# Atmospheric $CH_4$ and $N_2O$ measurements near Greater Houston area landfills using a QCL-based QEPAS sensor system during *DISCOVER-AQ 2013*

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A quartz-enhanced photoacoustic absorption spectroscopy (QEPAS)-based gas sensor was developed for methane ($CH_4$) and nitrous-oxide ($N_2O$) detection. The QEPAS-based sensor was installed in a mobile laboratory operated by Aerodyne Research, Inc. to perform atmospheric $CH_4$ and $N_2O$ detection around two urban waste-disposal sites located in the northeastern part of the Greater Houston area, during *DISCOVER-AQ*, a NASA Earth Venture during September 2013. A continuous wave, thermoelectrically cooled, 158 mW distributed feedback quantum cascade laser emitting at 7.83 μm was used as the excitation source in the QEPAS gas sensor system. Compared to typical ambient atmospheric mixing ratios of $CH_4$ and $N_2O$ of 1.8 ppmv and 323 ppbv, respectively, significant increases in mixing ratios were observed when the mobile laboratory was circling two waste-disposal sites in Harris County and when waste disposal trucks were encountered. 

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Atmospheric $CH_4$ and $N_2O$ mixing ratios were measured during the September 2013 Houston-based NASA field campaign *DISCOVER-AQ* (Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality, www.discover-aq.larc.nasa.gov/science.php). These gases play a major role in global warming, with 100-year time horizon global warming potentials of 25 ($CH_4$) and 298 ($N_2O$) [1,2]. According to the Environmental Protection Agency, landfills constitute the third largest source of $CH_4$ emission in the United States, while $N_2O$ emissions are mainly associated with agricultural soil management [3]. Limited measurements of $N_2O$ have been reported in landfill areas. Hence $N_2O$ emission measurements as a function of the environmental conditions within a landfill site and of the nitrogen content of the waste being disposed are needed [4].

During the last 10 years, different techniques, such as tunable diode laser absorption spectroscopy [5,6], photoacoustic absorption spectroscopy [7], and cavity-enhanced absorption spectroscopy [8] were employed for $CH_4$ and $N_2O$ detection. In this work, we used the quartz-enhanced photoacoustic (QEPAS) technique to perform atmospheric measurements of these two targeted trace gas species. QEPAS has been used since 2002 to detect, with high sensitivity and selectivity, numerous trace gas species with absorption lines in the mid-infrared range [9–19]. The QEPAS-based sensor system uses a 7.83 μm continuous wave (CW), thermoelectrically cooled (TEC) distributed feedback (DFB) quantum cascade laser (QCL) (AdTech Optics, Part No. HHL-12-25), with an output power of 158 mW. A commercial quartz tuning fork (QTF) with a resonant frequency ($f_0$) of 32.768 kHz and a high-quality factor of $\sim 10^4$ at atmospheric pressure is employed as a resonant transducer in our QEPAS sensor. The emitted QCL beam is modulated at half of the QTF resonant frequency ($f = f_0/2$) in order to perform second-harmonic ($2f$) detection for sensitive $CH_4$ and $N_2O$ concentration measurements [20]. The interaction between the QCL modulated beam and a trace gas leads to the generation of acoustic waves that mechanically bend the QTF prongs. Hence the electrode pairs of the QTF will be electrically charged due to the quartz piezoelectricity. The QTF electrical response is acquired via a transimpedance amplifier with a feedback resistor of 10 MΩ. In addition, the QEPAS signal can be enhanced ~10 times by adding to the QTF sensor architecture a micro-resonator composed of two tubes that are placed at both sides of the QTF. The dimensions of the tubes, length and inner diameter, have been optimized experimentally [21].

The developed QEPAS sensor was installed in the Aerodyne Research, Inc. mobile laboratory (AML) in order to perform $CH_4$ and $N_2O$ atmospheric concentration measurements. The specific characteristics of the AML and its previous monitoring activities are described elsewhere [22]. Considering the importance of $CH_4$ emissions from landfills and the potential of $N_2O$ generation from these waste-disposal sites, the mixing ratios of these gas species around two urban solid waste disposal sites in the Greater Houston, Texas, area (WM Atascocita and BFI McCarty landfills) were monitored. The results of this study are described in this manuscript.

The schematic of the QEPAS sensor is depicted in Fig. 1. The optical characterizations of the 7.83 μm CW TEC DFB-QCL and the QEPAS sensor setup used for

 

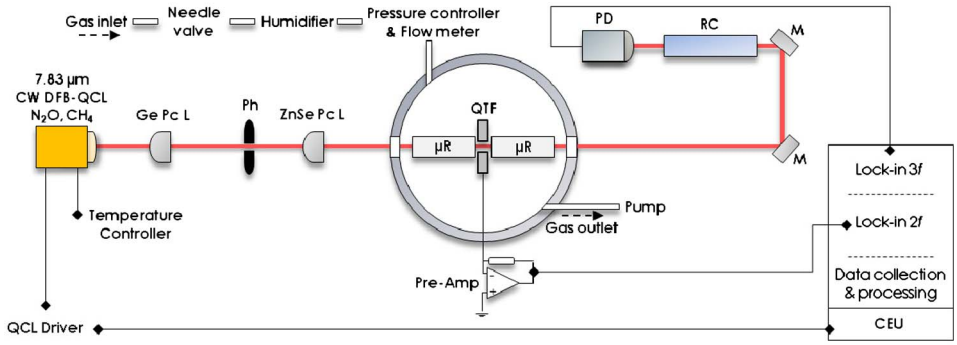


Fig. 1. $CH_4$ and $N_2O$ QEPAS sensor schematic. Ge Pc L and ZnSe Pc L, germanium and zinc selenide planoconvex lenses; Ph, pinhole; M, mirror; QTF, quartz tuning fork; μR, acoustic microresonator; RC, reference cell; PD, pyroelectric-detector; CEU, control electronics unit for the QEPAS based sensor system.

this campaign were described in detail elsewhere [23]. Moreover, sensor properties, such as sensitivity, selectivity, linearity, and stability also were demonstrated [23].

A water-cooling system and a high-capacity cup mount (dB Engineering, Inc.; slm 1A) were added to the QEPAS sensor in order to maintain the QCL temperature at 21.5°C (temperature in the AML van ranged between 26°C and 34°C) and to isolate the system from vibrations induced by road bumps, respectively. Two urban solid-waste disposal sites, WM Atascocita and BFI McCarty landfills, were selected to perform atmospheric $CH_4$ and $N_2O$ measurements on three dates: September 7, 10, and 26, 2013. During these measurements, the wind direction was predominantly east–northeast with an average wind speed of 3 mph. The starting point of the AML was Channelview, Texas, which is located in the eastern part of the Greater Houston area. First, all the sensor parameters, shown in Table 1, were set in order to determine and optimize the $2f$ QEPAS sensor signal. Atmospheric $CH_4$ or $N_2O$ measurements started when the AML van approached a specific landfill site (i.e., WM Atascocita or BFI McCarty) and continued as the AML circled the landfill and stopped at several arbitrary locations along its perimeter.

The targeted $CH_4$ and $N_2O$ absorption lines are located at 1275.04 $cm^{-1}$ and 1275.49 $cm^{-1}$, respectively. In this wavenumber range, the $CH_4$ and $N_2O$ absorption line strengths are weak [$S_{CH_4} = 3.729 \times 10^{-20}$ $cm^{-1}/(molecule/cm^{-2})$, $S_{N_2O} = 1.407 \times 10^{-19}$ $cm^{-1}/(molecule/cm^{-2})$]. However, employing an intense (>120 mW) laser excitation source in the QEPAS sensor system, such as a 7.83 μm CW TEC DFB-QCL, leads to excellent minimum detection limits ($1\sigma$) of 13 ppbv for $CH_4$ and 6 ppbv for $N_2O$, respectively, as reported previously [23]. Figure 2 depicts atmospheric $CH_4$ and $N_2O$ $2f$ QEPAS signals with a 1 s averaging time at the AML Channelview starting point. These signals are optimized, prior to beginning continuous measurements, in terms of the QTF calibration ($f_0$ and $Q$), amplitude of modulation, and current scanning range by using the control electronics unit (CEU) and an internally developed LabView program, respectively. After the optimization step, we performed $CH_4$ or $N_2O$ continuous measurements in a $3f$ line-locking mode. This mode is activated by integrating into our QEPAS sensor setup a 5 cm long reference cell (Wavelength Reference, Inc.) filled with a calibrated content of 0.5% $CH_4$ and 1% $N_2O$ at 100 Torr and a pyroelectric detector. The $CH_4$ and $N_2O$ $2f$ QEPAS signal amplitudes depicted in Fig. 2 correspond to 1.8 ppmv and 323 ppbv concentrations, respectively.

During *in situ* monitoring of $CH_4$ and $N_2O$, it is feasible to verify the QEPAS measured concentrations by comparing them with values measured by the AML van-based "QCL mini monitor" multipass optical sensor with a $CH_4$ detection sensitivity of 0.3 ppbv and $N_2O$ detection sensitivity of 0.060 ppbv, both in 1 s [24]. The two types of sensors yield the same $CH_4$ and $N_2O$ concentrations within <5% difference, thus verifying the precision and stability of the reported QEPAS sensor.

On September 7, 2013, atmospheric $CH_4$ measurements at and around the WM Atascocita landfill were carried out. These measurements were performed from 12:00 to 16:28 pm central daylight time (CDT) as shown in Fig 3. The $CH_4$ mixing ratio remained stable at 1.8 ppmv, until the AML van approached the WM Atascocita, Texas, landfill at ~14:10 pm, when a $CH_4$ plume of 10 ppmv was detected.

The highest $CH_4$ plumes (mixing ratios of 53, 14, and 25 ppmv) were generated by waste trucks passing close to the AML. The second AML trip, shown in Fig. 4, started by first optimizing the QEPAS sensor system parameters and subsequently performing atmospheric $CH_4$ measurements at and around the BFI McCarty landfill, Texas, 77078 on September 10, 2013. These measurements were performed between ~8 am and noon CDT.

**Table 1. $CH_4$ and $N_2O$ QEPAS Sensor Parameters**

| Date | Targeted Gas Molecule | Landfill | DFB-QCL Temperature (°C) | DFB-QCL Current Scanning Range (mA) | DFB-QCL Power (mW) | Amplitude of Modulation (mA) | Pressure inside the ADM (Torr) |
|---|---|---|---|---|---|---|---|
| 09/07/2013 | $CH_4$ (1275.04 $cm^{-1}$) | Atascocita | 21.5 | 485–498 | 158 | 4 | 130 |
| 09/10/2013 | $CH_4$ (1275.04 $cm^{-1}$) | BFI McCarty | 21.5 | 485–498 | 158 | 4 | 130 |
| 09/26/2013 | $N_2O$ (1275.49 $cm^{-1}$) | BFI McCarty | 21.5 | 437–448 | 123 | 4 | 130 |

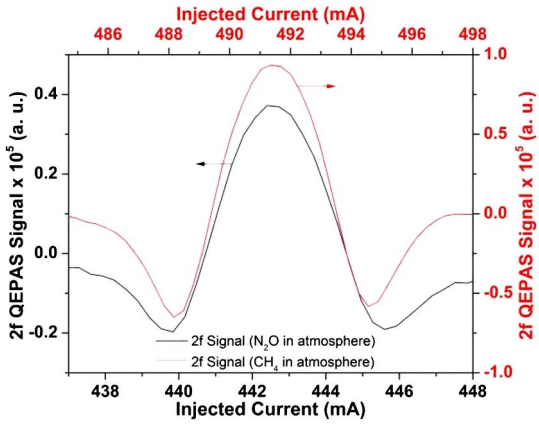


Fig. 2. $2f$ QEPAS signal of atmospheric $CH_4$ and $N_2O$ at Channelview (starting point of AML field trip measurements) for $CH_4$ on September 7, 2013, and for $N_2O$ on September 26, 2013. The pressure inside the ADM of the QEPAS-based sensor was set to $P = 130$ Torr.

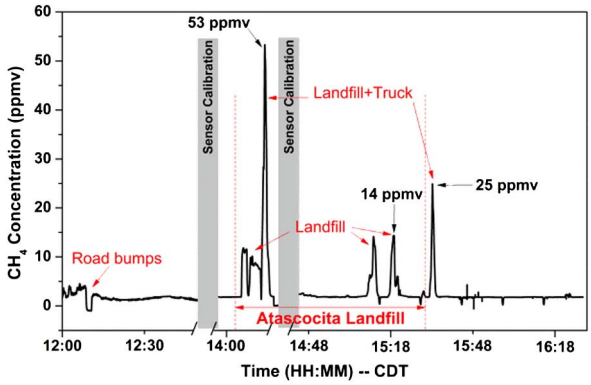


Fig. 3. $CH_4$ mixing ratios at and around the WM Atascocita, Texas 77396 landfill on September 7, 2013.

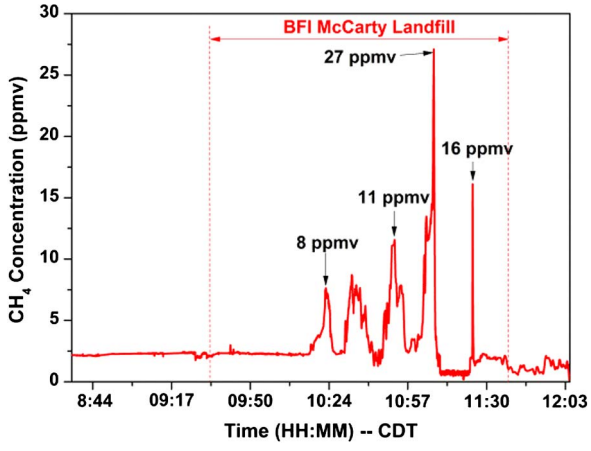


Fig. 4. $CH_4$ mixing ratios around the BFI McCarty landfill, Texas 77078 on September 10, 2013.

The average $CH_4$ mixing ratio detected near the BFI McCarty landfill was ~5 ppmv based on averaging over measurements from 10:10 am until 11:40 am, while the highest mixing ratios observed, 16 and 27 ppmv, were related to waste trucks passing near the AML.

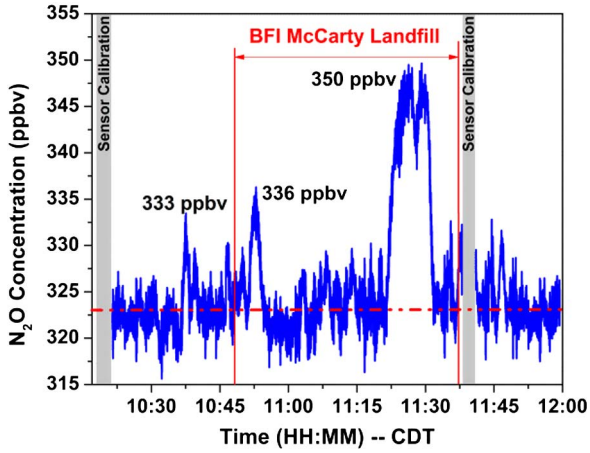


Fig. 5. $N_2O$ mixing ratios at and around the BFI McCarty landfill on September 26, 2013.

The third AML trip, shown in Fig. 5, was based on monitoring atmospheric $N_2O$ levels in the atmosphere around the BFI McCarty landfill on September 26, 2013.

The measurements were performed between 10:15 am and 12:00 pm CDT. The $N_2O$ level remained stable at its natural abundance near 323 ppbv. However, when waste trucks passed close to the AML at two different times, 10:37 and 10:52 am, two spikes of $N_2O$ were observed clearly, corresponding to 333 and 336 ppbv, respectively.

Furthermore, mixing ratios of approximately 350 ppbv of $N_2O$ were detected while the AML was circling the landfill from 11:22 to 11:32 am.

In this study, we demonstrated the performance of a mid-infrared QCL-based QEPAS sensor system installed in the AML to perform continuous, atmospheric $CH_4$ and $N_2O$ measurements at and around two urban waste landfills, BFI McCarty and Atascocita, located in the northeastern part of Greater Houston. QEPAS allows performance of sensitive measurements in a very small (few $mm^3$) gas sample, which is suitable for applications requiring a compact, lightweight, and low-cost sensor architecture. The sensor system employed a 7.83 μm CW TEC 158 mW DFB-QCL as an excitation source. $2f$ and $3f$ harmonic detection was used for optimum sensor sensitivity and line-locking operation mode, respectively. The QEPAS sensor measurements were verified by comparing them with values observed by an ARI ultra-sensitive QCL-based multipass gas cell sensor system [24]. Enhancements of ~8 ppmv of $CH_4$ and ~30 ppbv of $N_2O$ compared to their natural abundances were detected when the AML was next to the landfills or circling them at a distance of ~200 m. Due to dilution, mixing ratios decreased to background levels when the circling distance exceeded ~400 m. Furthermore, the sensor clearly detected enhanced $CH_4$ and $N_2O$ as a result of waste trucks driving close to the AML. An ultracompact QCL-based QEPAS $CH_4$ and $N_2O$ sensor system is planned and will be based on integrating novel surface-mounted digital electronics in order to reduce the size of the sensor system. In addition, the data-acquisition system and the QCL controllers will be designed so as to allow the simultaneous detection of atmospheric $CH_4$ and $N_2O$.

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