DATASET ID: MeX_netflux_2005_2006.txt
DATASET TITLE: Halomethane and methane net fluxes in northern Alaskan tundra, Barrow and Toolik Lake, 2005-2006
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FUNDING SOURCE: NSF Office of Polar Programs: ARC/ARCSS/SNACS Grant # 0435870: Halomethane gas exchange in northern Alaskan coastal ecosystems
README VERSION: "MeX_2005_2006_README.pdf" v 1.0 (April 24, 2009)

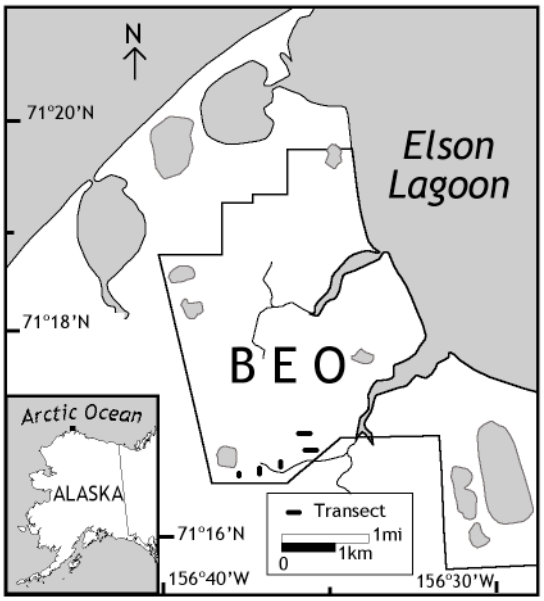
I. INTRODUCTION

The objectives of our research were to quantify fluxes of environmentally important trace gases between the coastal tundra and atmosphere, including the methyl halides (CH_3Br, CH_3Cl and CH_3I), chloroform ($CHCl_3$) and methane (CH_4), and to understand the environmental and biological controls on these fluxes. This understanding helps us predict how Arctic climate and microtopography changes would affect these radiatively active trace gas fluxes. The methyl halides and chloroform are ozone-depleting compounds, while methane is a potent greenhouse gas. This research was funded by the NSF Office of Polar Programs (Study of the Northern Alaskan Coastal System)

II. FIELD SAMPLING

A. Physical location of field sites

Research was conducted at 2 field sites on the North Slope of Alaska: the Barrow Environmental Observatory (BEO, 71°N, 157° W) and around the Toolik Lake Long Term Ecological Research site (TOOLIK, 69°N, 149°-150° W).



Two BEO campaigns occurred in 2005: from June 21-26 and from August 17-22. A third BEO campaign was conducted the following year, from July 20-25, 2006. Twenty sites were measured for each outing, divided into 5 transects of 4 plots spaced 10-50 meters apart (Figure 1). These sites covered the predominant microtopographic features, including high-centered polygon, low-centered polygon, polygon edge, ice wedge channel, wet meadow and drained lake basin.

Figure 1. Five transects on the southeast portion of the BEO. The first two transects (eastern sites) are located on a drained lake basin and accessed via boardwark, while the other three transects cover a range of hydrologic and microtopographic regimes.

The Toolik Lake region campaign occurred from August 17-20, 2006, at the end of the growing season. Sixteen sites were measured during this outing and covered the predominant vegetation types except for large riparian shrubs. Sampling sites included ecotypes classified as acidic as well as nonacidic (http://www.uaf.edu/toolik/gis/).

B. Time period covered by the data

The total time period ranged from June 21, 2005 to August 20, 2006. Specific data collection times were: June 21-26, 2005 (BEO), August 17-22, 2005 (BEO), July 20-25, 2006 (BEO) and August 17-20, 2005 (Toolik Lake). The compiled dataset here represents the combined data sets reported in the following publications: [*Rhew et al., 2007; Teh et al., 2009; Rhew et al., 2008*].

III. MEASUREMENT METHODS

A. Instrument description

Air canister samples were measured twice using an Agilent 6890N/5973 gas chromatograph/ mass spectrometer (GC/MS) with a custom-built cryotrapping and sample introduction system [*Rhew et al.*, 2007]. Gas chromatographic separation occurs on a 60 meter, 1.4 μm film thickness DB-VRX capillary column (J&W Scientific) The chromatography allows the following compounds to be measured in each gas sample, in order of elution, with target ions specified: CFC-12 (m/z=85), CH_3Cl (m/z=50, 52), CH_3Br (m/z = 94, 96), CFC-11 (m/z=103), CH_3I (m/z =142), CFC-113 (m/z=153), $CHCl_3$ (m/z=83,85) and CCl_4 (m/z=117, 119). Calibration curves were constructed by trapping and injecting different sized aliquots of a whole air standard collected at Trinidad Head, California and calibrated at the Scripps Institution of Oceanography on the SIO-2005 scale.

Methane and CO_2 samples were analyzed using a Shimadzu GC-14A gas chromatograph (Shimadzu Scientific Inc., Columbia, MD), equipped with Porapak-Q column, a flame ionization detector (FID) for CH4 analysis and a thermal conductivity detector (TCD) for CO_2 determination [*Teh et al., 2005*]. Gas standards were prepared by Scott Specialty Gases (Scott Specialty Gases, Plumsteadville, PA), and contained 10.5 ppmv CH_4 and 950 ppmv CO_2.

B. Precision and minimum detectable fluxes

At ambient concentrations, the precisions (1 σ) based on daily standards after applying drift corrections are calculated to be better than 3% for CH_3Cl, CH_3Br, and the CFCs, 2-4% for $CHCl_3$, and better than 12% for CH_3I. Precision was approximately 1.5 % for CH_4 and 1.0 % for CO_2.

Given the instrumental precisions and typical conditions for flux chamber sampling, we estimate the minimum detectable fluxes of CH_3Cl, CH_3Br, CH_3I, and $CHCl_3$ to be 17, 0.29, 0.11, and 1.2 nmol m^{-2} d^{-1}, respectively.

IV. DATA COLLECTION AND PROCESSING

A. Flux chamber sampling

Gas fluxes were measured using two-component, mirror-polished aluminum, static flux chambers (188 L volume, 0.264 m^2 surface area). At each chamber site, an open-ended base (61 L) was seated in the soil, typically 1-2 days prior to measurement. To start the chamber experiment, the lid (127 L) was placed in a water channel surrounding the lip of the base, creating an airtight seal. Enclosures lasted 32-40 minutes with three air samples drawn from the chamber at 15-20 minute intervals into previously evacuated canisters (1L electropolished stainless steel or 3L silica-lined stainless steel). A vent tube was opened during sampling to allow for pressure equilibration, and ambient air samples were collected to make a correction for this dilution effect. Two internal fans mixed the chamber air, and the chamber was shrouded with reflective insulation to mitigate internal temperature fluctuations. Chamber and ambient temperatures were measured, along with the barometric pressure, depth of chamber placement, soil temperatures at 5 and 10 cm depth, and plant coverage. Additional measurements in 2006 included water table depth, active layer depth, and volumetric water content at 0-5 cm (Theta Probe ML2x, Dynamax Inc.). Also, in 2006, all chambers included a small addition of $^{13}CH_3Cl$, $^{13}CH_3Br$, and F-113 at the beginning of the enclosure for determining gross fluxes using a stable isotope tracer technique. For consistency in this dataset, only net fluxes are reported here.

B. Calculating fluxes

To calculate fluxes, a linear least squares regression was applied to the chamber headspace concentration of each gas versus time. A positive slope indicates net emission, while a negative slope represents net uptake. For sites showing net uptake, first order uptake rates were calculated by plotting the natural log of the concentration versus time, with the slope representing the uptake rate constant (k). Uptake rates were normalized to initial concentrations of **535.7 ppt CH_3Cl** and **10.4 ppt CH_3Br**, representative of their estimated mean northern Hemisphere baseline mole fractions [*Simmonds et al.*, 2004]. In our notation, positive fluxes indicate net emission, while negative fluxes indicate net consumption of the compounds of interest. Because uptake rates are first order, you can adjust uptake rates to alternative ambient concentrations. To do so, determine the ratio of new concentration to the concentration used here, and multiply that ratio to the uptake flux. (note: does not apply to sites of net emission, which were calculated using linear regressions).

C. Determining hydrologic regime

The hydrologic regime of chamber sites was based on the amount of surface area covered by standing water and the degree of soil saturation: "flooded" (50-100% standing water, ~100% soil moisture), "wet" (1-50% standing water, ≥70% soil moisture), "moist" (no standing water, ≥70% soil moisture, <5 cm water table depth), "drained" (no standing water, 30-70% soil moisture, 25 cm average water table depth), and "dry" (no standing water, <30% soil moisture, and >40 cm water table depth).

D. Plant sampling and processing

In June and August, 2005, all live above-ground vegetation was harvested at all non-boardwalk sites (Sites 9-20). Plant samples were sorted between live and dead portions and oven dried at 60 to 65 ºC for over 24 hours to determine live above ground biomass densities. Because the June sites were harvested for plant material, different sites were chosen in August within 10 meters of the original ones. Predominant vascular plant species were identified as the ones that together account for >80% of the live vascular dry biomass. In 2006, plants were not harvested and predominant plant classifications were assessed as general vegetation types.

E. Description of quality control procedures

In a few instances in 2005 (denoted by ** in the dataset), the t=40 sample was either compromised or below our detection limit (<5 ppt for CH_3Cl, <1 ppt for CH_3Br) because of rapid uptake rates. In these cases, uptake rates were based on a two-point linear fit between t=1 and t=20. In 2006, flux chamber times were shortened to 32 minutes to avoid this problem.

The number of moles of air in the chamber was calculated based on the volume of enclosed headspace (adjusted by the depth of base placement), chamber temperature, and pressure. Ambient temperature and pressure were monitored in the field. Flux errors were estimated by propagating errors associated with the calculation of number of moles of air in the chamber (volume, internal temperature, and ambient pressure uncertainties) and with the calculation of the slope of concentrations. In 2005, this regression error was calculated using 68% confidence intervals for the regression coefficients. In 2006, we used the standard error on the linear regression slope coefficient, which is equivalent to the 95% confidence interval divided by the student's critical value, using n=number of measurements (typically 6).

V. DATA FORMAT

A. Software output

Data file was created using Microsoft Excel 2008 for Mac, Version 12.1.7 (090302), and exported as a tab-delimited text (.txt) file.

B. Data format and layout

Column

1. **Site (#):** Unique identifier for flux chamber experiment, in order of occurrence
2. **Site (BEO/TL):** Barrow Environmental Observatory (BEO), Toolik Lake region (TL)
3. **Transect (A-H):** A-E indicate transects at the BEO. F-H indicate similar topographic conditions around Toolik Lake, and are generally (but not always) clustered nearby.
4. **Latitude (degrees):**
5. **Latitude (minutes):** Precision given to level measured by hand-held GPS. Estimated to be accurate to ~6 m when minutes are 5 digits (xx.xxx).
6. **Longitude (degrees):**
7. **Longitude (minutes):**
8. **Date (yyyymmdd)**
9. **Hydrological_regime**: See Section IV.C
10. **Soil_Temp_10cm (°C):** soil temperature measured @ 10 cm with thermocouples
11. **Air_temp:** air temperature measured within chamber using thermocouple
12. **CH_4 ($mmol\_m^{-2}\_d^{-1}$):** flux in millimoles per square meter per day
13. **err-CH_4 (same):** error on flux using same units as previous column
14. **CO_2 ($mmol\_m^{-2}\_d^{-1}$):** flux in millimoles per square meter per day
15. **err-CO_2 (same):** error on flux using same units as previous column
16. **CH_3Cl ($nmol\_m^{-2}\_d^{-1}$):** flux in nanomoles per square meter per day
17. **err-CH_3Cl (same):** error on flux using same units as previous column
18. **CH_3Br ($nmol\_m^{-2}\_d^{-1}$):** flux in nanomoles per square meter per day
19. **err-CH_3Br (same):** error on flux using same units as previous column
20. **CH_3I ($nmol\_m^{-2}\_d^{-1}$):** flux in nanomoles per square meter per day
21. **err-CH_3I (same):** error on flux using same units as previous column
22. **$CHCl_3$ ($nmol\_m^{-2}\_d^{-1}$):** flux in nanomoles per square meter per day
23. **err-$CHCl_3$ (same):** error on flux using same units as previous column
24. **Water_Table_depth (cm)**: average (n=9) depth to water table or to bedrock measured from surface at center of 9 sectors within the chamber (divide surface area into a 3x3 grid)- 2006 only
25. **Volumetric_Water_content (%vol/vol):** average (n=9) volumetric water content reading for the same 9 points within the chamber footprint (2006 only).
26. **Gravimetric_water_content (%):** Water content (water mass/total mass) measured from a 0-5 cm core taken at the center of the chamber site, as determined by oven drying at 105°C for at least overnight. (August 2005, 12 sites only.)
27. **Total_unsaturated_zone_volume (L):** Total volume of tundra peat between the surface and the water table/bedrock, calculated by summing up the separately calculated volumes of the 9 sectors within the chamber footprint. (2006 only)
28. **Unsaturated_zone_waterfree_volume (L):** Total Unsaturated Zone Volume minus the total estimated water volume within that zone; unfilled pore space. (2006 only)
29. **Total sphagnum (g/m^2):** dry weight of sphagnum moss collected between surface and peaty layer, normalized to square meter (Transects C-E, 2005 only).
30. **Live_sphagnum (g/m^2):** dry weight of green sphagnum moss in chamber footprint, normalized to square meter (Transects C-E, 2005 only).
31. **Total_Carex_aquatilis (g/m^2):** dry weight of Carex aquatilis (live and dead) in chamber footprint, normalized to square meter (Transects C-E, 2005 only)
32. **Live_Carex_aquatilis (g/m^2):** dry weight of live Carex aquatilis in chamber footpring, normalized to square meter (Transects C-E, 2005 only).
33. **C/N (g/g)**: ratio measured in soil core (August 2005, 12 sites only.)
34. **Predominant_vascular_plants (species_given_when_identified):** Predominant vascular plants that account for >80% of the live vascular dry biomass, listed in order of predominance. Biomass not estimated for boardwalk sites (1-8). Cover types for Toolik Lake were determined by inputing the GPS co-ordinates for each site into the Toolik Field Station GIS data base (http://www.uaf.edu/toolik/gis/index.html).

C. Description of flags, codes used in the data, and definitions

NaN: measurement not conducted or available.

n.s.: When calculated flux errors exceed the flux, 'n.s.' is written in both the flux and the error columns to indicate 'not significant'

****** : During 2005, several flux chambers drew down concentrations to near or below detection limits, which yielded very large and uncertain fluxes. For these sites, the flux was calculated using only the first two points, using a linear fit, and are indicated by '**' appended to the flux error number.

D. Data version number and date

Version 1.1 (April 25, 2009) of "MeX_netflux_2005_2006.txt"

E. Data remarks

These data are published in [*Rhew et al., 2007; Teh et al., 2009; Rhew et al., 2008*], with the following notes:

a. BEO sampling dates in 2005 are one day earlier in this corrected dataset than listed in Table 1 of Rhew et al., 2007.

b. 2005 CH_4, CO_2, CH_3Cl, CH_3Br and CH_3I flux data is in final form as of January 17, 2007.

c. 2006 CH_4 data is missing error estimates in this dataset, which may be added in a future update when located.

d. 2006 methyl halide net fluxes were presented in [*Teh et al., 2009*] and re-calculated again in 2009 for the purpose of consistency in this archival dataset here. These updated fluxes use the same Matlab script used to calculate the 2005 fluxes (with the slight variation of the error on the slope, as noted in section IV.E. above). Fluxes calculated by [*Teh et al., 2009*] differed slightly because of different weighting of uncertainties and different treatment of leakage from venting of static chamber. However, these differences are believed to be insignificant within the error of the flux.

F. Software compatibility

The files are suitable for opening in Microsoft Excel versions through 2008 or other spreadsheet software.

VI. REFERENCES

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Simmonds, P.G., R.G. Derwent, A.J. Manning, P.J. Fraser, P.B. Krummel, S. O'Doherty, R.G. Prinn, D.M. Cunnold, B.R. Miller, H.J. Wang, D.B. Ryall, L.W. Porter, R.F. Weiss, and P.K. Salameh, AGAGE observations of methyl bromide and methyl chloride at Mace Head, Ireland, and Cape Grim, Tasmania, 1998-2001, J. Atmos. Chem., 47 (3), 243-269, 2004.

Teh, Y.A., O. Mazéas, A. Atwood, T. Abel and R.C. Rhew, Hydrologic regulation of methyl chloride and methyl bromide fluxes in Alaskan Arctic tundra. *Global Change Biology*, doi:10.1111/j.1365-2486.2008.01749.x (2009).

APPENDIX: Header on Dataset

DATASET ID = MeX_netflux_2005_2006.txt
DATASET TITLE = Halomethane and methane net fluxes in northern Alaskan tundra, Barrow and Toolik Lake, 2005-2006
PI / DATA CONTACT: Rhew, Robert (University of California at Berkeley)
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DATA COVERAGE START DATE: 20050621
DATA COVERAGE STOP DATE: 20060725
LOCATION = Barrow and Toolik Lake, Alaska
DATA VERSION = 1.1 (24 April 2009)
REMARKS: Missing data = NaN
REMARKS: Minimum detectable fluxes follow:
REMARKS: CH_3Cl is 17 nmol m^{-2} d^{-1}
REMARKS: CH_3Br is 0.28 nmol m^{-2} d^{-1}
REMARKS: CH_3I is 0.11 nmol m^{-2} d^{-1}
REMARKS: $CHCl_3$ is 1.2 nmol m^{-2} d^{-1}
REMARKS: CH_4 minimum detectable flux is 0.03 mmol m^{-2} d^{-1}
REMARKS: Below minimum detectable flux = n.s.
REMARKS: *Predominant vascular plants that account for >80% of the live vascular dry biomass, listed in order of predominance. Biomass not estimated for boardwalk sites (1-8).
REMARKS: Cover types for Toolik Lake were determined by inputing the GPS co-ordinates for each site into the Toolik Field Station GIS data base (http://www.uaf.edu/toolik/gis/index.html).
REMARKS: ** denotes a flux based on 2 point linear fit (t=1 and t=20)
REMARKS: lat/long ~ 6 meters accuracy when minutes are 5 digits (xx.xxx)
REMARKS: See “MeX_2005_2006_README.pdf” for descriptions of columns.