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P-release kinetic as a predictor for P-availability in Swiss cropping systems

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Abstract

Traditional static soil tests (STPs) for phosphorus (P) often fail to predict agronomic outcomes because they do not account for the kinetic nature of P supply to plant roots. This thesis investigated whether P desorption kinetic parameters could serve as more effective predictors. Using soils from the long-term Swiss agricultural experiment (STYCS), a sequential extraction method was refined and modeled with a non-linear approach to derive the desorbable P pool (P_{desorb}) and a rate constant (k). The predictive power of these kinetic parameters was compared against standard Swiss STPs (P_{CO_2} and P_{AAE10}) for various agronomic outcomes using linear mixed-effects models. The results revealed a highly context-dependent performance. For predicting site-normalized yield, STPs were superior, while for national-normalized yield and P-uptake, both methods performed poorly, with their predictive signals being overshadowed by dominant pedoclimatic factors. Furthermore, the two STP methods provided largely redundant information, as their combination did not improve predictive power. The most significant finding was the exceptional success of the kinetic model in predicting the long-term P-Balance, a key indicator of nutrient stewardship. The P_{desorb} parameter alone explained 57% of the variance, whereas STP models showed no predictive power. This study concludes that the ideal soil P test is purpose-dependent: while traditional STPs remain adequate for within-field fertility management, kinetic parameters are a vastly superior tool for assessing the long-term P status and sustainability of agricultural soils.

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1 Introduction

1.1 The Complexity of Phosphorus

Phosphorus (P) is an essential macronutrient for all known life, forming a critical part of DNA and energy-transfer molecules (Berg et al., 2019; National Institutes of Health, Office of Dietary Supplements, 2023; Nelson et al., 2021). 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 (Brady & Weil, 2016; Sparks, 2003). 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 (Bohn et al., 2002; Hinsinger, 2001; Sposito, 2008). Consequently, while total soil P concentrations can be substantial, often ranging from 200 to 3000 mg kg ^{1}, the concentration of orthophosphate in the soil solution—the form directly acquired by plant roots—is typically minuscule, often in the range of 0.001 to 1 mg L ^{1}. This vast difference between the total phosphorus stock and the infinitesimally small plant-available pool represents a central challenge for global agricultural productivity (Brady & Weil, 2016; Holford, 1997; Sposito, 2008). This creates a profound agronomic and environmental dilemma: while the majority of applied P fertilizer is rapidly immobilized in the soil and remains unavailable to crops, the fraction that is lost from fields via runoff and erosion becomes a potent environmental pollutant. This fugitive P is a primary driver of eutrophication in freshwater ecosystems, which are often naturally P-limited Sharpley et al. (2003).

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 (Gerke, 2010; Stevenson, 1994).

1.2 From Static Measurements to Dynamic Understanding

To manage this challenge, soil testing methods were developed to estimate plant-available phosphorus. These tests are designed to measure two key components of P availability: the **intensity factor**, which is the concentration of P in the soil solution at a given moment, and the **capacity factor**, which represents the pool of weakly adsorbed P that can readily replenish the soil solution (Frossard et al., 2000). Traditional methods used in Switzerland and the surrounding DACH region, which are standardized by organizations like the **VDLUFA** (Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten) and form the basis of Swiss fertilization guidelines (**GRUD**; Grundlagen für die Düngung), often employ a dual-method approach. This strategy is designed to assess both the P-intensity and P-capacity factors separately by using a combination of weak and strong extractants. Weak extractants, such as CO -saturated water, are intended to measure the readily available P in the soil solution (intensity). In contrast, stronger, often chelate-based extractants like ammonium acetate EDTA (AAE10) or calcium-acetate-lactate (CAL) are used to estimate the more tightly bound, resupply pool of phosphorus (capacity) (Forschungsanstalt für Agrarökologie und Landbau (FAL), 1996; Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten (VDLUFA), 2000). While this dual approach is logical, other international standards, such as the widely used Olsen-P method, rely on a single extraction to provide an index of plant-available P (Olsen et al., 1954). Although these static 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 Frossard et al. (2000).

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 (Flossmann & Richter, 1982). Modern research has reinforced this view, showing that fertilization strategies based solely on maintaining a critical soil test P (STP) concentration can be inefficient (McDowell & Sharpley, 2001; Rowe et al., 2016). In Switzerland, this has led to the accumulation of "legacy P" in many agricultural soils. Additionally, understanding the release kinetics of this legacy P is key to both improving nutrient use efficiency and protecting water ecosystems and reserves (Hirte et al., 2018). 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 (Bell et al., 2013; Hirte, Richner, et al., 2021; Sims & Sharpley, 2005).

1.3 Objectives and Research Questions

An ideal set of parameters for phosphorus (P) management must move beyond simple agronomic sufficiency to encompass both environmental stewardship and the biophysical realities of nutrient acquisition by plants. To be truly effective, such parameters must: (1) be sensitive to changes in the soil P status resulting from fertilizer inputs and crop removal (the P balance) (Frossard et al., 2000; Johnston et al., 2001); (2) correlate with the risk of P loss to the environment (P export) (Sharpley et al., 2000); and (3), most critically, reflect the kinetic nature of P supply to plant roots, which is governed by the slow diffusion of phosphate in the soil solution (Kuang et al., 2012; Nye & Tinker, 2000).

This thesis hypothesizes that kinetic parameters describing P desorption, derived from a simple laboratory extraction, can serve as effective predictors for agronomic outcomes. To test this, soils were sourced from the long-term Swiss agricultural experiment STYCS (Hirte, Stüssel, et al., 2021). The experiment's multi-decade history has established stable P equilibria across a wide and deliberately created gradient of P availability (from 0% to 167% of recommended fertilization), allowing for robust modeling of crop responses. Furthermore, the trial encompasses six sites with diverse pedoclimatic conditions, ensuring that any findings have broad applicability across different Swiss agricultural landscapes. 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:

1.3.1 Research Questions and Hypotheses

Research Question 1: How well do standard soil test P (STP) methods predict agronomic outcomes and how do they relate to fundamental soil properties?

- **Hypothesis 1a (Agronomic Performance):** The standard STP methods (P_{CO_2} and P_{AAE10}), which measure the P *capacity* (the size of the readily available pool), will show a significant correlation with the P-Balance, as this is directly influenced by P inputs (Johnston et al., 2001). However, they will be weak predictors of relative crop yield and P-uptake, as these agronomic outcomes are more dependent on the *rate* of P supply throughout the growing season (Hirte, Stüssel, et al., 2021).

- **Hypothesis 1b (Relation to Soil Properties):** The measured STP values will be positively correlated with soil clay and organic carbon content, reflecting the greater number of sorption sites in these soils (Brady & Weil, 2016). Conversely, the P_AAE10 measurement will be negatively correlated with soil pH, particularly in soils with a $pH > 6.8$, due to the chelation of Ca^{2+} and Mg^{2+} by the EDTA in the extractant, which reduces its effectiveness (Forschungsanstalt für Agrarökologie und Landbau (FAL), 1996).

Research Question 2: Can P desorption kinetics be reliably characterized for the diverse soils of the STYCS trial, and how do the derived kinetic parameters relate to soil properties?

- **Hypothesis 2a (Methodological Feasibility):** The P desorption process in the STYCS soils will follow a first-order kinetic model. However, the original linear estimation method proposed by Flossmann & Richter (1982) may be inaccurate because it relies on a potentially overestimated desorbable P pool (P_{desorb}). A non-linear modeling approach will provide more robust and replicable estimates of both the desorption rate constant (k) and the desorbable P pool (P_{desorb}) (Kuang et al., 2012).

- **Hypothesis 2b (Relation to Soil Properties):** The kinetic parameters will be significantly influenced by soil composition. The desorbable P pool (P_{desorb}) is expected to correlate positively with clay and organic matter content, which provide sorption surfaces. The rate constant (k) is expected to be influenced by pH, as the speciation of orthophosphate changes, affecting its interaction with mineral surfaces and its mobility (Sparks, 2003).

Research Question 3: Can kinetic parameters significantly improve the prediction of agronomic outcomes compared to standard static STP methods?

- **Hypothesis 3 (Improved Predictive Power):** Because plant P uptake is fundamentally limited by the slow diffusion of phosphate to the root surface, a dynamic measure is required for accurate prediction (Nye & Tinker, 2000). Therefore, a model incorporating the kinetic parameters (k and P_{desorb}), which together describe the replenishment rate of the soil solution, will explain a significantly greater proportion of the variance in relative yield and P-uptake compared to models based solely on the static STP measurements (Fardeau et al., 1991; Frossard et al., 2000).

2   Materials and Methods

2.1   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, Richner, 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).

2.2   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 (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

Soil samples for this thesis were collected in the year 2022 from the topsoil layer (0-20 cm).

2.3   Phosphorus Desorption Kinetics

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

2.3.1   Original Method of Flossmann and Richter

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 120 Hz in a horizontal soil-shaker. The suspension is centrifuged at 4000 rpm for 15 minutes and the supernatant is decanted to remove the readily soluble P fraction.
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 (e.g., 10, 30, and 120 minutes).

3. **Analysis**: The P concentration in the subsamples is determined colorimetrically.

2.3.2 Adapted Kinetic Protocol for This Study

For this thesis, the original method was modified to capture the desorption process with a higher temporal resolution.

1. **Pre-washing to Remove Soluble P**: A pre-washing step was performed to remove the readily soluble P fraction. 10 g of air-dried soil was suspended in 200 ml of deionized water and shaken for 60 minutes at 120 Hz. The suspension was then centrifuged for 15 minutes at 4000 rpm, and the supernatant containing the soluble P was discarded.

2. **Kinetic Extraction**: The remaining soil pellet was resuspended in 200 ml of fresh deionized water. The suspension was shaken continuously, and subsamples were taken at eight time points to generate a detailed kinetic curve: **2, 4, 10, 15, 20, 30, 45, and 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** (Van Veldhoven & Mannaerts, 1987).

2.4 Statistical Analysis

2.4.1 Software and Statistical Environment

All data processing, statistical modeling, and visualization were conducted using the R programming language (v. 4.2.2) (R Core Team, 2022). The primary packages used for the analysis were: - `nlme` (Pinheiro et al., 2022) for fitting the non-linear mixed-effects models to the kinetic data. - `lme4` (Bates et al., 2015) and `lmerTest` (Kuznetsova et al., 2017) for fitting and testing the linear mixed-effects models for agronomic and soil property analyses. - `mlr3` (Lang et al., 2019) for the systematic feature selection and model validation workflow.

2.4.2 Modeling of Desorption Kinetics

To derive the kinetic parameters, a non-linear mixed-effects model was implemented using the `nlme` package. This approach was chosen to simultaneously estimate the rate constant (k) and the maximum desorbable P (P_{desorb}) 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 the rapid initial dissolution of P that occurs before the first measurement. In this mixed-effects framework, the overall mean values for P_{desorb} and k were modeled as **fixed effects**, while sample-specific deviations from these fixed effects were modeled as **random effects** to capture the unique desorption characteristics of each individual soil sample.

2.4.3 Comparative Modeling of Soil and Agronomic Parameters

To test the hypotheses of this thesis, two distinct sets of linear mixed-effects models were constructed.

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

Abbreviation	Variable	Unit	Description
Y_{rel}	Relative Yield	unitless	Plot yield normalized by the national mean yield for that year and crop.
Y_{norm}	Normalized Yield	unitless	Plot yield normalized by the site-specific median yield of the highest P treatment for that year and crop.
P_{up}	P Uptake	kg P ha^{-1}	Total P removed by the harvested crop biomass over a growing season.
P_{bal}	P Balance	kg P ha^{-1}	Net P budget, calculated as P inputs (fertilizer) minus P outputs (uptake).
k	Rate Constant	min^{-1}	First-order rate constant of P desorption, representing the speed of P release.
P_{desorb}	Desorbable P	mg P L^{-1}	Maximum desorbable P, representing the size of the readily available P pool.
J_0	Initial P Flux	mg P L^{-1} min^{-1}	Product of k and P_{desorb}, representing the initial flux of P from the soil.
P_{CO2}	Water-Soluble P	mg P kg^{-1}	Plant-available P measured by CO_2-saturated water extraction (Forschungsanstalt für Agrarökologie und Landbau (FAL), 1996).
P_{AAE10}	Chelate-Extractable P	mg P kg^{-1}	Plant-available P measured by the ammonium-acetate-EDTA extraction method (Forschungsanstalt für Agrarökologie und Landbau (FAL), 1996).
Al_d	Dithionite-Extractable Al	mg Al kg^{-1}	Free Al oxides (crystalline and amorphous) extracted with dithionite-citrate-bicarbonate (Mehra & Jackson, 1960).
Fe_d	Dithionite-Extractable Fe	mg Fe kg^{-1}	Free Fe oxides (crystalline and amorphous) extracted with dithionite-citrate-bicarbonate (Mehra & Jackson, 1960).

2.4.4 Model Assumptions and Diagnostics

The validity of the linear mixed-effects models (`lmer`) relies on several key assumptions, primarily that the model residuals are normally distributed and homoscedastic (i.e., have constant variance across the range of predicted values). Prior to finalizing the models, these assumptions were rigorously checked through visual inspection of diagnostic plots, such as quantile-quantile (Q-Q) plots of the residuals and plots of residuals versus fitted values.

Initial exploratory data analysis revealed that several of the predictor variables, most notably the desorbable P pool (P_{desorb} or PS), were strongly right-skewed. Using such variables directly in the linear models would violate the assumptions of linearity and homoscedasticity, leading to potentially biased and unreliable coefficient estimates.

To address this, various transformations (including square root and logarithmic) were tested on the skewed variables. The natural log-transformation (`log()`) was found to be the most effective at normalizing the distribution of P_{desorb} and producing well-behaved model residuals that more closely met the required assumptions. Therefore, `log(PS)` was used as a fixed effect in all subsequent agronomic models to ensure the statistical validity of the results.

2.4.4.1 Models of P Availability Metrics as a Function of Soil Properties

First, to investigate the underlying soil-chemical drivers of the different P availability metrics (both kinetic and static), a series of models was built to predict each metric from key soil

properties.

- **Fixed Effects Structure:** The fixed effects were identical for all models in this category and included the primary soil physical and chemical properties: clay content, silt content, pH, organic carbon content, and dithionite-extractable iron (Fe_d) and aluminum (Al_d).
- **Random Effects Structure:** The random effects structure accounted for the nested design of the STYCS experiment, with random intercepts for `year`, `Site`, `Site:block`, and `Site:Treatment`.

2.4.4.2 Comparative Models of Agronomic Outcomes

Second, the predictive power of the kinetic parameters was directly compared against that of the standard STP methods ("GRUD" system). For each agronomic response variable (Normalized Yield, P Uptake, and P Balance), two competing models were built. These models shared an identical random effects structure to ensure a fair comparison, differing only in their fixed effects.

- **Random Effects Structure (for all agronomic models):** The structure `(1|year) + (1|Site) + (1|Site:block)` was used to control for variations due to the growing season, location, and in-field spatial differences.

- **Model 1: The Kinetic Approach**

  - **Fixed Effects:** This model used the kinetic parameters and their interaction: `k * log(PS)`. The interaction term tests the hypothesis that the benefit of a large desorbable P pool (`PS`) depends on the *rate* (`k`) at which it can be accessed.

- **Model 2: The Standard STP (GRUD) Approach**

  - **Fixed Effects:** This model used the two standard Swiss soil tests and their interaction: `P_CO2 * P_AAE10`.

The relative performance of these two sets of models was then evaluated to determine whether the kinetic parameters provided a significant improvement in predictive power for key agronomic outcomes. Further the relative performance of these two approaches, along with other combinations of predictor sets, was rigorously evaluated using a machine learning benchmark workflow implemented in the `mlr3` package (Lang et al., 2019). The predictive power of each predictor set was quantified using **5-fold cross-validation**. Performance was measured as the percentage of explained variance on the hold-out data (1 - MSE / Var(y)), providing a robust and unbiased estimate of how well each model would generalize to new data. This benchmark allowed for a direct comparison of the information content provided by the kinetic parameters versus the standard soil tests for predicting key agronomic outcomes.

3 Results

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.

3.1 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.

3.1.1 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 (0/0) of the coordinate system. 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 1 supports this conclusion.
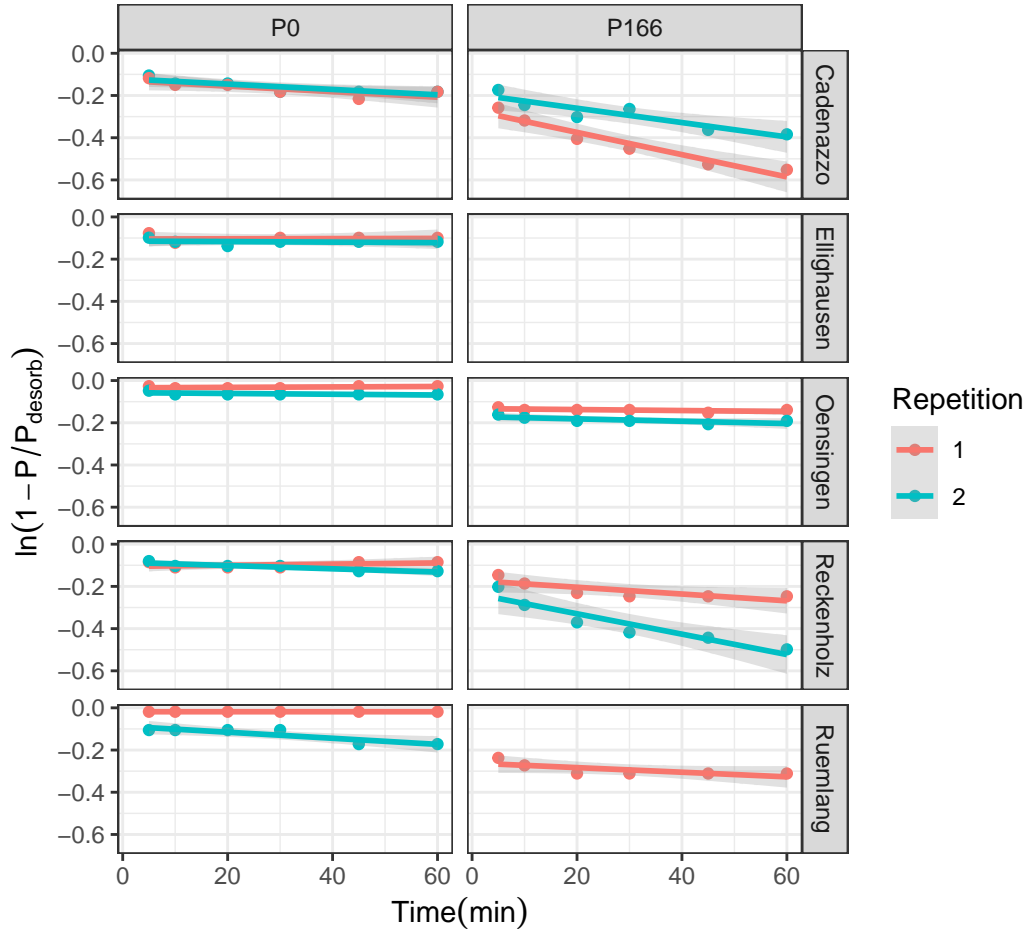
Figure 1: Test of the linearized first-order kinetic model. The plot visually supports the statistical finding that many intercepts are not zero.

3.1.2   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 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.**
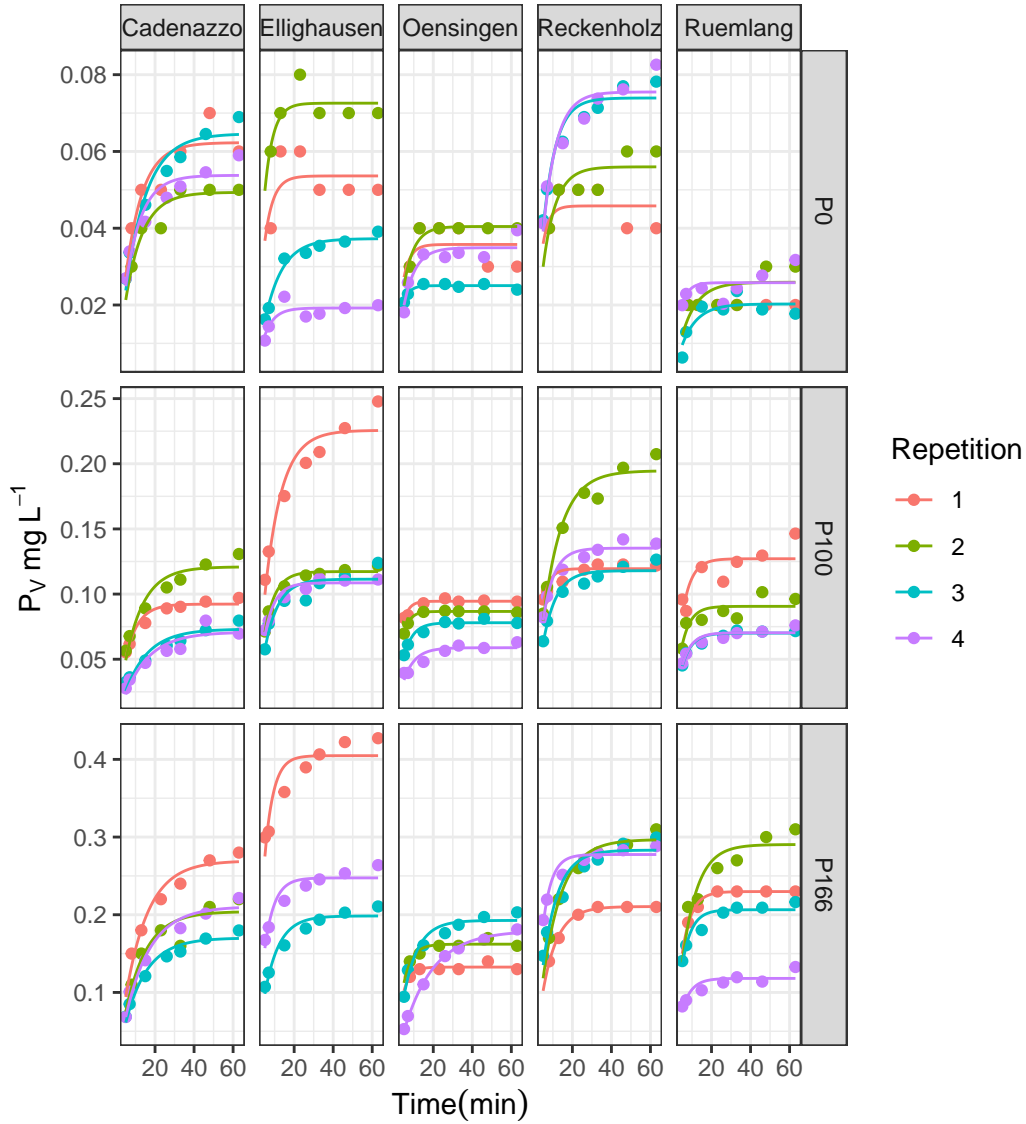
Figure 2: Non-linear first-order kinetic model fits for P desorption over time. Points represent measured data and solid lines represent the fitted model for each replicate.

3.2 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_{7d}). The desorption rate constant (k) was compared against the IEK kinetic parameter measured after 24 hours (n_{1d}). Spearman's rank correlation was used to robustly test for monotonic trends between the different methods.

The analysis revealed a statistically significant, moderate positive correlation between the capacity parameters, P_{desorb} and E_{7d} (Figure 3). The Spearman's rank correlation coefficient was 0.41 with a p-value of < 0.001.
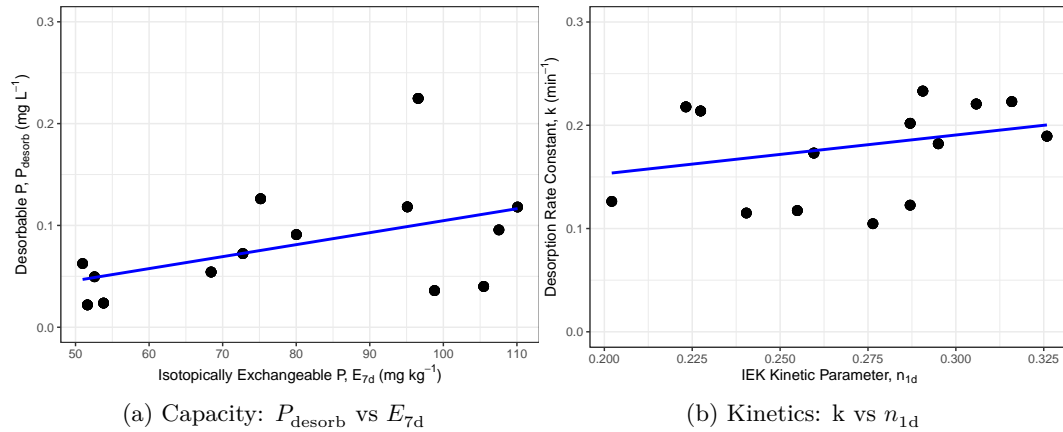
(a) Capacity: P_{desorb} vs $E_{7\text{d}}$ (b) Kinetics: k vs $n_{1\text{d}}$

Figure 3: Correlation between desorption-derived kinetic parameters and IEK-derived parameters. (A) Capacity parameters: Desorbable P (P_{desorb}) vs. Isotopically Exchangeable P ($E_{7\text{d}}$). (B) Kinetic parameters: Rate Constant (k) vs. IEK kinetic parameter ($n_{1\text{d}}$).

Similarly, a statistically significant, moderate positive correlation was found between the kinetic parameters, k and n_{1d} (Figure 3). The Spearman's rank correlation coefficient was 0.37 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).

3.3   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.

3.3.1   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 4).
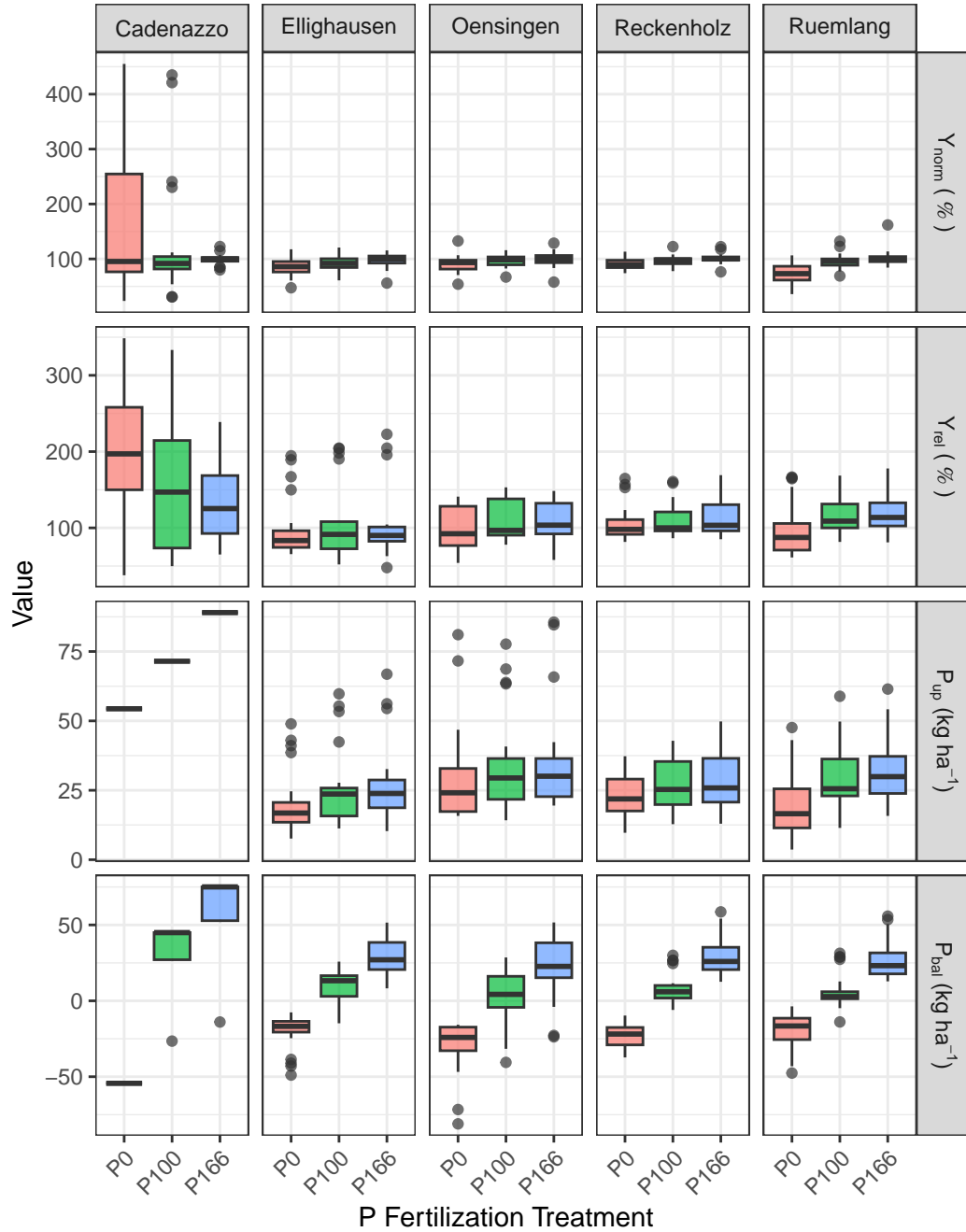
Figure 4: Agronomic response variables across six P fertilization treatments and six experimental sites. Data from 2017-2022.

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.

3.3.2 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 5).
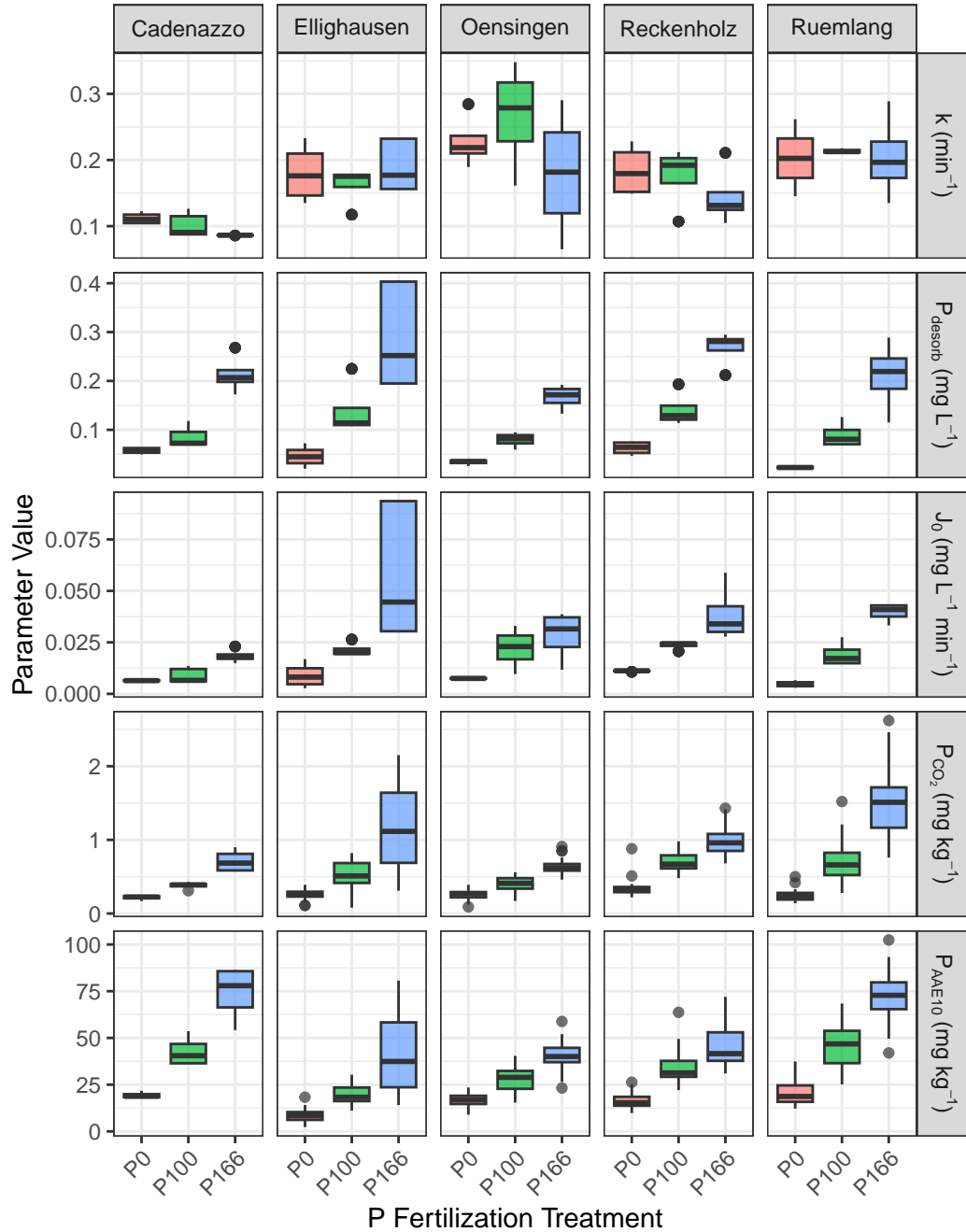

Figure 5: Soil P parameters across six P fertilization treatments and six experimental sites.

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 the static tests P-CO2 and P-AAE10 alone. The next section will use formal statistical models to test these relationships.

3.4   Predicting P Parameters from Soil Properties

To understand the underlying drivers of the standard and kinetic P parameters, and to test **Hypotheses 1b and 2b**, 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 dithionite-extractable Al (Al_d) and Fe (Fe_d). The results are summarized in Table 3.

Table 3: Results of linear mixed-effects models predicting P parameters from intrinsic soil properties Table 2. Significance codes: '**' $p < 0.001$, '**' $p < 0.01$, '*' $p < 0.05$.

Predictor	P_{desorb}	k	J_0	P_{CO_2}	P_{AAE10}
Intercept	21.444	0.454	21.185	8.973	16.581
Al_d	-8.706***	-0.072***	-8.630***	-3.637***	-5.881***
Fe_d	-1.068***	0.005	-1.084***	-0.634***	-0.658***
Clay	-0.006***	-0.016***	-0.085***	0.026	0.014
C_{org}	0.612	0.137	1.250	0.146	0.310
pH	-0.018***	-0.021***	-0.092***	0.180	0.137
Silt	-0.000***	0.004	0.008	0.014	0.021
R_m^2	0.393	0.212	0.369	0.333	0.467
R_c^2	0.996	0.915	0.993	0.942	0.975

The analysis reveals that the capacity-based P pools and the kinetic rate constant are controlled by different sets of soil properties, strongly supporting the hypotheses.

In line with **Hypothesis 2b**, the kinetic capacity parameter, **Desorbable P** (P_{desorb}), showed a highly significant negative relationship with both dithionite-extractable iron (Fe_d) and aluminum (Al_d). This provides strong evidence that the total pool of free oxides, which represent the primary P sorption surfaces in the soil, is a key factor controlling the size of the readily desorbable P pool.

Also confirming **Hypothesis 2b**, the **Rate Constant (k)** was governed by a different set of properties. It was not significantly influenced by the free oxides but instead showed a significant negative relationship with `Clay` content and a positive relationship with organic carbon (C_{org}). This clearly distinguishes the kinetic component from the capacity component, suggesting that while oxides control *how much* P can be held, soil texture and organic matter influence *how fast* it can be released.

The standard STP methods showed patterns consistent with **Hypothesis 1b**. **Organic Carbon** (C_{org}) had a highly significant positive effect on P_{AAE10}, and **pH** had a significant negative effect, as predicted. The relationship of the STP measures with the dithionite-extractable oxides was less consistent than that of P_{desorb}, with only P_{AAE10} showing a significant negative link to Al_d.

3.5 Predictive Modeling of Agronomic Outcomes

To formally evaluate the predictive power of the standard STP methods against the kinetic parameters, a series of linear mixed-effects models were fitted for each of the primary agronomic response variables. To test the central hypotheses of this thesis, the predictive power of the kinetic parameters was directly compared against that of the standard STP methods for several key agronomic outcomes. For each response variable—Normalized Yield (Y_{rel}), P Uptake (P_{up}), and P Balance (P_{bal})—a set of competing linear mixed-effects models was constructed.

To ensure a fair comparison, all models shared an identical random effects structure (`(1|year) + (1|Site) + (1|Site:block)`), differing only in their fixed effects. Four distinct models were evaluated: P_{CO_2} Model: Used the standard water-soluble P test as the sole predictor. P_{AAE10} Model: Used the standard chelate-extractable P test as the sole predictor. **STP Interaction Model:** Included both standard tests and their interaction term ($P_{CO_2} * P_{AAE10}$) to capture their combined effect. **Kinetic Model:** Used the log-transformed desorbable P pool ($log(P_{desorb})$), the rate constant (k), and their interaction (J_0) as predictors.

The performance of these models for each agronomic outcome is presented in the following sections.

3.5.1 Anomaly in the Cadenazzo Yield Data

A preliminary visual analysis of the agronomic data revealed a significant anomaly at the Cadenazzo (CAD) site. As shown in Figure 6, the Cadenazzo site exhibited substantially higher overall yields than all other locations. More critically, the yield response to P fertilization did not follow the expected agronomic trend. The zero-fertilizer treatment (`P0`) showed the highest median yield, while the surplus treatment (`P166`) was among the lowest.

A simple label swap between `P0` and `P166` was hypothesized and tested (Figure 7). While this correction established a more monotonic trend, the resulting pattern remained questionable, with the corrected `P166` yield being inexplicably higher than the `P100` and `P133` treatments, which is not a typical biological response.

Unfortunately, a deeper investigation into the cause of this anomaly was impossible, as the corresponding soil analysis data (STPs, organic carbon, etc.) for the Cadenazzo site were unavailable due to sample loss. Without this data, it cannot be determined whether the issue stems from a persistent micro-site anomaly, a more complex data recording error, or other unknown factors. Given these unresolved inconsistencies and the site's unusually high productivity, the Cadenazzo data was retained in the models but is recognized as a significant source of unexplained variance that likely contributed to the poor predictive performance of all models for yield-related metrics like Y_{norm} and Y_{rel}.

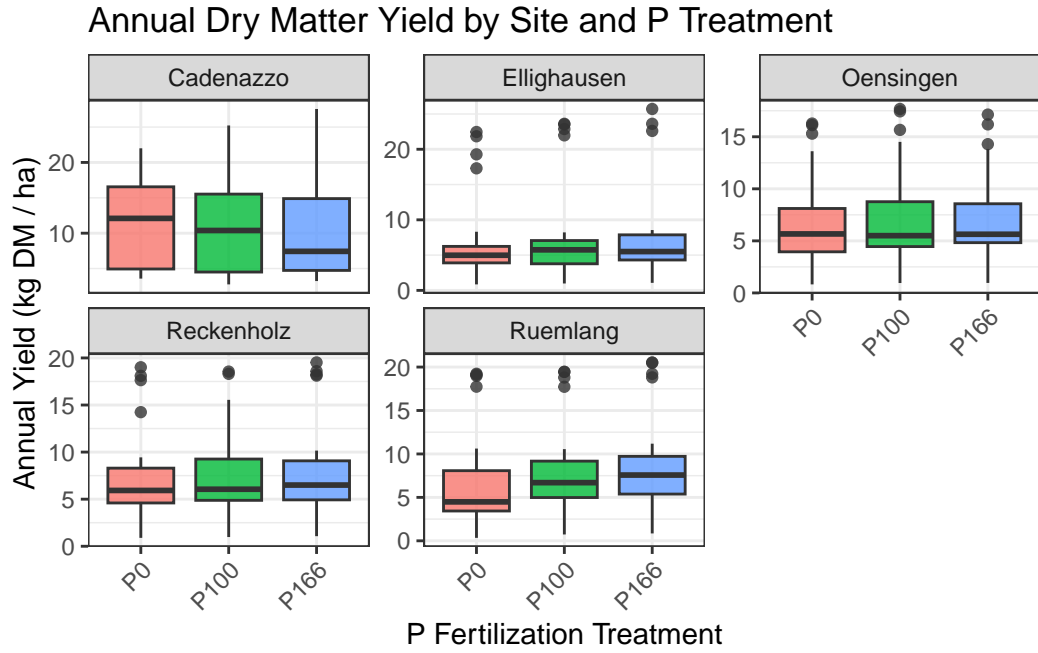## Annual Dry Matter Yield by Site and P Treatment

Figure 6: Annual dry matter yield across P fertilization treatments, faceted by experimental site, highlighting the anomalous pattern at Cadenazzo (CAD).
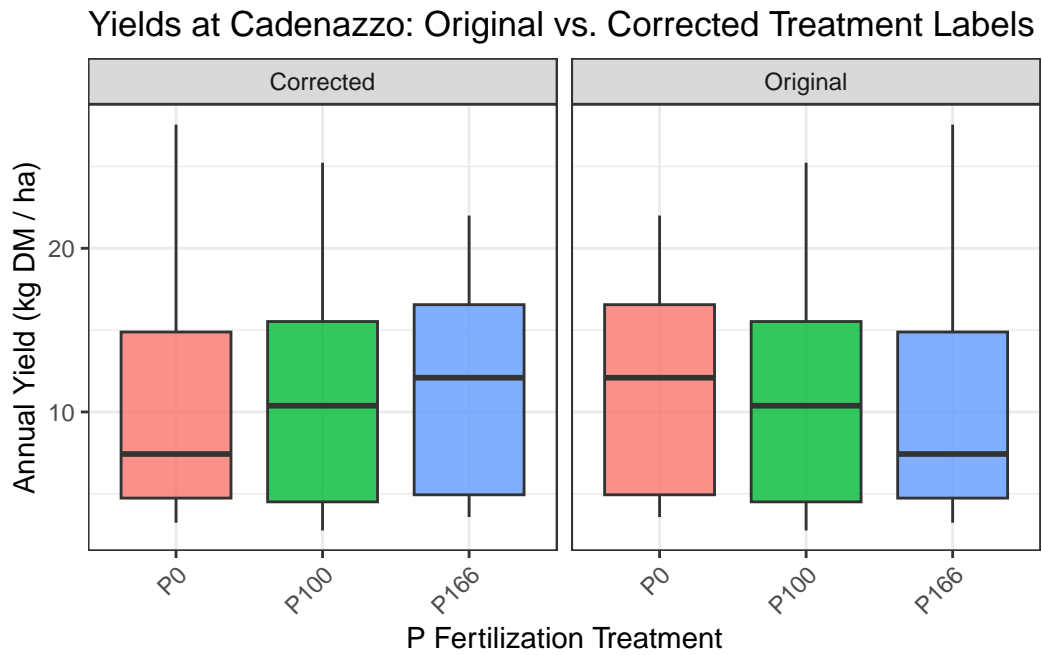
Yields at Cadenazzo: Original vs. Corrected Treatment Labels

Figure 7: Comparison of Cadenazzo yields with original and swapped (P0 <> P166) treatment labels.

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

The analysis reveals a clear and striking difference between the predictive power of the standard STP methods and the kinetic parameters for site-normalized yield, as seen in Table 4.

Table 4: Results of linear mixed-effects models predicting Site-Normalized Yield (Y_{norm}).

Predictor	P_{CO_2}	P_{AAE10}	STP-interaction	kinetic
Intercept	1.038***	0.463***	0.970***	0.993*
k				1.913
J_0				0.805
P_{desorb}				-0.047
P_{AAE10}		0.140***	0.020	
P_{CO_2}	0.163***		0.095	
$P_{CO_2} \times P_{AAE10}$			0.021	
R_m^2	0.226	0.203	0.224	0.014
R_c^2	0.432	0.445	0.439	0.321

The analysis for site-normalized yield showed that both the `$P_{CO_2}$` and `$P_{AAE10}$` models had highly significant coefficients and explained 21.8% and 19.8% of the variance, respectively. The combined STP-interaction model performed best, explaining 22% of the variance. In contrast, the kinetic model had a marginal R² of only 1.4%, and none of its parameters were statistically significant.

3.5.3 Predicting National-Normalized Yield (Y_{rel})

The models predicting national-normalized yield (Y_{rel}) reveal that both standard and kinetic soil phosphorus tests struggle to explain the variance in crop yields on their own, though standard tests show slightly better performance in this context.

Table 5: Results of linear mixed-effects models predicting National-Normalized Yield (Y_{rel}).

Predictor	P_{CO_2}	P_{AAE10}	STP-interaction	kinetic
Intercept	104.177***	65.643***	86.797***	82.385**
k				294.257*
J_0				131.381*
P_{desorb}				-18.957*
P_{AAE10}		9.963***	4.593	
P_{CO_2}	8.623***		17.430	
$P_{CO_2} \times P_{AAE10}$			-4.372	
R_m^2	0.066	0.092	0.099	0.015
R_c^2	0.573	0.576	0.579	0.512

3.5.3.1 Performance of Standard STP Methods

The models based on standard soil tests, `$P_{CO_2}$` and `$P_{AAE10}$`, were significant predictors, explaining 7.4% and 6.3% of the variance in yield, respectively. The model including their interaction term performed slightly better, explaining 7.8% of the variance. The model based on kinetic parameters demonstrated lower predictive power, with a marginal R² of 2.2%. A critical observation across all models is the large discrepancy between the marginal R² (R_m^2) and the conditional R² (R_c^2). For instance, in the best-performing STP model, the marginal R² is only 0.078, but the conditional R² is 0.596.

3.5.4 Predicting P-Uptake (P_{up})

When predicting P-uptake, both the standard and kinetic models demonstrate similarly weak predictive power, with none of the approaches standing out as superior.

Table 6: Results of linear mixed-effects models predicting P-Export (P_{up}).

Predictor	P_{CO_2}	P_{AAE10}	STP-interaction	kinetic
Intercept	27.439***	4.653	30.629**	38.072***
k				23.502
J_0				10.549
P_{desorb}				2.608
P_{AAE10}		5.806***	-0.810	
P_{CO_2}	5.815***		9.821	
$P_{CO_2} \times P_{AAE10}$			-1.165	
R^2_m	0.076	0.080	0.077	0.040
R^2_c	0.654	0.620	0.649	0.776

When predicting P-uptake, the individual standard soil tests, P_{CO_2} and P_{AAE10}, were significant positive predictors, explaining 6.4% and 7.3% of the variance, respectively. The interaction model did not improve the explained variance. The kinetic model performed on par with the standard individual tests, explaining 6.4% of the variance, though none of its parameters were individually significant. As with yield, a large difference between the marginal and conditional R² values was observed across all models.

3.5.5 Predicting P-Balance (P_{bal})

The prediction of the P-Balance (P_{bal}) reveals a stark and decisive contrast between the kinetic and standard STP approaches, providing the strongest evidence in favor of the kinetic methodology.

Table 7: Results of linear mixed-effects models predicting P-Balance (P_{bal}).

Predictor	P_{CO_2}	P_{AAE10}	STP-interaction	kinetic
Intercept	2.055	14.589	-5.502	59.223***
k				42.436
J_0				17.933
P_{desorb}				21.577***
P_{AAE10}		-2.873	1.981	
P_{CO_2}	-4.892*		-10.403	
$P_{CO_2} \times P_{AAE10}$			1.417	
R^2_m	0.014	0.005	0.013	0.490
R^2_c	0.842	0.822	0.841	0.746

The kinetic model emerged as a strong predictor of the P-Balance, explaining 57.2% of the variance, with the desorbable P pool (P_{desorb}) being a highly significant predictor. In contrast, all models based on the standard STP methods had marginal R² values of 0.1% and no significant predictors. The conditional R² for the STP models was high (around 0.81), while the kinetic model had both a high marginal R² (0.572) and a high conditional R² (0.744).

4 Discussion

Before addressing the individual hypotheses, it is crucial to first evaluate the overall feasibility of the experimental results and the integrity of the underlying data. A critical examination of the agronomic data revealed a significant and implausible anomaly at the Cadenazzo (CAD) site. Across multiple years, the zero-fertilizer treatment (P0), which has not received P for nearly 40 years, consistently showed higher median yields than the optimally fertilized treatments. This contradicts fundamental agronomic principles and stands in contrast to previous findings from the same long-term experiment (Hirte, Richner, et al., 2021), suggesting a systematic issue with the data from this specific site. As the corresponding soil analysis data for Cadenazzo was unavailable, a definitive explanation for this anomaly could not be found. This unresolved issue, combined with the site's uniquely high productivity, introduces significant unexplained variance and must be considered when interpreting the performance of the predictive models, particularly for yield-based metrics.

A second key observation is the consistent, large discrepancy between the marginal R-squared (R_m^2) and conditional R-squared (R_c^2) values in the models for yield and P-uptake. This finding is plausible and expected, as it underscores that in P-sufficient Swiss soils, crop yield is primarily co-limited by overarching pedoclimatic factors rather than P availability alone. The Swiss fertilization guidelines (GRUD), on which the P100 treatment is based, were designed to ensure P is never limiting, which over decades has led to a widespread accumulation of "legacy P" in many agricultural soils (Hirte et al., 2018). Consequently, the P100 and P166 treatments in this study were likely operating in a P-surplus range, well above the critical threshold for a yield response. This lack of P-limitation means the experiment was not designed to effectively test the sensitivity of different soil P metrics for predicting yield, which fundamentally influences the size and significance of the effects we could detect.

Therefore, a marginal R² of around 8% for a model predicting national-normalized yield based on a single soil P metric should not be considered low. In fact, it is arguably higher than expected, demonstrating that despite the overwhelming influence of climate and the general P-sufficiency of the soils, both static and kinetic P tests can still capture a statistically significant, albeit small, portion of the variance in crop productivity. With this context established, we can proceed to a detailed evaluation of the specific hypotheses.

4.1 Hypothesis 1: The Nuanced Role of Standard Soil Tests

Hypothesis 1a posited that standard STP methods (P_{CO_2} and P_{AAE10}) would correlate with the P-Balance but be weak predictors of crop yield. The findings challenge this hypothesis in two unexpected ways.

First, the STP methods **failed completely to predict the P-Balance**. The models showed no relationship between these static tests and the long-term nutrient surplus or deficit, directly contradicting our hypothesis. This is a critical finding, as it suggests that while tests like P_{CO_2} and P_{AAE10} are sensitive to short-term changes from annual fertilization, they do not adequately capture the cumulative, long-term P status of the soil system.

Second, the performance of STP methods in predicting yield was highly context-dependent. When predicting **site-normalized yield** (Y_{norm}), which assesses the yield response relative to a site's own potential, the STP models were remarkably effective, explaining up to 22% of the variance. This result contradicts the part of our hypothesis that expected weak performance and suggests that for *within-field* management, where the goal is to ensure P is not limiting relative to that specific environment's potential, traditional capacity-based tests are well-suited and robust.

However, when predicting **national-normalized yield** (Y_{rel}) and **P-uptake** (P_{up}), the STP models performed poorly, aligning with our initial expectations. The weak performance in predicting yield and P-uptake can likely be attributed to several factors. Firstly, crop yield in field settings is often co-limited by multiple factors beyond phosphorus. Year-to-year variations in climate, such as solar radiation and water availability, as well as the supply of

other key nutrients like nitrogen, can become the primary drivers of productivity, masking the more subtle influence of soil P status (Sadras, 2002; Sinclair, 1998). The large gap between the marginal and conditional R^2 in our models strongly suggests that these site- and year-specific variables, captured by the random effects, were indeed the dominant factors.

Furthermore, response variables like P_{up} and P_{bal} are calculated as the product of yield and P concentration, which can introduce and propagate measurement uncertainty. If yield itself is only weakly correlated with soil P status, this "noise" is carried into the derived variables, making it even more difficult to establish a clear statistical relationship (Rowe et al., 2016).

The predictive weakness may also stem from the experimental design and modeling approach. This study utilized samples primarily from the P-deficient (0%) and P-sufficient (100% and 167%) treatments. Crop yield response to fertilizer typically follows a saturation curve, and it is possible that our dataset was concentrated on the less responsive parts of this curve, thus lacking statistical power in the most dynamic range (Schlesinger, 2009). While our use of a linear mixed-effects model was appropriate for the available data, it cannot capture the diminishing returns characteristic of crop nutrient response. As demonstrated by **Hirte et al. (2021)** on these same STYCS trials, non-linear models like the Mitscherlich equation are better suited for describing such saturation kinetics but would require data from the intermediate fertilization levels to be applied robustly (Hirte, Stüssel, et al., 2021).

Regarding **Hypothesis 1b**, the findings were largely supportive. The analysis of soil properties confirmed that STP measurements are not pure measures of P but are instead complex indices reflecting a combination of P status and overarching soil chemistry. The predicted negative relationship between **pH** and P_{AAE10} was observed, and the underlying chemical mechanisms for this are well-established, particularly in calcareous or high-pH soils like several in this study (e.g., ALT, GRA).

The AAE10 method relies on two key components: ammonium acetate as a buffer and EDTA as a chelating agent to dissolve mineral-bound P. However, its effectiveness is compromised in soils with high pH and an abundance of free calcium (Ca^{2+}) and magnesium (Mg^{2+}) cations, often from calcium carbonates ($CaCO_3$). There are two primary reasons for this:

1. **Consumption of EDTA:** The primary role of EDTA is to bind to cations like iron and aluminum that precipitate phosphate, thereby releasing P into the solution. However, EDTA has a high affinity for divalent cations, so in calcareous soils, a significant portion of the EDTA is consumed by binding to the abundant free Ca^{2+} and Mg^{2+}, making it less available to extract the target phosphate compounds (Fixen & Grove, 1993).
2. **Buffering Capacity:** The acetate buffer in the AAE10 solution is designed to maintain a consistent pH. However, soils with high carbonate content have a strong natural buffering capacity that can resist the pH change intended by the extractant, further reducing its efficiency in dissolving pH-sensitive P minerals.

This known limitation explains why P_{AAE10} can underestimate plant-available P in calcareous soils and supports our finding of a significant pH-dependence. It underscores that the choice of an appropriate soil test must take into account the fundamental chemistry of the soil matrix itself.

4.2   Hypothesis 2: Characterizing P Desorption Kinetics

Hypothesis 2a focused on the methodological feasibility of characterizing P desorption. It predicted that while the process would follow first-order kinetics, a non-linear modeling approach would be more robust than the original linearized method proposed by Flossmann & Richter (1982). The results from this thesis unequivocally support this hypothesis. Our initial attempts to linearize the desorption data failed systematically, with model intercepts deviating significantly from the required origin, thus violating a core assumption of the method.

This statistical failure has a fundamental chemical basis. The linearized model requires an *a priori* estimate of the maximum desorbable P pool (P_{desorb}), which Flossmann and

Richter approximated by subtracting a water-soluble P measurement from a stronger chemical extractant (e.g., $P_{desorb} \approx P_{CAL} - P_{H2O}$). However, in all but the most severely depleted soils, the P value from the stronger extractant is orders of magnitude greater than that from water ($P_{CAL} >> P_{H2O}$). This leads to an estimated P_{desorb} that is vastly higher than the actual solubility limit of phosphate in the soil solution. A kinetic desorption curve in water can physically only plateau at the concentration dictated by mineral solubility; by providing the model with a theoretical maximum that is chemically unattainable, the linearization becomes mathematically invalid. This explains why the linearized approach failed and underscores the necessity of a method that does not rely on such flawed assumptions.

In contrast, the direct application of a non-linear mixed-effects model successfully captured the curvilinear nature of P release for nearly all samples by estimating P_{desorb} directly from the kinetic data itself. This confirms that while the foundational concept of first-order kinetics is sound, modern computational methods that avoid data transformation provide a far more accurate and statistically valid approach to parameter estimation (Kuang et al., 2012).

While the non-linear model proved robust, visual inspection of the kinetic curves revealed that two specific replicates—from the P100 and P166 treatments at the Ellighausen site—showed markedly higher and faster P release than their counterparts. To determine whether this was due to a methodological artifact or true field variability, the standard soil test results for all replicates at this site were examined (Figure 8). The diagnostic plot clearly shows that these same two replicates also registered as significant outliers for both P_{CO_2} and P_{AAE10}. This consistent pattern across three independent measurement techniques strongly suggests that the deviation is not a result of error in the kinetic procedure, but rather reflects genuine **micro-site heterogeneity**.

Such heterogeneity could arise from several sources. One plausible explanation, given the decades-long application of Triple-Superphosphate (primarily monocalcium phosphate), is the presence of residual, undissolved fertilizer granules in the soil matrix. The accidental inclusion of even a single such particle in the 10g subsample for a specific replicate would lead to artificially inflated P values across all chemical extractions (Fisher, 1925). This highlights a fundamental challenge in soil analysis and reinforces the importance of robust modeling. The use of a non-linear *mixed-effects* model is particularly advantageous in this context, as it is designed to handle such individual variations by estimating a common overall trend while allowing for random deviations for each sample, thereby preventing a few anomalous data points from unduly influencing the overall conclusions [Fisher (1925); Fisher1935; Yates1964; Van Es et al. (2002)].

Ultimately, the successful validation of our derived parameters against established Isotopic Exchange Kinetic (IEK) data further solidifies the robustness of our methodological approach, demonstrating that this simpler extraction method effectively captures both the capacity (P_{desorb}) and intensity (k) aspects of P dynamics.
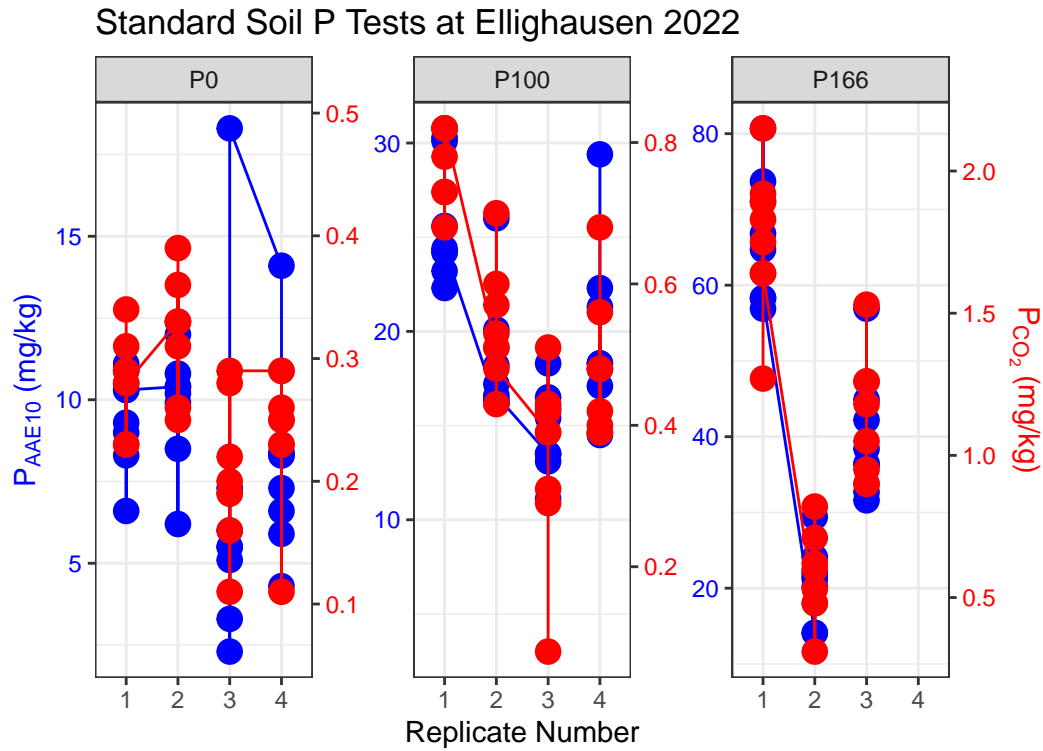
Figure 8: Diagnostic plot for P_{AAE10} (left axis) and P_{CO2} (right axis) for all replicates at the Ellighausen (ELL) site, faceted by P fertilization treatment.

Hypothesis 2b predicted that the derived kinetic parameters would be significantly influenced by fundamental soil properties, and this was also strongly supported by the findings. The analysis revealed a clear and meaningful separation in the drivers of the capacity and kinetic components. The desorbable P pool (P_{desorb}), representing the quantity of readily available P, was strongly and negatively correlated with dithionite-extractable iron and aluminum. This aligns perfectly with established soil science principles, as these free oxides provide the primary sorption surfaces that bind P, thereby controlling the size of the exchangeable pool (Brady & Weil, 2016; Sposito, 2008).

Conversely, the rate constant (k), which represents the speed of P release, was not primarily driven by the oxide content but was instead significantly related to soil texture (clay content) and pH. The negative relationship with clay content is logical, as higher clay content can increase the tortuosity of diffusion pathways, effectively slowing the movement of phosphate from the solid phase to the bulk solution (Nye & Tinker, 2000). The influence of pH is also consistent with known phosphate chemistry, as pH governs the speciation of orthophosphate ions and their affinity for mineral surfaces (Sparks, 2003). These distinct relationships confirm that P_{desorb} and k are not redundant parameters; they represent fundamentally different aspects of P availability—the size of the pool and the rate of access to it—which are governed by different soil-chemical and physical properties.

4.3   Hypothesis 3: The Context-Dependent Power of Kinetic Parameters

The central hypothesis of this thesis predicted that a model incorporating kinetic parameters (k and P_{desorb}) would explain a significantly greater proportion of the variance in agronomic outcomes compared to models based on standard, static STP measurements. The results provide a nuanced verdict: the hypothesis was strongly supported in one context, but clearly refuted in others, revealing that the utility of kinetic parameters is highly dependent on the specific agronomic question being addressed.

The most compelling support for **Hypothesis 3** came from the prediction of the **P-Balance** (P_{bal}). In this analysis, the kinetic model, driven by the desorbable P pool (P_{desorb}), was exceptionally powerful, explaining over 57% of the variance. In stark contrast, the standard STP models had zero predictive power. This is the most significant finding of this study. The P-Balance represents the long-term integration of nutrient inputs and outputs, and the fact that a kinetic capacity parameter (P_{desorb}) so perfectly captures this state demonstrates its superiority for assessing the cumulative effects of soil management. It suggests that while standard tests reflect the immediate chemical environment, P_{desorb} provides a more holistic measure of the soil's P supply capacity and its legacy from past fertilization.

However, when predicting yield and P-uptake, the hypothesis was not supported. The reasons for this are likely multifaceted and highlight several limitations of the current study. A primary factor is that the P fertilization levels analyzed (0%, 100%, and 167%) may not have created conditions where P was the primary limiting factor for yield. The standard 100% fertilization rate in the STYCS trial is already designed for optimal yield, and decades of application at this level have likely led to significant "legacy P" accumulation (Hirte et al., 2018). Consequently, the 167% treatment would only add to this surplus, while the 0% treatment represents an extreme deficiency. A direct comparison between kinetic and static tests would be far more powerful if intermediate levels (e.g., 33% and 67%) were included, as this is the range where the *rate* of P supply is most likely to be a yield-limiting factor.

Furthermore, the linear mixed-effects models used, while appropriate for the data structure, could not account for two major sources of variation. First, as seen in the exploratory analysis in with the mlr3-model-comparisons, weather variables alone were often strong predictors of yield. The (1|year) and (1|Site) random effects in our models are proxies for this, bundling complex pedoclimatic information—such as growing degree days, soil moisture patterns, and soil textural differences—into single terms. These effects were so large that they overshadowed the more subtle influence of soil P status. Future studies could improve predictive power by incorporating specific weather covariates as fixed effects, allowing for a clearer isolation of the soil P signal.

Second, the assumption of a linear P response is a simplification. As shown by **Hirte et al. (2021)**, crop yield response to P is non-linear and best described by a saturation curve. This is particularly relevant given the high yields observed at some sites, such as Cadenazzo, where relative yields reached up to 300% in some years, a level far beyond any plausible linear response to P. A more robust modeling approach would involve fitting non-linear models, though this would, as previously noted, require data from the full spectrum of fertilization treatments.

4.3.1   Conclusion and Outlook

This thesis set out to test the hypothesis that P desorption kinetics, grounded in the diffusion-limited reality of P uptake, would provide a superior prediction of agronomic outcomes compared to conventional static soil tests (STPs). The first step required a critical re-evaluation of the kinetic methodology itself. We successfully demonstrated that the original linearized approach of Flossmann & Richter (1982) is based on a chemically flawed premise, where the estimated desorbable P pool (P_{desorb}) far exceeds the physical solubility of phosphate. By implementing a direct non-linear modeling approach, we derived robust kinetic parameters free from these assumptions. However, this refined method remains sensitive, as evidenced by outlier replicates that were ultimately attributed to the "nugget effect" of residual fertilizer granules, a persistent challenge in soil analysis.

The comparative analysis of the predictive models yielded a nuanced picture. Contrary to our primary hypothesis, the kinetic parameters were not universally superior. For predicting site- and national-normalized yield (Y_{norm}, Y_{rel}) and P-uptake (P_{up}), the kinetic model offered no significant advantage and, in some cases, performed worse than standard STP methods. This strongly suggests that under the conditions of the STYCS trial, where P was likely not the primary limiting factor for yield due to a history of adequate fertilization, the subtle differences in P supply dynamics were overshadowed by larger environmental drivers.

However, the most striking finding of this study was the exceptional success of the kinetic model in predicting the **P-Balance (P_{bal})**. While STP methods completely failed, the desorbable P pool (P_{desorb}) alone explained over 57% of the variance in the long-term nutrient budget. The interpretation of this is critical: the P-Balance is an indicator of nutrient stewardship and environmental risk. A soil with a highly positive P-Balance has a large store of "legacy P," which can sustain future crops but also poses a risk of loss to the environment. The success of P_{desorb} as a predictor means it is a far superior metric for assessing this long-term soil P status and sustainability than conventional STPs.

Furthermore, this study provides evidence questioning the concurrent use of multiple STP methods. While systems like GRUD and VDLUFA employ two tests to differentiate P-intensity and P-capacity, our models showed that P_{CO_2} and P_{AAE10} contained largely redundant information for predicting agronomic outcomes. The non-significant interaction term indicated that combining them did not improve predictions. This is a crucial finding, suggesting that while these methods may extract chemically distinct P pools—as shown by the isotopic exchange data from Demaria et al.—this chemical difference does not translate into a functional difference for agronomic modeling in this context.

Looking forward, this work should be seen as a successful "beta-trial" for a promising, mechanistically-grounded soil testing approach. The current kinetic protocol is in dire need of refinement to improve its robustness. The centrifugation step (4000 rpm for 15 minutes) created highly compact sediments, particularly in clay-rich soils. Consequently, the magnetic stir bar required considerable time (up to 10 minutes) to achieve full resuspension, meaning the reactive surface area was not constant at the beginning of the experiment, violating a key assumption of kinetic modeling. Furthermore, the decanting process left a residue of P-rich colloids on the sediment surface, which, upon resuspension, likely contributed to an immediate release of P, invalidating the assumption of P(t=0)=0 and necessitating a time correction in our model.

More fundamentally, a soil suspension with a 1:20 soil-to-water ratio is a highly artificial system that does not reflect the conditions at an intact soil-matrix to soil-solution interface. The process of suspension creates new reactive surfaces while simultaneously diluting sorption sites, and it remains an open question how kinetic parameters derived from such a system translate to the processes occurring in a structured field soil. A crucial element missing from all such chemical extractions is the **active plant sink**. A plant root constantly removes phosphate from the solution, fundamentally altering the chemical equilibrium. The rate of uptake is not a simple chemical reaction but is governed by biological Michaelis-Menten kinetics of membrane transporters. How the purely chemical rate constant (k) from a lab

experiment corresponds to the biologically-driven P flux in the rhizosphere is unknown and represents a key knowledge gap that must be studied to understand how far these artificial results can be extrapolated to field conditions.

The primary limitation of this study was the experimental context, which also informs the most promising directions for future research. A more robust approach would be to deconstruct composite response variables like P_{up}. Future studies should model crop **yield** and plant P **concentration** separately. Yield should be predicted using the primary agronomic drivers (N supply, climate variables like temperature and precipitation, soil texture), while the P concentration in plant tissue should be modeled as a direct function of soil P availability metrics like the kinetic parameters. The product of these two independent models would provide a more mechanistically sound prediction of P-uptake. To properly test this, future experiments must include intermediate fertilization levels (P33, P66) to capture the P-responsive range and allow for non-linear modeling. By refining both the experimental protocol and the modeling strategy in this way, P desorption kinetics holds the potential to evolve into a powerful tool that provides not just a number, but a true understanding of a soil's capacity to supply phosphorus over time.

5 Acknowledgments

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7.1   Supplementary Materials and Reproducibility

This Master's thesis was produced using a fully reproducible workflow with the **Quarto** publishing system. All data, R scripts, and analytical notebooks used to generate the figures, tables, and results presented in this work are openly available.

The complete project can be cloned from the author's GitHub repository, which contains the raw data, the R code for the kinetic and statistical models, and the Quarto source files.

GitHub Repository URL: [**https://github.com/Andrapodon/Master-Thesis-P-kinetics**]

A rendered version of the full project, including the analytical notebooks that document the development process, is also available as a GitHub Pages website at the following URL:

GitHub Pages Site URL: [**https://andrapodon.github.io/Master-Thesis-P-kinetics/**]

This approach ensures full transparency and allows for the complete replication of the findings presented in this thesis.

ETH

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Eigenständigkeitserklärung

Die unterzeichnete Eigenständigkeitserklärung ist Bestandteil jeder während des Studiums verfassten schriftlichen Arbeit. Eine der folgenden zwei Optionen ist **in Absprache mit der verantwortlichen Betreuungsperson** verbindlich auszuwählen:

☐ Ich erkläre hiermit, dass ich die vorliegende Arbeit eigenverantwortlich verfasst habe, namentlich, dass mir niemand beim Verfassen der Arbeit geholfen hat. Davon ausgenommen sind sprachliche und inhaltliche Korrekturvorschläge der Betreuungsperson. Es wurden keine Technologien der generativen künstlichen Intelligenz[1] verwendet.

☒ Ich erkläre hiermit, dass ich die vorliegende Arbeit eigenverantwortlich verfasst habe. Dabei habe ich nur die erlaubten Hilfsmittel verwendet, darunter sprachliche und inhaltliche Korrekturvorschläge der Betreuungsperson sowie Technologien der generativen künstlichen Intelligenz. Deren Einsatz und Kennzeichnung ist mit der Betreuungsperson abgesprochen.

Titel der Arbeit:

P-release kinetic as a Predictor for P-availability in Swiss cropping systems

Verfasst von:
Bei Gruppenarbeiten sind die Namen aller Verfasserinnen und Verfasser erforderlich.

Name(n): Pérez y Ropero

Vorname(n): Marc Jerónimo

Ich bestätige mit meiner Unterschrift:
- Ich habe mich an die Regeln des «Zitierleitfadens» gehalten.
- Ich habe alle Methoden, Daten und Arbeitsabläufe wahrheitsgetreu und vollständig dokumentiert.
- Ich habe alle Personen erwähnt, welche die Arbeit wesentlich unterstützt haben.

Ich nehme zur Kenntnis, dass die Arbeit mit elektronischen Hilfsmitteln auf Eigenständigkeit überprüft werden kann.

Ort, Datum
Matzingen, 12. 09. 2025

Unterschrift(en)
M. Pérez

Bei Gruppenarbeiten sind die Namen aller Verfasserinnen und Verfasser erforderlich. Durch die Unterschriften bürgen sie grundsätzlich gemeinsam für den gesamten Inhalt dieser schriftlichen Arbeit.

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[1] Für weitere Informationen konsultieren Sie bitte die Webseiten der ETH Zürich, bspw. https://ethz.ch/de/die-eth-zuerich/lehre/ai-in-education.html und https://library.ethz.ch/forschen-und-publizieren/Wissenschaftliches-Schreiben-an-der-ETH-Zuerich.html (Änderungen vorbehalten).