Minimum Detectable ICOS Flux

To compute the minimum detectable flux I'm following the procedure used by Parkin et.al 2012 https://acsess.onlinelibrary.wiley.com/doi/epdf/10.2134/jeq2011.0394. Parkin et.al. computed minimum detection limit parameters for 3 and 4 measurements per incubation, however with the ICOS we get a few hundred measurements for each incubation. I repeated the Monte Carlo simulation using the larger number of measurements possible with the ICOS.

First I need to compute the standard deviation and CV of the system. Parkin used CV, I used standard deviation, since the standard deviation instead of the CV is the input parameter to the `rnorm` function.

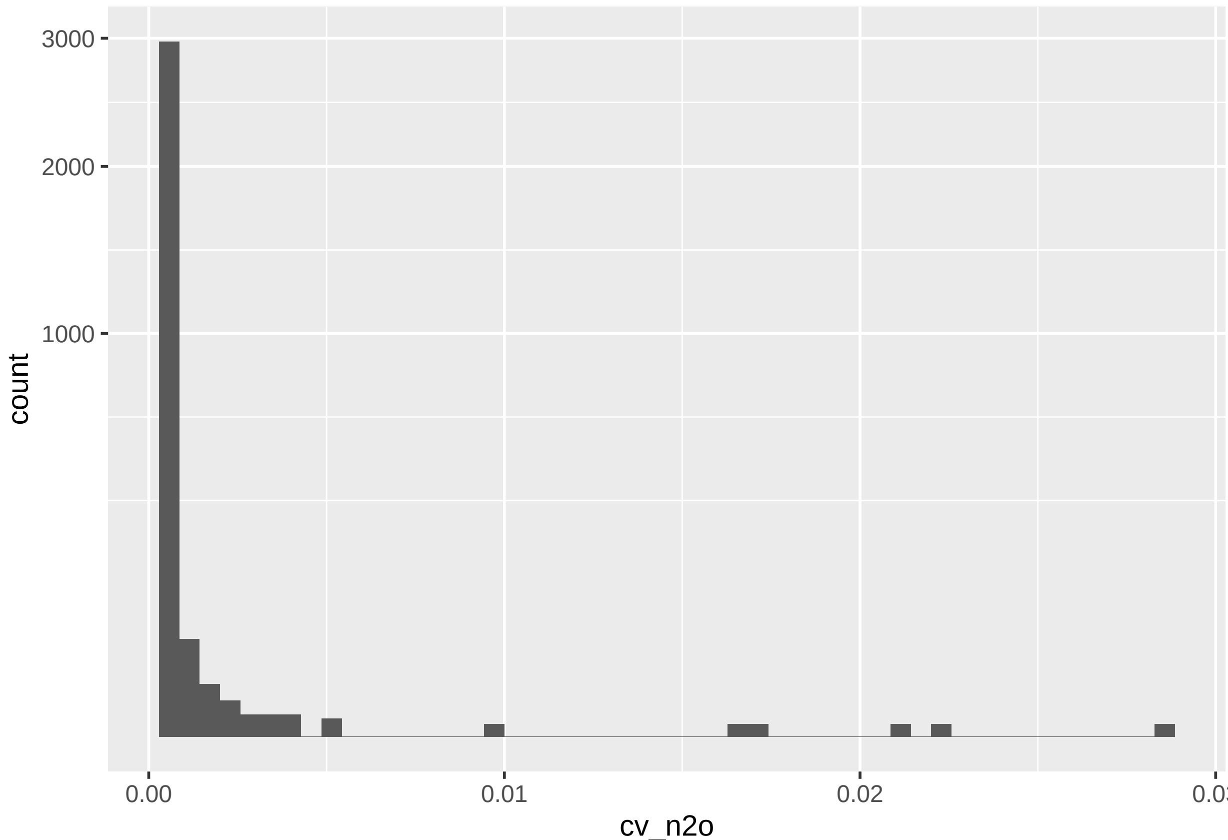
Taking all the zero fluxes (where the metal plate was installed), we compute the mean, standard deviation, median number of samples per incubation, and CV from each incubation.

```
points %>%
  group_by(id) %>%
  summarize(avg_n2o = mean(n2o_ppm), sd_n2o = sd(n2o_ppm), number = n()) %>%
  mutate(cv_n2o = sd_n2o/avg_n2o) %>%
  summarize(mean_n2o= mean(avg_n2o), mean_sd = mean(sd_n2o),
            max_cv = max(cv_n2o), min_cv = min(cv_n2o), mean_cv=mean(cv_n2o),
            median_n = median(number))
```

```
## # A tibble: 1 x 6
##   mean_n2o  mean_sd max_cv   min_cv  mean_cv median_n
##      <dbl>    <dbl>  <dbl>    <dbl>    <dbl>    <int>
## 1    0.350 0.000228 0.0285 0.000464 0.000652      210
```

Plotting the distribution of CV's it looks to be clustered on the low end.

```
points %>%
  group_by(id) %>%
  summarize(avg_n2o = mean(n2o_ppm), sd_n2o = sd(n2o_ppm)) %>%
  mutate(cv_n2o = sd_n2o/avg_n2o) %>%
  ungroup() %>%
  ggplot(aes(cv_n2o)) + geom_histogram(bins=50)  + scale_y_sqrt()
```



I define a function to draw 210 samples (which was the average number of sample points we have per incubation) from a random distribution (`rnorm(number, mean, std)`) with a mean of 0.350 ppm and a standard deviation of 0.000228 (computed from the zero flux data). Then I join it with a sequence (1..210) which would represent the second and divide by 30 to simulate minutes (we get one measurement every 2 seconds). I join the minute and ppm values into a data.frame and fit a linear model `ppm = a + b second` and extract the slope `b` component.

```
sim = function() {
  minute = seq(1,210)/30
  ppm=rnorm(210, 0.350, 0.000228)
  data = data.frame(minute, ppm)
  summary(lm(ppm ~ minute, data=data))$coefficients[[2,1]]
}
```

Running through one iteration of the function with the intermediate results, shows that the last result returns just the slope intercept.

```
minute = seq(1,210)/30
ppm=rnorm(210, 0.350, 0.000228)
data = data.frame(minute, ppm)
head(data)
```

```
##       minute       ppm
## 1 0.03333333 0.3500176
## 2 0.06666667 0.3498557
## 3 0.10000000 0.3500429
## 4 0.13333333 0.3497786
## 5 0.16666667 0.3498983
## 6 0.20000000 0.3498768
```

```r
summary(lm(ppm ~ minute, data=data))$coefficients
```

```
##                 Estimate   Std. Error      t value   Pr(>|t|)
## (Intercept) 3.499445e-01 2.891115e-05 12104.138453 0.00000000
## minute      1.257812e-05 7.128201e-06     1.764557 0.07910598
```

```r
summary(lm(ppm ~ minute, data=data))$coefficients[[2 ,1]]
```

```
## [1] 1.257812e-05
```

Next I define a function to run a number of simulations using the `sim` function, arranging the resulting slopes in order and taking the last number of the top 5% or 1% of the numbers to be the minimum detectable flux. Running the function 100000 times with a 5% and a 1% significance level.

```r
mdl = function(runs, significance, sim_function) {
  replicate(runs, sim_function()) %>%
  enframe(name='id', value='flux') %>%
  arrange(flux)  %>%
  # mutate(row_id =row_number()) %>%
  slice_head(n=runs * significance) %>%
  slice_tail()
}
```

The minimum detectable slope at a 5% confidence level is (we have two tails so we use 0.025 as the cutoff)

```r
mdl(100000, 0.025, sim)
```

```
## # A tibble: 1 x 2
##      id       flux
##   <int>      <dbl>
## 1 93180 -0.0000152
```

and at a 1% confidence level

```r
mdl(100000, 0.005, sim)
```

```
## # A tibble: 1 x 2
##      id       flux
##   <int>      <dbl>
## 1 44447 -0.0000202
```

Since the minimum detectable slopes are symmetrical, the minimum detectable slope is around +/- 0.015 ppb/min at a 5% confidence level and +/- 0.02 ppb/min at a 1% confidence level.

Defining a function to compute flux

```r
flux <- function(slope, molecular_weight, air_temperature, height) {
  ug_minute = (slope * molecular_weight * 1)/(0.0821 * (air_temperature + 274.15))
  area =  pi * 14.1^2/10000
  volume = pi * 14.1^2 * (height- 0.2) / 1000
  flux_ug_m_hr = (ug_minute * volume * 60)/area
  flux_ug_m_hr * 0.01 * 24
}
```

Assuming 20C and 30 cm chamber height we would get

```r
flux(0.000015, 28, 20, 30)
```

```
## [1] 0.07463045
```

```r
flux(0.000020, 28, 20, 30)
```

```
## [1] 0.09950726
```

For our chambers that would work out to an MDL of +/-74 mg/ha/day at a 5% confidence level and +/-99 mg/ha/day at a 1% confidence level.

The mean slopes for the zero flux samples (-0.0072 ppb/min) is less than the computed minimum detectable limit.

```r
points %>%
  distinct(id, n2o_slope) %>%
  summarize(n2o_mean_slope = mean(n2o_slope))
```

```
## # A tibble: 1 x 1
##   n2o_mean_slope
##            <dbl>
## 1    -0.00000724
```

Which works out to about 18 mg/ha/day.

During the fall run-in period we observed 89 negative fluxes out of 1744 total fluxes. Of the negative fluxes 25 were below the MDL. However, if we filter out fluxes where the co2_r2 < 0.8 we end up with 4 negative fluxes below the MDL and if we filter out fluxes where the co2_r2 < 0.8 and the n2o_r2 < 0.5 we end up with no negative fluxes below the MDL.

Christiansen et. al. 2015 (https://doi.org/10.1016/j.agrformet.2015.06.004) proposed a method to compute the minimum detectable flux based on the published noise figure of the instrument used. He proposed $\frac{Aa}{tc}\frac{VP}{SRT}$ where Aa is the analytic accuracy of the instrument, tc is the closure time in hours V is the chamber volume, P the atmospheric pressure in Pa, S the surface area of the soil, R the gas constant and T the temperature in Kelvin.

Nickerson 2019 (https://eosense.com/wp-content/uploads/2019/11/Eosense-white-paper-Minimum-Detectable-Flux.pdf) proposed replacing instrument precsion with the standard error of the instrument precision by replacing the first element of the equation by $\frac{Aa}{tc\sqrt{(tc/p)}}$ where p is the sampling period of the instrument.

Setting up the conditions for our chambers and computing with the Christiansen approach I get the following in mg/ha/day

```r
# chamber closure in hours
tc = 210/30/60
# period in hours
p = 2/3600
# pressure in Pa
pressure = 101325
# temperature in K
temperature = 20 + 271
# surface area in m2
surface = 0.5 * 0.5
# gas constant for m3 Pa K-1 mol-1
R = 8.31446261815324
# volume in m2
volume = surface * 0.15
# precision in ppm
Aa = 2/1000

(Aa /tc ) * ((volume * pressure)/(surface * R * temperature)) * 28 * 24 / 10000 * 1000
```

```
## [1] 7.236577
```

while using the modified Nickerson approach I get:

```
(Aa / (tc * sqrt(tc/p))) * ((volume * pressure)/(surface * R * temperature)) * 28 * 24 / 10000 * 1000
```

```
## [1] 0.4993712
```

both are siginficantly lower than the Parkin approach and the actual zero flux measurements.

Lab GC

we took 30 air samples to establish an error estimate

```
air <- read_parquet("./cvresults.parquet")
ch4 <- air %>%
  filter(str_detect(Sample,'^A')) %>%
  filter(!str_detect(Sample, 'STD')) %>%
  select(Vial, ch4_ppm)
n2o_co2 <- air %>%
  filter(str_detect(Sample,'^B')) %>%
  filter(!str_detect(Sample, 'STD')) %>%
  select(Vial, n2o_ppm, co2_ppm)
lab_data <- merge(ch4, n2o_co2)
```

lets get the CV for N2O

```
lab_data %>%
  summarize(avg_n2o = mean(n2o_ppm), sd_n2o = sd(n2o_ppm), number = n()) %>%
  mutate(cv_n2o = sd_n2o/avg_n2o) %>%
  summarize(mean_n2o= mean(avg_n2o), mean_sd = mean(sd_n2o),
            max_cv = max(cv_n2o), min_cv = min(cv_n2o), mean_cv=mean(cv_n2o),
            median_n = median(number))
```

```
##    mean_n2o     mean_sd     max_cv     min_cv    mean_cv median_n
## 1 0.2079897 0.002634633 0.01266713 0.01266713 0.01266713       30
```

defining a lab simulation procedures drawing 4 samples for each incubation.

```
sim_lab = function() {
  minute = seq(1,4)*15
  ppm=rnorm(4, 0.208, 0.00263463)
  data = data.frame(minute, ppm)
  summary(lm(ppm ~ minute, data=data))$coefficients[[2,1]]
}
```

Again the minimum detectable slope at a 5% confidence level is (we have two tails so we use 0.025 as the cutoff)

```
mdl(100000, 0.025, sim_lab)
```

```
## # A tibble: 1 x 2
##      id      flux
##   <int>     <dbl>
## 1 28570 -0.000154
```

and at a 1% confidence level

```
mdl(100000, 0.005, sim_lab)
```

```
## # A tibble: 1 x 2
```

```
##      id      flux
##   <int>     <dbl>
## 1 60899 -0.000204
```

In the lab GC our detection limit is basically 10x higher. I think this is mainly due to only using 4 samples instead of 210., The minimum detectable slope is around +/- 0.15 ppb/min at a 5% confidence level and +/- 0.2 ppb/min at a 1% confidence level.

Assuming 20C and 30 cm chamber height and re-using our flux function we would get

```
flux(0.00015, 28, 20, 30)
```

```
## [1] 0.7463045
```

```
flux(0.00020, 28, 20, 30)
```

```
## [1] 0.9950726
```

For our chambers that would work out to an MDL of +/-746 mg/ha/day at a 5% confidence level and +/-995 mg/ha/day at a 1% confidence level.