Master Thesis

Marc Pérez

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 derivates 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

```
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
```

```
Loading required package: carData
```

```
Loading required package: Matrix
```

```

Attaching package: 'Matrix'
```

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

    expand, pack, unpack

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


Attaching package: 'nlme'

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

    lmList


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

Registered S3 methods overwritten by 'MuMIn':
  method        from
  nobs.multinom broom
  nobs.fitdistr broom


Attaching package: 'sjmisc'

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

    replace_na
```

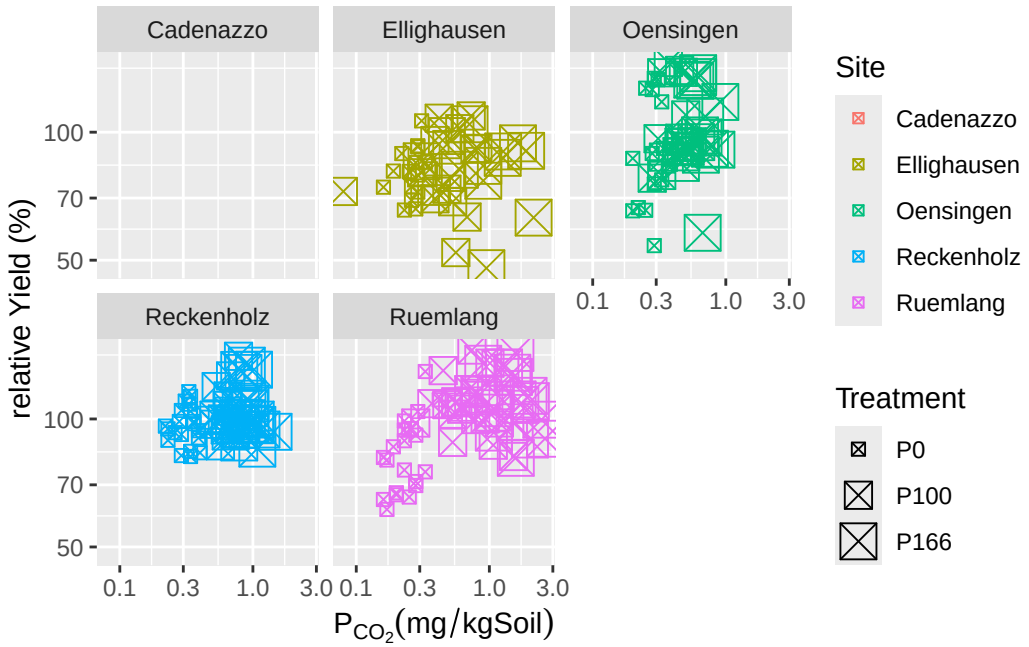
Research Questions:

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

- Hypothesis I: The measurements of the 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. C_P relates strongly to the amount of Phosphorus applied, the P-balance might well be siginificantly correlated to C_P but not explain a lot of variance.

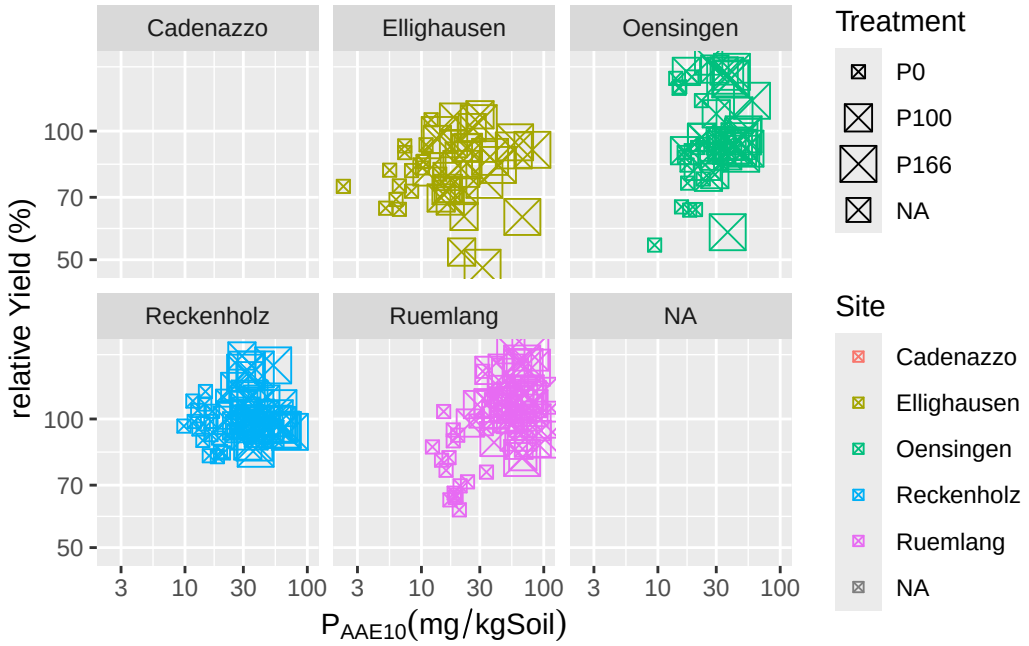
```
Warning: Using size for a discrete variable is not advised.

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

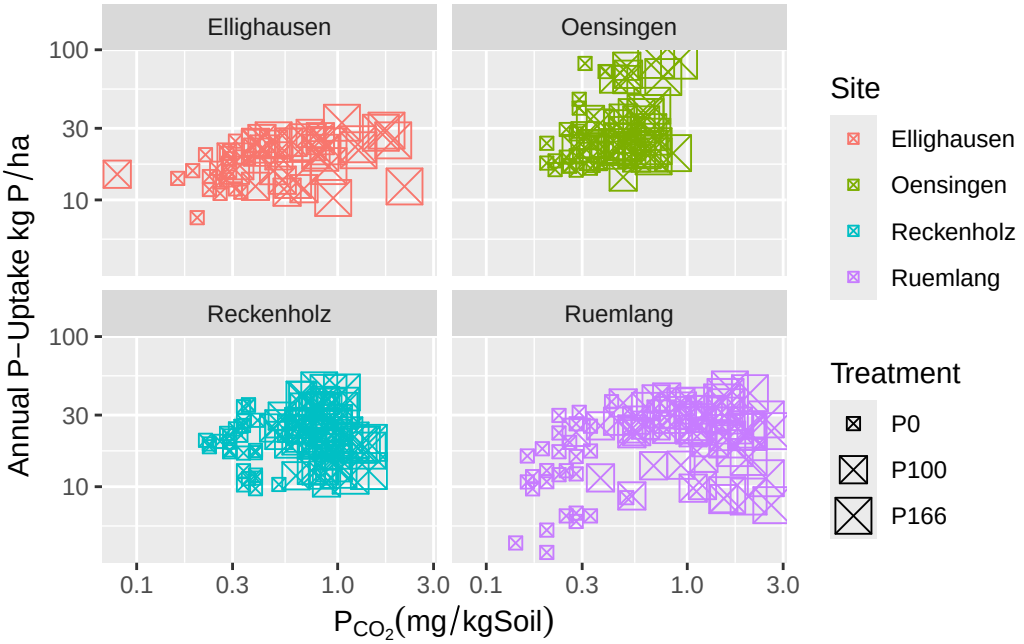



```
Warning: Using size for a discrete variable is not advised.
```

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

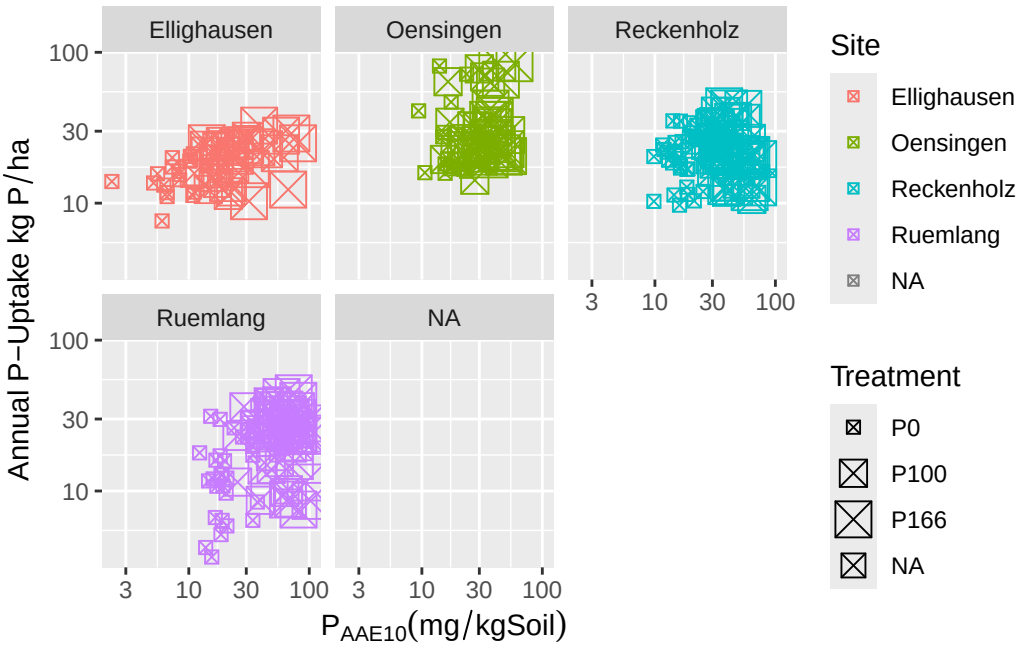


```
Warning: Using size for a discrete variable is not advised.
```




```
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()`).
```

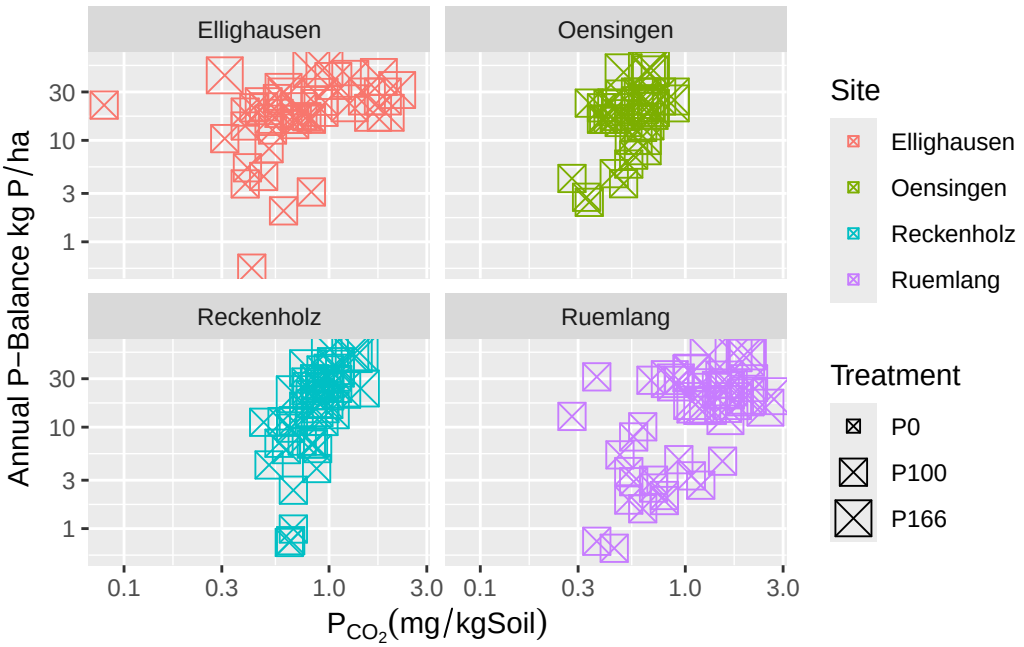



```
Warning: Using size for a discrete variable is not advised.
```

```
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()`).
```

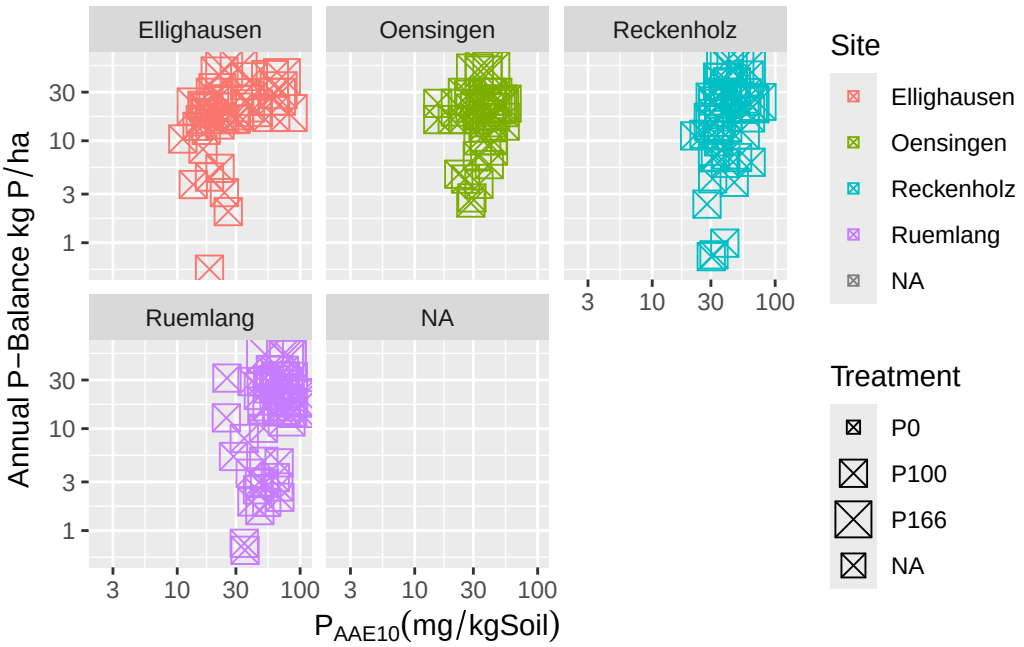



```
Warning: Using size for a discrete variable is not advised.
```

```
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:

```
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.


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.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  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],
```

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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.


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:

```
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

                   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

# Indices of model performance

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

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.

```
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

           R2m       R2c
[1,] 0.6044325 0.8244053

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

           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.

```
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_pr
                       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


                   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


# Indices of model performance

AIC     |    AICc |     BIC |  RMSE |  Sigma
-------------------------------------------
```

```
765.695 | 779.948 | 821.647 | 9.989 | 10.270


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

                   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

# Indices of model performance

AIC     |    AICc |     BIC |   RMSE |  Sigma
-----------------------------------------------
804.491 | 809.807 | 840.097 | 11.738 | 11.738
```

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.

```
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
```

```
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')


            R2m       R2c
[1,] 0.03304352 0.8042098


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

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')


            R2m       R2c
[1,] 0.01723874 0.6121275

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

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')


           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.

```
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

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    0.314
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)

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

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)

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

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 $PS = [P_{\text{Olsen/CAL}}] - [P_{H_2O}]$, 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.

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

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.
```

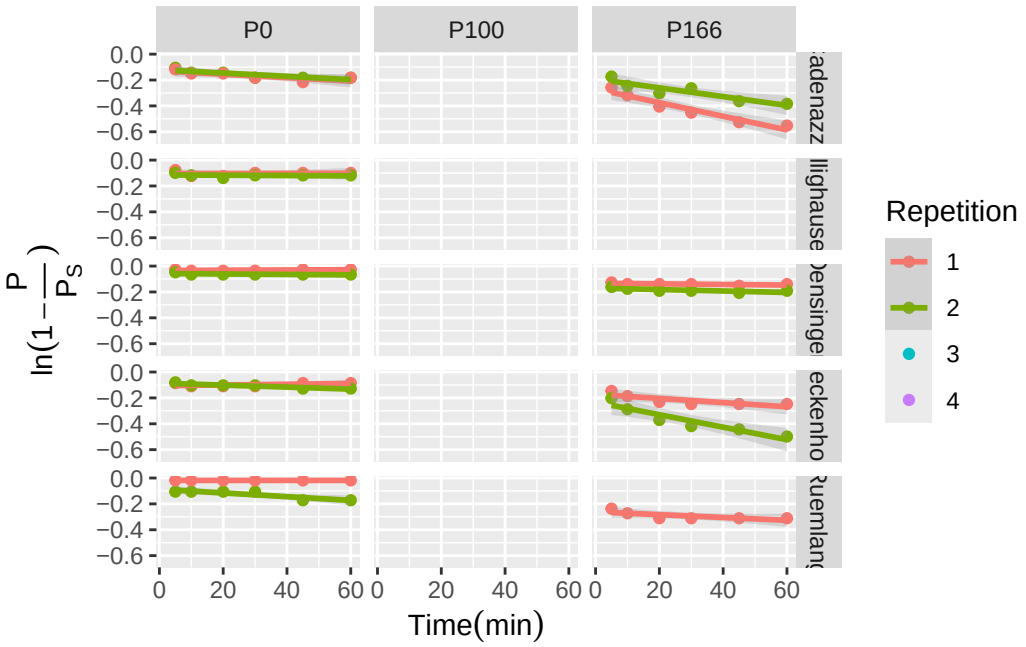
```
                       Estimate   Std. Error       t value     Pr(>|t|)
Cadenazzo_P0_1     -1.318800e-03 0.0004483906 -2.941186e+00 4.466020e-03
Cadenazzo_P0_2     -1.272378e-03 0.0004483906 -2.837654e+00 5.984783e-03
Cadenazzo_P100_1              NA           NA            NA           NA
Cadenazzo_P100_2              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

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

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

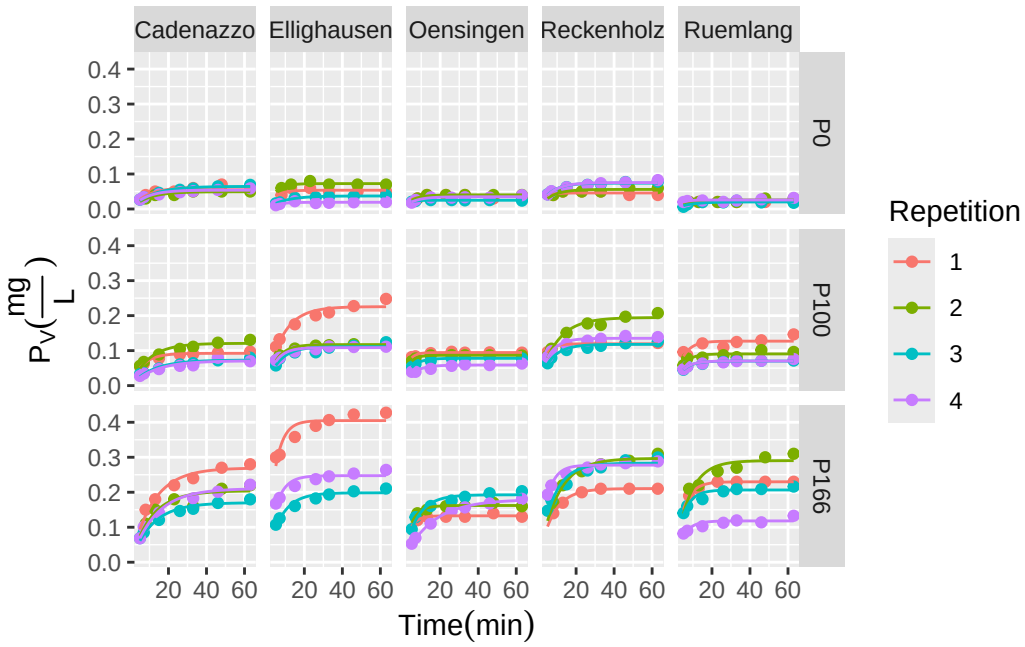
Warning: Removed 292 rows containing missing values or values outside the scale range
(`geom_point()`).
```



The relation can be improved:

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

```
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:

```
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'!

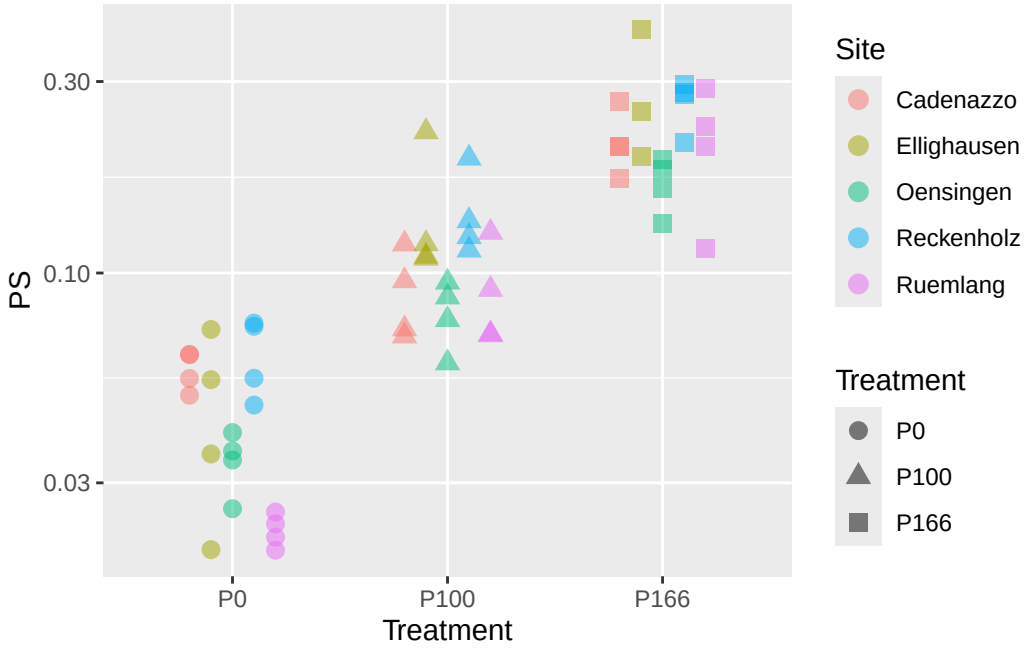
Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded
```

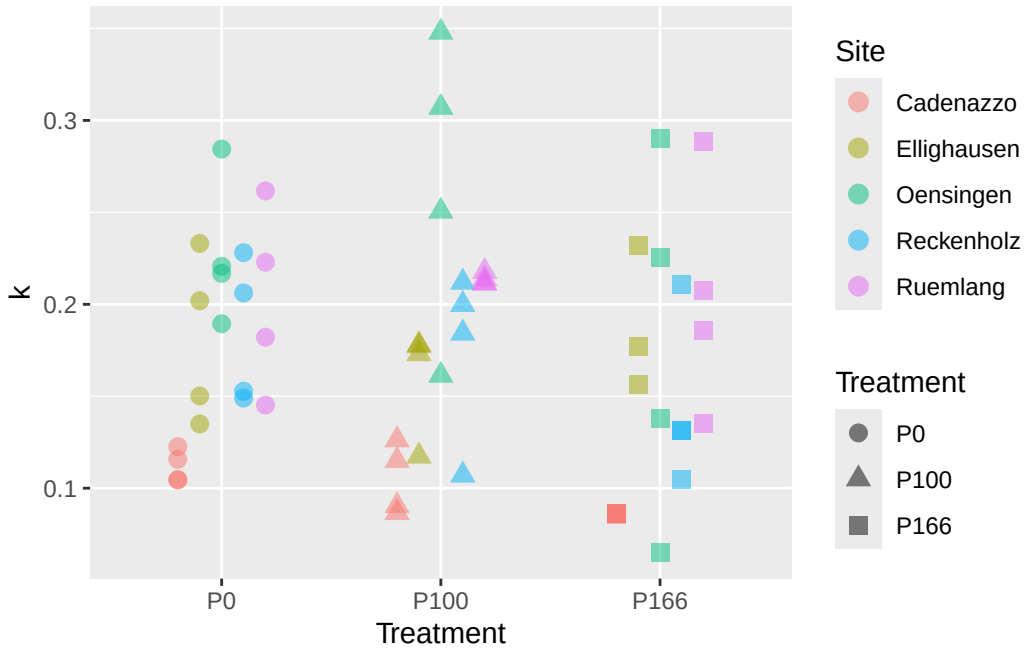
```
Warning in nlme.formula(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)), fixed = PS + :
Iteration 1, LME step: nlminb() did not converge (code = 1). Do increase
'msMaxIter'!

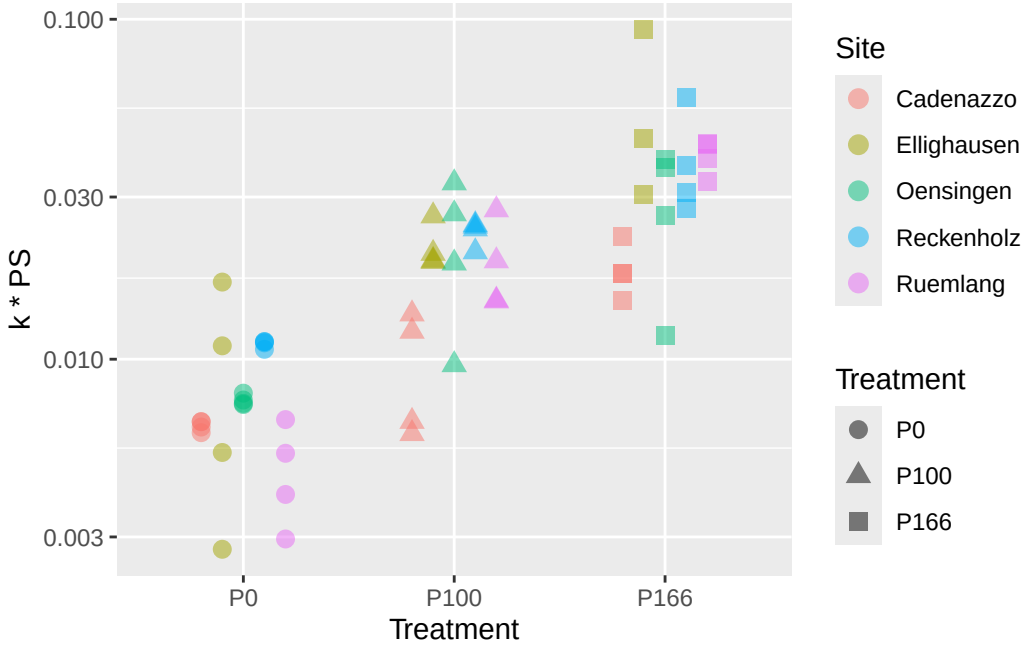
Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded
Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded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

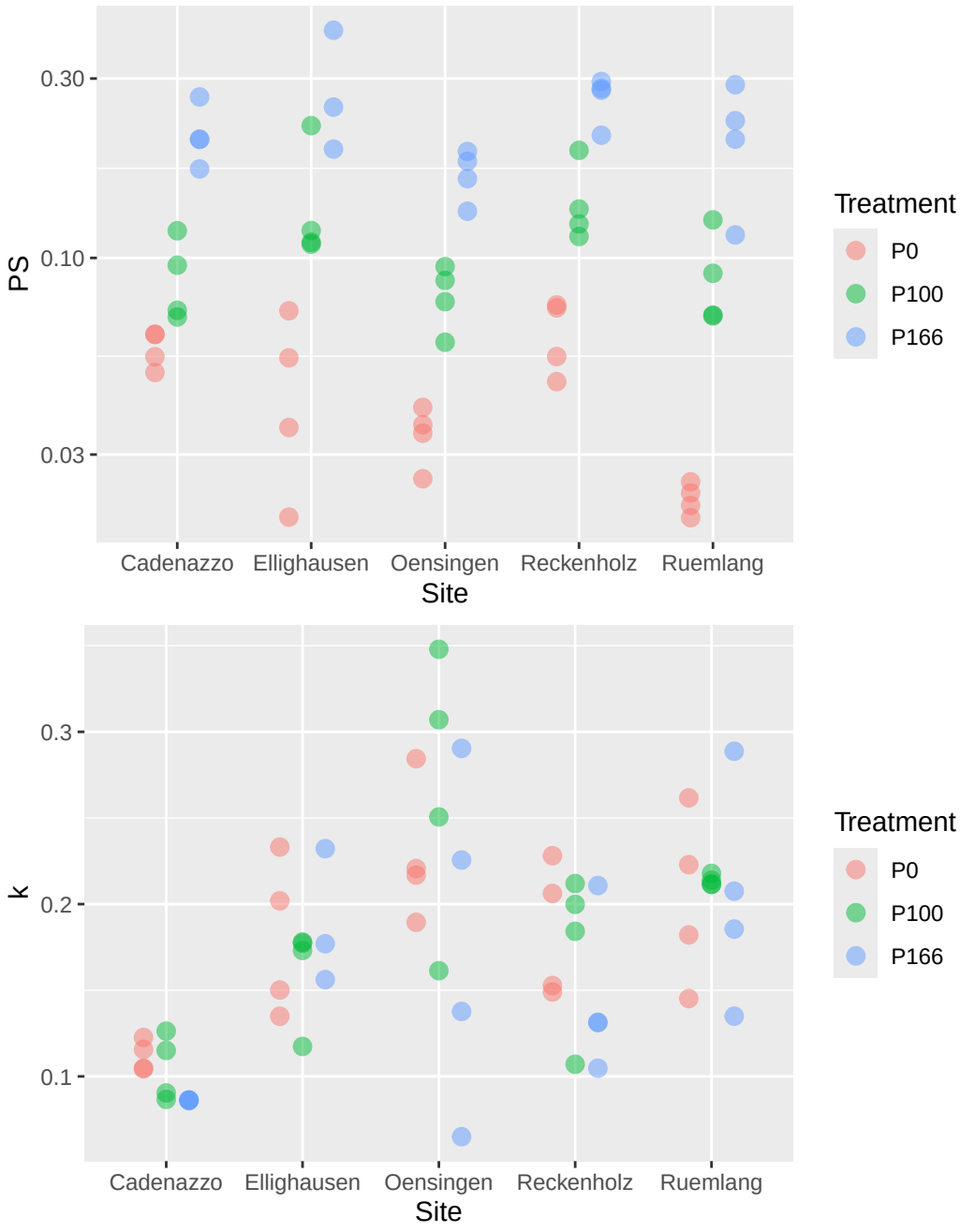
Warning in nlme.formula(Pv.mg.L. ~ PS * (1 - exp(-k * t.dt)), fixed = PS + :
Singular precision matrix in level -1, block 1

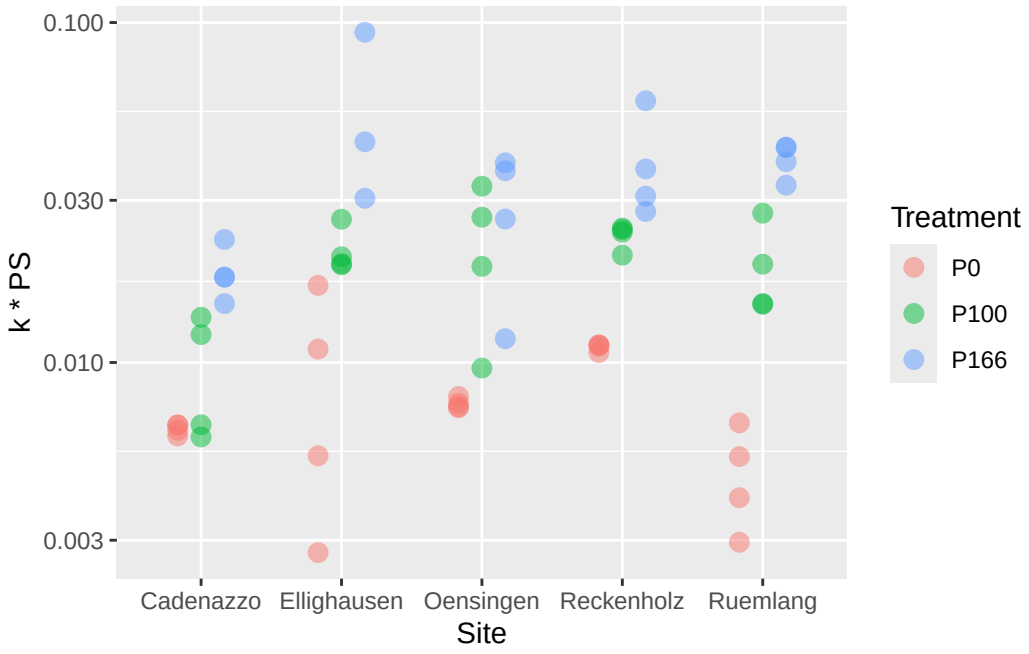
Warning in data.frame(PS = fixef["PS"], k = fixef["k"], ui = lvl, Site =
d.tmp[1, : row names were found from a short variable and have been discarded
```




k
0.3
0.2
0.1
P0
P100
P166
Treatment
Site
Cadenazzo
Ellighausen
Oensingen
Reckenholz
Ruemlang
Treatment
P0
P100
P166


k * PS
0.100
0.030
0.010
0.003
P0
P100
P166
Treatment
Site
Cadenazzo
Ellighausen
Oensingen
Reckenholz
Ruemlang
Treatment
P0
P100
P166


PS
0.30
0.10
0.03
Cadenazzo
Ellighausen
Oensingen
Reckenholz
Ruemlang
Site
Treatment
P0
P100
P166
k
0.3
0.2
0.1
Cadenazzo
Ellighausen
Oensingen
Reckenholz
Ruemlang
Site
Treatment
P0
P100
P166




```
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


     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)

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


     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 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


     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)


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


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


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  0.00995 **
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)


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



     Simultaneous Tests for General Linear Hypotheses

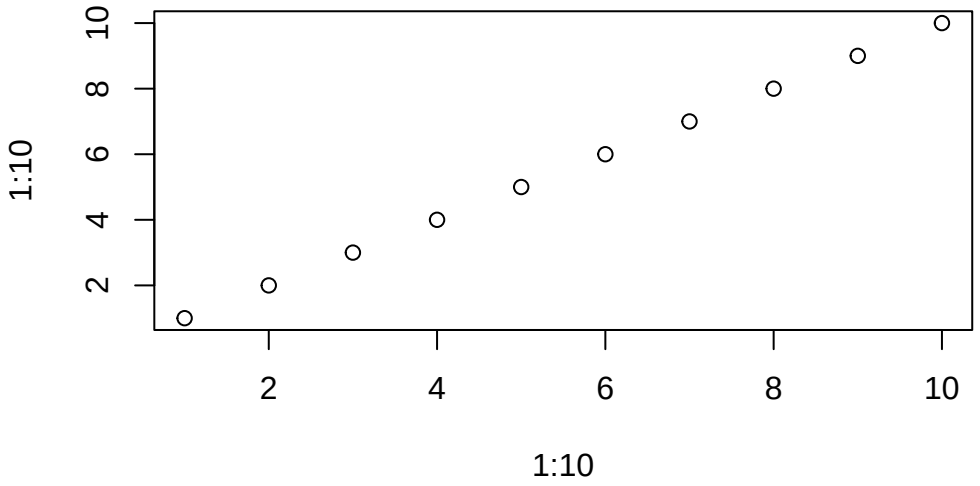
Fit: lmer(formula = I(log(k * PS)) ~ soil_0_20_clay + soil_0_20_pH_H2O +
    soil_0_20_Corg + soil_0_20_silt + Treatment + (1 | year) +
    (1 | Site) + (1 | Site:block) + (1 | Site:Treatment), data = D)

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

```
[1] 19
```



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.