Master Thesis

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Abstract

Hier kommt das Abstract

Preface

Abstract

(Knuth 1984)

Introduction

The Complexity of Phosphorus

Phosphorus (P) is an essential macronutrient for all known life, forming a critical part of DNA and energy-transfer molecules. In soils—where organic, mineral, and aqueous phases interface—its behavior is complex. In the presence of oxygen, P exists almost exclusively as orthophosphate (PO_4^{3-}) and its protonated forms (HPO_4^{2-} or $H_2PO_4^-$), depending on the soil pH. These dissolved phosphate species are highly reactive; they are subject to adsorption onto the surfaces of clays and oxides and can precipitate with cations like calcium, iron, and aluminum to form minerals with low solubility. Consequently, while the total amount of P in a soil can be large, only a small fraction is in the soil solution at any given moment, posing a central challenge for agriculture. The efficacy of P fertilization is often low due to these rapid immobilization processes, and P lost from agricultural fields can become an environmental pollutant, disturbing P-limited aquatic ecosystems.

Soil organic matter (SOM) adds another layer of complexity to these interactions. Organic acids released during the decomposition of SOM can compete with phosphate for the same adsorption sites on mineral surfaces, which can increase P concentrations in the soil solution. Furthermore, humic substances can form stable complexes with cations like Al³ and Fe³ , preventing them from precipitating phosphate and thereby enhancing its availability. The efficacy of P fertilization is often low due to these rapid and competing immobilization processes, and P lost from agricultural fields can become an environmental pollutant, disturbing P-limited aquatic ecosystems. ## From Static Measurements to Dynamic Understanding

To manage this challenge, traditional soil testing methods (e.g., Olsen-P, AAE10, CO -water) were developed to quantify the **size of the readily available P pool**. This static measurement is often referred to as the **"capacity factor"**. While these tests are invaluable for basic fertility assessment, they do not capture the dynamic nature of P supply. A crucial missing piece of information is the rate at which P is replenished into the soil solution from the solid phase after being taken up by plant roots. This replenishment rate, or **"kinetic factor"**, is vital for sustaining crop growth, especially during periods of high demand.

The importance of these dynamics is not a new concept. As early as 1982, **Flossmann and Richter** argued that characterizing the kinetics of P release was essential for refining fertilizer recommendations beyond what static tests alone could offer. Modern research has reinforced this view, showing that fertilization strategies based solely on maintaining a critical soil test P (STP) concentration can be inefficient. In Switzerland, this has led to the accumulation of "legacy P" in many agricultural soils, and understanding the release kinetics of this legacy P is key to both improving nutrient efficiency and protecting water quality. Furthermore, critical STP levels are not constant; they are influenced by

pedoclimatic factors like soil texture and temperature, making a "one-size-fits-all" approach to fertilization suboptimal.

Objectives and Research Questions

An ideal set of parameters for P management should meet several criteria. The parameters should correlate strongly with P export and P balance in a steady-state system. They must also respond to fertilizer inputs and, most importantly, capture the diffusive, kinetic nature of P supply to plant roots.

This thesis hypothesizes that **kinetic parameters describing P desorption, derived from a simple laboratory extraction, can serve as effective predictors for agronomic outcomes.** Using soils from the long-term STYCS experiment in Switzerland, this study employs a modified version of the Flossmann & Richter kinetic test to derive the desorption rate (k) and the desorbable P pool (P^S). The performance of these new kinetic parameters will be compared against standard STP methods (P_{CO_2} and P_{AAE10}) by addressing the following research questions:

1. Is the P desorption kinetic method replicable and effective for the soils from the STYCS trial?
2. How do the kinetic coefficients, k and P^S, correlate with key soil properties (organic carbon, clay content, pH)?
3. How well do the standard STP methods (P_{CO_2} & P_{AAE10}) predict crop yield, P export, and P balance?
4. Can the kinetic parameters, k and P^S, improve the prediction of these agronomic outcomes compared to the standard static tests?

Materials and Methods

The Long-Term Phosphorus Fertilization Experiment

The soil samples for this thesis originate from a set of six long-term field trials in Switzerland, established by Agroscope between 1989 and 1992. The primary objective of these experiments was to validate and re-evaluate Swiss phosphorus (P) fertilization guidelines by assessing long-term crop yield responses to varying P inputs across different pedoclimatic conditions. A detailed description of the experimental design and site characteristics can be found in Hirte et al. (2021).

The experiment was set up as a **completely randomized block design** with four field replications at each site. The core of the experiment consists of six fixed-plot treatments representing different P fertilization levels, which were applied annually as superphosphate before tillage and sowing. These levels were based on percentages of the officially recommended P inputs: 0% (Zero), 33% (Deficit), 67% (Reduced), 100% (Norm), 133% (Elevated), and 167% (Surplus).

Experimental Sites

The six experimental sites are located in the main crop-growing regions of Switzerland: **Rümlang-Altwi (ALT)**, **Cadenazzo (CAD)**, **Ellighausen (ELL)**, **Grabs (GRA)**, **Oensingen (OEN)**, and **Zurich-Reckenholz (REC)**. The key soil properties are summarized below.

Table 1: Soil characteristics of the six long-term experimental sites. Data adapted from Hirte et al. (2021).

Site	Soil Type (WRB)	Clay (%)	Sand (%)	Organic C (g/kg)	pH (H2O)
ALT	Calcaric Cambisol	22	48	21	7.9
CAD	Eutric Fluvisol	8	40	14	6.3
ELL	Eutric Cambisol	33	31	23	6.6
GRA	Calcaric Fluvisol	17	34	16	8.3
OEN	Gleyic-calc. Cambisol	37	32	24	7.1
REC	Eutric Gleysol	39	25	27	7.4

Source: Article Notebook

Soil samples for this thesis were collected on [Your Sampling Date] from the topsoil layer (0-20 cm). [Add any further specific details about your sampling strategy here].

Phosphorus Desorption Kinetics

The analysis of phosphorus (P) desorption kinetics was based on the principles of sequential extraction established by Flossmann and Richter (1982). The original method is described below, followed by the specific protocol adapted for this study.

Original Method of Flossmann and Richter (1982)

The foundational method aims to characterize the P replenishment capacity of the soil. The procedure is as follows:

1. **Removal of Soluble P**: 17.5 g of air-dried soil is shaken with 350 ml of deionized water for one hour at 25 ± 1°C. The suspension is centrifuged and the supernatant is decanted to remove the readily soluble P fraction. This first extract is referred to as:
   - **Solution A**: Contains easily soluble P, which is discarded.
2. **Kinetic Extraction**: The remaining soil pellet is resuspended with another 350 ml of deionized water. Subsamples of the suspension are taken at specific time intervals, yielding the following extracts for kinetic analysis:
   - **Solution B**: Subsample taken after **10 minutes**.
   - **Solution C**: Subsample taken after **30 minutes**.
   - **Solution D**: Subsample taken after **120 minutes**.
3. **Analysis**: The P concentration in Solutions B, C, and D is determined colorimetrically using the molybdenum blue method according to Murphy and Riley (1962).

Adapted Kinetic Protocol for This Study

For this thesis, the original method was modified to capture the desorption process with a higher temporal resolution and using a different soil-to-solution ratio.

1. **Soil Suspension**: 10 g of air-dried soil was suspended in 200 ml of deionized water. Unlike the original protocol, a pre-washing step to remove soluble P was not performed, meaning the measured desorption includes both the release of readily soluble P and the subsequent replenishment from the solid phase.

2. **Kinetic Extraction**: The suspension was shaken continuously, and subsamples were taken at eight time points to generate a detailed kinetic curve. The resulting extracts were:

   - **Extract 1**: Subsample taken after **2 minutes**.
   - **Extract 2**: Subsample taken after **4 minutes**.
   - **Extract 3**: Subsample taken after **10 minutes**.
   - **Extract 4**: Subsample taken after **15 minutes**.
   - **Extract 5**: Subsample taken after **20 minutes**.
   - **Extract 6**: Subsample taken after **30 minutes**.
   - **Extract 7**: Subsample taken after **45 minutes**.
   - **Extract 8**: Subsample taken after **60 minutes**.

3. **Analysis**: Each subsample was immediately filtered. The concentration of orthophosphate in the filtered extracts was determined colorimetrically using the **malachite green method**.

Statistical Analysis

The statistical workflow involved two main stages: 1) estimating the P desorption kinetic parameters from the laboratory data, and 2) using these parameters to model the agronomic outcomes from the long-term field experiment.

Modeling of Desorption Kinetics

To derive the kinetic parameters, a non-linear mixed-effects model (`nlme`) was implemented. This approach was chosen to simultaneously estimate the rate constant (k) and the maximum desorbable P (P_{desorb})

directly from the time-series data for each soil sample. The model was fitted to the exact solution of the first-order rate equation:

$$P(t) = P_{desorb} \times (1 - e^{-k \times t'})$$

Where $P(t)$ is the P concentration at time t, and t' is an adjusted time ($t_{\min} + 3$ min) to account for rapid initial P dissolution. The overall means for P_{desorb} and k were modeled as **fixed effects**, while sample-specific deviations for both parameters were modeled as **random effects** to capture the unique characteristics of each soil sample.

Modeling of Agronomic Responses

The estimated kinetic parameters were merged with the agronomic and soil chemistry dataset from the years 2017-2022. A series of linear mixed-effects models were then constructed to evaluate the predictive power of these parameters.

Variables Used in the Models

The response and predictor variables used in the linear mixed-effects models are defined in the table below.

Table 2: Description of variables used in the agronomic models.

Abbreviation	Full.Name	Role	Description
Y_{rel}	Relative Yield	Response	Plot yield normalized by the national mean yield for that year and crop.
Y_{norm}	Normalized Yield	Response	Plot yield normalized by the site-specific median yield of the highest P treatment for that year and crop.
P_{up}	P Uptake	Response	Total P removed by the harvested crop biomass over a growing season (kg P ha⁻¹).
P_{bal}	P Balance	Response	Net P budget, calculated as P inputs (fertilizer) minus P outputs (uptake) (kg P ha⁻¹).
k	Rate Constant	Predictor	First-order rate constant of P desorption, representing the speed of P release (min⁻¹).
P_{desorb}	Desorbable P	Predictor	Maximum desorbable P, representing the size of the readily available P pool (mg P L⁻¹).
J_0	Initial P Flux	Predictor	Product of k and P_{desorb}, representing the initial flux of P from the soil.
P_{CO2}	Water-Soluble P	Predictor	Plant-available P measured by the CO -saturated water extraction method (mg P kg⁻¹).
P_{AAE10}	Chelate-Extractable P	Predictor	Plant-available P measured by the ammonium-acetate-EDTA extraction method (mg P kg⁻¹).

Source: Article Notebook

Linear Mixed-Effects Model Structure

Linear mixed-effects models (`lmer`) were used to test the relationships between the predictor variables and each of the three response variables. The structure of these models was designed to account for the nested nature of the long-term experiment. A general form of the model is:

Response Variable ~ Fixed Effects + (1 | Random Effects)

- **Fixed Effects**: These represent the main explanatory variables of interest whose effects we wanted to quantify. The fixed effects included the kinetic parameters (k, P_{desorb}, J_0) and the standard soil P tests (P_w, P_{AAE10}), along with their interactions.
- **Random Effects**: These were included to control for non-independence among observations. By including `(1 | Site)`, `(1 | Year)`, and `(1 | Crop)` as random intercepts, the model accounts for

baseline differences in the response variable that are attributable to the specific location, growing season, or crop type, allowing for a more accurate estimation of the fixed effects.

To identify the most informative and parsimonious model, a systematic feature selection process was conducted using the `mlr3` machine learning framework. This involved training and evaluating different combinations of predictor variables using nested cross-validation to ensure the robustness of the final selected model.

All statistical analyses were performed in the R environment, utilizing the `nlme` package for kinetic modeling and the `lme4`, `lmerTest`, and `mlr3` packages for the final agronomic modeling and feature selection.

Results

The results of this study are presented in two main parts. First, the direct effects of the long-term phosphorus (P) fertilization treatments on both the agronomic outcomes and the soil P test parameters are explored visually. This descriptive analysis provides an overview of the main trends across the different experimental sites. Second, the relationships between the soil P predictors and the agronomic responses are formally evaluated using linear mixed-effects models.

Effects of Fertilization on Agronomic and Soil Parameters

To visualize the primary effects of the long-term P fertilization treatments, the key response and predictor variables were plotted for each treatment level across all six experimental sites.

Agronomic Responses to P Fertilization

The long-term application of different P fertilization levels had a pronounced impact on the primary agronomic outcomes, including two different metrics for yield, P Uptake (P_{up}), and P Balance (P_{bal}). The response, however, varied considerably between the different sites (Figure X.1).
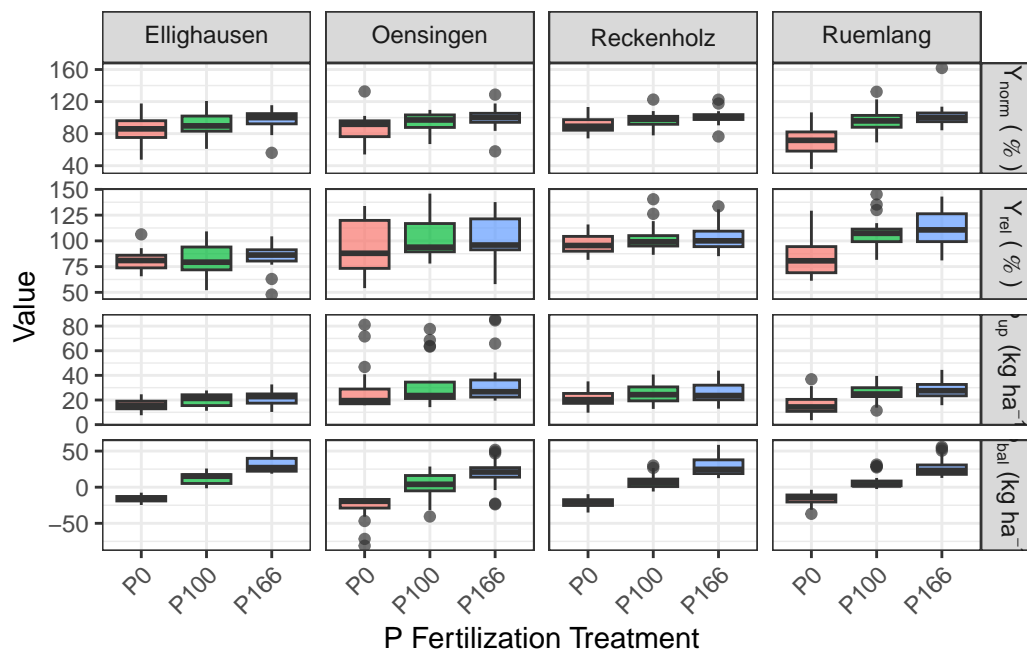

Figure 1: Agronomic response variables across six P fertilization treatments and six experimental sites. Points represent the median of replicates for each crop and year from 2017-2022.

Source: Article Notebook

(Placeholder for Figure X.1)

Yield Metrics (Y_{norm} and Y_{rel}): Both yield metrics, now displayed as percentages, showed a generally positive response to P fertilization, especially at the lower treatment levels. The site-normalized yield (Y_{norm}) clearly shows the response relative to the site's potential for that year, with most yields plateauing around the Norm (100%) treatment. The national-normalized yield (Y_{rel}) provides a broader context, showing how the yields at each site compare to the national average. At some high-productivity sites, even the zero-P treatment produced yields above the national average (i.e., $> 100\%$), while at others, yields remained below average even with high fertilization.

P Uptake (P_{up}): Phosphorus uptake by crops followed a similar trend to yield, increasing with fertilization. However, unlike yield, P uptake often continued to increase at the highest fertilization levels. This suggests that at high P supply, plants engaged in "luxury consumption," taking up more P than was required for additional biomass production.

P Balance (P_{bal}): The P balance showed a strong, linear relationship with the fertilization treatment, which is expected by definition. The Zero and Deficit treatments consistently resulted in a negative P balance, indicating that crops were mining P from soil reserves. The Norm treatment was generally close to a neutral balance, while the Elevated and Surplus treatments led to a significant P surplus, contributing to the accumulation of legacy P in the soil.

Soil P Parameters as a Function of P Fertilization

The different soil P test parameters, including the standard STP methods and the newly derived kinetic parameters, all responded to the long-term fertilization treatments (Figure X.2).
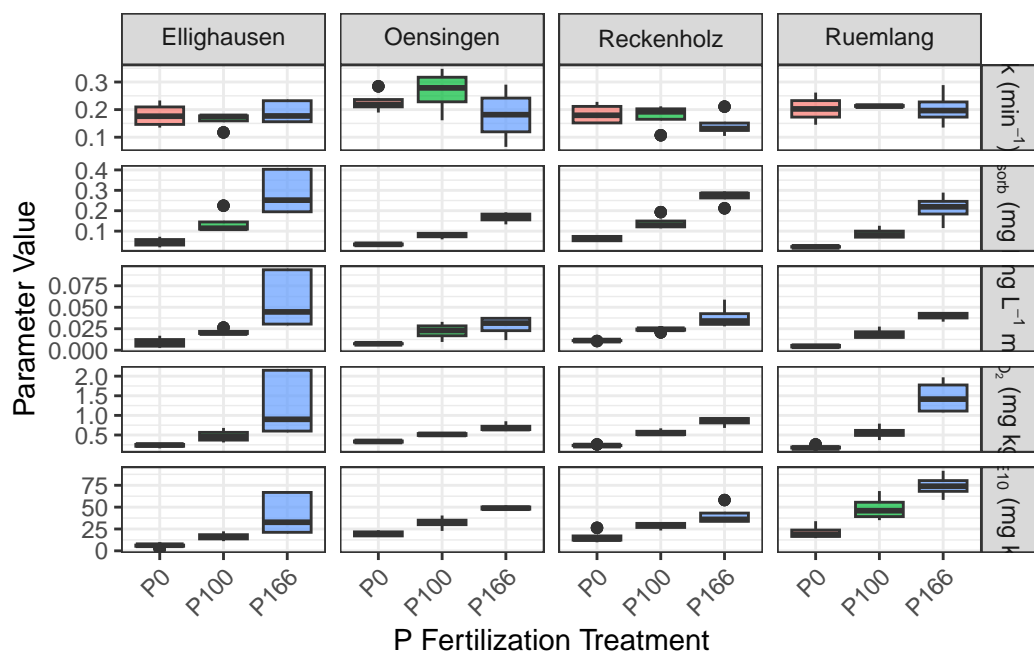

Figure 2: Soil P parameters across six P fertilization treatments and six experimental sites. Points represent the mean of replicates.

Source: Article Notebook

(Placeholder for Figure X.2)

Standard STPs (P_{CO_2} and P_{AAE10}): Both standard soil P tests showed a clear and consistent increase with rising P fertilization levels across all sites. This confirms that both methods are sensitive to changes in the soil P status resulting from long-term management. The absolute values, however, differed significantly between sites, reflecting the influence of soil properties like clay content and pH on P retention.

Kinetic Parameters (k, P_{desorb}, and J_0): * **Desorbable P (P_{desorb}):** This parameter, representing the size of the readily desorbable P pool, behaved very similarly to the standard STPs. It increased steadily with P fertilization, confirming its role as a "capacity" indicator. * **Rate Constant (k):** The rate constant, representing the speed of P release, showed a more complex pattern. At most sites, k did

not show a strong, consistent trend with fertilization, or in some cases, it slightly decreased at very high P levels. This suggests that while fertilization increases the *amount* of available P, it may not necessarily increase the intrinsic *release rate* from the soil matrix. * **Initial P Flux** (J_0)**:** As the product of P_{desorb} and k, the initial P flux integrates both the size of the pool and its release rate. It showed a strong positive response to fertilization, driven primarily by the increase in P_{desorb}. This parameter effectively captures the overall P-supplying power of the soil.

These initial observations suggest that while all P metrics are sensitive to fertilization, the kinetic parameters, particularly the rate constant k, may provide unique information about the soil's P dynamics that is not captured by static tests alone. The next section will use formal statistical models to test these relationships.

Discussion

Conclusion

Acknowledgments

Legal Disclosure

References

Knuth, Donald E. 1984. "Literate Programming." *Comput. J.* 27 (2): 97–111. https://doi.org/10.1093/comjnl/27.2.97.

Appendix

Supplements