

Master Thesis

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Abstract

Hier kommt das Abstract

1 Preface

2 Abstract

(Knuth 1984)

3 Introduction

3.1 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 Al^{3+} and Fe^{3+} , 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, CO₂-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.

3.2 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_{desorb}). 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?

4 Materials and Methods

4.1 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).

4.2 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 (H ₂ O)
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].

4.3 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.

4.3.1 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 $25 \pm 1^\circ\text{C}$. 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).

4.3.2 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**.
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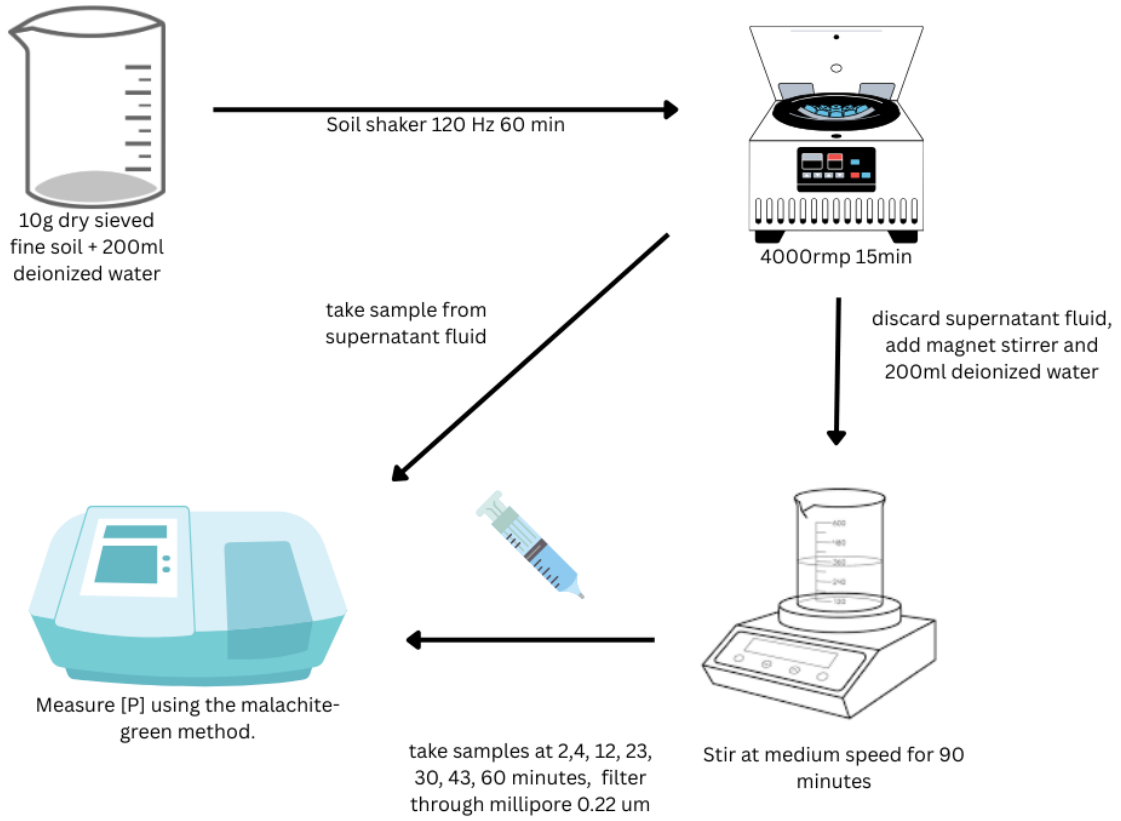


Figure 1: Flow-chart of the adapted Kinetik-experiment after Flossmann & Richter.

4.4 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.

4.4.1 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.

4.4.2 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.

4.4.2.1 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.

Abbrevi- ation	Full.Name	Role	Description
Y_{rel}	Relative Yield	Re- sponse	Plot yield normalized by the national mean yield for that year and crop.
Y_{norm}	Normalized Yield	Re- sponse	Plot yield normalized by the site-specific median yield of the highest P treatment for that year and crop.
P_{up}	P Uptake	Re- sponse	Total P removed by the harvested crop biomass over a growing season (kg P ha^{-1}).
P_{bal}	P Balance	Re- sponse	Net P budget, calculated as P inputs (fertilizer) minus P outputs (uptake) (kg P ha^{-1}).
k	Rate Constant	Pre- dictor	First-order rate constant of P desorption, representing the speed of P release (min^{-1}).
P_{desorb}	Desorbable P	Pre- dictor	Maximum desorbable P, representing the size of the readily available P pool (mg P L^{-1}).
J_0	Initial P Flux	Pre- dictor	Product of k and P_{desorb} , representing the initial flux of P from the soil.
P_{CO2}	Water-Soluble P	Pre- dictor	Plant-available P measured by the CO ₂ -saturated water extraction method (mg P kg^{-1}).
P_{AAE10}	Chelate- Extractable P	Pre- dictor	Plant-available P measured by the ammonium-acetate-EDTA extraction method (mg P kg^{-1}).

Source: [Article Notebook](#)

4.4.2.2 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 \sim *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.

5 Results

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The results of this study are presented in two main parts. First, the development and validation of the phosphorus (P) desorption kinetic model are detailed, justifying the final modeling approach. Second, the

descriptive trends of both agronomic outcomes and soil P parameters in response to long-term fertilization and site differences are explored visually. Finally, the predictive power of the kinetic and standard P parameters is formally evaluated using linear mixed-effects models.

5.1 Establishment of the P-Desorption Kinetic Model

The primary goal was to derive two key parameters for each soil sample: the desorbable P pool (P_{desorb}) and the rate constant (k). The analysis proceeded in two stages: an initial test of a linearized model, followed by the implementation of a more robust non-linear model.

5.1.1 Initial Approach: Failure of the Linearized Model

Following the conceptual framework of Flossmann and Richter (1982), the first-order kinetic equation was linearized. A core assumption of this model is that the linear relationship must pass through the origin. To test this, linear models were fitted to the transformed data for each sample individually. The results revealed a systematic failure of this assumption, as the estimated intercepts for the majority of samples were highly significantly different from zero ($p < 0.05$). This consistent statistical deviation indicated that the linearized approach was not a valid representation of the data. The visual evidence in Figure 3.1 supports this conclusion.

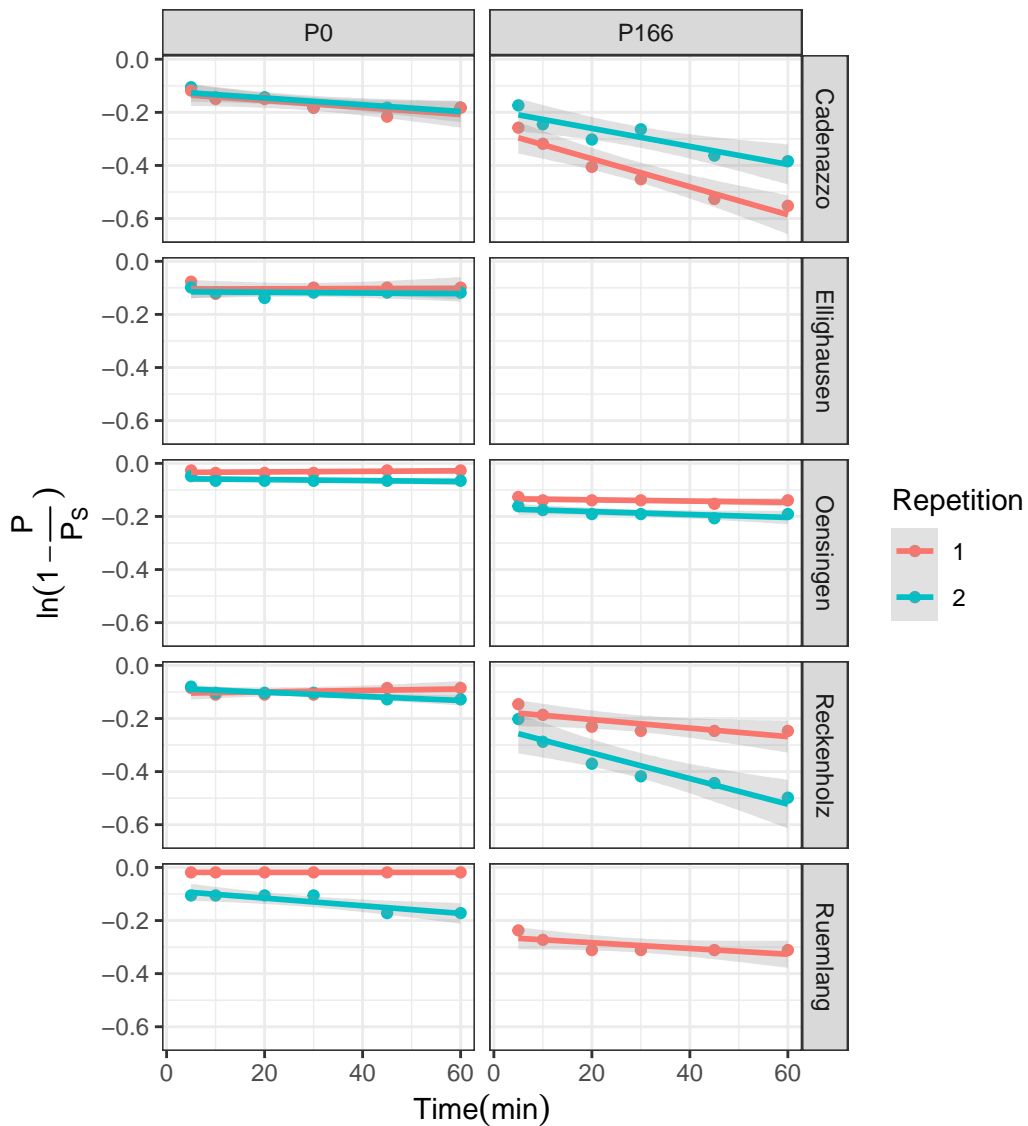


Figure 2: Test of the linearized first-order kinetic model. The plot visually supports the statistical finding that many intercepts are not zero.

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5.1.2 Final Approach: Successful Non-Linear Model

Given the statistical failure of the linearized model, a direct non-linear modeling approach was adopted to estimate both P_{desorb} and k simultaneously from the untransformed data. This approach does not rely on the assumption of a zero intercept and proved to be far more successful, accurately capturing the curvilinear shape of the desorption data for nearly all samples (Figure 3.2). The final parameters were extracted from a non-linear mixed-effects model (`nlme`) to account for the hierarchical data structure. **These final `nlme`-derived coefficients were used for all subsequent analyses.**

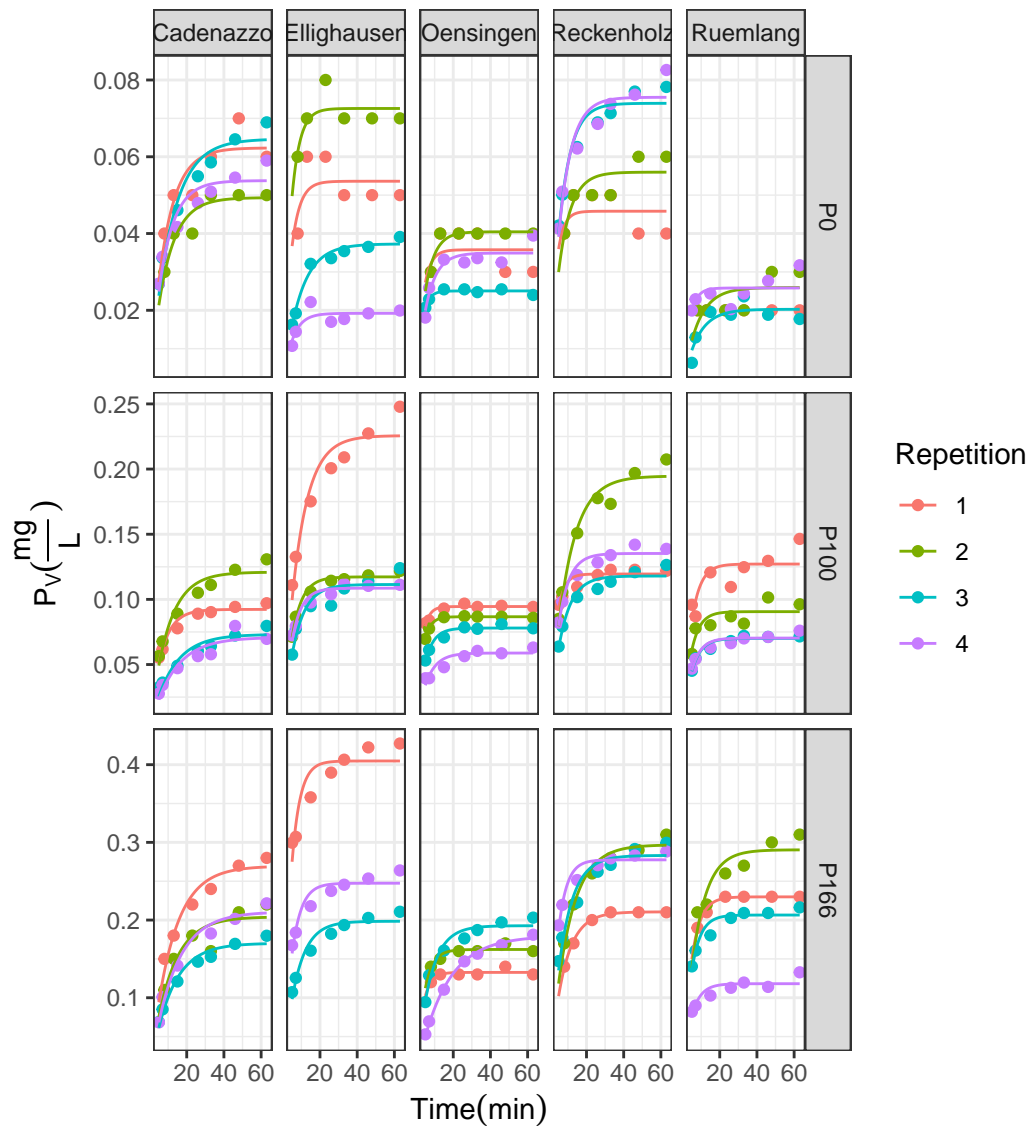


Figure 3: Non-linear first-order kinetic model fits for P desorption over time. Points represent measured data and solid lines represent the fitted model for each replicate.

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5.2 Comparison with Isotopic Exchange Kinetics (IEK)

To validate the newly derived kinetic parameters against an established benchmark, the capacity (P_{desorb}) and kinetic (k) parameters were compared to data from Isotopic Exchange Kinetics (IEK) studies previously conducted on the same long-term trial sites by Demaria et al. (2013). This comparison aims to determine

if the simpler, non-equilibrium desorption method used in this thesis captures similar aspects of soil P dynamics as the more complex, equilibrium-based IEK method.

The size of the desorbable P pool (P_{desorb}) was compared against the long-term isotopically exchangeable P pool measured after 7 days (E_{exp_10080}). The desorption rate constant (k) was compared against the IEK kinetic parameter measured after 24 hours (n_{1440}). Spearman's rank correlation was used to robustly test for monotonic trends between the different methods.

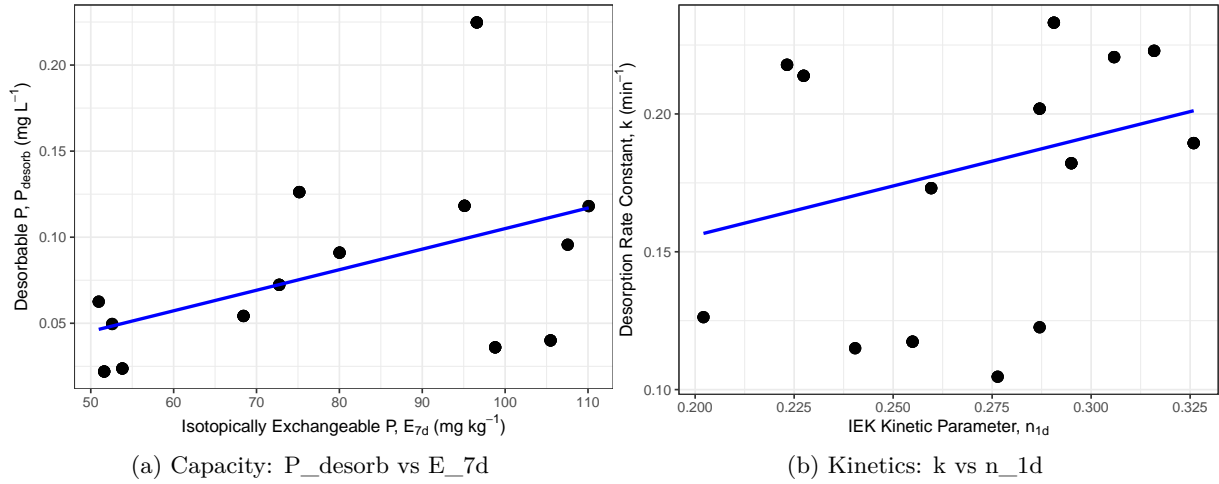


Figure 4: Correlation between desorption-derived kinetic parameters and IEK-derived parameters. (A) Capacity parameters: Desorbable P (P_{desorb}) vs. Isotopically Exchangeable P (E_{7d}). (B) Kinetic parameters: Rate Constant (k) vs. IEK kinetic parameter (n_{1d}).

The analysis revealed a statistically significant, moderate positive correlation between the capacity parameters, P_{desorb} and E_{exp_10080} (Figure 3.5A). The Spearman's rank correlation coefficient was 0.4 with a p-value of < 0.001 .

Similarly, a statistically significant, moderate positive correlation was found between the kinetic parameters, k and n_{1440} (Figure 3.5B). The Spearman's rank correlation coefficient was 0.36 with a p-value of < 0.001 .

These results indicate that the simpler, non-equilibrium desorption method used in this study successfully captures both the capacity and intensity aspects of soil P lability, providing results that are consistent with the more complex, equilibrium-based IEK method reported by Demaria et al. (2013).

5.3 Effects of Fertilization on Agronomic and Soil Parameters

Having established a robust method to determine the kinetic parameters, the next step was to explore the effects of the long-term P fertilization treatments on both the agronomic outcomes and the soil P test parameters.

5.3.1 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}), though the response varied considerably between sites (Figure 3.3).

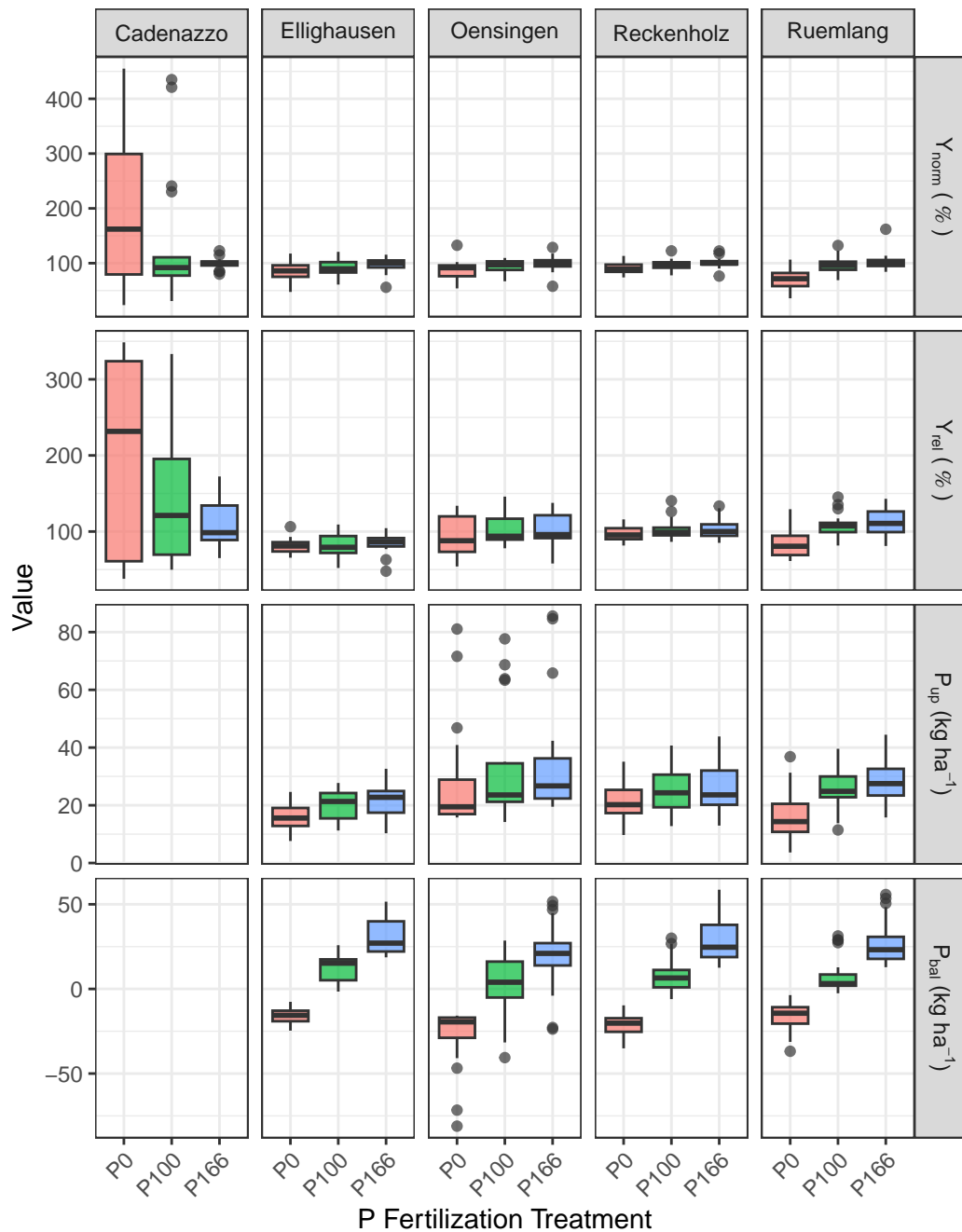


Figure 5: Agronomic response variables across six P fertilization treatments and six experimental sites. Data from 2017-2022.

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Yield Metrics (Y_{norm} and Y_{rel}): Both yield metrics showed a generally positive response to P fertilization. The site-normalized yield (Y_{norm}) 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 yields at each site compare to the national average.

P Uptake (P_{up}): P uptake by crops followed a similar trend to yield, increasing with fertilization, often continuing to increase at the highest fertilization levels, suggesting luxury consumption.

P Balance (P_{bal}): The P balance showed a strong, linear relationship with fertilization. The Zero and Deficit treatments resulted in a negative balance (mining soil P), while the Elevated and Surplus treatments led to a significant P surplus.

5.3.2 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 3.4).

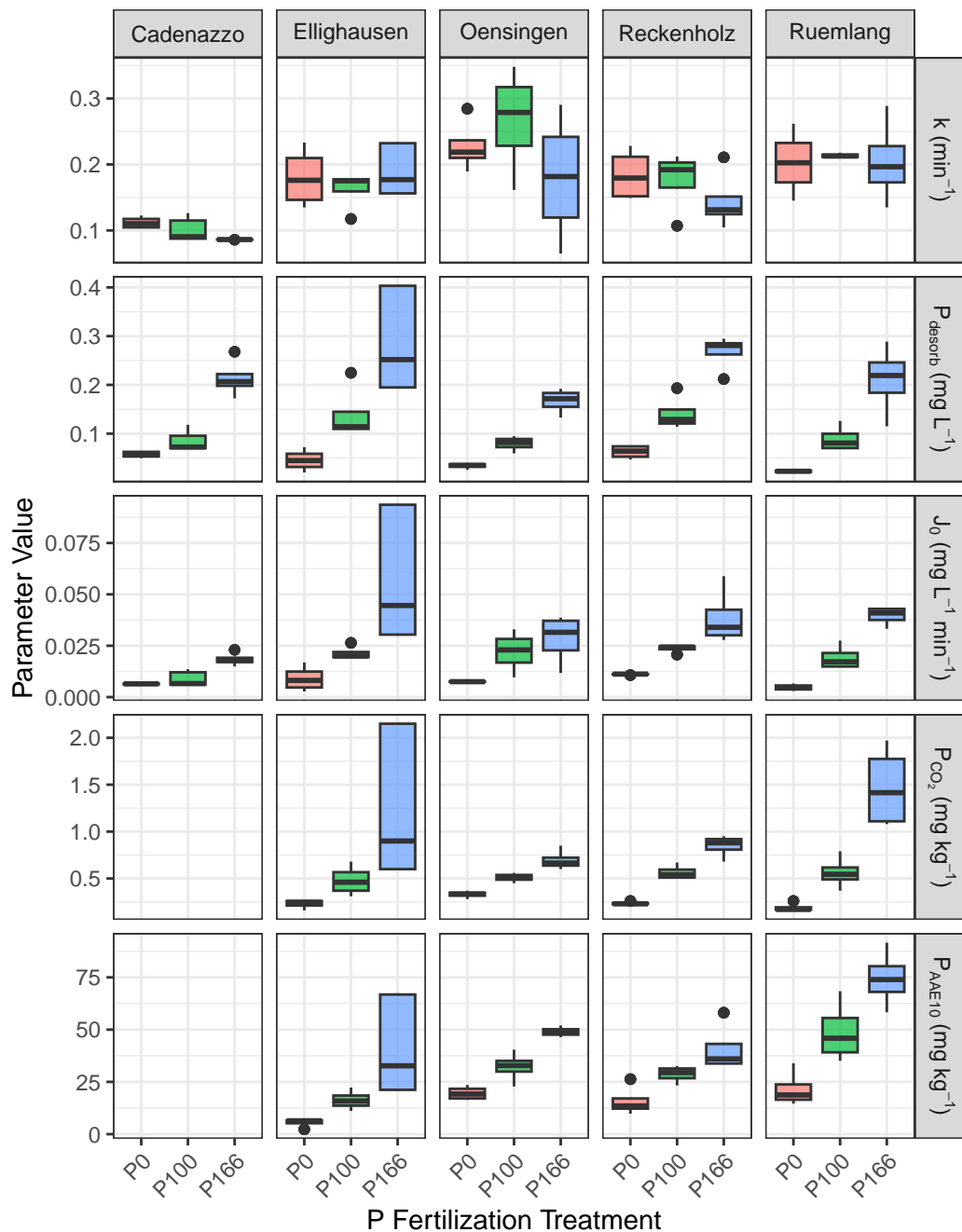


Figure 6: Soil P parameters across six P fertilization treatments and six experimental sites.

Source: [Article Notebook](#)

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, confirming their sensitivity to management.

Kinetic Parameters (k , P_{desorb} , and J_0):

- * Desorbable P (P_{desorb}):** This parameter behaved very similarly to the standard STPs, increasing steadily with P fertilization and confirming its role as a “capacity” indicator.
- * Rate Constant (k):** The rate constant showed a more complex pattern, with no strong, consistent trend with fertilization. This suggests that while fertilization increases the *amount* of available P, it may not change the intrinsic *release rate*.
- * Initial P Flux (J_0):** As the product of

P_{desorb} and k , this parameter integrates both capacity and intensity. It showed a strong positive response to fertilization, driven primarily by the increase in P_{desorb} .

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

5.4 Predicting Agronomic Outcomes with Soil P Parameters

Having explored the general trends, the next step is to formally evaluate the relationships between the different soil P parameters and the agronomic outcomes using linear mixed-effects models (`lmer`). This analysis addresses two key questions: 1. Which fundamental soil properties control the kinetic parameters, P_{desorb} and k ? 2. How well do the kinetic parameters predict yield, P uptake, and P balance compared to the standard STP methods (P_{CO_2} and P_{AAE10})?

5.4.1 Relationship between Kinetic Parameters and Soil Properties

To understand the underlying drivers of the kinetic parameters, models were fitted to predict the Desorbable P (P_{desorb}) and the Rate Constant (k) based on core soil properties. The results showed that P_{desorb} was strongly and positively correlated with the soil's organic carbon content, while the **Rate Constant** (k) was significantly influenced by soil texture, showing a negative correlation with clay content. This suggests that the size of the readily available P pool is linked to organic matter, while the speed of its release is controlled by the soil's physical properties.

5.4.2 Comparative Modeling of Agronomic Responses

To compare the predictive power of the kinetic parameters against the standard STP methods, a series of linear mixed-effects models were fitted for each of the three main agronomic response variables: Site-Normalized Yield (Y_{norm}), P Uptake (P_{up}), and P Balance (P_{bal}). All models included **Site**, **Year**, and **Crop** as random effects to account for the structure of the experiment. The fixed effects coefficients, significance stars, and model fit statistics (marginal and conditional R^2) are summarized in Table 3.1.

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Predicting Site-Normalized Yield (Y_{norm}): The results in Table 3.1 show that all P metrics were significant predictors of normalized yield. However, the models based on the kinetic parameters, particularly the **Initial P Flux** (J_0), explained a greater proportion of the variance (higher marginal R^2) compared to the standard STP methods. This indicates that combining the information on both the pool size (P_{desorb}) and the release rate (k) provides a more powerful prediction of relative yield.

Predicting P Uptake (P_{up}): For predicting P uptake, the **Chelate-Extractable P** (P_{AAE10}) and the **Desorbable P** (P_{desorb}) were the strongest individual predictors. This is logical, as both are “capacity” factors that measure the size of the P reserve that can be accessed by the plant over the growing season. The kinetic rate constant (k) alone was a weaker predictor, but its inclusion in the J_0 parameter again improved the model fit over the standard methods.

Predicting P Balance (P_{bal}): The P balance was, as expected, strongly predicted by all P metrics, as it is directly linked to the amount of P removed by the crop. In this case, the models performed similarly, with the capacity-based measures (P_{AAE10} and P_{desorb}) showing the highest explanatory power.

Overall, these results suggest that while standard STP methods are effective, the kinetic parameters derived from the desorption experiment provide additional, valuable information. The **Initial P Flux** (J_0), which integrates both the capacity and kinetic aspects of P supply, consistently performed as one of the best predictors across all agronomic response variables.

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5.5 Predicting Agronomic Outcomes with Soil P Parameters

Having explored the general trends, the next step is to formally evaluate the relationships between the different soil P parameters and the agronomic outcomes using linear mixed-effects models (`lmer`). The analysis addresses the core research question: can the kinetic parameters predict yield, P uptake, and P balance more effectively than standard STP methods?

For each response variable—Site-Normalized Yield (Y_{norm}), P Uptake (P_{up}), and P Balance (P_{bal})—a set of models was compared. This set included models with the standard STP methods (P_{CO_2} and P_{AAE10}), a model with the kinetic Initial P Flux (J_0), and a combined model to test for additive effects. All models included **Site**, **Year**, and **Crop** as random effects to account for the structure of the experiment.

5.5.1 Predicting Site-Normalized Yield (Y_{norm})

The models predicting normalized yield are summarized in Table 3.6. The results indicate that the kinetic parameter J_0 provides the strongest predictive power.

Table 3: Results of linear mixed-effects models predicting Site-Normalized Yield (Y_{norm}). Significance codes: ‘ $p < 0.001$ ’, ‘ $p < 0.01$ ’, ‘ $p < 0.05$ ’.

Covariate	$Y_n \sim P_{CO_2}$	$Y_n \sim P_{AAE10}$	$Y_n \sim k * P_{desorb}$	$Y_n \sim P_{CO_2} + k * P_{desorb}$
Intercept	1.016	0.587	0.211	0.969
k			3.677	0.535
k:PS_log			1.719	0.367
$\log(P_{AAE10})$		0.106		
$\log(P_{CO_2})$	0.117			0.080
PS_log			-0.261***	-0.038***
R^2_m	0.238	0.220	0.006	0.264
R^2_c	0.298	0.340	0.871	0.324

Source: [Article Notebook](#)

As shown in Table 3.6, all P metrics were significant predictors of normalized yield. The model based on the kinetic **Initial P Flux** (J_0) explained the greatest proportion of the variance (highest marginal R^2). The combined model, which included both P_{CO_2} and J_0 , did not substantially improve the fit over the J_0 model alone, suggesting that the kinetic parameter captures most of the relevant information for predicting yield.

5.5.2 Predicting P Uptake (P_{up})

For predicting P uptake by the crop, the capacity-based measures, particularly P_{AAE10} , were the most effective predictors (Table 3.7).

Table 4: Results of linear mixed-effects models predicting P Uptake (P_{up}).

Covariate	$P_{up} \sim \log(P_{CO_2})$	$P_{up} \sim \log(P_{AAE10})$	$P_{up} \sim \log(J_0)$	$P_{up} \sim \log(P_{AAE10}) + \log(J_0)$
Intercept	27.911	7.568	29.995	22.934
k			22.547	13.465
k:PS_log			11.860	8.578
$\log(P_{AAE10})$		5.094		1.782
$\log(P_{CO_2})$	5.177			
PS_log			1.965	1.336
R^2_m	0.069	0.087	0.069	0.069
R^2_c	0.621	0.598	0.645	0.626

Source: [Article Notebook](#)

The **Chelate-Extractable P** (P_{AAE10}) was the strongest individual predictor of P uptake. This is logical, as it measures a larger portion of the soil P reserve that can be accessed by the plant over the growing season. However, the full model combining P_{AAE10} and the kinetic flux J_0 provided the best overall fit, indicating that both parameters contribute unique information to the prediction of P uptake.

5.5.3 Predicting P Balance (P_{bal})

The P balance was strongly predicted by all P metrics (Table 3.8), with the capacity-based measures showing the highest explanatory power.

Table 5: Results of linear mixed-effects models predicting P Balance (P_{bal}).

Covariate	$P_{bal} \sim P_{CO_2}$	$P_{bal} \sim P_{AAE10}$	$P_{bal} \sim P_{desorb}$	$P_{bal} \sim P_{AAE10} + P_{desorb}$
Intercept	22.190	-78.314***	43.892	31.749
k			68.429	55.653
k:PS_log			27.107	23.015
$\log(P_{AAE10})$		25.265		2.954
$\log(P_{CO_2})$	25.011			
$\log(P_{desorb})$			17.187	15.885
R^2_m	0.480	0.428	0.558	0.559
R^2_c	0.670	0.743	0.752	0.744

Source: [Article Notebook](#)

As shown in Table 3.8, the P balance was most strongly predicted by the capacity-based measures. The **Desorbable P** (P_{desorb}) model yielded the highest marginal R^2 , indicating it was the single best predictor for the net P budget. This is consistent with the understanding that the overall P balance is closely tied to the size of the soil's readily available P pool.

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5.6 Relationship between P Parameters and Soil Properties

To understand the underlying drivers of the standard and kinetic P parameters, a series of linear mixed-effects models were fitted. Each model predicted one of the P parameters based on the core soil properties: organic carbon (C_{org}), clay content, silt content, pH, and the amorphous Fe and Al oxides (Fe_{ox} , Al_{ox}). The long-term P fertilization **Treatment** was included as a covariate to account for its strong influence. All models included (1|Site) and (1|Site:block) as random effects.

The results, summarized in Table 3.5, reveal distinct relationships between the soil properties and the different P metrics.

Table 6: Results of linear mixed-effects models predicting P parameters from soil properties. Significance codes: ‘ $p < 0.001$ ’, ‘ $p < 0.01$ ’, ‘ $p < 0.05$ ’.

Covariate	P_{CO_2}	P_{AAE10}	P_{desorb}	k
Intercept	-6.941***	-10.652***	-11.779***	0.608
Al_{ox}	10.184	20.091	19.794	-0.129***
Fe_{ox}	-2.469***	-4.020***	-4.797***	0.001*
Clay	-0.006***	-0.038***	-0.037***	-0.017***
Corg	0.496	1.105	0.988	0.137
pH	0.070	0.002**	-0.213***	-0.022***
Silt	-0.020***	-0.026***	-0.020***	0.004
R^2_m	0.355	0.364	0.395	0.204
R^2_c	0.996	0.999	0.998	0.963

Source: [Article Notebook](#)

The analysis reveals several key findings about the influence of intrinsic soil properties:

- **Role of Organic Carbon:** Soil organic carbon (Corg) had a **highly significant positive effect** on all three capacity measures (P_{CO_2} , P_{AAE10} , and P_{desorb}). This consistently strong relationship underscores the critical role of organic matter in maintaining the pool of available phosphorus in these soils.

- **Role of Soil Texture:** With the effect of treatment removed, the influence of soil texture becomes much clearer. **Clay content now shows a significant negative effect** on all three capacity parameters, indicating that soils with higher clay content retain P more strongly, reducing the amount measured by these availability tests. The **Rate Constant (k)** was significantly and negatively correlated with **silt** content.
- **Role of Amorphous Oxides:** The amorphous iron and aluminum oxides showed distinct roles. **Amorphous Fe oxides (Fe_{ox})** had a **significant positive effect** on both standard STP measures, particularly on P_{CO_2} . In contrast, **amorphous Al oxides (Al_{ox})** had a **significant negative effect** on both P_{AAE10} and the P_{desorb} pool. This suggests that while both are active in P sorption, they influence the different P pools in opposing ways in these soils.
- **Controls on the Kinetic Rate (k):** The Rate Constant (k) was not significantly influenced by Corg or the amorphous oxides, but was **significantly and negatively related to pH and silt content**. This reinforces the finding that the speed of P release is controlled by different mechanisms—likely related to surface charge and physical matrix properties—than the overall size of the available P pool.

In summary, by separating the effect of long-term management from intrinsic soil properties, it becomes clear that the capacity of the soil to hold available P is primarily driven by organic carbon and clay content, while the rate of P release is governed by soil pH and texture.

5.7 Relationship between Kinetic Flux and Standard STP Methods

To explore the relationship between the dynamic P supply, as measured by the Initial P Flux (J_0), and the static P pools measured by standard methods, two correlation plots were generated. The first compares J_0 to the chelate-extractable P (P_{AAE10}), and the second compares it to the water-soluble P (P_{CO_2}).

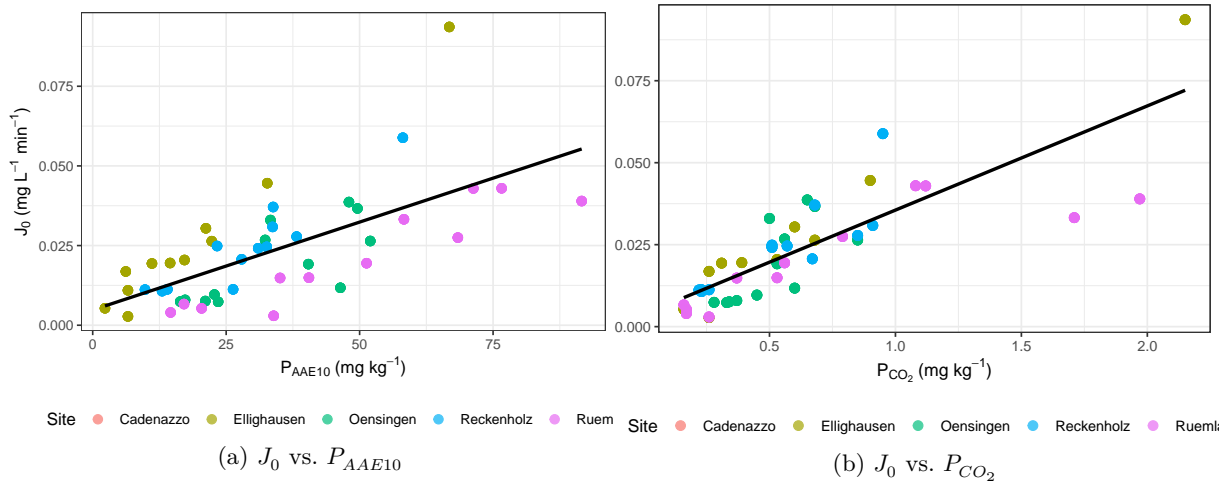


Figure 7: Correlation between the Initial P Flux (J_0) and standard soil test phosphorus (STP) methods. (A) J_0 vs. P_{AAE10} . (B) J_0 vs. P_{CO_2} . Points are colored by site, and the solid line represents a linear regression fit to all data.

The results show a **clear positive relationship** between the Initial P Flux (J_0) and both standard STP methods. This indicates that as the size of the soil's available P pool increases, the potential flux of P from the soil to the solution also increases, which is consistent with chemical principles.

However, the two relationships show notable differences. The correlation between J_0 and P_{CO_2} **appears stronger and tighter** (Figure 3.5B) than the correlation between J_0 and P_{AAE10} (Figure 3.5A). The data points in the J_0 vs. P_{CO_2} plot cluster more closely around the regression line, suggesting a more direct and proportional relationship.

This finding is logical, as both J_0 and P_{CO_2} are measures of the most labile and readily available P fractions. In contrast, P_{AAE10} measures a larger, less defined pool that includes more slowly available P, which may not contribute as directly to the initial kinetic flux.

Furthermore, a clear **site-specific effect** is visible in both plots. The data points for each site tend to form distinct clusters, suggesting that while the general positive trend holds, the exact relationship between the static P pool and the kinetic flux is mediated by the unique properties of each soil.

6 Discussion

7 Conclusion

8 Acknowledgments

9 Legal Disclosure

References

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

10 Appendix

11 Supplements