

Master Thesis

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Hier kommt das Abstract

Preface

Abstract

(Knuth 1984)

Introduction

Complexity of Phosphorous

Phosphorous displays a wide range of behaviours in soils, in places where organic, mineral and aqueous phases interface. In phases that contain oxygen Phosphorous is almost exclusively present as several derivatives of Orthophosphate PO_4^{3-} . It can be found as organic molecules as anhydric- and ester-groups, being needed by all known species as a constituent of DNA and energy transfer-processes. It can be present as anorganic Phosphate either as mono-orthophosphate PO_4^{3-} or poly-orthophosphate $HO - (PO_2)_n - OH$, where it can strongly interact with water, forming, depending on pH HPO_4^{2-} or $H_2PO_4^-$. The dissolved species of phosphate are subject to adsorption to clay- and oxide-surfaces of the solid soil-phase, they also form fallout-products such as Apatite, Vivianite etc. With the present metal-cations in the solution. While the solubility constant of most phosphate-salts are comparably low (Wert eingeben), meaning that the fallout and formation of minerals happens at low chemical activities of phosphate, phosphate often is leached from soil-surface-layers, heavily reducing the efficacy of P-fertilization and presenting a disturbance to P-limited ecosystems. Those phenomena, many of them being physicochemically controlled, are influenced by parameters such as pH, ionic-strength, clay-content, specific-surface of the solid phase, amorphous $Fe(OH)_3$ -content, amorphous $Al(OH)_3$ -content, in short the phenomena depend heavily on the composition, distribution and geometry of the soil. Those properties are considered to be stable respectively

long-term properties of a soil, when looked at it with the interest of modelling the transport processes of Phosphate in soils. Factors such as water-content, temperature, vegetation and precipitation are factors that temporally can vary fast and to a certain degree unpredictably. Organic forms of phosphates, prominently DNA or oligonucleotides and phytate are also subject to physicochemical reactions, mainly decomposition, but are foremost controlled in their presence by enzymatic processes, where i.e. plants form phytates in seeds to provide the embryo a compact and specific reserve of phosphate, but many bacteria possess via Phytases the ability to hydrolyse phytate and use it for their own means. To assess and cover those phenomena, models, dynamically describing the motion of Phosphorous in soils, differentiate several pools of Phosphorous, most prominently the organic-P, dissolved-P, adsorbed-P, mineral-P, where the difference in temporal behaviour, such as the mean-reside-time can lead to a differentiation between labile-P, semi-labile-P and so on.

Plants as Phosphate sinks

When a soil is used agronomically, P-sinks such as leaching and plant P-uptake

```
#|include: false
#|echo: false

library(multcomp)
```

```
Loading required package: mvtnorm
```

```
Loading required package: survival
```

```
Loading required package: TH.data
```

```
Loading required package: MASS
```

```
Attaching package: 'TH.data'
```

```
The following object is masked from 'package:MASS':
```

```
geyser
```

```
library(car)
```

Loading required package: carData

```
library(tidyr)  
library(lme4)
```

Loading required package: Matrix

Attaching package: 'Matrix'

The following objects are masked from 'package:tidyr':

expand, pack, unpack

```
library(ggplot2)  
library(ggtext)  
library(ggpmisc)
```

Loading required package: ggpp

Registered S3 methods overwritten by 'ggpp':

method	from
heightDetails.titleGrob	ggplot2
widthDetails.titleGrob	ggplot2

Attaching package: 'ggpp'

The following object is masked from 'package:ggplot2':

annotate

```
library(nlme)
```

Attaching package: 'nlme'

The following object is masked from 'package:lme4':

lmList

```
library(latex2exp)
library(kableExtra)
library(broom)
library(dplyr)
```

Attaching package: 'dplyr'

The following object is masked from 'package:kableExtra':

group_rows

The following object is masked from 'package:nlme':

collapse

The following object is masked from 'package:car':

recode

The following object is masked from 'package:MASS':

select

The following objects are masked from 'package:stats':

filter, lag

The following objects are masked from 'package:base':

intersect, setdiff, setequal, union

```
library(MuMin)
```

Registered S3 methods overwritten by 'MuMIn':

```
method      from
nobs.multinom broom
nobs.fitted  broom
```

```
library(sjPlot) # table functions
library(sjmisc) # sample data
```

Attaching package: 'sjmisc'

The following object is masked from 'package:tidyr':

```
replace_na
```

```
library(lme4) # fitting models
library(report)
library(performance)

load("~/Documents/Master Thesis/Master-Thesis-P-kinetics/data/results_coefficient_analysis")
```

Research Questions:

How well can current GRUD measurements of C_P predict the relative Yield, P-Uptake and P-Balance?

- Hypothesis I: The measurements of the equilibrium concentrations of Phosphorus in a solvent do not display significant effects on relative Yield and consequently P-Uptake, since it is strongly dependent on yield. C_P relates strongly to the amount of Phosphorus applied, the P-balance might well be significantly correlated to C_P but not explain a lot of variance.

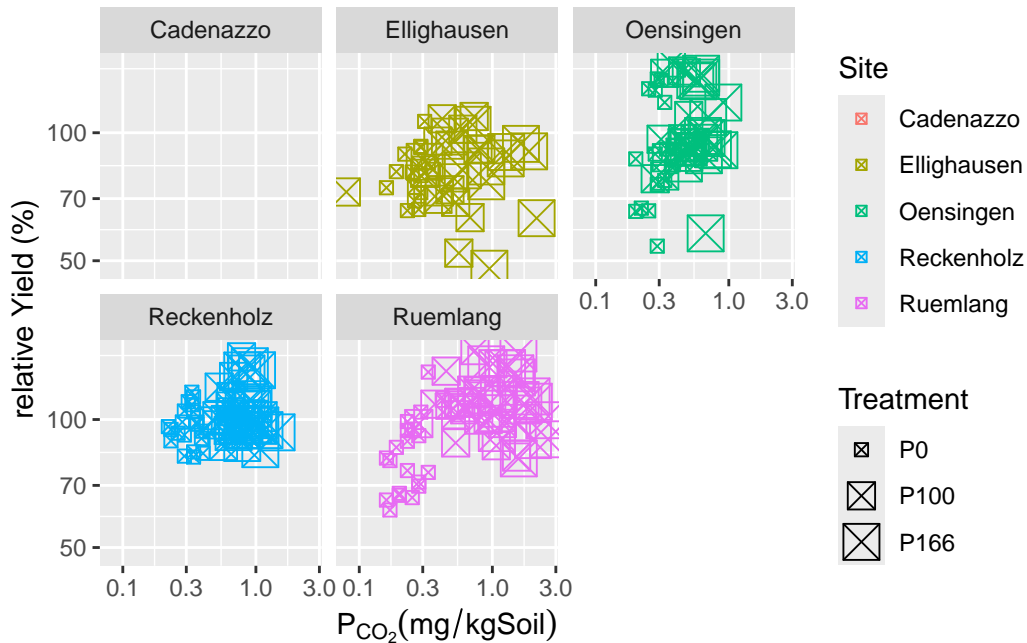
```
#|code-fold: true
#|tidy: true
#|echo: false

ggplot(D[D$soil_0_20_P_CO2!=0,], aes(y=Ymain_rel, x=soil_0_20_P_CO2, col=Site, size = Treatment)) +
  geom_point(shape = 7) +
  scale_x_log10() + scale_y_log10() +
  labs(x=TeX("$P_{CO_2}$ (mg/kg Soil)$"),
```

```
y="relative Yield (%)" +  
facet_wrap( ~ Site, nrow = 2)
```

Warning: Using size for a discrete variable is not advised.

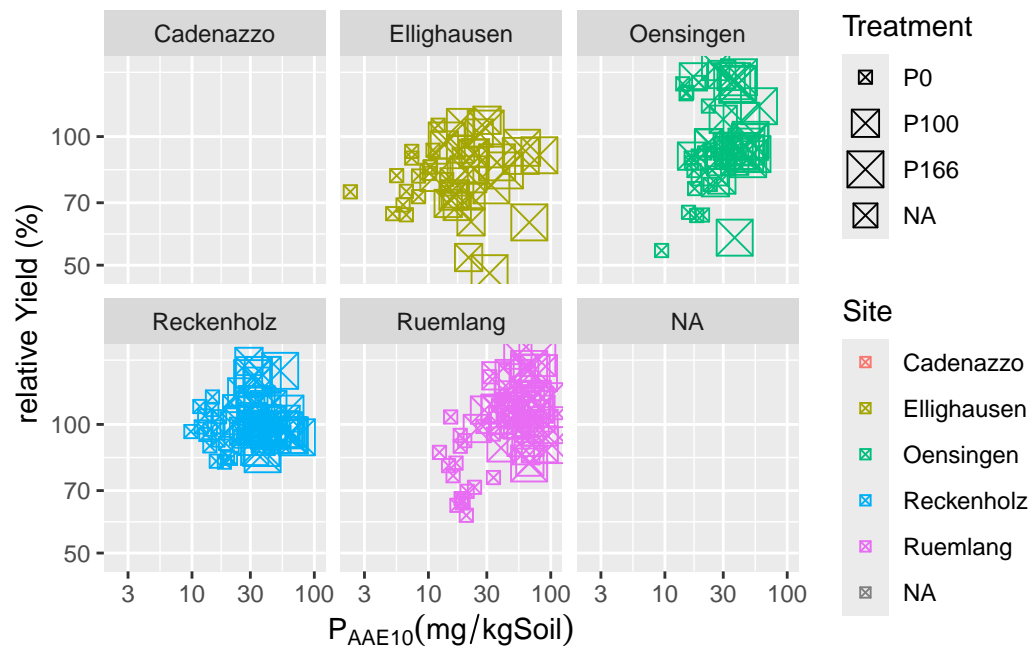
Warning: Removed 200 rows containing missing values or values outside the scale range (`geom_point()`).



```
ggplot(D[D$soil_0_20_P_AAE10!=0,],aes(y=Ymain_rel, x=soil_0_20_P_AAE10, col=Site, size = Tre  
geom_point(shape = 7) +  
scale_x_log10() + scale_y_log10() +  
labs(x=TeX("$P_{AAE10}(mg/kg Soil)$"),  
y="relative Yield (%)") +  
facet_wrap( ~ Site, nrow = 2)
```

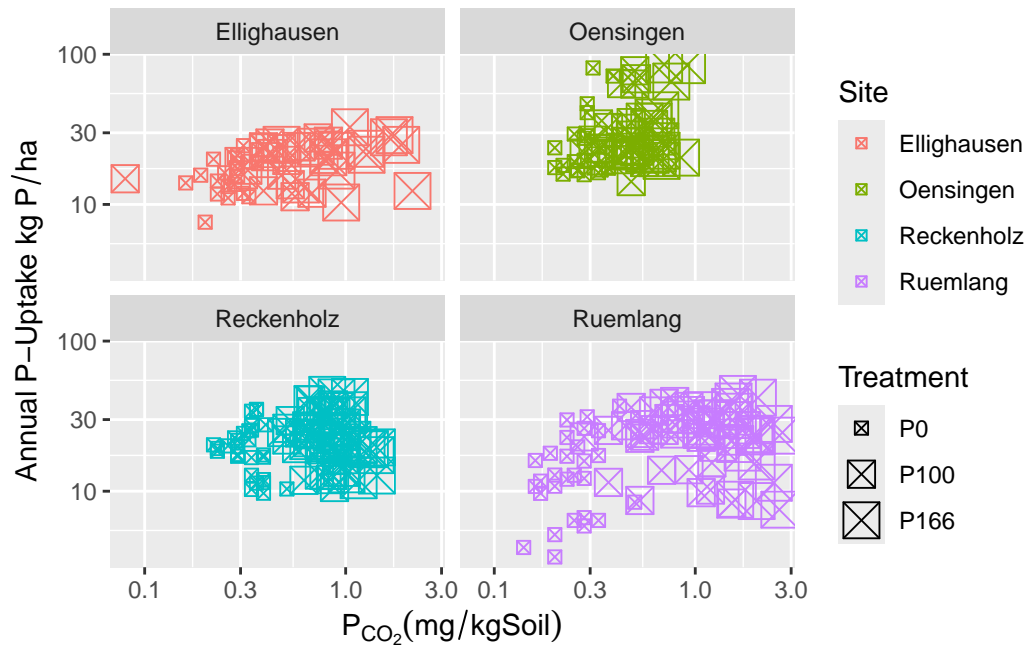
Warning: Using size for a discrete variable is not advised.

Warning: Removed 259 rows containing missing values or values outside the scale range (`geom_point()`).



```
ggplot(D[D$soil_0_20_P_CO2!=0&D$annual_P_uptake!=0,], aes(y=annual_P_uptake, x=soil_0_20_P_CO2)) +
  geom_point(shape = 7) +
  scale_x_log10() + scale_y_log10() +
  labs(x=TeX("$P_{CO_2}$ (mg/kg Soil)"),
       y=TeX("Annual P-Uptake $kg~P/ha$")) +
  facet_wrap(~ Site, nrow = 2)
```

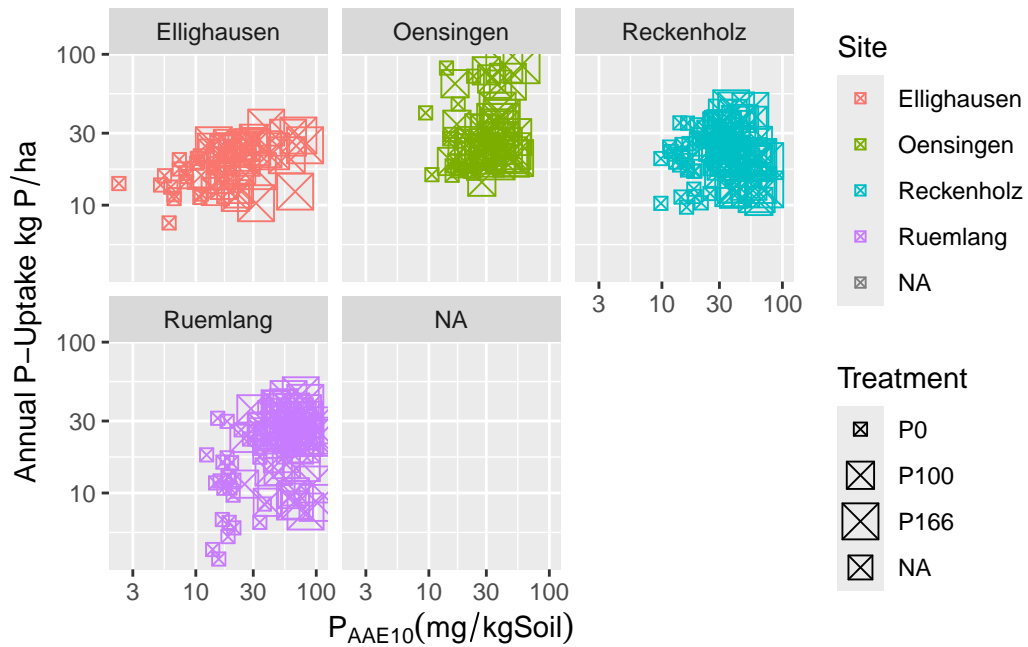
Warning: Using size for a discrete variable is not advised.



```
ggplot(D[D$soil_0_20_P_AAE10!=0&D$annual_P_uptake!=0,],aes(y=annual_P_uptake, x=soil_0_20_P_
  geom_point(shape = 7) +
  scale_x_log10() + scale_y_log10() +
  labs(x=TeX("$P_{AAE10}(mg/kg Soil)$"),
        y=TeX("Annual P-Uptake $kg~P/ha$")) +
  facet_wrap( ~ Site, nrow = 2)
```

Warning: Using size for a discrete variable is not advised.

Warning: Removed 50 rows containing missing values or values outside the scale range (`geom_point()`).



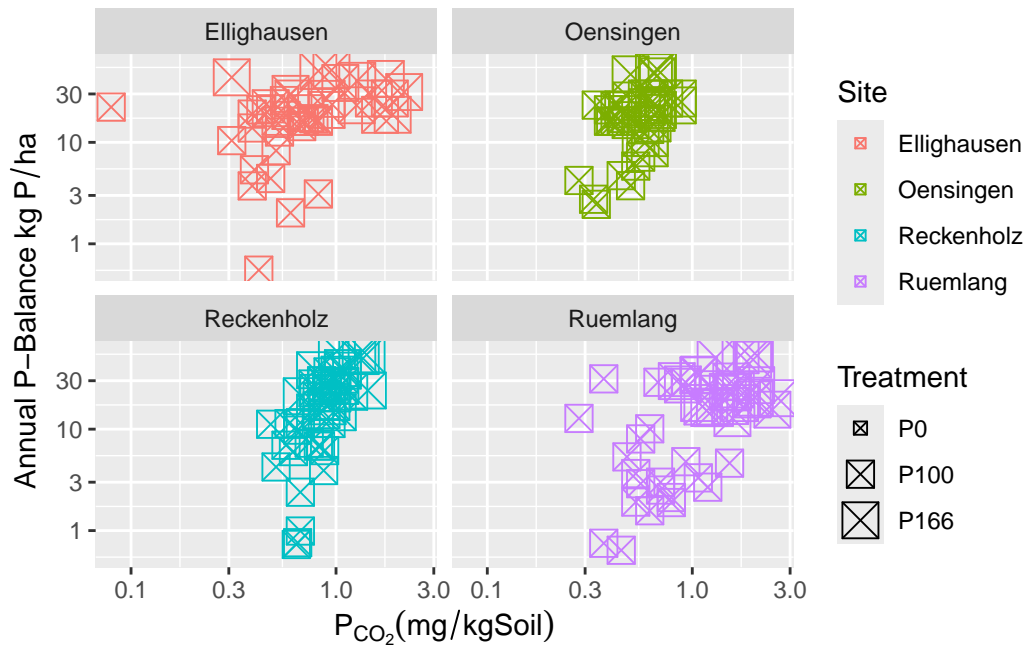
```
ggplot(D[D$soil_0_20_P_CO2!=0&D$annual_P_balance!=0,],aes(y=annual_P_balance, x=soil_0_20_P_
  geom_point(shape = 7) +
  scale_x_log10() + scale_y_log10() +
  labs(x=TeX("$P_{CO_{2}}(mg/kg Soil)$"),
        y=TeX("Annual P-Balance $kg~P/ha$")) +
  facet_wrap( ~ Site, nrow = 2)
```

Warning: Using size for a discrete variable is not advised.

Warning in transformation\$transform(x): NaNs produced

Warning in scale_y_log10(): log-10 transformation introduced infinite values.

Warning: Removed 131 rows containing missing values or values outside the scale range (`geom_point()`).



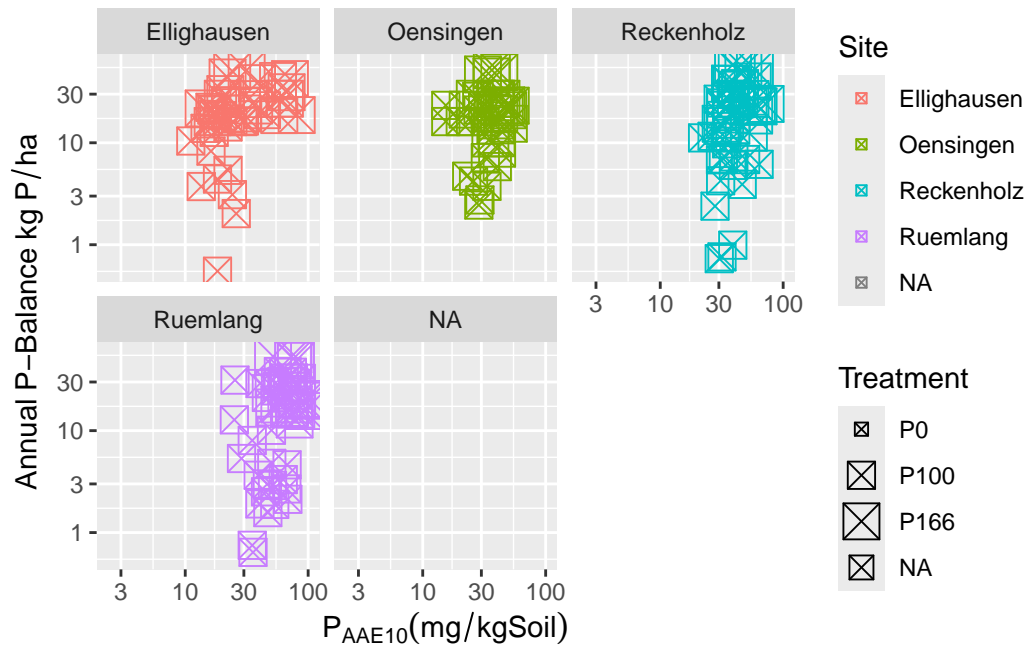
```
ggplot(D[D$soil_0_20_P_AAE10!=0&D$annual_P_balance!=0,],aes(y=annual_P_balance, x=soil_0_20_P_AAE10)) +
  geom_point(shape = 7) +
  scale_x_log10() + scale_y_log10() +
  labs(x=TeX("$P_{AAE10}(mg/kg Soil)$"),
       y=TeX("Annual P-Balance $kg~P/ha$")) +
  facet_wrap( ~ Site, nrow = 2)
```

Warning: Using size for a discrete variable is not advised.

Warning in transformation\$transform(x): NaNs produced

Warning in scale_y_log10(): log-10 transformation introduced infinite values.

Warning: Removed 187 rows containing missing values or values outside the scale range (`geom_point()`).



Now we want to check the strength of the models in terms of R^2 and the significance of the effects in terms of p-values:

```
#|code-fold: true
#|tidy: true
#|echo: false

#tab_model(fit.grud.Yrel,fit.grud.Puptake,fit.grud.Pbalance)
report(fit.grud.Yrel)
```

Loading required namespace: lmerTest

Formula contains log- or sqrt-terms.

See `help("standardize")` for how such terms are standardized.

boundary (singular) fit: see `help('isSingular')`

Formula contains log- or sqrt-terms.

See `help("standardize")` for how such terms are standardized.

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We fitted a linear mixed model (estimated using REML and nloptwrap optimizer) to predict `Ymain_rel` with `soil_0_20_P_CO2`, `soil_0_20_P_AAE10` and `Treatment` (formula: `Ymain_rel ~ log(soil_0_20_P_CO2) + log(soil_0_20_P_AAE10) + Treatment`). The model included year as random effects (formula: `list(~1 | year, ~1 | Site, ~1 | Site:block, ~1 | Site:Treatment)`). The model's total explanatory power is substantial (conditional $R^2 = 0.58$) and the part related to the fixed effects alone (marginal R^2) is of 0.10. The model's intercept, corresponding to `soil_0_20_P_CO2 = 0`, `soil_0_20_P_AAE10 = 0` and `Treatment = P0`, is at 70.66 (95% CI [38.22, 103.10], $t(202) = 4.30$, $p < .001$). Within this model:

- The effect of `soil_0_20_P_CO2 [log]` is statistically non-significant and positive (beta = 1.16, 95% CI [-6.67, 8.98], $t(202) = 0.29$, $p = 0.771$; Std. beta = -0.28, 95% CI [-0.97, 0.42])
- The effect of `soil_0_20_P_AAE10 [log]` is statistically non-significant and positive (beta = 8.10, 95% CI [-0.14, 16.33], $t(202) = 1.94$, $p = 0.054$; Std. beta = 0.93, 95% CI [0.17, 1.68])
- The effect of `Treatment [P100]` is statistically non-significant and positive (beta = 4.06, 95% CI [-5.90, 14.02], $t(202) = 0.80$, $p = 0.422$; Std. beta = 0.29, 95% CI [-0.18, 0.76])
- The effect of `Treatment [P166]` is statistically non-significant and positive (beta = 1.60, 95% CI [-10.64, 13.84], $t(202) = 0.26$, $p = 0.797$; Std. beta = 0.20, 95% CI [-0.39, 0.80])

Standardized parameters were obtained by fitting the model on a standardized version of the dataset. 95% Confidence Intervals (CIs) and p-values were computed using a Wald t-distribution approximation.

```
report(fit.grud.Puptake)
```

Formula contains log- or sqrt-terms.

See `help("standardize")` for how such terms are standardized.
boundary (singular) fit: see `help('isSingular')`

Random effect variances not available. Returned R^2 does not account for random effects.

Formula contains log- or sqrt-terms.

See `help("standardize")` for how such terms are standardized.
boundary (singular) fit: see `help('isSingular')`

Random effect variances not available. Returned R^2 does not account for random effects.

We fitted a linear mixed model (estimated using REML and nloptwrap optimizer) to predict annual_P_uptake with soil_0_20_P_CO2, soil_0_20_P_AAE10 and Treatment (formula: annual_P_uptake ~ log(soil_0_20_P_CO2) + log(soil_0_20_P_AAE10) + Treatment). The model included year as random effects (formula: list(~1 | year, ~1 | Site, ~1 | Site:block, ~1 | Site:Treatment)). The model's explanatory power related to the fixed effects alone (marginal R2) is 0.05. The model's intercept, corresponding to soil_0_20_P_CO2 = 0, soil_0_20_P_AAE10 = 0 and Treatment = P0, is at 14.25 (95% CI [-3.31, 31.81], t(402) = 1.59, p = 0.112). Within this model:

- The effect of soil 0 20 P CO2 [log] is statistically non-significant and positive (beta = 2.08, 95% CI [-1.75, 5.92], t(402) = 1.07, p = 0.286; Std. beta = 0.15, 95% CI [-0.29, 0.60])
- The effect of soil 0 20 P AAE10 [log] is statistically non-significant and positive (beta = 0.82, 95% CI [-3.27, 4.91], t(402) = 0.40, p = 0.693; Std. beta = 0.16, 95% CI [-0.35, 0.66])
- The effect of Treatment [P100] is statistically non-significant and positive (beta = 1.52, 95% CI [-2.04, 5.09], t(402) = 0.84, p = 0.401; Std. beta = 0.12, 95% CI [-0.10, 0.35])
- The effect of Treatment [P166] is statistically non-significant and positive (beta = 1.18, 95% CI [-3.83, 6.19], t(402) = 0.46, p = 0.643; Std. beta = 0.10, 95% CI [-0.22, 0.42])

Standardized parameters were obtained by fitting the model on a standardized version of the dataset. 95% Confidence Intervals (CIs) and p-values were computed using a Wald t-distribution approximation.

```
report(fit.grud.Pbalance)
```

Formula contains log- or sqrt-terms.

See help("standardize") for how such terms are standardized.
boundary (singular) fit: see help('isSingular')

Random effect variances not available. Returned R2 does not account for random effects.

Formula contains log- or sqrt-terms.

See help("standardize") for how such terms are standardized.
boundary (singular) fit: see help('isSingular')

Random effect variances not available. Returned R2 does not account for random effects.

We fitted a linear mixed model (estimated using REML and nlptwrap optimizer) to predict annual_P_balance with soil_0_20_P_CO2, soil_0_20_P_AAE10 and Treatment (formula: annual_P_balance ~ log(soil_0_20_P_CO2) + log(soil_0_20_P_AAE10) + Treatment). The model included year as random effects (formula: list(~1 | year, ~1 | Site, ~1 | Site:block, ~1 | Site:Treatment)). The model's explanatory power related to the fixed effects alone (marginal R²) is 0.51. The model's intercept, corresponding to soil_0_20_P_CO2 = 0, soil_0_20_P_AAE10 = 0 and Treatment = P0, is at -16.64 (95% CI [-35.71, 2.43], t(402) = -1.72, p = 0.087). Within this model:

- The effect of soil 0 20 P CO2 [log] is statistically significant and negative (beta = -5.00, 95% CI [-9.65, -0.35], t(402) = -2.12, p = 0.035; Std. beta = -0.05, 95% CI [-0.48, 0.37])
- The effect of soil 0 20 P AAE10 [log] is statistically non-significant and negative (beta = -1.12, 95% CI [-6.04, 3.80], t(402) = -0.45, p = 0.655; Std. beta = -0.43, 95% CI [-0.90, 0.03])
- The effect of Treatment [P100] is statistically significant and positive (beta = 22.38, 95% CI [18.03, 26.72], t(402) = 10.13, p < .001; Std. beta = 1.12, 95% CI [0.91, 1.33])
- The effect of Treatment [P166] is statistically significant and positive (beta = 38.89, 95% CI [32.78, 44.99], t(402) = 12.52, p < .001; Std. beta = 1.95, 95% CI [1.65, 2.26])

Standardized parameters were obtained by fitting the model on a standardized version of the dataset. 95% Confidence Intervals (CIs) and p-values were computed using a Wald t-distribution approximation.

here I also show the non linear mixed models, following the Mitscherlich saturation curve:

```
#|code-fold: true
#|echo: false

library(nlme)

# Make sure grouping variables are factors
D$year <- as.factor(D$year)
D$Site <- as.factor(D$Site)
D$block <- as.factor(D$block)
D$crop <- as.factor(D$crop)
# Fit the model
fit.mitscherlich.CO2.Yrel <- nlme(
```

```

Ymain_rel ~ A * (1 - exp(-k * soil_0_20_P_CO2 + E)),
fixed = A + k + E ~ soil_0_20_clay + soil_0_20_pH_H2O + ansum_sun + ansum_prec,
random = A ~ 1 | year/Site/block,
data = D,
start = c(
  A = 220, A1 = 0, A2 = 0, A3 = 0, A4 = 0,
  k = 0.05, k1 = 0, k2 = 0, k3 = 0, k4 = 0,
  E = -3, E1 = 0, E2 = 0, E3 = 0, E4 = 0
),
control = nlmeControl(maxIter = 500),
na.action = na.omit
)

summary(fit.mitscherlich.CO2.Yrel)

```

Nonlinear mixed-effects model fit by maximum likelihood

Model: Ymain_rel ~ A * (1 - exp(-k * soil_0_20_P_CO2 + E))

Data: D

	AIC	BIC	logLik
	744.5163	792.8389	-353.2581

Random effects:

Formula: A ~ 1 | year

A.(Intercept)

StdDev: 0.001170608

Formula: A ~ 1 | Site %in% year

A.(Intercept)

StdDev: 1.560869

Formula: A ~ 1 | block %in% Site %in% year

A.(Intercept) Residual

StdDev: 4.988193e-05 10.27543

Fixed effects: A + k + E ~ soil_0_20_clay + soil_0_20_pH_H2O + ansum_sun + ansum_prec

	Value	Std.Error	DF	t-value	p-value
A.(Intercept)	193.7899	63.1614	48	3.0681695	0.0035
A.soil_0_20_clay	-0.0020	0.3174	48	-0.0062559	0.9950
A.soil_0_20_pH_H2O	2.1577	3.3046	48	0.6529475	0.5169
A.ansum_sun	-0.0321	0.0178	48	-1.7992514	0.0783
A.ansum_prec	-0.0582	0.0193	48	-3.0115355	0.0041
k.(Intercept)	1052.4990	607.1499	48	1.7335077	0.0894

k.soil_0_20_clay	0.1588	0.1220	48	1.3012499	0.1994
k.soil_0_20_pH_H2O	-49.3388	28.7546	48	-1.7158575	0.0926
k.ansum_sun	-0.2481	0.1432	48	-1.7328670	0.0895
k.ansum_prec	-0.2283	0.1294	48	-1.7646583	0.0840
E.(Intercept)	267.9738	165.2244	48	1.6218779	0.1114
E.soil_0_20_clay	0.2363	0.1424	48	1.6594850	0.1035
E.soil_0_20_pH_H2O	-8.7078	5.6370	48	-1.5447609	0.1290
E.ansum_sun	-0.0690	0.0422	48	-1.6349736	0.1086
E.ansum_prec	-0.0863	0.0509	48	-1.6957763	0.0964

Correlation:

	A.(In)	A.s_0_20_	A._0_20_H	A.nsm_s	A.nsm_p	k.(In)	k.s_0_20_
A.soil_0_20_clay	-0.526						
A.soil_0_20_pH_H2O	-0.768	0.646					
A.ansum_sun	-0.911	0.297	0.539				
A.ansum_prec	-0.566	-0.105	0.077	0.518			
k.(Intercept)	0.250	-0.143	-0.354	-0.165	-0.070		
k.soil_0_20_clay	0.178	-0.103	-0.273	-0.109	-0.039	0.641	
k.soil_0_20_pH_H2O	-0.250	0.146	0.356	0.163	0.068	-1.000	-0.645
k.ansum_sun	-0.249	0.141	0.351	0.165	0.071	-1.000	-0.629
k.ansum_prec	-0.252	0.142	0.356	0.165	0.073	-0.998	-0.671
E.(Intercept)	0.260	-0.151	-0.360	-0.173	-0.076	0.998	0.630
E.soil_0_20_clay	0.193	-0.061	-0.287	-0.126	-0.073	0.944	0.796
E.soil_0_20_pH_H2O	-0.262	0.164	0.375	0.169	0.065	-0.996	-0.629
E.ansum_sun	-0.258	0.146	0.353	0.176	0.077	-0.997	-0.617
E.ansum_prec	-0.255	0.141	0.352	0.168	0.084	-0.996	-0.665
	k._0_20_H	k.nsm_s	k.nsm_p	E.(In)	E.s_0_20_	E._0_20_H	E.nsm_s
A.soil_0_20_clay							
A.soil_0_20_pH_H2O							
A.ansum_sun							
A.ansum_prec							
k.(Intercept)							
k.soil_0_20_clay							
k.soil_0_20_pH_H2O							
k.ansum_sun	0.999						
k.ansum_prec	0.998	0.996					
E.(Intercept)	-0.997	-0.998	-0.997				
E.soil_0_20_clay	-0.943	-0.941	-0.955	0.940			
E.soil_0_20_pH_H2O	0.996	0.995	0.993	-0.997	-0.930		
E.ansum_sun	0.996	0.998	0.994	-0.999	-0.937	0.995	
E.ansum_prec	0.995	0.995	0.998	-0.997	-0.957	0.992	0.995

Standardized Within-Group Residuals:

Min	Q1	Med	Q3	Max
-----	----	-----	----	-----


```
-3.52454696 -0.29064469 0.01534025 0.42451197 4.41233128
```

Number of Observations: 94

Number of Groups:

```

      year      Site %in% year block %in% Site %in% year
      2              8              32

```

```
anova(fit.mitscherlich.CO2.Yrel)
```

	numDF	denDF	F-value	p-value
A.(Intercept)	1	48	5602.523	<.0001
A.soil_0_20_clay	1	48	24.781	<.0001
A.soil_0_20_pH_H2O	1	48	16.273	0.0002
A.ansum_sun	1	48	3.585	0.0644
A.ansum_prec	1	48	3.689	0.0607
k.(Intercept)	1	48	41.991	<.0001
k.soil_0_20_clay	1	48	7.496	0.0086
k.soil_0_20_pH_H2O	1	48	0.758	0.3883
k.ansum_sun	1	48	0.424	0.5182
k.ansum_prec	1	48	16.020	0.0002
E.(Intercept)	1	48	25.335	<.0001
E.soil_0_20_clay	1	48	0.152	0.6987
E.soil_0_20_pH_H2O	1	48	0.931	0.3396
E.ansum_sun	1	48	0.253	0.6170
E.ansum_prec	1	48	2.876	0.0964

```
model_performance(fit.mitscherlich.CO2.Yrel)
```

Indices of model performance

```

AIC      |      AICc |      BIC |      RMSE |      Sigma
-----
796.042 | 806.312 | 844.365 | 10.189 | 10.275

```

```
r.square.CO2 <- 1-sum(residuals(fit.mitscherlich.CO2.Yrel)^2)/sum((D$Ymain_rel-mean(D$Ymain_rel
```

With the covariate and random effect used as by Juliane Hirte we obtain $R^2 = 0.9749806$, I don't know how to interpret that, I fear that the model is overfitting data.

How do GRUD-measurements of C_P relate to the soil properties C_{org} -content, clay-content, silt-content and pH?

- Hypothesis II: Given the known capacity of clay and silt compounds to adsorb orthophosphate a positive correlation between C_P (for both CO_2 and AAE10) and silt- and clay-content. C_{org} has been reported to positively influence the capacity of Phosphorus as well, it is plausible it also shows a positive correlation with C_P . AAE10 also deploys Na_4EDTA which is easily captured by Mg^{2+} and Ca^{2+} , therefore it is officially by GRUD advised against being used in soils with $pH > 6.8$, therefore C_P -AAE10 will presumably be negatively correlated to pH.

```
#|code-fold: true
#|echo: false
```

```
anova(fit.soil.CO2)
```

Type III Analysis of Variance Table with Satterthwaite's method

	Sum Sq	Mean Sq	NumDF	DenDF	F value	Pr(>F)
soil_0_20_clay	0.0118	0.01181	1	48.798	0.1428	0.7071250
soil_0_20_pH_H2O	0.0686	0.06858	1	65.341	0.8297	0.3657041
soil_0_20_Corg	0.2993	0.29934	1	37.017	3.6216	0.0648334 .
soil_0_20_silt	0.0665	0.06645	1	22.514	0.8040	0.3793909
Treatment	4.8977	2.44886	2	5.827	29.6281	0.0008839 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```
fit.soil.CO2 |> r.squaredGLMM()
```

	R2m	R2c
[1,]	0.6044325	0.8244053

```
anova(fit.soil.AAE10)
```

Type III Analysis of Variance Table with Satterthwaite's method

	Sum Sq	Mean Sq	NumDF	DenDF	F value	Pr(>F)
soil_0_20_clay	0.0491	0.0491	1	58.650	1.1361	0.2908517
soil_0_20_pH_H2O	0.2473	0.2473	1	75.287	5.7214	0.0192552 *
soil_0_20_Corg	0.2830	0.2830	1	45.764	6.5490	0.0138669 *
soil_0_20_silt	0.0572	0.0572	1	87.560	1.3231	0.2531704

```
Treatment      7.5352  3.7676      2  4.841 87.1720 0.0001598 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

```
fit.soil.AAE10 |> r.squaredGLMM()
```

```
      R2m      R2c
[1,] 0.5157062 0.9219818
```

Can the Inclusion of the net-release-kinetic of Orthophosphate improve the model power of predicting relative Yield, P-Uptake and P-Balance?

- Hypothesis III: Given the comparably low solubility of PO_4^{3-} in the water-soil interface, most P is transported to the rhizosphere via diffusion. As a consequence the intensity of PO_4^{3-} might not adequately account for the P-uptake in the harvested plant. Since the diffusion process is in its velocity a kinetic and in its finally reached intensity a thermodynamic process, the inclusion of kinetic parameters might well improve the performance.

```
#|code-fold: true
#|echo: false

fit.mitscherlich.PS.Yrel <- nlme(
  Ymain_rel ~ A * (1 - exp(-r * PS + E)),
  fixed = A + r + E ~ k + soil_0_20_clay + soil_0_20_pH_H2O + ansum_sun + ansum_prec,
  random = A ~ 1 | year/Site/block,
  data = D,
  start = c(
    A = 220, A1 = 0, A2 = 0, A3 = 0, A4 = 0, A5 = 0,
    r = 1, r1 = 0, r2 = 0, r3 = 0, r4 = 0, r5 = 0,
    E = -1, E1 = 0, E2 = 0, E3 = 0, E4 = 0, E5 = 0
  ),
  control = nlmeControl(maxIter = 500),
  na.action = na.omit
)

summary(fit.mitscherlich.PS.Yrel)
```

```
Nonlinear mixed-effects model fit by maximum likelihood
Model: Ymain_rel ~ A * (1 - exp(-r * PS + E))
```

```

Data: D
      AIC      BIC    logLik
756.704 812.6565 -356.352

Random effects:
Formula: A ~ 1 | year
      A.(Intercept)
StdDev:    0.001434366

Formula: A ~ 1 | Site %in% year
      A.(Intercept)
StdDev:          4.135705

Formula: A ~ 1 | block %in% Site %in% year
      A.(Intercept) Residual
StdDev:  2.098085e-05 10.26954

Fixed effects:  A + r + E ~ k + soil_0_20_clay + soil_0_20_pH_H2O + ansum_sun +      ansum_p
               Value Std.Error DF    t-value p-value
A.(Intercept)   159.3520   91.1962 45    1.7473529 0.0874
A.k             -25.4193   30.3021 45   -0.8388642 0.4060
A.soil_0_20_clay    0.3554    0.4095 45    0.8678259 0.3901
A.soil_0_20_pH_H2O  4.9194    4.3133 45    1.1405232 0.2601
A.ansum_sun       -0.0257    0.0269 45   -0.9524325 0.3460
A.ansum_prec      -0.0623    0.0288 45   -2.1634395 0.0359
r.(Intercept)   2284.8408 1418.9108 45    1.6102779 0.1143
r.k             334.2789   237.5217 45    1.4073615 0.1662
r.soil_0_20_clay  -3.5798    2.4890 45   -1.4382872 0.1573
r.soil_0_20_pH_H2O -100.7852  62.7013 45   -1.6073858 0.1150
r.ansum_sun      -0.5390    0.3332 45   -1.6176110 0.1127
r.ansum_prec     -0.5023    0.3122 45   -1.6088164 0.1147
E.(Intercept)    63.8366   53.9968 45    1.1822310 0.2433
E.k             22.9236   12.6296 45    1.8150670 0.0762
E.soil_0_20_clay   0.0488    0.0483 45    1.0101435 0.3178
E.soil_0_20_pH_H2O -1.1850    1.4792 45   -0.8010865 0.4273
E.ansum_sun      -0.0174    0.0144 45   -1.2077238 0.2335
E.ansum_prec     -0.0327    0.0228 45   -1.4328213 0.1588
Correlation:
               A.(In) A.k      A.s_0_20_ A._0_20_H A.nsm_s A.nsm_p r.(In)
A.k           0.088
A.soil_0_20_clay -0.504 0.082
A.soil_0_20_pH_H2O -0.747 -0.263 0.589
A.ansum_sun     -0.931 -0.071 0.340    0.565

```

A.ansum_prec	-0.623	-0.130	-0.077	0.165	0.539		
r.(Intercept)	0.326	-0.153	-0.221	-0.392	-0.249	-0.108	
r.k	0.164	-0.283	-0.081	-0.174	-0.128	-0.052	0.807
r.soil_0_20_clay	-0.221	0.216	0.118	0.266	0.165	0.076	-0.935
r.soil_0_20_pH_H2O	-0.325	0.173	0.223	0.380	0.251	0.108	-0.996
r.ansum_sun	-0.333	0.140	0.226	0.404	0.254	0.111	-0.999
r.ansum_prec	-0.310	0.161	0.206	0.378	0.236	0.099	-0.997
E.(Intercept)	0.336	-0.151	-0.213	-0.385	-0.260	-0.129	0.976
E.k	0.235	-0.071	-0.120	-0.322	-0.171	-0.081	0.832
E.soil_0_20_clay	0.089	-0.084	0.010	-0.122	-0.076	-0.035	0.551
E.soil_0_20_pH_H2O	-0.327	0.025	0.193	0.390	0.248	0.145	-0.779
E.ansum_sun	-0.334	0.165	0.212	0.376	0.264	0.124	-0.979
E.ansum_prec	-0.299	0.180	0.189	0.351	0.227	0.108	-0.985

r.k	r.s_0_20_	r._0_20_H	r.nsm_s	r.nsm_p	E.(In)	E.k
-----	-----------	-----------	---------	---------	--------	-----

A.k

A.soil_0_20_clay

A.soil_0_20_pH_H2O

A.ansum_sun

A.ansum_prec

r.(Intercept)

r.k

r.soil_0_20_clay -0.943

r.soil_0_20_pH_H2O -0.836 0.942

r.ansum_sun -0.778 0.919 0.990

r.ansum_prec -0.828 0.950 0.990 0.994

E.(Intercept) 0.799 -0.916 -0.979 -0.972 -0.969

E.k 0.888 -0.891 -0.845 -0.815 -0.845 0.809

E.soil_0_20_clay 0.334 -0.413 -0.524 -0.566 -0.560 0.491 0.335

E.soil_0_20_pH_H2O -0.603 0.703 0.798 0.774 0.751 -0.867 -0.706

E.ansum_sun -0.795 0.913 0.979 0.977 0.973 -0.995 -0.787

E.ansum_prec -0.855 0.955 0.982 0.979 0.992 -0.972 -0.850

E.s_0_20_	E._0_20_H	E.nsm_s
-----------	-----------	---------

A.k

A.soil_0_20_clay

A.soil_0_20_pH_H2O

A.ansum_sun

A.ansum_prec

r.(Intercept)

r.k

r.soil_0_20_clay

r.soil_0_20_pH_H2O

r.ansum_sun

r.ansum_prec

```

E.(Intercept)
E.k
E.soil_0_20_clay
E.soil_0_20_pH_H2O -0.210
E.ansum_sun        -0.538      0.824
E.ansum_prec       -0.572      0.746      0.977

```

Standardized Within-Group Residuals:

Min	Q1	Med	Q3	Max
-3.62053951	-0.40518895	0.02478129	0.53746770	4.15921453

Number of Observations: 94

Number of Groups:

year	Site %in%	year block %in%	Site %in%	year
2		8		32

```
anova(fit.mitscherlich.PS.Yrel)
```

	numDF	denDF	F-value	p-value
A.(Intercept)	1	45	2488.4068	<.0001
A.k	1	45	2.3144	0.1352
A.soil_0_20_clay	1	45	2.2731	0.1386
A.soil_0_20_pH_H2O	1	45	29.8949	<.0001
A.ansum_sun	1	45	6.5752	0.0137
A.ansum_prec	1	45	2.6606	0.1098
r.(Intercept)	1	45	21.0005	<.0001
r.k	1	45	1.9181	0.1729
r.soil_0_20_clay	1	45	0.1437	0.7064
r.soil_0_20_pH_H2O	1	45	6.0053	0.0182
r.ansum_sun	1	45	0.1454	0.7048
r.ansum_prec	1	45	9.4644	0.0036
E.(Intercept)	1	45	26.4308	<.0001
E.k	1	45	0.9943	0.3240
E.soil_0_20_clay	1	45	0.0699	0.7926
E.soil_0_20_pH_H2O	1	45	0.0668	0.7973
E.ansum_sun	1	45	0.8021	0.3752
E.ansum_prec	1	45	2.0530	0.1588

```
model_performance(fit.mitscherlich.PS.Yrel)
```

```
# Indices of model performance
```

AIC	AICc	BIC	RMSE	Sigma
765.695	779.948	821.647	9.989	10.270

```
r.square.PS <- 1-sum(residuals(fit.mitscherlich.PS.Yrel)^2)/sum((D$Ymain_rel-mean(D$Ymain_re

fit.mitscherlich.kPS.Yrel <- nlme(
  Ymain_rel ~ A * (1 - exp(-k * PS + E)),
  fixed = A + E ~ soil_0_20_clay + soil_0_20_pH_H2O + ansum_sun + ansum_prec,
  random = A ~ 1 | year/Site/block,
  data = D,
  start = c(
    A = 220, A1 = 0, A2 = 0, A3 = 0, A4 = 0,
    E = -1, E1 = 0, E2 = 0, E3 = 0, E4 = 0
  ),
  control = nlmeControl(maxIter = 500),
  na.action = na.omit
)

summary(fit.mitscherlich.kPS.Yrel)
```

Nonlinear mixed-effects model fit by maximum likelihood

Model: Ymain_rel ~ A * (1 - exp(-k * PS + E))

Data: D

AIC	BIC	logLik
757.7736	793.3798	-364.8868

Random effects:

Formula: A ~ 1 | year

A.(Intercept)

StdDev: 0.00112278

Formula: A ~ 1 | Site %in% year

A.(Intercept)

StdDev: 0.008239412

Formula: A ~ 1 | block %in% Site %in% year

A.(Intercept) Residual

StdDev: 2.69498e-05 11.73805

Fixed effects: A + E ~ soil_0_20_clay + soil_0_20_pH_H2O + ansum_sun + ansum_prec

	Value	Std.Error	DF	t-value	p-value
A.(Intercept)	2690.1350	985.2790	53	2.730328	0.0086
A.soil_0_20_clay	5.8621	3.0618	53	1.914606	0.0609
A.soil_0_20_pH_H2O	-75.2347	37.4744	53	-2.007628	0.0498
A.ansum_sun	-0.7671	0.2684	53	-2.858049	0.0061
A.ansum_prec	-0.6208	0.2478	53	-2.505009	0.0154
E.(Intercept)	0.6989	0.5030	53	1.389531	0.1705
E.soil_0_20_clay	0.0069	0.0040	53	1.715683	0.0921
E.soil_0_20_pH_H2O	-0.0352	0.0289	53	-1.219687	0.2280
E.ansum_sun	-0.0004	0.0002	53	-2.210431	0.0314
E.ansum_prec	-0.0002	0.0002	53	-1.427522	0.1593

Correlation:

	A.(In)	A.s_0_20_	A._0_20_H	A.nsm_s	A.nsm_p	E.(In)	E.s_0_20_
A.soil_0_20_clay	-0.024						
A.soil_0_20_pH_H2O	-0.857	0.189					
A.ansum_sun	-0.963	-0.098	0.725				
A.ansum_prec	-0.873	-0.184	0.620	0.829			
E.(Intercept)	0.197	-0.757	-0.214	-0.136	-0.092		
E.soil_0_20_clay	-0.791	0.449	0.717	0.719	0.574	-0.393	
E.soil_0_20_pH_H2O	0.014	0.643	0.399	-0.184	-0.246	-0.593	0.197
E.ansum_sun	0.266	0.555	-0.317	-0.204	-0.330	-0.800	-0.088
E.ansum_prec	-0.040	0.243	-0.140	-0.016	0.345	-0.562	-0.030
	E._0_20_H	E.nsm_s					

A.soil_0_20_clay
A.soil_0_20_pH_H2O
A.ansum_sun
A.ansum_prec
E.(Intercept)
E.soil_0_20_clay
E.soil_0_20_pH_H2O
E.ansum_sun
E.ansum_prec

Standardized Within-Group Residuals:

Min	Q1	Med	Q3	Max
-2.72142747	-0.51960209	-0.04192907	0.54601061	4.70468829

Number of Observations: 94

Number of Groups:

year	Site %in%	year	block %in%	Site %in%	year
2		8			32


```
anova(fit.mitscherlich.kPS.Yrel)
```

	numDF	denDF	F-value	p-value
A.(Intercept)	1	53	14865.096	<.0001
A.soil_0_20_clay	1	53	474.026	<.0001
A.soil_0_20_pH_H2O	1	53	0.724	0.3986
A.ansum_sun	1	53	286.635	<.0001
A.ansum_prec	1	53	305.097	<.0001
E.(Intercept)	1	53	1.553	0.2182
E.soil_0_20_clay	1	53	3.035	0.0873
E.soil_0_20_pH_H2O	1	53	0.401	0.5295
E.ansum_sun	1	53	3.082	0.0850
E.ansum_prec	1	53	2.038	0.1593

```
model_performance(fit.mitscherlich.kPS.Yrel)
```

```
# Indices of model performance
```

AIC	AICc	BIC	RMSE	Sigma
804.491	809.807	840.097	11.738	11.738

```
r.square.kPS <- 1-sum(residuals(fit.mitscherlich.kPS.Yrel)^2)/sum((D$Ymain_rel-mean(D$Ymain_rel))^2)
```

With the covariate and random effect used as by Juliane Hirte we obtain $R^2 = 0.9759552$, I don't know how to interpret that, I fear that the model is overfitting data, the same might be true for the model that used $k \times PS$ as a predictor with $R^2 = 0.9667951$.

I also tried more conservative models, where I log-transformed the concentrations and PS, also I was more cautious with random effects. This resulted in coefficients that were not as straight-forward as the mitscherlich coefficients to interpret.

```
#|code-fold: true
#|echo: false
#|tidy: true

# relative Yield
anova(fit.kin.Yrel)
```

Type III Analysis of Variance Table with Satterthwaite's method

	Sum Sq	Mean Sq	NumDF	DenDF	F value	Pr(>F)
k	146.11	146.11	1	151.805	0.4824	0.4884
log(PS)	44.91	44.91	1	226.958	0.1483	0.7005
Treatment	740.92	370.46	2	4.838	1.2232	0.3716
k:log(PS)	324.35	324.35	1	172.913	1.0710	0.3022

```
summary(fit.kin.Yrel)
```

Linear mixed model fit by REML. t-tests use Satterthwaite's method [
lmerModLmerTest]

Formula: Ymain_rel ~ k * log(PS) + Treatment + (1 | year) + (1 | Site) +
(1 | Site:block) + (1 | Site:Treatment)

Data: D

REML criterion at convergence: 2326.3

Scaled residuals:

Min	1Q	Median	3Q	Max
-2.6718	-0.5771	-0.0119	0.5429	3.2858

Random effects:

Groups	Name	Variance	Std.Dev.
Site:block	(Intercept)	0.00	0.000
Site:Treatment	(Intercept)	19.21	4.383
year	(Intercept)	790.71	28.120
Site	(Intercept)	382.97	19.570
Residual		302.86	17.403

Number of obs: 271, groups:

Site:block, 20; Site:Treatment, 15; year, 6; Site, 5

Fixed effects:

	Estimate	Std. Error	df	t value	Pr(> t)
(Intercept)	111.004	21.926	41.379	5.063	8.98e-06 ***
k	48.164	69.342	151.805	0.695	0.488
log(PS)	-2.362	6.133	226.958	-0.385	0.701
TreatmentP100	8.891	5.689	13.161	1.563	0.142
TreatmentP166	9.868	8.140	36.868	1.212	0.233
k:log(PS)	30.223	29.205	172.913	1.035	0.302

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```

Correlation of Fixed Effects:
              (Intr) k      lg(PS) TrP100 TrP166
k              -0.438
log(PS)         0.700 -0.685
TretmntP100    -0.405 -0.178 -0.354
TretmntP166    -0.488 -0.156 -0.455  0.799
k:log(PS)      -0.421  0.945 -0.750 -0.155 -0.152
optimizer (nloptwrap) convergence code: 0 (OK)
boundary (singular) fit: see help('isSingular')

```

```
fit.kin.Yrel |> r.squaredGLMM()
```

```

              R2m      R2c
[1,] 0.03304352 0.8042098

```

```

# P-Uptake
anova(fit.kin.Puptake)

```

Type III Analysis of Variance Table with Satterthwaite's method

	Sum Sq	Mean Sq	NumDF	DenDF	F value	Pr(>F)
k	41.986	41.986	1	456.19	0.3035	0.5819
log(PS)	6.315	6.315	1	457.82	0.0457	0.8309
Treatment	129.470	64.735	2	443.37	0.4680	0.6266
k:log(PS)	39.416	39.416	1	457.86	0.2850	0.5937

```
summary(fit.kin.Puptake)
```

Linear mixed model fit by REML. t-tests use Satterthwaite's method [
lmerModLmerTest]

Formula: annual_P_uptake ~ k * log(PS) + Treatment + (1 | year) + (1 |
Site) + (1 | Site:block) + (1 | Site:Treatment)
Data: D

REML criterion at convergence: 3672.2

Scaled residuals:

Min	1Q	Median	3Q	Max
-2.6530	-0.5097	0.0716	0.5600	4.9444

Random effects:

Groups	Name	Variance	Std.Dev.
Site:block	(Intercept)	0.00	0.000
Site:Treatment	(Intercept)	0.00	0.000
year	(Intercept)	182.70	13.517
Site	(Intercept)	29.44	5.426
Residual		138.32	11.761

Number of obs: 471, groups:
Site:block, 20; Site:Treatment, 15; year, 8; Site, 5

Fixed effects:

	Estimate	Std. Error	df	t value	Pr(> t)
(Intercept)	17.7701	9.6386	84.5771	1.844	0.0687 .
k	18.2855	33.1889	456.1925	0.551	0.5819
log(PS)	0.6425	3.0068	457.8227	0.214	0.8309
TreatmentP100	2.0741	2.3774	447.4842	0.872	0.3834
TreatmentP166	2.0186	3.6421	430.0571	0.554	0.5797
k:log(PS)	7.5234	14.0934	457.8642	0.534	0.5937

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Correlation of Fixed Effects:

	(Intr)	k	lg(PS)	TrP100	TrP166
k	-0.511				
log(PS)	0.778	-0.710			
TretmntP100	-0.481	-0.166	-0.410		
TretmntP166	-0.554	-0.128	-0.482	0.871	
k:log(PS)	-0.486	0.943	-0.770	-0.146	-0.134

optimizer (nloptwrap) convergence code: 0 (OK)
boundary (singular) fit: see help('isSingular')

```
fit.kin.Puptake |> r.squaredGLMM()
```

	R2m	R2c
[1,]	0.01723874	0.6121275

```
anova(fit.kin.Pbalance)
```

Type III Analysis of Variance Table with Satterthwaite's method

	Sum Sq	Mean Sq	NumDF	DenDF	F value	Pr(>F)
k	20.3	20.3	1	457.51	0.0960	0.7568
log(PS)	12.9	12.9	1	455.60	0.0613	0.8046

```
Treatment 15488.3 7744.1      2 379.27 36.7144 2.658e-15 ***
k:log(PS)   10.1   10.1      1 455.83  0.0477   0.8272
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

```
summary(fit.kin.Pbalance)
```

```
Linear mixed model fit by REML. t-tests use Satterthwaite's method [
lmerModLmerTest]
```

```
Formula: annual_P_balance ~ k * log(PS) + Treatment + (1 | year) + (1 |
      Site) + (1 | Site:block) + (1 | Site:Treatment)
Data: D
```

```
REML criterion at convergence: 3854.5
```

```
Scaled residuals:
```

```
      Min      1Q  Median      3Q      Max
-3.8654 -0.5354 -0.0249  0.5914  3.3879
```

```
Random effects:
```

```
Groups      Name      Variance Std.Dev.
Site:block  (Intercept)  0.00   0.000
Site:Treatment (Intercept) 0.00   0.000
year        (Intercept) 51.80   7.197
Site        (Intercept) 21.44   4.631
Residual                    210.93  14.523
```

```
Number of obs: 471, groups:
```

```
Site:block, 20; Site:Treatment, 15; year, 8; Site, 5
```

```
Fixed effects:
```

```
              Estimate Std. Error      df t value Pr(>|t|)
(Intercept)   -16.980     10.354 231.810  -1.640   0.102
k              -12.679     40.918 457.507  -0.310   0.757
log(PS)        -0.916      3.701 455.596  -0.248   0.805
TreatmentP100   21.950      2.907 382.869   7.552 3.18e-13 ***
TreatmentP166   37.991      4.435 317.155   8.566 4.74e-16 ***
k:log(PS)       -3.788     17.345 455.832  -0.218   0.827
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

```
Correlation of Fixed Effects:
```

```
(Intr) k      lg(PS) TrP100 TrP166
```

```

k                -0.590
log(PS)          0.888 -0.713
TretmntP100     -0.542 -0.165 -0.407
TretmntP166     -0.627 -0.126 -0.481  0.868
k:log(PS)       -0.565  0.944 -0.776 -0.140 -0.126
optimizer (nloptwrap) convergence code: 0 (OK)
boundary (singular) fit: see help('isSingular')

```

```
fit.kin.Pbalance |> r.squaredGLMM()
```

```

          R2m          R2c
[1,] 0.4228263 0.5715903

```

Are the kinetic coefficients k and PS (k can be interpreted as the relative speed of desorption, PS is the equilibrium concentration of PO_4^{3-} of the observed desorption in the dried fine earth-water suspension 1:20 by weight) related to soil properties?

- Hypothesis IV: Clay particles as well as organic compounds with negative surface charges provide surfaces for P-sorption, especially their structure, but in general their respective concentration in a soil can be expected to significantly influence the kinetic and thermodynamic of the P-desorption reaction. The pH dictates the form of orthophosphate, with $pH < 6.5$, the predominant form will be $H_2PO_4^-$, this should reduce electrical interactions and increase the movement- and therefore diffusion-speed.

```

#|code-fold: true
#|tidy: true
#|echo: false

anova(fit.soil.PS)

```

```

Type III Analysis of Variance Table with Satterthwaite's method

          Sum Sq Mean Sq NumDF  DenDF  F value    Pr(>F)
soil_0_20_clay    0.0719   0.0719     1 70.835    2.3900 0.1265690
soil_0_20_pH_H2O  0.0152   0.0152     1 89.035    0.5061 0.4787086
soil_0_20_Corg    0.4704   0.4704     1 65.081   15.6423 0.0001915 ***
soil_0_20_silt    0.1061   0.1061     1 70.745    3.5286 0.0644392 .
Treatment        10.0459   5.0230     2  6.055  167.0386 5.047e-06 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```

```
summary(glht(fit.soil.PS))
```

```
Warning in RET$pffunction("adjusted", ...): Completion with error > abseps
Warning in RET$pffunction("adjusted", ...): Completion with error > abseps
```

Simultaneous Tests for General Linear Hypotheses

```
Fit: lmer(formula = log(PS) ~ soil_0_20_clay + soil_0_20_pH_H2O +
  soil_0_20_Corg + soil_0_20_silt + Treatment + (1 | year) +
  (1 | Site) + (1 | Site:block) + (1 | Site:Treatment), data = D)
```

Linear Hypotheses:

	Estimate	Std. Error	z value	Pr(> z)
(Intercept) == 0	-4.53113	0.74437	-6.087	<0.001 ***
soil_0_20_clay == 0	0.01718	0.01111	1.546	0.535
soil_0_20_pH_H2O == 0	0.03974	0.05587	0.711	0.976
soil_0_20_Corg == 0	0.55587	0.14055	3.955	<0.001 ***
soil_0_20_silt == 0	-0.02635	0.01403	-1.878	0.314
TreatmentP100 == 0	1.06832	0.10058	10.622	<0.001 ***
TreatmentP166 == 0	1.84388	0.10133	18.197	<0.001 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
(Adjusted p values reported -- single-step method)

```
#summary(glht(fit.PS))
```

```
# Fazit: PS wird von treatment stark beeinflusst, k eher nicht (dafür von site)
anova(fit.soil.k)
```

Type III Analysis of Variance Table with Satterthwaite's method

	Sum Sq	Mean Sq	NumDF	DenDF	F value	Pr(>F)
soil_0_20_clay	0.0098143	0.0098143	1	69.314	10.0428	0.002277 **
soil_0_20_pH_H2O	0.0091422	0.0091422	1	102.384	9.3551	0.002838 **
soil_0_20_Corg	0.0014112	0.0014112	1	98.359	1.4440	0.232372
soil_0_20_silt	0.0046704	0.0046704	1	75.910	4.7792	0.031888 *
Treatment	0.0059043	0.0029521	2	5.405	3.0209	0.131613

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```
summary(glht(fit.soil.k))
```

```
Warning in RET$pfunction("adjusted", ...): Completion with error > abseps
Warning in RET$pfunction("adjusted", ...): Completion with error > abseps
Warning in RET$pfunction("adjusted", ...): Completion with error > abseps
```

Simultaneous Tests for General Linear Hypotheses

```
Fit: lmer(formula = k ~ soil_0_20_clay + soil_0_20_pH_H2O + soil_0_20_Corg +
  soil_0_20_silt + Treatment + (1 | year) + (1 | Site) + (1 |
  Site:block) + (1 | Site:Treatment), data = D)
```

Linear Hypotheses:

	Estimate	Std. Error	z value	Pr(> z)
(Intercept) == 0	0.074168	0.150771	0.492	0.9965
soil_0_20_clay == 0	-0.007001	0.002209	-3.169	0.0100 *
soil_0_20_pH_H2O == 0	0.033720	0.011024	3.059	0.0152 *
soil_0_20_Corg == 0	-0.034533	0.028737	-1.202	0.7767
soil_0_20_silt == 0	0.005864	0.002683	2.186	0.1652
TreatmentP100 == 0	0.003910	0.015506	0.252	0.9999
TreatmentP166 == 0	-0.031147	0.015685	-1.986	0.2547

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
(Adjusted p values reported -- single-step method)

```
anova(fit.soil.kPS)
```

Type III Analysis of Variance Table with Satterthwaite's method

	Sum Sq	Mean Sq	NumDF	DenDF	F value	Pr(>F)
soil_0_20_clay	0.0055	0.00551	1	77.626	0.1043	0.747639
soil_0_20_pH_H2O	0.3773	0.37731	1	101.942	7.1335	0.008807 **
soil_0_20_Corg	0.0105	0.01052	1	93.639	0.1990	0.656575
soil_0_20_silt	0.0036	0.00360	1	80.228	0.0681	0.794743
Treatment	4.0339	2.01697	2	5.847	38.1329	0.000442 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```
summary(glht(fit.soil.kPS))
```


Warning in RET\$pfunction("adjusted", ...): Completion with error > abseps

Simultaneous Tests for General Linear Hypotheses

```
Fit: lmer(formula = I(log(k * PS)) ~ soil_0_20_clay + soil_0_20_pH_H2O +
  soil_0_20_Corg + soil_0_20_silt + Treatment + (1 | year) +
  (1 | Site) + (1 | Site:block) + (1 | Site:Treatment), data = D)
```

Linear Hypotheses:

	Estimate	Std. Error	z value	Pr(> z)
(Intercept) == 0	-6.657570	1.107392	-6.012	<0.001 ***
soil_0_20_clay == 0	-0.005316	0.016463	-0.323	0.9997
soil_0_20_pH_H2O == 0	0.216354	0.081005	2.671	0.0477 *
soil_0_20_Corg == 0	0.094691	0.212278	0.446	0.9980
soil_0_20_silt == 0	0.005221	0.020000	0.261	0.9999
TreatmentP100 == 0	1.064948	0.189188	5.629	<0.001 ***
TreatmentP166 == 0	1.634290	0.190050	8.599	<0.001 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

(Adjusted p values reported -- single-step method)

Is the method presented by Flossmann and Richter (1982) with the double extraction replicable with the soils from the STYCS-trial?

- Hypothesis V: The authors expect the desorption kinetics to follow a 1. order kinetic, with the relation:

$$\frac{dP}{dt} = PS(1 - e^{-kt})$$

where PS is estimated as $PS = [P_{\text{Olsen}/\text{CAL}}] - [P_{H_2O}]$, denoted as the semi-labile P-pool. The Olsen- and CAL-method deploy extractants that increase the solubility by more than order of magnitude. This presents the problem, that the estimation of PS is likely to high. It was chosen by the authors in order to make the equation linearizable, so if the linearization is not well behaved, a non-linear regression might deliver a better estimation of both parameters.

```
#|code-fold: true
#|tidy: true
#|echo: false

res <- lmList(Y1 ~ t.min. | uid, d[d$Repetition==1|d$Repetition==2,],na.action = na.pass)
```

Warning: 12 times caught the same error in lm.fit(x, y, offset = offset, singular.ok = singular.ok, ...): NA/NaN/Inf in 'y'

```
summary(res)
```

Warning in summary.lm(el): essentially perfect fit: summary may be unreliable

Call:

Model: Y1 ~ t.min. | uid

Data: d[d\$Repetition == 1 | d\$Repetition == 2,]

Coefficients:

(Intercept)

	Estimate	Std. Error	t value	Pr(> t)
Cadenazzo_P0_1	-0.12891945	0.01537006	-8.387702	4.332766e-12
Cadenazzo_P0_2	-0.12037045	0.01537006	-7.831491	4.433395e-11
Cadenazzo_P100_1	NA	NA	NA	NA
Cadenazzo_P100_2	NA	NA	NA	NA
Cadenazzo_P166_1	-0.26932199	0.01537006	-17.522512	6.499702e-27
Cadenazzo_P166_2	-0.19243796	0.01537006	-12.520316	2.550625e-19
Ellighausen_P0_1	-0.10464296	0.01537006	-6.808236	3.136905e-09
Ellighausen_P0_2	-0.11438112	0.01537006	-7.441815	2.257472e-10
Ellighausen_P100_1	NA	NA	NA	NA
Ellighausen_P100_2	NA	NA	NA	NA
Ellighausen_P166_1	NA	NA	NA	NA
Oensing_P0_1	-0.03432646	0.01537006	-2.233333	2.882091e-02
Oensing_P0_2	-0.05745952	0.01537006	-3.738407	3.819350e-04
Oensing_P100_1	NA	NA	NA	NA
Oensing_P100_2	NA	NA	NA	NA
Oensing_P166_1	-0.13275856	0.01537006	-8.637481	1.527196e-12
Oensing_P166_2	-0.17051390	0.01537006	-11.093902	6.616653e-17
Reckenholz_P0_1	-0.10545869	0.01537006	-6.861308	2.519112e-09
Reckenholz_P0_2	-0.08557888	0.01537006	-5.567897	4.753375e-07
Reckenholz_P100_1	NA	NA	NA	NA
Reckenholz_P100_2	NA	NA	NA	NA
Reckenholz_P166_1	-0.17172348	0.01537006	-11.172600	4.839473e-17
Reckenholz_P166_2	-0.23296391	0.01537006	-15.156998	1.712692e-23
Ruemlang_P0_1	-0.01851905	0.01537006	-1.204878	2.324269e-01
Ruemlang_P0_2	-0.08675331	0.01537006	-5.644307	3.515958e-07
Ruemlang_P100_1	NA	NA	NA	NA
Ruemlang_P100_2	NA	NA	NA	NA
Ruemlang_P166_1	-0.26153690	0.01537006	-17.016002	3.315417e-26

Ruemlang_P166_2	NA	NA	NA	NA
t.min.				
	Estimate	Std. Error	t value	Pr(> t)
Cadenazzo_P0_1	-1.318800e-03	0.0004483906	-2.941186e+00	4.466020e-03
Cadenazzo_P0_2	-1.272378e-03	0.0004483906	-2.837654e+00	5.984783e-03
Cadenazzo_P100_1	NA	NA	NA	NA
Cadenazzo_P100_2	NA	NA	NA	NA
Cadenazzo_P166_1	-5.270369e-03	0.0004483906	-1.175397e+01	4.905164e-18
Cadenazzo_P166_2	-3.394812e-03	0.0004483906	-7.571105e+00	1.316077e-10
Ellighausen_P0_1	4.952586e-05	0.0004483906	1.104525e-01	9.123759e-01
Ellighausen_P0_2	-1.260933e-04	0.0004483906	-2.812130e-01	7.794010e-01
Ellighausen_P100_1	NA	NA	NA	NA
Ellighausen_P100_2	NA	NA	NA	NA
Ellighausen_P166_1	NA	NA	NA	NA
Oensingeng_P0_1	1.049070e-04	0.0004483906	2.339634e-01	8.157164e-01
Oensingeng_P0_2	-1.837559e-04	0.0004483906	-4.098121e-01	6.832320e-01
Oensingeng_P100_1	NA	NA	NA	NA
Oensingeng_P100_2	NA	NA	NA	NA
Oensingeng_P166_1	-2.320568e-04	0.0004483906	-5.175327e-01	6.064639e-01
Oensingeng_P166_2	-5.531502e-04	0.0004483906	-1.233635e+00	2.215861e-01
Reckenholz_P0_1	2.780943e-04	0.0004483906	6.202053e-01	5.371956e-01
Reckenholz_P0_2	-7.752286e-04	0.0004483906	-1.728914e+00	8.836252e-02
Reckenholz_P100_1	NA	NA	NA	NA
Reckenholz_P100_2	NA	NA	NA	NA
Reckenholz_P166_1	-1.609218e-03	0.0004483906	-3.588876e+00	6.216266e-04
Reckenholz_P166_2	-4.831330e-03	0.0004483906	-1.077482e+01	2.367928e-16
Ruemlang_P0_1	8.878899e-20	0.0004483906	1.980171e-16	1.000000e+00
Ruemlang_P0_2	-1.438957e-03	0.0004483906	-3.209160e+00	2.032261e-03
Ruemlang_P100_1	NA	NA	NA	NA
Ruemlang_P100_2	NA	NA	NA	NA
Ruemlang_P166_1	-1.090605e-03	0.0004483906	-2.432266e+00	1.764226e-02
Ruemlang_P166_2	NA	NA	NA	NA

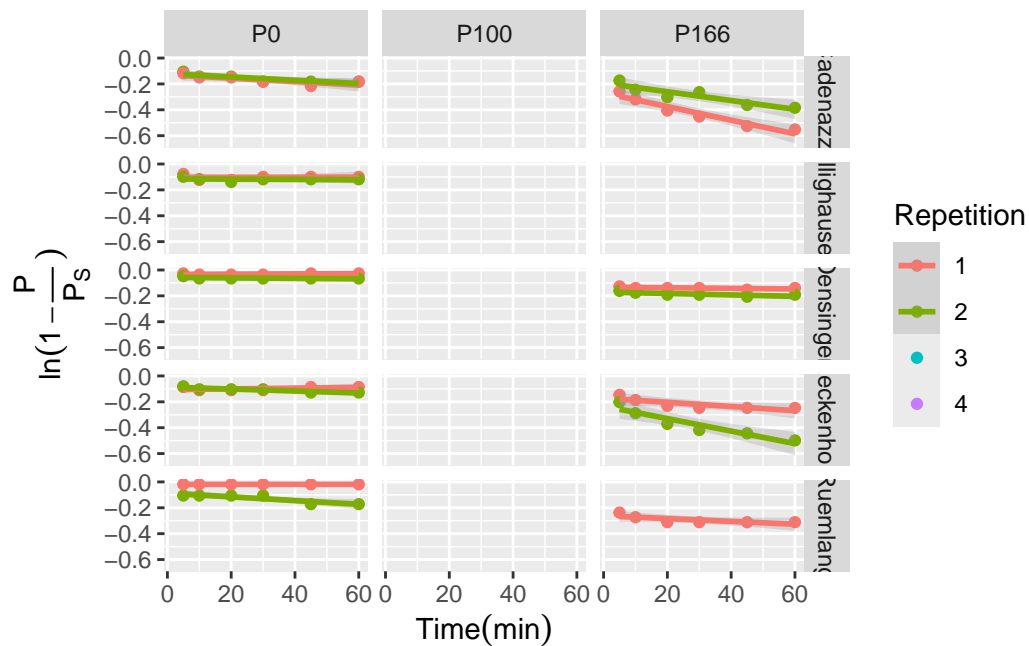
Residual standard error: 0.02119011 on 68 degrees of freedom

```
ggplot(d, aes(y=Y1, x=t.min., col = Repetition)) +
  geom_point() +
  facet_grid(Site ~ Treatment) +
  labs(x=TeX("$Time$ (min)$"),
       y=TeX("$\ln(1-\frac{P}{P_S})$")),
  geom_smooth(method="lm", alpha = 0.3)
```

```
`geom_smooth()` using formula = 'y ~ x'
```

Warning: Removed 292 rows containing non-finite outside the scale range
(`stat_smooth()`).

Warning: Removed 292 rows containing missing values or values outside the scale range
(`geom_point()`).



The relation can be improved:

```
#|code-fold: true
#|tidy: true
#|echo: false
```

```
Res <- nlsList(Pv.mg.L. ~ PS * (1 - exp(-k * (t.dt))) | uid, d[, c("Pv.mg.L.", "uid", "t.dt")])
```

Warning: 1 error caught in nls(model, data = data, control = controlvals, start = start): singular gradient

```

# summary(Res)
# d$nls_pred <- predict(Res)

# Extract coefficients from the nlsList results
nls_coefs <- coef(Res)
nls_coefs$uid <- rownames(nls_coefs)

# Merge coefficients back to the main dataset
d_plot <- merge(d, nls_coefs, by = "uid")

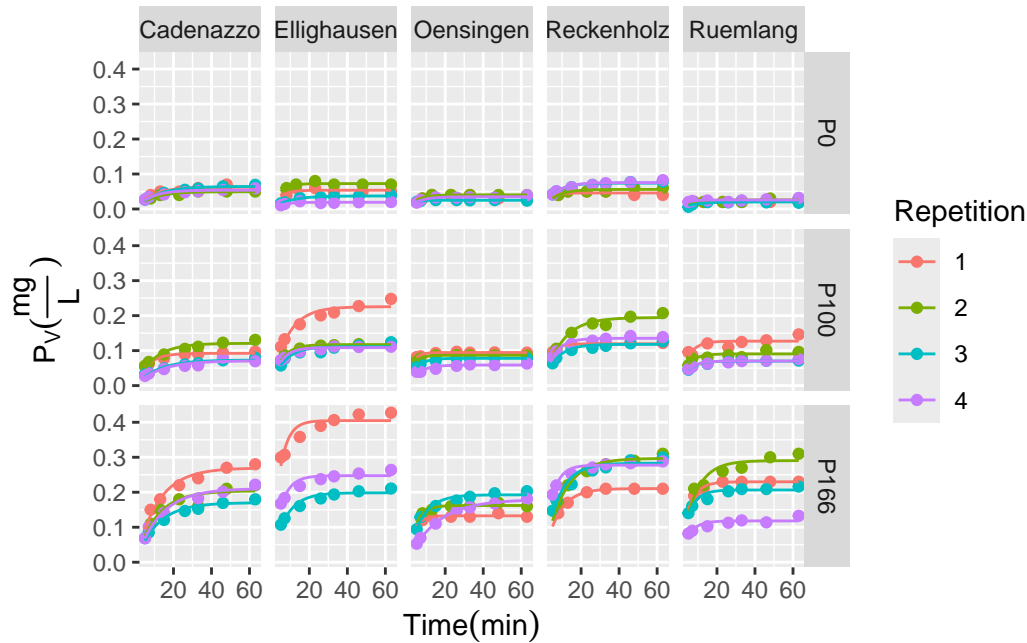
# Most straightforward approach - create curves manually
time_seq <- seq(min(d$t.dt, na.rm = TRUE), max(d$t.dt, na.rm = TRUE), length.out = 100)

# Create prediction data
pred_data <- d_plot %>%
  select(uid, Site, Treatment, Repetition, PS, k) %>%
  distinct() %>%
  crossing(t.dt = time_seq) %>%
  mutate(pred_Pv = PS * (1 - exp(-k * (t.dt))))

# Final plot
p1 <- ggplot() +
  geom_point(data = d_plot, aes(y = Pv.mg.L., x = t.dt, col = Repetition)) +
  geom_line(data = pred_data, aes(x = t.dt, y = pred_Pv, col = Repetition), size = 0.5) +
  facet_grid(Treatment ~ Site) +
  labs(x = TeX("$Time (min)$"),
       y = TeX("$P_{V}(\\frac{mg}{L})$")); suppressWarnings(print(p1))

```

Warning: Using `size` aesthetic for lines was deprecated in ggplot2 3.4.0.
 i Please use `linewidth` instead.



Now we see how those parameters depend on the treatment:

```
#|code-fold: true
#|tidy: true
#|echo: false

d$ui <- interaction(d$Site, d$Treatment)

nlme.coef.avg <- list()
nlme.coef <- list()
for (lvl in levels(d$ui)){
  d.tmp <- subset(d, ui == lvl)
  # first get nlsList coefs for comparison only (unused)
  temp_nls <- coef(nlsList(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)) | uid,
    d.tmp[, c("Pv.mg.L.", "uid", "t.dt")],
    start = list(PS = 0.1, k = 0.2)))
  nlsList_coefs <- c(apply(temp_nls, 2, \(x) c(mean=mean(x), sd=sd(x))))
  names(nlsList_coefs) <- c("PS.mean", "PS.sd", "k.mean", "k.sd")

  # now do the real thing
  model4 <- nlme(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)),
    fixed = PS + k ~ 1,
    random = PS + k ~ 1 | uid,
    data = d.tmp[, c("Pv.mg.L.", "uid", "t.dt")],
```

```

        start = c(PS = 0.05, k = 0.12),
        control = nlmeControl(maxIter = 200))
coef(model4)
fixef <- model4$coefficients$fixed
ranefs <- ranef(model4)
colnames(ranefs) <- paste0("ranef_", colnames(ranefs))
nlme.coef[[lvl]] <- cbind(coef(model4), ranefs, Rep=1:nrow(ranef(model4)), ui=lvl, Site=d
nlme.coef.avg[[lvl]] <- data.frame(PS=fixef["PS"], k=fixef["k"], ui=lvl, Site=d.tmp[1, "Si
}

```

Warning in nlme.formula(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)), fixed = PS + :
Iteration 1, LME step: nlminb() did not converge (code = 1). Do increase
'msMaxIter'!

Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded
Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded
Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded

Warning in nlme.formula(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)), fixed = PS + :
Iteration 1, LME step: nlminb() did not converge (code = 1). Do increase
'msMaxIter'!

Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded

Warning: 1 error caught in nls(model, data = data, control = controlvals, start
= start): singular gradient

Warning in nlme.formula(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)), fixed = PS + :
Iteration 1, LME step: nlminb() did not converge (code = 1). Do increase
'msMaxIter'!

Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded
Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded

Warning in nlme.formula(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)), fixed = PS + :
Iteration 1, LME step: nlminb() did not converge (code = 1). Do increase
'msMaxIter'!

Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded

Warning in nlme.formula(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)), fixed = PS + :
Iteration 1, LME step: nlminb() did not converge (code = 1). Do increase
'msMaxIter'!

Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded
Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded

Warning in nlme.formula(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)), fixed = PS + :
Iteration 1, LME step: nlminb() did not converge (code = 1). Do increase
'msMaxIter'!

Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded

Warning in nlme.formula(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)), fixed = PS + :
Iteration 1, LME step: nlminb() did not converge (code = 1). Do increase
'msMaxIter'!

Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded

Warning in nlme.formula(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)), fixed = PS + :
Iteration 1, LME step: nlminb() did not converge (code = 1). Do increase
'msMaxIter'!

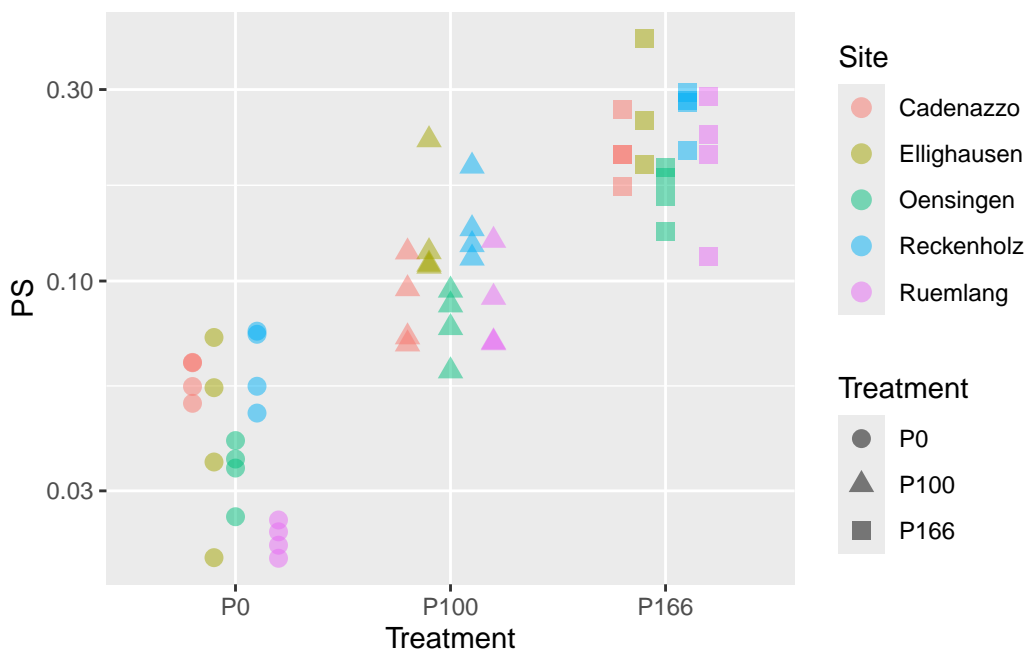
Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded
Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded
Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded


```
Warning in nlme.formula(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)), fixed = PS + :
Singular precision matrix in level -1, block 1
```

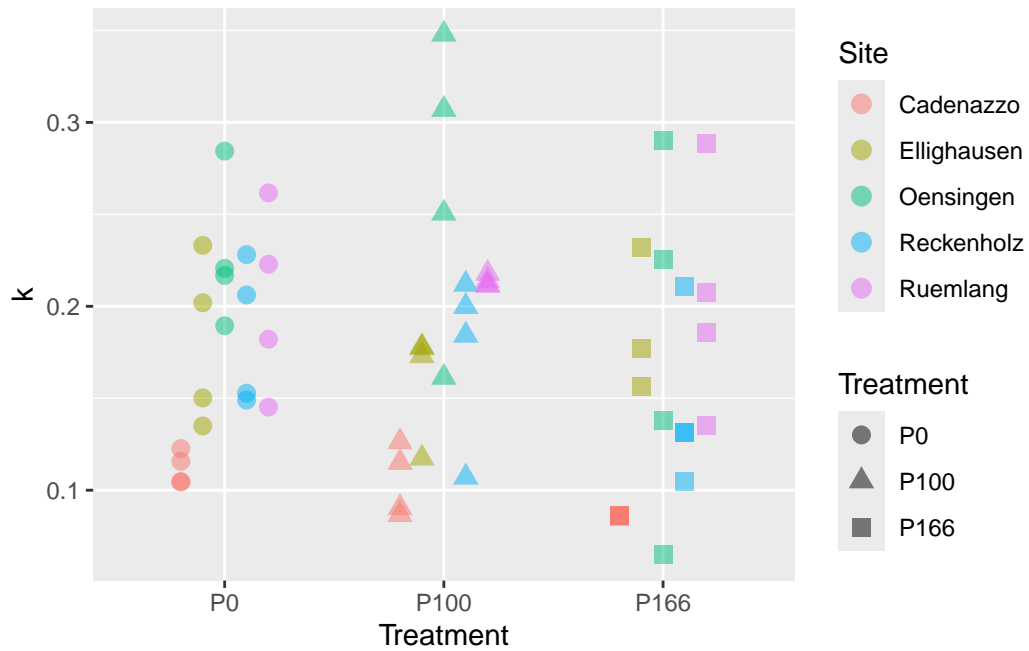
```
Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded
```

```
nlme.coef.avg <- do.call(rbind, nlme.coef.avg)
# folgendes datenset wollen wir benutzen um ihn mit dem Boden zu kombinieren
nlme.coef <- do.call(rbind, nlme.coef)
points <- geom_point(position=position_dodge(width=0.5), size = 3, alpha = 0.5)

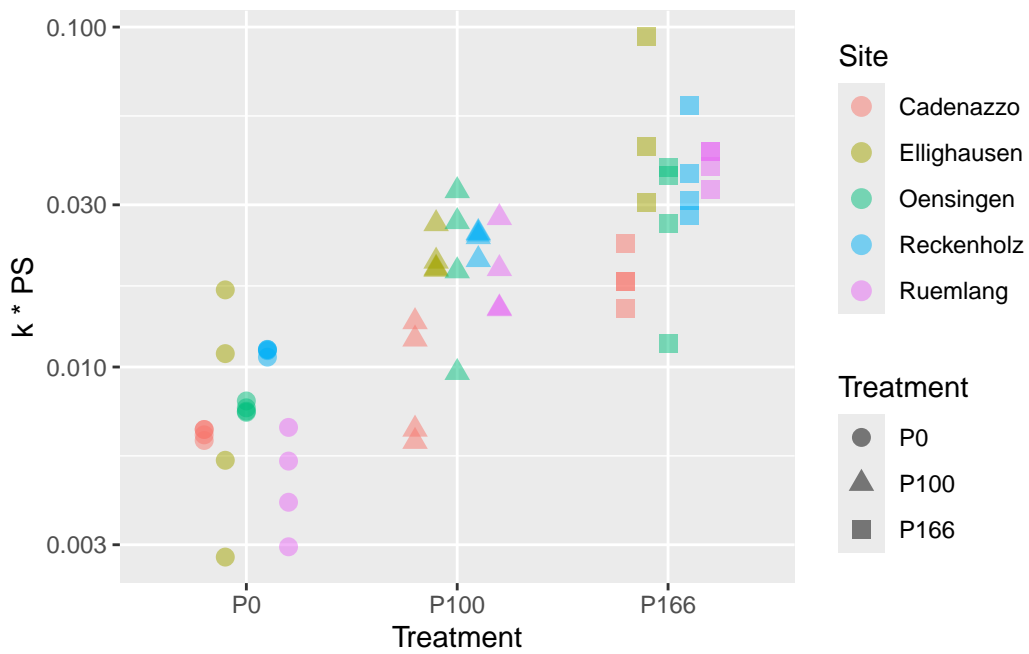
ggplot(nlme.coef, aes(y=PS , x=Treatment, col=Site, pch=Treatment)) + points + scale_y_log10
```



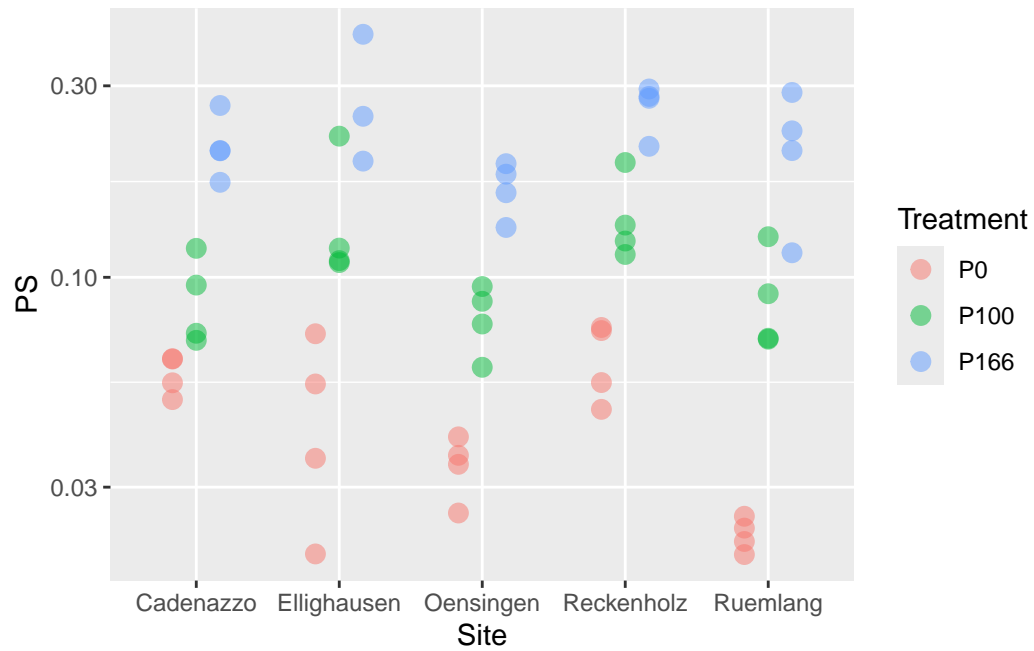
```
ggplot(nlme.coef, aes(y=k , x=Treatment, col=Site, pch=Treatment)) + points
```



```
ggplot(nlme.coef, aes(y=k*PS, x=Treatment, col=Site, pch=Treatment)) + points + scale_y_log10()
```



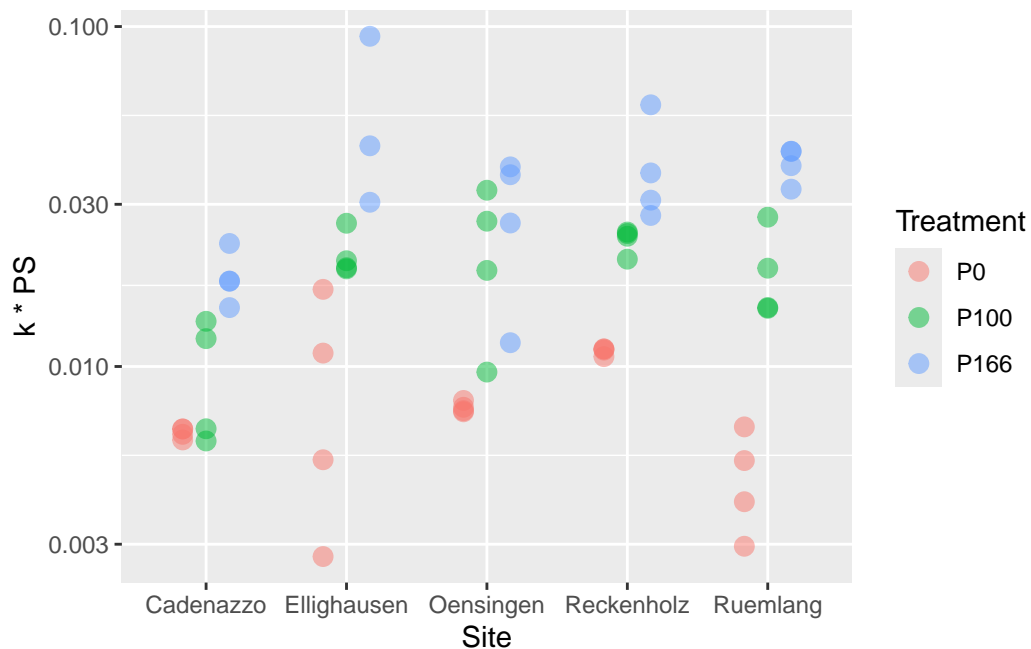
```
ggplot(nlme.coef, aes(y=PS, x=Site, col=Treatment)) + points + scale_y_log10()
```



```
ggplot(nlme.coef, aes(y=k , x=Site, col=Treatment)) + points
```



```
ggplot(nlme.coef, aes(y=k*PS, x=Site, col=Treatment)) + points + scale_y_log10()
```



```
# k PS macht von der interpretation her Sinn
# aber PS ist log-normal verteilt
```

```
fit.PS <- lm(log(PS) ~ Treatment + Site, nlme.coef)
fit.k <- lm(k ~ Treatment + Site, nlme.coef)
fit.kPS <- lm(I(log(k*PS)) ~ Treatment + Site, nlme.coef)
```

```
Anova(fit.PS)
```

Anova Table (Type II tests)

Response: log(PS)

	Sum Sq	Df	F value	Pr(>F)
Treatment	27.6260	2	154.7655	< 2.2e-16 ***
Site	3.0383	4	8.5104	2.324e-05 ***
Residuals	4.6411	52		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```
summary(glht(fit.PS, mcp(Treatment = "Tukey")))
```

Simultaneous Tests for General Linear Hypotheses

Multiple Comparisons of Means: Tukey Contrasts

Fit: `lm(formula = log(PS) ~ Treatment + Site, data = nlme.coef)`

Linear Hypotheses:

	Estimate	Std. Error	t value	Pr(> t)
P100 - P0 == 0	0.91948	0.09447	9.733	<1e-09 ***
P166 - P0 == 0	1.68127	0.09580	17.550	<1e-09 ***
P166 - P100 == 0	0.76179	0.09580	7.952	<1e-09 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
(Adjusted p values reported -- single-step method)

```
# Fazit: PS wird von treatment stark beeinflusst, k eher nicht (dafür von site)
Anova(fit.k)
```

Anova Table (Type II tests)

Response: k

	Sum Sq	Df	F value	Pr(>F)
Treatment	0.007374	2	1.6124	0.2092
Site	0.108427	4	11.8547	6.442e-07 ***
Residuals	0.118902	52		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```
summary(glht(fit.k, mcp(Treatment = "Tukey")))
```

Simultaneous Tests for General Linear Hypotheses

Multiple Comparisons of Means: Tukey Contrasts

Fit: `lm(formula = k ~ Treatment + Site, data = nlme.coef)`

Linear Hypotheses:

	Estimate	Std. Error	t value	Pr(> t)
P100 - P0 == 0	0.003111	0.015121	0.206	0.977
P166 - P0 == 0	-0.022243	0.015334	-1.451	0.323
P166 - P100 == 0	-0.025354	0.015334	-1.653	0.233

(Adjusted p values reported -- single-step method)

```
Anova(fit.kPS)
```

Anova Table (Type II tests)

Response: I(log(k * PS))

	Sum Sq	Df	F value	Pr(>F)
Treatment	22.4177	2	68.5970	2.609e-15 ***
Site	3.9298	4	6.0124	0.0004703 ***
Residuals	8.4969	52		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```
summary(glht(fit.kPS, mcp(Treatment = "Tukey")))
```

Simultaneous Tests for General Linear Hypotheses

Multiple Comparisons of Means: Tukey Contrasts

Fit: lm(formula = I(log(k * PS)) ~ Treatment + Site, data = nlme.coef)

Linear Hypotheses:

	Estimate	Std. Error	t value	Pr(> t)
P100 - P0 == 0	0.9127	0.1278	7.140	<1e-04 ***
P166 - P0 == 0	1.5035	0.1296	11.599	<1e-04 ***
P166 - P100 == 0	0.5908	0.1296	4.558	<1e-04 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

(Adjusted p values reported -- single-step method)

```
anova(fit.soil.PS)
```

Type III Analysis of Variance Table with Satterthwaite's method

	Sum Sq	Mean Sq	NumDF	DenDF	F value	Pr(>F)
soil_0_20_clay	0.0719	0.0719	1	70.835	2.3900	0.1265690
soil_0_20_pH_H2O	0.0152	0.0152	1	89.035	0.5061	0.4787086
soil_0_20_Corg	0.4704	0.4704	1	65.081	15.6423	0.0001915 ***
soil_0_20_silt	0.1061	0.1061	1	70.745	3.5286	0.0644392 .
Treatment	10.0459	5.0230	2	6.055	167.0386	5.047e-06 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```
#summary(glht(fit.PS))
# Fazit: PS wird von treatment stark beeinflusst, k eher nicht (dafür von site)
anova(fit.soil.k)
```

Type III Analysis of Variance Table with Satterthwaite's method

	Sum Sq	Mean Sq	NumDF	DenDF	F value	Pr(>F)
soil_0_20_clay	0.0098143	0.0098143	1	69.314	10.0428	0.002277 **
soil_0_20_pH_H2O	0.0091422	0.0091422	1	102.384	9.3551	0.002838 **
soil_0_20_Corg	0.0014112	0.0014112	1	98.359	1.4440	0.232372
soil_0_20_silt	0.0046704	0.0046704	1	75.910	4.7792	0.031888 *
Treatment	0.0059043	0.0029521	2	5.405	3.0209	0.131613

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```
summary(glht(fit.soil.k))
```

Warning in RET\$pf(function("adjusted", ...): Completion with error > abseps

Warning in RET\$pf(function("adjusted", ...): Completion with error > abseps

Warning in RET\$pf(function("adjusted", ...): Completion with error > abseps

Simultaneous Tests for General Linear Hypotheses

```
Fit: lmer(formula = k ~ soil_0_20_clay + soil_0_20_pH_H2O + soil_0_20_Corg +
  soil_0_20_silt + Treatment + (1 | year) + (1 | Site) + (1 |
  Site:block) + (1 | Site:Treatment), data = D)
```

Linear Hypotheses:

	Estimate	Std. Error	z value	Pr(> z)
(Intercept) == 0	0.074168	0.150771	0.492	0.99651

```

soil_0_20_clay == 0    -0.007001    0.002209   -3.169   0.00995 **
soil_0_20_pH_H2O == 0  0.033720    0.011024    3.059   0.01508 *
soil_0_20_Corg == 0   -0.034533    0.028737   -1.202   0.77661
soil_0_20_silt == 0    0.005864    0.002683    2.186   0.16535
TreatmentP100 == 0     0.003910    0.015506    0.252   0.99993
TreatmentP166 == 0    -0.031147    0.015685   -1.986   0.25355

```

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
(Adjusted p values reported -- single-step method)

```
anova(fit.soil.kPS)
```

Type III Analysis of Variance Table with Satterthwaite's method

	Sum Sq	Mean Sq	NumDF	DenDF	F value	Pr(>F)
soil_0_20_clay	0.0055	0.00551	1	77.626	0.1043	0.747639
soil_0_20_pH_H2O	0.3773	0.37731	1	101.942	7.1335	0.008807 **
soil_0_20_Corg	0.0105	0.01052	1	93.639	0.1990	0.656575
soil_0_20_silt	0.0036	0.00360	1	80.228	0.0681	0.794743
Treatment	4.0339	2.01697	2	5.847	38.1329	0.000442 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```
summary(glht(fit.soil.kPS))
```

Simultaneous Tests for General Linear Hypotheses

Fit: lmer(formula = I(log(k * PS)) ~ soil_0_20_clay + soil_0_20_pH_H2O +
soil_0_20_Corg + soil_0_20_silt + Treatment + (1 | year) +
(1 | Site) + (1 | Site:block) + (1 | Site:Treatment), data = D)

Linear Hypotheses:

	Estimate	Std. Error	z value	Pr(> z)
(Intercept) == 0	-6.657570	1.107392	-6.012	<0.001 ***
soil_0_20_clay == 0	-0.005316	0.016463	-0.323	0.9997
soil_0_20_pH_H2O == 0	0.216354	0.081005	2.671	0.0479 *
soil_0_20_Corg == 0	0.094691	0.212278	0.446	0.9980
soil_0_20_silt == 0	0.005221	0.020000	0.261	0.9999
TreatmentP100 == 0	1.064948	0.189188	5.629	<0.001 ***
TreatmentP166 == 0	1.634290	0.190050	8.599	<0.001 ***

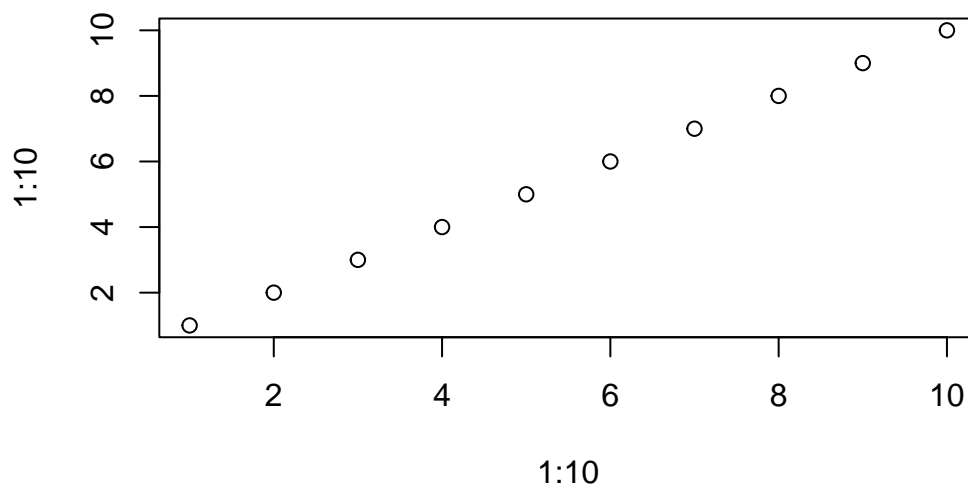
Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
(Adjusted p values reported -- single-step method)

Method

```
print(19)
```

```
[1] 19
```

```
plot(1:10,1:10)
```



Results

Discussion

Conclusion

Acknowledgments

Legal Disclosure

References

Appendix

Supplements

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