An inversion algorithm for the detection of methane over the wetlands by open-path FTIR in various atmospheric conditions

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An intelligent inversion algorithm has been developed to determine the path averaged concentration of methane over wetlands from open-path Fourier-Transform InfraRed (FTIR) measurements. The algorithm, based on a Doesn't-Use-Derivative (DUD) non-linear least-squares method, is robust and yields accurate methane concentrations for all atmospheric conditions. Fifty-eight spectral channels were needed to accurately determine the concentration of methane in the presence of other absorbing gases, especially for water vapor at 100 percent humidity. Tests were made for mixtures of the first 12 gases on the HITRAN database at typical ambient concentrations. The algorithm is described with particular attention to applications of methane fluxes over Northern-Hemisphere wetlands.

Introduction

Methane is the most abundant greenhouse gas in the troposphere after water and carbon dioxide[1] and, on a per molecule basis, is 24.5 times more effective as a greenhouse gas than carbon dioxide.[2] At ~1750 ppbv, its current globally averaged tropospheric mixing ratio is more than twice as high as in preindustrial times.[3] Estimates of atmospheric conditions based on ice core chemistry indicate that the current methane mixing ratio is unprecedented over the past 420 000 years.[4] In addition, ice core data indicate that methane concentrations have been well-correlated with temperature over the long term.[4$6] It is likely that increased emissions from wetlands in response to climate change played a major role in the link between temperature and methane.[1]

Wetlands are the most important natural source of global methane emissions. Current estimates of methane emissions from natural sources are about 160 Tg CH_4/year,[2] with roughly 115 Tg CH_4/year originating from wetlands.[7] Approximately two-thirds of freshwater wetlands are located in high-latitude, remote regions.[8] These regions are expected to be disproportionately affected by global climate change and, at the same time, are difficult to access and therefore difficult to study. It is also unclear how wetland methane emissions will respond to global climate change. Several studies have shown that methane emissions increase with increasing temperature and soil moisture content (e.g., Refs. 9$12). Thus, there is a potential for a positive feedback loop with increasing temperatures resulting in increased methane emissions. It has been speculated that this response has contributed to the rise in net methane emissions over the last 2$5 years.[1] However, more studies are needed of methane emissions from wetlands in order to better constrain estimates of wetland methane emissions and to predict how they respond to climate change.

Current methods for analyzing methane emissions fall into two major categories: chamber-based methods and eddy correlation flux measurements that utilize direct measurement of atmospheric concentrations and analysis of micro-meteorological conditions. To date, most studies of methane emissions from wetlands have utilized chamber-based methods.[13] In this approach, gases that accumulate in the headspace of a closed chamber are sampled and analyzed, usually by GC$FID. This approach is sensitive, with a minimum detectable flux of ~ 0.6 Umol·m$^{$2}·h$^{$1} (Ref. 13), which is well below a œtypicalB wetland methane flux of 20 Umol·m$^{$2}·h$^{$1} (Ref. 14). However, it has several disadvantages. Because they require an accumulation time, chamber methods cannot be used to make continuous, real-time measurements and may be affected by non-steady-state diffusion. Installation of chambers disturbs the habitat and can sometimes lead to artificially high emission rates.[15] Chambers must be placed over a small area that is unlikely to be representative of the entire ecosystem. In addition, installation and monitoring chambers is labor-intensive and is not amenable to remote operation. These factors make it difficult to utilize chambers to comprehensively determine methane emission dynamics from heterogeneous wetland ecosystems, especially those found in remote, high-latitude environments.

Micrometeorological flux-gradient and nocturnal boundary layer methods when combined with Fourier-Transform InfraRed (FTIR) spectroscopy[16] have a number of advantages over the chamber methods. They can operate continuously for long periods of time without the need for human intervention, thus allowing continuous data. Several gases can be monitored simultaneously by the FTIR method as long as the instrument has sufficient spectral resolution and/or the absorption regions of the gases are not overlapping. Some of the disadvantages of the method are that the measurements must be used in combination with independent micrometeorological measurements such as vertical wind velocities in order to determine the fluxes of the trace gases. For a number of important trace gases the natural fluxes are below the detection limit of the method.

Both of the above methods measure the flux at a point source. Inferring the correct footprint of the emission from point source measurements can be prone to error.

In the current study, an inversion algorithm is developed for methane emissions from wetland ecosystems data that would come from a moderate resolution (0.05 cm^{-1}), portable FTIR instrument. Such an instrument is capable of remote operation and can provide real-time continuous measurements. The data yield path average concentrations, hence they are more representative of large areas, and when data are taken over several paths (i.e., several reflecting mirrors are employed) 2-D concentration maps[17] can be generated. In order to make such an instrument useful an intelligent inversion algorithm must be developed to consider data taken in a variety of meteorological conditions. In Section 1 the development of the algorithm is presented. Section 2 surveys applications where such a system and inversion algorithm would be useful. In the last section the work presented here is summarized.

1. Development of the inversion algorithm for FTIR measurements

Open path FTIR is an attractive choice for measuring the concentrations of trace atmospheric constituents. Some of the desirable properties of the open path FTIR are the ability to measure multiple trace gases simultaneously, cover a very broad spectral region, and make measurements that are representative of the path. Open path FTIR liberates one from having to calculate an average concentration across a path from a set of discrete measurements by providing the path average directly. When multiple paths are probed 2-D concentration profiles can be generated. This is a very desirable attribute for some applications.

The method of FTIR is well known and described in the literature, for the example, the Proceedings of the Aspen Conference.[18]

The suitability of high resolution FTIR for identification of trace atmospheric molecular species has been demonstrated by the California Institute of Technology's Jet Propulsion Laboratory (JPL) experiment: Atmospheric Trace Molecules Observed by Spectroscopy (ATMOS).[19] Government agencies (NASA, USAF) have also used large scale, expensive, high-resolution instruments and shown suitability of FTIR for trace atmospheric molecular species identification.[20–24] FTIR is theoretically sound for this application.

There are other relevant FTIR experiments. One, under Canadian government sponsorship,[25–28] showed that the FTIR approach is applicable to ground based, long path length use. This experiment, however, had only 1 cm^{-1} resolution and was not designed to identify and separate trace species. Gosz et al. did a parallel U. S. effort, with nearly identical experimental design.[29]

Lower resolution instruments (e.g. 1 cm^{-1}), though commonly available and often installed as air quality analyzers, are inadequate for the task when the trace molecules are not previously defined. Instruments with resolution better than 1 cm^{-1} are needed to apportion the spectrum, that is, to partition the spectrum with respect to the observed species components. Murcray et al. (Refs. 30, 31) have found that while 0.1 cm^{-1} resolution can be successful, 1 cm^{-1} resolution is inadequate for such apportionment. Hence, an instrument with at least 0.1 cm^{-1} or higher resolution should be used.

Given a field instrument of adequate resolution spectra can be recorded in many atmospheric conditions. The absorption of water vapor often makes regions of the spectrum useless in moderate to high relative humidity conditions. The aim of this study is to assess if an inversion routine can be developed that would allow measuring methane flux from the surface of wetlands using open path FTIR in a wide range of atmospheric conditions. This type of application requires a precise measurement, for the objective is to discern the vertical concentration profile of methane over the wetland. The vertical concentration gradient is combined with boundary layer meteorological measurements to calculate a flux of methane out of the surface of the wetland into the free atmosphere.

The goal of the work is to retrieve accurate, precise methane concentration values from open path FTIR measurements. Before developing an instrument and deploying it in the field, it is necessary to assure that such an approach will yield the needed data. As such, the development of the inversion algorithm that will answer these questions was done by utilizing synthetic spectra calculated from line parameters contained on the HITRAN database as the measured spectrum. The first 12 molecular species listed on the database were retained for the calculations and are listed along with their assumed ambient concentrations in Table 1.

Table 1. Molecules, tropospheric concentrations and retrieved concentrations with percent difference for the atmospheric conditions of the study

Molecule	Initial concentration*	Retrieved concentrations					
		296 K, 10% RH	Diff, %	296 K, 50% RH	Diff, %	296 K, 100% RH	Diff, %
H_2O**		2.75E-03	2.84E-02	1.38E-02	2.72E-01	2.75E-02	2.01E-01
CO_2	3.5E-04	3.4976E-04	6.91E-02	3.4803E-04	5.62E-01	3.4803E-04	5.62E-01
O_3	2.0E-07	2.0053E-07	2.66E-01	1.9974E-07	1.32E-01	1.9955E-07	2.25E-01
N_2O	3.0E-07	2.9972E-07	9.43E-02	3.0018E-07	5.83E-02	3.0018E-07	5.93E-02
CO	5.0E-07	5.0027E-07	5.40E-02	4.9964E-07	7.14E-02	4.9950E-07	9.98E-02
CH_4	**1.5E-06**	**1.4986E-06**	**9.33E-02**	**1.4995E-06**	**3.33E-02**	**1.4978E-06**	**1.49E-01**
O_2	0.2095	0.2095	NA	0.2095	NA	0.2095	NA
NO	5.0E-07	5.0713E-07	1.43E+00	4.9609E-07	7.81E-01	4.8982E-07	2.04E+00
SO_2	2.0E-07	1.8723E-07	6.38E+00	1.2575E-07	3.71E+01	1.2505E-07	3.75E+01
NO_2	5.0E-07	5.0102E-07	2.04E-01	5.1910E-07	3.82E+00	5.1944E-07	3.89E+00
NH_3	2.5E-08	2.4952E-08	1.91E-01	2.6435E-08	5.74E+00	2.6461E-08	5.84E+00
HNO_3	5.0E-08	5.1264E-08	2.53E+00	5.1037E-08	2.07E+00	5.0985E-08	1.97E+00
Molecule	Initial concentration*	278 K, 10% RH	Diff, %	278 K, 50% RH	Diff, %	278 K, 100% RH	Diff, %
H_2O**		8.5630E-04	5.67E-01	4.2715E-03	3.34E-01	8.5419E-03	3.21E-01
CO_2	3.50E-04	3.4764E-04	6.74E-01	3.4781E-04	6.27E-01	3.4780E-04	6.30E-01
O_3	2.00E-07	1.9996E-07	2.15E-02	1.9998E-07	1.05E-02	1.9988E-07	5.90E-02
N_2O	3.00E-07	3.0020E-07	6.63E-02	3.0035E-07	1.15E-01	3.0034E-07	1.12E-01
CO	5.00E-07	4.9950E-07	9.94E-02	4.9977E-07	4.60E-02	4.9976E-07	4.78E-02
CH_4	**1.50E-06**	**1.4992E-06**	**5.47E-02**	**1.4999E-06**	**2.00E-03**	**1.4998E-06**	**1.47E-02**
O_2	0.2095	2.0950E-01	NA	2.0950E-01	NA	2.0950E-01	NA
NO	5.00E-07	4.9576E-07	8.49E-01	4.9615E-07	7.69E-01	4.9610E-07	7.80E-01
SO_2	2.00E-07	1.3835E-07	3.08E+01	1.3614E-07	3.19E+01	1.3513E-07	3.24E+01
NO_2	5.00E-07	5.1707E-07	3.41E+00	5.1722E-07	3.44E+00	5.1730E-07	3.46E+00
NH_3	2.50E-08	2.6223E-08	4.89E+00	2.6251E-08	5.00E+00	2.6263E-08	5.05E+00
HNO_3	5.00E-08	-2.382E-03	4.76E+06	2.2610E-03	4.52E+06	-3.955E-02	7.91E+07

* Molecular concentrations are tropospheric values obtained from Seinfeld and Pandis (Ref. 40).

**Initial concentration of water vapors corresponds to 10, 50, and 100% relative humidity.

The calculation of the synthetic spectra assumed typical atmospheric concentrations of the trace gases, see Table 1. Simulations were done at 296 and 278 K, with a path length of 250 m, atmospheric pressure of 1 atm, and relative humidity values of 10, 50, and 100 percent. Contributions from line wings were taken to extend 25 cm^{-1} to either side of line center. The molecular absorption across an open, horizontal path is modeled by the Beer–Lambert Law with a Lorentzian line shape, and the monochromatic transmission is given by

$$T(\nu) = \exp\left\{-\sum_k \left[\sum_{if} \frac{S_{if}}{\pi} \frac{\gamma_{if} P_T}{[(\nu_0 - \nu_{if})^2 + (\gamma_{if} P_T)^2]}\right] N_L P_k L\right\},$$

(1)

where N_L is the Loschmidts number $2.479 \cdot 10^{19}$ molec/(m³·atm) at 296 K, L is the length of the path, P_T is the total pressure, the subscript, if, denotes the line $i \to f$ of the kth molecule, γ is the half-width, ν_0 is the line center vacuum position, S is the line strength, and P_k is the partial pressure of the kth molecule. The parameters S, γ, and ν_0 are all taken from the HITRAN 96 database. The spectra were determined over a wavenumber range 800 cm^{-1} to 4500 cm^{-1}. The calculations were made at three different values of relative humidity thus producing three different spectra that are the foundation of the study.

The synthetic spectra were then convolved with an instrument response function of resolution 0.08 cm^{-1} and random Gaussian noise with a standard deviation derived from an assumed signal to noise ratio of 80:1 was added, where 1 is the standard deviation of the random noise with zero mean. Note, this is a conservative estimate of the S/N ratio of the instrument.

These spectra were analyzed and compared with plots of the pure methane spectrum. The nature of the infrared spectra at the earth's surface is very crowded with absorption features from many different trace gases. It is impossible to «look at» methane without seeing other trace gases. Thus, the quality of the fit for methane will depend on the quality of the fit over the entire spectral region. NLLS fits of all the trace gases simultaneously overcome the problem of overlapping lines from competing species. A number of channels (spectral micro-windows) were chosen to optimize the retrieval of methane concentrations for the typical range of atmospheric conditions over the wetlands. Tests considered the temperature range 278 to 296 K and relative humidity values of 10, 50, and 100 percent. These channels included regions where methane absorbed with minimum competition from the

other 11 species as well as regions where the other trace gas concentrations could be determined accurately. The channels are listed in Table 2.

Table 2. Channels used for the retrieval of methane

Channel	Range, cm^{-1}		Channel	Range, cm^{-1}		Channel	Range, cm^{-1}	
1	805	807	21	1227	1238	41	2115	2124
2	808	849	22	1240	1244	42	2125	2135
3	855	908	23	1245	1257	43	2140	2145
4	910	921	24	1261	1264	44	2147	2151
5	922	947	25	1273	1280	45	2153	2161
6	949	1015	26	1281	1284	46	2164	2186
7	1017	1041	27	1291	1296	47	2188	2205
8	1042	1066	28	1298	1304	48	2207	2275
9	1068	1091	29	1898	1901	49	2391	2500
10	1092	1106	30	1978	1986	50	2500	2600
11	1107	1110	31	2000	2006	51	2600	2700
12	1112	1120	32	2010	2015	52	2700	2800
13	1122	1136	33	2028	2033	53	2800	2900
14	1138	1149	34	2047	2060	54	2900	2933
15	1154	1165	35	2067	2074	55	2934	2954
16	1166	1173	36	2079	2081	56	2955	2965
17	1175	1186	37	2082	2087	57	2975	2980
18	1188	1198	38	2091	2096	58	2980	2990
19	1199	1210	39	2098	2100			
20	1213	1217	40	2101	2113			

The basic idea for reducing concentrations from a measurement is as follows. The FTIR instrument makes a measurement of the transmission of radiation through the path. There are a number of other factors contained in the measurement that must be understood, such as the instrument line shape, effects of phase error, the background, the 0% and 100% transmission levels, and apodization of the signal. These factors must be modeled in the least-squares (LS) fit approach. The transmission, T, is defined as the ratio of the observed intensity over the incident intensity; the absorbance is given by $-\log T$. Most LS algorithms choose to work in absorbance space because it casts the problem in a linear space. This however requires the 0% and 100% transmission levels and many of the corrections to be known accurately. A more robust approach is to remain in transmission space and solve the problem using a non-linear least-squares (NLLS) fit approach. Although this is more time consuming and difficult computationally, it has many advantages. The baseline and 100% transmission levels, phase error, aperture and jitter effects, etc. can now be included in the solution. Using accurate models to describe these effects reduces their influence on the final reduced concentrations. The NLLS fitting algorithm, developed here, is a derivative-free Gauss–Newton algorithm[32] that (except for the additional evaluations needed for starting) gives one iteration for each function evaluation under normal conditions. The Gauss–Newton approach is fast and has intimate connections with maximum likelihood estimation algorithms[33–36] and the modern methods of robust estimation.[37] This algorithm is ideally suited to the reduction of spectra.[38]

The NLLS method requires the specification of a numerical model, in this case the Beer–Lambert Law, which takes parameter estimates and calculates a synthetic spectrum. The parameter estimates, **P**, (bold type indicates a vector quantity) are used to calculate $f(\mathbf{P})$, which is a non-linear function in the parameter values. The goal is to minimize the function:

$$RSS(\mathbf{P}) = \sum_i [y_i - f_i(\mathbf{P})]^2, \qquad (2)$$

where y_i is ith component of the observed (measured) data, and $f_i(\mathbf{P})$ is the corresponding calculation. The elements of **P** are the variable parameters that are used in $f_i(\mathbf{P})$, which is Beer's Law. The only parameters that are unknown (variable) are the concentrations of the molecules, and all the other parameters used in the calculation are the atmospheric conditions and data from the HITRAN database. The NLLS estimates of the concentrations are the estimates that provide the smallest sum of the square differences. The summation occurs over all of the points in each of the 58 channels.

NLLS has the desirable properties of being asymptotically efficient, and asymptotically consistent. This is to say that as the number of observations goes to infinity, the variance in the parameter estimates decreases to smaller values and the systematic errors go to zero. Thus, any difference between the observed and calculated spectra may be attributable to random Gaussian noise, and not to any inaccuracies in the models used to calculate the spectrum.[39]

The NLLS method used in this study was a modified version of the Doesn't Use Derivatives (DUD) algorithm.[32] DUD requires that only the synthetic spectra be calculated and not the derivatives of synthetic function (Beer–Lambert Law). The process involves approximating $f(\mathbf{P})$ by an affine function of **P** near an initial estimate of **P⁰**. This sets up an approximate linear least squares problem that is solved with the solution becomes the new **P⁰**. This process continues until successive estimates of **P⁰** do not change significantly.

Table 1 presents the results of the inversion algorithm for the 12 trace gases considered in this work. The assumed tropospheric trace gas concentrations are values taken from Seinfeld and Pandis,[40] and are listed in the second column. The upper part of the table are for 1 atm and 298 K conditions and the lower part of the table are for 1 atm and 278 K. The derived concentration of the trace gases and the percent difference from the simulation value are then given for the 10% RH, 50% RH, and 100% RH spectra. Under all conditions of relative humidity and temperatures considered here, the retrieved methane concentrations are very good with a maximum percent difference of 0.1.

2. Discussion

Wetlands are ideal sites to test the utility of the field path FTIR system for measuring methane fluxes

since, unlike most upland ecosystems, they are known strong sources of methane. High emissions from wetlands would be expected to provide relatively steep gradients of atmospheric methane even during daytime periods when air is most unstable. For example, while Griffith et al.[16] reported that the daytime gradients of atmospheric methane in an agriculture field were not steep enough to compute fluxes, Friborg et al.[41] readily measured daytime fluxes from an arctic fen using eddy correlation techniques. An FTIR beam path of 250 m would be very useful for determining methane emissions in wetlands since wetland fluxes exhibit strong temporal[42] and horizontal[43] heterogeneity. Hence, a technique that averages this heterogeneity would yield a better estimate of the ecosystem flux than one that samples only one point. In addition, by deploying several mirrors, it is possible to use the FTIR system for the acquiring data to construct a two- or three-dimensional map of methane concentrations in the air above a wetland.

A primary goal of methane flux studies is to accurately estimate methane emissions over relatively large spatial scales.[42,44] Although many studies have utilized enclosure techniques (chambers) to estimate methane fluxes,[45$47] extrapolating flux chamber data is fraught with uncertainty since chamber footprints are of the order of 1.0 m^2 or less. Micrometeorological techniques that use relatively high towers increase the measurement footprint, which for data collected at 12 m height are less than 1000 m from the tower, with the bulk of the flux contribution originating from surfaces 100$200 m upwind.[48] The FTIR utilizes a 250 m path length that opens the possibility of using a horizontal path in the field that would yield methane data representing an average concentration over that distance. This differs from a previous FTIR application where point source samples were collected and passed through an enclosed FTIR cell.[16] Deployment of mirrors in the field should improve the accuracy of estimating fluxes since the footprint will be better constrained. These measurements still require at least two vertical data points for a gradient to be calculated and they require knowledge of meteorological parameters needed to calculate a flux. Eddy correlation fluxes are computed from covariances between vertical wind and concentrations of trace gases[49] and the former can be acquired from a sonic anemometer (e.g., Gill Instruments, Ltd) deployed on a short meteorological tower (< 3.0 m) placed in the middle of the habitat of interest.[41] Depending on the physical heterogeneity of the terrain, it may be necessary to use more than one tower to adequately determine the wind field, but a single tower should suffice for relatively homogenous terrain and for night emissions estimated by nocturnal boundary layer methods.[16] However, the field deployed FTIR would be most advantageous when the horizontally averaged data are combined with appropriate micrometeorology data under more complex atmospheric conditions. Ideally, the path of the FTIR

beam should be perpendicular to wind direction, although a parallel path may still yield reasonable flux estimates.

Although methane is an important gas, FTIR can measure a variety of gases, which allows for studies of several important gases simultaneously. For example, wetlands are known sources of volatile sulfur gases such as dimethylsulfide and hydrogen sulfide,[50] and some wetlands emit nitrogen oxides.[51] The technology could also be applied to uplands, which are noted sources of nitrogen oxides[52,53] and sinks for carbonyl sulfide,[54] among others. Therefore, with the application of appropriate algorithms, it should be possible to obtain uninterrupted data for multiple gases for extended periods of time in a variety of environments.

Summary

A non-linear least-squares spectral inversion algorithm has been developed to take the spectra produced by a moderate resolution (0.08 cm$^{$1}$) open-path FTIR instrument and produce path averaged concentrations for a number of atmospheric trace gases. Here the emphasis was on methane. In order to reproduce the concentrations of the simulated spectra to high accuracy, it was necessary to choose fifty-eight channels to correctly model the other trace gases that interfere with the methane signal. The algorithm was tested at several levels of relative humidity and worked well under all conditions tested. Thus, coupled with a portable FTIR system the algorithm could produce continuous data via remote operation.

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