P - P_t and plant available P (measured with the double lactate method – P-DL) and the P-leaching were studied. The trials have been carried out on 56 simple non-weighable lysimeters (NWLYS) between 1997 and 2015. The NWLYS used consisted of a sheet steel vessel with a quadratic surface area of 1 m² and a total depth of 1.25 m. After the installation of the vessel a 25-cm thick filter layer (sand over gravel over stone gravel) was placed at the bottom of the lysimeter. A drainage pipe was installed inside the filter layer to collect seepage and to discharge it into a storage tank in the lysimeter cellar. The lysimeter vessels were filled manually with disturbed soil material (two layers 0-30 cm and 31–100 cm) from different agricultural used sites in Eastern Germany. Overall, the relationships between soil P-test levels and the P-concentrations in leachates indicate, that the recommended P-fertilizations and the target levels in soil according to advisory boards in Germany as well as the guidelines of the European Water Framework Directive must be reduced in order to prevent freshwater systems to undesired P-pollution and eutrophication.

InnoSoilPhos – a new long-term research program in Germany

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InnoSoilPhos (“Innovative solutions to sustainable Soil Phosphorus management”) is a new multidisciplinary research program in the frame of the BonaRes-call of the German Ministry for Research and Technology (BMBF). Objectives of the 9-year-research program are to develop solutions for optimizing soil phosphorus (P) fertility as a basis for a future bio-economy that lowers our dependency on finite phosphate rock reserves, and vulnerability to increasing mineral P fertilizer prices. Eleven workgroups throughout Germany are funded in the first 3-year-period. The research addresses four main areas (1 to 4) which correspond to the scales at which the P issue requires research-based solutions: (1) the atomic and molecular, (2) the plot- to field-, (3) the field- to catchment-, and finally, (4) the societal scale. These four main areas are further subdivided into 10 closely interlinked work packages (WPs). WPs1.1 and 1.2 investigate the fundamentals of P binding at extremely contrasting mineral surfaces by combining sorption experiments with quantum-chemical modelling. In WP1.3 the microbe-mediated processes of P solubilisation, mobilisation, uptake, storage and transport will be disclosed at the genetic, transcriptomic and metabolomic level. The spatial distribution of differently accessible P species in top- and subsoil compartments is studied in WP1.4. At a larger scale in WP2, long-term P fertilizer trials, established by consortium members and soil samples from all relevant long-term trials in Germany and adjacent EU countries, are used for more detailed process-studies of the soil-plant P cycling than ever before (WP2.1). Furthermore, new pot and plot experiments are established to reach a comparative assessment of all novel P recycling materials (WP2.2). These data, along with literature and still unpublished data on P fertilizer effects will be statistically evaluated in meta-analyses to strengthen the scientific basis for P fertilizer recommendations (WP2.3). Optimizing soil P fertility at the catchment scale requires the monitoring of P losses, detecting their “hot spots” and “hot moments” in order to minimize these losses (WP3). Finally, the WP4 will put forward the economic and societal dimension of the P issue. The presentation briefly describes the project, gives examples for scientific achievements in the first 18 month and highlights links to other P-research programs in the EU and beyond.

P2.31

Intraspecific diversity of the rhizodeposition of *Lupinus angustifolius* L. regarding the phosphorus mobilization in the soil

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The cropping of lupines (*Lupinus spp.*) for protein production is rising worldwide. The growth of lupines is often limited by P deficiency, caused by low P bioavailability in soils. The rhizodeposition is a leading control of the P mobilization in the soil, i.e. especially by the release of phosphatases and organic acids. In the present study 20 genotypes of *L. angustifolius* (19 accessions from different geographic origins and the cultivar Boruta) were tested on their molecular-chemical composition of the rhizodeposition in P-deficiency by pyrolysis-field ionisation mass spectrometry (Py-FIMS) and on the phosphatase and β -glucosidase activities in the rhizosphere soil.

The intraspecific diversity of the composition of the rhizodeposits was especially large for the relative abundance of carbohydrates and in this way in a specific impact on the microbial activity in the rhizosphere by selective promotion under some genotypes by easily available C sources for the microbial rhizosphere community. This was confirmed by a large variation in the thermal stability of the rhizodeposits of different genotypes, a varying pH level in identical cultivation conditions and in varying activities of alkaline and acid phosphomonoesterases and β -glucosidase in the rhizosphere. Furthermore, the data revealed a strong variation in the release of alkaloids into the rhizosphere during the growth with a further impact on the microbial activity. In conclusion, the use of the quality of the rhizodeposition as an indicator of the potential for P mobilization in P-deficient soils highlighted a broad intraspecific diversity within *L. angustifolius*. This is a promising basis for a selection of highly P efficient genotypes within this species for further breeding strategies of productive cultivars.

Fungal soil bioinoculants and their skills to improve phosphorus slow solubilisation and release

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Phosphorus is one of the most important nutrients for plant development and deficiencies in soil limit agricultural crop yields worldwide since its soluble forms rapidly become insoluble or unavailable to organisms. This forces growers to repeated applications of fertilizers to crops, resulting in eutrophication and other ecological challenges. The global P reserves are projected to be depleted in 50 years, raising concern over food production for the human population which is thought to increase in next decades. The use of microorganisms, fungi and bacteria, as biological fertilizers is a growing practice and the subject of intense research. Fungi are ubiquitous in soil and can be dominant components of the microbiota in many soil types. Among the potentialities of fungi to be employed in innovative forms of soil amendment, the ability of some fungal species in the leaching of minerals and elements' chelation and translocation has been yet very little evaluated and even less exploited. The aim of this study was to identify the best P biofertilizers among the tested fungal species for their application in agricultural soil, in order to increase the P availability for plant development from insoluble tricalcium phosphate (TCP). We tested selected fungal isolates (29 species: 4 Zygomycota and 25 Ascomycota) with different life strategies on Pikovskaya's medium containing 5% TCP. Fungal growth was evaluated by diametric extension of colonies and biomass yield in order to also consider the density of fungal mycelium. The surface pH of the agar was measured at specific intervals across the diameter of the Petri dish with a pH meter. The halo zones around the colonies were assessed and the solubilising efficiency was calculated according to different indexes. The solubilised phosphorus in broth cultures and the P content of fungal biomass were estimated by colorimetric methods. Different patterns of solubilisation by fungi were described and related to fungal growth. The results of the study provided evidence on some saprotrophic fungi ability to mobilize P from insoluble compounds, and thus release it with different speeds. P forms slowly released by fungi in soil can become available to plants at a sustainable rate. This study integrates the number of P solubilising fungal species and shed the light on mechanisms and parameters that are important to be considered in the choice of efficient soil P-biofertilizers.

P2.33

Activity of enzymes in the rhizosphere and in the leaves of agricultural crops as affected by water supply in combination with phosphorus deficiency

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The activity of enzymes in soil and plants is strongly affected by growing factors. The effects of phosphorus (P) and water deficiency on the growth processes and enzyme activities in the rhizosphere and leaves of sudan grass (*Sorghum bicolor* x *Sorghum sudanese*), amaranth (*Amaranthus cruentus*), soybean (*Glycine max*) and rye (*Secale cereale*) were investigated in an outdoor pot experiment, using a loamy sand with a suboptimal P supply. Two water regimes were applied with 70% (control) and 30% (drought) of soil water holding capacity. After eight weeks of growing time soil samples from the rhizosphere and crop leaves were collected and analysed for enzyme activities, proline content, shoot biomass and P uptake. The results showed that water deficiency reduced plant height, shoot biomass and nutrient uptake. The activity of enzymes however was affected differently by water supply and also varied widely in dependence of the tested crops. Water stress usually induced a decrease of rhizosphere protease (PR) activity, whereas the arylsulfatase (AS) activity was not affected by water supply. Water shortage reduced microbial activity in soil measured as the activity of the dehydrogenase (DHA) as well as the activities of the acid phosphatase (AcP) and alkaline phosphatase (AIP) in combination with soybean and rye, but not in combination with amaranth and sorghum. The activities of AcP, AIP, and phosphodiesterase in leaves were found to be higher for all crops under water stress. Proline as a stress hormone was also accumulated under these conditions. For enzymes, which are not directly involved in the P turnover like the nitrate reductase, glutamine synthetase, and glycolate oxidase decreased activities in leaves were observed of the stressed plants. It became clear that enzymes are relatively sensitive regarding environmental stress but their activities are also strongly dependent on crop species.

The effect of *Penicillium bilaii* inoculation on plant and root growth, root architecture and P uptake of oil seed rape in a low P soil

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Rock phosphate is a limited and non-renewable resource; thus a more sustainable and efficient use of P in agriculture is crucial for global food security. The inoculation of P-solubilizing microorganisms, such as *Penicillium bilaii*, in soil or on seeds and roots has shown a potential to increase growth and P nutrition of crop plants. However, the colonization and persistence of *P. bilaii* and its effect on plant and root growth is still not well understood.

The aim of this study was therefore to investigate the effect of *P. bilaii* inoculation on plant and root growth and P uptake of oil seed rape (*Brassica napus*). The main hypothesis was that inoculation with *P. bilaii* increases the root length and of oil seed rape and that this will lead to higher plant growth and P uptake.

A 5-weeks pot experiment has been conducted in low P soil under three levels of P fertilization (0, 20, 40 mg total P kg⁻¹ soil). The pots were specially constructed rhizoboxes (40 x 20 x 2.2 cm) with one transparent side, where the root growth was followed and recorded during the experiment. After harvest, roots were washed and scanned for root length determination, and the shoot and root dry matter and P content in shoots and roots determined.

The analyses are currently on-going and preliminary biomass data show significant effect of P fertilization level, and interactions with the *P. bilaii* inoculation. The poster will include the complete dataset.

P2.35

Rhizobacterial impact on plant P acquisition

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Even if phosphate (P) concentration in soils is high, P often is hardly available for plants. Rhizosphere bacteria may acquire even low Pi concentrations (down to 110 nM) using their high P affinity uptake system. Our results from in silico, in vitro and in vivo studies decipher versatile rhizobacterial strategies to mineralize and solubilize phosphate from diverse organic and mineral compounds. Both, single selected P-solubilizing bacterial strains and the whole microbial community may alter the P-availability in soils.

Selected P-solubilizing bacterial strains

Besides well-known direct P-mobilization mechanisms of organic acid production, Fe-chelating and indirect root growth-promoting mechanisms via phytohormone production, we group in vitro and in silico P-solubilizing bacteria according their strategies to solubilize different hardly available P- compounds. Genome comparison unraveled alternative strategies, which are analyzed in in vitro gene expression studies.

Soil microbial community

Although P_{mic} (P in the microbial biomass) is the smallest fraction, consisting only of 1% (1.7-5.5 mg kg⁻¹ soil) of total extractable P (HNO₃, 300-600 mg kg⁻¹ soil in our experiment), it has a tremendous function in P cycling processes in soils for keeping fertilized mineral P within the biological cycle and acting as a suitable indicator for predicting plant P-availability. That indicator improves tailored P-fertilization strategies.

Looking at selected bacterial strains as well as on microbial community level will help to gain deeper insights into bacterial mediated plant P acquisition.

Measuring P in soil microbial biomass: the use of soil- and treatment-specific extraction efficiency kP determined by ^{33}P labeling

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Phosphorus in microbial biomass (P_{mic}) is an important source of potentially available P for plant nutrition. Therefore, measuring P_{mic} represents an important issue for understanding P cycle in soils and terrestrial ecosystems.

Our research was aimed to determine i) P immobilization as dependent on soil type and the amount of easily available substrate glucose and ii) soil type-specific extraction efficiency factors kP. Individual kP were estimated by ^{33}P labeling and measuring ^{33}P recovery in microbial biomass in four soil types. The soils were collected from a climatic gradient with increasing mean annual temperature and progressive decrease in annual precipitation: Podzol (Corg 3.3%, $p\text{H}_{\text{H}_2\text{O}}$ 3.5), Phaeozem (Corg 1.4%, $p\text{H}_{\text{H}_2\text{O}}$ 5.6), Chernozem (Corg 3.4%, $p\text{H}_{\text{H}_2\text{O}}$ 6.9), and Kastanozem (Corg 1.9%, $p\text{H}_{\text{H}_2\text{O}}$ 8.3). kP were determined separately for control (unfertilized) soil and soil enriched with glucose and inorganic P source. ^{33}P input to microbial DNA was also determined.

Soils were treated with i) ^{33}P -orthophosphate spike (0.1 mg P kg^{-1} as K_2HPO_4 , 0.4 kBq g^{-1}) or ii) with the ^{33}P -orthophosphate spike, glucose ($4000 \text{ mg C kg}^{-1}$) and inorganic P source (soil mg P kg^{-1}) and incubated during 3 days. P_{mic} was determined by direct fumigation and anion exchange membrane (AEM) techniques. P concentration in extracts was determined by the malachite green (MG) colorimetric procedure, and ^{33}P enrichment by radioactivity. ^{33}P recovery after ^{33}P sorption and ^{31}P - ^{33}P isotopic exchange were also determined. DNA were extracted with the kit MP BIO.

Potentially available P immobilized in microbial biomass was shown to be an important source for plant P nutrition: it prevailed over P percentage in easily available water-extractable forms in all soil types. Extraction efficiency kP were soil type-dependent with significant deviations from mean 0.40 widely used for P_{mic} measurements. kP values in glucose amended (0.35-0.81) were higher than in glucose untreated soils (0.19-0.38). Total P_{mic} , labeled $^{33}\text{P}_{mic}$ and labeled ^{33}P -DNA pools in glucose amended soils were also higher than those in glucose untreated soils. ^{33}P in microbial biomass was mainly recovered in DNA (up to 80% of $^{33}\text{P}_{mic}$).

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P2.37

Sustainable agriculture and phosphorus management practices in the Everglades agricultural area

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Soil sustainability, water conservation and nutrient management are the cornerstone of sustainable agriculture. In the 450,000 acres of the Everglades Agricultural Area (EAA) of South Florida, farming practices have long been mindful of phosphorus (P) management as it relates to sufficiency and efficiency of P utilization. Over two decades of P best management practices have resulted in 3001 metric-ton of P load reduction from the EAA to downstream ecosystems. Some of the ongoing research will be highlighted in this presentation.

During the summer, more than 50,000 acres of fallow sugarcane land is available for rice production. The net value of growing flooded rice in the EAA as a rotational crop with sugarcane far exceeds its monetary return. Soil conservation, improvement in tilth and P load reduction are only some of the benefits. With no P fertilizer applied, a two-year field trial on flooded rice showed improved outflow P concentrations by up to 40% as a result of particulate setting and plant P uptake. Harvested whole grain rice can effectively remove 15 kg ha⁻¹ of P from a rice field per growing season.

In parts of the EAA where soils are sandy, the application of using locally derived organic amendments as potential P fertilizer has gained interest over the past few years. The use of local agricultural and urban organic residues as amendments in sandy soils of South Florida provide options to enhance soil properties and improve sugarcane yields, while reducing waste and harmful effects of agricultural production on the environment. A lysimeter study was conducted to determine the effect of mill ash and three biochar types (rice hulls, yard waste, horse bedding) on sugarcane yields, soil properties, and drainage water quality in sandy soils. Mill ash and rice hull biochar increased soil TP, Mehlich 3-P (M3-P), and cation exchange capacity (CEC) compared to the control. TP and M3-P content remained constant after 9 months, CEC showed a significant increase over time with rich hull biochar addition.

Future projects include the utilization of aquatic vegetation, such as chara and filamentous algae as bio-filters in farm ditches to reduce P load. This will be achieved by circulating high P concentration farm canal water through the ditches prior to being discharged off site. Optimizing the flow through the ditches will allow the aquatic vegetation to uptake P. The vegetation will ultimately be harvested and incorporated back on to the fields.

Industry perspectives on agricultural phosphorus use efficiency

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Over the past century, the use of phosphorus fertilizer has contributed substantially to productivity increases on agricultural cropland. This contribution has not been uniform globally or within regions, but has ranged from rapid accumulations of surpluses in some soils to depletions limiting crop yield in others. The industry's 4R Nutrient Stewardship concept, while focusing on application of the right phosphorus source at the right rate at the right time and in the right place, includes a full systems approach to sustainability improvement, assessing management choices through key performance indicators related to impacts that include farmland productivity, nutrient use efficiency, soil health, water quality, and food and nutrition security. Nutrient use efficiency is directly and indirectly implicated in some of the indicators related to the United Nations Sustainability Development Goals, and in agricultural metrics being proposed in the private sector for the food supply chain. To fully represent the contribution of phosphorus to sustainable crop production, any metric of phosphorus use efficiency requires complementary indicators. Water quality, for example, requires a separate indicator, because the losses that impact water quality are small relative to the amounts used, rendering phosphorus use efficiency at best a very crude approximation of loss potential. On the other hand, management choices for timing and placement that have little influence on phosphorus use efficiency can have large impacts on losses that impact water quality. Interpretation of phosphorus use efficiency demands clarity in presentation, as crop recovery of applied phosphorus in the short term differs strongly from that in the long term. The International Plant Nutrition Institute has worked closely with stakeholders to develop a range of nutrient performance indicators that reflect the diversity of impacts that come from nutrient best management practice. This presentation aims to explain and provide support for the use of specific forms of phosphorus use efficiency in the context of other indicators relevant to sustainable crop nutrition, with examples from various regions around the world.

P2.39

Phosphorus fertilization: Phosphate reuse as part of circular economy

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Phosphorus (P) is an essential nutrient for living beings. Currently the sustainability of phosphorus fertilization goes towards the reduction of P mineral fertilizers and to the increased reuse of P incorporated in other sources such as organic wastes and composts. However, it's nowadays possible to separate by technological procedures P from these products in particular sewage sludge. The product obtained is called struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) and could be used directly as a P fertilizer or as a raw material. This work aims to assess P availability to crops in the following P sources: compost from sewage sludge (CSS), poultry manure compost (CPM) and struvite (SV) by comparing with single superphosphate (SSP). The work evaluate (i) P forms quantified by a sequential fractionation scheme in all P sources, (ii) the recovery of added P by a test used with agronomic purpose viz. Olsen P (iii) fertilizer P use by crop using a micropot experiment. The sequential fractionation scheme of Traore et al. (1999) was used: in a compost: solution ratio of 1:200 the first extraction was with H_2O , the second with 0.5 M NaHCO_3 (pH 8.5), the third with 0.1 M NaOH and finally with 1 M HCl . In CSS and CPM organic P was also quantified in the first three fractions. Each P fertilizer has been added to a dystic cambisol with a pH=4.5 and poor in available P, at a rate corresponding to 26 kg P ha^{-1} . The treatments were incubated during 4 months at 25°C and 70% of field capacity. With these incubated fertilized soils a micropot experiment was performed in a growth chamber during 6 weeks, using *Secale cereale* L. as plant test and fertilizer P use by crop was evaluated. The results showed that SV had 29% of P_i in the first two fractions in relation to all P_i forms, CSS and CPM had 58 and 50% respectively and SSP 85%. Concerning HCl-P_i fraction SV had 27% of all P_i forms, CSS and CPM had 35 and 44% respectively and SSP 15%. In composts ~90% of total P are in P_i forms. P recovery by Olsen test shows significant differences, ranged between 0.50 (CSS) and 0.87 (SSP). P recovery was in the order $\text{CSS} \sim \text{CPM} < \text{SSP}$ and $\text{SV} \sim \text{SSP}$. In the micropot experiment shoot dry weight, P uptake, the apparent P recovery and the partial factor of productivity of rye were similar between all treatments. The results suggest that all fertilizers have the same ability to provide P to crops in the short time and in acid soils

Future sustainable phosphorus management: Optimum P-supplies of agricultural soils to meet efficiency, consistency and sufficiency

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As consequences of till now non-sustainable official P recommendations for arable and grassland soils in Germany i.e. by VDLUFA (1997-2015) influenced by lobby mainly to promote mass consumption and corresponding production of animal food (i.e. 68% more meat than tolerable) actually about 73% of the agricultural soils of Germany are hypertrophied with P (and 78% with K). This has led to a not tolerable surplus of about 755 kg P/ha in the agricultural soils during 1950 to 2007 and doubled their total P (and K) contents. Thus the actual P-Input (2010) by mineral fertilizers of 6 kg P/ha.yr or by animal manure of 12 kg P/ha.yr can be compensated by using this soil P surplus for the next 125 and 63 years respectively. P efficiency in agriculture is actually about 55% P efficiency of the total system human nutrition is only about 3% but 92% is stored in agricultural soils and "only" 5% are P input into the hydrosphere. Nevertheless corresponding average 5fold too high input of 772 g P/ha .yr from agriculture into surface water of Germany has not changed during 1983 to 2005. On the other hand for some future decades there is no need for any P input into these P (and K) hypertrophied soils: Agriculture can and must use these soils as future "P (and K) bank". Correspondingly the future P recommendations for arable and grassland soils supplies of 3-5 mg CAL-P (100g soil will guarantee on a long term about 98% of maximum yields changing actual P surplus from 9.5 to -7.5 kg P/ha .yr and (apparent) P-efficiency from 55 to 288% respectively. There are no needs for mineral fertilizer P and imported or mineral P feed because P input by recycled P from animal manure as well as sustainable waste and waste water management are sufficient for future sustainable P balance of agriculture with 60% less animal production and consumption as well as corresponding plant production. Additionally the 80% needed reduction to 143 g P/ha .yr of average P input into the hydrosphere resp. into the surface water by agriculture will be met (Pconsistency) and - if other affluence countries will follow these future P recommendations - also to maintain the world's mineral P reserves considerably longer than actually 300 years (P consistency and P sufficiency). Finally aimed is reactive C-, N-, P-, (K-) emission neutrality of agriculture, human nutrition and bio energy management implemented by sustainable de-intensification within these affluence countries.

P2.41

Agronomic efficiency of P recycling products from waste water treatment and rendering by-products

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In Germany, P demand of agriculture is mainly satisfied by farmyard manures or slurries and mineral fertilization. However, there is a great potential to utilize phosphorus from alternative sources by recycling sewage sludge (SS), meat and bone meal (MBM) and their ashes (SSA, MBMA), and by precipitating P from waste water or sewage sludge (struvite). Currently unused P from these sources amounts to the average sum of P supplied to the fields in the form of mineral fertilizer each year. The German Fertilizer Ordinance has already provided type descriptions for a variety of P fertilizers made from recycling materials. The efficiency of a P fertilizer can be estimated by various chemical extraction methods also defined in the Fertilizer Ordinance, both on national and on EU level. In order to verify such estimates, vegetation trials are needed. Three vegetation trials (two modified Neubauer exhaustion trials in quartz sand and a full vegetation period trial in soil) were carried out to investigate the agronomic efficiency of P recycling products including fertilizers made from struvite, (thermochemically treated) SSA, MBM, and MBMA. While these products are generally not water soluble, their plant availability may be estimated by their solubility in neutral ammonium citrate (NAC). Precipitation products (struvites) display a high solubility (90-100%) in NAC, while MBM and most ash-based products (both MBMA and SSA) are only partly soluble in this extractant (less than 50% down to 15% for MBMA). If SSA is treated with NaSO₄, however, Na-silicophosphates form, increasing the solubility in NAC up to about 63%. Accordingly, struvites (and partly also SSA treated with NaSO₄) are able to achieve dry matter yields and P uptakes in the same order of magnitude as conventional mineral fertilizers such as SSP, TSP or DAP, while MBM, MBMA and other SSA based products remain below this level in most cases.

Benchmarking P and N use efficiency in Irish farm systems to motivate practice change

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Agriculture faces the challenge of achieving sustainable, profitable production while maintaining environmental quality. In Ireland, for example, ambitious national growth targets for agricultural output have been set but, at the same time, Ireland, like other countries, must meet international environmental obligations in terms of water quality and greenhouse gas (GHG) emissions. Conventional agricultural production is highly dependent on nutrient inputs of P and N in fertilizer and feed and poor use efficiency of these resources is associated with losses to the environment and impacts on water quality, GHG emissions, air quality, acidification and biodiversity. Stakeholders are increasingly interested in the environmental performance and efficiency of different farming systems and seek reliable indicators of improvements in sustainability. Nutrient accounting systems (farm nutrient balance and use efficiency) have been proposed as a means of assessing nutrient management efficiency at farm level while also providing an indicator of environmental pressure. We report initial results from a study of Irish farm systems, using nationally representative data from the National Farm Survey (part of the EU Farm Accountancy Data Network) to assess P and N balances and use efficiencies across different farm systems and set benchmark indicators for those systems that could be used to motivate practice change and improvement in resource use efficiency, and reduce overall environmental pressure, at farm level. We discuss the approach taken to classify farming systems for this purpose and to developing benchmark indicators. We explore the potential for application of a farm benchmarking tool to drive practice change on farm and the potential impact such change could have nationally, in terms of reduced environmental pressure in the form of farm nutrient surpluses.

P2.43

Management of phosphorus in agriculture in Poland - production and environmental aspects

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Phosphorus (P) is an essential building block of life as there is no substitute for its use to produce food and feed. The objective of P fertilization is to add an adequate (in regard to soil test P) amount of P to produce the economic yield. Unbalanced P management leads to P wastage, the lower cost-effectiveness of production and water quality impairment. The aim of this paper is to analyze the structure and trends in the consumption of phosphorus mineral fertilizers and to draw gross phosphorus balance in Poland (NUTS -1 level) and by regions (NUTS-2 level). In Poland, P for agriculture is mainly applied as compound fertilizers, among which diammonium phosphate represents the greatest share. An average P consumption rate in Poland declined slightly since 2008, currently reaching 24.4 kg P₂O₅·ha⁻¹ UAA. The differences in intensity of farming, measured by the consumption of PMF reached more than 200%, and this differentiation has intensified for years. The polarization of Polish agriculture is also confirmed by GPB outcome, as differences between provinces are in the range of -1.9 kg P·ha⁻¹ UAA in Małopolskie to 7.7 kg P·ha⁻¹ UAA in Wielkopolskie region. The differences in crop and animal production in Poland are largely conditioned by both organizational and production management, which conjointly affect the agricultural phosphorus use efficiency.

Mitigation of phosphorus losses from agriculture -synthesis of a Swedish phosphorus research programme

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During 2009-2013, a phosphorus (P) research programme was carried out with the overall aim to increase the knowledge about P losses from Swedish agriculture to waters, and to develop mitigation methods. It was funded by the Swedish Farmers' Foundation for Agricultural Research, the Swedish Board of Agriculture and the Swedish Environmental Protection Agency. In total, 3.6 million Euro was invested in 24 research projects. In this paper, a synthesis of these projects is presented.

Several of the projects examined or identified indicators for risk assessment of sources of potential P losses, mobilization and transport. This has facilitated development of methods for quantifying and showing within-field variations, which in turn enables targeting hotspots and placement of cost-efficient mitigation measures. The studied mitigation measures included:

- Animal production; feeding recommendations for P, and risks associated with grazing animals,
- Management of arable fields; tillage strategies, cover crops, structure liming, and P application with fertilizers and manure,
- Management of field edges and watercourses; buffer strips, reactive filters and small sedimentation ponds.

The research has contributed to development of risk assessment tools for use in advisory service on farms and has been important for implementation of the Water Framework Directive in Sweden. Some of the most useful outcomes were:

- P recommendations for feeding of cows and horses, and P content of faeces as an indicator of overfeeding,
- Methods for identification of hot-spot areas for P losses in outdoor horse paddocks, and recommendations of measures for reducing risks of P losses,
- Methods for identification of hydrologically active areas in arable fields, and for construction of high-resolution maps of erosion risks and placement of buffer zones within fields or along field edges,
- Recommendations for application of animal manure and risk assessment of long-term effects of manure use,
- The role of the topsoil and subsoil P content, P sorption capacity and transport pathways for the risk of P leaching in relation to the effect of crop, cover crop and tillage practices,
- The importance of soil structure for reducing P losses, and structure liming as one of the most promising measure on clay soils,
- The amount of sediment transport in streams, and the effect of reactive filters and small ponds for reducing transport of particulate P in the agricultural landscape.

P2.45

Measures to reduce phosphorus losses from agricultural land in Sweden

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Sweden has a long coast line along the Baltic Sea and a large number of lakes. A large proportion of the arable land consists of clay soils, and in some regions soil content of P is rather high due to high livestock density. Work has been going on since the 1980s to reduce P losses to rivers, lakes and seas. In 2001, the advisory campaign Focus on Nutrients started. Over the years, 10 000 farmers have received in average 3 voluntary farm visits each. Financial support for measures to reduce P losses is also available in the Rural Development Program (RDP). Further measures are now implemented to meet requirements in the EU Water Framework Directive.

To reduce the risk of excessive fertilization there is a limit of 22 kg P/ha in manure and other organic fertilizers applied, as an average for 5 years. In vulnerable zones manure application is prohibited during the winter and restricted in the autumn. National recommendations for fertilization are published yearly. Well-functioning drainage is an important prerequisite for efficient crop production and low nutrient losses. Free advice is provided in the topic within Focus on Nutrients. Structure liming and lime filter ditches are important to improve soil structure and reduce P losses from clay soils. Investment support has been available for some years. Structure liming has increased significantly. 5 400 ha were limed to improve soil structure in 2012 and 6 100 ha in 2014. Agri-environmental payments are available for buffer zones within vulnerable zones. In 2013, 4 600 farmers had established buffer zones on 11 800 ha. Investment support is available for wetlands and ponds designed to catch phosphorus. Since 1990 ca 10 000 ha of wetlands were constructed. Only 34 ponds designed to catch phosphorus were constructed until 2013, but the number is expected to increase. From 2016 investment support is available in the RDP for construction of two stage ditches, controlled drainage and lime filters.

The surplus in the P balance has decreased and is now close to zero as an average for the whole country. On farms receiving advice in Focus on Nutrients, surpluses in the farm gate balance were reduced by 38% (1.8 kg/ha) on dairy farms and 83% (6.4 kg/ha) on pig farms over a 10 year period. A trend analysis showed a clear downward trend in total P concentrations and transport in 65 small agricultural rivers during 20 years. The decrease was greatest in regions where most measures have been done and Focus on Nutrients has been going on.

Influence of phosphorous fertilization on copper phytoextraction and antioxidant enzymes in castor bean (*Ricinus Communis L.*)

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Application of phosphorus is one of the essential agricultural strategies for enhancing the efficiency of phytoremediation of heavy metal contaminated soil. This study investigated the beneficial effect of three types of phosphate fertilizers (i.e., oxalic acids-activated phosphate rock (APR), $\text{Ca}(\text{H}_2\text{PO}_4)_2$, and NaH_2PO_4) in the range of 0-600 mg P kg^{-1} soil on the castor bean growth, antioxidants (antioxidative enzymes and glutathione - GSH etc.), and Cu uptake. Results showed that, the addition of phosphorus fertilizers significantly increased the dry weight of castor bean and the Cu concentration in roots, resultantly increased the amount of Cu uptake by castor bean. The phosphorus concentration in shoots and roots were both increased, and comparatively $\text{Ca}(\text{H}_2\text{PO}_4)_2$ treatment increased the most. The application of APR, NaH_2PO_4 and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ reduced the malondialdehyde (MDA) contents, and decreased the superoxide dismutase (SOD) and catalase (CAT) contents in castor bean leaves. Moreover, GSH concentration increased with the increasing levels of phosphorus in soil and also the accumulation of phosphorus in shoots, as compared to control. These results demonstrate that addition of phosphorus fertilizers can enhance the resistance of castor bean to Cu and effectively increase extracting efficiency of Cu by castor bean from contaminated soils.

Key words: Copper, Castor Bean, Antioxidant Enzymes, Phosphorus Fertilizer

P2.47

Genetic analysis of phosphorus utilization in Japanese quail

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The ability of poultry to use phosphorus (P) of plant feed ingredients is low and poultry diets are commonly supplemented with feed phosphates of mineral origin. One approach to save global limited P reserves and to reduce P losses into the environment is to improve the P utilization (PU) in poultry via breeding methods. Our objective was to investigate the genetic background of PU in a Japanese quail animal model. The genetic variance components of PU were estimated in a F1 cross of an unselected random-bred Japanese quail line. A total of 200 unsexed juvenile quail were individually housed in metabolic compartments to measure individual PU between day 10 and 15 of life. The low-P diet contained 3.9 g P/kg dry matter and had a Calcium (Ca):P ratio of 1.6:1.0. The average PU was 72% with a high phenotypic variation. The heritability was estimated to be 0.09, and a large standard error reflected an insufficient power of the design. Therefore, in a second step a large F2 cross of two on social behavior divergent selected Japanese quail lines was generated. 888 F2 individuals were housed under similar experimental conditions as describe above, and phenotyped for PU, bodyweight gain (BWG), and feed per gain ratio (F:G). To describe the complex interrelationships between the traits, structural equation models (SEM) were used. Three recursive structural coefficients ($\lambda_{F:G,PU}$, $\lambda_{BWG,PU}$, $\lambda_{BWG,F:G}$) were selected a priori based on biological knowledge. λ_{ij} describes the rate of change of trait i with respect to trait j for a model with a recursive effect of trait j on trait i . The heritability of PU was 0.14. An estimated $\lambda_{F:G,PU}=0.177$ indicates that increasing PU improves F:G. The overall effect of PU on BWG was 0.374, i.e. increasing PU by 1% increases BWG by 0.374 g. The genetic correlations were negative between PU and F:G and positive between PU and BWG. Applying SEMs allow a clear distinction between direct and indirect genetic effects and contribute to a better biological understanding of the relationship between the complex traits. In the third step QTL were mapped for PU using the dataset of the large F2 crosswith around 350 SNP markers of known chromosomal positions. Because the marker density was only sparse, a line cross model and a paternal half-sib model were applied for QTL linkage mapping. For PU two (one) QTL were identified at a 5% (1%) chromosome-wide significance level. However there was no overlap in detected QTL between the models.

Zinc and phosphorus accumulation in wheat as affected by organic matter amendment and *Bacillus subtilis* inoculation

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Phosphorus (P) fertilization can promote zinc (Zn) deficiency. This is one of the most commonly studied antagonistic interactions in plant nutrition. Organic matter and microbial activity has proved to affect the bioavailability of both nutrients. Although the effect of inoculation with microorganisms on P uptake by plants has been widely studied, the effect on the availability of Zn to plants has been rarely reported.

This work was aimed at studying the influence of a labile organic source, β -cellulose, which is expected to increase microbial activity in soil, and the inoculation with *Bacillus subtilis* on P and Zn uptake in wheat grown in pots with two representative Mediterranean soils under different P fertilizer treatments: unfertilized, phosphate rock, and potassium phosphate. P and Zn concentration in plant tissues, dry matter yield, and two enzymatic activities, dehydrogenase (DHA) and β -glucosidase, were studied.

Total Zn uptake by plants was decreased by the application of the more soluble P source. There was not any enhancement of β -glucosidase throughout the experiment, but DHA increased at the end of the crop cycle. This may reveal a change in the profile of the microbial communities in the soil. Total Zn and P in aerial biomass was related to DHA in *B. subtilis* inoculated plants. Thus, it seems that, in this case, Zn and P uptake was related to microbial activity in the rhizosphere. This effect can be explained by the ability of rhizospheric microorganisms to mobilize Zn, as well as P. The application of cellulose resulted in an improved accumulation of P and Zn in the aerial parts of plants grown on unfertilized plant media, and also in Zn concentration (by 30%) in grains in one the less calcareous soil. In the case of cellulose treatment, however, no relationship between uptake and microbial activities were observed, thus revealing a different pattern than in *B. subtilis* inoculated plants. Overall, cellulose application resulted in an increased microbial activity estimated as DHA. Thus, its potential effect can be also related to an increased microbial activity in the rhizosphere. Results reveal the potential benefits on P and Zn nutrition of an increased microbial activity in the growing media, which can lead to a significant biofortification of wheat grains.

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P2.49

Estimation of total available P to plants in representative by using different P extraction methods

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Phosphorus fertilizer is required when P supply from soil is not enough to face plants demand. Soil P supply is assessed by using soil P test (SPT). However, the accuracy of widely used SPTs, such as Olsen P, is usually limited by the fact that they cannot encompass all P-related factors potentially affecting P availability to plants. More precise P fertilization schemes require a deeper knowledge of soil properties affecting the accuracy of SPTs or the development of more precise SPTs based on single and easily performable extraction methods. The aim of this work was to study different chemical- and sink-based P extraction methods to assess available P to plants in soil. To this end, a P starvation experiment was performed to estimate total available P to plants in soil (TAP). A cumulative P uptake curve was obtained as the relationship between cumulative P uptake and P concentration in 0.01 M CaCl₂ extracts. TAP was considered as the amount of P in the cumulative P uptake curve for a P concentration at which no P extraction was expected. Chemical extractants used were: 0.5 M NaHCO₃; 0.27 M Na citrate + 0.11 M NaHCO₃ (CB), the two first sequential extractions in the Ruíz et al. (1997) fractionation scheme (0.1 M NaOH + CB). P-sink extractions used were performed with anion exchange resins (AER) in Cl⁻ and HCO₃⁻ forms.

Overall, extraction using P sinks (AERs) performed better than single chemical extractions, including Olsen P. Best estimations for TAP were obtained with HCO₃⁻ AER (R²=87%). Cl-AER explained 77% of variance in TAP, and when phytase-hydrolyzable P in NaOH and CB extracts was also taken into account, 86% of TAP was explained; the fraction of Fe in oxides ascribed to poorly crystalline oxides increased TAP explained by Cl-AER to 84%. Better performance of resins when compared with Olsen P can be explained because AER extractions showed more significant correlations with P buffer capacity and with the fraction of Fe in oxides ascribed to poorly crystalline Fe oxides than other indices tested. Best results obtained with HCO₃⁻-AER are likely explained because this extraction reflects most of the factors affecting the equilibrium of inorganic P between solid and liquid phases in soils and consequently affecting P availability to plants.

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An aerial, black and white photograph of a city, likely Stockholm, Sweden, showing a dense urban area with numerous buildings and a large body of water in the background. The text is overlaid on the upper portion of the image.

Theme 3: Phosphorus Recycling: Technologies and Product Applications

Theme 3

Phosphorus Recycling - Technologies and Product Applications

Oral Presentations

Responsible scientist: Jens Tränckner (University of Rostock, Germany)

Keynote Speaker: Christian Kabbe (Berlin Centre of Competence for Water, Germany)

Phosphorous is a strategic resource for which there is neither substitute nor replacement. This calls for fostering both the recovery of P and its return into the nutrient cycle, i.e., recycling. In recent years, many initiatives, extensive research, and several demonstration projects on P-recycling have been launched and realized at different scales. Technologies aimed at P recovery and recycling have been developed to tap this precious element from different sources, yielding various recyclates or even final products, but full-scale applications are limited. These efforts have been accompanied by continued research and political discussions on the implementation of effective P recycling strategies. In its focus on phosphorous recycling, this session will host a series of implementation-oriented discussions: Which technological approaches are promising from legal, logistic, and marketing perspectives? What can be learned from the experience with full-scale recovery, recycling, and product valorization? Which key hurdles must be overcome or bypassed to implement P recovery and recycling in and across different economic sectors?

Keywords: recycling technologies, recovery, valorization, hurdles, full-scale application

Keynote abstract:

Circular economy – Challenges and opportunities for phosphorus recycling

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Circular economy for nutrients! How to transfer buzz words into solid results? To sustain good harvests, each year millions of tons of fossil phosphorus have to be mined and processed, while the potential to recover and recycle this essential resource remain untapped or is just inefficiently used as in the case of sewage sludge, manure and food waste. To provide alternatives to argued traditional nutrient recycling routes and to allow more flexibility and more precise application, various technical solutions have been developed in recent years. They allow to recover phosphorus providing renewable mineral compounds suitable as raw material for industries like fertilizer production or even as ready-to-use “renewable” fertilizer. These alternative solutions can be categorized into two principle routes, the recovery from solid and from liquid phases of waste. Combinations including phase transfer between the both are considered as well.

This contribution provides an overview of promising technologies for phosphorus recovery from waste streams, but also reveals recently developed and implemented synergies with nitrogen recovery. It discusses aspects regarding their wide-spread application but also limitations with special regards to environmental but also economic impacts. Not only the technologies themselves, also the obtained renewable materials and their valorization options are addressed. A powerful tool to quantify these impacts is represented by sound Life Cycle Assessment (LCA). Of course, to avoid misleading interpretation, data quality and correct system boundaries are crucial elements for soundness of the results and drawn conclusions relevant for policy and decision making.

Under the light of already existing and feasible technologies, future focus should be laid upon bringing them to the market and not just to increase the spectrum of technologies. The current legal framework and the low prices for raw materials have to be considered as market barriers.

At current price levels for fossil phosphate rock and other raw materials, only legal requirements seem to be likely to boost a wide-spread implementation of phosphorus recovery and recycling from the wastewater stream. The creation a level playing field for fertilisers, no matter if they are made of fossil or of secondary sources is a first step. This has to be flanked by the definition of End-of-Waste criteria for recovered nutrients and binding recycling targets comparable to the CO₂ emission reductions goals. Otherwise, neither recovery nor recycling technologies will be widely implemented in Europe unless they are already providing operational or monetary benefits to its operators under current conditions.

The current revision of the European fertilizer regulation within the European Commission’s circular economy package provides a concrete example or even

template, what issues have to be coped with and what measures have to be taken to create a level playing field for both, primary and secondary based materials destined for fertilizer use. Still, the so-called technical nutrient recovery is lacking a demand-side driven market pull for recovered (secondary) nutrients and the biggest challenge will be the bridging of the gap between supply (recovery) and demand (recycling). Whereas in the past, the focus of nutrient recovery technologies was laid upon high recovery rates for single nutrients, now energy efficiency, synergies and cost become more and more important. Resource efficiency can never be tackled for just one nutrient alone. Hence, sustainable phosphorus management can only be achieved by sustainable nutrient and energy management. And here the link to the other macro-nutrient nitrogen is most prominent.

What about value chains? What can already be done up-stream, before or while the waste is created? Sure, prevention of waste should be of highest priority, we cannot avoid it entirely. But, we have to do what we can do to generate waste in such forms supporting down-stream recovery and recycling. Society has to redefine priorities as well as we have to look for easy to implement, rather integrative solutions instead of reinventing the wheel, creating fancy parallel (infra)-structures. Finally, only if we manage to transform our resource exhaustive, growth of consumption driven economy into a well-balanced circular economy, the paradigm shift from waste towards renewable resource will be accomplished.

There is a lot of know-how already waiting to be shared with huge potential to be creatively transformed into innovation. Our future will be shaped by the ones who dare, not by the ones who fear! Think forward, act circular!

Key words: Phosphorus Recovery, Recycling, Life Cycle Assessment, Circular Economy, Value

Global flows of nitrogen and phosphorus embedded in agricultural products and recycling potential

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Increasing agricultural production and trade during the past decades has gone along with increasing mobilization of nutrients from agricultural fields and across country borders embedded in traded commodities. We used agricultural production, trade and consumption statistics mainly from the FAOSTAT database combined with nutrient contents of more than 500 agricultural commodities to quantify the mobilization from the field, flows of nutrients embedded in trade and their final consumption globally with a focus on nitrogen (N) and phosphorus (P). From 1961 until 2011, the amounts of nutrients extracted from agricultural fields has increased for N from about 25 Tg to nearly 100 Tg a⁻¹ and for P from 5 Tg to 16 Tg a⁻¹. More than 50% of both nutrients were embedded in cereals, followed by fodder crops and oil crops in the 1960s. The fraction embedded in cereals has since decreased greatly while the fractions embedded in oil crops and fodder have increased.

Presently, about 20% of both nutrients become subject to international trade each year as compared to about 10% in the 1960s. The primary importer for N and P embedded in agricultural and food products since the 1980s until today is Europe (EU). While its main trade flows in terms of embedded nutrients originated from intra-EU trade, North America (NA) and Central & South America (CSA) in the 1980s, NA has become negligible in recent years, while intra-EU trade is strongly dominating. Also Asia's (AS) imports of embedded nutrients had been strongly dependent on exports from NA in the 1980s, but are presently strongly diversified with large volumes of N and P imported from intra-AS trade, CSA, EU and Oceania besides NA. A decrease in nutrient import diversification was found for CSA where NA is across the whole time period the most important trade partner.

The utilization of agricultural products has not changed substantially since the 1960s with about 50% of both nutrients embedded in food, 30% in fodder and the remaining part in seeds, waste and other utilizations such as chemical non-food compounds. Hence, with appropriate recovery technologies, up to 50% of nutrients mobilized from agricultural fields (corresponding to about 40% of mineral fertilizer) could be recovered from sanitation systems and household waste assuming high efficiency. This would allow for a substantial diversification in mineral fertilizer supply concerning that especially P fertilizer presently originates from only few countries globally.

Evaluation of pyrolysis chars from sewage sludge as phosphorus fertilizers

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Phosphorus (P) contained in sewage sludge holds the main proportion of P currently lost in waste streams, and options to recycle it for use in agriculture are therefore needed. Pyrolysis of sewage sludge is a promising local alternative to centralized sewage sludge incineration. During pyrolysis, pathogens and organic pollutants are destroyed and a carbon-rich substrate commonly known as biochar is formed. We evaluated pyrolysis of sewage sludge at temperatures between 350-800°C as well as sintering of pyrolysis char with alkali salts. The products were first characterized with respect to elemental composition and solubility of P in alkaline ammonium citrate. They were then applied in pot experiments with neutral and acidic soils in order to determine P uptake by ray grass (*Lolium multiflorum*) and changes in soil pH, available P and cation exchange capacity. Pyrolysis increased the concentration of P from about 35 g kg⁻¹ in the original sewage sludge to about 50 g kg⁻¹ in the pyrolysis chars, and the concentration of other elements also increased, except for cadmium and mercury which were partly lost during pyrolysis. Concentrations of polyaromatic hydrocarbons were below the threshold allowed by the European Biochar certificate. The solubility of P in alkaline ammonium citrate decreased with increasing pyrolysis temperature, being >90% for char produced at 350-400°C but only 26% and 8% for char produced at 600°C and 800°C, respectively. In contrast, plant P uptake was greatest for char produced at 600°C, with an apparent P use efficiency of 13%, compared to 37% in the case of triple super phosphate. After alkali treatment of char produced at 600°C, however, P use efficiency (30-32%) and solubility in alkaline ammonium citrate (about 80%) increased. Interactions between soil pH and P use efficiency of the various products are currently being investigated, since chars produced at low temperatures likely contain iron and aluminum phosphates, whereas various calcium phosphates are present after pyrolysis at higher temperatures and especially after sintering of char with alkali salts. In conclusion, pyrolysis changed plant availability of P only slightly as compared to the parent sewage sludge, but post-treatment with alkali salts increased plant P availability to levels comparable to triple super phosphate. Advantages and disadvantages of these approaches will be discussed.

A thermochemical process for P-fertilizer production from sewage sludge ashes investigated from lab to industrial scale

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Sewage sludge ashes (SSA) contain up to 13% P and are thus promising raw materials for fertilizer production. However, SSAs also contain heavy metals and the main P-bearing mineral phases whitlockite and aluminium phosphate are poorly bioavailable. We developed and patented a process that produces fertilizers from SSA addressing the above mentioned challenges. SSA is thermochemically treated at $\sim 950^{\circ}\text{C}$ under reducing conditions (reductive: dry sewage sludge) in a rotary kiln together with an alkali compound such as sodium or potassium sulfate, hydroxide or carbonate. Some undesired trace elements such as As, Hg, Pb and Cd are evaporated and separated via off gas treatment system. The poorly soluble phosphates are transformed into calcium alkali phosphates (CaNaPO_4 or CaKPO_4) that are not water soluble but completely soluble in neutral ammonium citrate solution (NAC). Pot experiments showed that the fertilizer performance of the treated SSA containing calcium alkali phosphates as the single P-bearing mineral phase was comparable to the performance of triple superphosphate. The PNAC-solubility of fertilizer products correlated very well with the resulting contents of calcium alkali phosphates and the P-uptake of plants in pot experiments. The effect of the ratio alkali/P on the PNAC-solubility was investigated by crucible experiments and trial series with a medium scale rotary kiln using different SSAs and alkali phosphates. The effects of operational parameters such as the temperature and the retention time were investigated as well as concurring side reactions of the alkali compounds e.g. with SiO_2 present in SSA. The alkali/P ratio must be roughly adjusted at 2 to achieve 100% PNAC-solubility for a common type of SSA. A demonstration trial with an output of 2 t recycling fertilizer was carried out in an industrial rotary kiln (product output 30 kg/h). The PNAC-solubility of the product varied between 60% and 80% during the 4 days campaign showing that the transformation of the mineral P-phases to calcium alkali phosphates was not complete. This was observed although the amount of Na_2SO_4 additive was dosed according to the results of the pre-investigations. Structure analysis by XRD showed that besides the target compound CaNaSO_4 also some $\text{Ca}_3(\text{PO}_4)_2$ remained in the SSA as well as some unreacted Na_2SO_4 additive. Obviously, the conditions in the industrial rotary kiln were not optimal for the process showing that some process aspects have to be reconsidered for the scale-up.

Impact of co-incineration of refuse derived fuels (RDF) on sewage sludge ash quality with focus on P-recovery

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Recovery of phosphorus (P) from sewage sludge ash (SSA) is a promising approach to recycle P from municipal wastewater. However, municipal sewage sludge is characterized by a low net calorific value (NCV) due to its high water content and thus, mono-incineration of a solely mechanically dewatered sludge without pre-drying proves to be difficult. While newly built mono-incineration plants can be adapted to incinerate low-calorific fuels, existing facilities previously used for the combustion of other fuels/wastes can face energy-related restrictions when trying to switch to mono-incineration of sewage sludge. An alternative to pre-drying is co-firing of high-calorific waste. Yet due to partly high heavy metal (HM) concentrations and fluctuating quality their application is limited when trying to achieve a proper ash quality for future P-recovery. Therefore, a thorough evaluation of their potential and limitations is deemed necessary.

In this work samples of waste-oil, different fractions of plastic waste and meat and bone meal (MBM) were analysed in laboratory. Subsequently, the ash quality resulting from co-incineration of sewage sludge (30% TS) and varying amounts of these wastes depending on their calorific value was simulated. Results revealed that waste-oil has little effect on SSA quality, due to its low ash content and little amounts of HMs. Only for Cr and Ni the increase in maximum values is noteworthy. The simulated co-firing of plastic waste raised HM-content in the ash significantly, while simultaneously lowering P-content by 1-2 pp. Certain high-quality plastic fractions show potential when only looking at the mean composition of the resulting ash. Nevertheless, the large variation in HM-content can provoke high concentration fluctuations and is not in accordance with the need to maintain a rather constant ash quality for P-recovery. Furthermore, due to high Cl content in mixed plastic waste the risk of unfavourable formation of persistent organic pollutants and corrosion is increased. As often demonstrated in other research, MBM lowered HM content and added the benefit of higher P content.

In conclusion waste-oil and MBM are evaluated as viable waste fractions to obtain high energy outputs and a good ash quality and should be further investigated, while co-firing of plastic waste is only considered possible for the fractions of highest quality, but is likely not economically feasible due to their high market price.

Phosphorus recycling in the mineral fertilizer industry - co-processing of sewage sludge ash during chemical wetphosphoric acid production

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Introduction Phosphoric acid (PA) is by far the most important precursor for phosphorus containing mineral fertilizer. Thus, phosphorus recycling by utilizing existing PA production facilities for co-processing of SSA together with rock phosphate is a promising alternative to existing recycling routes.

In PA production rock phosphate is digested by sulfuric acid producing a slurry consisting of PA and gypsum. In the subsequent filtration section gypsum and PA are separated. Good filtration properties are crucial for economic plant operation. It is well known that impurities contained in the rock phosphate can effect gypsum crystal shape and size distribution and therefore filtration properties.

Research questions

- 1) Which effects do metals typically contained in SSA have on gypsum crystallization under simulated conditions of PA production?
- 2) Do leaching characteristics of phosphorus from SSA under conditions of PA production differ from those of rock phosphate?
- 3) Do process strategies exist to integrate co-processing of SSA in a way that unwanted release of metals into the acid can be limited without affecting phosphorus release?

Experimental Acid Leaching experiments were conducted with different ashes metal content of leachates was analyzed by ICP-OES.

Crystallization experiments were conducted in a semi-batch crystallizer. The effect of the following metals on crystallization kinetics was investigated: Al, Fe, Mg, Cu, Zn, Mn. Additionally some experiments were conducted using real SSA leachates.

Results Digestion experiments reveal that the leaching characteristics of metals differs from ash to ash. Still, trends for certain elements can be observed. A process scheme for co-processing is proposed.

Crystallization experiments show that the investigated impurities have a significant effect on kinetics of gypsum crystallization. In the experimental setup chosen filtration rate only changes in very few cases. In few cases phase transition from gypsum to calcium sulfate hemihydrate is observed.

Conclusion Co-Processing of SSA in PA production is a promising alternative to the proposed phosphorus recycling technologies. It is cost effective by utilizing existing production facilities and increases chances of market acceptance of the recycling product by supplying a known product.

Innovatively simple technology for phosphate recovery using a bifunctional adsorption-aggregation agent

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Although many technologies have been available for phosphate (Pi) recovery and recycling, their implementation has often been hampered by cost problems. A simple, low-cost technology for Pi recovery has been developed using a bifunctional adsorption-aggregation agent, i.e. amorphous calcium silicate hydrates (A-CSHs). A-CSHs are obtained simply by treating solid wastes containing calcium silicates with hydrochloric acid. Such wastes, for example unwanted concrete sludge, are abundantly available from the cement industry. Unlike crystalline calcium silicate hydrates, A-CSHs readily release calcium and silicate ions in water and form insoluble ion aggregates in the presence of Pi. Importantly, the calcium-silicate-Pi ion aggregates can easily settle as sediments without adding any other chemical coagulants. The acid-treatment was essential for preparing the bifunctional adsorption-aggregation agent from calcium silicate-rich solid wastes. A-CSHs could exhibit higher Pi removability and settleability, compared to CaCl_2 and $\text{Ca}(\text{OH})_2$ that have been used as conventional Pi precipitation agents. In addition, unlike CaCl_2 and $\text{Ca}(\text{OH})_2$, no carbonate inhibition was observed with the Pi recovery using A-CSHs. The unique ability of A-CSHs allowed us to develop an innovatively simple, low-cost technology for Pi recovery from liquid wastes. The Pi recovery process required only one batch reactor in which Pi is simultaneously removed and precipitated with A-CSHs. The Pi-rich ion aggregates could be recovered by filtration using filter cloth bags. Demonstration experiments have been performed using a mobile pilot-scale plant at a full-scale wastewater treatment plant (WWTP). Experimental results have showed that approximately 80% Pi could be recovered from anaerobic sludge digestion liquor which was rejected water from a membrane-type solid-liquid separator for digested sludge at the WWTP. The levels of heavy metals such as Cd, As, Pb, Ni, and Cr were much lower than their regulatory standards for fertilizer. The recovered Pi product could be used as a source of Pi for recycled fertilizers such as wood waste composts. The efficacy of the recovered Pi product was confirmed by plant cultivation tests. The present technology could make a great contribution to not only the recovery of Pi from liquid wastes but also the valorization of calcium silicate-rich solid wastes for recycling.

Cost-efficient phosphorus removal in rural waste water treatment plants (WWTP)

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It is generally agreed that increased Phosphorus fractions (P) in the aquatic environment lead to eutrophication of the water body and should therefore be eliminated in waste water treatment plants (WWTP). Generally effluent values for P are in EU only defined for large WWTP. So in Germany only WWTP with a size >10'000 population equivalents (PE) have to comply with defined maximum effluent. However, in rural areas most of the WWTP are smaller than 10'000 PE, like Mecklenburg Vorpommern (MV) in this case, where 552 of the 608 WWTP belongs to size class 1 to 3, i.e. <10'000 PE. The cumulative P emission of all WWTP smaller than 10'000 PE with no P emission limitations is higher as the cumulative P emission of all WWTP greater than 10'000 PE. Against this background, the central question that motivates this paper is the reduction of P in small WWTP, here, for the case study of Mecklenburg-Vorpommern. The investigation has been divided in four consecutive steps:

- 1.) Quantification of P emissions for small WWTP in MV,
- 2.) Identifying the optimization potential by operational methods,
- 3.) Calculation of the costs of the removal by precipitation and the P admission into biomass,
- 4.) Prioritization of most relevant plants using cost-efficiency criteria.

The steps 2 to 3 were so far elaborated with 20 (jointly with the authorities) pre-selected plants, with high total emissions or a high relative P-ratio to the total P load at the ambient water body. The challenge of this study was on the one hand the diversity of the process engineering of the rural WWTP and on the other hand to create cost efficient solutions. For quantification of the P emission a database from the authorities containing the monitored P-concentrations and flows at the effluent of the WWTP. Additionally, the average P-load of the water body was calculated from measured P-concentration and regionalized discharge data. CAPEX and OPEX were comparatively calculated. For evaluating the priority of the plants, three evaluation criteria were selected, which combine the emission and ambient water based approach of WFD with the social impact:

- 1.) The divergence from the LAWA-RAKOON guidance value,
- 2.) The cost per % P reduction in the receiving water in the immission based approach,
- 3.) The cost per total mass P removed in the emission approach. Most efficient actions could be realized in those plants, where all three criteria are high.

Theme 3

Phosphorus Recycling - Technologies and Product Applications

Poster Presentations

P3.1

Adsorptive phosphate recovery in decentralized wastewater treatment - From adsorbent screening to phosphorus recovery in pilot test

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EU Water Framework Directive calls for a good chemical status of natural water bodies. Therefore, in Germany, a phosphorus emission limiting value for small wastewater treatment plants (SWTPs) of 2 mg/L P is under discussion^[1].

The applicability of conventional phosphorus removal techniques (e.g. chemical precipitation, Bio-P) in SWTPs is limited. Alternatively, an engineered adsorption process could be an useful option. Potential key benefits are: the possibility of phosphorus recovery by desorption, no need for on-site storage of chemicals, high tolerance in terms of fluctuating parameters (e.g. volumetric flow, concentration of phosphorus, etc.), easy to perform by a simple, space-saving, and low maintenance integration in existing SWTPs.

Therefore, we investigated different adsorbents to determine general properties, such as specific surface area or particle size, as well as maximum loading capacities and kinetic parameters for the phosphate adsorption. For this purpose we have selected five different granular ferric (hydr)oxides, three iron containing hybrid anion exchangers, an iron containing activated carbon, an aluminum oxide and an iron-lanthanum binary oxide.

Based on the adsorbent characteristics (e.g. data of adsorption equilibrium and kinetics), the linear driving force model was applied to predict the breakthrough behavior in a fixed-bed adsorber with an adsorbent volume of about 30 dm³. According to the modeling results, pilot tests are conducted using GEH® 104.

Many studies show a declining adsorption capacity during the alkaline regeneration step (desorption). A declining reload capacity hinders the reusability of the adsorbent tremendously. Therefore, an innovative regeneration method was developed. It consists of an acidic preconditioning step followed by an alkaline desorption. This method allows a complete removal of phosphate and enables an efficient reload of the adsorbents for multiple times (>15 tested)^[2].

The resulting alkaline liquid contains nearly 100% of the removed phosphorus and is used for precipitation with lime. With a content of 30...33% P₂O₅ the precipitate could be used as a slow-release fertilizer. The transfer of pollutants originating in wastewater (e.g. organic contaminants, heavy metals) to the precipitate can be neglected.

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Lanthanum and magnetic nanoparticles composites for phosphorus recovery

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Communities in the North American Great Lakes region have been severely affected by tap water bans while the fisheries, agricultural and tourism sectors are threatened by the build-up of toxin producing algae stemming from high phosphorus levels. This suggests that in-lake phosphorus removal efforts are needed in addition to ongoing efforts to limit external phosphorus loading. Modified clays are increasingly being used to inactivate inorganic phosphorus but this approach does not allow for nutrient removal and there are concerns that this phosphorus may eventually be desorbed. Composites of lanthanum and magnetic nanoparticles have high phosphorus sorbing capacities and allow phosphorus removal by the use of magnets but it is unclear how effective these materials will be in ponds and lakes. Thus, we conducted a series of lab-scale studies to understand their binding behaviour as the first stage in determining their potential. Based on these results, we have identified priorities for further research.

P3.3

Screw pyrolysis for phosphorous recovery - The example of chicken manure

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Phosphorus is a non-renewable resource, present in large amounts in wastewater and livestock residues such as sewage sludge, digestate and manures from animal breeding. An important characteristic is the local or regional appearance of such streams. Moreover, livestock residues have calorific values in the range of 10 to 14 MJ/kg on dry basis, which are suitable to substitute fossil fuels for power generation. Therefore, thermo-chemical processes are attractive to exploit all the potential of livestock residues, i.e. phosphorus and other nutrients recovery, the energetic valorization as well as the hygienization and the destruction of pharmaceuticals. However, the immediate plant availability of phosphorous in the ashes of combustion processes is rather poor. The suitability of pyrolysis processes for phosphorous recovery was investigated in bench-scale with the proprietary KIT screw pyrolysis technology. The KIT pyrolysis enables the controlled degradation of solid and pasty organic materials providing a carbonized solid product, the pyrolysis char, and a particle-free vapor/gas fraction due to integrated hot gas filtration. Phosphorus is enriched almost completely in the char. The gaseous products may be used for autothermal operation of the pyrolysis process and for power and heat production in decentral installations, respectively.

As an example for phosphorous-enriched biogenic waste about 100 kg of pelletized chicken manure were pyrolyzed in the KIT screw pyrolysis reactor to understand the main degradation steps during the thermo-chemical conversion and to analyze the phosphorous compounds in the products. Pyrolysis was performed at temperatures between 250°C (Torrefaction) and 500°C. Besides the mass and energy balancing, the pyrolysis char was characterized in detail by means of elemental analysis, metals and mineral composition, respectively. SEM and XRD analysis were applied in order to evaluate the structure of the chars and the distribution of phosphorous compounds. Finally, elution tests were carried out using different DIN Standard procedures to evaluate the "plant availability" of phosphorus in the chars. First results show a clear relation between pyrolysis temperature, mineral composition and elution availability. The work encourages further investigation of screw pyrolysis technology for nutrients recovery via pyrolysis char and the more detailed analysis of phosphorous compounds as well as their availability for plant nutrition.

Investigating residual products from thermal conversion of sewage sludge as potential inoculation carriers for phosphorus-solubilizing *Penicillium bilaiae*

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Thermal processes converting organic wastes to bioenergy result in residual ashes/biochars which are often rich in plant nutrients such as phosphorus (P). However, the P contained in these products is often poorly bioavailable for plants. The materials may also possess characteristics such as high porosity or water holding capacity which make them potentially interesting to be used as microbial carriers. If ashes or biochars could be used both as a P source for plants and at the same time as an inoculation carrier for phosphate solubilizing microorganisms (PSM), applied to increase their P availability, this could prove to be a highly interesting bio-based fertilizer product.

The aim of this study was therefore to explore the ability of a PSM, *Penicillium bilaiae*, to grow on and solubilize P from different ashes/biochars to evaluate their potential as inoculant carriers and fertilizers.

In a first step *Penicillium bilaiae* was grown on different products from thermal conversion of sewage sludge: slow pyrolysis biochar (SP), fast pyrolysis biochar (FP), low temperature gasification ash (LT-CFBG), high temperature gasification ash (TS-G) and ash from sludge incineration (FB-I). The potential carrier materials were supplemented with a nutrient solution with two levels of glucose: 13 and 26 mg glucose.g⁻¹ material, respectively. AT 10 and 30 days after inoculation, pH, colony forming units (CFU), water-extractable P and organic anions in the materials were determined.

Penicillium bilaiae was able to grow on all tested materials, with CFU counts significantly higher in FP compared to the other materials. An increase in water-extractable P was observed in SP, LT-CFBG and FB-I, which was accompanied with a drop in pH of the materials and the production of mainly citric acid. The amount of soluble P was significantly higher when the high amount of glucose had been applied prior to inoculation. The most efficient combination to release water soluble P was FB-I combined with the highest glucose concentration, resulting in the soluble P level increasing more than ten-fold after 10 days.

On the basis of the high P solubilisation observed from sewage sludge incineration ash, we are currently optimizing *Penicillium bilaiae* growth and activity on this potential carrier/fertilizer material, results will be presented at the conference.

P3.5

Enhancing P-solubilisation by *Penicillium bilaiae* from sewage sludge ash through addition of different carbon and nitrogen sources

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Incineration ash from sewage sludge has a high phosphorus (P) content, but plant P-availability typically remains rather low. The fungus *Penicillium bilaiae* has shown the ability to solubilize P from this type of ash. The capacity of soil microbes to break down insoluble P forms has been described as heavily dependent on the nature and availability of carbonaceous materials found in soil. One of the main mechanisms associated to P solubilisation is the production and excretion of organic acids, which needs a primary source of carbon (C). The incineration ash, however provides no or only low amount of C and nitrogen (N) for growth and P-solubilisation activity of *P. bilaiae*.

The aim of this study was therefore to explore the response of *P. bilaiae* P-solubilisation activity on incinerated ash to the addition of different C and N sources in micro-incubation experiments.

In a first step, the release of water-soluble P by *P. bilaiae* was recorded over a 16 day-period with different C and N combinations to determine the optimal sampling time. In the following experiment, the effect of eight simple C-sources combined with NO_3^- only, NH_4^+ only or $(\text{NH}_4^+)+(\text{NO}_3^-)$, respectively on P-solubilisation from ash were tested. The test was then repeated with the best combinations of C and N sources in different concentrations in a factorial design. *P. bilaiae* showed the highest P-solubilisation from incineration ash after 12 days of incubation. Among the different C and N combinations tested, fructose and xylose combined with NH_4^+ only and $(\text{NH}_4^+)+(\text{NO}_3^-)$ as well as raffinose with $(\text{NH}_4^+)+(\text{NO}_3^-)$ allowed the release of the highest amount of water soluble-P by *P. bilaiae* corresponding to a 125 fold increase in ash water-soluble P though still only equivalent to 0.8% of ash total P. The factorial design with the different substrate concentrations revealed a greater P-solubilisation by *P. bilaiae* when the C-source was provided in a higher concentration. The amount of water-soluble P was higher with fructose, xylose or raffinose in combination with $(\text{NH}_4^+)+(\text{NO}_3^-)$ producing a 250 fold increase in soluble P equivalent to around 2% of ash total P.

These and further results to be presented at the conference show a promising perspective to use incinerated ash from sewage sludge combined with *P. bilaiae* and suitable C and N sources as a biofertilizer.

Mobilization and leaching of phosphorus and cadmium in soils amended with different bone-/activated chars

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It has been shown that bone char (BC) application may have the beneficial “double-effect” of mobilizing P for plant nutrition and immobilizing plant-available Cd (Siebers & Leinweber 2013; Morshedizad et al. 2016). These studies, however, were done under equilibrium conditions, which are simple to set up but eventually do not adequately reflect field conditions. Therefore, we studied the effect of BC, surface-modified BC (BCplus) and activated char (AC) application in different particle-size classes (0.2-0.5, 0.5-1, 1-2 and 2-4 mm) on the P- and Cd-mobilization in a combined incubation-leaching experiment. The column leaching experiment, using a rainfall simulation system, was conducted on treatments control, AC (0.2-0.5 mm), BC (4 particle-size), BCplus (4 particle-sizes) and BC (4 particle-sizes) plus AC (0.2-0.5 mm) at 500 mg P kg⁻¹ on two different soils for 1, 5, 13, 34 and 70 days of incubation. The P-concentrations in leachates were increased significantly by BC and BCplus of 0.5-1 mm size during whole incubation period. AC application reduced the P-release from BC in all treatments. Minimum Cd-concentration was obtained soils amended with the smallest BC particles. The addition of BCplus and AC significantly increased the Cd-concentrations in leachates so that the more Cd was leached as particle-sizes became larger. The results indicate that the P-release from BCs was larger under non-equilibrium conditions compared to the previous routine incubation extraction experiments. The presentation also will report the most recent synchrotron based-P speciations of single BC particles that were isolated from the soil after finalization of the incubation/leaching cycles.

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P3.7

Plant availability of phosphorous in sewage sludge compost

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Tailing dumps, open-cast coal mining pits and landfills are characteristic areas in central Germany. For the sake of the environment they must be covered with suitable materials to obtain a vegetation layer. This measure reduces leachate and the transport of hazardous solutes. An alternative material which can be used for the establishment of the vegetation layer may be sewage sludge compost (SSC). It fulfills typical requirements of a soil like texture or water holding capacity and has a high content of organic matter as well as macronutrients. Because in future phosphorus (P) will become a rarer element for fertilization of plants investigations regarding the plant availability of this essential nutrient in SSC's are necessary. To solve this question pot and in-situ field trials at a waste dump in Thuringia (Germany) have been carried out.

In the field trials the recultivation layer has a thickness of 30 cm. Three mixture ratios between SSC and a loamy sand were tested. SSC were added at 0, 15 and 30% by volume. In a pot experiment the same variants were tested and moreover the pure sewage sludge with an amount of 5 t/ha and a sewage sludge compost with an amount of 10 t/ha were used in the mixture with soil. During the two years field trail the following crops were established at the recultivation layer: *Zea mays*, *Agropyron elongatum*, *Silphium perfoliatum*, energy gras (mixture from *Trifolium pratense*, *Medicago sativa*, *Phleum pratense*), *Secale cereale*. In the pot experiment the above mentioned mixture ratios were repeated and two variants were tested: planted with *Lolium perenne* and without plants.

During two years samples were taken from the different recultivation layers and analyzed regarding total phosphorous (Pt), plant available phosphorous (double-lactate method- P-DL) and plant available phosphorous (calcium-acetate-lactate-method- P-CAL). Furthermore, the P uptake by plants were measured.

First results showed differences between the Pt and the different extraction methods (P-DL, P-CAL) in the field and the pot-experiments. There is a tendency that in the pot experiments the P-DL content increased with raised amounts of SSC. Further results regarding P availability and P balancing will be displayed. Recommendations for the practical application of the tested materials will be discussed.

Phosphate solubilizing microorganisms as fertility tools for nutrient deficient soils of Cameroon

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Phosphate solubilizing microorganisms (PSM) are able to increase the phosphate availability in soils containing high P contents which are only hardly or even not available to plants. To improve the P utilization efficiency of sparingly soluble phosphates or rock phosphates, PSM were isolated from acidic soils of Cameroon and screened for their phosphate solubilizing ability on agar plates and in shaking cultures supplied with rock phosphates (RP) of different origins (Malian, Moroccan and Mexican RP). They were subsequently tested either single or in consortia on maize, common bean and soya bean grown in pots filled with non-sterile and sterilized soils amended with Malian RP for their aptitude in promoting plant growth. The index of bacterial induced P solubilization ranged between 1.33-2.71 with an average of 2.01. *Enterobacter* sp. (41B) was the only strain showing halo zones on plates supplemented with all the three different rock phosphates. In shaking culture, all the four strains were able to mobilize phosphorus from all rocks. However and again, *Enterobacter* sp. (41B) was the strain with the highest P solubilizing activity, producing 1032.92 $\mu\text{gP g}^{-1}$ in seven days culture, followed by *Klebsiella* sp. (113B) with an average of 643.68 $\mu\text{gP g}^{-1}$ over the three rock phosphates. Single inoculation treatments with *Klebsiella* sp. (113B), *Enterobacter* sp. (41B) and *Pseudomonas* sp. (1B) induced the highest plant growth responses of 59.3%, 231.4%, 251% increase in dry matter of maize, common bean and soya bean plants respectively. However, a combination of the different PSM strains allowed obtaining the highest plant growth responses in all three plant species. These results suggest that the use of rock phosphate combined with the co-inoculation of PSM strains in soil with low fertility provides a sustainable alternative to the use of industrial fertilizers for maize, common beans and soya bean production.

Keywords: Phosphate solubilizing microorganisms, Rock phosphate, Maize, Common bean, Soya bean.

P3.9

Phosphorus limited aquaponics – Causes and consequences

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High accumulation of nutrients in recirculation aquaculture systems (RAS) is particularly interesting for the combined production of fish and plants - aquaponics (AS) (Palm et al. 2014). Literature lacks information on management of commercial AS. Nutrient concentrations in the aquaculture indicate a high N:P-ratio. To investigate the potential without P supplementation, we conducted two experiments at the aquaponic research facilities in the "Fishglashouse" of Rostock University.

Experiment 1

We chose to manipulate the nutritional profile of the system water by altering stocking density of the fish. We hypothesized, that increase in stocking density would result in proportional increase of nutrient levels. We stocked catfish at "extensive" (35 fish tank⁻¹); "semi-intensive" (70 fish tank⁻¹) "intensive" (140 fish tank⁻¹) densities. Physical water quality was determined from Monday to Friday. Stocking density affected N:P-ratio: extensive: 15:1, semi-intensive: 12:1, intensive: 9:1. This was unexpected and contradicts our hypothesis. We conclude, that increased stocking density stimulates denitrification.

Experiment 2

The effects of RAS effluent water of intensive and extensive stocking density (experiment 1) were tested on performance of Moroccan mint (*Mentha* spp.) in a coupled, AS. A commercial fertilizer solution served as control. Each group was tested in triplicate. Water quality was determined from Monday to Friday. When water exchange commenced, water quality was determined before and after water exchange. Nutrient analysis was performed using an automated discrete analyzer. Plant performance was mainly indicated by increase of biomass. Mean biomass harvest were: control: 11.2 g ± 5.3 g, extensive: 17.4 g ± 4.7 g, intensive: 31.8 g ± 13.8 g. We conclude, that Moroccan mint can be cultivated without additional supplementation of P in AS.

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Sugarcane bagasse ash as alternative nutrient sources for plant nutrition

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Brazil, with the 39% of global harvest in 2015, is the largest sugarcane producer worldwide. The cane juice used for sugar and ethanol production is of a great relevance for Brazilian economy. To meet the projected demand of fuel-ethanol (61.1 BL) by 2021, the ethanol production needs to increase by 65% compared to the marketing year 2014/15. One of the strategies to cover growing demand is to expand the sugarcane cultures by occupying new agricultural areas with unfavourable agro-climatic conditions. Consequently, the Brazilian farmers will rely more on mineral fertiliser for maximising the yields as they do already nowadays.

To extract sugar, the canes are crushed and the solid by-product, so called bagasse, is burned. Consequently high amounts of bagasse ash are produced. In 2014 the production is estimated to have reached 5 Mt/year and is expected to rise in near future. So far bagasse ashes are considered as waste polluting the environment. However the ashes contain varying amounts of minerals essential for plant-nutrition that can be recycled as fertiliser. Since the plant-nutrient availability of the ashes depend on incineration conditions, the aim of the project "ASHES" is to find optimal processing conditions for maximising the ashes nutrient availability for plants, mainly P, and increase the fertilisation effects. The aim of the experiment was to analyse the bagasse ash from Brazil (unknown incineration conditions) as a source of P for plants. Preliminary results showed that high amounts of bagasse ash (30 and 45 t/ha) reduced the germination of soybeans in sand. Furthermore, pre-germinated maize and soybean seedlings were transplanted in nutrient poor substrates (sand and a mixture of sand/nutrient poor soil) with (i) five doses of bagasse ash (0, 5, 15, 30 and 45 t/ha) and (ii) four mineral fertiliser controls containing equivalent P-amounts supplemented through ash amendments. The maximal plant growth of maize and soybeans was reached at supplemented bagasse ash dose of 30 t/ha. The growth of these plants was comparable to mineral controls growing in substrates with equivalent amounts of P.

These preliminary results allowed to determine the potential and limitations of bagasse ash with unknown incineration conditions and should be verified in running experiment. This experiment will be used as reference for determining the fertilisation effects of well-defined bagasse ash, provided by project partners, on maize and soybeans.

P3.11

PARFORCE – An innovative technology for phosphate recovery from secondary raw materials

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The recovery of phosphate from secondary raw materials represents a major technological challenge for waste management. From a materials-policy point of view it will be essential for the German phosphorus supply. Besides the often proposed usage of sewage sludge ashes (SSA) additional secondary phosphate containing resources like production or animal residues should be focused, too. Until now there is no process available on the market which can operate economically. Main obstacles are high costs of chemicals, e. g. acids, bases and precipitants, missing process reliability (corrosion) or formation of non-marketable by-products like gypsum by sulfuric acid leaching.

The PARFORCE technology is invented in Freiberg and will solve these challenges. PARFORCE is an acronym which stands for Phosphoric Acid Recovery From Organic Residues and Chemicals by Electrochemistry. It is a zero waste process which can use different primary and secondary phosphate containing raw materials. These includes for example apatite, production and fermentation residues, calcium phosphates, bone meal ashes or luminescent materials. One of its main advantages in comparison to other phosphate recycling processes is the reduction of the chemical demand to a minimum. The problem is solved by recycling of the leaching acid for raw material digestion. In addition, the production of marketable by-products like lime is another economic advantage, which drives the PARFORCE process economically.

Currently the process is scaled up to a demonstration plant for a throughput of about one ton per day feedstock material, within the scope of a spin-off project. The technological and economically feasibility is performed for phosphate containing production residues and bone meal ashes.

Tailored calcium silicate hydrates as adsorbents for the phosphorus recovery from wastewater

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Calcium silicate hydrates (CSH) are a product of quartz, unhydrated lime and water, generated under elevated temperature and pressure conditions. Their specific surface area and their surface charge make them an ideal adsorption material. Due to the fact that it is traded in a granulated form it can be directly used for a phosphorus recovery in the waste water treatment sector.

First practical experience in the use of CSH as an adsorbing material for a phosphorus recovery from waste water has been gained from the so called P-RoC process, developed by the Karlsruhe Institute of Technology. The synthetic CSH used in this process came from an industrial production guaranteeing standardized properties. But nonetheless these CSH-phases are not optimized in terms of a phosphorus adsorption.

On the other hand a lot of scientific research has been done to synthesize CSH with an increased phosphorus uptake-rate using well-defined chemicals and parameters under laboratory conditions. These were prepared only in small amounts and neither is a production on a large scale economic nor is it technologically realized.

To overcome the gap between the already commercially available but less effective CSH and the ones highly optimized but only generated in the laboratory, in this investigation the raw materials for CSH were compounded in various ratios and processed under different temperature and pressure conditions to obtain well-defined CSH-phases with an improved phosphorus adsorption behaviour. Simultaneously these CSH should be suitable for a large scale production. The products have been characterized by XRF and XRD. In further experiments the adsorption capacity of the individual CSHs has been investigated and compared to the CaO/SiO₂-ratio as well as to the temperature and pressure conditions in the course of the hydrothermal reaction.

P3.13

Phosphate recovery from aqueous wastes by hydrotalcite-type clay materials

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Hydrotalcite-type materials, also called layered double hydroxides (LDHs), are a family of naturally occurring anionic clays. They are represented by the empirical formula $[M_{2+1-x}M_{3+x}(OH)_2]_x^+ (An-x/n) \cdot mH_2O$, where: M^{2+} are divalent cations (Mg^{2+} , Zn^{2+} , Ca^{2+} , etc.), M^{3+} are trivalent cations (Al^{3+} , Fe^{3+} , Mn^{3+} , etc) and An^- are interlayer anions (CO_3^{2-} , NO_3^- , etc). These materials can be used in phosphate sorption due to their large surface areas, high anion-exchange capacity, and flexible interlayer region accommodating various anionic species. Moreover, their chemical composition can be easily tuned allowing not only a high ion exchange capacity but also high selectivity towards phosphate ions. However, the powder form of the hydrotalcite-like (HT) materials is not suitable for real wastewater treatment due to the mass transfer limitations, difficulty in handling as well as recovery at the end of the process. This study focuses on shaping of the hydrotalcite-like materials into microspheres with a tuned pore structure for phosphate recovery from aqueous waste streams. The HT powders were processed into suspensions containing sodium alginate polymer, which can be cross-linked further into a coagulation bath encompassing Ca^{2+} ions. The research combines physico-chemical characterization (XRD, SEM, porosity measurements), material shaping (zeta potential and viscosity measurements of the slurries and suspensions) and phosphate sorption testing by UV-vis Spectroscopy.

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Porous filter material for trapping phosphate from agricultural drainage water

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Agricultural drainage water contributes substantially to the phosphate loads of streams, lakes and coastal zones, and in Denmark agricultural discharges makes up the largest source. For tile drained soils – soluble phosphate in the drainage water may be removed via flow-through filters located at end of the pipe before the water is discharged into streams and lakes. As flows may be high filter materials should consist of larger particles to allow a high hydraulic conductivity of the filter, and at the same time the material should sorb phosphate fast, and with high affinity without sorption sites being depleted over longer periods. In addition desorption should be low and the material should perform well at pH 5-7. For this purpose we investigated the performance of a calcined diatomaceous earth porous material (CDE) coated with iron oxides. This material has a high internal porosity and it is physically stable; coating with a high-affinity sorbent like iron oxide is expected to produce a material that can sorb phosphate quickly and which can store substantial quantities of phosphate in the particle interior. Calcined diatomaceous earth ("moler"; 2–4 mm particle size) was soaked in acid iron(III) chloride solutions, and the iron(III) absorbed precipitated as iron(III) (hydr)oxides. The final products with added iron(III) contents between 1.1 and 19.6 wt% had specific surface areas varying between 40 and 80 m² g⁻¹.

Initial observations by SEM-EDX showed that phosphate was quickly absorbed into the interior of CDE particles. Batch experiments showed that sorption kinetics could be described as a second order reaction (Ritchie equation) with half lives between 200 and 1000 min to reach saturation for steady state phosphate concentrations between 0.5 and 5 mg L⁻¹. Sorption was pH dependent with a 4 fold increase in sorption going from pH 8 to 4. Mini-column experiments showed that a CDE containing 11.2 wt% Fe could sorb up to 4.5 g P kg⁻¹ at a phosphate inlet concentration of 1 mg L⁻¹. Experiments with medium sized columns (10 cm diameter; 19 cm long) packed with CDE containing 1.1% iron retained more than 50% of an inlet phosphate concentration of 0.15 mg L⁻¹ at a flow rate of 2 L h⁻¹. Due to ideal hydraulic properties, good physical stability, a substantial phosphate sorption capacity, and tunable phosphate sorption affinity the iron oxide coated CDE filter material has a marked potential for use in agricultural drainage water filters.

P3.15

Urine – An efficient fertilizer product in closed nutrient cycle

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Source separated human urine is rich in essential nutrients like nitrogen and phosphorus. For the first time in Finland a research project named BIOUREA, studies in a large scale the efficiency and safety of utilizing urine based fertilizer products in agriculture. In the project also technologies for the collection and management of urine is developed and tested and aims to acquire official and social acceptance for using these fertilizers in agriculture in Finland. Urine is collected and stored in order to make it safe for to use as fertilizer. Fertilization experiments are implemented on selected crops by contract farmers. Urine is analyzed for contents of pathogens and a selection of harmful substances. Project also collects dry toilet solids and evaluates the nutritional value of the collected biomasses after composting.

Cost and life cycle review comparing urine collection infrastructure and the current wastewater treatment system is carried out. As end result, the BIOUREA-project creates a model and recommendations for usage of urine derivatives in agriculture in Finland. The project is implemented during 2015–2016 and currently the fertilizer experiments are ongoing.

The project theme is very sensitive in Finland and work is needed to influence the attitudes and prejudices of public, decision makers, politicians and officials towards the reuse of toilet fertilizers. One aim of the project is to produce solid scientific data about the benefits and efficiency of these fertilizer products and show with the model the opportunities of alternatives in closing the nutrient loop in communities. Project generates public discussion, media releases and social events relating utilization of urine and toilet compost in agriculture.

The project is implemented by Tampere University of Applied Sciences (TAMK), Global Dry Toilet Association (Huussi ry) and the Finnish Environment Institute (SYKE) as a joint project. The project also involves The Central Union of Agricultural Producers and Forest Owners (MTK) as well as other experts as well as cooperation farmers. The project is funded by the Ministry of the Environment.

Low-cost recyclable filter media for phosphate elimination

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There are several technological approaches available to eliminate phosphate from liquid phase. Well known P - precipitation and sedimentation processes represents classical approach demanding application of chemicals (e.g. Fe_2O_3 , polymers), direct operation of process and sludge/sediment management. Whereas the latter represents the main challenge, especially in Germany after introduction of new sludge application regulation in agriculture, as the fulfilment primarily the requirements of EU WFD. This restriction leads to the acceleration of the demand in phosphor elimination with sequent recycling technologies. One of which is filtration with further recycling either of the entire filter or backwash material. Therefore, the objective of the study is to find appropriate low-cost filter media, which is able to bind phosphate without water quality deterioration and afterwards recycled. The specific tasks of the presented study are limited to the background investigations and include (i) choice of the low-cost material; (ii) laboratory experiments to define the sorption capacity in a range of phosphate concentration; (iii) test of the material on emission of pollutants.

Based on results of other published studies, the activated bio-chars (AC) have been chosen as pilot filter media for experiments. The AC's for tests have been produced as pellet from digestate, wood waste pellet, tires, chicken excrement, bones, and afterwards milled and wet sieved ($45\ \mu\text{m}$). Dried AC's suspended in phosphate solution ($0,05\text{--}10\ \text{mg/l}$) and in deionized water in triples have been stirred for 24 hours in batch-reactors. After filtration ($0,6\ \mu\text{m}$ CA) the phosphate concentrations have been defined by ascorbic acid method. As marker for pollutants emission the COD, TC, DOC and TN have been analysed in filtrate of water series.

The preliminary lab results have shown that there is a variable potential for application of AC as filter media for phosphate elimination in studied concentration range of phosphate. Whereby, the row material of AC is the decisive factor for media performance as for sorption capacity as well as in pollutants emission. Nevertheless, further investigation of the materials in "natural" solutions (e.g. field drainage water, small WWTP) are required in order to confirm their applicability.

P3.17

Phosphorus transformations in agro-industrial by-products induced by pyrolysis

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Thermal treatment of organic waste materials recovered from agro-industrial practices has the potential to transform these resources into valuable fertiliser products such as biochar. We utilise synchrotron-based, X-ray absorption near-edge structure (XANES) and solution nuclear magnetic resonance (NMR) spectroscopies to characterise P species in the following waste materials, as well as the biochars derived from pyrolysis treatment of the materials: poultry litter, pig slurry, bone meal, sewage sludge, wetland reeds, rice husks, cocoa husks and acacia bark. Preliminary findings indicate that several of the biochars have markedly different forms of P from their source materials, with implications for the plant availability of the P in amended agricultural soils. Linear combination fitting (LCF) of P K-edge XANES spectra using up to 25 reference compounds revealed relatively good fits with the following standards: $\text{FePO}_4 \cdot x\text{H}_2\text{O}$, $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$, apatite, $\text{Mg}_2\text{O}_7\text{P}_2$ and ATP-2Na salt. Although it is unlikely that the XANES LCF accounted for all spectral features, the relative proportions of these species were used to infer broad changes in P speciation due to pyrolysis.

Apatite-group minerals were identified as the dominant form of P in most materials; e.g., in the three manure / sludge samples (poultry, pig and sewage), these accounted for approximately 40% of total P. However, whilst this proportion in the pig slurry and sludge remained effectively unchanged by pyrolysis, that in poultry litter increased to as much as 71%. Proportions of other P species also varied, both among the raw materials and their pyrolysed counterparts, and also as a function of the pyrolysis treatment. For example, after pyrolysis, the most distinct change in the three manure / sludge samples was an increase in pyrophosphate ($\text{Mg}_2\text{O}_7\text{P}_2$), with the relative abundance ranging from 19 to 37% in the biochars compared with 8 to 25% in their raw materials. Similar shifts in pyrophosphate were observed in the reed plant material. Observed decreases in long-chain polyphosphates possibly account for some of the increases in pyrophosphates as it is known that the pyrolysis of manures, sludges and plant material fragment the former into the latter. Analysis of the corresponding ^{31}P -NMR spectra and chemical P extractions will provide a clearer explanation of these and other P transformations in the context of potential fertiliser value.

Phosphorus recovery from anaerobic digested sludge as struvite

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Phosphorus, one of key nutrients in agricultural fields, has been wasted even though it is indispensable to get high and stable harvest yield. As Japan depend a large part of phosphorus on import, we have been making many efforts to not only reduce consumption but recover it from waste for sustainable development. We had already installed the first phosphorus recovery facility in 1998 and since then it has been successfully recovering some 300 kg struvite from every 500 m³ of anaerobic digested sludge filtrate in SWTP (Yoneda, 1999). The product has been distributed in commerce as chemical compound fertilizer in Japan.

Hitachi Zosen applied this system with some modification for the study of short-way phosphorus recovery from raw anaerobic digested sludge. As the result of the pilot test, phosphate conc. in raw sludge was almost doubled comparing with other digested sludge in SWTP with combined sewer system. The removal ratio of phosphate was 89% and the recovery ratio of removed phosphate was reached up to 90%.

The recovered struvite obtained in this study shows very similar to the theoretical struvite contents. Cadmium content is extremely small and it means cadmium contamination will be less than 3.6 mg-Cd/kg-P₂O₅ of the product which is lower than 20 mg specified as the severest regulation in the latest draft proposal relating to cadmium in fertilizers by the European Commission. The other harmful contaminations caused by nitrite, mercury, lead, and arsenic, are also quite low compared with the tolerance regulation of The Fertilizer Control Law in Japan.

We also confirmed decrease of struvite-scale formation in the downstream of the pilot plant as expected.

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P3.19

Sewage sludge ash (SSA) from incineration plants as a potential source of phosphorus

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An importance of issues related to phosphorus recovery from waste materials results from European Union (UE) legislation, which indicated phosphorus (P) as a critical raw material (CRM). Due to the risks of a shortage of supply and its impact on the economy, which is greater than other raw materials, the proper management of phosphorus resources is required in order to achieve global P security. One of the potential secondary P source is waste, eg. sewage sludge ash (SSA) generated in incineration plants. Currently, sewage sludge incineration is extensively practiced in some European countries such as the Netherlands, Switzerland, Austria and Germany.

The paper presents the possibility of the usage of SSA generated in Polish incineration plants as a secondary source of phosphorus. Currently, 11 large incineration plants with fluidized-bed furnaces (7 installations) and grate stoker furnaces (4 installations) are operated. Moreover, small installations, serving small towns and villages were also built and they are planned in future. Approx. 43,000 Mg of SSA per year is produced in incineration plants and according to the Polish National Waste Management Plan 2014 (NWMP) further steady growth is predicted. This indicates a great potential for recycle phosphorous from SSA and reintroduction it in the value chain, as a component of fertiliser which can be applied directly in the field. An average phosphorus content in SSA from Polish incineration plants is around 9.7%, though 3,000- 4,000 Mg of phosphorus per year can be recycled and introduced back into the environment. The total amount of available phosphorus in SSA vary from plant to plant depending on amount of incinerated sewage sludge and its quality. It contributes to the fact that new different technology solutions (e.g. mobile/ stationary phosphorus recovery installations) should be developed and implemented in the following years. The creation of database focused on collection and sharing the data about P amount recovered in EU and Polish installations is indicated as a helpful tool in development of an efficient P management model for Poland.

Key words: sewage sludge incineration, sewage sludge ash (SSA), phosphorus (P), phosphorus recovery, zero waste, circular economy (CE), small and large sewage sludge incineration plants

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Development of a technology for recovering resources from livestock waste

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There is a large amount of compost at the regions with a concentration of hog farms area in Japan. The compost is produced by hog farm much beyond the local demand. The surplus compost is over using into farmlands and natural environment. Hitachi Zosen has developed a system for recycling surplus compost with the aim of solving environmental problems in these regions. The system is established a series of processes for carbonizing compost with a self-recovering indirect heating system, which does not use fuel, and efficiently separating the phosphorus accumulated on the grainy surface of the bio-char to enhance phosphorus concentration. Furthermore, succeed to produce SSP (Single Super Phosphate) fertilizer mixed with the bio-char and phosphate rock, which met Japanese standards quality. And it was confirmed that the bio-char was as effective as chemical and organic fertilizer resources.

Moreover, Hitachi Zosen accomplished a running by self-recovering indirect heating system. Energy input was not required for kiln heating except for a pilot burner. The ratio of energy input of pilot burner was only 3%. Nearly all of the Phosphorus present in compost from pig manure can be accumulated on the surface of the hydrothermally treated bio-char. The phosphorus concentration was 15% in bio-char (P_2O_5). All conditions were cleared for Japanese standard of SSP. Bio-char has as a feature of highly solubility than phosphate rock. This means that phosphorus in bio-char is easy to leach in the soil. These results suggest that the surplus compost will be converted into valuable materials without fuel.

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P3.21

Decision tool for predicting P fertilisation effects of secondary resources

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Substituting mineral phosphorus (P) fertiliser with P in secondary resources is a crucial step towards increased P sustainability. In order to achieve P recycling in practice, it is essential to know the relative agronomic efficiency (RAE) of secondary resources compared with mineral fertiliser. Therefore, simple laboratory methods are required that can be used to predict RAE when fertilisation plans are established. We applied different laboratory methods to 20 secondary resources and compared the methods in terms of their ability to predict RAE measured as the first harvest of ryegrass (*Lolium multiflorum*) of a bioassay with a nutrient-deficient blend of sand and sphagnum peat as experimental soil. Based on this systematic comparison, we suggest a decision tool for predicting RAE of secondary resources:

If P in the secondary resource in question has been precipitated with Al and/or Fe, as in the case of chemically precipitated sewage sludge, we suggest predicting the RAE by the concentration of Al and Fe in the product according to:

$$\text{RAE} = 25.7 - 4.6 \times \text{Al} - 3.0 \times \text{Fe}; R^2 = 0.73, n = 11$$

In other secondary resources, P is probably mainly present as Ca phosphates of differing solubility. The solubility of stable Ca phosphates decreases with increasing soil pH. Therefore, we suggest predicting RAE by application of one of two different chemical extraction methods depending on pH in the target soil.

At soil pH <6.5, we propose predicting RAE of the secondary resource according to:

$$\text{RAE} = 1.6 \times \text{H}_2\text{O extractable P} + 48.9; R^2 = 0.65, n = 9$$

The fraction of H₂O-soluble P indicates a secondary resource's ability to increase soil solution concentration and replenish the P concentration after plant P uptake.

At soil pH >6.5, we propose predicting RAE of the secondary resource according to:

$$\text{RAE} = 4.2 \times \text{Olsen extractable P} + 23.6; R^2 = 0.77, n = 9$$

Olsen P, which is buffered at pH 8.5, was the only extraction method that was significantly correlated with RAE at soil pH >6.5 because it extracted least P from those secondary resources that contained the largest fractions of stable Ca phosphates (e.g. hydroxyapatite).

The suggested decision tool is a first attempt to propose simple laboratory methods that allow consideration of the RAE of secondary resources in fertilisation plans. The more data available for a decision tree, the closer the prediction will be to the real fertilisation effects.

Fertilizer replacement value of digestate, processed animal manure, compost, biochar and struvite as renewable P sources

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Biomass processing in the bioeconomy results in new products with potential as alternative P fertilizer. 90% of the biomass fed to biogas plants leaves the reactor in form of digestate. Digestate contains large amounts of nutrients and organic matter (OM), and has therefore a high potential as renewable nutrient source or soil conditioner. Digestate processing is widely adopted by the biogas producers. On large scale pig and cattle farms, manure processing is also increasingly introduced. Further processing of digestate, manure and waste streams may result in biochar and struvite production. We aimed at forecasting the P fertilizer replacement value (PFRV) based on the chemical composition of these renewable P sources.

In greenhouse pot trials we assessed the PFRV for 19 processed digestates, 10 types of processed animal manure, 2 composts, 2 struvites, 5 biochars and 18 blends. The DM and OM content ranged from 4.2 to 93.3% and 1.4 to 83.9%/DM, respectively. The P content had a range of 0.3 to 12.1%/DM. The soil used for the pot trial was a sandy loam soil with C% 1.6, pH-KCl 5.4, N% 0.15 and a P-AL of 4 mg P/100 g dry soil. The P content was low, which makes differences in bioavailability of P detectable in plant growth. The different products were mixed through the soil at an amount equivalent to 90 kg P₂O₅/ha. Extra mineral NK was supplied to reach a minimum dose of 180 kg Nmin/ha and 180 kg K₂O/ha. *Lolium multiflorum* L. subsp. *Westerwoldicum* was sown in the pots and the DM crop yield and P export were measured to determine the PFRV as an estimator of P bioavailability ($PFRV = [(X_{org}, fertilizer - XP_0) / (XP_{90} - XP_0)] * 100$, with X=DM yield or P export). The references for this calculation were P₀ (no P) and P₉₀ (90 kg P₂O₅/ha triple superphosphate).

The PFRV ranged from 46 to 170%. This suggests that some organic fertilizers have a slow release of P, or P is present in unavailable forms (FRV <100%). On the contrary, some organic fertilizers result in more bioavailable P than triple superphosphate (FRV >100%). Organic acids released by the organic fertilizers can compete with P adsorption on Ca, Fe or Al binding sites and eventually stimulate P desorption or prevent P adsorption. Although the pot trials are still ongoing, we already observed a significant negative correlation ($R^2=0.37$; $p<0.001$) between the PFRV and the Ca:P molar ratio. Results on the link between P bioavailability and the composition of the organic fertilizers will be presented.

P3.23

Bone char as novel alternative phosphorus fertilizer: from submicroscopic characterization to fertilization experiments

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Bone char (BC) could be an alternative P fertilizer that contributes to closed P cycles in food production and reduces heavy metal contamination of soil from mineral P fertilizers. Since BC consists mainly of hydroxylapatites its low P solubility is a problem. To overcome this limitation we produced and tested a surface-modified BC (BCplus). Both chars (BC and BCplus) were characterized by wet-chemical, electron microscopic (SEM and EDX) and synchrotron-based techniques (XANES, μ -XANES). These analyses showed the modification of elemental contents & distribution at BCplus-surfaces along with rather small changes in the bulk P solubility in laboratory tests. For example, the concentration of sulfur increased from <0.1 mass-% in BC up to 27 mass-% in BCplus as confirmed by distinct S-peaks in electron microscopic observations BCplus contrasting to BC. Additionally, single particle analyses by electron microscopy and XANES (bulk and μ -) revealed changes in P-speciation during the vegetation period. For BC, transformations from Ca-P (86%) into Mg-P- (59%), Fe/Al-P- phases can be shown (30%). BCplus contained $(\text{NH}_4)_2\text{HPO}_4$ and Porg-compounds, parts of which were transformed into metal-P-phases in soil. P-uptake and yields in pot and field trials showed differences in fertilization effects of BC and BCplus although trends are not yet consistent. In the first experimental year of a field trial yield of the BCplus treatment increased in average by 10% in comparison to the BC treatment, whilst in the second year a yield decrease by 9% was observed. Furthermore, stronger impacts of the initial soil P-status on fertilization effects were recorded in the second experimental year. The latest soil (P enzymes, microbial biomass P, soil P tests) and plant data (P-concentrations, P-uptake and crop yields) covering 3 years of experiments will be reported and correlated with the findings on the single bone char particles.

Plant phosphorus availability in biochar and ashes from sewage sludge processed by different thermal conversion technologies

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Thermal conversion of phosphorus (P)-rich waste materials such as sewage sludge offers several advantages: generation of bioenergy, up-concentration of plant nutrients facilitating transport and distribution, and destruction of a wide range of organic pollutants and pathogens in the raw material. It is well-known that different thermal processes modify the chemical and physical structure of the feedstock in different ways, which also affects P speciation and plant availability in the residual ashes or biochars. There are, however, not many investigations that systematically compare the P fertilizer value of ashes and biochars produced by converting the same feedstock in different thermal processes.

In this study, 25 tons sewage sludge from a representative Danish wastewater treatment plant were converted on different thermal platforms, including sludge incineration, sludge pyrolysis and two different sludge gasification processes. A final oxidation step was additionally applied as an option to increase P bioavailability in pyrolysis- and gasification chars. The particle size range of the assessed materials was aligned and their P fertilizer value was tested in a pot experiment in an acidic soil with spring wheat as a test crop. Water-extractable soil P after the addition of the different materials was additionally determined.

All materials greatly increased plant biomass compared to the untreated control. The pyrolysis chars and one incineration ash had a fertilizer value comparable to that of unconverted sludge and mineral fertilizer and better than the gasification ashes. However, downstream oxidation significantly improved P availability in low-temperature gasification ash and increased plant biomass production by almost 50%. Likewise, oxidation of pyrolysis char markedly increased the plant available P content in soil after material incorporation, however, the effect was not that clearly reflected in plant growth.

Under the conditions tested, incineration or pyrolysis of sewage sludge resulted in products with a high P fertilizer value. Results also showed that downstream oxidation of pyrolysis- and gasification chars can increase soil P availability as well as plant growth. In general, the results of the study showed that changes in the design and settings of the thermal conversion processes can significantly influence P availability in the residual material.

P3.25

Application of sugar cane ashes and mycorrhiza fungi to different Cuban soils

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In Cuba, sugar cane ash is produced in enormous quantities as a residue of the island's sugar industry and stored in outdoor piles, constituting an environmental risk. At the same time, a lack of research prevents the adequate use of cane ash as an amendment for soils poor in phosphorus (P), which are often inadequately low fertilized due to the high prices of imported chemical fertilizers. The objective of this work was to determine the effect of increasing rates of sugar cane ash, alone or accompanied with mycorrhiza fungi or compost, on the soil P availability and plant growth compared with the effect of chemical NPK fertilizer. Field studies and pot experiments were carried out with different crops and soils (sugar cane and maize on Eutric Oxisols and Inceptisols). The soil P concentrations (extraction with H_2SO_4 0,1 N) were suboptimal. The sugar cane ash had a P concentration of about 0.8 %. The mycorrhiza (*Glomus intraradices* and *Glomus hoi*-like strains) was applied as commercial product EcoMic®. The results showed a promoting effect of sugar cane ashes on the soil P availability and on the plant growth. The adequate cane ash dosages varied from 2.5 to 10 t ha^{-1} , depending on soil characteristics, although, 10 t ha^{-1} was frequently the most favourable. It was also remarkable that the effect of only 5 t ha^{-1} ash, when accompanied with the mycorrhiza substrate, was almost similar to that of 10 t ha^{-1} ash alone, and higher than the application of 5 t ha^{-1} ash alone. Ash application also had an influence on the P solubilizing bacteria population. The results showed that sugar cane ash can be an adequate substitute for highly soluble P fertilizers in Cuban agriculture.

Can P extractions of waste products predict their P fertiliser value?

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A more sustainable exploitation of the world's phosphorus (P) resources is essential. Many waste products contain high P concentrations. The question is whether the P in these products is available to plants and whether they are suitable as alternative P fertilisers.

This study aimed to investigate the relationship between the products P characteristics and their fertiliser values by characterizing the different P species in a range of waste products combined with plant P uptake measured in pots. The effect of soil type was also tested by including three soils in the pot experiment. The products (two sewage sludge's, two biomass ashes, struvite, composted household/park waste, meat and bone meal (MBM), MBM biochar, two industrial sludge's, soft rock phosphate) were applied with a target dose of 30 kg P ha⁻¹ and compared to mineral P fertilizer. Spring Barley was used as test crop and the experiment was repeated in two growing seasons. All soils had low P status but differed in texture and regional origin.

The P species were characterized in all products with different P extraction methods, among others were water-extractable P (Pw), total P on bicarbonate-extractable P (BeTP, modified Olsen P) and total P (TP). Total above-ground dry mass and total P uptake was determined in barley, and the relative P fertilisation effect of the products was compared to mineral P fertiliser.

Fertiliser values showed significant positive correlation with the BeTP concentration in products ($r=0.685-0.927$, $P<0.05$) and with the TP concentration ($r=-0.661$, $P<0.05$, one soil type only), whereas there was no significant relationship with the Pw concentration in the products. Other product extraction methods (e.g. resin, oxalate, 2% citric acid) are also tested, but analyses are not finished yet. Different soil types resulted in significant differences in fertiliser values. The fertiliser values varied significantly between the products from about 0% (e.g. Biochar and Soft Rock P) to about 100% (e.g. Struvite and industrial sludge).

These findings indicate that different P species characterizations of waste products can help to specify whether a product is suitable as a P fertiliser with short-term effects. The results also indicate that fertiliser values of waste products depend on the soil characteristics.

P3.27

Phosphorous in raw and hydrothermally carbonized sewage sludges

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Sewage sludges from waste water treatment plants are known as materials containing phosphorous from human activities. Because of different environmental harmful or otherwise problematic ingredients, these sludges may no longer be used in agriculture. On the other hand, sewage sludges are possible secondary sources of phosphorous with a remarkable potential.

Hydrothermal carbonization may be a suitable instrument for exploitation of sewage sludges. Using the HTC conversion technique an efficient production of HTC-coal as a solid fuel and a decomposition of organic pollutants for agriculture application are both possible. In the case of fuel application phosphorous shall be dissolved from the coal and being recycled in a separate recycling process. To estimate the possibilities for utilization of hydrothermally treated sewage sludge as a farm fertilizer, knowledge about the distribution of phosphorous during the HTC process is important. Therefore the influence of HTC-treatment on the distribution of phosphorous and possibility of phosphorous extraction was investigated.

Applying inorganic acids both, an extraction of phosphorous and a changing of the distribution and the type of phosphorous compounds are possible.

In the present study fresh and hydrothermally carbonized sewage sludges were treated concerning an extraction protocol to identify the contents of total, organic and inorganic phosphorous. The extraction solutions were measured with inductively coupled plasma optical emission spectrometry.

The distribution of inorganic and organic phosphorous in fresh material was nearly the same. After HTC-treatment the content of inorganic phosphorous was considerably higher than the content of organic phosphorous.

The HTC is one of the most efficient possibilities for the application of sewage sludges from medium size plants, and these results enable a phosphorous management integrated in the conversion process. A targeted influence on distribution of phosphorous can also be used for the production of storable fertilizer out of excess manure.

The influence of the composting process on plant availability of phosphorus in a green waste compost and in a mixture of green waste compost and ash from a biomass power plant

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Objective: Presently The Recycling-Park Harz company sells about 3000 tons of biomass ash a year as a fertilizer to farmers. As the farmers are interested in the availability of nutrients – especially of phosphorus –, we carried out some preliminary laboratory experiments relating to the nutrient availability of ash and the effect of the composting process on the ash. The basic idea is that nutrient availability might be enhanced by composting the ashes. Owing to the microbial activity arising in the course of the composting process, parts of the small ash grains might dissolve and thus release nutrients such as phosphorus.

Materials and Methods: Later we decided - in collaboration with the University of Rostock - to carry out a more realistic open field trial on the composting plant of Recycling-Park Harz in Heudeber. For this experiment two compost windrows the size of 100 cubic meters were built. The first windrow contained only shredded green waste, the second contained both green waste and ash. The materials were analyzed for nutrients, pollutants and microbial activity. The windrows were arranged in November 2014. They were turned over once a month and their temperature was measured continuously. Samples were taken at the beginning, after a month, after two months and after four months, by the end of the trial. The samples were analyzed at the Rostock laboratory.

Results:

1. The total phosphorus content in the dry matter increased considerably in both materials after one month of composting and remained approximately the same over the last three months.
2. The content of citrate-soluble phosphorus rose in both windrows over the entire testing period. Citrate-soluble phosphorus amounted to about 80% of total phosphorus.
3. The water-soluble phosphorus content remained virtually unchanged in both windrows over the entire testing period. It ended up between 2 and 5% of total phosphorus.

Conclusions: There seems to be evidence of a significant increase in citrate-soluble phosphorus during the composting period. The increase takes place in the mere compost as well as in the ash-compost mixture. The composting process over a period of four months results in a doubling of the citrate-soluble-phosphorus content in both materials. As a result, it can be concluded that the composting process leads to an increase in plant available phosphorus in green waste compost and green waste compost mixed with ash from biomass power plants alike.

P3.29

A more efficient and sustainable fertilization through recycling phosphorus as struvite

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To secure food production, changes in phosphorus (P) management are necessary. The use of mineral P fertilizers need to be reduced and new nutrient management strategies like the use of alternative P sources together with a more tuning and efficient fertilization need to be implemented.

In this frame struvite is a promising example of a clean and recycled phosphorus source. Besides positive agronomic results in terms of yields and P uptake, investigations regarding P availability for plants with different strategies to uptake P, with different root systems and with different soil pH are required to improve the production process and therefore the quality of this product.

In this study, a greenhouse experiments was carried out to determine P fertilizing effect of struvite compared with triple superphosphate (TSP), an a control without P applications. Two different crops (maize and lupine) with different P acquisition strategies and different root geometry and morphology were used. Nitrogen (N) source is another significant factor affecting plant P acquisition because N-induced change in rhizosphere pH can affect the solubility of P. Therefore two different N sources (ammonium and nitrate) were applied for each treatment.

The aim of this study was to compare the effect of the struvite and TSP in crop yield, P dynamics in the rhizosphere and changes in root architecture, as well as observe the differences between plant species with different nutrient-acquisition strategies and at different soil pH (modified by applying nitrogen as NH_4^+ or NO_3^-). The differences on plant yield between fertilizers were weekly analyzed during the experiment, measuring the leaf area with an automatic noninvasive phenotyping device.

Struvite had as high P recovery as TSP. In both species ammonium resulted in a significantly greater P uptake (g/root surface area), but not greater total uptake as plants fertigated with nitrate had greater root surface area. Possibly ammonium uptake resulted in rhizosphere acidification and thereby greater mobilization and uptake of P. An increase in the leaf area compared with no P control was earlier observed in the TSP treatment, however after the second week no differences were observed between both treatments.

We propose that struvite can be used as a sustainable phosphorus fertilizer on acidic sandy soils, however deeper studies of the effect of recycled products on rhizosphere dynamics are necessary to have a more efficient fertilization.

An aerial, black and white photograph of a city, likely Stockholm, Sweden, showing a dense urban area with numerous buildings and a large body of water (the harbor) in the background. The text is overlaid on the upper portion of the image.

**Theme 4: Syntheses of and
with Phosphorus-Containing
Compounds**

Theme 4

Syntheses of and with Phosphorus-Containing Compounds

Oral Presentations

Responsible Person: Marko Hapke, Thomas Werner (both from the Leibniz Institute for Catalysis)

Keynote speaker: Christian Müller (Freie Universität Berlin, Institute for Chemistry and Biochemistry – Anorganic Chemistry, Berlin, Germany)

This session considers P compounds in all oxidation states, ranging from low-valent compounds in low oxidation states to those regularly used for catalytic purposes and beyond. The structural versatility of P has led to the isolation of a large number of unusual novel P species, and thus to detailed studies of their often fascinating properties. In lectures and poster sessions, the many facets of the synthetic chemistry of phosphorus, the vast applications for catalytic purposes, as well as analytic and theoretical studies of P compounds in all their versatility will be presented.

Keywords: phosphorus compounds, synthesis, catalytic application, oxidation states, properties

Keynote abstract:

Recent developments in the chemistry of low-coordinate phosphorus heterocycles

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Low-coordinate phosphorus compounds have recently regained noticeable interest as the very peculiar stereoelectronic and coordination properties of such $\lambda^3\sigma^2$ -species differ significantly from classical trivalent $\lambda^3\sigma^3$ -phosphanes. These special characteristics can have interesting effects in applications, such as homogeneous catalysis or material science.

Due to a modular synthetic approach, we have lately demonstrated the access to various donor-functionalized 2,4,6-triaryl- λ^3 -phosphinines (phosphabenzenes, type **A**, Figure 1), including phosphorus derivatives of 2,2'-bipyridine and terpyridine. By making use of the chelate effect, we could demonstrate for the first time that neutral P,N and anionic P,C hybrid ligands form easily coordination compounds with transition metal centers in both low as well as medium to high oxidation states, which is an important aspect for applications in more applied research fields.

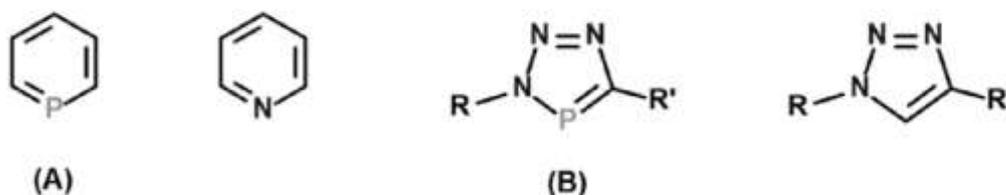


Figure 1. Phosphinine (**A**) and triazaphosphole (**B**) and comparison with their nitrogen-analogues.

Inspired by these findings, we started to investigate also other classes of functionalized, low-coordinate phosphorus compounds. We anticipated that derivatives of 3*H*-1,2,3,4-triazaphospholes (type **B**, figure 2) are suitable candidates, as they can generally be prepared in a modular “click”-reaction, starting from azides and phosphalkynes. First results show indeed, that this powerful tool can be used as well for the straightforward and simple preparation of donor-substituted, chelating triazaphospholes.

This lecture will focus on the design and preparation of especially pyridyl-functionalized phosphinines and triazaphospholes. The access to such compounds provides new perspectives for areas of chemical research, which are otherwise dominated by transition metal complexes based on pyridine-, bipyridine- and terpyridine-based ligands. A detailed comparison of the here-presented low-coordinate phosphorus compounds with their structurally related nitrogen-counterparts, having an identical substitution pattern, will be provided.

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Hydrolysis stability of bidentate phosphites utilized as modifying ligands in the Rh-catalyzed n-regioselective hydroformylation of internal olefins

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The stability of ligands and catalysts is an almost neglected issue in homogeneous catalysis, but crucial for successful application of this methodology in technical scale.^[1] We have studied the effect of water on phosphites being the most applied co-catalysts in the n-regioselective homogeneous Rh-catalyzed hydroformylation of olefins.^[2] The stability of the bidentate nonsymmetrical diphosphite L1, as well as its two monophosphite constituents L2 and L3, towards hydrolysis was investigated by means of in situ NMR spectroscopy under similar conditions as applied in industry. Hydrolysis pathways, intermediates and kinetics were clarified. DFT calculations were used to support the experimentally found data. The acylphosphite unit L2, which reacts with water in an unselective manner, was proven to be much less stable than the phenolphosphite L3. The stability of the bidentate ligand L1 can therefore mainly attributed to its phenolphosphite moiety. With an excess of water the hydrolysis of L1 and L2 as well as their Rh-complexes is first order with respect of the phosphite. Surprisingly, coordination to Rh significantly stabilizes the monodentate ligand L2, while in strong contrast the bidentate ligand L1 decomposes faster in the Rh complex. NMR spectroscopy provided evidence for the existence of species from decomposition of phosphites, which can likewise coordinate as ligands to the metal. Electron-withdrawing groups in the periphery of the acylphosphite moiety decrease the stability of L1, whereas 3,5-disubstituted salicylic acid derivatives with bulky groups showed superior stability.

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A new strategy for the synthesis of P-chiral ligands for asymmetric catalysis

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In asymmetric reactions aiming the synthesis of compounds with high enantioselective purity the application of chiral phosphorus-ligands as co-catalysts for transition metals plays a pivotal role. In contrast to the vast number of chiral bidentate diphosphines bearing the chiral information in the backbone of the carbon skeleton only a few phosphorus ligands are known with a stereogenic P-atom (e.g. DiPAMP, Duanphos, BisP). This situation is quite astonishing because a chiral P-atom allows the closest contact between ligand and prochiral substrate through the coordination sphere of the metal and therefore the most efficient chirality transfer can be expected.

Based on the well-established method for the synthesis of P-chiral monophosphines developed mainly by Jugé et al. we intended to synthesize P-chiral versions of the prominent, but achiral Xantphos- and DPEPhos-type ligands by the simultaneous introduction of both P-chiral groups in the corresponding carbon backbone. Surprisingly, the targeted diphosphines could not be obtained by this protocol. Only by a decisive modification of the Jugé approach, the desired ligands could be prepared. By the new pathway more than 60 individuals of the new chiral ligand type were accessible. First results to use them in asymmetric catalytic reactions will be simultaneously reported.

Rhodium diphosphine complexes in homogeneous catalysis – How to use the catalysts more efficiently?

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Fundamental objectives in chemical catalysis research are reducing the required energy, avoiding by-products and increasing the yields to have a cost-efficient, ecologically sensitive and sustainable use of existing resources. Thus the main focus is generally on the consumed reagents such as the metal of the selected catalyst, the substrates and the solvent.

Another approach for higher efficiency of a catalyzed reaction is to get the in-depth knowledge of the formation of the active catalyst from the corresponding precatalyst. A precondition for an efficient use of the catalyst is that the active catalyst is formed completely.

But depending on the catalyst precursor, the ligand, the solvent and possible additives, several types of complexes could be observed besides the desired active catalyst. The time for complete catalyst formation differs also for several catalyst systems.

In this presentation an overview of possible activation and deactivation phenomena during the formation of rhodium catalysts containing diphosphine ligands is shown. Corresponding rhodium diphosphine complexes are characterized by means of ³¹P-NMR spectroscopy and X-ray analysis. The main focus is on the monitoring of the formation of these complexes by means of quantitative UV/vis spectroscopy. Stability constants of relevant rhodium diphosphine complexes were determined and are discussed.

CO₂ valorization utilizing new P-based catalysts

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The chemical fixation of CO₂ into valuable products has attracted much attention in recent years.^[1] In this context the conversion of CO₂ with epoxides to the corresponding cyclic carbonates is an attractive and extensively studied reaction.^[2] The obtained products find numerous applications.^[3] There have been several reports on the utilization of organocatalysts in this reaction.^[2] However, for efficient conversion of the substrates they often require harsh reaction conditions and/or long reaction times. We are generally interested in the synthesis of cyclic carbonates from petrochemical as well as renewable feedstocks.^[4] Recently we reported efficient sustainable metal-based two component catalyst systems enabling the conversion of CO₂ with epoxides under mild conditions.^[4b, 4c] Subsequently a structural design concept for one-component organocatalysts was proposed which proved to be viable.^[4g, 4h] Herein we report the preparation of various P-based organocatalysts for the conversion of petrochemical as well as bio-based epoxides. We were able to determine structure activity relationships and we identified the most active catalyst for the conversion of small mostly petro-based epoxides. We optimized the reaction conditions and under these conditions the desired products could be obtained in good to excellent yields. Notably, similar P-organocatalysts can also be employed for the conversion of larger fatty acid and bio-oil derived epoxides.

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Phosphorus-based organocatalysts for base free catalytic Wittig reaction

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One of the most fundamental methods for the construction of C=C double bonds is the Wittig-reaction.^[1] In the last few years there have been several publications on catalytic Wittig reactions based on achiral phosphanes.^[2] We are also interested in the synthesis and application of phosphorus based organo[-]catalysts.^[3] In this context we reported the first enantioselective catalytic Wittig reaction as well as the first microwave assisted version.^[3a,b] We also envisioned a base free catalytic Wittig reaction based on a three step process. Simple phosphanes serve as organocatalysts, which attacks an acceptor substituted alkene, in this case, diethyl maleate. By a [1,2]-H-shift the corresponding ylide is formed^[4] in the absence of a base. The conversion with a carbonyl compound, e.g. aldehyde, provides the respective succinate. The in situ reduction of the formed phosphine oxide regenerates the catalyst and closes the catalytic cycle. We will report mechanistic investigation by ¹H NMR, which confirm both the ylide formation and the proposed reaction sequence. The reaction is stereoselective and various products are obtained in excellent yields up to 95% and high E selectivities. Those highly functionalized alkenes might serve as a scaffold for further functionalizations. We will also present our effort in this context.

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P-N-Compounds as synthons in cyclisation reactions

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Phosphorus chemistry has always been a source of unusual reactivity paired with a resulting incredible broad variety of structural motifs with different non-metallic as well as metallic elements. In recent years the chemistry of P-N-containing synthons and derived reaction products with different unsaturated reaction partners has found increasing interest due to the interesting properties of the obtained compounds as well as the synthetic possibilities they offer. Species containing P-N multiple bonds are highly reactive and difficult to handle. However, the application of such precursor compounds enables the release of these reactive species by adding another reagent like a Lewis acid in solution to avoid the necessity to prepare such reactive species beforehand. The contribution will deal with the reactivity of such in situ-prepared P-N species with different unsaturated substrates, especially alkenes, alkynes and dienes, to obtain so far unknown cyclisation products and to observe the mechanism of such reactions by spectroscopic methods like NMR (Nuclear Magnetic Resonance). The effect of the used additives like Lewis acids is investigated as well as the possible preparation and application of alternative sources of P-N synthons and sophisticatedly designed unsaturated substrates.

Highly tunable organic-inorganic hybrid materials based on the utility of vanadium organophosphonate clusters

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The development of novel organic-inorganic hybrid materials based on the utility of phosphonate ligands is attracting growing attention since interesting properties with relevance to different applications may be obtained.¹ One approach to prepare such kind of materials is based on the utility of fluoride-templated vanadium organophosphonate cluster compounds, in which the V/P/O framework, bearing different organic moieties R, assembles around the fluoride template to form a complex organic-inorganic hybrid anionic cluster which is balanced by the charge-compensating cation M.

In this contribution, $[(V_2O_3)_2(RPO_3)_4F]^-$ cluster as building block supported by different phosphonium and/or transition metal ion as a charge compensating M cation have been designed, synthesized and characterized by single crystal XRD, such as $Ph_4P[(V_2O_3)_2(PhPO_3)_4,F]$, $Ph_4P[(V_2O_3)_2(CH_3PO_3)_4,F]$, $Ni(2,2\text{-bipy})_3[(V_2O_3)_2(tBuPO_3)_4,F]$, and $[Co(NCCH_3)_6][(V_2O_3)_2(PhPO_3)_4,F]_2$. In contrast to most mixed-metal organophosphonates, these compounds are soluble and stable in polar organic solvents. Therefore, the intact cluster structure in solution can be easily proved by multinuclear NMR (1H , ^{19}F , ^{31}P and ^{51}V) and EPR spectroscopy upon one-electron reduction.

Varying the R group of the phosphonate ligand and the type and charge of the M cations by using functional phosphonium or transition metal ions with ligand spheres of different geometric constraint gives the opportunity to highly tune the solubility, thermal stability and redox properties of vanadium phosphonate cluster compounds. This could open a wealth of opportunities in solid-state chemistry to design and synthesize materials for specific application.

Theme 4
**Syntheses of and with Phosphorus-Containing
Compounds**
Poster Presentations

P4.1

In situ infrared-spectroscopic investigations on heterogeneous catalysts for the hydroformylation of alkenes

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Hydroformylation is the reaction of alkenes with synthesis gas to yield aldehydes. The reaction is among the few multi-ton scale industrial processes utilizing homogenous catalysts such as phosphine or phosphite modified complexes of rhodium or cobalt. Although the application of heterogeneous catalysts are connected with a number of procedural and economic advantages, the development of applicable catalyst systems is still a challenge.^[1] Promising concepts represent supported ionic liquid-phase catalysts (SILP) and catalysts based on porous organic ligands (POLs).^[2,3]

The upcoming KataPlasma project deals with new heterogeneous catalyst systems for the rhodium catalyzed hydroformylation. Organic polymers are treated in a low temperature plasma using reactive gases to deposit anchor groups. Another feasible strategy is the plasma-assisted polymerization of suitable monomers as a thin film on the surface of an inorganic support such as silica, alumina or carbon-based materials. Subsequently, ligands (e.g. phosphines, phosphites) are attached to the backbone followed by the loading with rhodium. These materials are applied in model reactions to examine their catalytic performance and stability with respect to catalyst recycling.

For in situ IR-spectroscopic studies, heterogeneous catalyzed hydroformylations are performed in a customized ATR cell which is fitted into a modified Bruker Matrix FTIR-spectrometer. The catalyst is placed directly on the ATR crystal while the cell is continuously fed with solvent-educts-mixture from a pressure reactor system via a micro-gear-pump. This arrangement allows us to collect IR-spectra of the working catalyst at distinct time intervals under reaction conditions. The resulting IR-spectra contain structural and quantitative information about the occurring catalyst species. FTIR-spectroscopic data is treated with chemometric software tools such as PCD (pure component decomposition) for the recovery of pure component spectra. Since the formed organometallic intermediates are in most cases not isolable, vibrational spectra calculated by DFT methods can support the subsequent interpretation of the experimental data beneficially.

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Synthesis of annular PNP containing ligands

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From a synthetic point of view, the chemistry of phosphorus is challenging and does not always follow the predicted routes. Tervalent phosphorus compounds are not only crucial in biological systems but are proven to be extremely versatile ligands. Their interaction with transition metals affords a large number of complexes which might find a use in the field of homogenous catalysis, both in academic research and industrial applications. ^[1]

A common product class are phosphorus compounds containing nitrogen. Established PNP ligands such as Diphosphinoamines^[2] or PNP pincer-type ligands^[3] are well known and investigated. However annular PNP containing compounds are less attended and with regard to their catalytic potential as ligands barely examined.

We developed a selective synthesis of annular PNP ligands by varying and optimizing the reduction of dihalogenated PNP-fragments. Consequently the preparation of novel ring-shaped PNP-compounds succeeded, which could find application as potential ligands in coordination chemistry and homogeneous catalysis.

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P4.3

Synthesis of new bidentate tertiary P-stereogenic triaryl phosphines

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New bidentate tertiary P-stereogenic triaryl phosphines based upon 9,9-dimethylxanthene, 2,7-di-tert-butyl-9,9-dimethylxanthene, diphenyl ether or dibenzofuran were synthesized via di-ortho-lithiation of the backbones and phosphorylation with tertiary diaryl phosphines. The resulting ligands were coordinated to several rhodium and palladium complexes and investigated with respect to their influence on the selectivity of hydrogenation and allylation reactions.

Synthesis and properties of cobalt-phosphite complexes

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Compared to phosphine ligands, phosphite ligands play a significantly less important role in transition metal-mediated homogeneous catalysis. However, they possess several features making them highly interesting substitutes for phosphines. Although they coordinate strongly to transition metals as well, the bonds can often be cleaved more easily compared to the corresponding phosphines, releasing the catalytically active metal center under rather mild conditions.

Recently we have found that complexes of the Cp(cyclopentadienyl)-Co(I)-fragment with phosphites or phosphite-olefin combinations exhibit several interesting features for catalysis, including the stabilisation of the metal fragment and their release by thermal or photochemical treatment. Such complexes, most of them prepared for the first time, have been applied in cyclisation reactions of alkynes and nitriles, yielding pyridines.

However, the complex formation still needs further investigation for a better mechanistic understanding and the possibility to scale up the synthesis, due to a collaboration with a company to commercialise these complexes. Additionally, phosphites with different electronic and steric properties should be investigated as ligands in these reactions to systematically analyse the molecular properties of the obtainable complexes of the type CpCo(Olefin)[P(OR)₃] and their behavior in catalytic reactions.

P4.5

Synthesis of carbonate-bearing hydroxyl apatite (CHAP) via calcite transformation: Calibration of stable isotope (C, O) and monovalent cation partitioning

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Carbonate-bearing hydroxyl-apatite (CHAP) is of fundamental and applied interest to the (bio)geochemical, paleontological, medical and material scientific communities, since it forms the basic mineral phase in human and animal teeth and bones. In addition, it is found in non-biogenic phosphate deposits, thereby presenting a sedimentary sink in the global biogeochemical phosphorus cycle, and also being a resource for human needs. The stable isotope and foreign element composition of biogenic CHAP is widely used to estimate the formation conditions. This requires careful experimental calibration under well-defined boundary conditions.

Within the DFG project EXCALIBOR, synthesis of carbonate-bearing hydroxyapatite was conducted via the transformation of synthetic calcite powder in aqueous solution as a function of time, pH, and temperature using batch-type experiments. The aqueous solution was analyzed for the carbon isotope composition of dissolved inorganic carbonate (gas isotope mass spectrometry), the oxygen isotope composition of water (laser Raman scattering), and the cationic composition. The solid was characterized by powder X-ray diffraction, micro Raman and FTIR spectroscopy, SEM-EDX, elemental analysis (EA, ICP-OES) and gas isotope mass spectrometry.

Temperature was found to significantly impact the transformation rate of calcite to CHAP. Upon complete transformation, CHAP was found to contain up to 5% wt carbonate, depending on the solution composition (e.g., pH), both incorporated on the A and B type position of the crystal lattice. The oxygen isotope fractionation between water and CHAP decreased with increasing temperature with a tentative slope shallower than those reported in the literature for apatite, calcite or aragonite, so far.

The presence of dissolved NH_4^+ , K^+ or Na^+ in aqueous solution led to partial incorporation into the CHAP lattice. It was found that Na^+ was strongly preferred compared to K^+ and pronounced wrt NH_4^+ , which is explained by the difference of the radii of the monovalent cations. Distribution coefficients ($D(\text{Na-K})$ and $D(\text{Na-NH}_4)$) are derived that can be used to estimate fluid compositions from natural abiotic apatite.

Chromium catalysts with phosphorus-based ligands for the selective ethylene oligomerization

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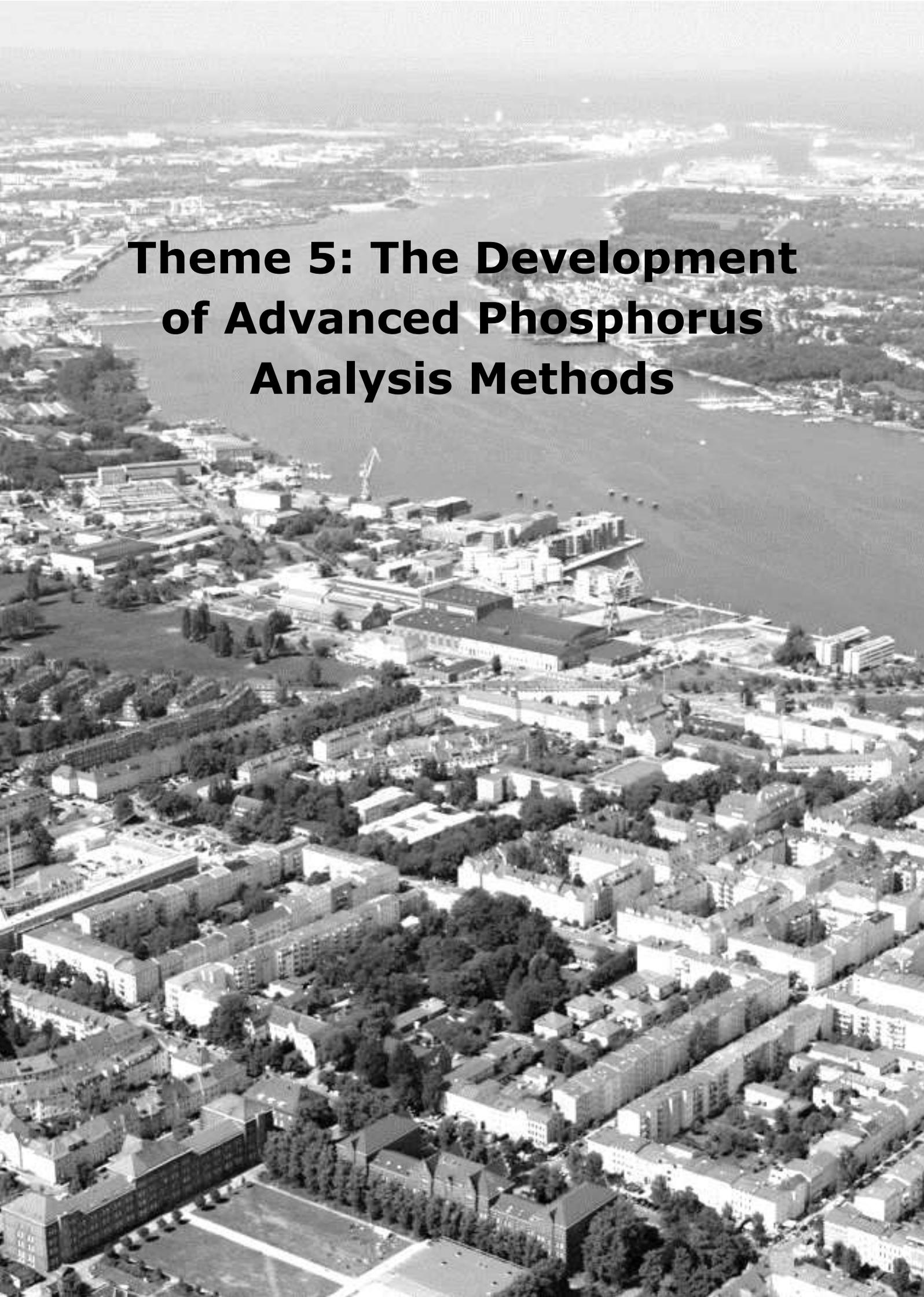
Ligands with phosphorus as constituent parts are an important class of ligand because their electronic and steric properties can be altered in a systematic and predictable way over a very wide range by varying the substituents.

Due to their high reactivity, Linear Alpha Olefins (LAOs) are important intermediates for a variety of industrial relevant chemical reactions. Their utilization is strongly dependent on the chain length, which also entails different physical properties. The quantitatively most important usage of LAOs is as comonomers in the production of high density (HDPE) and linear low density polyethylene (LLDPE (C4-C8)). Other significant applications are in the synthesis of plasticizer alcohols (C10-C16) or oil field chemicals and wax replacements (C16-C30+). LAOs can be produced by cracking of Fischer-Tropsch products. Currently the main suppliers of LAOs rely on full-range ethylene oligomerization technologies. These technologies are based on homogeneous catalysts, which are all producing even numbered olefins ranging from four to more than 30 carbon atoms. The composition of the product mixture follows mathematical distributions (e.g. Schulz-Flory or Poisson), reflected by the statistically determined chain growth/ β -hydride-elimination mechanism. Though the product distribution of these processes can be tuned to a minor degree by changing process parameters, the range of flexibility remains strongly limited.

During the past few years, several research groups developed selective catalytic routes to 1-hexene and 1-octene focusing on homogeneous chromium-based catalyst systems in order to match the market demand. P and N donor ligands yielded the most promising results. A catalyst system for the trimerization of ethylene, comprising the chromium source $\text{Cr}(\text{acac})_3$, a ligand $\text{Ph}_2\text{P-N}(\text{iPr})\text{-P}(\text{Ph})\text{-N}(\text{iPr})\text{H}$ (Ph = phenyl, iPr = isopropyl), dodecyltrimethylammonium chloride as modifier and triethylaluminium as activator, is presented.^[1] The synthesis of further ligands with P-N-P motif, their coordination chemistry and their applications in the catalytic oligomerization of ethylene are described.^[2]

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An aerial, black and white photograph of a city, likely Stockholm, Sweden, showing a dense urban area with numerous buildings and a large body of water (the Baltic Sea) in the background. The text is overlaid on the upper portion of the image.

Theme 5: The Development of Advanced Phosphorus Analysis Methods

Theme 5

The Development of Advanced Phosphorus Analysis Methods

Oral Presentations

Responsible scientists: Peter Leinweber (University of Rostock, Germany), Detlef Schulz-Bull (Leibniz Institute for Baltic Sea Research Warnemünde, Rostock, Germany)

Keynote Speaker: Barbara J. Cade-Menun (*Agriculture & Agri-Food Canada, Swift Current Research and Development Centre, Saskatchewan, Canada*)

This session will address the many novel and advanced analytical approaches that enable the identification, speciation, and quantification of P-containing compounds in environmental and technical systems. The respective methods include quantum-chemical and other modeling approaches, synchrotron-based techniques, nuclear magnetic resonance spectroscopy, and mass spectrometry, the latter often combined with gas- or liquid-chromatographic separations or other chemical-analytical methods. Among the analytical targets are P compounds in complicated environmentally relevant mixtures such as sediment, soil, by-products, and waste. An additional focus will be the many natural and anthropogenic P compounds in biological systems and their medical applications.

Keynote abstract:

Phosphorus research and ^{31}P -NMR spectroscopy: Current knowledge and future directions

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Phosphorus (P) is an essential nutrient for all organisms and is a key regulator of productivity in terrestrial and aquatic ecosystems. Organic P, in which P is bonded with carbon (C), comprises half or more of the total P in many ecosystems. However, the cycling of organic P is still poorly understood compared to that of the simplest inorganic P form, orthophosphate. Organic P forms include phosphate monoesters (inositol phosphates, sugar phosphates, and mononucleotides), orthophosphate diesters (DNA, RNA, phospholipids, and lipoteichoic acids), phosphonates with a C-P bond; inorganic P forms include orthophosphate and complex inorganic P forms composed of chains of orthophosphate (pyrophosphate, polyphosphate). All of these vary in their production by and bioavailability to various organisms, and in their environmental reactivity, including sorption to mineral surfaces. In light of this, identifying and quantifying P forms in environmental samples such as soil, manure, water and sediments can improve nutrient management for crop growth while minimizing water quality impairment. However, studies of P cycling have often been limited by methodology.

The technique that has most advanced our knowledge of P, particularly organic P, in environmental samples is ^{31}P nuclear magnetic resonance spectroscopy (^{31}P -NMR). The only naturally occurring P isotope is ^{31}P ; as such, ^{31}P -NMR is a quantitative technique if the P concentration of the analyzed sample is known. Both solid-state and liquid-state (also known as solution) ^{31}P -NMR experiments can be conducted. However, the low P concentrations and the presence of iron and other paramagnetic ions in most environmental samples produce solid-state ^{31}P -NMR spectra with broad, poorly resolved peaks. As such, solution ^{31}P -NMR experiments are most common for environmental samples. These allow larger samples to be extracted and concentrated to increase the total P in the ^{31}P -NMR tube. Extraction also allows the effects of paramagnetic ions to be reduced, resulting in higher resolution spectra. The most commonly used extractant is 0.25 M NaOH+0.05 M Na₂EDTA. Through recent advances, almost all of the organic P species in extracts of soils and sediments can be identified with careful spiking experiments. And when solution ^{31}P is coupled with techniques that characterize inorganic P species, such as P K-edge X-ray absorption near-edge structure (XANES) spectroscopy, almost all the P forms in environmental samples can be identified.

Phosphorus forms were first characterized by ^{31}P -NMR in soil samples by Newman and Tate, in 1980. Since then, more than 200 papers have been published using solution ^{31}P -NMR in soil science, including soils from temperate

and tropical regions and from natural and managed systems. There have been nearly 80 papers using both solid-state and solution ^{31}P -NMR for manure, composts and other wastes. Over 60 papers have been published in limnology, including studies of sediments in lakes, rivers and wetlands. There have also been studies characterizing P in dissolved and particulate samples from the water column in lakes and rivers, and in colloidal material transported from soils. However, this technique is still underutilized in oceanography, where fewer than 20 papers using solid-state or solution ^{31}P -NMR have been published. In addition, differences in methodologies among research groups still hamper our ability to compare results among research groups or across research disciplines.

This presentation will present an overview of the use of ^{31}P -NMR in soil science, limnology and oceanography, highlighting current knowledge in these disciplines as well as knowledge gaps and analytical problems to be addressed. It will also discuss research needs and future research directions.

New evidences on impact of glyphosate binding in soil: A molecular-level picture

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Glyphosate is a phosphonated derivate of the amino acid glycine and became the most important herbicide in the world with 650,000 t annually use. Binding and mobilization in soil depends on factors such as pH, texture, mineralogy and organic carbon but the role of individual factors are discussed controversially in the literature (Vereecken et al. 2004; Borggaard et al. 2008). Generally, glyphosate is considered to be strongly bound and readily mineralized. However, recent observations contrast to these assumptions:

- (1) glyphosate remains in soil for years although it should be decomposed by microbial activity within some days (Bergström et al. 2011);
- (2) glyphosate was found in groundwater and the Baltic Sea (Skeff et al. 2015).

To shed more light into the behavior of glyphosate in the environment, we investigated 24 soil samples that differed in (1) texture, (2) pH, (3) pedogenic oxides, mobile metals and phosphates and (4) organic matter content and composition. Furthermore, molecular modeling of glyphosate-soil-interaction is established via quantum chemical calculation. Adsorption experiments were carried out in the concentration range 10 – 150 mg L⁻¹ and the data were fitted to FREUNDLICH-models. Correlations between soil properties and adsorption parameters showed:

- (1) Soil organic matter (SOM) content as well as
- (2) soil texture and
- (3) Al and Cu content strongly affected adsorption but
- (4) pH in the range 4 to 7.1 had no effect.

The influence of SOM was investigated by pyrolysis-field ionization mass spectrometry and results suggest amides, carbohydrates and phenols as potential binding partners for glyphosate. Quantum-chemical modeling was conducted to calculate binding energies between glyphosate and selected representatives of SOM compound classes, and these data agreed with the experimental results. Details regarding the complexation, H-bond-formation and binding energies of glyphosate with the modeled SOM molecular system have been explored. Currently, we study the effect of an oligopeptide that showed the highest calculated binding energy for glyphosate adsorption. Preliminary results indicate a complexation potential of peptides in the soil solution which may explain glyphosate leaching and transport into waterways. Furthermore, we study potential of biochars for retaining glyphosate at the field scale.

Novel spectroscopic techniques to examine soil phosphorous speciation

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Determination of soil phosphorus (P) speciation is vital for understanding P retention and transport in soils. Current methods for soil P speciation rely heavily on sequential chemical extractions which are ex situ and can introduce artifacts during the analysis procedure. To overcome limitations of current methods for examining the P speciation, non-invasive spectroscopic techniques can be used to analyze soils in situ. This study evaluates synchrotron-based techniques to elucidate mechanisms for P bonding in soils. Agricultural soils have been collected throughout the Chesapeake Bay watershed (USA) to examine P speciation. Micro-scale X-ray fluorescence (XRF) imaging and X-ray absorption near-edge spectroscopy (XANES) at the P K-edge has been performed at the X15B beamline at the National Synchrotron Light Source and the 14-3 beamline at Stanford Synchrotron Radiation Lightsource. Initial studies have used XRF to correlate the presence of P with Fe, Ca, and Al. Micro-scale XANES spectra were compared to spectra of standards with known chemical composition to identify mineral Ca phosphates and adsorbed phosphate to Al-oxides. Future studies will seek to identify additional chemical information using extended X-ray absorption fine-structure (EXAFS) spectroscopy.

In situ-IR-spectroscopy for the study of kinetic and mechanistic aspects of alkene hydroformylation with metal catalysts modified by phosphorus(III) ligands

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In order to study mechanistic aspects of catalytic reactions, heterogeneous as well as homogeneous, one approach is to couple kinetic investigations with spectroscopic techniques. For the study of hydroformylation reactions, high-pressure in situ spectroscopic methods, especially FTIR- and NMR-spectroscopy, provide important structural and quantitative information about catalytically relevant complexes under reaction conditions.^[1,2] The treatment of FTIR-spectroscopic data with chemometric software tools to obtain pure component spectra and their concentration profiles is often necessary to extract the maximum information from respective experiments.^[3] In our group selected hydroformylation reactions are studied with homogeneous and heterogeneous transition metal catalysts modified by phosphorus(III) ligands such as phosphines and phosphites. Those phosphorus(III) ligands represent co-catalysts which have a crucial impact on the catalytical activity and chemo-/regioselectivity. Reactions for in situ IR-spectroscopic studies are performed in semi-batch reactor systems which are coupled with a high pressure transmission IR cell or ATR cell and an automated sampling device for ex situ gas chromatographic analysis.^[2] FTIR-spectroscopic data is treated with the chemometric software tool PCD (pure component decomposition) for the recovery of pure component spectra and their associated concentration profiles. The interpretation of experimental IR-spectra of catalytic complexes, which are in most cases non-isolable and sometimes present in low concentrations only, are supported beneficially by considering vibrational spectra calculated by DFT methods. Thus, important structural aspects such as complex geometry and the coordination mode of the phosphorus(III) ligands can be clarified.

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Quantification of enzyme-mediated hydrolysis by means of the oxygen isotope ratio of phosphate in grassland and forest soils

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Organic P (Po) contributes 30-50 % to total P concentrations in soil. Plants and microorganisms developed strategies to contribute to the transformation of Po to inorganic P (Pi) by synthesizing enzymes capable of hydrolyzing Po. Commonly, assays with substrate additions are used to characterize potential enzyme activity which differs from actual enzyme activity. We present an approach based on $\delta^{18}\text{O}$ values of resin-extractable Pi ($\delta^{18}\text{OP}$) in soil. This approach relies on the incorporation of O atoms of ambient water into phosphate that results from the hydrolysis of Po by enzymatic activity. We added waters differing in the O isotope composition to soil prior to laboratory (grassland soils) or field (forest soils) incubation. The slope of the linear regression of $\delta^{18}\text{OP}$ values on $\delta^{18}\text{O}$ values in soil water was used to quantify the incorporation factor (α) of water-O into Pi in soil and to identify pathways based on apparent fractionation factors. In the laboratory incubation of grassland soils, the actual incorporation of water-O into Pi was small ($\alpha=5.7\pm 2.1\%$) calling for cautious interpretations of potential enzyme activities. Apparent fractionation factors associated with extra- and intra-cellular enzymatic reactions suggest that between 0.6% and 2.3% of Pi in soil originated from extra-cellular Po mineralization. Between 3.4% and 5.1% of Pi in soil was released by living cells.

For the in-situ incubation of forest soils, the incorporation factor of water-O into resin-extractable Pi was 0.25 (\pm standard error 0.05) indicating that, averaged across all resin-extractable phosphate molecules, one out of four O atoms originated from enzymatic incorporation of water-O atoms. Potential monoesterase activity and the incorporation factor α were significantly related ($p=0.03$) with 84% of the variation in α remaining unexplained. This might be caused by the contribution of phosphate molecules without any water-O incorporation and of enzymatic reactions of other Po compounds (pyrophosphatase, diester etc.). Labile and moderately labile Pi fractions (NaHCO_3 -extractable + NaOH -extractable) explained nearly half of the variation in the incorporation factor α ($p=0.001$). In general, we found no significant effects of tree species or land use intensity on potential or actual enzyme activities in the forests under study ($0.05 < p < 0.83$). In conclusion, our approach offers unique insights into actual enzymatic processes involved in Pi release in soil.

Separation of inositol phosphate isomers in environmental samples by ion-exchange chromatography coupled with electrospray ionization tandem mass spectrometry

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A LC-ESI-MS/MS method for isomeric separation of inositol phosphates (InsP_n) in environmental samples originating from different sources such as soil, manure/compost, and aquatic sediments has been developed. The method includes a single NaOH-EDTA extraction step, centrifugation and direct injection of a particle free solution into an ion chromatographic column. Isomeric separation was achieved with an ammonium carbonate gradient compatible with electrospray ionization tandem mass spectrometric detection. Data collection was done in negative ESI mode with multiple reaction monitoring (MRM) recording several transitions for each InsP_n.

Extensive method development was conducted to address several performance parameters such as, preserved separation efficiency, signal stability, detection limits etc. The method provides enhanced long term stability compared to a previous method¹ and up to 100 samples has been analyzed in a single run batch without any need to clean the ion source.

The use of LC-ESI-MS/MS provides a sensitive tool for the identification and quantification of both higher and lower orders of InsP_n in environmental samples. The presented method makes it possible to directly analyze samples from different origin with good selectivity and sensitivity. The detection limit was between 0.03-0.16 μM for the different InsP_n, corresponding to 37-99 ng P/g sample DW. The method has shown to be able to analyze more than 200 samples without any severe matrix effects. This allows future study of the fate of inositol phosphates in the environment possible.

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Application of high resolution mass spectrometry to the characterisation of organic phosphorus in environmental matrices

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Cycling of phosphorus (P) in the environment plays a fundamental role in agricultural production and the health of freshwater ecosystems. However, the contribution of organic phosphorus (P_o) species to biological processes, particularly eutrophication, is not fully understood. Characterisation of P_o in water quality testing is based on an operational definition. This is sufficient for studying bulk chemistry processes, but provides limited insights into the role of organic phosphorus in the environment.

Attempts to characterise P_o in more detail have mostly focused on the use of nuclear magnetic resonance (NMR) spectroscopy. NMR can identify classes of P_o compounds, for example phosphate monoesters, or diesters, however, potentially many tens or hundreds of compounds can contribute to a given signal in an NMR spectrum, since individual molecular species of P_o cannot be resolved. In contrast, high resolution mass spectrometry (HRMS) has become a powerful tool in the analysis of complex biological samples and is being widely used in the field of metabolomics. Thousands of compounds can be resolved simultaneously with the capability being extended still further by combination with liquid chromatography (LC) to provide enhanced characterisations and quantitative determinations.

This paper presents results to date from the development and application of electrospray-HRMS and LC/HRMS techniques to the determination of P_o from complex environmental matrices, including: agricultural manures, i.e. pig manure, cow manure, and poultry litter, wastewater effluents and river water extracts. We aim to demonstrate how molecular characterisation of P_o opens up the possibility of studying the transformation and transport processes involving P_o in the environment to better understand the role P_o plays in the P cycle, in particular the eutrophication of freshwater ecosystems.

Real-time monitoring of oxygen isotope exchange between phosphate and water using Raman spectrometry

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Oxygen isotopes associated to phosphorus (P) can be used to trace different sources and biological processes in the environmental P-cycle. While under ambient conditions, abiotic effects on the oxygen isotopic composition of phosphate are minimal and can be neglected, extracellular and intracellular enzymes can lead to the exchange of oxygen between phosphate and water. This exchange is subject to isotopic fractionations that have been determined for several combinations of phosphatases and substrates. However, little is known about the kinetics of oxygen isotope exchange during biological cycling of phosphate, which is important to interpret variations in the oxygen isotope composition of phosphate in the environment. Raman spectroscopy is a powerful technique to address this gap of knowledge, because it allows to detect mass dependent vibrations of oxygen atoms in phosphates. In a time-experiment under abiotic conditions with ^{18}O enriched phosphate, we observed that the oxygen exchange rate increases with increasing temperatures from 100°C to 135°C . In a second set of experiments at 22°C , we added the intracellular enzyme pyrophosphatase from baker's yeast, which lead to a rapid oxygen exchange despite the high energy barrier of the reaction. Small increases of the cofactor concentration (MgCl_2) in solution translated into an increase in the enzyme-catalyzed exchange rate, highlighting the sensitivity of the instrument to monitor the effect of changing conditions in the analyzed system. These results show that Raman spectroscopy is a viable tool to measure oxygen isotope exchange between phosphate and water in real-time, offering a much faster approach compared to conventional methods, which require time consuming wet chemistry protocols prior mass spectrometric analysis. To our knowledge, this is the first study applying Raman spectroscopy to measure oxygen isotope exchange rates between phosphate and water under abiotic and biotic conditions, proposing a new method for future research in aqueous systems and maybe even in soils.

Theme 5

**The Development of Advanced Phosphorus
Analysis Methods**

Poster Presentations

P5.1

Can laser-induced breakdown spectroscopy be used as an accurate and fast method for determining total phosphorus in soils?

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Phosphorus (P) enrichment in agricultural soils can be seen as a valuable resource for future crop production in a global context of limited phosphate rock reserves, but it also poses the risk of P losses to surface waters. In order to improve the utilization of soil P, agricultural management strategies have to take into account P distribution in soil profiles as well as patterns of P accumulation in the landscape. Given the prospect of spatially differentiated soil and crop management for a more resource-efficient crop production, there is a great interest in mapping the P pool at a higher spatial resolution in fields. This calls for new, much cheaper methods of P determination than the conventional chemical methods.

As a spectroscopic method, Laser-Induced Breakdown Spectroscopy (LIBS) is a low-cost, rapid, and a potentially in situ deployable full elemental analysis that can be used to measure P directly in soil samples. However, LIBS has not been systematically tested for soil P analysis and has not gone beyond a proof-of-concept for P analysis, yet. The aim of this study is to develop a practical method for determining total soil P by means of LIBS. This includes a thorough evaluation of the sensitivity and reproducibility of the LIBS method for P analyses.

We will present the results of a comprehensive testing of LIBS for total P analysis in soils. A relevant set of several hundred soil samples from different Danish soil archives have been selected for this work. Subsets of these samples represent gradients of soil P in combination with gradients of soil texture either from the same field site or from different geologies in Denmark. Soil samples are analyzed for TP by a standard wet-chemical method (perchloric acid digestion) providing reference data. Calibration and prediction models for TP are developed with the help of chemometric methods based on measured LIBS spectra and reference data. We expect to obtain a good correlation between signal intensity and emission line ranges with total P concentrations. We also expect to be able to evaluate interferences with other elements in order to find the best spectral characterization of P for a representative range of agricultural soils. Overall, we expect that LIBS can be used as an accurate method for TP soil determination and faster than standard chemical methods.

Quantification of inorganic polyphosphates in activated sludge by ^{31}P NMR spectroscopy

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Phosphorus (P) is a limited resource ^[1], and this makes the recovery of P from waste water an attractive way to simultaneously reduce the P loading in the environment and increase the recycling of P. The development of new P recovery strategies from waste water treatment plants (WWTPs) requires knowledge of the detailed speciation of P through the WWTP, including both waste water streams and sewage sludge.

Inorganic polyphosphate with the general formula $\text{H}_2\text{PO}_3\text{-}[\text{PO}_3]_n\text{-H}_2\text{PO}_3$ is present in the activated sludge in WWTPs due to polyphosphate accumulating bacteria, and the quantification of inorganic polyphosphate is therefore of interest in the mapping of the P speciation.

Solution state ^{31}P NMR is often used for identification of organic P species in the environmental sciences and has earlier been used for identification of poly-P ^[2-4]. Solution state NMR advantageous with regards to resolution and NMR experiment time, but for environmental samples, the need for extraction leads to the risk of incomplete extraction or hydrolysis ^[3,5].

The objective here is to develop a method for extraction of activated sludge samples for ^{31}P solution state NMR, which precisely identifies and quantifies polyphosphate without hydrolysis of the polyphosphate during the extraction. Solid state ^{31}P NMR (SSNMR) is here used to study the efficiency of the extraction method for solution state NMR, as SSNMR directly probes the P species present and can give insight into the P speciation before extraction. Through a combination of solution state ^{31}P NMR and ^{31}P SSNMR polyphosphate we observe that polyphosphate is not hydrolyzed during extraction and that all polyphosphate in the activated sludge is extracted.

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P5.3

Carbonate effect on phosphate crystallization from polyphosphate

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Municipal wastewater sludge contains a significant fraction of condensed phosphates (polyphosphate) due to the action of polyphosphate accumulating bacteria (PAO's). In anaerobic digesters, the PAO depolymerize their polyphosphate stores as an energy source in this anaerobic environment. Polyphosphate depolymerisation consequently increases the dissolved inorganic phosphate concentration; as a consequence, struvite precipitation occurs. The possibility of precipitating carbonated calcium phosphate (apatite) minerals before the anaerobic digestion step with inorganic phosphate from the polyphosphate stores requires some understanding of the interactions between calcium, carbonate, and fluoride with polyphosphate anions.

Preliminary Raman spectroscopy and powder x-ray diffraction data suggest that there is a role for carbonate and fluoride in the depolymerisation of polyphosphate and subsequent formation of apatite. Carbonate ions may contribute an oxygen to the polyphosphate depolymerisation process, and fluoride may alter the interaction of calcium with the polyphosphate ion, facilitating its depolymerization. The preliminary Raman data that focuses on the energy changes in the different P-O bond energies of polyphosphates in different environments will be presented.

Development and validation of an analytical method for the determination of glyphosate, glufosinate, AMPA and 2-AEP in seawaters

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Phosphonates are a class of organophosphorus components including a C-P bond in their chemical structures, which makes them extremely resistant to thermal decomposition and chemical hydrolysis. Phosphonates comprise a significant fraction of the marine dissolved organic phosphorus pool. The presence of these substances in the environment can be derived from anthropogenic sources (e.g. herbicides, pharmaceuticals, etc.) or they naturally occur in different microbial taxa (e.g. phosphonolipids, antibiotic, etc.). Glyphosate and glufosinate are post-emergence, non-selective, broad spectrum herbicides intensively used in agricultural and non-agricultural areas. Aminomethylphosphonic acid (AMPA) is the most frequently detected metabolite of glyphosate in soil, water and plants. 2-aminoethyl-phosphonate (2-AEP) is a biogenic phosphonate which has been identified from many types of plankton feeders and marine invertebrates. The properties of these phosphonates such as low molecular weight, low volatility, thermal liability, and high water solubility make their analysis using gas chromatography (GC) and liquid chromatography (LC) very challenging, especially in the marine environment (i.e. low concentrations and complex matrices). In a previous work we developed a fast LC-MS/MS analytical method in order to study the presence of glyphosate and AMPA in the Baltic estuaries and their potential transport to the Baltic Sea. The data obtained clearly depicted the transport of both contaminants to the Baltic Sea. Concentration ranges observed were 28 to 1690 ng/L and 45 to 4156 ng/L for glyphosate and AMPA, respectively. However, the method is not sensitive enough for their determination in the Baltic Sea. Thus, we developed and validated a sensitive method for the analysis of glyphosate, glufosinate, AMPA and 2-AEP in seawaters. The method was based on LC-MS/MS after a derivatization (FMOC-Cl) and a pre-concentration step using solid phase extraction (SPE). Satisfactory validation parameters including linearity, precision, analytes stability, limits of detection and quantification were obtained.

A sensitive method in hand allows monitoring of the contaminants glyphosate, glufosinate and AMPA in the marine environment. Moreover, due to a lack of analytical methods for 2-AEP determination in several environmental compartments the method developed in our study can be considered as a baseline method which facilitates its identification and quantification in the marine environment.

P5.5

A microextraction method for the simultaneous determination of 20 organo phosphorous pesticides from marine water samples

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To protect crops from pests like insects, fungi and competing herbs pesticides are used worldwide. In contrast to the organo chlorine pesticide compounds such as DDT or Lindane which were applied globally in huge amounts after World War II and until the 1980ies, the group of organo phosphorous pesticides (OPP) exhibit less persistency in the environment and much higher toxicity requiring lower application dosage. Therefore, the OPP herbicides are considered as "modern" herbicides and, thus, comprise one third of the in Germany applied herbicides, i. e., more than 5,500 t of active substances sold in Germany were OPP, e. g., Tolclophos-methyl or Pirimiphos-methyl.

Spray off during application and run off after significant rainfall transfer the applied pesticides into surface water in which they have been occasionally detected throughout the world. Moreover, with surface water streams, pesticides may reach rivers and oceans, where they may exert their toxic properties to estuarine and marine organisms, too.

Throughout the last couple of years, sensitive detection methods for the quantification of pesticides and contaminants in matrices like soil, food and beverage were developed. In particular, for the analysis of environmental samples enrichment methods are of importance in order to detect analytes in sub trace levels.

We will report on the optimization and validation of a multi method for the simultaneous extraction and fortification of 20 OPP compounds from river and sea water based on ultrasound assisted liquid-liquid micro extraction with subsequent GC-MSMS analysis.

Investigation of soil legacy phosphorus transformation in long-term agricultural fields using sequential fractionation, P K-edge XANES and solution P-NMR Spectroscopy

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Understanding legacy phosphorus (P) build-up and draw-down from long-term fertilization is essential for effective P management. Using replicated plots from Saskatchewan, Canada, with P fertilization from 1967-1995 followed by either P fertilization or P cessation (1995-2010), soil P was characterized in surface and subsurface layers using sequential fractionation, P K-edge X-ray absorption near-edge structure (XANES) and solution ^{31}P nuclear magnetic resonance (P-NMR) spectroscopy. Legacy P from a 28-yr build-up was sufficient for 15 years of wheat cultivation, resulting in no significant differences in crop yield in 2010. In surface soils, soil test (Olsen) P decreased significantly in unfertilized plots compared with 1995, which was reflected in declining aluminum (hydr)oxide-associated inorganic P by fractionation and XANES. Furthermore, XANES analysis revealed a decrease of calcium-associated P in 2010-unfertilized soils at both depths and an increase of Fe (hydr)oxides-associated P in the 2010-fertilized and -unfertilized surface soils relative to the 1995 soils. Increased total organic P and orthophosphate diesters by P-NMR and accumulated inositol hexaphosphate by XANES were observed in surface soils with P fertilization cessation. In subsurface soils, few legacy P transformations were detected. These results provide important information about legacy P to improve agricultural sustainability while mitigating water quality deterioration.

P5.7

Characterizing phosphorus in snowmelt runoff from cattle winter bale-grazing sites in Saskatchewan Canada

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The feeding of bales of dry hay or straw over the winter to beef cattle spatially dispersed over annual cropland or pastures (i.e. bale-grazing) has become common practice on the Canadian Prairies, replacing confined winter feeding in drylot pens. In addition to saving producers the cost of spreading manure, it is assumed that the direct deposit of urine and feces will enhance soil fertility significantly. However, this practice also increases the risk of nutrient loss during spring snowmelt runoff while soils are still frozen, which is the main source of runoff on the Prairies. A five-year study was conducted in Swift Current Saskatchewan to determine the effects of in-field winter bale grazing on soil fertility and on snowmelt runoff, using 350 m² microwatersheds established in Russian wild rye (RWR) and crested wheat grass (CWG) pastures. These pastures were bale-grazed in alternate years, each for two years total, and were compared to controls with no bale-grazing or with fall-spread, unincorporated manure. Runoff samples were collected during each annual snowmelt event (spring 2009-2013), and were analyzed for total dissolved P, total particulate P and soluble molybdate reactive phosphate (MRP). Runoff samples were filtered within 24 h of collection, and P forms in dissolved and particulate samples from the first day of runoff for each year of the project were characterized with ³¹P-NMR spectroscopy. The number of runoff events per year, and average runoff volume, varied greatly from one year to the next. This in turn influenced nutrient loss in runoff. Dissolved MRP ranged from 0.5 to 7 mg L⁻¹, with no clear patterns related to the year of bale-grazing. Particulate P ranged from 0.2 to 2.8 mg L⁻¹, and was generally higher in the years with bale-grazing. Loss of MRP in runoff from fall-spread manure was often as high as for bale-grazing, but particulate P losses were lower. Particulate P contained a variety of P forms, including organic P forms of microbial origin, while dissolved P was predominantly inorganic phosphate, but annual variations were observed.

Suitability of methods for analyzing plant available P-fractions in digestates of biogas plants

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Digestates of biogas plants are used as organic fertilizers, but there is no standard method for the extraction and determination of plant available phosphorus in digestates. Various extraction methods for different phosphorus (P) species in different matrixes are described in literature. The total P content of soils and fertilizers is usually extracted by aqua regia, while plant available P fractions in soils and composts are extracted commonly by CAL (calcium-ammonium-lactate) and water. The German fertilizer ordinance recommends the extraction of fertilizer materials by NAC (neutral-ammonia-citrate) for determining plant available P-fractions. Digestates are comparable to composts rather than mineral fertilizers which leaves open the question of a suitable method to evaluate plant available P-fractions in digestates. In the presented study it was shown that the CAL and NAC-extraction methods extract P in the same order of magnitude (CAL: 19 g/kg DM (dry matter), NAC 21 g/kg DM, total P 22 g/kg DM), which indicates that both methods are comparable in their extraction force. Besides the extraction procedure, there are also different methods for the measurement of the P-contents in extracts available. The two most common ones are the colorimetric assay with P being determined photometrically as molybdate-blue-complex and by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry), respectively. The colorimetric assay tends to overestimate P-contents due to matrix effects during the formation of the molybdate-complex, some measurements of CAL-extracts showed up to 18 % higher P-contents than the determined total P-content. The sensitivity of the colorimetric assay against matrix effects in the presence of various metal ions such as Fe, Al, Mn, Ca, K and Mg is well-known. This made ICP-OES measurement the preferable method of analysis in this study as these minerals occur in significant amounts in digestates. Different extraction procedures have been employed and different methods of P determination were tested.

P5.9

Predicting plant available phosphorus – Is DGT better than classical soil analyses?

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Optimizing phosphorus (P) application is important both for efficient use of limited mineral P reserves and for limiting P losses to the watercourses. It has been claimed that classical soil extractions only provide a snapshot of a certain P fraction and do not reflect the soil processes that are active during plant P uptake. P supply to plant roots is dependent on both the rate of P release from the soil and the transport rate in the soil pores. Thereby, both chemical P characteristics and physical soil parameters, such as pore volume and pore size distribution, are important for P supply to plant roots. The DGT (Diffusive gradient in thin films) is aimed to mimic these soil processes by measuring the diffusive P supply.

Materials and methods

In Norway, the P-AL method (Egnér et al. 1960) is the standard test for agricultural soils. In a greenhouse trial with barley (*Hordeum vulgare*), 19 soils from 11 different sites were included. At three of the sites soils were collected from long term fertilizer trials. P-AL in soil varied from very low to very high (P-AL 1.6-23 mg P/100 g). Pots received 0 or 10 mg P kg⁻¹ soil given as triple superphosphate. Nitrogen and potassium (120 mg kg⁻¹ soil) were applied to all pots. Plants were harvested at start of heading. Response to P application was measured as total dry matter yield and P uptake in aboveground biomass. Response to P application and P uptake by zero P application were related to P-AL and DGT (48 hr. exposure) measurements.

Results

The crop response to P fertilization decreased with increasing P-AL and DGT concentrations. P-AL and DGT explained relative crop response equally well, with coefficient of determination (R^2) of 0.73 and 0.76, respectively. For 17 of the soils, P-AL and DGT were quite close related ($R^2=0.73$). However, when relating P-AL and DGT measurements to P uptake by zero P application, the DGT values were better predictors for P uptake than P-AL with R^2 of 0.77 and 0.17 for DGT and P-AL, respectively. The low R^2 for P-AL was mainly caused by two soils with a high yield level, probably caused by favorable physical soil conditions. The physical factors favorable for plant growth are maybe the same as those favorable for P diffusion, resulting in better fit for DGT than P-AL.

Conclusion

The classical soil extraction P-AL could predict the crop response to P application as well as DGT, even though the soil's ability to deliver P to plant roots was better reflected by DGT than by classical soil extractions.

Microdialysis of soil P: A means to mimick root uptake?

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Standard procedures to assess P availability in soils are based on batch experiments with various extractants. However, in most soils P nutrition is less limited by bulk stocks but by slow diffusion of phosphate through the soil solution. More comparable to the root's approach is to strip phosphate locally from the solid phase by lowering the soil-solution concentration, which can be achieved by establishing an infinite diffusional sink, e.g. by resins or the "diffusive gradient in thin films" (DGT) technique. An alternative diffusive sampling technique is microdialysis (MD), well established in pharmacokinetics. Briefly, this method uses miniaturized flow-through probes where the perfusate gets in diffusive contact to the external solution by a semipermeable membrane. It is quite evident, that important aspects of P supply to roots resemble MD sampling. This is not only the mostly diffusive transport and insignificant contribution of mass flow, but also an elongated capillary tube-like geometry of absorption. The diameter of typical commercial MD probes is around 500 μm . One additional inherent feature of microdialysis is the possibility to release low-molecular substances from the perfusate by diffusion into the matrix, such as carboxylates. However, MD has yet not been used for P in soils, possibly due to the challenge to analyze rather small samples with only trace concentrations of P. We tested MD in topsoils of an acid beech forest, of an unfertilized grassland and of a fertilized crop site. Three perfusates have been tested: 1 mM KNO_3 , electrolyte + 0.1 mM citric acid, and electrolyte + 1 mM citric acid. We observed rates of uptake into the probes in a range between $1.5 \cdot 10^{-15}$ and $6.7 \cdot 10^{-14}$ $\text{mol s}^{-1} \text{cm}^{-1}$ in case of no citrate addition which is very close to reported root-uptake rates. Surprisingly, these uptake rates were mostly independent of the bulk stocks. Citrate addition increased P yields only in the case of the non-acid crop site. The observed results could be reproduced by a cylindrical diffusion model with flow rates that are most sensitive to the adsorption coefficient. We conclude that microdialysis is a promising tool to complement existing P-analytical procedures, especially when spatial aspects such as depletion zones or topological synergisms between emitting and receiving structures are in focus.

P5.11

Phosphate-bound oxygen isotope ratio analysis: A new tool for the characterization of phosphorus cycling in anoxic groundwater

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The analysis of the isotopic composition of phosphate-bound oxygen ($\delta^{18}\text{O-Pi}$) constitutes a promising and innovative tool in the environmental sciences. Despite its increasing application, this approach has not been applied to anoxic groundwater so far. Anoxic groundwater with PO_4^{3-} concentrations exceeding 2 mg/L is a common feature of Holocene aquifers in Southeast Asia. In combination with traditional hydrochemical analyses, conclusions can be drawn regarding (i) the source and (ii) the intensity of the biological P turnover based on $\delta^{18}\text{O-Pi}$ signatures.

The aim of our study was to adopt existing protocols for $\delta^{18}\text{O-Pi}$ analysis (Gruau et al. 2005, Tamburini et al. 2010) to the special requirements of anoxic groundwater that is characterized by high concentrations of compounds interfering with the IRMS analysis (i.e., As , SO_4^{2-} , HCO_3^- , Cl^- , DOC).

To test our method, samples were collected from anoxic groundwater at a field site located in the Red River Delta in Vietnam. Dissolved PO_4^{3-} was fully separated from groundwater by co-precipitation with Fe hydroxides. Later, Fe precipitates were dissolved in diluted HNO_3 and PO_4^{3-} was precipitated as AMP for purification. In a next step, AMP was dissolved and the PO_4^{3-} precipitated in form of struvite. Struvite was then dissolved and filtered through an ion exchange resin before PO_4^{3-} was finally precipitated as Ag_3PO_4 , which was analyzed for $\delta^{18}\text{O-Pi}$ by Py-EA-IRMS.

The method proved reliable and prevented an isotopically fractionating loss of PO_4^{3-} during the elaborate sample preparation. $\delta^{18}\text{O-Pi}$ values determined for seven groundwater test samples range from $+14.5 \pm 0.1$ to $+16.8 \pm 0.3$ ‰VSMOW. Resulting $\delta^{18}\text{O-Pi}$ signals are slightly overlain by traces of As in the final Ag_3PO_4 precipitates. Although the method requires further fine tuning, our study constitutes a successful proof of concept and will serve as a solid base for further investigations related to the cycling of P in anoxic aquifers.

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Phosphorus extraction from various environmental and biological materials

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This presentation has two major goals: the introduction of an easy and robust method to convert all phosphorus compounds into phosphate (as well as all nitrogen into nitrate). The second aim is a presentation of quality management tools, as they were used abundantly in this method evaluation study. These are determination limits of the whole procedures, not only the final quantification step. A control chart system is further recommended as it is used in all environmental agencies to record blanks, standards and replicates.

The sub-boiling digestion procedure at 90°C (Huang & Zhang 2009) turned out to be very reliable, easy to manage, low-cost and as a high throughput method to digest various materials. This result is good news especially to all laboratories, which cannot afford laboratory microwave systems. The digestates can be investigated further with any method wanted. The digestate is clear and without discoloration if an acid is used in combination with an oxidation agent. Digestates in nitric acid cannot be measured by the molybdenum blue method.

The digestion is easiest in combusted material (450°C for 4 h), but may be effective in dry matter also (first results). Samples must be neutralised for storage, but do not need to be filtered as long as they are measured manually (not by flow analysers).

P5.13

Using extended X-ray absorption fine structure (EXAFS) spectroscopy at the phosphorus (P) K-edge to determine the local atomic environment of P in bonechar

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Bonechar is usually produced by pyrolysis of animal carcass. This material is not only important from an agricultural point of view, under which it can serve as an important source of phosphorus (P) to plants, but also from an environmental standpoint as its production reduces environmental liability arising from animal carcass disposal.

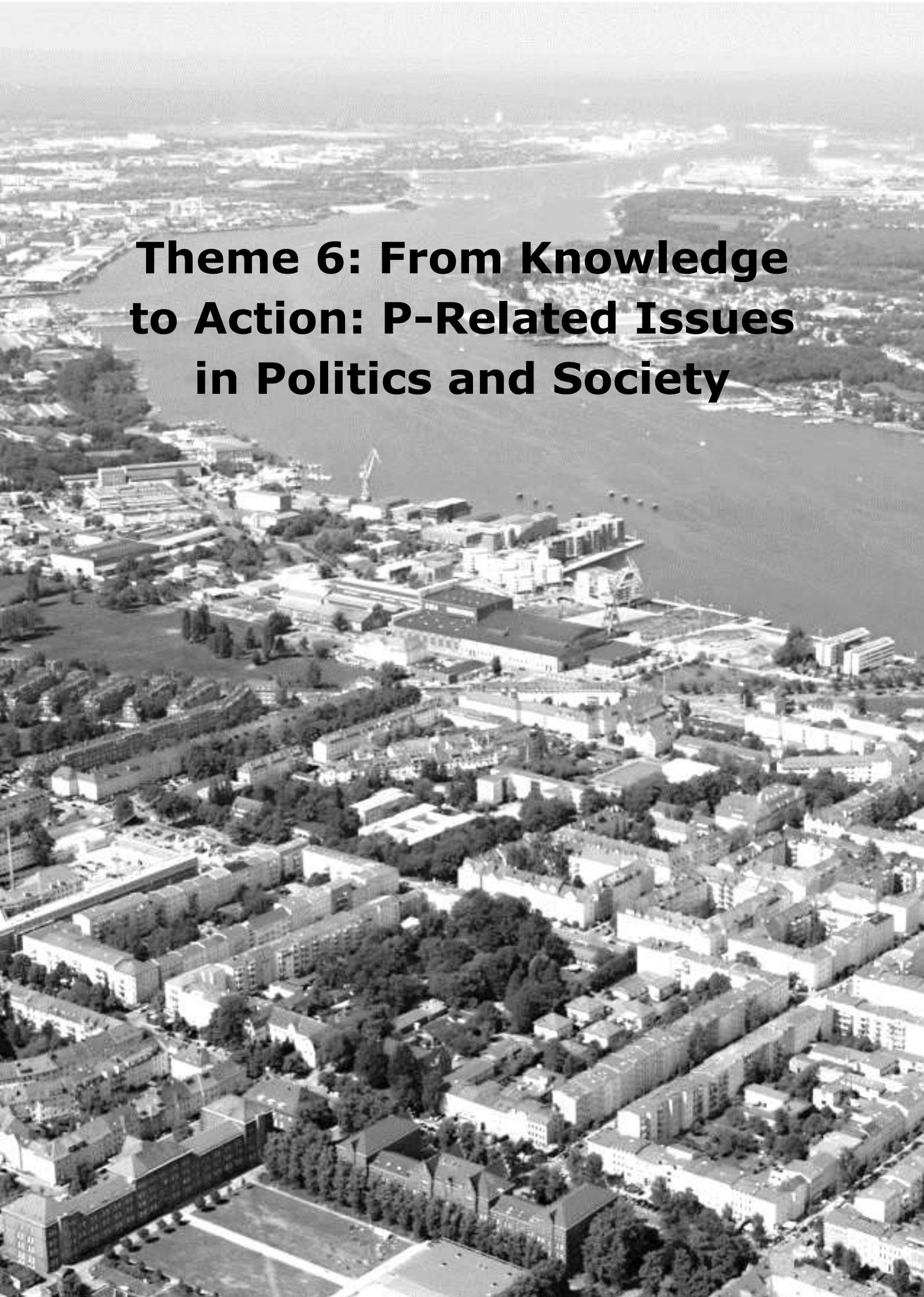
Biological apatites, like bone, have a smaller crystal size, more carbonate substitutions and a significant OH deficiency, overall resulting in greater solubility in comparison with its counterpart geological apatites (Zwetsloot et al., 2013). Because of the high temperatures to which bones are subjected during pyrolysis for bonechar production, it follows that significant modifications in the chemical and physical structure of bone occur. The end products usually vary in crystallinity, abundance of Ca and the way the later coordinates with PO₄ in the mineral lattice. Important thought the coordination of PO₄ with Ca is in these materials, as it implies changes in solubility, this information has been overlooked, presumably, due to the lack of availability of techniques capable of directly accessing the local coordination environment of such light elements. Therefore, improving our understanding on how pyrolysis temperature and feedstock source affect bonechar crystallinity and Ca-PO₄ coordination can be advantageous for the production of more effective P fertilizers.

EXAFS spectroscopy is a powerful analytical technique that can provide direct detailed structural information on the local environment of an atom.

To date, the use of P-EXAFS spectroscopy has been limited to the determination of the bonding configurations of P at the mineral/water interfaces (Abdala et al., 2015a, b). We, however, showed a novel use of such a powerful technique to determine what the changes in the local atomic environment of P in bonechar were as a function of pyrolysis temperature, either at T= 550 or 800 °C.

Even though mineral crystallinity, based on XRD analysis, varied little between the two materials, P-EXAFS analysis showed changes in Ca-PO₄ coordination in bonechar when pyrolysis temperature was raised from 550 to 800 °C.

Our results proved P-EXAFS spectroscopy being a promising technique to assess the local coordination environment of PO₄ in natural materials exhibiting a high degree of heterogeneity such as bonechars.

An aerial, black and white photograph of a city, likely Oslo, Norway, showing a dense urban area with numerous buildings and a large body of water in the background. The text is overlaid on the upper portion of the image.

**Theme 6: From Knowledge
to Action: P-Related Issues
in Politics and Society**

Theme 6

From Knowledge to Action: P-Related Issues in Politics and Society

Oral Presentations

Responsible scientist: Felix Ekardt (University of Rostock and Research Unit Sustainability and Climate Policy)

Keynote Speaker: Susanne Stoll-Kleemann (University of Greifswald, Germany)

This session examines the policy measures and societal changes that promote or prevent a sounder, more informed use of phosphorus. So far, P supplies have been addressed in tentative proclamations rather than in legally binding measures. However, traditional regulatory measures focusing on single actions, i.e., the command-and-control approach, are unlikely to suffice as solutions to resource and environmental problems. Instead, P problems are more appropriately viewed as quantity-related. Additional economic instruments will be needed to avoid enforcement deficits, prohibit rebound and shifting effects, and promote recycling while decreasing P consumption. Whether policy measures, including economic instruments, will contribute simultaneously to solving environmental problems regarding land use, resources, biodiversity loss, and climate change remains to be seen.

Keynote Abstract:

Meat consumption, human behavior and phosphorus

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High meat consumption is linked to unsustainable inputs of phosphorus as a major fertilizer to grow feed crops which cover 60-70% of all agricultural land. For example since the “nutrient and livestock revolutions” the use of phosphorus has tripled. The worldwide demand for meat and further animal-based products will increase over time due to continuing prosperity in industrialized countries and further demographic and economic growth in developing and transition countries like China. To meet this demand, intensive agriculture based on large inputs of phosphorus fertilizer with its ongoing multiple negative impacts on the environment (such as eutrophication and deoxygenation of the sea) seems necessary.

Based on this issue, we argue that – together with minimizing food wastage – a reduction in meat- and dairy-product consumption has the potential to reduce the negative consequences of phosphorus accumulation significantly together with further problems for human beings and nature (e.g. health problems, food insecurity, climate change, biodiversity loss and deforestation).

Our research includes an analysis of possible avenues to reduce the production and consumption of animal products predominately in industrialized countries. We present the outcomes of a systematic meta-analysis of over 140 studies about economic and psychological mechanisms, which could become suitable leverage points for this change in production and diets.

Results indicate that the deep cultural integration of animal products in the majority of human diets, low prices for animal products, as well as cognitive dissonance - the unconscious denying of uncomfortable facts in order not to change habits or to admit grievances - are factors regarding the reduction of animal-product consumption.

We suggest that political and economic measures (by internalizing environmental and social costs or by abolishing existing subsidies) are of paramount importance to give animal-based food their true production prices. Furthermore, expanding the infrastructure for a plant-based diet, including appropriate nudges as well as educational measures are essential tools to increase people’s awareness for this issue of concern. Overall, all measures should foster the reduction of animal-product consumption to a level consistent with planetary boundaries.

EU regulatory and policy objectives relevant to sustainable agricultural land and phosphorus use

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Feeding the growing world population in the future and saving the natural resources base is one of the main future challenges. Agricultural systems are highly dependent on scarce and qualitative worsening mineral P resources from phosphate rock. At the same time, we are confronted with a proceeding biodiversity loss, ongoing soil degradation and the effects of global climate change for which agriculture is one main contributor. The ever growing pressure on natural resources through intensive land use and the reliance on fossil fuels is at the core of these closely interlinked problems.

Within EU Environmental policy a set of more than 60 specific legally binding targets and almost 70 non-binding objectives in the different environmental policy areas subsist. Many of those objectives are closely related to the challenge of disrupted nitrogen and phosphorus cycles. Whether EU goals such as reaching a "good ecological status" for water bodies by 2015 or halting biodiversity loss by 2020 or net land take until 2050 will be achieved, largely depends on the development of agriculture, being one of the main polluters in many sectors of environmental legislation. These EU objectives and targets, are currently starting to raise significant pressure on national policy makers: some of the goals set for 2015 have not been achieved, the 2020 deadlines are approaching quickly.

Taking a critically reflected closer look at those normative guidelines set by EU environmental legislation and policy and their legal status will help us to understand, within which normative framework agricultural land use needs to evolve if those goals and targets are taken seriously, which limits for further intensification of agriculture arise and thus, which government strategies have to be combined – like efficiency and sufficiency strategies – to foster the development and support of an effective P governance.

Changing animal food consumption as part of phosphorus regulation?

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While livestock production is land and emissions intensive, global meat and dairy consumption is still on the rise. Using arable land for feed stuff strongly contributes to various environmental and resource problems such as soil degradation, biodiversity loss, water pollution and climate change as well as further issues which are among others related to P. Our presentation will analyze whether regulating meat consumption might be part of effective P regulation through the backdoor. Regulating animal food consumption and/or production however raises complex questions for basic human rights like freedom to choose one's dietary habits or economic rights. We will focus on economic instruments on EU level, starting with Common Agricultural Policy (CAP). Beyond existing policy frameworks, alternative economic incentives will be discussed including those aiming at regulating meat consumption through demand and production. It will be analyzed how economic instruments aiming at sufficiency could work and where leverage points for consumption could be. Market instruments will be considered, which raise prices for a key resource for example land use, P by itself or CO₂ triggering changes in food supply, food prices and consequently consumption patterns. It will be shown that it is possible to regulate P issues as well as other environmental problems by addressing animal food consumption. Finally, we will shortly compare this to nudging approaches, so far mainly considered in public health programs, as options for incentives towards a certain diet. From the methodological point of view, our contribution is based in governance analysis.

What influences the achievement of optimal soil P status at farm level?

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The Republic of Ireland was one of a minority of EU member states to include direct controls on phosphorus (P) fertilisers in its EU Nitrates Directive National Action Plan, first introduced in 2006. Total allowable chemical P fertiliser application limits are based on soil P status and crop demand with reductions for any organic manure P or concentrate animal feed P imported. The Teagasc Agricultural Catchments Programme (ACP) now into its third phase (2007-2019) is involved in the on-going evaluation of the effectiveness of regulations introduced under the EU Nitrates Directive across the Republic of Ireland. The ACP works with 300 farmers across six case study catchments (generally 6-10 km²). This paper uses soil P data from 2 soil censuses, 4 year apart (2008-09 and 2012-13), to examine changes in soil P status across a cohort of farms participating in the ACP. The analysis will explore whether farmers are moving to a more optimal soil P status based on results of the 1st and 2nd soil census. Additionally, the research explores the effect of farm system, contact with agricultural advisors, environmental and management factors on the achievement of optimal soil P status.

German fertiliser legislation: current and future rules on phosphorus

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With a surplus of only 2 kg P/ha*a, the German national phosphorus balance is almost in equilibrium (van Dijk et al. 2015), comparing to neighboring countries like the Netherlands (22 kg P/ha*a) or Belgium (23 kg P/ha*a). However, in regions with a high density of livestock production, e.g. in the northwest of Germany, P surpluses can reach 20 kg P /ha*a and more. During a concentration process of several decades, P from animal liquid manure accumulated in soils of this region (Tóth et al 2014, Römer, 2014).

The current fertilisation ordinance allows a surplus of 8,7 P/ha*a on farm level. In the ministerial draft for an amendment of this ordinance (2015), this surplus shall be reduced to 4,4 P/ha*a. According to the expected new regulation, a certain P-surplus will still be tolerated, although fertilisation on soils oversupplied with P shall not exceed plant needs. Present and future regulation do not stipulate sampling and analysing plots smaller than one hectare, so the rules only apply to larger plots.

Additional legal provisions have been adopted on Federal State level (especially Lower Saxony, North Rhine-Westphalia) in order to improve regional, supra-regional and transnational control of animal manure transport. Insights into interregional manure transports will be presented as well as predictions on the increase of manure exports after amending the fertilisation ordinance.

However, all these measures do not aim at a sustainable use of P from animal faeces. Since 2014, P is listed by the European Commission as a critical raw material which should be used economically. In the short term, the input of P in regions with intensive animal husbandry and thus high soil P concentrations could be reduced, and more P could be exported to arable farming regions in need of P. A further concentration of animal production in the hot spot-regions should be counteracted i.e. by means of building permissions based on building law and immission control legislation.

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Strategies for mitigating China's phosphorus resource crisis

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More than 80% of global phosphorus (P) mining occurs for the production of P fertilizers. Consumption of P chemical fertilizers in China has exceeded 12.5 million tons P_2O_5 per year since 2008, representing a third of the global total. The future needs of China's agriculture industry are anticipated to remain at least 10.5 million tons of P fertilizers annually to maintain an adequate level of average soil Olsen-P and meet the demands of grain production. The depletion of P will fundamentally impact China as well as the world. We can take the following precautionary measures to reduce consumption of P fertilizers and preserve P as a necessary resource: (1) adjusting the structure of P fertilizers and rationing the use of middle-grade and low-grade P resources; (2) reusing one-third of P from these organic resources in agriculture can replace 4.85 million tons of P fertilizers; (3) reducing the use of P fertilizers for paddy fields of China. 20 mg P kg^{-1} of soil Olsen-P content is enough to maintain high rice production in paddy soils. Chinese paddy soil accounts for 22% of China's total cultivated land area, and this can save 1.16 million tons of P fertilizers. With these measures, the future demand for P fertilizer in Chinese agriculture can be reduced from 10.50 million tons to 4.49 million tons annually, with a concomitant approximate reduction in consumption of P mining from 60 million tons to 30 million tons. P depletion can be postponed based on the China's current resources of P.

Theme 6

From Knowledge to Action: P-Related Issues in Politics and Society

Poster Presentations

P6.1

Phosphate rock – The chance and need for zero waste activity

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The intense scientific discussions have highlighted the urgent need to further develop strategies for sustainable efficient use of phosphorus. These issues are currently focused on the local to national scale (e.g. responsible use of phosphate fertilizer to avoid unnecessary pollution to soils and waterways). However, it does not reveal the 'true' global sustainability issues with regard to phosphorus, as much of the phosphate fertilizer in European countries is derived from overseas export markets, and this part of the chain of phosphate from source to sink remains oblique with respect to its inherent sustainability.

The 'greener' concept of total resource utilization, comprehensive extraction, zero waste activity (i.e. the idea to use the entire of a mined material) maybe achievable to improve the environmental credibility of phosphate fertilizer used in Europe. Among the primary resource phosphorus, phosphate ores and in particularly sedimentary phosphate ores contain a number of valuable impurities, namely rare earth elements (REE) and uranium (U), in relevant concentrations. At present, without extracting REEs and uranium during fertilizer production process results in these elements accumulating in the final fertilizer product (phosphor-gypsum tailings). As a consequence, these valuable resources are lost and may have subsequent disadvantages effects on our environment. The two largest phosphate producers in Guizhou province (China): Wengfu Group and Kailin Group have now realized the potential for zero waste phosphate rock mining and subsequently started tailings processing with the final goal of achieving zero phosphogypsum accumulation by 2025. This work highlights the motivation behind the planned zero waste phosphate rock processing activity in China and discusses to what extend such a process may be favorable for phosphate rock producers elsewhere.

Most large European countries do import phosphate for the fertilization of agricultural crop production. The best current estimates for Germany indicate 114-228 ton U yr⁻¹ applied to German agricultural land during the 60 years (equivalent to ca. 1 kg U ha⁻¹). Based on agricultural land area and national fertilizer information available, it can expected that similar amounts of U are annually added to agricultural soils in the United Kingdom, possibly even more in France and Spain. These initial rough estimates clearly highlight the need and potential for U (and REE) recovery from phosphate rocks at the European scale.

On the potential of mussel farms as nutrient retention measure in an eutrophied lagoon

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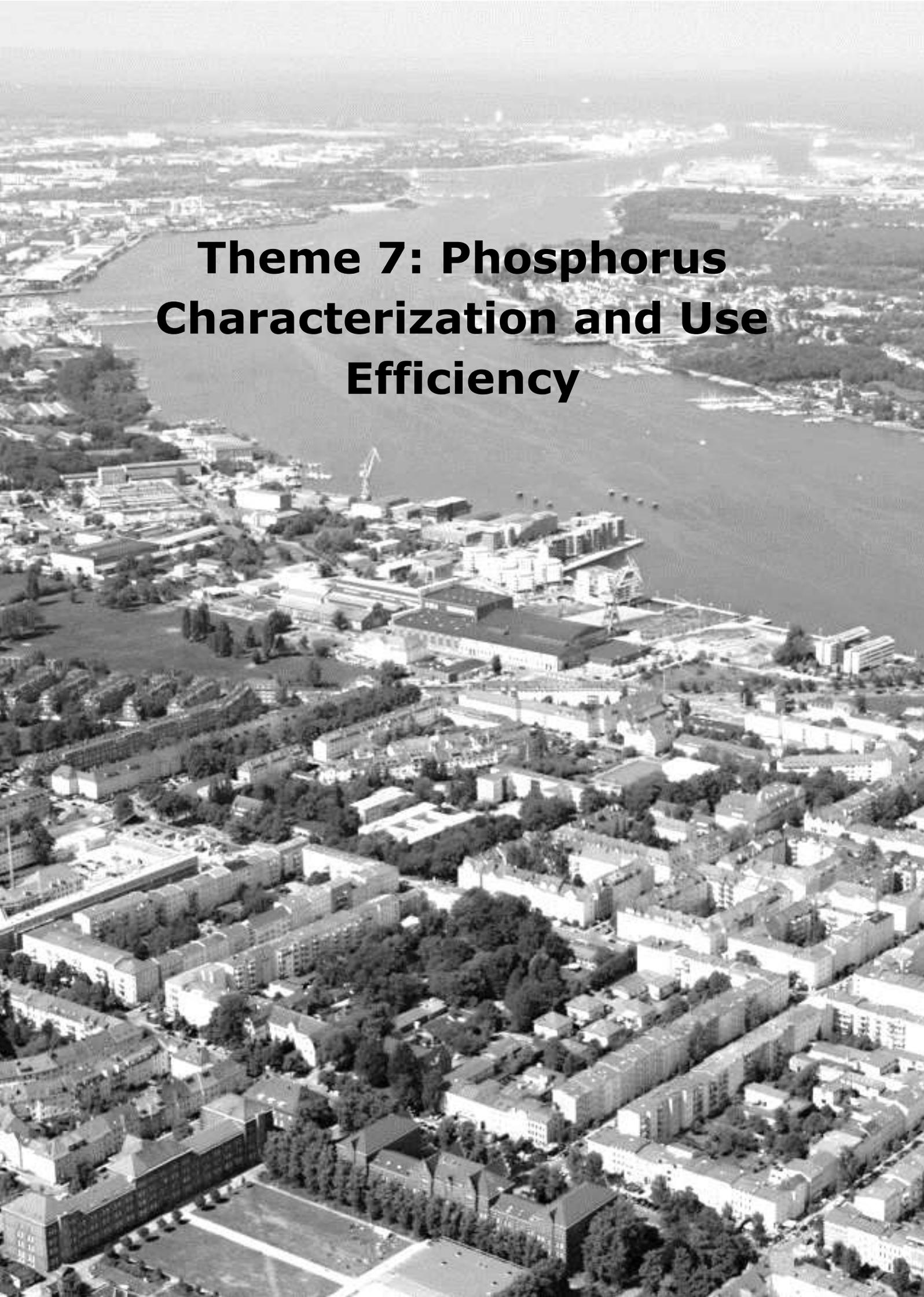
Many coastal waters like Szczecin Lagoon are highly eutrophied and characterized by high amounts of Phytoplankton and dissolved inorganic nutrients. Since the eutrophication is mainly caused by high nutrient loads from land, their reduction was seen for a long time as the best measure to increase the water quality. But exceptions exist, that do not show an improvement of water quality although nutrient loads were reduced, e.g. the Small Bay of Szczecin Lagoon. Instead a combination of load reductions and sea-based measures seem necessary to achieve the Good Ecological state like it is defined in the Water Framework Directive. Mussel farms are seen as one possible sea-based measure to increase the internal nutrient retention and enhance the removal of biomass, if the mussels are harvested. First estimates by Schernewski et al. (2012) have shown, that per year up to 1000 t of Nitrogen and 70 t of Phosphorus could be removed from Szczecin Lagoon. By combining economic, social and ecologic aspects this removal can be further optimized to bring the removal to a (theoretical) carrying capacity. Therefore, a broad bench of modeling and observations is conducted in Small Bay of Szczecin Lagoon, showing promising results with respect to the filtration by mussels, as well as problematic aspects like the increase of Phosphate-concentrations in the sediments below a test farm in Lake Usedom. To achieve a permanent improvement of water quality mussel farms could be potentially used to improve the growing conditions of submerged macrophytes.

P6.3

Phosphorus-related services of sediments in German coastal seas - Aspects of the SECOS project

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Mostly, marine sediments are the main locations of modification and accumulation of input into coastal and marginal seas. So far, their key positions as central reactors in land-sea interaction are insufficiently studied and assessed. In the joint project SECOS, distribution and quantitative relevance of sedimentary services in the range of the outer coastal waters of the German Baltic are mapped and modeled including projection of future scenarios. A major aim is, to advance the development of management tools and to support political and administrative planning processes along the European Marine Strategy Framework Directive (MSFD), in order to combine an optimal economic use of the coastal sea with the sustainable conservation of its natural structures and functions, thus contributing to Ecosystem Approach to Management (EAM). Looking at the nutrient fluxes and exchange processes at the sediment-water interface, phosphorus represents a key compound influencing the water body with consequences to its ecological state. In SECOS, new water quality targets were proposed for German Baltic waters, including phosphorus. These recommendations are based on a modeling approach combining the river basin flux model MONERIS with ERGOM-MOM, a three-dimensional ecosystem model of the Baltic Sea. Information about the spatial distribution of different phosphorus species is incorporated into the Baltic Sea Atlas, the central project output.

An aerial, black and white photograph of a city. A large river flows through the upper half of the image. In the foreground and middle ground, there is a dense urban area with many buildings, interspersed with trees. A large industrial or port area is visible along the riverbank, featuring several large buildings and cranes. The background shows a hazy cityscape extending to the horizon.

Theme 7: Phosphorus Characterization and Use Efficiency

Theme 7

Phosphorus Characterization and Use Efficiency

Oral Presentations

This is an additional session with selected Abstracts from other topics. It is being held to respond to the overwhelming number of submitted Abstracts for oral presentations.

Organic phosphorus forms in Baltic Sea sediments

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An ecologically important pool of phosphorus in the Baltic Sea surface sediment is bound to organic matter. During sediment diagenesis, a share of organically bound phosphorus is mineralized, and dissolved phosphorus is recycled to the water column, while the other share is present also in older sediment layers and thus apparently resistant to degradation. However, methods to identify and quantify different organic phosphorus forms are limited.

We have applied newly developed methods to specifically detect three different organic phosphorus forms in accumulation sediment profiles from different parts of the Baltic Sea; P bound into DNA, lipids, and as inositol. The concentrations of these organic phosphorus forms varied between 2 to 6% of the total phosphorus content in the surface sediment. In general terms, all three organic phosphorus forms declined in concentration with increased sediment depth, indicating a labile character of these P forms, and thus representing a significant contribution to the pool of P to be recycled to the water column.

The long-term storage of phosphorus via vivianite formation in iron rich surface sediments is prevented by nitrate

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It is known for a long time that nitrate can have a similar function for the binding of phosphorus (P) in lake sediments as the presence of molecular oxygen. In lake management, it is crucial to define and to quantify the role of nitrate for internal P cycle at different geochemical settings. A key function of the effect of nitrate is assigned to the sedimentary inventory and mobility of iron (Fe). In a laboratory experiment with sediment cores it has been tested, how their P uptake capacity is changing at oxygen-free conditions in dependence of the sediment Fe content with and without the presence of nitrate. An Fe poor sediment of Lake Langer See, Brandenburg, Germany, was amended by ferric iron (FeCl_3) to adjust different iron contents (12, 28 and 68 mg Fe/g dw). These cores were incubated in comparison to two additional lakes differing in their natural sediment iron content, being Lake Tegeler See with 33 mg Fe/g dw and Lake Müggelsee with 63 mg Fe/g dw. The P uptake capacity was realized by constantly adding P to adjust a P concentration of 2 to 10 mg/l in the sediment overlying water. The cumulative P uptake of sediment depended mainly on its iron content. The artificial iron addition compensated the nitrate effect since enough iron for P binding was still available under anaerobic conditions. However, different mechanisms contributed to the P uptake of sediment: In the presence of nitrate, added P was mainly bound to reducible Fe (BD-P), whereas, without nitrate a considerable proportion of P was detectable as NaOH-SRP. In the absence of nitrate, during earlier sediment diagenesis vivianite could be formed since (1) the addition of Fe shifted the molar S to Fe ratio from 2.5 to 0.5, and (2) Fe^{2+} was available at the sediment surface in high concentrations. The laboratory experiments show that nitrate can stimulate the temporary P binding onto oxidized Fe. But it becomes also obvious that nitrate can prevent the possible formation of vivianite by keeping the iron oxidized. Consequently, low iron contents diminish the nitrate effect because of missing potential P binding sites, whereas high iron contents of the sediment determine the P uptake independent whether nitrate is present or absent at the sediment surface.

Inefficiencies associated with phosphorus fertilization of a grazed pasture system

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For sustainable agriculture it is important that P fertilizer inputs are managed to optimize productivity and economic return with minimal environmental impact. The finite nature of the world's phosphate rock reserves also demand that P fertilizer be used as efficiently as possible, as P is a key nutrient that underpins global food security. The P-balance efficiency, fate and distribution of P applied to soil was measured in a grazed temperate pasture system in Southern Australia, where accumulation of P in soil is the major inefficiency associated with fertilizer use. Clover-based pastures were fertilized annually from 1994 with soluble P fertilizer (mainly triple-superphosphate) to achieve levels of soil P fertility that were either 'near-optimum' for maximum pasture growth or where the system was deliberately 'over'-fertilized, along with a non-fertilized control. Systems were grazed by sheep at different set rates of stocking. From 1994 to 2006, P balance studies (based on cumulative inputs and outputs) across the grazing treatments indicated that 89-93% of the P applied as fertilizer was retained within the systems. Between 2001-2006, where the soils were maintained at near-constant levels of 'plant available' P, as determined by soil test P (STP), 83-88% of the annual fertilizer inputs in the optimal-fertility treatment (average input of 9.5 kg P/ha/yr) accumulated in soil. This was confirmed by sequential extraction of soil P fractions, where on average 72%, and 16% of the total P applied as fertilizer was recovered in the 0-10 and 10-20 cm layers of surface soil, respectively. Within the extracted fractions, 33 to 37% of the recovered P over the top 20 cm was in inorganic forms and on average 37% in organic forms, with the remainder occurring in the residual P fraction. The accumulated inorganic P was predominantly associated with the NaOH extractable fraction and for organic P in the NaHCO₃ fraction. Across all P treatments, net accumulation of P in the soil was not influenced by sheep stocking rate, but was higher in systems maintained at higher STP concentration. This indicates that development of plant species and systems that are able to yield well at lower levels of STP concentration will accumulate less P and thus be more P-efficient. Soil managed with lower STP concentration will also carry lesser environmental risk because P losses (i.e., by runoff, leaching and erosion) are strongly related to the STP concentration of the soil.

A complementary set of methods to characterize P availability from fertilizers of varying origin and solubility

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Due to the limitation of global phosphorus (P) reserves, recycling fertilizers produced from heterogeneous P-rich biowastes such as sewage sludge, slaughterhouse waste or animal manures will become increasingly relevant. Various waste treatment processes further increase the diversity of products. Standard extractions to predict P bioavailability in fertilizers and soils have often been developed and calibrated for a limited range of substrates. It is therefore needed to assess the accuracy and predictive power of P tests on a wider range of P-rich substrates, including conventional and recycling fertilizers.

We investigated a set of complementary approaches to characterize fertilizer P availability. Using standard methods of fertilizer analysis (H₂O, 2% formic acid, 2% citric acid and neutral ammonium citrate extractions) in combination with comparatively new approaches (diffusive gradient in thin films (DGT), depletion-induced desorption of P from fertilizer, and imaging of P diffusion in soil from granulated fertilizer), more information about the characteristics of P fertilizers is expected to be gained than with standard extracts alone. The method evaluation was conducted on 13 P fertilizers of contrasting origins and solubility, with a 6-week pot trial (*Secale cereale*) in a carbonate-free soil (pH H₂O=6.8) as reference.

The range of P availability in the fertilizer test set was wide and homogeneously distributed. While the sewage sludge biochars performed worst, chicken manure and struvite (magnesium ammonium phosphate) were as efficient as conventional superphosphate. The DGT method explained nearly 90% of variance in plant growth (Mitscherlich equation fitting) while the coefficients of correlation between plant growth and P extracted by standard extracts were much lower. Implemented in combination with chemical imaging, these extracts could nevertheless help understand and predict the P release dynamics from granulated fertilizer.

Overall, our results indicate the potential of a selected set of complementary methods to characterize highly contrasting P fertilizers and to help optimize their use in agriculture.

Soil phosphorus tests compared on established European long-term trials: which test is the winner?

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A variety of tests for available soil phosphorus (P) is used worldwide, each with a historical and local background. The test ranging from intensity based ones, indicating P solubility to quantity based ones, i.e. near complete total soil P extraction.

A study was set up to identify the most suitable soil P test in a fully comparative way by using the same set of soils of contrasting fields on a set of soil P tests. The requirement for this is to find P response trials in which various fertilizer responses are only related to varying P doses. Soil samples (n=254) were collected from the plough layer of 12 fields complying to these conditions. The soils were collected from the field or from archived soil collection and were gathered in Belgium (2), France (3), Germany (1), United Kingdom (5) and Sweden (1). In all these fields different P fertilisation doses during several years (3-123 years) resulted in differences in soil P status and a significant P response in all 12 fields, sometimes for different crops per field. The relative response, i.e. the crop yield relative to that in highest P rate, ranged between 6.5 and 107.1%. Soil P availability was measured in the 254 gathered soil samples by different methods: (1) extraction with ammonium lactate and acetate at pH 3.75 (Egnér et al. 1960); (2) extraction with 0.5 M NaHCO₃ (Olsen et al. 1954); (3) extraction with 0.01 M CaCl₂ (Houba et al. 2000); (4) extraction with ammonium oxalate (Schwertmann 1964), with possibility to calculate the phosphate saturation degree (5) diffusive gradient in thin film technique (DGT) (Degryse et al., 2009). For each method, the relative yield, i.e. the obtained yield divided by the maximum yield observed on the same field, was plotted versus the measured soil P availability. A Mitscherlich curve was fitted on all data and on the data of every field separately. The "critical soil P availability" was defined as that concentration related to 95% relative yield.

The best soil P test was determined based on several indices: R² of the Mitscherlich curve, coefficient of variance (CV) of the field specific critical values, CV of the crop type specific critical value, the amount of fault positive or fault negative results included. The performances of the tests are approximately equal and differences between the soil P tests are minimal. A more detailed statistical analysis still need to be done, and the results of this analysis will be presented during the conference.

Placement of P and N to improve crop nutrient acquisition and yield: a meta-analysis

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In farming soils, plant-available phosphorous (P) and nitrogen (N) may be insufficient for crop production although total P or N concentrations are high. Therefore, P and/or N fertilizer is commonly applied to field soil by broadcast although broadcast does not ensure that a significant part of applied fertilizer is available for optimal root uptake. Fertilizer placement in soil, which refers to precise application of specific fertilizer formulations close to seeds or plant roots to ensure high nutrient availability, may be a more effective alternative to broadcast application. With focus on P-nutrition, our objectives were: (1) to compile existing techniques for fertilizer placement in soil; and (2) to quantify the relative effects of subsurface fertilizer placement to fertilizer broadcast on crop performance. We reviewed literature on fertilizer placement and performed a meta-analysis according to baseline contrasts on the relative effects of fertilizer placement to fertilizer broadcast on yield, nutrient composition of plant parts and on nutrient uptake. For the meta-analysis, we used 1022 datasets published in 40 field studies from 1982 to 2015. Results revealed that fertilizer placement led to 3.7% higher yield, 3.7% higher concentration of nutrients in plant parts and 11.9% higher nutrient uptake than fertilizer broadcast. For urea+phosphate, ammonium+phosphate, urea, ammonium and soluble phosphate uncombined, fertilizer placement of led respectively to 27.3%, 14.7%, 11.6%, 3.8% and 0.0% increase in yield in comparison to broadcast. Increase in relative yield and relative nutrient uptake from subsurface placement of urea, urea+phosphate, ammonium or ammonium+phosphate to increase with increasing placement depth down to more than 10 cm. Effects of placing of sparingly soluble alternative P fertilizers combined with ammonium or urea in subsurface soil has been hardly investigated and remains unknown. Results show that deep subsurface placement of ammonium (\pm P) or urea (\pm P), solid or liquid manure is more effective to improve nutrient uptake and yield than broadcast.

Re-evaluation of phosphorus fertilizer recommendations based on meta-analyses of long-term field experiments

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Phosphorus fertilizer recommendations in most European countries are based on plant available soil P contents which are assessed using various extraction procedures. The interpretation of these soil P contents in terms of soil fertility classes is based on the yield increase which has been observed in long-term field experiments. This traditional scheme has resulted in excessive P fertilizer recommendations in the past decades, causing widespread diffuse P losses and eutrophication problems, and excessive exploitation of geological P resources. Moreover, in this approach site and soil specific conditions are accounted for only inadequately. In a recent meta-analysis of long-term fertilizer experiments throughout Germany, using a novel approach of data mining, classification and regression tree analysis and various soil and site parameters, we showed that P fertilizer rates based on these traditional recommendation schemes often failed to result in adequate yield increases, and thus, were in general too high (Kuchenbuch & Buczko 2011). In the ongoing "InnoSoilPhos" project, this novel approach is being expanded and refined by including a much larger database of P fertilizer experiments from all over Germany and additional relevant site and soil parameters which have probably an impact on the adequate P fertilizer rates. The previous database of long-term P fertilizer experiments has been enlarged and comprises about 5000 data sets from about 11 field experiments in different soil and climatic zones throughout Germany. The data encompass all five soil P content classes and all crop types which are relevant in Germany. Statistical evaluations using various classification and regression tree approaches, multiple linear and nonlinear regression analysis and mixed models indicate that besides soil phosphorus content and fertilizer amount, the type of fertilizer, soil texture and soil organic matter content have a large influence on the effectiveness of phosphorus fertilization. In a next step, those results will be utilized to modify and specify existing practical phosphorus fertilizer recommendations.

Distribution of phosphorus-containing colloids in shallow groundwater from a small agricultural catchment as revealed by the combination of ultrafiltration, ultracentrifugation, ICP-MS and XANES data

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Colloids (1~1000 nm) are major phosphorus (P) carrier phases in soil solutions. Their size and composition is therefore essential to understand the transport of P in soils, as is important to unravel what are the factors and processes that control the composition and spatio-temporal distribution of colloids in soils at catchment scale. Most studies developed so far on the role of colloids in P transport in soil solutions have, however, focused on lab extracts and it is still unclear whether lab extracts and natural soil solutions fit well each other with respect to P speciation and colloidal P composition.

Here, we compared the P speciation and colloidal P compositions in soil solutions from two transects (K and G) set in an intensively farmed catchment, using both natural soil solutions and lab extracted solutions (NaCl 0.001 M). For this purpose, we used a combination of ultrafiltration (UF), ultracentrifugation, inductively coupled plasma mass spectrometry (ICP-MS) and X-ray absorption near edge structure spectroscopy (XANES) techniques. XANES data evidenced no difference in terms of P speciation between lab extracted colloids and bulk soil samples, however revealing a strong enrichment of P in the extracted colloids, hence confirming the role of colloids as a major P carrier phase in agricultural soils. In natural soil solutions, total dissolved P (TDP) was similar in transects K and G, while molybdate reactive dissolved P (MRDP) was nearly 10 times higher in transect G than in Transect K. UF-ICP-MS data showed that the natural and lab extracted colloids consisted of a homogeneous mixture of Fe(Al)-oxides and organic matter, despite strong spatial variations of colloidal P proportion in natural waters (from 25 to 70%). Overall, transect G soil solutions showed high proportions of true dissolved MRDP (up to 65%), while transect K being richer in colloidal P and true dissolved organic P. UF-ICP-MS data from lab extractions, however, did not reveal the same difference in P speciation, all extracts being dominated by colloidal P and MRDP in roughly the same proportions. So far, the cause of this difference is not clearly identified.

Though confirming the important role of colloids as a major P carrier phase in agricultural soils, results from this study indicate that natural soil solutions and lab extracts may yield different results regarding P speciation in soils, and that care should be exercised in extrapolating lab data to field situation.

Delta18O-P as a marker for depth resolved microbial turnover of phosphorus in native and cropped Australian Vertosols

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Australia has the largest area of Vertosols (70.5 M ha) among all countries worldwide. A major feature of these soils is that they form deep cracks due to soil expansion and contraction leading to top- and subsoil mixing. Mixing of the soil column may lead to increased microbial activity in deeper soil layers and thus increased biogeochemical activity. Increased microbial activity might lead to greater turnover of potentially scarce soil nutrients like phosphorus (P), thus mediating the availability of subsoil P stocks to plants. A promising technique to evaluate microbial P turnover and accessibility is the d18O-P technique. Bonding between oxygen (O) and P is stable under abiotic conditions. Hence, there is strong evidence suggesting that the use of d18O natural abundance of soil phosphates (d18O-P) can track bedrock origins where microbial and root enzyme activity is absent. In contrast, when biological activity is present, there is rapid O exchange between soil phosphates and water. Hence, the higher the biological involvement in soil P turnover, the more the d18O-P value will deviate from the original d value in the bedrock.

The aim of this study was to identify the microbial turnover of P at depth in native and cotton-cropped vertisols. We divided soil cores into 5 subsamples according to depth (0-15, 15-30, 30-50, 50-70, and 70-100 cm) from native, continuous cotton, and cotton rotations and analyzed the ratio between 18O and 16O in phosphate. Overall, microbial activity at depth was also determined by measuring carbon dioxide evolution using a Respicond VII. The calculated theoretical equilibrium value for the studied sites was 17.0‰. The d18O values of the cropped sites were lower in the topsoil (11.4‰; 0-15 cm) compared to the deepest subsoil layers (14.4‰; 70-100 cm) and also the equilibrium value. The d18O was uniformly distributed between 15-100 cm. The lower d18O values in the topsoil layer were not anticipated as normally d18O is higher in topsoil due to evaporation-fractionation processes. However, the dry climate and low rainfall in the sampling area, as well as lower clay content of the topsoil layer, may explain this. Generally, the d18O-P technique seems to be a suitable approach in order to study the accessibility and turnover of P Australian Vertosols and indicated that there still is some potential to make P more available in these soils.

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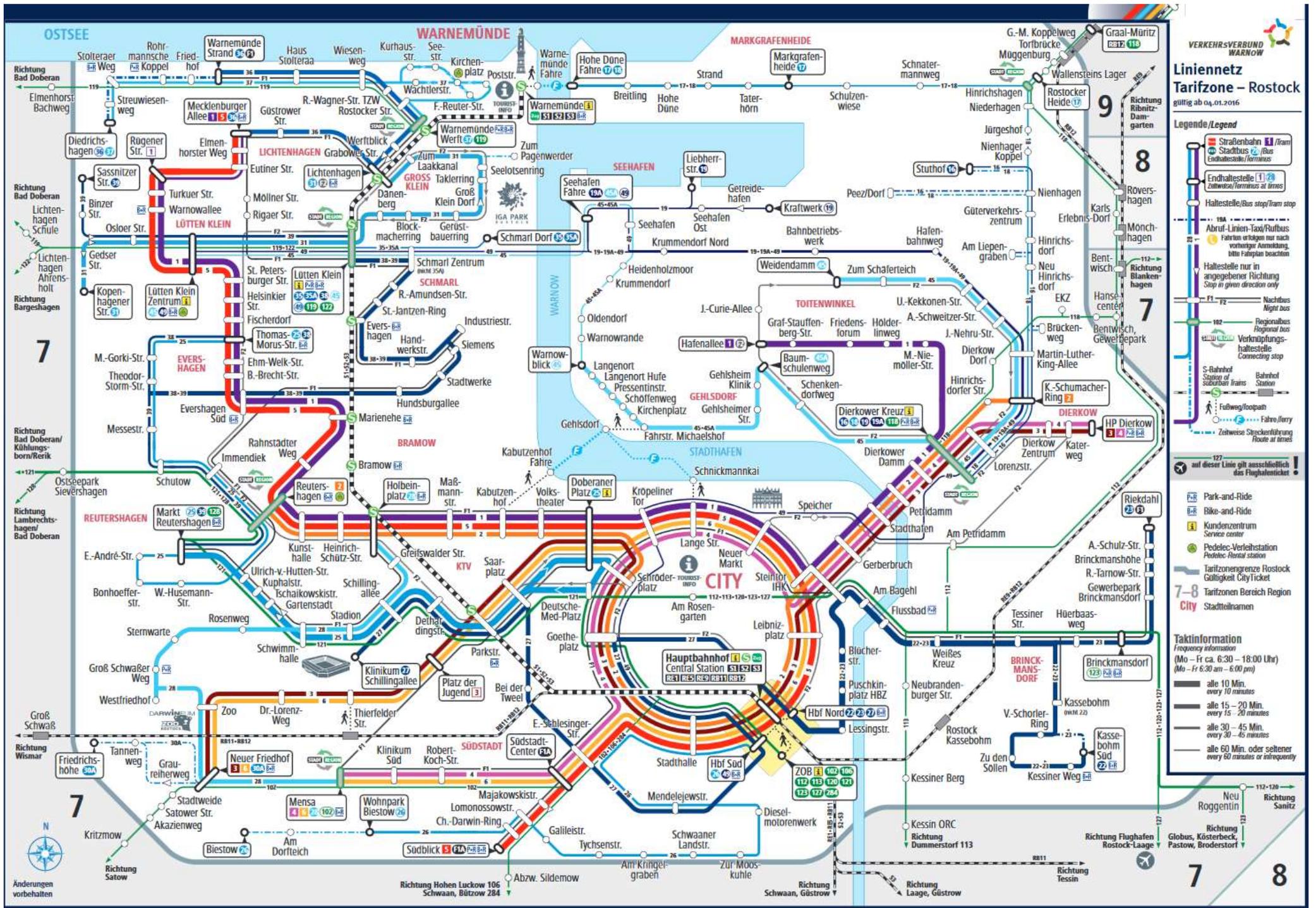
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Notes



Linienetz Tarifzone – Rostock

gültig ab 04.01.2016

Legende / Legend

- Strassenbahn / Tram
- Stadtbuss / Bus
- Endhaltestelle / End stop
- Haltestelle / Bus stop / Tram stop
- Abruf-Linien-Taxi / Rufbus
- Haltestelle nur in angegebener Richtung / Stop in given direction only
- Nachbus / Night bus
- Regionalbus / Regional bus
- Verknüpfungshaltestelle / Connecting stop
- S-Bahnhof / Station of suburban trains
- Bahnhof / Station
- Fußweg / Footpath
- Fähre / Ferry
- Zeichweise Streckenführung / Route at times

127 auf dieser Linie gilt ausschließlich das Flughafenicket

- Park-and-Ride
- Bike-and-Ride
- Kundenzentrum / Service center
- Pedelec-Verleihstation / Pedelec Rental station
- Tarifzongrenze Hostock / Tarifzone CityTicket
- 7-8 Tarifzonen Bereich Region
- City / Stadtteilnamen

Taktinformation
Frequency information

(Mo – Fr ca. 6:30 – 18:00 Uhr)
(Mo – Fr 6:30 an – 6:00 pm)

- alle 10 Min. / every 10 minutes
- alle 15 – 20 Min. / every 15 – 20 minutes
- alle 30 – 45 Min. / every 30 – 45 minutes
- alle 60 Min. oder seltener / every 60 minutes or infrequently

