Long open-path, TDL based system for monitoring methane background concentration for deployment at Jungfraujoch High Altitude Research Station-Switzerland

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A new, long open-path instrument for monitoring of the background methane concentration path-averaged over 1000m will be presented. The instrument allows monitoring of water vapor concentration as well. The instrument is built on the monostatic scheme (transceiver – distant retroreflector). A VCSEL tunable diode laser (TDL) with a central wavelength of 1654 nm is used as a light source. The receiver is built around a 20 cm Newtonian telescope. To avoid distortions in the shape of a methane line, caused by atmospheric turbulences, the methane line is scanned within 1μs. Fast InGaAs photodiodes and a 200 MHz, 14 bit ADC are used to achieve this scanning rate. The expected concentration resolution for the above mentioned path-lengths is of the order of 1 ppb with accuracy better than 5%.

The instrument is developed at the Swiss Federal Institute of Technology – Lausanne (EPFL) Switzerland and will be used within the GAW+ CH program for long-term monitoring of background methane concentration in the Swiss Alps. After completing the ongoing initial tests at the EPFL, the instrument will be installed in 2012 at the High Altitude Research Station Jungfraujoch (HARSJ). The HARSJ is located at 3580 m ASL and is one of the 24 global GAW stations and carries on continuous observations of a number of trace gasses, including methane. One of the goals of the project is to compare path-averaged to ongoing point measurements of methane in order to identify possible influence of the station. Future deployments of a copy of the instrument could include the Colombian part of Amazonia and Siberian wetlands.

1. Introduction

A number of gases are involved in the anthropogenic enhancement of the greenhouse effect. The most important of these greenhouse gases (GHGs) are carbon dioxide (CO_2); methane (CH_4); nitrous oxide (N_2O); halocarbons (HC); and tropospheric ozone (O_3). Methane has a special place among these gases since its global warming potential is 25 times or even 72 times larger than the potential of CO_2 in 100 yr. and 20 yr. time horizons respectively [1]. Beside the direct radiative forcing (RF), estimated to +0.48 Wm^{-2} methane has important indirect effect because of its chemical reactivity resulting in a total RF of +0.7 Wm^{-2}. The indirect radiative effects of methane result mostly from reaction with atmospheric OH. This reaction: reduces the OH concentration, leading via a positive feedback to an enhancement of methane and some HC lifetimes; produces additional CO_2; enhances stratospheric water vapor; and increases tropospheric ozone concentration through the methane production chain. Because of concentrations lower than those of CO_2, at present methane has the second-largest radiative forcing (RF) effect after CO_2.

Methane is emitted by natural and anthropogenic sources with anthropogenic sources accounting for 60% of the total CH_4 budget at present. The main natural sources are wetlands, termites, oceans, geological sources, methane hydrates, and wildfire. The most important anthropogenic sources are energy production, (including mining, fossil fuel production, distribution and use), rice agriculture, ruminant animals, landfills, waste treatment and biomass burning. The main methane sinks are the oxidation by tropospheric OH, oxidation in soils and loss to stratosphere.

Methane concentrations have increased almost 2.5 times since 1750 reaching 1774 ppb in 2005. Systematic measurements over the last 25 years show a 30% increase in methane concentrations during that period. This increase is not monotonic, with greater than 1% per year growth rates in the late 1970 and early 1980, slowing down to zero or negative values during 1999-2005 with substantial interannual variations in the period 1988-2005. Recent data show renewed growth of atmospheric methane [2] during last years. The reasons for the decrease and variability in the CH_4 growth rate and the implications for future changes are not understood although a number of hypotheses were suggested [1]. In response to an increase in global average temperature, large quantities of methane can be released in relatively short time scales from geological storage, such as methane hydrates and permafrost and through biogenic processes. The global temperature increase can cause significant increase in methane concentrations since 70% of the atmospheric methane originates from biogenic sources, which are highly sensitive to climate variables. Recent studies have shown that the permafrost contains approx. 500-900 Gt carbon, up to 30 % of which can be converted in methane by microorganisms during thawing [3, 4, 5]. In response to climate warming, permafrost has already begun to thaw, with extreme projections that by the end of the century it will have thawed almost completely. Climate changes also affect the stability of methane hydrates beneath the ocean where ~4 Tt are stored [6]. The latest observations of the Siberian Arctic shelf suggest that 900 Gt methane are stored there in methane hydrate deposits and as a free gas below the hydrate deposits. There is high probability that 50 Gt methane of this storage can be released abruptly at any time due to

the changes in sea water temperatures, related to the melting of Arctic ice, or as a result of geological events [7, 8, 9]. Data from September 2005 show high (12000%) CH_4 super saturation of surface water, and high (up to 8 ppm) CH_4 concentration in the atmospheric layer above the sea surface over the East Siberian Shelf [7].

Currently several networks and governmental organizations systematically measure methane concentration in surface air [1]. NOAA/GMD is the most geographically extensive network operating 40 surface air flask-sampling sites and acquiring data almost weekly since 1983 [10]. GAGE/AGAGE network operates 5+3 sites equipped with automatic systems with sampling rates up to 36 samples/24h since late 1980 [11]. All networks use exclusively the gas chromatograph (GC) technique with a flame ionization detector (FID) for measuring CH_4 concentration. With a proper calibration, this technique can supply measurements with relatively good sensitivity and precision of 0.2-1%. Since the measurement process depends on a number of external parameters, to achieve sufficient correlation among measurements taken with different instruments and between consecutive runs taken with the same instrument, the GC requires calibration with a precise standard gas mixture before every sample measurement. Drifts and shifts in the standard scale [12] may require reassessment of the whole data series. In addition, GC instruments have relatively high initial price and operational costs because of the need of expensive consumables (high and very-high purity gases), the need of special environment (housing), and regular maintenance by qualified personnel. Since the sampling is done at a fixed point, the measurements can be easily altered by sample taking and can be affected by local sources, sinks, or local transport, particularly in poorly mixed atmospheres as in the case of wetlands where concentration can vary by orders of magnitude for distances of several meters. Therefore, point measurements lack the spatial representativeness needed for modeling purposes. Because of all these factors GC are not suitable for the enlargement of the existing CH_4 networks as envisaged in the GAW 2008-2015 strategic plan especially in Arctic and tropical regions.

Infrared (IR) spectral analysis techniques such as Fourier Transform Infrared (FTIR) or Tunable Laser Absorption Spectroscopy (TLAS) are widely used for accurate quantitative measurements of trace gas concentrations [13]. The concentration is derived from IR absorption measured over an optical path. The sensitivity and the precision of these measurements depend strongly on the path-length. To achieve sufficient sensitivity and precision for trace concentration measurements, the path length is extended either by using multiple-path cells or measuring over long-path in open air (referred to herein as "open-path" or OP). The multiple-pass technique allows compact instrumental design and relatively easy calibration but being a point measurement technique suffers from the same drawbacks as the GC technique mentioned above. In the OP technique the concentration measurements are averaged over an extended path, and therefore are much less affected by local unrepresentative fluctuations in gas concentration than measurements taken with point sensors. The passive open-path FTIR method uses the Sun as a light source and has been used to produce continuous, long time series of high quality, total column GHGs data [14]. The FTIR method, however, is limited to only daytime and clear weather conditions. The active OP-FTIR can be operated around the clock but the achievable absorption paths are usually short (< 1000 m) because of the use of non-coherent light sources, which leads to low sensitivity. Both OP-FTIR methods require significant resources and expert knowledge to ensure proper deployment, operation, and final data production. Furthermore, FTIR instruments are delicate and have moving parts, which makes them difficult to deploy in field conditions.

The advances in semiconductor laser science and technology has made available tunable, sources for real-time TLAS monitoring of a large number of molecular species in the IR. Tunable Diode laser (TDL)and Quantum Cascade Laser (QCL) based point measurements of a number of trace gases including CO_2, CH_4, O_3 N_2O and other have been successfully demonstrated in recent years [15, 16, 17, 18, 19, 20] and commercial instruments [21, 22, 23] have become available recently. The majority of these experiments and most commercial instruments are however, designed for point observations. Some successful OP experiments have been carried out in the late 1970, but because of the lack of suitable laser sources, these type measurements did not find wide applications. Recently with the appearance of new laser sources, OP measurements of methane have been reported and commercial instruments [24] are available. These instruments however are designed mostly for detecting gas leaks or measuring higher than background concentrations.

In this paper we describe a new, TDL based OP instrument for monitoring of the background methane concentration. The instrument is developed at the Swiss Federal Institute of Technology – Lausanne (EPFL) Switzerland and will be used within the GAW+ CH program for long-term monitoring of background methane concentration in the Swiss Alps. After completing the ongoing initial tests at the EPFL, the instrument will be installed in 2012 at the High Altitude Research Station Jungfraujoch (HARSJ). The HARSJ is located at 3580 m ASL and is one of the 24 global GAW stations and carries on continuous observations of a number of trace gasses, including methane. One of the goals of the project is to compare path-averaged to ongoing point measurements of methane in order to identify possible influence of the station. Future deployments of a copy of the instrument could include the Colombian part of Amazonia and Siberian wetlands.

2. Theory of operation

The OP TDL technique employs the absorption spectroscopy principle to obtain species concentration. The concentration C is derived from the measured over the sample length L light transmittance $T(\nu)$ as

$$C = \frac{\ln T(\nu)}{\sigma(\nu)L}$$

where $\sigma(v)$ is wavelength (v) dependant absorption cross section, specific for the detected substance. The transmittance is measured by sweeping repeatedly the laser wavelength across an absorption line of the species being detected. The transmittance measured outside of the absorption line is used to correct for light losses other than species absorption. To achieve sufficient sensitivity (of the order of ppbv), the open-path monitoring uses long optical paths through the atmosphere. This gives a path-averaged value of the species concentration.

The main features of the OP TDL method, which make it a valuable technique for atmospheric measurements, can be summarized as:

- As a high-resolution spectroscopic technique it is virtually immune to interferences by other species, a problem that plagues most competing methods.
- As a differential spectroscopic technique the method allows straightforward calibration and cancelation of background absorption
- Concentration measurements are averaged over an extended path, and therefore are much less affected by local unrepresentative fluctuations in gas concentration than measurements taken with point sensors.
- It offers continuous measurements at time-constants of tens of seconds or so with ppb or sub-ppb low detection limit. The time-constant of the technique can be traded off against sensitivity and this can allow flux measurements of relatively abundant species by the eddy-flux correlation technique.
- Measurements can be made in regions of difficult access, especially above ground level.
- There is no material contact between gas and sensor and thus there is no degradation of the gas being measured or "poisoning" of the sensor.
- Several species can be measured simultaneously with a single laser
- It is a general technique. The same instrument can easily be converted from one species to another by changing the laser or the laser temperature. Furthermore, the number of simultaneously measured species can be extended by multiplexing the outputs of several lasers.

3. Instrument design and deployment

The instrument consists of a transmitter-receiver and distant retroreflector operated in monostatic configuration as shown in Fig. 1. The transmitter-receiver is designed as a compact block built around the receiving telescope. The transmitter uses a Vertical Cavity Surface Emitting Laser (VCSEL) with a central wavelength 1.654 μm, current-tuned over 3 nm. The relatively wide tuning range of the laser allows simultaneous measurements of water vapor using a water vapor absorption band centered at approx. 6047.8 cm^{-1}. The laser radiation is collimated by an off-axis parabolic mirror and directed to the retroreflector along the telescope optical axis. For alignment purposes a green tracing laser beam is transmitted coaxially to the IR laser beam. The telescope is Newtonian type with 20 cm diameter of the main mirror. Peltier cooled InGaAs photodiode and a low-noise transimpedance amplifier are used in the receiver. To avoid distortions in the line shape, caused by atmospheric turbulences, the methane line is scanned within 1μs. The acquisition is carried out by a fast 14 bit, 200 MHz ADC card installed in a PC. The laser, the collimating optics, and the receiver detector are fixed on the telescope. A retroreflector with 15 cm clear aperture was assembled from flat mirrors using the technology for building and alignment developed at EPFL. The instrument is controlled via LabView based software. To ensure better than 1 ppb accuracy the data treatment software will take into account the actual atmospheric pressure and temperature measured at the two ends of the optical path and laser power variations.
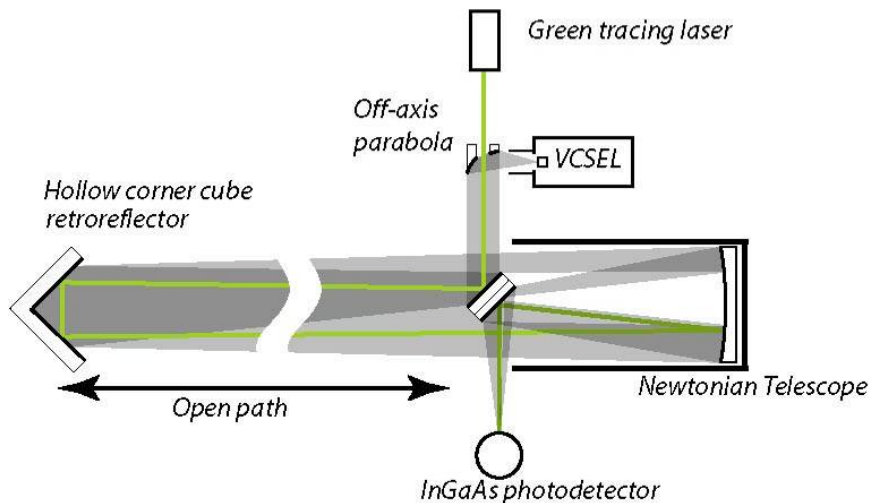

Fig. 1. Optical schema of the instrument. The enclosures of the transceiver and the retroreflector are not shown here for simplicity.
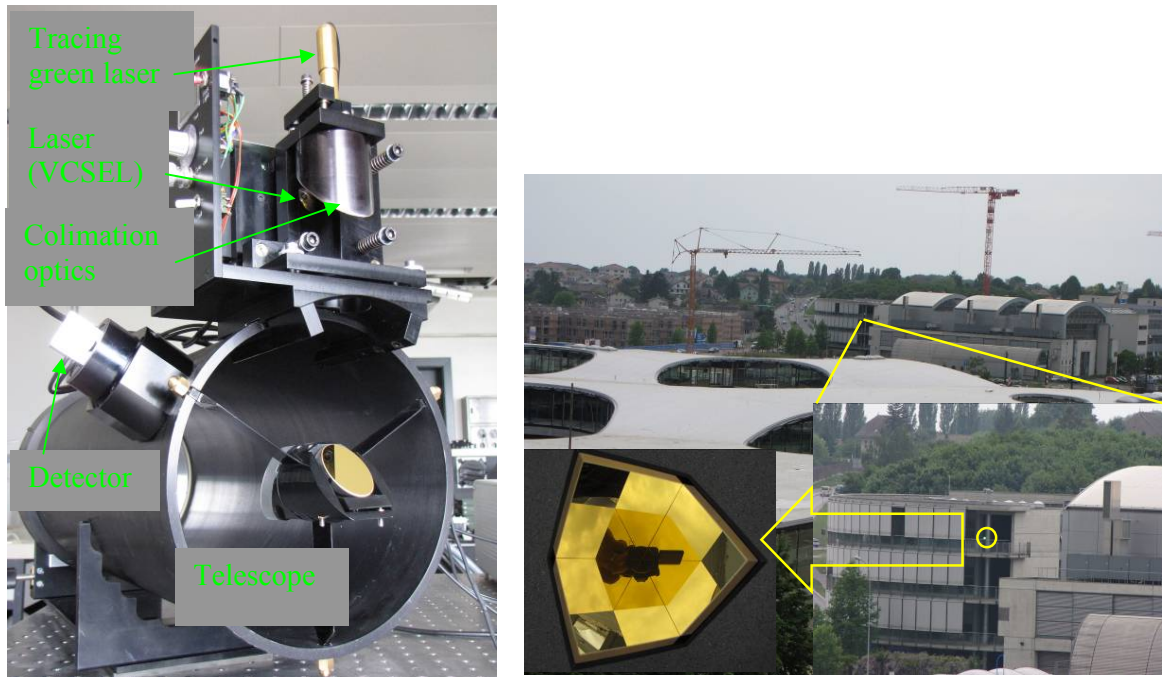
Fig. 2 *Left* A photograph of the open-path instrument for monitoring background methane concentration. *Right pane;l* Instrument transceiver. L*eft panel*. The measuring site at EPFL showing the position of the retroreflector. The inset shows a close picture of the retroreflector.

The instrument has already been built and extensive tests measurements over 1000 m optical path has been carried out. A picture of the instrument is shown on the left panel of Fig. 2. The right panel of the same figure shows the deployed at the EPFL campus indicating the position of the retroreflector.

A comparison between a simulated (using HITRAN database) and experimentally measured atmospheric absorption taken during the tests is shown in Fig. 3. Well-expressed methane and water vapor spectral features are clearly seen in the figure. The signal level and signal to noise ratio allow us to estimate that the measurement of ambient CH_4 concentrations with accuracy and precision better than 1 ppb is feasible with the current configuration for acquisition times of the order of tens of seconds. The lower detection limit for water vapor is expected to be of the order of tens of ppb.

Fig.3. Atmospheric absorption spectrum in the vicinity of 6047 cm^{-1} CH$_4$ line. *Upper panel*, HITRAN [25] based simulation; 1.79 ppm CH$_4$, 4% H$_2$O, 1000 m optical path. *Lower panel,* Measured over 1000 m path length spectrum. The signal is averaged over 2000 laser pulses (0.5 s), time for scanning the CH$_4$ line 1µs.

After completing the ongoing initial tests at the EPFL, the instrument will be installed in 2012 at the High Altitude Research Station Jungfraujoch (HARSJ). Due to its high-altitude location (3580 m ASL) the HARSJ is situated most of the time in the free troposphere allowing background trace gas monitoring. HARSJ is one of the 24 global GAW stations and carries on continuous observations of a number of trace gasses, including methane by a gas chromatograph and an FTIR system. The transceiver will be installed in the Sphinx observatory of HARSJ and two possible positions of the retroreflector are envisaged; a PTT station at approx. 1.1 km west from HARSJ and the surroundings of Mönchsjohhütte hut at approx 2.3 km NE from HARSJ (Fig. 5). The PTT station is located at an altitude of 3800 m ASL and has suitable infrastructure allowing easy installation and maintenance of the retroreflector. The Mönchsjohhütte hut is located at 3627 m ASL and is accessible part of the year.
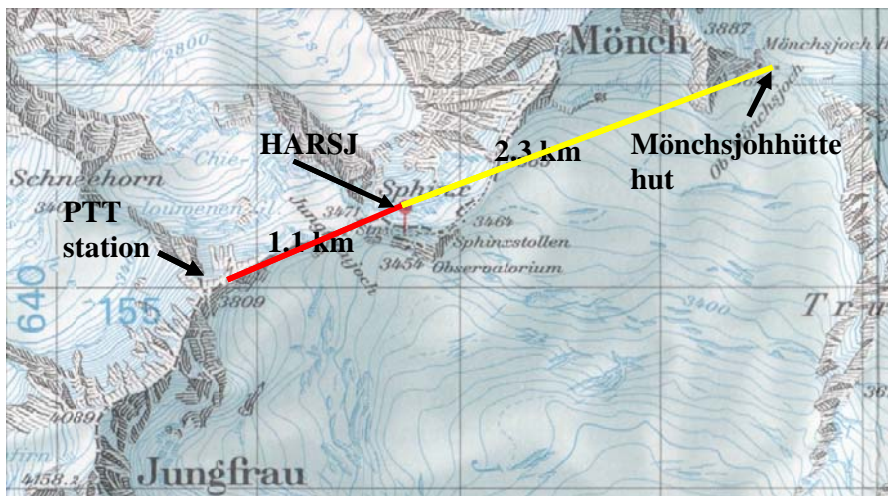

Fig. 4. Possible optical paths from HARSJ

The next phase of the project is due for experimental measurements, comparison with the operational at Jungfraujoch point and remote measurements and analysis of the results. To define the weather dependence measurements will be carried out in different weather conditions. Because of the short acquisition time of the open-path mid IR system, measurements will be possible in scattered clouds in short time intervals. The comparison with the regular point gas chromatograph and TDL multi-pass cell measurements and with the FTIR space-averaged measurements will be carried out. The goal of the intercomparison is not only to verify the TDL-open-path data but also to identify possible influence of the emissions from the Jungfraujoch station and tourist sites on the point GHGs measurements. The Jungfraujoch is a very busy tourist site with a highly sophisticated infrastructure and up to 8'000 visitors per day; therefore there always exists the possibility that emissions from the Jungfraujoch tourist facilities can affect the point measurements of CH_4 and water vapor to a much larger extent than the long open path measurements. Since the TDL instrument will supply data averaged over one (two) kilometers this could possibly allow the identification of the Jungfraujoch station's influence on the GHGs measurements by studying the differences between the point and spatially averaged data, and visitor statistics and meteorological conditions.

4. Conclusion

A new, long open-path instrument for monitoring of atmospheric water vapor and background methane concentration path-averaged over 1000m was developed at the Swiss Federal Institute of Technology – Lausanne (EPFL) Switzerland. The instrument is built on the monostatic scheme (transceiver – distant retroreflector). Using an IR Vertical Cavity Surface Emitting Laser in the transmitter. The receiver is built around a 20 cm Newtonian telescope. To avoid distortions in the shape of a methane line, caused by atmospheric turbulences, the methane line is scanned within 1μs. Fast InGaAs photodiodes and a 200 MHz, 14 bit ADC are used to achieve this scanning rate.

The instrument will be used within the GAW+ CH program for long-term monitoring of background methane concentration in the Swiss Alps. After completing the ongoing initial tests at the EPFL, the instrument will be deployed in 2012 at the High Altitude Research Station Jungfraujoch (3580 m ASL). Future deployments of a copy of the instrument could include the Colombian part of Amazonia and Siberian wetlands.

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23. http://www.picarro.com/markets/greenhouse/

24. http://www.boreal-laser.com   The announced (web page) maximum path is 1000 m. According to a company engineer the real maximum path is 400 m with a possibility to extend the path length to 1000 m using a multi-retroreflector array that has to be developed specially. Our experience of using multi-reflector arrays with QCL and TDL systems shows that multi-reflector configuration when used with coherent sources produces dynamic interference fringes which compromise the measurement. The fringes are caused by the interference of the modulated by atmospheric turbulence beams that originate from individual retroreflectors. Paper on this subject is on preparation.