Online Analytical Chemistry notes: data analysis

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Overview

These notes are on analysis of data, including application of statistical models, that comes after data manipulation.

Multiple measurements on one experimental unit

We'll start with an important problem that runs through all this material: hypothesis testing or statistical inference requires replication at the experimental unit level. The *experimental unit* is the physical thing to which an experimental treatment is applied. Without this kind of replication, even millions of measurements will tell us nothing about an effect or a difference *in general*. Making multiple measurements on a single experimental unit results in data that may be called *structured* (an unfortunately vague term, perhaps). You might also see the terms *hierarchical*, *nested*, or *subsampling* used. In this case, the lack of *independence* among observations becomes a problem. Unfortunately, as Bello and Renter wrote:

"Yet, a staggering number of standard statistical methods commonly used for data analysis, particularly those taught in introductory statistics courses (e.g., correlations, z-tests, t-tests, traditional ANOVA, regression), implicitly assume that observations are mutually independent and that data structure is nonexistent. Most concerning, these critical assumptions often go understated, thus effectively disregarding any correlation patterns in the data induced by the hierarchical structure of data architecture. As a direct consequence, experimental replication is naively matched one-to-one with level of observation in the data (Stroup, 2013) and the inferential space is misrepresented (Tempelman, 2009). This oversight can have serious downstream implications for inference (Aitkin and Longford, 1986) and provide a false sense of security on results, meanwhile undermining RR."

This all relates to the *scope of inference*, or the population to which a statistical inference applies. While we might generally like our results to apply to a very broad population, a narrow one is more likely. And without replication of experimental units, the scope becomes very narrow.

Let's try to keep these general issues in mind as we explore some ways to analyze data generated from online measurements. But also, be sure to keep them in mind for design of experiments. Try to think about the ideal scope of inference and how replication at the experimental unit level can be done.

General ideas

For data analysis we will focus on relatively simple methods that can handle structured data. Some of the main ideas are:

1. Statistical models are not always needed
2. Statistical models can be difficult to appropriately apply *directly* to measurement data
3. Recognition of the expermental unit is essential
4. Response feature analysis is simple and circumvents problems with structured data
5. Nonlinear regression can be helpful for fitting complex models or feature extraction

6. Mixed-effects models are an easy and flexible approach for working with structured data

When it comes to statistical modeling, we will go over these four groups of methods:

1. Response feature analysis
2. Classical linear models
3. Mixed-effects models
4. Nonlinear regression

These four are related; some are used together.

No statistics needed

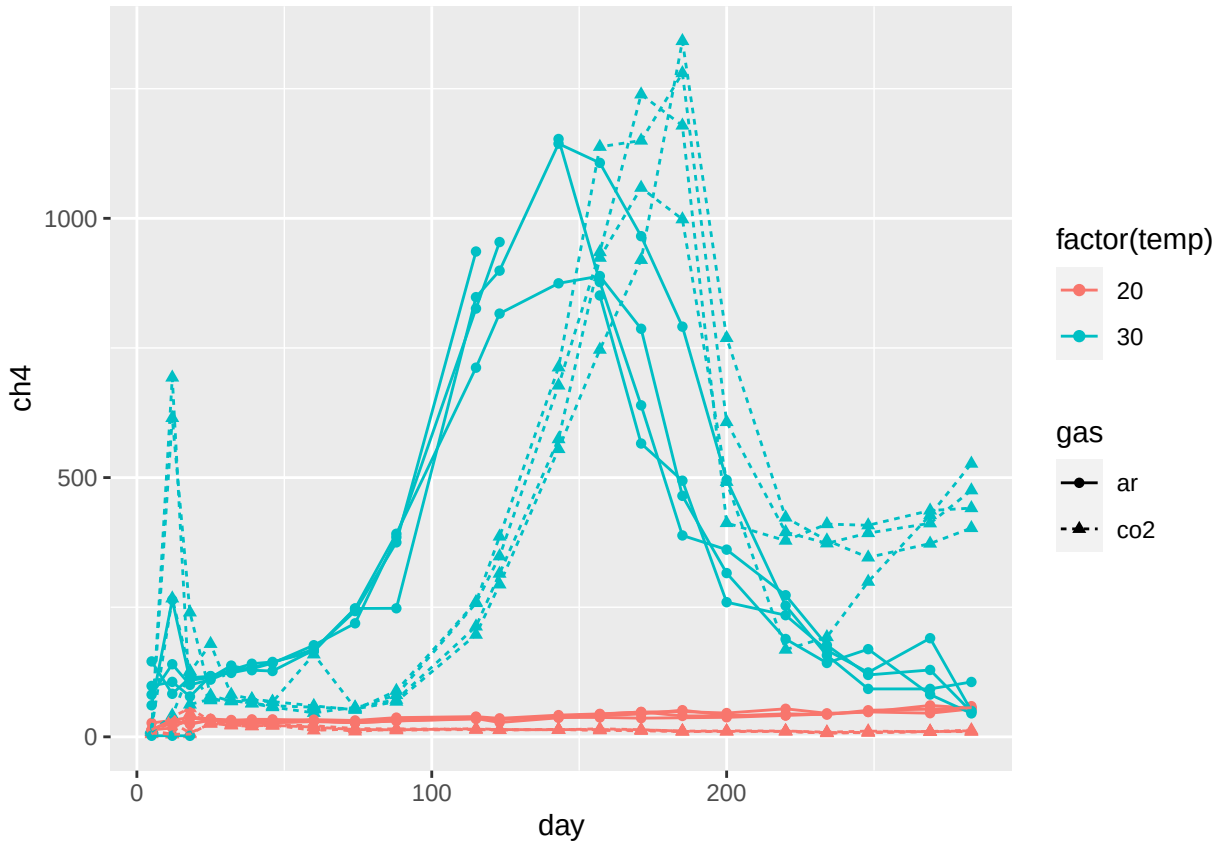
1. Methane emission in lab incubations

```
library(data.table)
dat <- fread('../../data/slurry_emis.csv')
dat
```

```
##      reactor     ch4      co2       flow day gas temp
##   1:      R1  11.374  338.300 0.06300000   5 co2   20
##   2:      R2   9.638  348.235 0.07300000   5 co2   20
##   3:      R3   5.221  320.180 0.08200000   5 co2   20
##   4:      R4   7.200  313.690 0.08100000   5 co2   20
##   5:      R5  16.000  371.500 0.08400000   5 co2   30
##  ---
## 350:     R12  59.150 1002.000 0.06121372 283  ar   20
## 351:     R13  48.320  858.300 0.06754617 283  ar   30
## 352:     R14  49.970  865.400 0.06860158 283  ar   30
## 353:     R15  45.260  837.200 0.06860158 283  ar   30
## 354:     R16 105.800  895.000 0.05910290 283  ar   30
```

```
library(ggplot2)
ggplot(dat, aes(day, ch4, colour = factor(temp), shape = gas, group = reactor, lty = gas)) +
  geom_point() + geom_line()
```

```
## Warning: Removed 6 rows containing missing values (`geom_point()`).
```



2. Ammonia volatilization dynamics

```
amm_int <- fread('../../data/NH3_emis_acid_interval.csv')
amm_int
```

```
##       pmid     ct      cta   dt             t_start               t_end     j_NH3
##    1: 1947   1.73   1.7333 1.73 2020-11-18 13:40:00 2020-11-18 15:24:00 0.0088216
##    2: 1947   3.46   3.4667 1.73 2020-11-18 15:24:00 2020-11-18 17:08:00 0.0000000
##    3: 1947   5.19   5.2000 1.73 2020-11-18 17:08:00 2020-11-18 18:52:00 0.0061700
##    4: 1947   6.92   6.9333 1.73 2020-11-18 18:52:00 2020-11-18 20:36:00 0.0136090
##    5: 1947   8.65   8.6667 1.73 2020-11-18 20:36:00 2020-11-18 22:20:00 0.0154260
##   ---
## 3485: 1982 178.19 178.5300 1.73 2020-12-16 23:49:00 2020-12-17 01:33:00 0.0100490
## 3486: 1982 179.92 180.2700 1.73 2020-12-17 01:33:00 2020-12-17 03:17:00 0.0098460
## 3487: 1982 181.65 182.0000 1.73 2020-12-17 03:17:00 2020-12-17 05:01:00 0.0095709
## 3488: 1982 183.38 183.7300 1.73 2020-12-17 05:01:00 2020-12-17 06:45:00 0.0099536
## 3489: 1982 185.11 185.4700 1.73 2020-12-17 06:45:00 2020-12-17 08:29:00 0.0116350
```

```
amm_plot <- fread('../../data/NH3_emis_acid_plot.csv')
amm_plot
```

```
##     pmid treat   app_date tan_app e_cum_final e_rel_final f
##  1: 1947  tank 2020-11-18   97.30      3.9108    0.040193 1
##  2: 1948  tank 2020-11-18   97.30      4.9536    0.050910 1
##  3: 1949 field 2020-11-18  103.60     13.6860    0.132110 1
##  4: 1950 field 2020-11-18  103.60     12.3270    0.118980 1
##  5: 1951  none 2020-11-18   95.20     20.0020    0.210100 1
```

```
##  6: 1952 field 2020-11-18  103.60     14.6960    0.141860 1
##  7: 1953  none 2020-11-18   95.20     19.9610    0.209670 1
##  8: 1954  tank 2020-11-18   97.30      5.3328    0.054808 1
##  9: 1955  none 2020-11-18   95.20     17.1320    0.179960 1
## 10: 1956  none 2020-11-25   71.75     25.1850    0.351020 2
## 11: 1957 field 2020-11-25   72.45     26.9790    0.372390 2
## 12: 1958  tank 2020-11-25   67.55      1.3104    0.019399 2
## 13: 1959 field 2020-11-25   72.45     20.7570    0.286510 2
## 14: 1960  tank 2020-11-25   67.55      1.8739    0.027741 2
## 15: 1961  none 2020-11-25   71.75     25.3840    0.353780 2
## 16: 1962  tank 2020-11-25   67.55      2.3160    0.034286 2
## 17: 1963 field 2020-11-25   72.45     23.5660    0.325270 2
## 18: 1964  none 2020-11-25   71.75     26.8990    0.374900 2
## 19: 1965  none 2020-02-12  151.20     20.4720    0.135400 3
## 20: 1966  tank 2020-02-12  118.30      3.3581    0.028386 3
## 21: 1967 field 2020-02-12  149.10     17.5260    0.117540 3
## 22: 1968 field 2020-02-12  149.10     17.5560    0.117750 3
## 23: 1969  tank 2020-02-12  118.30      3.1914    0.026977 3
## 24: 1970 field 2020-02-12  149.10     17.2320    0.115580 3
## 25: 1971  none 2020-02-12  151.20     25.9790    0.171820 3
## 26: 1972  tank 2020-02-12  118.30      3.1087    0.026278 3
## 27: 1973  none 2020-02-12  151.20     24.6010    0.162700 3
## 28: 1974  tank 2020-09-12   71.40      8.6166    0.120680 3
## 29: 1975  tank 2020-12-09   71.40      8.8196    0.123520 4
## 30: 1976 field 2020-12-09   65.10     15.6990    0.241150 4
## 31: 1977  none 2020-09-12   66.50     17.2490    0.259380 4
## 32: 1978 field 2020-09-12   65.10     14.6140    0.224490 4
## 33: 1979  none 2020-12-09   66.50     18.9850    0.285480 4
## 34: 1980  tank 2020-12-09   71.40      9.3760    0.131320 4
## 35: 1981 field 2020-12-09   65.10     14.6650    0.225270 4
## 36: 1982  none 2020-12-09   66.50     18.4340    0.277210 4
##     pmid treat   app_date tan_app e_cum_final e_rel_final f
```

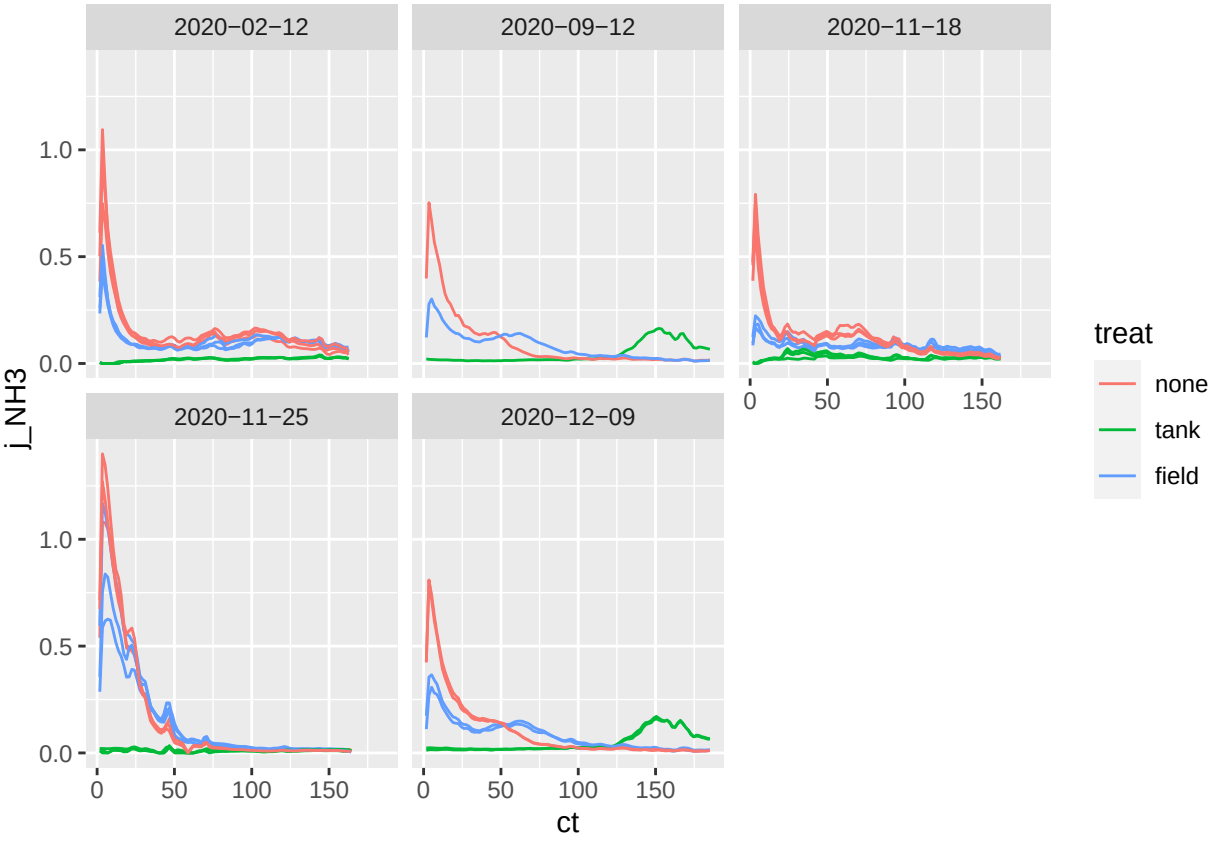
```
amm_plot[, treat := factor(treat, levels = c('none', 'tank', 'field'))]
```

```
amm <- merge(amm_plot, amm_int, by = 'pmid')
amm
```

```
##       pmid treat   app_date tan_app e_cum_final e_rel_final f      ct      cta   dt             t_sta
##    1: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   1.73   1.7333 1.73 2020-11-18 13:40:0
##    2: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   3.46   3.4667 1.73 2020-11-18 15:24:0
##    3: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   5.19   5.2000 1.73 2020-11-18 17:08:0
##    4: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   6.92   6.9333 1.73 2020-11-18 18:52:0
##    5: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   8.65   8.6667 1.73 2020-11-18 20:36:0
##   ---
## 3485: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 178.19 178.5300 1.73 2020-12-16 23:49:0
## 3486: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 179.92 180.2700 1.73 2020-12-17 01:33:0
## 3487: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 181.65 182.0000 1.73 2020-12-17 03:17:0
## 3488: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 183.38 183.7300 1.73 2020-12-17 05:01:0
## 3489: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 185.11 185.4700 1.73 2020-12-17 06:45:0
##                     t_end     j_NH3
##    1: 2020-11-18 15:24:00 0.0088216
##    2: 2020-11-18 17:08:00 0.0000000
##    3: 2020-11-18 18:52:00 0.0061700
##    4: 2020-11-18 20:36:00 0.0136090
```

```
##    5: 2020-11-18 22:20:00 0.0154260
##   ---
## 3485: 2020-12-17 01:33:00 0.0100490
## 3486: 2020-12-17 03:17:00 0.0098460
## 3487: 2020-12-17 05:01:00 0.0095709
## 3488: 2020-12-17 06:45:00 0.0099536
## 3489: 2020-12-17 08:29:00 0.0116350
```

```
library(ggplot2)
ggplot(amm, aes(ct, j_NH3, group = factor(pmid), colour = treat)) +
  geom_line() +
  facet_wrap(~ app_date)
```



Response feature analysis

The basic idea with response feature analysis is to extract or calculate some characteristic or *feature* from the multiple measurements made on an individual experimental unit. This process collapses what might be a large number of measurements to a single value–typically one per experimental unit. These values then become the observations you use in a statistical analysis. For datasets that show simple responses over time, it could be the slope and intercept that are used. The more complex patterns typical in our online measurements might suggest responses like the integrated totals, peak values, time of maxima, or even the simple mean value. Nonlinear regression could be used to extract some rate constant or other model parameter. Ideally the selected response should be one that is relevant and interesting–not just something that facilitates hypothesis testing. Selecting a response after viewing results runs the risk of invalidating any p values or other statistical results. So be careful to avoid too much "fishing". Here is an example with the data we have seen before where our response is integrated total emission.

Integration for response feature analysis

```
library(data.table)
```

```
amm_int <- fread('../../data/NH3_emis_acid_interval.csv')
amm_int
```

```
##       pmid     ct      cta   dt             t_start               t_end     j_NH3
##    1: 1947   1.73   1.7333 1.73 2020-11-18 13:40:00 2020-11-18 15:24:00 0.0088216
##    2: 1947   3.46   3.4667 1.73 2020-11-18 15:24:00 2020-11-18 17:08:00 0.0000000
##    3: 1947   5.19   5.2000 1.73 2020-11-18 17:08:00 2020-11-18 18:52:00 0.0061700
##    4: 1947   6.92   6.9333 1.73 2020-11-18 18:52:00 2020-11-18 20:36:00 0.0136090
##    5: 1947   8.65   8.6667 1.73 2020-11-18 20:36:00 2020-11-18 22:20:00 0.0154260
##   ---
## 3485: 1982 178.19 178.5300 1.73 2020-12-16 23:49:00 2020-12-17 01:33:00 0.0100490
## 3486: 1982 179.92 180.2700 1.73 2020-12-17 01:33:00 2020-12-17 03:17:00 0.0098460
## 3487: 1982 181.65 182.0000 1.73 2020-12-17 03:17:00 2020-12-17 05:01:00 0.0095709
## 3488: 1982 183.38 183.7300 1.73 2020-12-17 05:01:00 2020-12-17 06:45:00 0.0099536
## 3489: 1982 185.11 185.4700 1.73 2020-12-17 06:45:00 2020-12-17 08:29:00 0.0116350
```

```
amm_plot <- fread('../../data/NH3_emis_acid_plot.csv')
amm_plot
```

```
##     pmid treat   app_date tan_app e_cum_final e_rel_final f
##  1: 1947  tank 2020-11-18   97.30      3.9108    0.040193 1
##  2: 1948  tank 2020-11-18   97.30      4.9536    0.050910 1
##  3: 1949 field 2020-11-18  103.60     13.6860    0.132110 1
##  4: 1950 field 2020-11-18  103.60     12.3270    0.118980 1
##  5: 1951  none 2020-11-18   95.20     20.0020    0.210100 1
##  6: 1952 field 2020-11-18  103.60     14.6960    0.141860 1
##  7: 1953  none 2020-11-18   95.20     19.9610    0.209670 1
##  8: 1954  tank 2020-11-18   97.30      5.3328    0.054808 1
##  9: 1955  none 2020-11-18   95.20     17.1320    0.179960 1
## 10: 1956  none 2020-11-25   71.75     25.1850    0.351020 2
## 11: 1957 field 2020-11-25   72.45     26.9790    0.372390 2
## 12: 1958  tank 2020-11-25   67.55      1.3104    0.019399 2
## 13: 1959 field 2020-11-25   72.45     20.7570    0.286510 2
## 14: 1960  tank 2020-11-25   67.55      1.8739    0.027741 2
## 15: 1961  none 2020-11-25   71.75     25.3840    0.353780 2
## 16: 1962  tank 2020-11-25   67.55      2.3160    0.034286 2
## 17: 1963 field 2020-11-25   72.45     23.5660    0.325270 2
## 18: 1964  none 2020-11-25   71.75     26.8990    0.374900 2
## 19: 1965  none 2020-02-12  151.20     20.4720    0.135400 3
## 20: 1966  tank 2020-02-12  118.30      3.3581    0.028386 3
## 21: 1967 field 2020-02-12  149.10     17.5260    0.117540 3
## 22: 1968 field 2020-02-12  149.10     17.5560    0.117750 3
## 23: 1969  tank 2020-02-12  118.30      3.1914    0.026977 3
## 24: 1970 field 2020-02-12  149.10     17.2320    0.115580 3
## 25: 1971  none 2020-02-12  151.20     25.9790    0.171820 3
## 26: 1972  tank 2020-02-12  118.30      3.1087    0.026278 3
## 27: 1973  none 2020-02-12  151.20     24.6010    0.162700 3
## 28: 1974  tank 2020-09-12   71.40      8.6166    0.120680 3
## 29: 1975  tank 2020-12-09   71.40      8.8196    0.123520 4
## 30: 1976 field 2020-12-09   65.10     15.6990    0.241150 4
## 31: 1977  none 2020-09-12   66.50     17.2490    0.259380 4
```

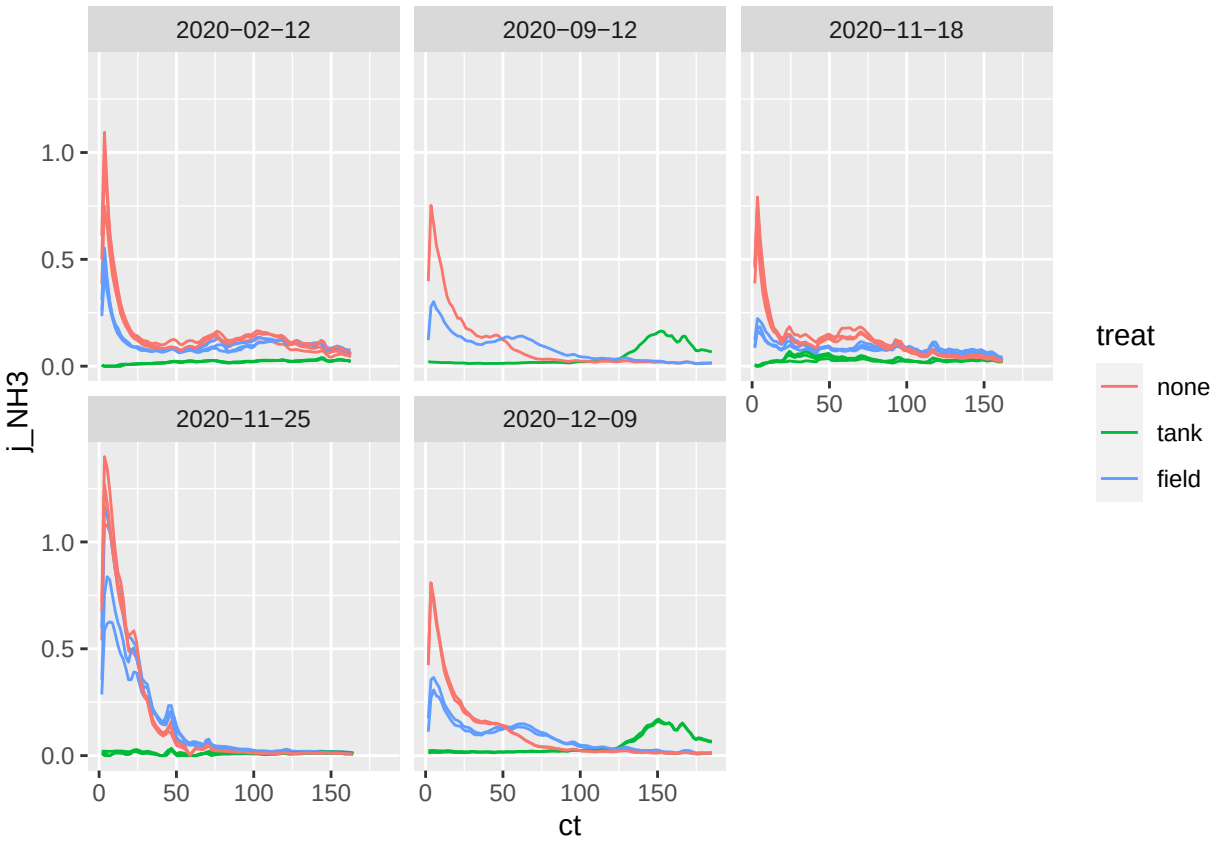
```
## 32: 1978 field 2020-09-12   65.10     14.6140    0.224490 4
## 33: 1979  none 2020-12-09   66.50     18.9850    0.285480 4
## 34: 1980  tank 2020-12-09   71.40      9.3760    0.131320 4
## 35: 1981 field 2020-12-09   65.10     14.6650    0.225270 4
## 36: 1982  none 2020-12-09   66.50     18.4340    0.277210 4
##     pmid treat   app_date tan_app e_cum_final e_rel_final f
```

```
amm_plot[, treat := factor(treat, levels = c('none', 'tank', 'field'))]
amm_plot[, app_date := factor(app_date)]
```

```
amm <- merge(amm_plot, amm_int, by = 'pmid')
amm
```

```
##       pmid treat   app_date tan_app e_cum_final e_rel_final f     ct      cta   dt             t_sta
##    1: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   1.73   1.7333 1.73 2020-11-18 13:40:0
##    2: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   3.46   3.4667 1.73 2020-11-18 15:24:0
##    3: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   5.19   5.2000 1.73 2020-11-18 17:08:0
##    4: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   6.92   6.9333 1.73 2020-11-18 18:52:0
##    5: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   8.65   8.6667 1.73 2020-11-18 20:36:0
##   ---
## 3485: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 178.19 178.5300 1.73 2020-12-16 23:49:0
## 3486: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 179.92 180.2700 1.73 2020-12-17 01:33:0
## 3487: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 181.65 182.0000 1.73 2020-12-17 03:17:0
## 3488: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 183.38 183.7300 1.73 2020-12-17 05:01:0
## 3489: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 185.11 185.4700 1.73 2020-12-17 06:45:0
##                     t_end     j_NH3
##    1: 2020-11-18 15:24:00 0.0088216
##    2: 2020-11-18 17:08:00 0.0000000
##    3: 2020-11-18 18:52:00 0.0061700
##    4: 2020-11-18 20:36:00 0.0136090
##    5: 2020-11-18 22:20:00 0.0154260
##   ---
## 3485: 2020-12-17 01:33:00 0.0100490
## 3486: 2020-12-17 03:17:00 0.0098460
## 3487: 2020-12-17 05:01:00 0.0095709
## 3488: 2020-12-17 06:45:00 0.0099536
## 3489: 2020-12-17 08:29:00 0.0116350
```

```
library(ggplot2)
ggplot(amm, aes(ct, j_NH3, group = factor(pmid), colour = treat)) +
  geom_line() +
  facet_wrap(~ app_date)
```




```
source('../../R-functions/mintegrate.R')
args(mintegrate)
```

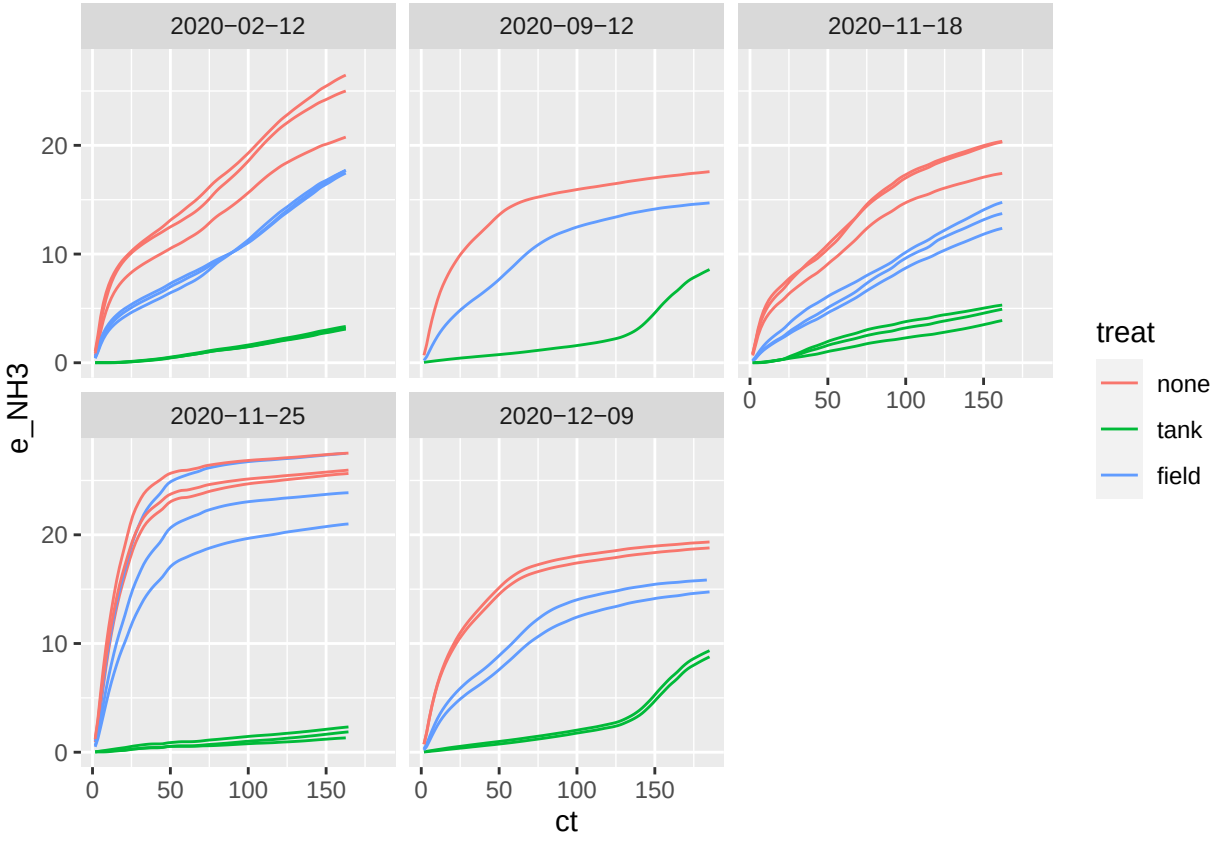
```
## function (x, y, method = "midpoint", lwr = min(x), upr = max(x),
##     ylwr = y[which.min(x)], value = "all")
## NULL
```

```
amm[, e_NH3 := mintegrate(ct, j_NH3, method = 'trap', lwr = 0), by = pmid]
amm
```

```
##       pmid treat   app_date tan_app e_cum_final e_rel_final f     ct      cta   dt             t_sta
##    1: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   1.73   1.7333 1.73 2020-11-18 13:40:0
##    2: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   3.46   3.4667 1.73 2020-11-18 15:24:0
##    3: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   5.19   5.2000 1.73 2020-11-18 17:08:0
##    4: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   6.92   6.9333 1.73 2020-11-18 18:52:0
##    5: 1947  tank 2020-11-18    97.3      3.9108    0.040193 1   8.65   8.6667 1.73 2020-11-18 20:36:0
##   ---
## 3485: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 178.19 178.5300 1.73 2020-12-16 23:49:0
## 3486: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 179.92 180.2700 1.73 2020-12-17 01:33:0
## 3487: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 181.65 182.0000 1.73 2020-12-17 03:17:0
## 3488: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 183.38 183.7300 1.73 2020-12-17 05:01:0
## 3489: 1982  none 2020-12-09    66.5     18.4340    0.277210 4 185.11 185.4700 1.73 2020-12-17 06:45:0
##                       t_end     j_NH3       e_NH3
##    1: 2020-11-18 15:24:00 0.0088216  0.01526137
##    2: 2020-11-18 17:08:00 0.0000000  0.02289205
##    3: 2020-11-18 18:52:00 0.0061700  0.02822910
##    4: 2020-11-18 20:36:00 0.0136090  0.04533794
##    5: 2020-11-18 22:20:00 0.0154260  0.07045321
```

```
##    ---
## 3485: 2020-12-17 01:33:00 0.0100490 18.72535479
## 3486: 2020-12-17 03:17:00 0.0098460 18.74256396
## 3487: 2020-12-17 05:01:00 0.0095709 18.75935958
## 3488: 2020-12-17 06:45:00 0.0099536 18.77624827
## 3489: 2020-12-17 08:29:00 0.0116350 18.79492241
```

```
ggplot(amm, aes(ct, e_NH3, group = factor(pmid), colour = treat)) +
  geom_line() +
  facet_wrap(~ app_date)
```




```
table(amm_plot[, .(app_date, treat)])
```

```
##             treat
## app_date     none tank field
##   2020-02-12    3    3     3
##   2020-09-12    1    1     1
##   2020-11-18    3    3     3
##   2020-11-25    3    3     3
##   2020-12-09    2    2     2
```

```
amm_tot <- amm[, .(e_NH3 = mintegrate(ct, j_NH3, method = 'trap', lwr = 0, value = 'total')), by = pmid]
amm_tot
```

```
##     pmid     e_NH3
##  1: 1947  3.888339
##  2: 1948  4.924019
##  3: 1949 13.726046
##  4: 1950 12.367994
```

```
##  5: 1951 20.369072
##  6: 1952 14.755975
##  7: 1953 20.311890
##  8: 1954  5.307757
##  9: 1955 17.422558
## 10: 1956 25.641761
## 11: 1957 27.487533
## 12: 1958  1.319052
## 13: 1959 20.998197
## 14: 1960  1.872497
## 15: 1961 25.953998
## 16: 1962  2.325047
## 17: 1963 23.870387
## 18: 1964 27.513122
## 19: 1965 20.759140
## 20: 1966  3.342990
## 21: 1967 17.682434
## 22: 1968 17.714323
## 23: 1969  3.174567
## 24: 1970 17.449584
## 25: 1971 26.459916
## 26: 1972  3.093773
## 27: 1973 24.999419
## 28: 1974  8.577115
## 29: 1975  8.772058
## 30: 1976 15.840716
## 31: 1977 17.579123
## 32: 1978 14.707340
## 33: 1979 19.341930
## 34: 1980  9.341222
## 35: 1981 14.748452
## 36: 1982 18.794922
##     pmid     e_NH3
```

```
amm_tot <- merge(amm_tot, amm_plot, by = 'pmid')
amm_tot[, e_NH3_rel := 100 * e_NH3 / tan_app]
amm_tot
```

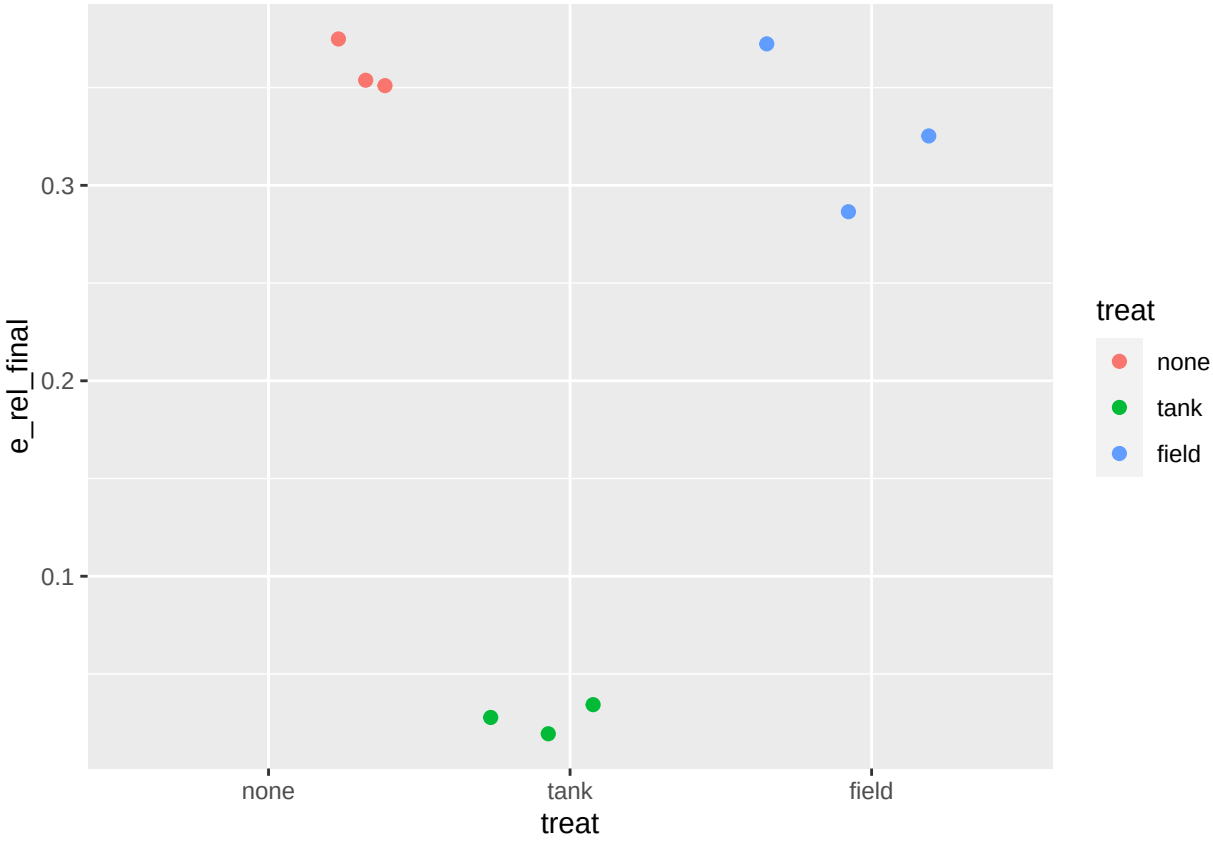
```
##     pmid     e_NH3 treat   app_date tan_app e_cum_final e_rel_final f e_NH3_rel
##  1: 1947  3.888339  tank 2020-11-18   97.30      3.9108    0.040193 1  3.996237
##  2: 1948  4.924019  tank 2020-11-18   97.30      4.9536    0.050910 1  5.060656
##  3: 1949 13.726046 field 2020-11-18  103.60     13.6860    0.132110 1 13.249079
##  4: 1950 12.367994 field 2020-11-18  103.60     12.3270    0.118980 1 11.938218
##  5: 1951 20.369072  none 2020-11-18   95.20     20.0020    0.210100 1 21.396084
##  6: 1952 14.755975 field 2020-11-18  103.60     14.6960    0.141860 1 14.243219
##  7: 1953 20.311890  none 2020-11-18   95.20     19.9610    0.209670 1 21.336018
##  8: 1954  5.307757  tank 2020-11-18   97.30      5.3328    0.054808 1  5.455044
##  9: 1955 17.422558  none 2020-11-18   95.20     17.1320    0.179960 1 18.301007
## 10: 1956 25.641761  none 2020-11-25   71.75     25.1850    0.351020 2 35.737646
## 11: 1957 27.487533 field 2020-11-25   72.45     26.9790    0.372390 2 37.940005
## 12: 1958  1.319052  tank 2020-11-25   67.55      1.3104    0.019399 2  1.952704
## 13: 1959 20.998197 field 2020-11-25   72.45     20.7570    0.286510 2 28.983018
## 14: 1960  1.872497  tank 2020-11-25   67.55      1.8739    0.027741 2  2.772016
## 15: 1961 25.953998  none 2020-11-25   71.75     25.3840    0.353780 2 36.172820
## 16: 1962  2.325047  tank 2020-11-25   67.55      2.3160    0.034286 2  3.441964
```

```
## 17: 1963 23.870387 field 2020-11-25   72.45     23.5660    0.325270 2 32.947393
## 18: 1964 27.513122  none 2020-11-25   71.75     26.8990    0.374900 2 38.345815
## 19: 1965 20.759140  none 2020-02-12  151.20     20.4720    0.135400 3 13.729590
## 20: 1966  3.342990  tank 2020-02-12  118.30      3.3581    0.028386 3  2.825858
## 21: 1967 17.682434 field 2020-02-12  149.10     17.5260    0.117540 3 11.859446
## 22: 1968 17.714323 field 2020-02-12  149.10     17.5560    0.117750 3 11.880834
## 23: 1969  3.174567  tank 2020-02-12  118.30      3.1914    0.026977 3  2.683489
## 24: 1970 17.449584 field 2020-02-12  149.10     17.2320    0.115580 3 11.703276
## 25: 1971 26.459916  none 2020-02-12  151.20     25.9790    0.171820 3 17.499944
## 26: 1972  3.093773  tank 2020-02-12  118.30      3.1087    0.026278 3  2.615193
## 27: 1973 24.999419  none 2020-02-12  151.20     24.6010    0.162700 3 16.534007
## 28: 1974  8.577115  tank 2020-09-12   71.40      8.6166    0.120680 3 12.012766
## 29: 1975  8.772058  tank 2020-12-09   71.40      8.8196    0.123520 4 12.285796
## 30: 1976 15.840716 field 2020-12-09   65.10     15.6990    0.241150 4 24.332897
## 31: 1977 17.579123  none 2020-09-12   66.50     17.2490    0.259380 4 26.434772
## 32: 1978 14.707340 field 2020-09-12   65.10     14.6140    0.224490 4 22.591920
## 33: 1979 19.341930  none 2020-12-09   66.50     18.9850    0.285480 4 29.085609
## 34: 1980  9.341222  tank 2020-12-09   71.40      9.3760    0.131320 4 13.082943
## 35: 1981 14.748452 field 2020-12-09   65.10     14.6650    0.225270 4 22.655071
## 36: 1982 18.794922  none 2020-12-09   66.50     18.4340    0.277210 4 28.263041
##     pmid     e_NH3 treat   app_date tan_app e_cum_final e_rel_final f e_NH3_rel
```

We will use a single field trial, to avoid getting too complicated at the start.

```
amm1 <- amm_tot[app_date == '2020-11-25', ]
```

```
ggplot(amm1, aes(treat, e_rel_final, colour = treat)) +
  geom_jitter(height = 0, size = 2)
```



Classical linear approach

In R, the function `lm()` (for linear model) gives you access to classical linear models.

```
mod0 <- lm(e_rel_final ~ treat, data = amm1)
summary(mod0)
```

```
##
## Call:
## lm(formula = e_rel_final ~ treat, data = amm1)
##
## Residuals:
##       Min        1Q    Median        3Q       Max
## -0.041547 -0.007743 -0.002787  0.007144  0.044333
##
## Coefficients:
##             Estimate Std. Error t value Pr(>|t|)
## (Intercept)  0.35990    0.01519  23.697 3.71e-07 ***
## treattank   -0.33276    0.02148 -15.492 4.58e-06 ***
## treatfield  -0.03184    0.02148  -1.483    0.189
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
##
## Residual standard error: 0.02631 on 6 degrees of freedom
## Multiple R-squared:  0.9799, Adjusted R-squared:  0.9732
## F-statistic: 146.2 on 2 and 6 DF,  p-value: 8.135e-06
```

The `aov()` function really just calls it up and returns output that is handled conveniently when using factors.

```
mod1 <- aov(e_rel_final ~ treat, data = amm1)
summary(mod1)
```

```
##             Df  Sum Sq Mean Sq F value   Pr(>F)
## treat        2 0.20229 0.10115   146.2 8.14e-06 ***
## Residuals    6 0.00415 0.00069
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

```
model.tables(mod1, 'means')
```

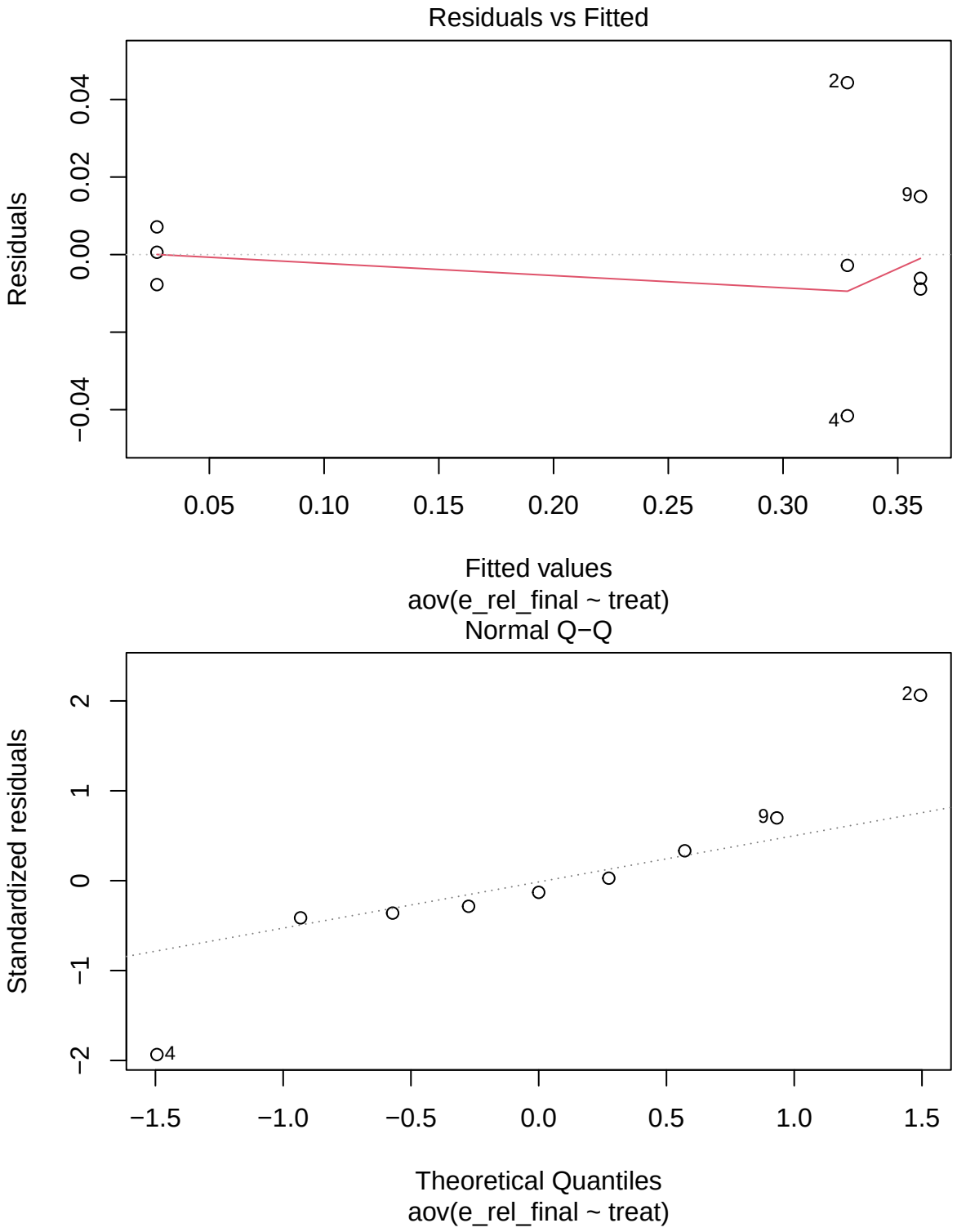
```
## Tables of means
## Grand mean
##
## 0.2383662
##
##  treat
## treat
##   none   tank  field
## 0.3599 0.0271 0.3281
```

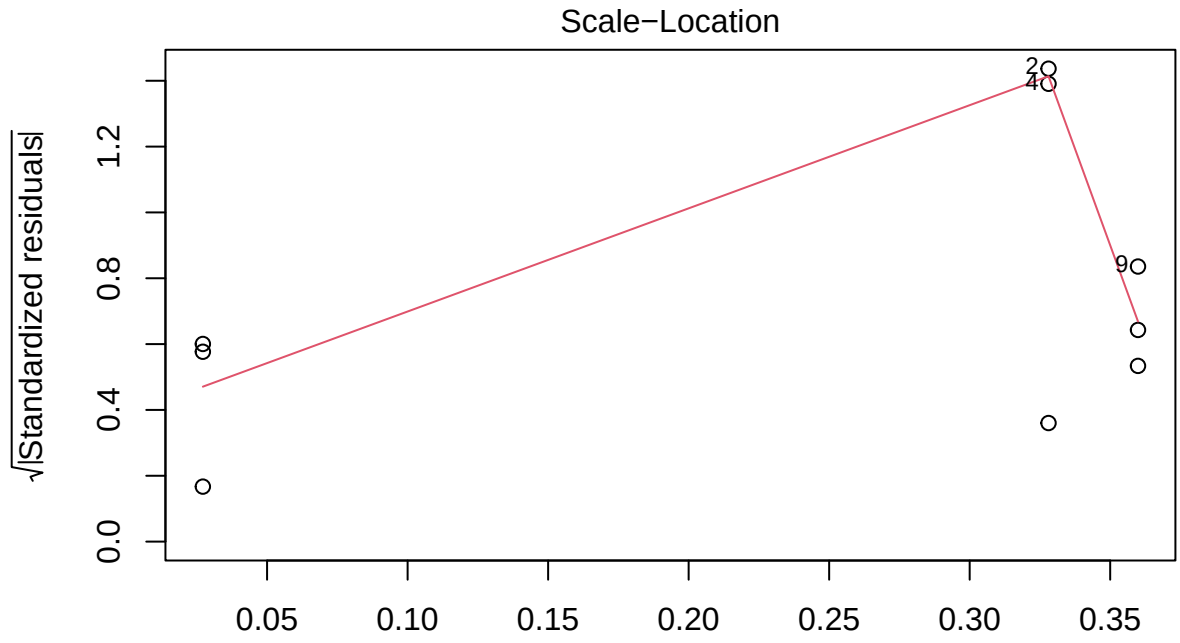
```
TukeyHSD(mod1)
```

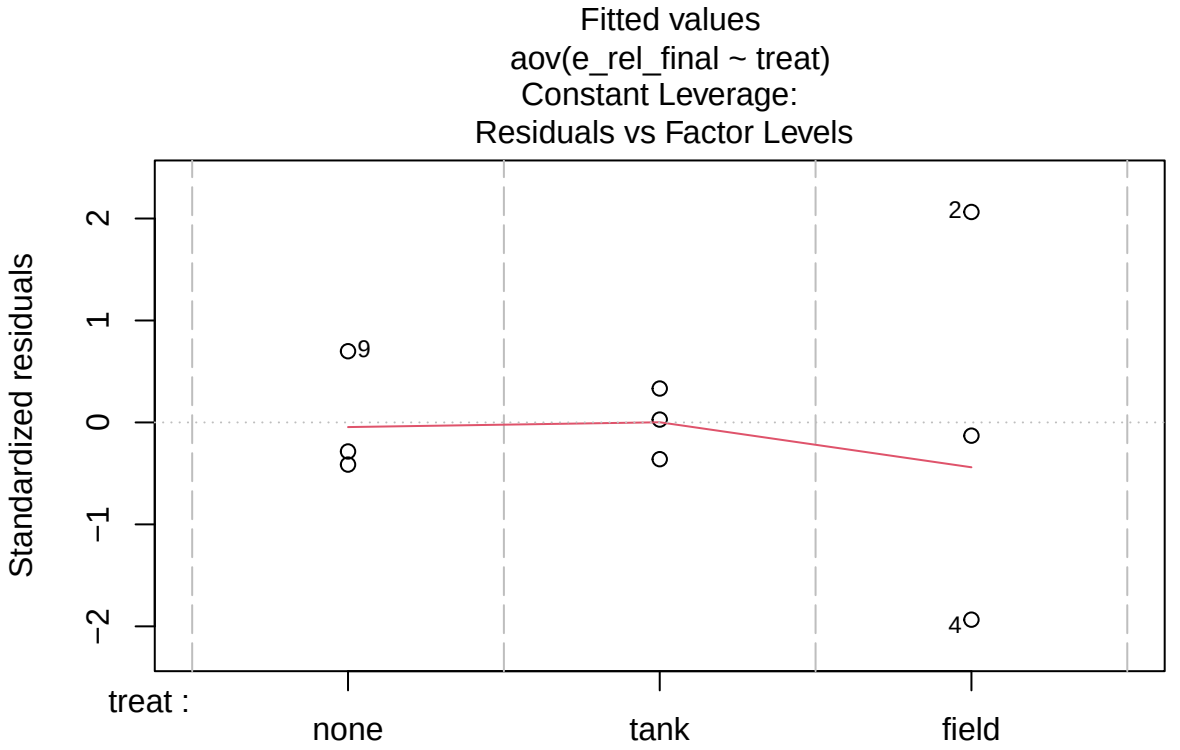
```
##   Tukey multiple comparisons of means
##     95% family-wise confidence level
##
## Fit: aov(formula = e_rel_final ~ treat, data = amm1)
##
## $treat
```

```
##                   diff         lwr         upr     p adj
## tank-none  -0.33275800 -0.39866041 -0.26685559 0.0000109
## field-none -0.03184333 -0.09774574  0.03405908 0.3627117
## field-tank  0.30091467  0.23501226  0.36681708 0.0000201
```

```
plot(mod1, ask = FALSE)
```








```
confint(mod1)
```

```
##                   2.5 %      97.5 %
## (Intercept)  0.32273703  0.39706297
## treattank   -0.38531438 -0.28020162
## treatfield  -0.08439971  0.02071304
```

In Python, we'll use the statsmodels module.

```
import statsmodels.formula.api as smf
```

```
import pandas as pd
```

```
amm_plot = pd.read_csv('../../data/NH3_emis_acid_plot.csv')
amm_plot['e_rel_final'] = 100 * amm_plot['e_rel_final']
amm1 = amm_plot[amm_plot['app_date'] == '2020-11-25' ]
amm1
```

```
##     pmid  treat    app_date  tan_app  e_cum_final  e_rel_final  f
## 9   1956   none  2020-11-25    71.75      25.1850      35.1020  2
## 10  1957  field  2020-11-25    72.45      26.9790      37.2390  2
## 11  1958   tank  2020-11-25    67.55       1.3104       1.9399  2
## 12  1959  field  2020-11-25    72.45      20.7570      28.6510  2
## 13  1960   tank  2020-11-25    67.55       1.8739       2.7741  2
## 14  1961   none  2020-11-25    71.75      25.3840      35.3780  2
## 15  1962   tank  2020-11-25    67.55       2.3160       3.4286  2
## 16  1963  field  2020-11-25    72.45      23.5660      32.5270  2
## 17  1964   none  2020-11-25    71.75      26.8990      37.4900  2
```

And we'll just use the response variable already given in the plot-level file.

```
mod1 = smf.ols('e_rel_final ~ C(treat, Treatment(reference = "none"))', amm1).fit()
mod1.summary()
```

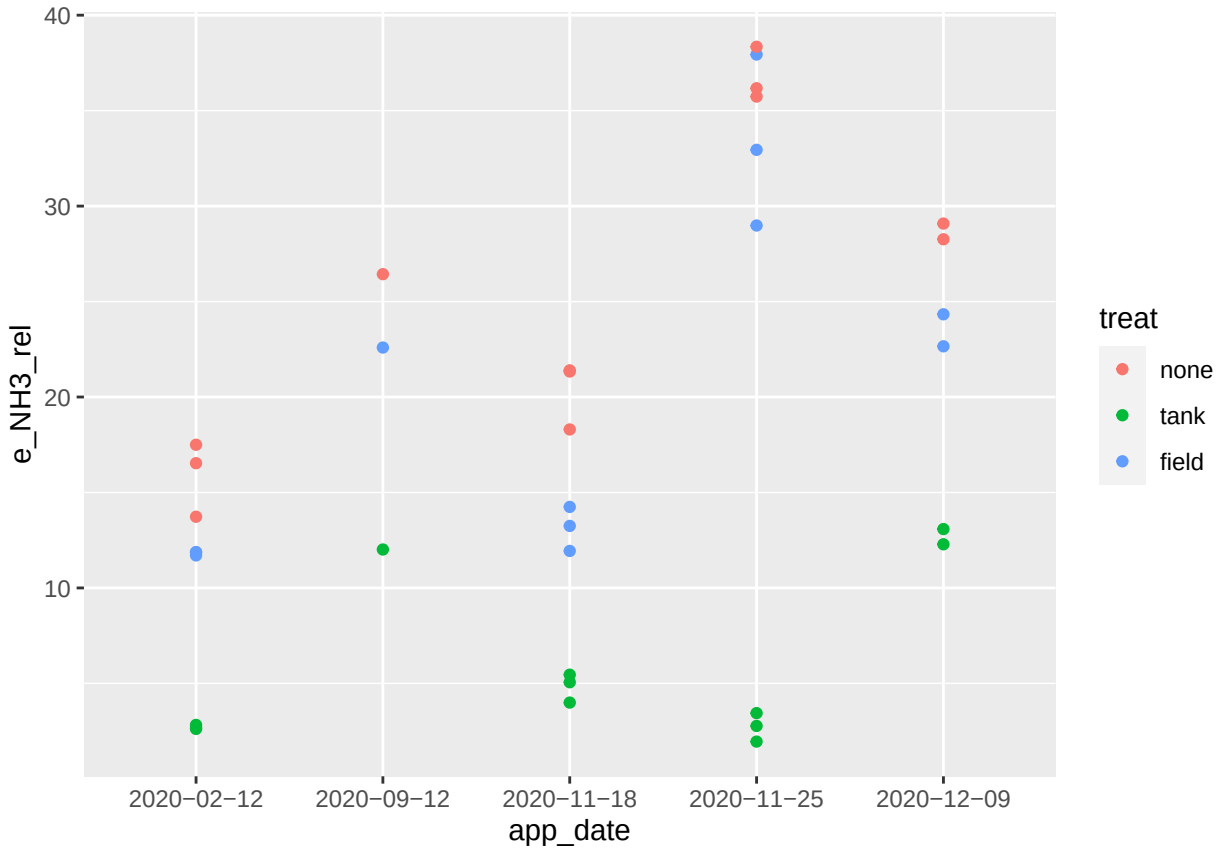
```
## <class 'statsmodels.iolib.summary.Summary'>
## """
##                             OLS Regression Results
## ==============================================================================
## Dep. Variable:            e_rel_final   R-squared:                       0.980
## Model:                            OLS   Adj. R-squared:                  0.973
## Method:                 Least Squares   F-statistic:                     146.2
## Date:                Wed, 28 Feb 2024   Prob (F-statistic):           8.14e-06
## Time:                        17:29:18   Log-Likelihood:                -19.651
## No. Observations:                   9   AIC:                             45.30
## Df Residuals:                       6   BIC:                             45.89
## Df Model:                           2
## Covariance Type:            nonrobust
## ================================================================================================
##                                                  coef    std err          t      P>|t|      [0.0
## ------------------------------------------------------------------------------------------------
## Intercept                                     35.9900      1.519     23.697      0.000      32.2
## C(treat, Treatment(reference="none"))[T.field]   -3.1843      2.148     -1.483      0.189      -8.4
## C(treat, Treatment(reference="none"))[T.tank]   -33.2758      2.148    -15.492      0.000     -38.5
## ==============================================================================
## Omnibus:                        2.408   Durbin-Watson:                   2.191
## Prob(Omnibus):                  0.300   Jarque-Bera (JB):                0.197
## Skew:                           0.199   Prob(JB):                        0.906
## Kurtosis:                       3.606   Cond. No.                         3.73
## ==============================================================================
##
## Notes:
## [1] Standard Errors assume that the covariance matrix of the errors is correctly specified.
## """
##
```

```
## /home/sasha/.local/share/r-miniconda/envs/r-reticulate/lib/python3.6/site-packages/scipy/stats/stats
##   "anyway, n=%i" % int(n))
```

Multiple dates

Can we handle this additional structure?

```
ggplot(amm_tot, aes(app_date, e_NH3_rel, colour = treat)) +
  geom_point()
```




```
amm_tot
```

```
##     pmid     e_NH3 treat   app_date tan_app e_cum_final e_rel_final f e_NH3_rel
##  1: 1947  3.888339  tank 2020-11-18   97.30      3.9108    0.040193 1  3.996237
##  2: 1948  4.924019  tank 2020-11-18   97.30      4.9536    0.050910 1  5.060656
##  3: 1949 13.726046 field 2020-11-18  103.60     13.6860    0.132110 1 13.249079
##  4: 1950 12.367994 field 2020-11-18  103.60     12.3270    0.118980 1 11.938218
##  5: 1951 20.369072  none 2020-11-18   95.20     20.0020    0.210100 1 21.396084
##  6: 1952 14.755975 field 2020-11-18  103.60     14.6960    0.141860 1 14.243219
##  7: 1953 20.311890  none 2020-11-18   95.20     19.9610    0.209670 1 21.336018
##  8: 1954  5.307757  tank 2020-11-18   97.30      5.3328    0.054808 1  5.455044
##  9: 1955 17.422558  none 2020-11-18   95.20     17.1320    0.179960 1 18.301007
## 10: 1956 25.641761  none 2020-11-25   71.75     25.1850    0.351020 2 35.737646
## 11: 1957 27.487533 field 2020-11-25   72.45     26.9790    0.372390 2 37.940005
## 12: 1958  1.319052  tank 2020-11-25   67.55      1.3104    0.019399 2  1.952704
## 13: 1959 20.998197 field 2020-11-25   72.45     20.7570    0.286510 2 28.983018
## 14: 1960  1.872497  tank 2020-11-25   67.55      1.8739    0.027741 2  2.772016
## 15: 1961 25.953998  none 2020-11-25   71.75     25.3840    0.353780 2 36.172820
```

```
## 16: 1962  2.325047  tank 2020-11-25   67.55      2.3160    0.034286 2  3.441964
## 17: 1963 23.870387 field 2020-11-25   72.45     23.5660    0.325270 2 32.947393
## 18: 1964 27.513122  none 2020-11-25   71.75     26.8990    0.374900 2 38.345815
## 19: 1965 20.759140  none 2020-02-12  151.20     20.4720    0.135400 3 13.729590
## 20: 1966  3.342990  tank 2020-02-12  118.30      3.3581    0.028386 3  2.825858
## 21: 1967 17.682434 field 2020-02-12  149.10     17.5260    0.117540 3 11.859446
## 22: 1968 17.714323 field 2020-02-12  149.10     17.5560    0.117750 3 11.880834
## 23: 1969  3.174567  tank 2020-02-12  118.30      3.1914    0.026977 3  2.683489
## 24: 1970 17.449584 field 2020-02-12  149.10     17.2320    0.115580 3 11.703276
## 25: 1971 26.459916  none 2020-02-12  151.20     25.9790    0.171820 3 17.499944
## 26: 1972  3.093773  tank 2020-02-12  118.30      3.1087    0.026278 3  2.615193
## 27: 1973 24.999419  none 2020-02-12  151.20     24.6010    0.162700 3 16.534007
## 28: 1974  8.577115  tank 2020-09-12   71.40      8.6166    0.120680 3 12.012766
## 29: 1975  8.772058  tank 2020-12-09   71.40      8.8196    0.123520 4 12.285796
## 30: 1976 15.840716 field 2020-12-09   65.10     15.6990    0.241150 4 24.332897
## 31: 1977 17.579123  none 2020-09-12   66.50     17.2490    0.259380 4 26.434772
## 32: 1978 14.707340 field 2020-09-12   65.10     14.6140    0.224490 4 22.591920
## 33: 1979 19.341930  none 2020-12-09   66.50     18.9850    0.285480 4 29.085609
## 34: 1980  9.341222  tank 2020-12-09   71.40      9.3760    0.131320 4 13.082943
## 35: 1981 14.748452 field 2020-12-09   65.10     14.6650    0.225270 4 22.655071
## 36: 1982 18.794922  none 2020-12-09   66.50     18.4340    0.277210 4 28.263041
##     pmid     e_NH3 treat   app_date tan_app e_cum_final e_rel_final f e_NH3_rel
```

```
mod2 <- aov(e_NH3_rel ~ treat * app_date, data = amm_tot)
summary(mod2)
```

```
##                Df Sum Sq Mean Sq F value   Pr(>F)
## treat           2 2486.4  1243.2  400.66  < 2e-16 ***
## app_date        4 1218.1   304.5   98.14 2.82e-13 ***
## treat:app_date  8  631.5    78.9   25.44 3.88e-09 ***
## Residuals      21   65.2     3.1
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

```
drop1(mod2, test = 'F')
```

```
## Single term deletions
##
## Model:
## e_NH3_rel ~ treat * app_date
##                Df Sum of Sq    RSS    AIC F value    Pr(>F)
## <none>                      65.16  51.36
## treat:app_date  8    631.51 696.67 120.66   25.44 3.878e-09 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

```
mod3 <- aov(e_rel_final ~ treat + app_date, data = amm_tot)
summary(mod3)
```

```
##             Df  Sum Sq Mean Sq F value   Pr(>F)
## treat        2 0.23732 0.11866   51.34 2.96e-10 ***
## app_date     4 0.11738 0.02935   12.70 4.33e-06 ***
## Residuals   29 0.06702 0.00231
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

```
coef(mod2)
```

```
##                   (Intercept)                     treattank                     treatfield
##                    15.9211805                   -13.2130007                    -4.1066620
##            app_date2020-09-12            app_date2020-11-18            app_date2020-11-25
##                    10.5135915                     4.4231892                    20.8309129
##            app_date2020-12-09  treattank:app_date2020-09-12 treatfield:app_date2020-09-12
##                    12.7531446                    -1.2090051                     0.2638098
##  treattank:app_date2020-11-18 treatfield:app_date2020-11-18  treattank:app_date2020-11-25
##                    -2.2940565                    -3.0942023                   -20.8168644
## treatfield:app_date2020-11-25  treattank:app_date2020-12-09 treatfield:app_date2020-12-09
##                     0.6447074                    -2.7769547                    -1.0736787
```

```
model.tables(mod2, 'means')
```

```
## Tables of means
## Grand mean
##
## 17.09293
##
##  treat
##      none   tank field
##     25.24  5.682 20.36
## rep 12.00 12.000 12.00
##
##  app_date
##     2020-02-12 2020-09-12 2020-11-18 2020-11-25 2020-12-09
##          10.15      20.35      12.78      24.25      21.62
## rep       9.00       3.00       9.00       9.00       6.00
##
##  treat:app_date
##        app_date
## treat   2020-02-12 2020-09-12 2020-11-18 2020-11-25 2020-12-09
##   none  15.92      26.43      20.34      36.75      28.67
##   rep    3.00       1.00       3.00       3.00       2.00
##   tank   2.71      12.01       4.84       2.72      12.68
##   rep    3.00       1.00       3.00       3.00       2.00
##   field 11.81      22.59      13.14      33.29      23.49
##   rep    3.00       1.00       3.00       3.00       2.00
```

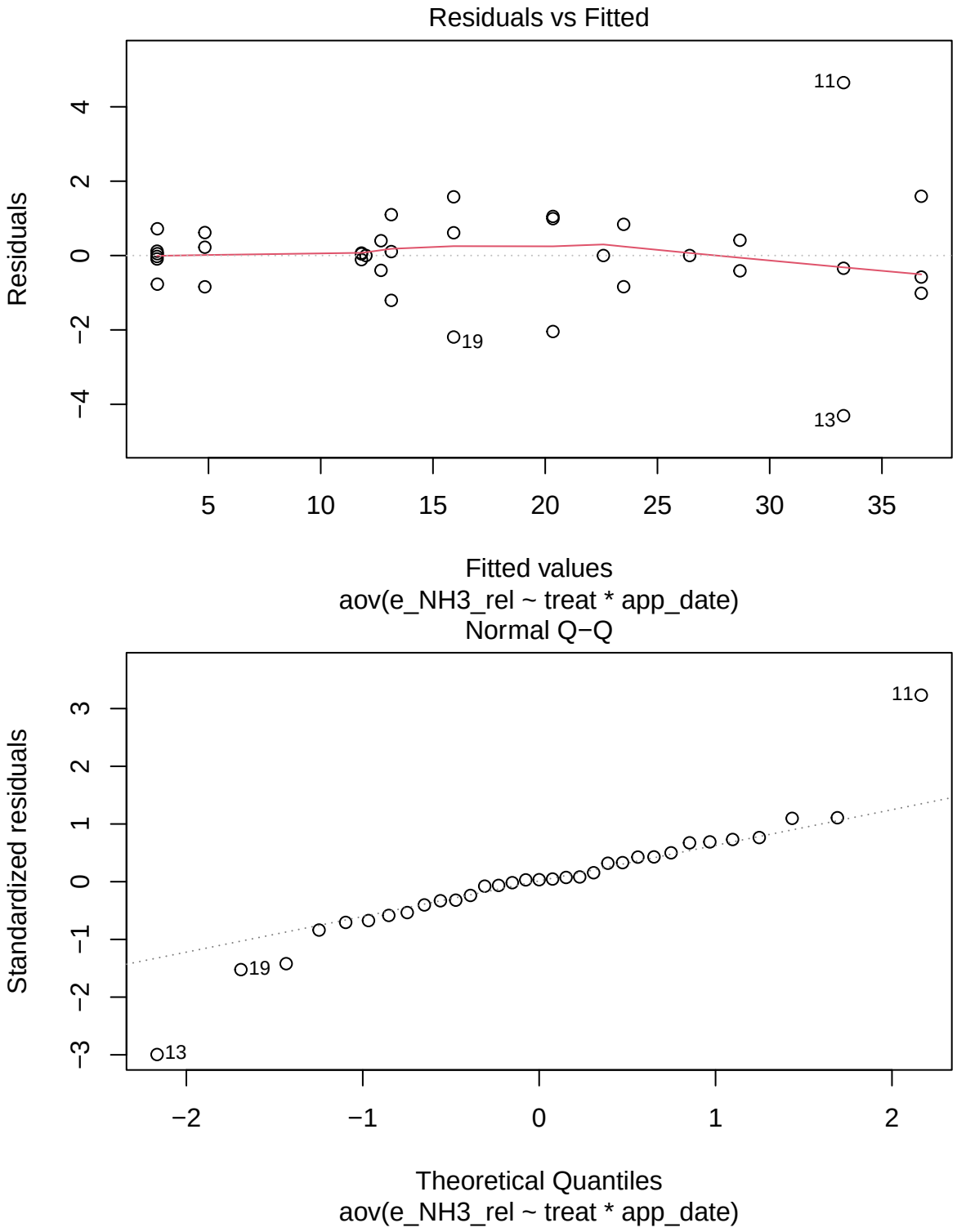
```
TukeyHSD(mod2, 'treat')
```

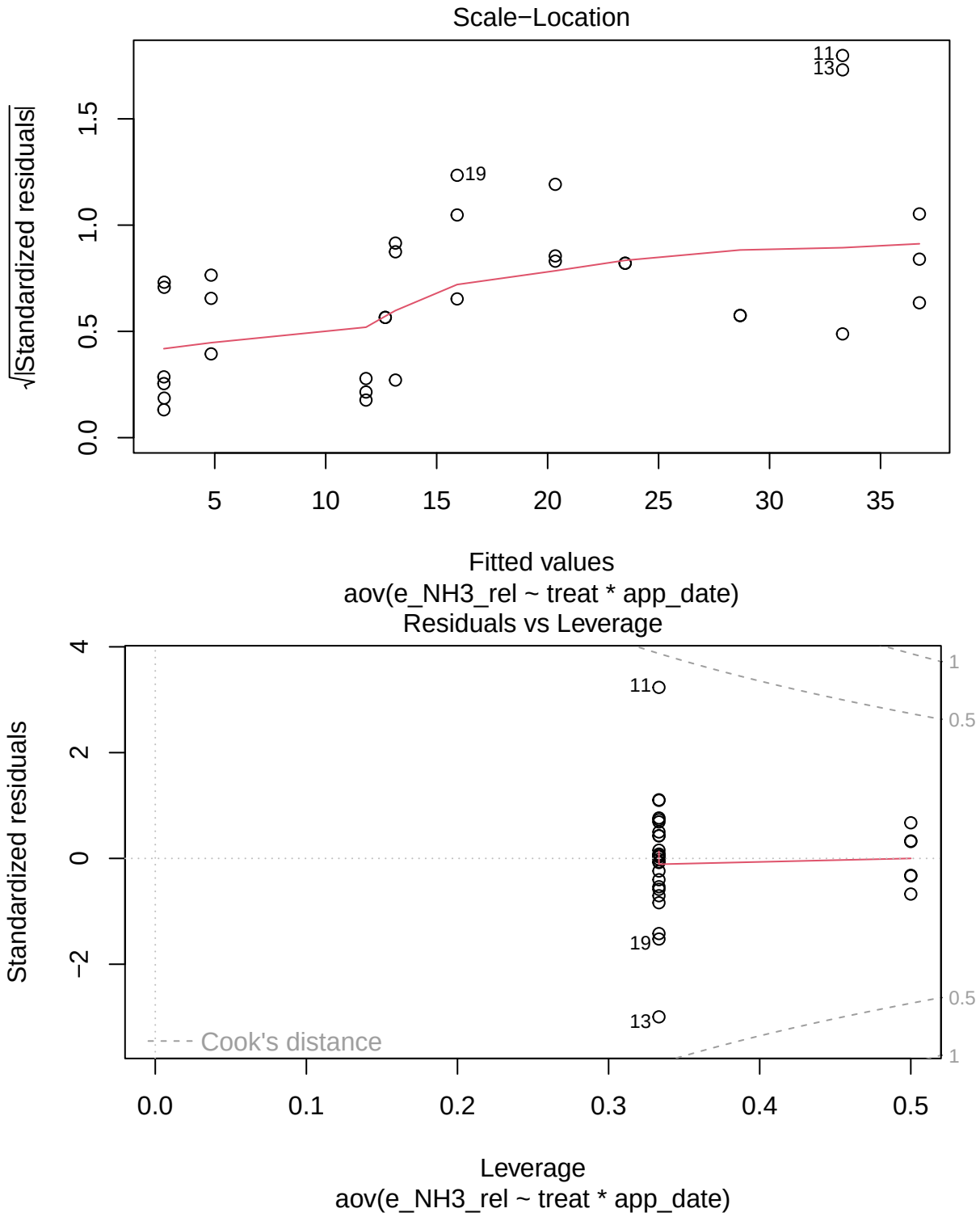
```
##   Tukey multiple comparisons of means
##     95% family-wise confidence level
##
## Fit: aov(formula = e_NH3_rel ~ treat * app_date, data = amm_tot)
##
## $treat
##                  diff        lwr        upr p adj
## tank-none  -19.554307 -21.366927 -17.741687 0e+00
## field-none  -4.875998  -6.688618  -3.063378 3e-06
## field-tank  14.678309  12.865689  16.490929 0e+00
```

```
plot(mod2, ask = FALSE)
```

```
## Warning: not plotting observations with leverage one:
```

```
##   28, 31, 32
```


Residuals vs Fitted
Residuals
Fitted values
aov(e_NH3_rel ~ treat * app_date)
Normal Q−Q
Standardized residuals
Theoretical Quantiles
aov(e_NH3_rel ~ treat * app_date)




```
confint(mod2)
```

```
##                                2.5 %     97.5 %
## (Intercept)                13.806203  18.036157
## treattank                 -16.204030 -10.221971
## treatfield                 -7.097691  -1.115633
## app_date2020-09-12          6.283638  14.743546
```

```
## app_date2020-11-18              1.432160   7.414218
## app_date2020-11-25             17.839884  23.821942
## app_date2020-12-09              9.409072  16.097217
## treattank:app_date2020-09-12   -7.191063   4.773053
## treatfield:app_date2020-09-12  -5.718249   6.245868
## treattank:app_date2020-11-18   -6.524011   1.935898
## treatfield:app_date2020-11-18  -7.324156   1.135752
## treattank:app_date2020-11-25  -25.046818 -16.586910
## treatfield:app_date2020-11-25  -3.585247   4.874661
## treattank:app_date2020-12-09   -7.506187   1.952278
## treatfield:app_date2020-12-09  -5.802911   3.655554
```

In Python. . .

```
amm_tot = amm_plot
amm_tot
```

```
##     pmid  treat    app_date  tan_app  e_cum_final  e_rel_final  f
## 0   1947   tank  2020-11-18    97.30       3.9108       4.0193  1
## 1   1948   tank  2020-11-18    97.30       4.9536       5.0910  1
## 2   1949  field  2020-11-18   103.60      13.6860      13.2110  1
## 3   1950  field  2020-11-18   103.60      12.3270      11.8980  1
## 4   1951   none  2020-11-18    95.20      20.0020      21.0100  1
## 5   1952  field  2020-11-18   103.60      14.6960      14.1860  1
## 6   1953   none  2020-11-18    95.20      19.9610      20.9670  1
## 7   1954   tank  2020-11-18    97.30       5.3328       5.4808  1
## 8   1955   none  2020-11-18    95.20      17.1320      17.9960  1
## 9   1956   none  2020-11-25    71.75      25.1850      35.1020  2
## 10  1957  field  2020-11-25    72.45      26.9790      37.2390  2
## 11  1958   tank  2020-11-25    67.55       1.3104       1.9399  2
## 12  1959  field  2020-11-25    72.45      20.7570      28.6510  2
## 13  1960   tank  2020-11-25    67.55       1.8739       2.7741  2
## 14  1961   none  2020-11-25    71.75      25.3840      35.3780  2
## 15  1962   tank  2020-11-25    67.55       2.3160       3.4286  2
## 16  1963  field  2020-11-25    72.45      23.5660      32.5270  2
## 17  1964   none  2020-11-25    71.75      26.8990      37.4900  2
## 18  1965   none  2020-02-12   151.20      20.4720      13.5400  3
## 19  1966   tank  2020-02-12   118.30       3.3581       2.8386  3
## 20  1967  field  2020-02-12   149.10      17.5260      11.7540  3
## 21  1968  field  2020-02-12   149.10      17.5560      11.7750  3
## 22  1969   tank  2020-02-12   118.30       3.1914       2.6977  3
## 23  1970  field  2020-02-12   149.10      17.2320      11.5580  3
## 24  1971   none  2020-02-12   151.20      25.9790      17.1820  3
## 25  1972   tank  2020-02-12   118.30       3.1087       2.6278  3
## 26  1973   none  2020-02-12   151.20      24.6010      16.2700  3
## 27  1974   tank  2020-09-12    71.40       8.6166      12.0680  3
## 28  1975   tank  2020-12-09    71.40       8.8196      12.3520  4
## 29  1976  field  2020-12-09    65.10      15.6990      24.1150  4
## 30  1977   none  2020-09-12    66.50      17.2490      25.9380  4
## 31  1978  field  2020-09-12    65.10      14.6140      22.4490  4
## 32  1979   none  2020-12-09    66.50      18.9850      28.5480  4
## 33  1980   tank  2020-12-09    71.40       9.3760      13.1320  4
## 34  1981  field  2020-12-09    65.10      14.6650      22.5270  4
## 35  1982   none  2020-12-09    66.50      18.4340      27.7210  4
```

```
mod2 = smf.ols('e_rel_final ~ C(treat, Treatment(reference = "none")) * app_date', amm_tot).fit()
mod2.summary()
```

```
## <class 'statsmodels.iolib.summary.Summary'>
## """
##                             OLS Regression Results
## ==============================================================================
## Dep. Variable:            e_rel_final   R-squared:                       0.986
## Model:                            OLS   Adj. R-squared:                  0.976
## Method:                 Least Squares   F-statistic:                     103.2
## Date:                Wed, 28 Feb 2024   Prob (F-statistic):           4.02e-16
## Time:                        17:29:21   Log-Likelihood:                -60.401
## No. Observations:                  36   AIC:                             150.8
## Df Residuals:                      21   BIC:                             174.6
## Df Model:                          14
## Covariance Type:            nonrobust
## ================================================================================================================
##                                                                    coef    std err
## ----------------------------------------------------------------------------------------------------------------
## Intercept                                                       15.6640      0.979     15.99
## C(treat, Treatment(reference="none"))[T.field]                  -3.9683      1.385     -2.86
## C(treat, Treatment(reference="none"))[T.tank]                  -12.9426      1.385     -9.34
## app_date[T.2020-09-12]                                          10.2740      1.959      5.24
## app_date[T.2020-11-18]                                           4.3270      1.385      3.12
## app_date[T.2020-11-25]                                          20.3260      1.385     14.67
## app_date[T.2020-12-09]                                          12.4705      1.548      8.05
## C(treat, Treatment(reference="none"))[T.field]:app_date[T.2020-09-12]     0.4793      2.770      0.17
## C(treat, Treatment(reference="none"))[T.tank]:app_date[T.2020-09-12]     -0.9274      2.770     -0.33
## C(treat, Treatment(reference="none"))[T.field]:app_date[T.2020-11-18]    -2.9243      1.959     -1.49
## C(treat, Treatment(reference="none"))[T.tank]:app_date[T.2020-11-18]     -2.1847      1.959     -1.11
## C(treat, Treatment(reference="none"))[T.field]:app_date[T.2020-11-25]     0.7840      1.959      0.40
## C(treat, Treatment(reference="none"))[T.tank]:app_date[T.2020-11-25]    -20.3332      1.959    -10.38
## C(treat, Treatment(reference="none"))[T.field]:app_date[T.2020-12-09]    -0.8452      2.190     -0.38
## C(treat, Treatment(reference="none"))[T.tank]:app_date[T.2020-12-09]     -2.4499      2.190     -1.11
## ==============================================================================
## Omnibus:                       10.510   Durbin-Watson:                   2.239
## Prob(Omnibus):                  0.005   Jarque-Bera (JB):               27.663
## Skew:                           0.066   Prob(JB):                     9.84e-07
## Kurtosis:                       7.292   Cond. No.                         20.6
## ==============================================================================
##
## Notes:
## [1] Standard Errors assume that the covariance matrix of the errors is correctly specified.
## """
```

```
mod3 = smf.ols('e_rel_final ~ C(treat, Treatment(reference = "none")) + app_date', amm_tot).fit()
mod3.summary()
```

```
## <class 'statsmodels.iolib.summary.Summary'>
## """
##                             OLS Regression Results
## ==============================================================================
## Dep. Variable:            e_rel_final   R-squared:                       0.841
## Model:                            OLS   Adj. R-squared:                  0.808
```

```
## Method:                 Least Squares   F-statistic:                     25.58
## Date:                Wed, 28 Feb 2024   Prob (F-statistic):           2.42e-10
## Time:                        17:29:21   Log-Likelihood:                -103.72
## No. Observations:                36   AIC:                             221.4
## Df Residuals:                    29   BIC:                             232.5
## Df Model:                         6
## Covariance Type:            nonrobust
## ==============================================================================================
##                                                 coef    std err          t      P>|t|      [0.0
## ----------------------------------------------------------------------------------------------
## Intercept                                    17.9143      1.963      9.128      0.000      13.9
## C(treat, Treatment(reference="none"))[T.field]   -4.6043      1.963     -2.346      0.026      -8.6
## C(treat, Treatment(reference="none"))[T.tank]  -19.0577      1.963     -9.710      0.000     -23.0
## app_date[T.2020-09-12]                       10.1247      3.205      3.159      0.004       3.5
## app_date[T.2020-11-18]                        2.6240      2.266      1.158      0.256      -2.0
## app_date[T.2020-11-25]                       13.8096      2.266      6.094      0.000       9.1
## app_date[T.2020-12-09]                       11.3722      2.534      4.488      0.000       6.1
## ==============================================================================
## Omnibus:                        3.175   Durbin-Watson:                   2.799
## Prob(Omnibus):                  0.204   Jarque-Bera (JB):                1.922
## Skew:                          -0.478   Prob(JB):                        0.383
## Kurtosis:                       3.606   Cond. No.                         6.10
## ==============================================================================
##
## Notes:
## [1] Standard Errors assume that the covariance matrix of the errors is correctly specified.
## """
```

Mixed-effects model

Mixed-effects models can be used for some really powerful stuff, but there is not always a clear advantage in understanding. Here we can use it to handle the data structure in an arguably more appropriate way.

```
library(lme4)
```

```
me1 <- lmer(e_NH3_rel ~ treat * (1|app_date), data = amm_tot)
summary(me1)
```

```
## Linear mixed model fit by REML ['lmerMod']
## Formula: e_NH3_rel ~ treat * (1 | app_date)
##    Data: amm_tot
##
## REML criterion at convergence: 215.3
##
## Scaled residuals:
##      Min       1Q   Median       3Q      Max
## -2.13052 -0.44537 -0.04327  0.68609  2.22431
##
## Random effects:
##  Groups   Name        Variance Std.Dev.
##  app_date (Intercept) 34.54    5.877
##  Residual             23.94    4.893
## Number of obs: 36, groups:  app_date, 5
##
## Fixed effects:
```

```
##             Estimate Std. Error t value
## (Intercept)   25.880      3.002   8.619
## treattank    -19.554      1.998  -9.789
## treatfield    -4.876      1.998  -2.441
##
## Correlation of Fixed Effects:
##            (Intr) trttnk
## treattank  -0.333
## treatfield -0.333  0.500
```

```
me2 <- lmer(e_NH3_rel ~ treat + (treat|app_date), data = amm_tot)
summary(me2)
```

```
## Linear mixed model fit by REML ['lmerMod']
## Formula: e_NH3_rel ~ treat + (treat | app_date)
##    Data: amm_tot
##
## REML criterion at convergence: 166.9
##
## Scaled residuals:
##      Min       1Q   Median       3Q      Max
## -2.44089 -0.42677 -0.00649  0.37310  2.76882
##
## Random effects:
##  Groups   Name        Variance Std.Dev. Corr
##  app_date (Intercept) 63.5789  7.9736
##           treattank   72.2202  8.4982   -0.83
##           treatfield   0.6801  0.8247    0.86 -1.00
##  Residual              2.9559  1.7193
## Number of obs: 36, groups:  app_date, 5
##
## Fixed effects:
##             Estimate Std. Error t value
## (Intercept)  25.7178     3.6034   7.137
## treattank   -18.8330     3.8728  -4.863
## treatfield   -4.9371     0.7932  -6.224
##
## Correlation of Fixed Effects:
##            (Intr) trttnk
## treattank  -0.829
## treatfield  0.309 -0.378
```

```
anova(me2, me1, test = 'Chisquare')
```

```
## refitting model(s) with ML (instead of REML)
```

```
## Data: amm_tot
## Models:
## me1: e_NH3_rel ~ treat * (1 | app_date)
## me2: e_NH3_rel ~ treat + (treat | app_date)
##     npar    AIC    BIC   logLik deviance  Chisq Df Pr(>Chisq)
## me1    5 235.16 243.08 -112.580   225.16
## me2   10 195.64 211.48  -87.822   175.64 49.517  5   1.74e-09 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

```
AIC(me2, me1)
```

```
##     df      AIC
## me2 10 186.8874
## me1  5 225.3088
```

```
coef(me1)
```

```
## $app_date
##            (Intercept) treattank treatfield
## 2020-02-12    18.83412 -19.55431  -4.875998
## 2020-09-12    27.99994 -19.55431  -4.875998
## 2020-11-18    21.27333 -19.55431  -4.875998
## 2020-11-25    31.93203 -19.55431  -4.875998
## 2020-12-09    29.35897 -19.55431  -4.875998
##
## attr(,"class")
## [1] "coef.mer"
```

```
coef(me2)
```

```
## $app_date
##            (Intercept) treattank treatfield
## 2020-02-12    16.68873 -13.89552  -5.459408
## 2020-09-12    27.14535 -15.77183  -5.201567
## 2020-11-18    19.43713 -14.46361  -5.384870
## 2020-11-25    36.67792 -33.73477  -3.498317
## 2020-12-09    28.63982 -16.29907  -5.141313
##
## attr(,"class")
## [1] "coef.mer"
```

```
coef(mod3)
```

```
##        (Intercept)          treattank         treatfield app_date2020-09-12 app_date2020-11-18
##         0.17914350        -0.19057683        -0.04604333         0.10124656         0.02624000
## app_date2020-11-25 app_date2020-12-09
##         0.13809611         0.11372156
```

```
coef(mod2)
```

```
##                   (Intercept)                     treattank                     treatfield
##                    15.9211805                   -13.2130007                    -4.1066620
##            app_date2020-09-12            app_date2020-11-18            app_date2020-11-25
##                    10.5135915                     4.4231892                    20.8309129
##            app_date2020-12-09  treattank:app_date2020-09-12 treatfield:app_date2020-09-12
##                    12.7531446                    -1.2090051                     0.2638098
##  treattank:app_date2020-11-18 treatfield:app_date2020-11-18  treattank:app_date2020-11-25
##                    -2.2940565                    -3.0942023                   -20.8168644
## treatfield:app_date2020-11-25  treattank:app_date2020-12-09 treatfield:app_date2020-12-09
##                     0.6447074                    -2.7769547                    -1.0736787
```

```
coef(me1)
```

```
## $app_date
##            (Intercept) treattank treatfield
## 2020-02-12    18.83412 -19.55431  -4.875998
## 2020-09-12    27.99994 -19.55431  -4.875998
```

```
## 2020-11-18    21.27333 -19.55431  -4.875998
## 2020-11-25    31.93203 -19.55431  -4.875998
## 2020-12-09    29.35897 -19.55431  -4.875998
##
## attr(,"class")
## [1] "coef.mer"
```

```
confint(me1, parm = c('treattank', 'treatfield'))
```

```
## Computing profile confidence intervals ...
```

```
##                 2.5 %      97.5 %
## treattank  -23.458561 -15.6500534
## treatfield  -8.780252  -0.9717443
```

```
coef(me2)
```

```
## $app_date
##            (Intercept) treattank treatfield
## 2020-02-12    16.68873 -13.89552  -5.459408
## 2020-09-12    27.14535 -15.77183  -5.201567
## 2020-11-18    19.43713 -14.46361  -5.384870
## 2020-11-25    36.67792 -33.73477  -3.498317
## 2020-12-09    28.63982 -16.29907  -5.141313
##
## attr(,"class")
## [1] "coef.mer"
```

```
confint(me2, parm = c('treattank', 'treatfield'))
```

```
## Computing profile confidence intervals ...
```

```
##                 2.5 %     97.5 %
## treattank  -27.142153 -10.497048
## treatfield  -6.740874  -3.245494
```

In Python, categorical variables are trickier to handle.

```
amm_tot
```

```
##     pmid  treat    app_date  tan_app  e_cum_final  e_rel_final  f
## 0   1947   tank  2020-11-18    97.30       3.9108       4.0193  1
## 1   1948   tank  2020-11-18    97.30       4.9536       5.0910  1
## 2   1949  field  2020-11-18   103.60      13.6860      13.2110  1
## 3   1950  field  2020-11-18   103.60      12.3270      11.8980  1
## 4   1951   none  2020-11-18    95.20      20.0020      21.0100  1
## 5   1952  field  2020-11-18   103.60      14.6960      14.1860  1
## 6   1953   none  2020-11-18    95.20      19.9610      20.9670  1
## 7   1954   tank  2020-11-18    97.30       5.3328       5.4808  1
## 8   1955   none  2020-11-18    95.20      17.1320      17.9960  1
## 9   1956   none  2020-11-25    71.75      25.1850      35.1020  2
## 10  1957  field  2020-11-25    72.45      26.9790      37.2390  2
## 11  1958   tank  2020-11-25    67.55       1.3104       1.9399  2
## 12  1959  field  2020-11-25    72.45      20.7570      28.6510  2
## 13  1960   tank  2020-11-25    67.55       1.8739       2.7741  2
## 14  1961   none  2020-11-25    71.75      25.3840      35.3780  2
## 15  1962   tank  2020-11-25    67.55       2.3160       3.4286  2
## 16  1963  field  2020-11-25    72.45      23.5660      32.5270  2
## 17  1964   none  2020-11-25    71.75      26.8990      37.4900  2
```

```
## 18  1965   none  2020-02-12   151.20      20.4720      13.5400  3
## 19  1966   tank  2020-02-12   118.30       3.3581       2.8386  3
## 20  1967  field  2020-02-12   149.10      17.5260      11.7540  3
## 21  1968  field  2020-02-12   149.10      17.5560      11.7750  3
## 22  1969   tank  2020-02-12   118.30       3.1914       2.6977  3
## 23  1970  field  2020-02-12   149.10      17.2320      11.5580  3
## 24  1971   none  2020-02-12   151.20      25.9790      17.1820  3
## 25  1972   tank  2020-02-12   118.30       3.1087       2.6278  3
## 26  1973   none  2020-02-12   151.20      24.6010      16.2700  3
## 27  1974   tank  2020-09-12    71.40       8.6166      12.0680  3
## 28  1975   tank  2020-12-09    71.40       8.8196      12.3520  4
## 29  1976  field  2020-12-09    65.10      15.6990      24.1150  4
## 30  1977   none  2020-09-12    66.50      17.2490      25.9380  4
## 31  1978  field  2020-09-12    65.10      14.6140      22.4490  4
## 32  1979   none  2020-12-09    66.50      18.9850      28.5480  4
## 33  1980   tank  2020-12-09    71.40       9.3760      13.1320  4
## 34  1981  field  2020-12-09    65.10      14.6650      22.5270  4
## 35  1982   none  2020-12-09    66.50      18.4340      27.7210  4
```

```
me1 = smf.mixedlm('e_rel_final ~ C(treat, Treatment(reference = "none")) + (1|f)', amm_tot, groups = am
```

```
## /home/sasha/.local/share/r-miniconda/envs/r-reticulate/lib/python3.6/site-packages/statsmodels/regres
##   warnings.warn(msg, ConvergenceWarning)
```

```
me1.summary()
```

```
## <class 'statsmodels.iolib.summary2.Summary'>
## """
##                           Mixed Linear Model Regression Results
## ============================================================================================
## Model:                          MixedLM           Dependent Variable:           e_rel_final
## No. Observations:               36                Method:                       REML
## No. Groups:                     36                Scale:                        24.4632
## Min. group size:                1                 Log-Likelihood:               -113.4857
## Max. group size:                1                 Converged:                    Yes
## Mean group size:                1.0
## --------------------------------------------------------------------------------------------
##                                                 Coef.  Std.Err.   z    P>|z|  [0.025  0.975]
## --------------------------------------------------------------------------------------------
## Intercept                                       18.677    2.252  8.293 0.000  14.263  23.091
## C(treat, Treatment(reference="none"))[T.field]  -4.604    2.855 -1.612 0.107 -10.201   0.992
## C(treat, Treatment(reference="none"))[T.tank]  -18.720    2.844 -6.583 0.000 -24.293 -13.146
## 1 | f                                           2.028    0.158 12.801 0.000   1.718   2.339
## Group Var                                      24.463
## ============================================================================================
##
## """
```

Including variation in treatment effects among dates is also tricky.

```
#me2 = smf.mixedlm('e_rel_final ~ C(treat, Treatment(reference = "none")) + (1|f) + (C(treat)|f)', amm_
#print(me1.summary())
```

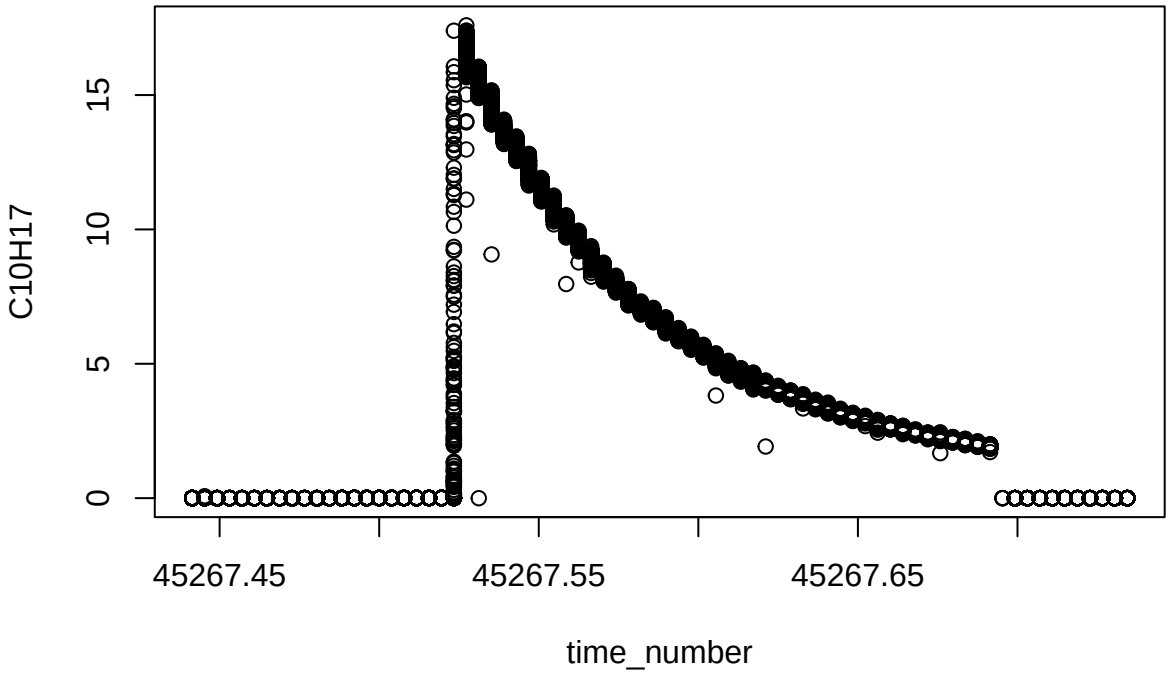
3. Nonlinear regression

Here we will use nonlinear regression to extract a rate constant from reaction chamber measurements.

```
ox <- fread('../../data/VOC_reaction.csv', skip = 2)
ox
```

```
##             time_string time_number     C1H3O2     C3H7O1     C2H5O2    C7H11O2       C10H17   C9H15O
##     1: 12/7/2023 10:34    45267.44 0.26983000 0.23759000 0.19983000 0.00494390 4.641300e-03 0.032477
##     2: 12/7/2023 10:34    45267.44 0.26303000 0.25205000 0.18137000 0.00074215 1.215800e-03 0.035656
##     3: 12/7/2023 10:34    45267.44 0.27097000 0.22796000 0.19361000 0.00399780 2.126600e-03 0.038066
##     4: 12/7/2023 10:34    45267.44 0.24479000 0.19712000 0.17835000 0.00546340 2.674500e-03 0.038752
##     5: 12/7/2023 10:34    45267.44 0.28258000 0.23840000 0.18143000 0.00438240 5.596100e-03 0.036147
##    ---
## 12733: 12/7/2023 17:38    45267.73 0.03405808 0.02747731 0.01098923 0.01535654 1.477731e-03 0.128273
## 12734: 12/7/2023 17:38    45267.73 0.03853077 0.02504192 0.01067731 0.01657769 6.119231e-04 0.130203
## 12735: 12/7/2023 17:38    45267.73 0.03404269 0.02224269 0.01141692 0.01477038 1.053115e-03 0.129607
## 12736: 12/7/2023 17:38    45267.73 0.03497692 0.02501538 0.01088462 0.01620885 8.473462e-04 0.128519
## 12737: 12/7/2023 17:38    45267.73 0.03452077 0.02439692 0.01039846 0.01530308 1.123654e-05 0.126469
##             C8H15O2   C9H15O2     C8H13O3     C9H15O3      C8H13O4      C9H15O4      C10H17O4
##     1:  0.002224600 0.0176530 0.001572400 0.00074916 -0.000329700  0.000333540  0.0010117000
##     2:  0.000274880 0.0176100 0.000050600 0.00132800  0.000026400  0.000302220 -0.0008735800
##     3: -0.000169370 0.0198280 0.001165100 0.00235960  0.000372220  0.000087300 -0.0004013000
##     4:  0.001921300 0.0244110 0.002060000 0.00228380 -0.000260980 -0.000734150  0.0007662200
##     5: -0.000215880 0.0164620 0.001499500 0.00194660 -0.000741000  0.000602880  0.0007395400
##    ---
## 12733:  0.002591538 0.1057462 0.004469231 0.01511654  0.001797462  0.001629615  0.0013644231
## 12734:  0.002445654 0.1070077 0.004283846 0.01568962  0.002281692  0.001849769  0.0009983462
## 12735:  0.002466885 0.1051923 0.003843115 0.01483231  0.001946538  0.001774385  0.0013291923
## 12736:  0.002529231 0.1074577 0.003875000 0.01596577  0.002222885  0.001807192  0.0008379615
## 12737:  0.002807692 0.1037269 0.003662269 0.01484231  0.001943769  0.002313885  0.0008159615
```

```
plot(C10H17 ~ time_number, data = ox)
```



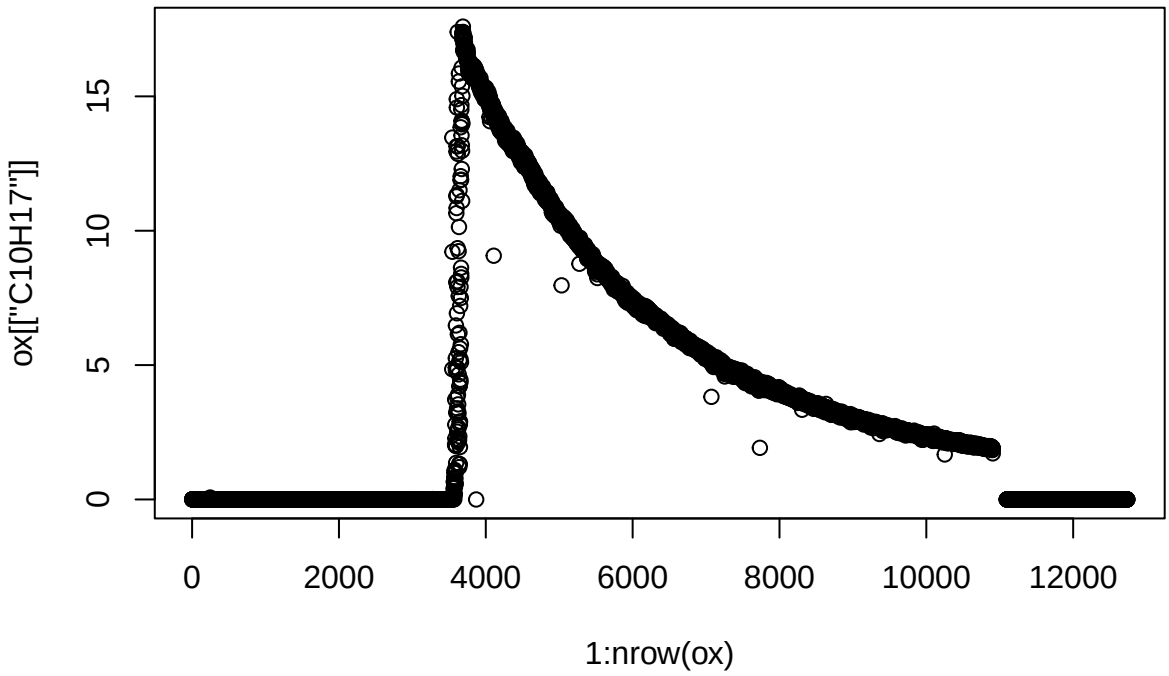

```
head(order(-ox[, C10H17]))
```

```
## [1] 3688 3689 3617 3690 3683 3692
```

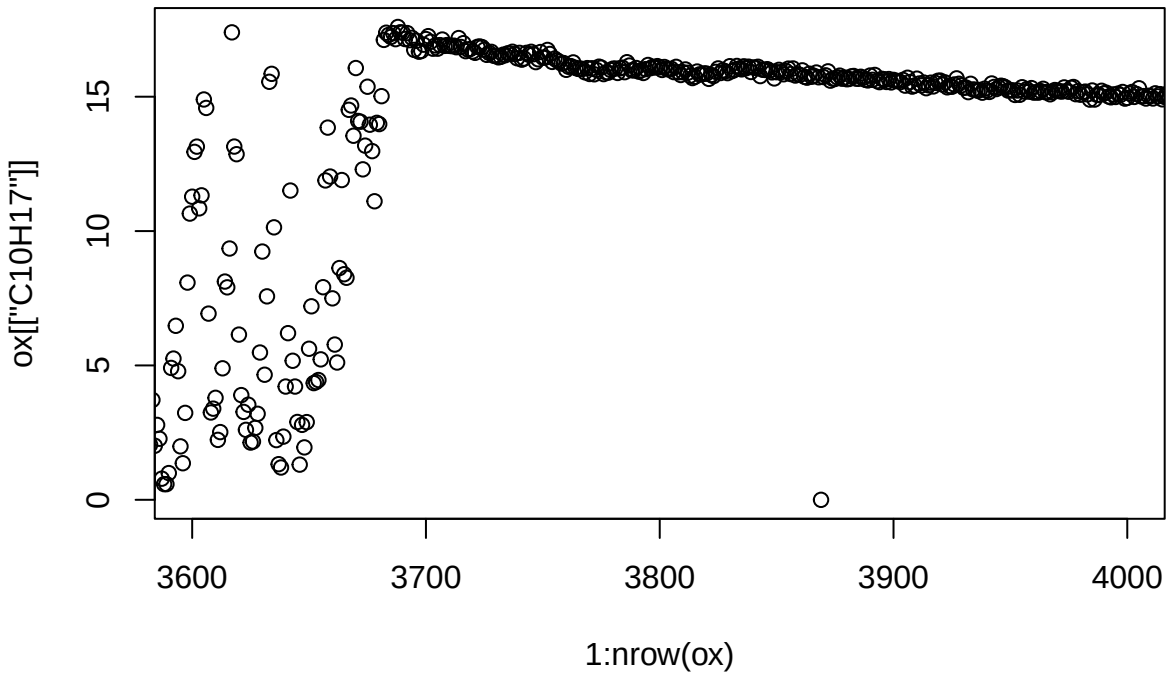
```
ox[3688, time_number]
```

```
## [1] 45267.53
```

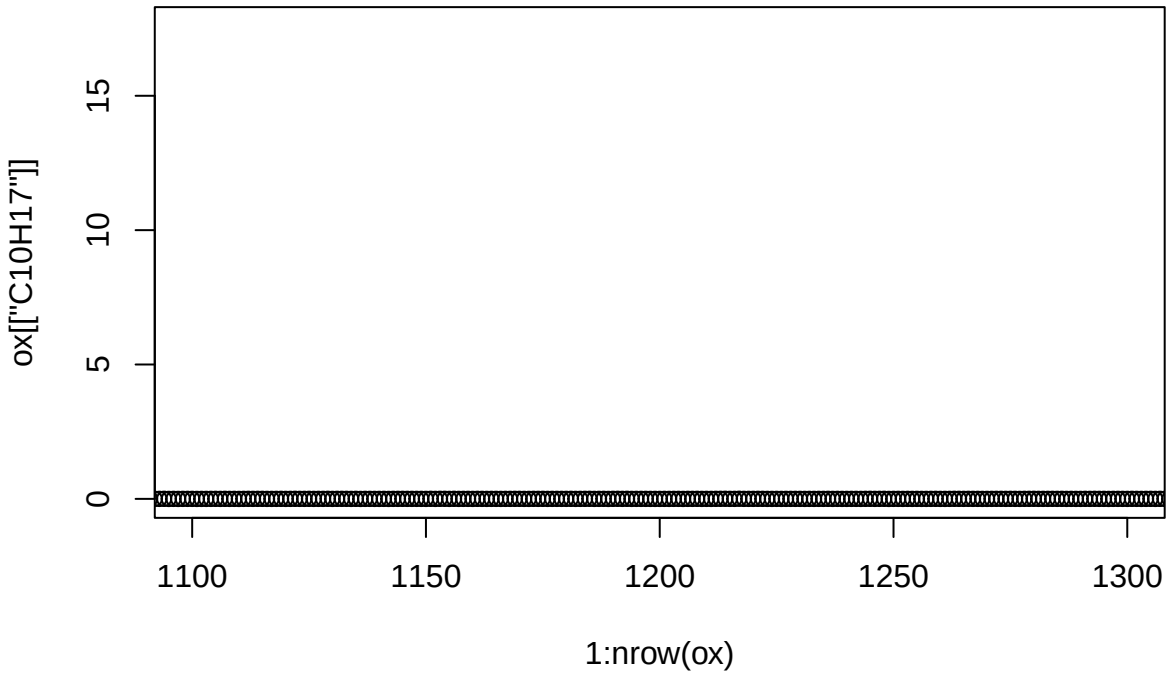
```
plot(1:nrow(ox), ox[['C10H17']])
```



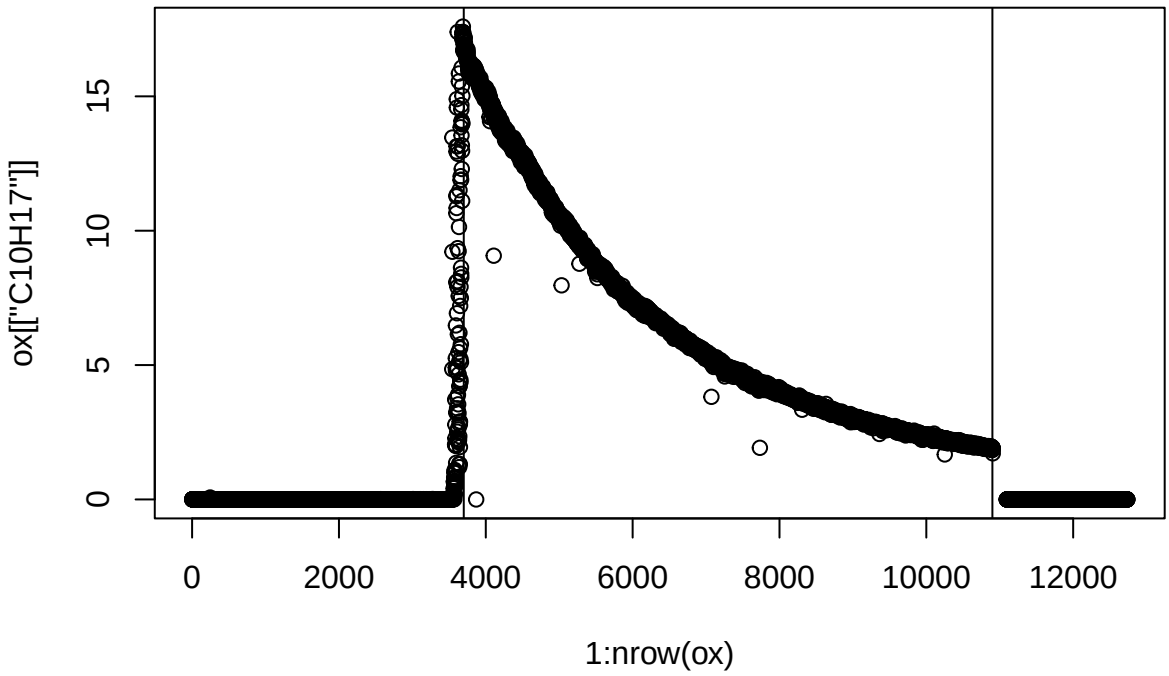

```
plot(1:nrow(ox), ox[['C10H17']], xlim = c(3600, 4000))
```



```
plot(1:nrow(ox), ox[['C10H17']], xlim = c(1100, 1300))
```

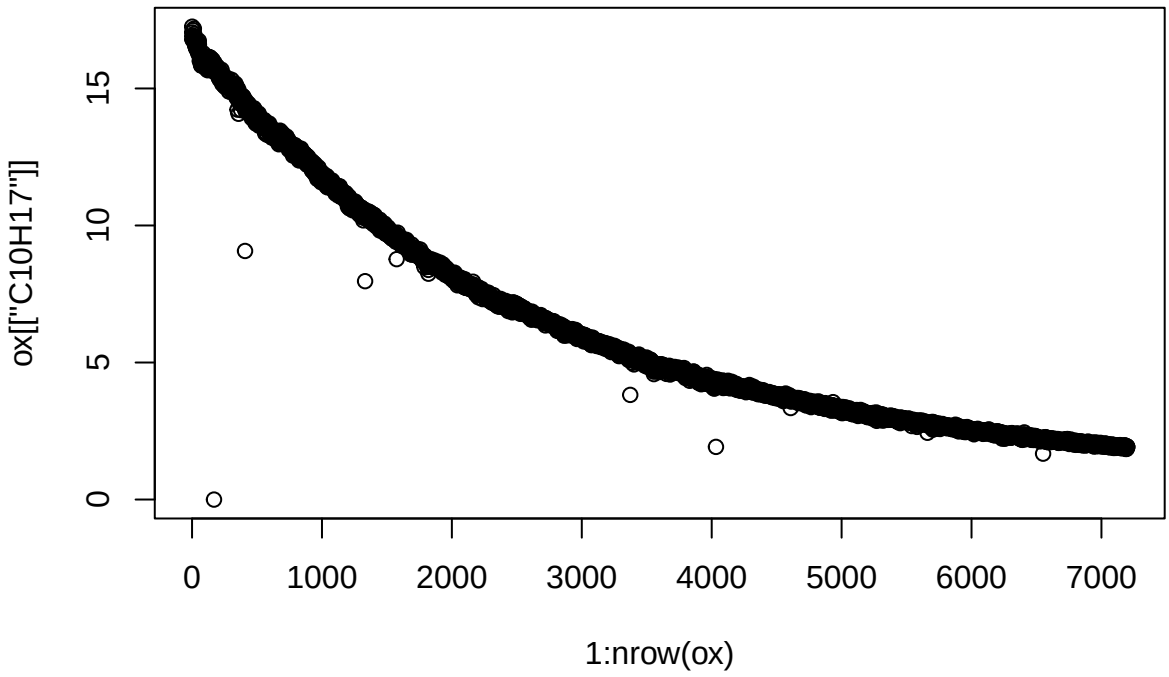



```
plot(1:nrow(ox), ox[['C10H17']])
abline(v = 3700)
abline(v = 10900)
```




```
ox <- ox[c(-1:-3700, -10900:-nrow(ox)), ]
```

```
plot(1:nrow(ox), ox[['C10H17']])
```




```
ox[, tsec := 1:nrow(ox)]
ox
```

```
##           time_string time_number  C1H3O2  C3H7O1  C2H5O2  C7H11O2  C10H17 C9H15O1   C8H15O2 C9H15O2
##    1: 12/7/2023 12:37    45267.53 0.48431 0.67633 0.27782 0.014327 17.2541 0.58644 0.0068041 0.15859
##    2: 12/7/2023 12:37    45267.53 0.53386 0.64853 0.27303 0.015742 17.0439 0.64274 0.0075032 0.14346
##    3: 12/7/2023 12:37    45267.53 0.49192 0.65911 0.26383 0.014787 16.7865 0.60899 0.0085258 0.16083
##    4: 12/7/2023 12:37    45267.53 0.51608 0.61097 0.27346 0.014162 16.9080 0.62952 0.0058579 0.14947
##    5: 12/7/2023 12:37    45267.53 0.53738 0.66043 0.26720 0.012270 16.7876 0.62864 0.0015246 0.15648
##   ---
## 7195: 12/7/2023 16:37    45267.69 1.32770 3.08730 0.57081 0.132810  1.9442 6.02930 0.0122850 1.80000
## 7196: 12/7/2023 16:37    45267.69 1.28920 2.99580 0.59899 0.117230  1.9277 6.01140 0.0145900 1.82750
## 7197: 12/7/2023 16:37    45267.69 1.25940 3.12300 0.56485 0.136080  1.9304 6.00870 0.0220580 1.81800
## 7198: 12/7/2023 16:37    45267.69 1.29540 3.07490 0.54210 0.122420  1.9194 5.98660 0.0193720 1.85040
## 7199: 12/7/2023 16:37    45267.69 1.33740 3.08580 0.56955 0.113580  1.9119 5.98520 0.0157170 1.83640
##         C8H13O3   C9H15O3     C8H13O4     C9H15O4    C10H17O4 tsec
##    1: 0.0045346 0.0059112  0.00024683 -0.00114750 -0.00115180    1
##    2: 0.0054259 0.0040023 -0.00030805  0.00007400  0.00037599    2
##    3: 0.0046067 0.0066372  0.00050152 -0.00140600  0.00049896    3
##    4: 0.0017105 0.0056087  0.00055994  0.00098229  0.00076083    4
##    5: 0.0075731 0.0053336  0.00057292  0.00045123  0.00065553    5
##   ---
## 7195: 0.0350790 0.0751170  0.01806400  0.01227200  0.00562280 7195
## 7196: 0.0337940 0.0689320  0.01303600  0.00786970  0.00882610 7196
## 7197: 0.0445080 0.0721900  0.01371000  0.01154300  0.00912240 7197
## 7198: 0.0423920 0.0695310  0.01351700  0.00877060  0.00459420 7198
## 7199: 0.0316910 0.0773430  0.01401900  0.00746740  0.00377230 7199
```

```
args(nls)
```

```
## function (formula, data = parent.frame(), start, control = nls.control(),
##     algorithm = c("default", "plinear", "port"), trace = FALSE,
##     subset, weights, na.action, model = FALSE, lower = -Inf,
```

```
##     upper = Inf, ...)
## NULL
```

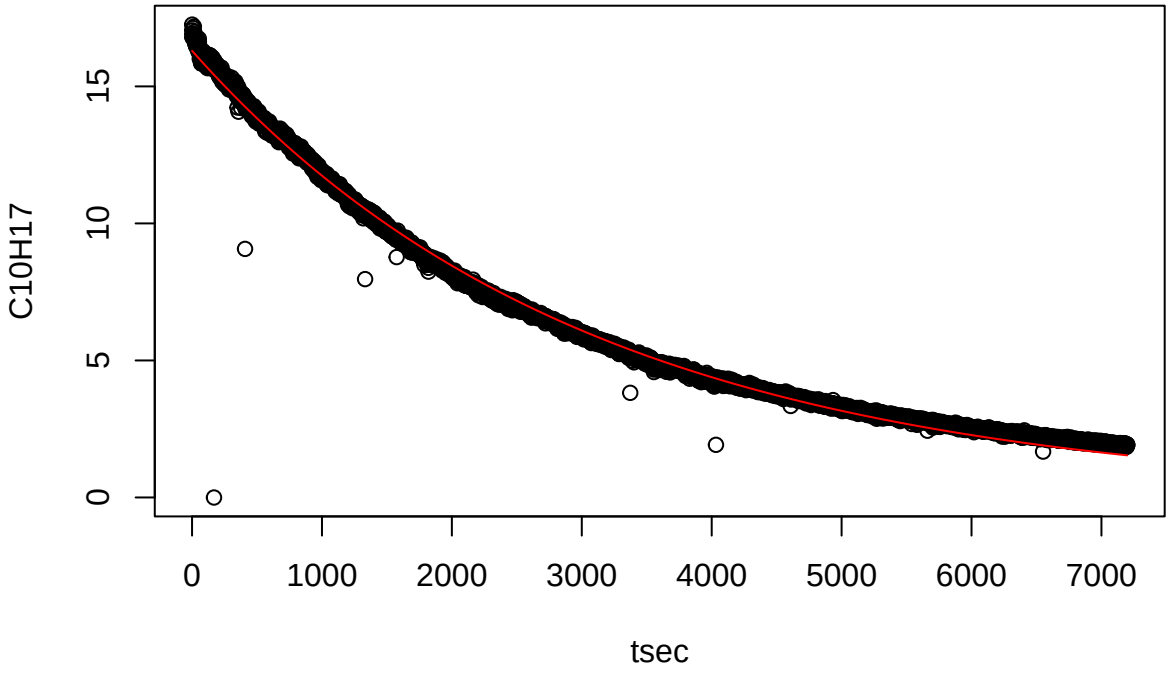
```
exp(-1 * 1:10)
```

```
##  [1] 3.678794e-01 1.353353e-01 4.978707e-02 1.831564e-02 6.737947e-03 2.478752e-03 9.118820e-04
##  [8] 3.354626e-04 1.234098e-04 4.539993e-05
```

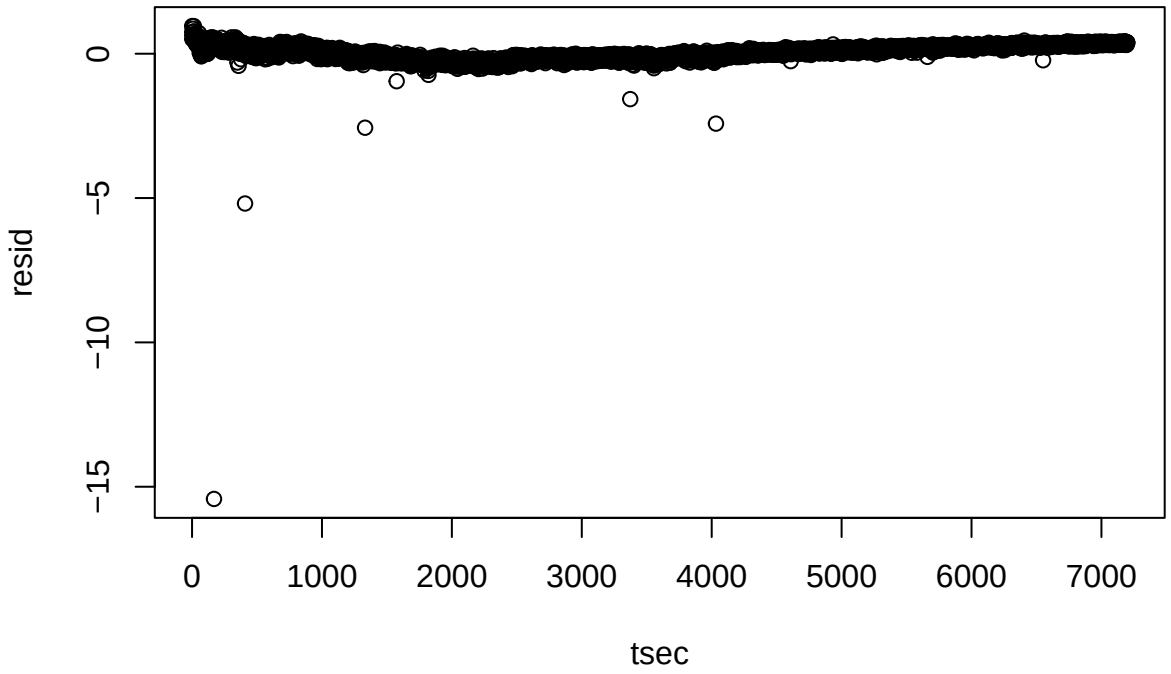
```
mod1 <- nls(C10H17 ~ c0 * exp(-k * tsec), start = c(c0 = 16, k = 1/4000), data = ox)
summary(mod1)
```

```
##
## Formula: C10H17 ~ c0 * exp(-k * tsec)
##
## Parameters:
##     Estimate Std. Error t value Pr(>|t|)
## c0 1.630e+01  1.126e-02  1448.3   <2e-16 ***
## k  3.280e-04  3.458e-07   948.5   <2e-16 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
##
## Residual standard error: 0.2983 on 7197 degrees of freedom
##
## Number of iterations to convergence: 5
## Achieved convergence tolerance: 1.485e-06
```

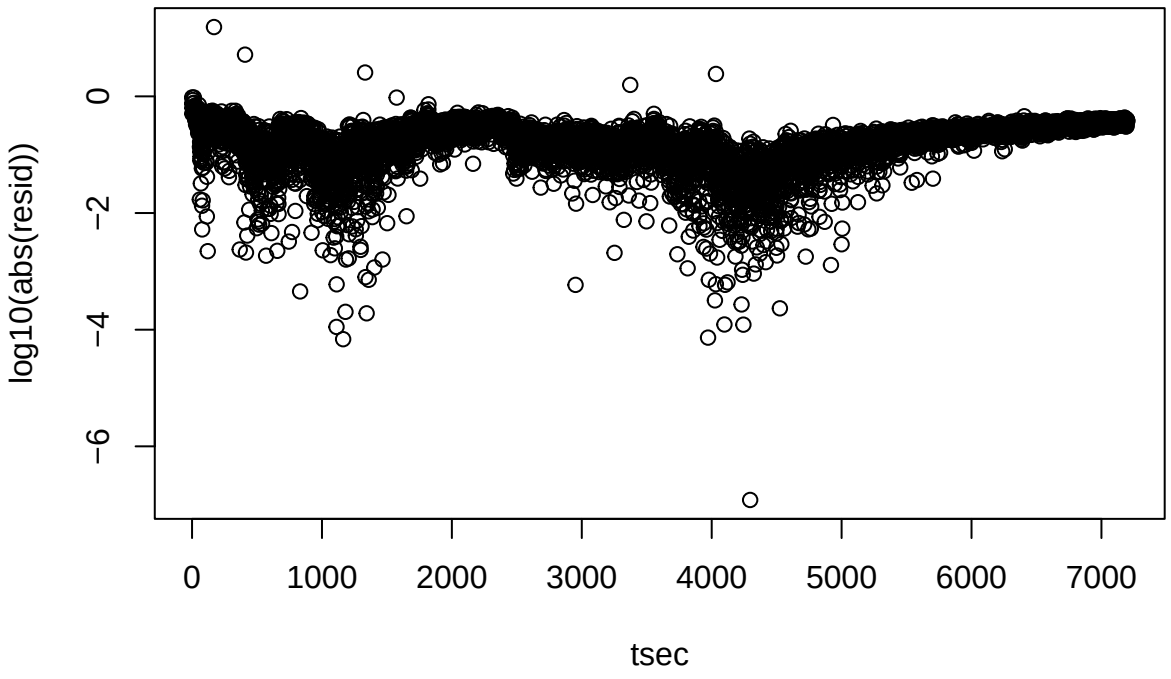
```
ox[, conc_pred := predict(mod1)]
ox[, resid := resid(mod1)]
plot(C10H17 ~ tsec, data = ox)
lines(conc_pred ~ tsec, data = ox, col = 'red')
```



```
plot(resid ~ tsec, data = ox)
```




```
plot(log10(abs(resid)) ~ tsec, data = ox)
```




```
ox <- ox[abs(resid) < 1, ]
```

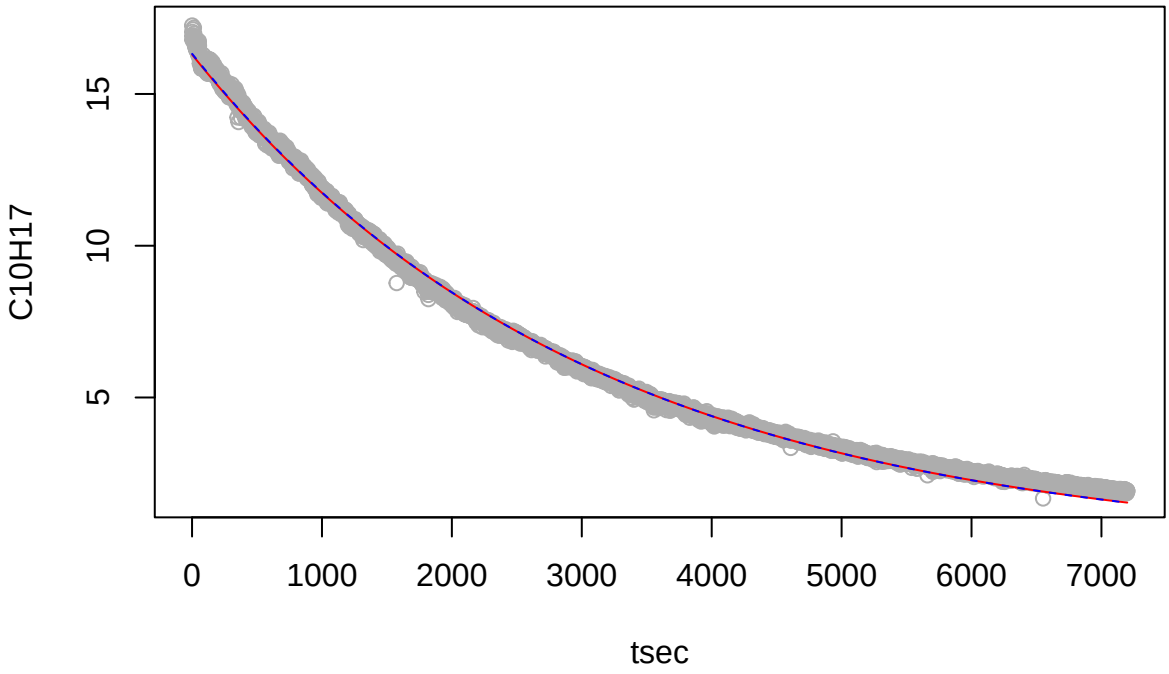
```
mod2 <- nls(C10H17 ~ c0 * exp(-k * tsec), start = c(c0 = 16, k = 1/4000), data = ox)
summary(mod2)
```

```
##
## Formula: C10H17 ~ c0 * exp(-k * tsec)
##
```

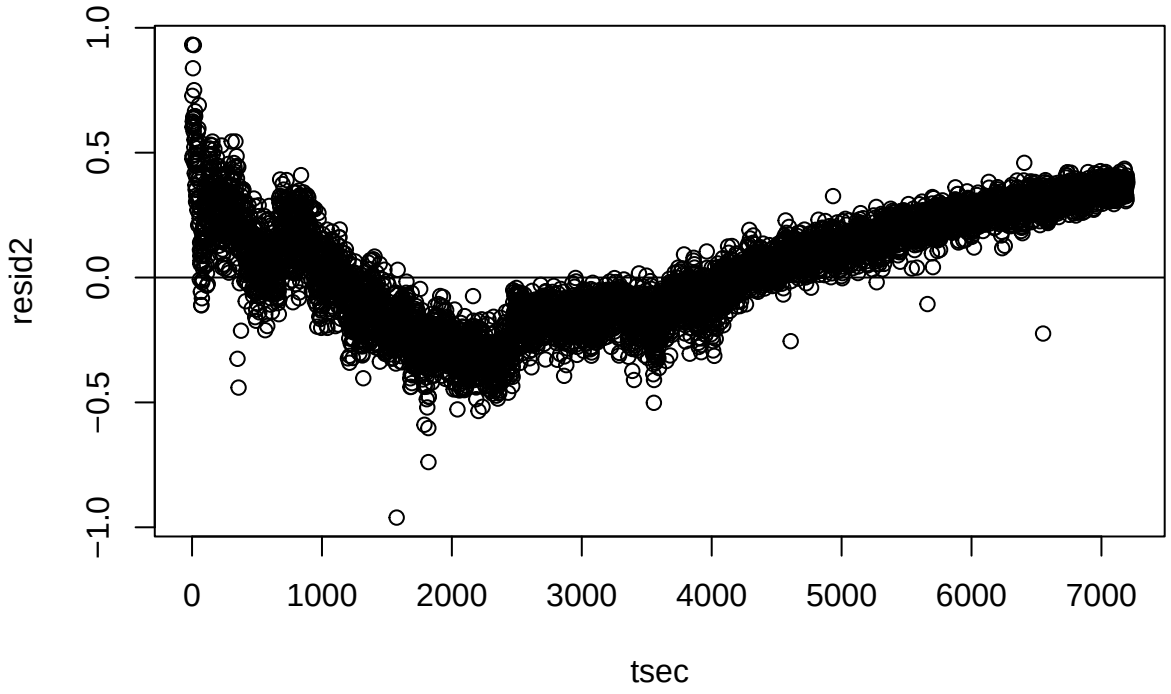
```
## Parameters:
##     Estimate Std. Error t value Pr(>|t|)
## c0 1.633e+01  8.458e-03    1930   <2e-16 ***
## k  3.285e-04  2.596e-07    1265   <2e-16 ***
## ---
## Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
##
## Residual standard error: 0.2238 on 7192 degrees of freedom
##
## Number of iterations to convergence: 5
## Achieved convergence tolerance: 2.163e-06
```

```
ox[, conc_pred2 := predict(mod2)]
ox[, resid2 := resid(mod2)]
```

```
plot(C10H17 ~ tsec, data = ox, col = 'gray68')
lines(conc_pred ~ tsec, data = ox, col = 'red')
lines(conc_pred2 ~ tsec, data = ox, col = 'blue', lty = 2)
```




```
plot(resid2 ~ tsec, data = ox)
abline(h = 0)
```


resid2
1.0
0.5
0.0
−0.5
−1.0
0
1000
2000
3000
4000
5000
6000
7000
tsec