Novel Approaches to Interpolating N$_2$O Flux Between Episodic Sampling Points and Improving Sampling Vial Storage Times

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Approaches to Temporal Sampling

- Periodic (e.g. weekly)
  - Convenient
  - Reasonable for system comparisons?
  - Can miss important emissions events

- Episodic
  - Targets episodes known to result in high fluxes
    (e.g. wet soil conditions, thaw, N additions)
  - Is NOT convenient (weekends, holidays)

- Combination
  - Flessa et al. 2002. Geoderma: “Weekly measurements of N$_2$O fluxes complemented by additional event-related flux determinations provided accurate estimates of total emissions”
Standard Method of Interpolating between Sampling Dates

• Trapezoidal Interpolation
  • Results depend strongly on sampling frequency, which defines area under the curve
  • For frequent sampling (e.g. daily), this method is likely adequate
  • For episodic sampling, less likely to be satisfactory
Sampling and Interpolating to Account for Temporal Variability of N$_2$O Emissions
Sampling and Interpolating to Account for Temporal Variability of N₂O Emissions

The graph shows the g N₂O-N ha⁻¹ d⁻¹ over time for different tillage practices: No Till (green), Chisel Till (blue), and Organic (yellow). The data points are distributed across various dates, highlighting the variability in N₂O emissions.
Common Method of Interpolating between Sampling Dates

→ Biological processes are not linear

Biological processes are not linear
Interpolating between Sampling Dates Based on Our Understanding of N\textsubscript{2}O Emissions Dynamics
Sampling and Interpolating to Account for Temporal Variability of N₂O Emissions

Data supplied by Tim Parkin, USDA-ARS, Iowa
Interpolating between Sampling Dates
Based on Our Understanding of N$_2$O Emissions Dynamics

$y = 568.73e^{-0.622x}$
$R^2 = 0.971$

Cavigelli, unpublished data
How Low Should Interpolated Values Go?

• Exponential decay interpolation results in very low values when there are large number of days between sampling points.

• Should a baseline value be used for interpolation after exponential decay reaches a certain level?

• Cumulative $\text{N}_2\text{O}$ emissions were only about 2% greater using a baseline value instead of using exponential decay curve to calculate values for all days between sampling dates.
Comparing Results of Linear vs. Exponential Interpolation Methods

Cavigelli, unpublished data

Cumulative 40 d $\text{N}_2\text{O}$ emissions (kg N ha$^{-1}$ d$^{-1}$)

<table>
<thead>
<tr>
<th>Method</th>
<th>NT</th>
<th>CT</th>
<th>Org</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trapezoidal</td>
<td>8.58</td>
<td>3.73</td>
<td>5.65</td>
</tr>
<tr>
<td>Exponential Decay</td>
<td>2.63</td>
<td>1.18</td>
<td>1.83</td>
</tr>
<tr>
<td>Trapezoidal/Exponential</td>
<td>3.3</td>
<td>3.2</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Sampling and Interpolating to Account for Temporal Variability of N$_2$O Emissions

Data supplied by Tim Parkin, USDA-ARS, Iowa
Assessing Exponential Decay Function Interpolation Using Automated Sampling Data

Data supplied by Tim Parkin, USDA-ARS, Iowa
(negative values converted to 0.001 for curve fitting)
Curve | Expon’l Decay | R² | Difference | Linear R²
--- | --- | --- | --- | ---
1 | $y=1394e^{-0.373x}$ | 0.74 | ~ | 0.75
2 | $y=123e^{-0.351x}$ | 0.55 | > | 0.48
3 | $y=111e^{-0.308x}$ | 0.57 | ~ | 0.59
4 | $y=136e^{-0.13x}$ | 0.66 | ~ | 0.63
5 | $y=499e^{-0.301x}$ | 0.80 | > | 0.54
6 | $y=3122e^{-0.303x}$ | 0.95 | > | 0.76
7 | $y=767e^{-0.257x}$ | 0.80 | > | 0.67
8 | $y=1463e^{-0.638x}$ | 0.90 | > | 0.75
9 | $y=269e^{-0.447x}$ | 0.88 | > | 0.81
10 | $y=3492e^{-0.463x}$ | 0.93 | > | 0.79
11 | $y=927e^{-0.246x}$ | 0.88 | > | 0.66
12 | $y=866e^{-0.366x}$ | 0.89 | > | 0.82
13 | $y=749e^{-0.309x}$ | 0.84 | ~ | 0.85
14 | $y=506e^{-0.579x}$ | 0.92 | > | 0.78
15 | $y=296e^{-0.37x}$ | 0.78 | > | 0.62

Data provided by Neville Millar et al., Michigan State U.
The graph shows the concentration of $\text{g N}_2\text{O-N ha}^{-1}\text{d}^{-1}$ over time (Day after sampling) for different samples labeled 1 to 15. The original curve is represented in red. The concentrations decrease exponentially with increasing days.
When to Sample to Capture Peaks?

Factors Controlling $\text{N}_2\text{O}$ Emissions

- Soil $\text{NO}_3$, $\text{NO}_2$, $\text{NH}_4$, DOC, DOC:$\text{NO}_3$, pH, Denitrifier enzyme status, Microbial community structure
- Oxygen (soil moisture)

1) Sampling when soils are wet is most important
When to Sample to Capture Peaks?

Factors Controlling $\text{N}_2\text{O}$ Emissions

- Soil NO$_3$, NO$_2$, NH$_4$, DOC, DOC:NO$_3$, pH, Denitrifier enzyme status, Microbial community structure
- Oxygen (soil moisture as surrogate)

2) Sampling when soils are dry not very important (can estimate those values with baseline value)
Sampling to Account for Temporal Variability of N$_2$O Emissions

Crucial to sample after each rain event

Data supplied by Tim Parkin, USDA-ARS, Iowa

Rainfall (mm): 1  6  16  29  7  22  3  3  45  1  11  34  7  44  19  9  5
Episodic Sampling to Account for Temporal Variability of N$_2$O Emissions

Data supplied by Tim Parkin, USDA-ARS, Iowa
Exponential Interpolation of Episodic Sampling “Data”

$y = 866e^{-0.366x}$

Cumulative $\text{N}_2\text{O}-\text{N}$ Emissions (kg ha$^{-1}$)

- Automated sampling: 33.5
- Sampling ~6 h after every rain event: 25.0 (75%)
- Sampling ~12 h after every rain event: 27.8 (83%)

Data supplied by Tim Parkin, USDA-ARS, Iowa
Linear Interpolation of Episodic Sampling “Data”

Cumulative N₂O-N Emissions (kg ha⁻¹)

- Automated sampling: 33.5
- Sampling ~6 h after every rain event: 54.6 (163%)
- Sampling ~12 h after every rain event: 62.6 (187%)

Data supplied by Tim Parkin, USDA-ARS, Iowa
Weekly Sampling to Account for Temporal Variability of N$_2$O Emissions

Data supplied by Tim Parkin, USDA-ARS, Iowa
Weekly Sampling to Account for Temporal Variability of $N_2O$ Emissions

Data supplied by Tim Parkin, USDA-ARS, Iowa
Exponential Interpolation of Weekly Sampling "Data"

Data supplied by Tim Parkin, USDA-ARS, Iowa
Exponential Interpolation of Weekly Sampling “Data”

\[ y = 866e^{-0.366x} \]

Cumulative N\(_2\)O-N Emissions (kg ha\(^{-1}\))

- Automated sampling: 33.5
- Sampling weekly B: 13.8

Data supplied by Tim Parkin, USDA-ARS, Iowa
Linear Interpolation of Weekly Sampling

“Data”

Automated sampling
Sampling weekly A linear
Sampling weekly B linear

Cumulative $\text{N}_2\text{O}-\text{N}$ Emissions (kg ha$^{-1}$ d$^{-1}$)

- Automated sampling: 33.5
- Sampling weekly A linear: 36.1 (108%)
- Sampling weekly B linear: 36.5 (109%)

Data supplied by Tim Parkin, USDA-ARS, Iowa
# Linear Interpolation of Weekly Sampling “Data”

<table>
<thead>
<tr>
<th>Sampling Day</th>
<th>Cumulative N$_2$O-N Emissions (kg ha$^{-1}$)</th>
<th>Percent of Automated (33.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monday</td>
<td>36.1</td>
<td>108</td>
</tr>
<tr>
<td>Tuesday</td>
<td>42.5</td>
<td>127</td>
</tr>
<tr>
<td>Wednesday</td>
<td>41.2</td>
<td>123</td>
</tr>
<tr>
<td>Thursday</td>
<td>36.5</td>
<td>109</td>
</tr>
<tr>
<td>Friday</td>
<td>27.6</td>
<td>83</td>
</tr>
<tr>
<td>Saturday</td>
<td>21.9</td>
<td>65</td>
</tr>
<tr>
<td>Sunday</td>
<td>20.9</td>
<td>62</td>
</tr>
</tbody>
</table>
Interim Conclusions

- Periodic sampling misses large peaks (depending on sampling interval)
- Linear interpolation of periodic sampling can provide the right answer for the wrong reason
- Episodic sampling makes more sense biologically
- Exponential decay interpolation is (probably?) necessary for episodic sampling
- Automated sampling can provide invaluable data to design manual sampling regimes
- Can regional sampling regimes be developed based on automated sample data sets?
How Frequently to Sample Following Soil Wetting?
Seasonal distribution of $N_2O$ flux
Unexpected daily patterns

Generally trends down

Enormous between-rep variability

Unpredictable peak timing
Exceptions

Immediately following fertilization
A new approach

Trapezoidal approximation describes total emissions over 7 days following rain.

Predict this value using measured fluxes.

Extend this model to rain events throughout the year.
Lognormally distributed data
GLMMs are appropriate
Consistent relationship: $R^2 = 0.85$
Vial Storage

- 84 frames × 4 vials per frame = 336 vials per sampling event
- 48h to analyze on GC
- Approximately 2-6 week turnaround time
- 4000 total vial inventory
Vial Storage

- 12 mL Exetainer from LabCo
- Standard rubber septa
- Flushed with $N_2$ gas for 60s before each sampling event
  - $O_2$ levels indicate a vial is leaky
Experimental Methods

• Vials with caps that had been used four times (16 total punctures in each septum)
• Four replicates
• Each week, 16 vials:
  – Flushed with N₂
  – Injected with either:
    10mL of N₂O-CO₂ standard gas (2ppm/1%)
    10mL of atmosphere
• Then stored for up to 10 weeks (@ lab conditions)
• Analyzed on two dates on GC:
  – “0-5 weeks”
  – “5-10 weeks”
No statistical relationship with CO$_2$
No statistical relationship with $\text{N}_2\text{O}$
No statistical relationship with $O_2$
Flushing

- Vials injected with either atmosphere or standard gas
  - 22g needles inserted
  - $N_2$ gas at 600cc/min
  - Exhaust
  - 0, 30, 60, 180 seconds of flow
Best practices

• Vials can be stored up to 10 weeks after sampling with no contamination nor leakage
  – Storage should be climate controlled (i.e. not the back of your sampling vehicle with diurnal temperature swings)
• Vials should be flushed with N2 gas to reduce O2 levels
  – Short flushing times (<30s) may be acceptable depending on flow rate
• We use septa 5 times (20 punctures with a 22g needle)
• We have not tested whether they could be used for more sampling events before replacement.