# 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 derivates of Orthophosphate 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 or poly-orthophosphate , where it can strongly interact with water, forming, depending on pH or . 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 -content amorphous -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.fitdistr broom

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

Learn more about sjmisc with 'browseVignettes("sjmisc")'.

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:

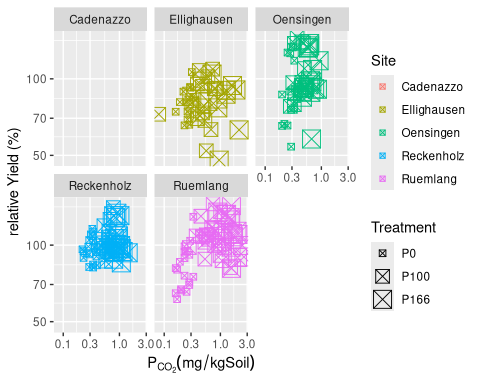
### How well can current GRUD measurements of predict the relative Yield, P-Uptake and P-Balance?

* Hypothesis I: The measurements of the equlibrium 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. relates strongly to the amount of Phosphorus applied, the P-balance might well be siginificantly correlated to 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.

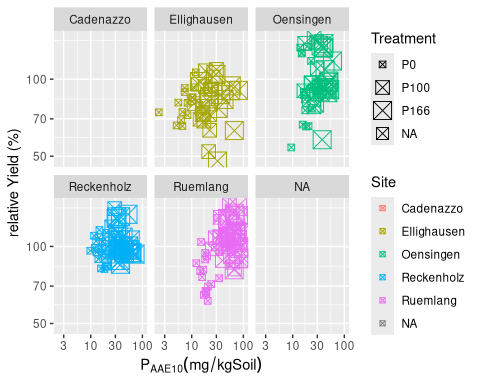
Warning: Removed 200 rows containing missing values or values outside the scale range  
(`geom\_point()`).



ggplot(D[D$soil\_0\_20\_P\_AAE10!=0,],aes(y=Ymain\_rel, x=soil\_0\_20\_P\_AAE10, col=Site, size = Treatment)) +  
 geom\_point(shape = 7) +   
 scale\_x\_log10() + scale\_y\_log10() +  
 labs(x=TeX("$P\_{AAE10}(mg/kg Soil)$"),  
 y="relative Yield (%)") +  
 facet\_wrap( ~ Site, nrow = 2)

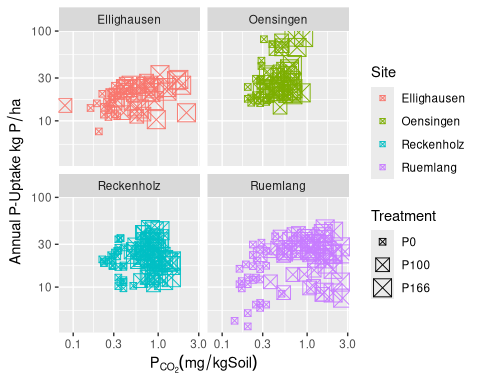
Warning: Using size for a discrete variable is not advised.

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, col=Site, size = Treatment)) +  
 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)

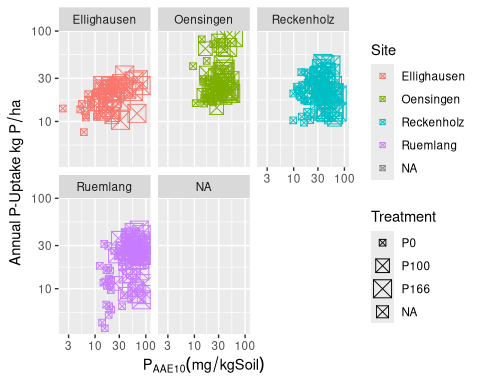
Warning: Using size for a discrete variable is not advised.



ggplot(D[D$soil\_0\_20\_P\_AAE10!=0&D$annual\_P\_uptake!=0,],aes(y=annual\_P\_uptake, x=soil\_0\_20\_P\_AAE10, col=Site, size = Treatment)) +  
 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()`).



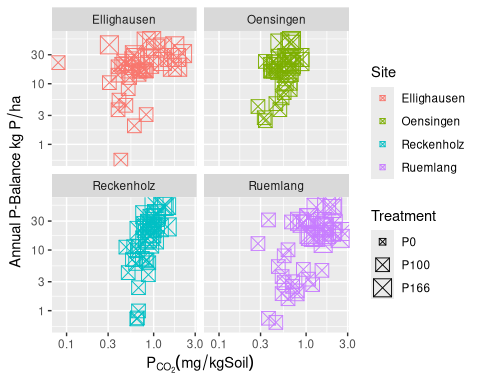
ggplot(D[D$soil\_0\_20\_P\_CO2!=0&D$annual\_P\_balance!=0,],aes(y=annual\_P\_balance, x=soil\_0\_20\_P\_CO2, col=Site, size = Treatment)) +  
 geom\_point(shape = 7) +   
 scale\_x\_log10() + scale\_y\_log10() +  
 labs(x=TeX("$P\_{CO\_{2}}(mg/kg Soil)$"),  
 y=TeX("Annual P-Balance $kg~P/ha$")) +  
 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()`).



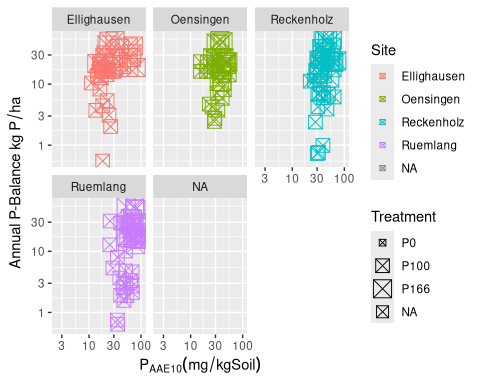
ggplot(D[D$soil\_0\_20\_P\_AAE10!=0&D$annual\_P\_balance!=0,],aes(y=annual\_P\_balance, x=soil\_0\_20\_P\_AAE10, col=Site, size = Treatment)) +  
 geom\_point(shape = 7) +   
 scale\_x\_log10() + scale\_y\_log10() +  
 labs(x=TeX("$P\_{AAE10}(mg/kg Soil)$"),  
 y=TeX("Annual P-Balance $kg~P/ha$")) +  
 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 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.

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

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 R2 = 0.58) and the part related  
to the fixed effects alone (marginal R2) 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 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 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 nloptwrap 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,na.rm=TRUE))^2,na.rm = TRUE)

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

### How do GRUD-measurements of relate to the soil properties -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 (for both and AAE10) and silt- and clay-content. has been reported to positively influence the capacity of Phosphorus as well, it is plausible it also shows a positive correlation with . AAE10 also deploys which is easily captured by and , therefore it is officially by GRUD advised against being used in soils with , therefore -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 in the water-soil interface, most P is transported to the rhizosphere via diffusion. As a consequence the intensity of 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\_prec   
 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\_rel,na.rm=TRUE))^2,na.rm = TRUE)  
  
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 0.329   
E.ansum\_prec -0.022 0.451   
  
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,na.rm=TRUE))^2,na.rm = TRUE)

With the covariate and random effect used as by Juliane Hirte we obtain 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 as a predictor with 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 and ( can be interpreted as the relative speed of desorption, is the equilibrium concentration of 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 dictates the form of orthophosphate, with , the predominant form will be , 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$pfunction("adjusted", ...): Completion with error > abseps  
Warning in RET$pfunction("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 0.313   
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 beeinfluss, 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 0.99651   
soil\_0\_20\_clay == 0 -0.007001 0.002209 -3.169 0.00957 \*\*  
soil\_0\_20\_pH\_H2O == 0 0.033720 0.011024 3.059 0.01524 \*   
soil\_0\_20\_Corg == 0 -0.034533 0.028737 -1.202 0.77733   
soil\_0\_20\_silt == 0 0.005864 0.002683 2.186 0.16562   
TreatmentP100 == 0 0.003910 0.015506 0.252 0.99993   
TreatmentP166 == 0 -0.031147 0.015685 -1.986 0.25391   
---  
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 0.0485 \*   
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:
* where is estimated as , 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 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

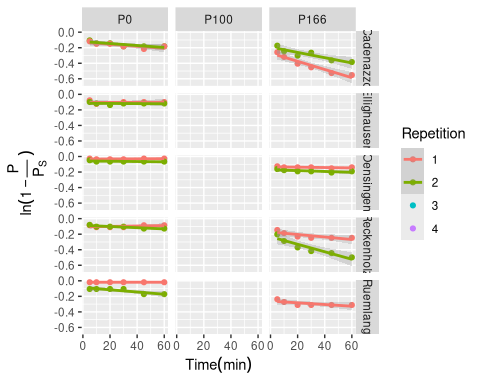
Call:  
 Model: Y1 ~ t.min. | uid   
 Data: d[d$Repetition == 1 | d$Repetition == 2, ]   
  
Coefficients:  
 (Intercept)   
 Estimate Std. Error t value Pr(>|t|)  
Cadenazzo\_P0\_1 -0.12891945 0.01537006 -8.387702 4.332766e-12  
Cadenazzo\_P0\_2 -0.12037045 0.01537006 -7.831491 4.433395e-11  
Cadenazzo\_P100\_1 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  
Oensingen\_P0\_1 -0.03432646 0.01537006 -2.233333 2.882091e-02  
Oensingen\_P0\_2 -0.05745952 0.01537006 -3.738407 3.819350e-04  
Oensingen\_P100\_1 NA NA NA NA  
Oensingen\_P100\_2 NA NA NA NA  
Oensingen\_P166\_1 -0.13275856 0.01537006 -8.637481 1.527196e-12  
Oensingen\_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  
Oensingen\_P0\_1 1.049070e-04 0.0004483906 2.339634e-01 8.157164e-01  
Oensingen\_P0\_2 -1.837559e-04 0.0004483906 -4.098121e-01 6.832320e-01  
Oensingen\_P100\_1 NA NA NA NA  
Oensingen\_P100\_2 NA NA NA NA  
Oensingen\_P166\_1 -2.320568e-04 0.0004483906 -5.175327e-01 6.064639e-01  
Oensingen\_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()`).



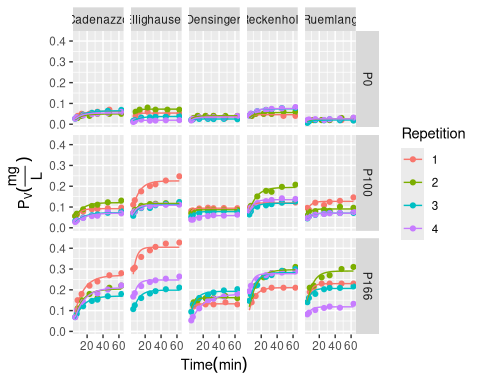
The relation can be improved:

#|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")], start=list(PS=0.1,k=0.2))

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 tratment:

#|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.tmp[1, "Site"], Treatment=d.tmp[1, "Treatment"], uid = rownames(coef(model4)))  
 nlme.coef.avg[[lvl]] <- data.frame(PS=fixef["PS"], k=fixef["k"], ui=lvl, Site=d.tmp[1, "Site"], Treatment=d.tmp[1, "Treatment"], uid = d.tmp$uid)  
}

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

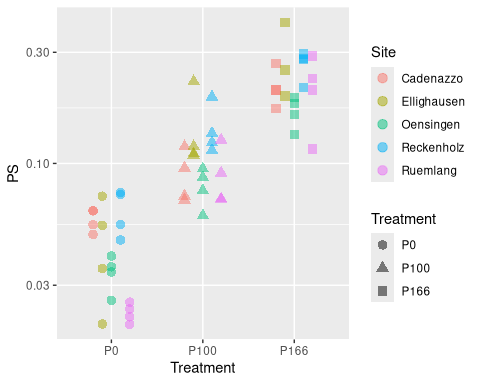
Warning in nlme.formula(Pv.mg.L. ~ PS \* (1 - exp(-k \* t.dt)), fixed = PS + :  
Iteration 1, LME step: nlminb() did not converge (code = 1). Do increase  
'msMaxIter'!

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

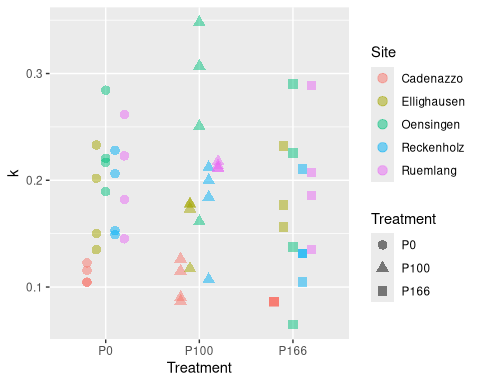
Warning in nlme.formula(Pv.mg.L. ~ PS \* (1 - exp(-k \* t.dt)), fixed = PS + :  
Singular precision matrix in level -1, block 1

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

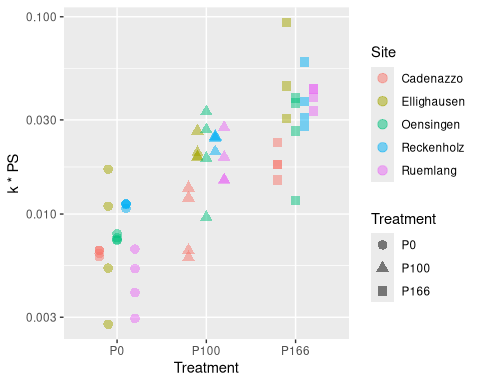
nlme.coef.avg <- do.call(rbind, nlme.coef.avg)  
# folgendes datenset wollen wir benutzen um ihn mit dem Boden zu kombinieren  
nlme.coef <- do.call(rbind, nlme.coef)  
points <- geom\_point(position=position\_dodge(width=0.5), size = 3, alpha = 0.5)  
  
ggplot(nlme.coef, aes(y=PS , x=Treatment, col=Site, pch=Treatment)) + points + scale\_y\_log10()



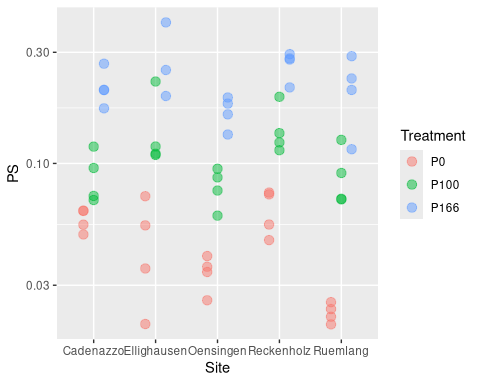
ggplot(nlme.coef, aes(y=k , x=Treatment, col=Site, pch=Treatment)) + points



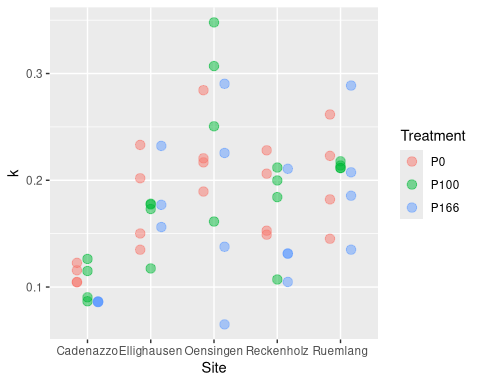
ggplot(nlme.coef, aes(y=k\*PS, x=Treatment, col=Site, pch=Treatment)) + points + scale\_y\_log10()



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-10 \*\*\*  
P166 - P0 == 0 1.68127 0.09580 17.550 < 1e-10 \*\*\*  
P166 - P100 == 0 0.76179 0.09580 7.952 1.01e-10 \*\*\*  
---  
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 beeinfluss, 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 beeinfluss, 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 0.0103 \*  
soil\_0\_20\_pH\_H2O == 0 0.033720 0.011024 3.059 0.0147 \*  
soil\_0\_20\_Corg == 0 -0.034533 0.028737 -1.202 0.7770   
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 0.2543   
---  
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 0.0476 \*   
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)