

Article

Carbon Dioxide and Methane at a Desert Site—A Case Study at Railroad Valley Playa, Nevada, USA

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Abstract: Ground based *in-situ* measurements of carbon dioxide (CO₂) and methane (CH₄) at the dry lakebed at Railroad Valley (RRV) playa, Nevada, USA (38°30.234' N, 115°41.604' W, elevation 1437 m) were conducted over a five day period from 20–25 June 2010. The playa is a flat, desert site with virtually no vegetation, an overall size of 15 km × 15 km and is approximately 110 km south-west of the nearest city, Ely (elevation 1962 m, inhabitants 4000). The measurements were taken in support of the vicarious calibration experiment to validate column-averaged dry air mole fractions of CO₂ and CH₄ (X_{CO₂} and X_{CH₄}) retrieved from the Greenhouse Gases Observing Satellite (GOSAT) which was launched in January 2009. This work reports on ground-based *in-situ* measurements of CO₂ and CH₄ from RRV playa and describes comparisons made between *in-situ* data and X_{CO₂} and X_{CH₄} from GOSAT.

Keywords: CO₂; CH₄; playa

1. Introduction

Carbon dioxide (CO₂) and methane (CH₄) are the first and second most important increasing greenhouse gases respectively. Before the industrial revolution, the concentration of CO₂ in the atmosphere was 280 ± 10 ppm for several thousand years [1-3]. The global average mixing ratio of tropospheric CO₂ in 2009 was 386.8 parts per million, ppm, with the seasonal cycle superimposed onto this average [4]. The amplitude of the ground-based seasonal cycle varies depending on location of the measurements; for example amplitudes of 15.5 ppm were reported at Ochsenkopf, Germany [5] whereas amplitudes of 30.4 ppm have been reported from the Zotino tall tower in central Siberia [6]. The atmospheric lifetime of CO₂ is a controversial topic. Some estimates describe a range of 50–200 years [7] and others claiming a far longer time in the order of magnitude of a few centuries [8]. The importance of CO₂ is amplified due to its long atmospheric life-time, its high global mean radiative forcing ($+1.66 \pm 0.17$ Wm⁻² [1]) and the fact that the average mixing ratio is increasing at a rate of 2 ppm/year [9] due to anthropogenic activities [1].

Since pre-industrial times the atmospheric concentration of CH₄ has more than doubled as a result of anthropogenic activities [1]. The most important sources of CH₄ are wetlands, rice fields, energy production, ruminants, landfills and biomass burning, contributing to a total of approximately 600 Tg emitted annually [1]. Recently (1999–2006) the increase in CH₄ mixing ratio started to stabilize, for reasons that are not well understood [10,11]. However, more recent reports suggest a renewed increase in atmospheric CH₄ [12,13]. The global average mixing ratio of tropospheric CH₄ in 2009 was 1.803 ppm [4] and the mean atmospheric lifetime of CH₄ is 8.4 years [1]. CH₄ is also considered the second most important trace gas in the atmosphere, in terms of its radiative forcing ($+0.48 \pm 0.05$ Wm⁻² [1]); hence CH₄ emissions have the ability to alter the state of the atmosphere on a global scale. CH₄ also plays an important role in the photochemistry of the atmosphere as it is primarily removed by oxidation with the hydroxyl radical (OH) and in so doing acts as a precursor for secondary pollutants, including ozone and eventually CO₂, CH₄ sinks also include soils and losses to the stratosphere.

Satellite data can be used to provide a better understanding of the atmospheric processes and CO₂ and CH₄ budgets. In January 2009, the Greenhouse Gases Observing Satellite (GOSAT) instrument was launched with the aim of measuring the column amounts of CO₂ and CH₄ [14]. GOSAT has a CO₂ target to achieve 4 ppm accuracy for a three month regional average using a combination of short-wavelength infrared, SWIR, and infrared, IR, channels [14-16]. This paper reports on ground-based *in-situ* measurements of CO₂ and CH₄ taken at a playa in Railroad Valley (RRV), Nevada during a field campaign in June 2010. The field campaign was part of a vicarious calibration experiment with the primary aim to validate column-averaged dry air mole fractions of CO₂ and CH₄ (X_{CO_2} and X_{CH_4}) retrieved from GOSAT. Comparisons of ground-based, *in-situ* data with X_{CO_2} and X_{CH_4} from GOSAT measurements taken on two cloud-free days are presented. Here, *in-situ* CO₂ and CH₄ data is presented from four measurement days to provide context to the daily and day-to-day variations and its potential relevance to satellite measurements.

2. Experimental

Ground-based atmospheric measurements of CO₂ and CH₄ were taken on a dry lakebed, or playa, at Railroad Valley (RRV), Nevada, USA (38°30.234' N, 115°41.604' W, height 1437 m) from 20–25 June 2010. The playa is a flat, high altitude desert site which makes up part of the Great Basin desert of the United States; except for several small oil fields, RRV is an area where local sources and sinks of carbon-species are expected to be minimal. The playa has virtually no vegetation, an overall size of 15 km × 15 km and is approximately 110 km south-west of the nearest city, Ely (elevation: 1962 m, inhabitants: 4000); the location and characteristics of the RRV site are such that it provides an estimate of well-mixed continental air. RRV playa is a radiometrically flat region and has been used to calibrate various satellite radiometers for many years [17-19]. The CO₂ and CH₄ measurements were part of a vicarious calibration of the GOSAT data; other measurements included solar irradiance, spectral albedo, bidirectional reflectance distribution function (BRDF), radiosonde (temperature, humidity profiles) and meteorological data (temperature, humidity, pressure, wind speed and direction) [19].

The CO₂ and CH₄ measurements were conducted using Wavelength-Scanned Cavity Ring-Down Spectroscopy (WS-CRDS) technique. The analyzer (Picarro Inc., CA, USA, model G1302) relies on the use of a high-finesse optical cavity consisting of three high-reflectivity mirrors (>99.995%), two lasers, a high-precision wavelength monitor, and photo-detectors to enable extremely precise and simultaneous measurements of CO₂ and CH₄. This technique has been described in detail elsewhere and is widely used as a ground-based and airborne-based instrument [6,20-22].

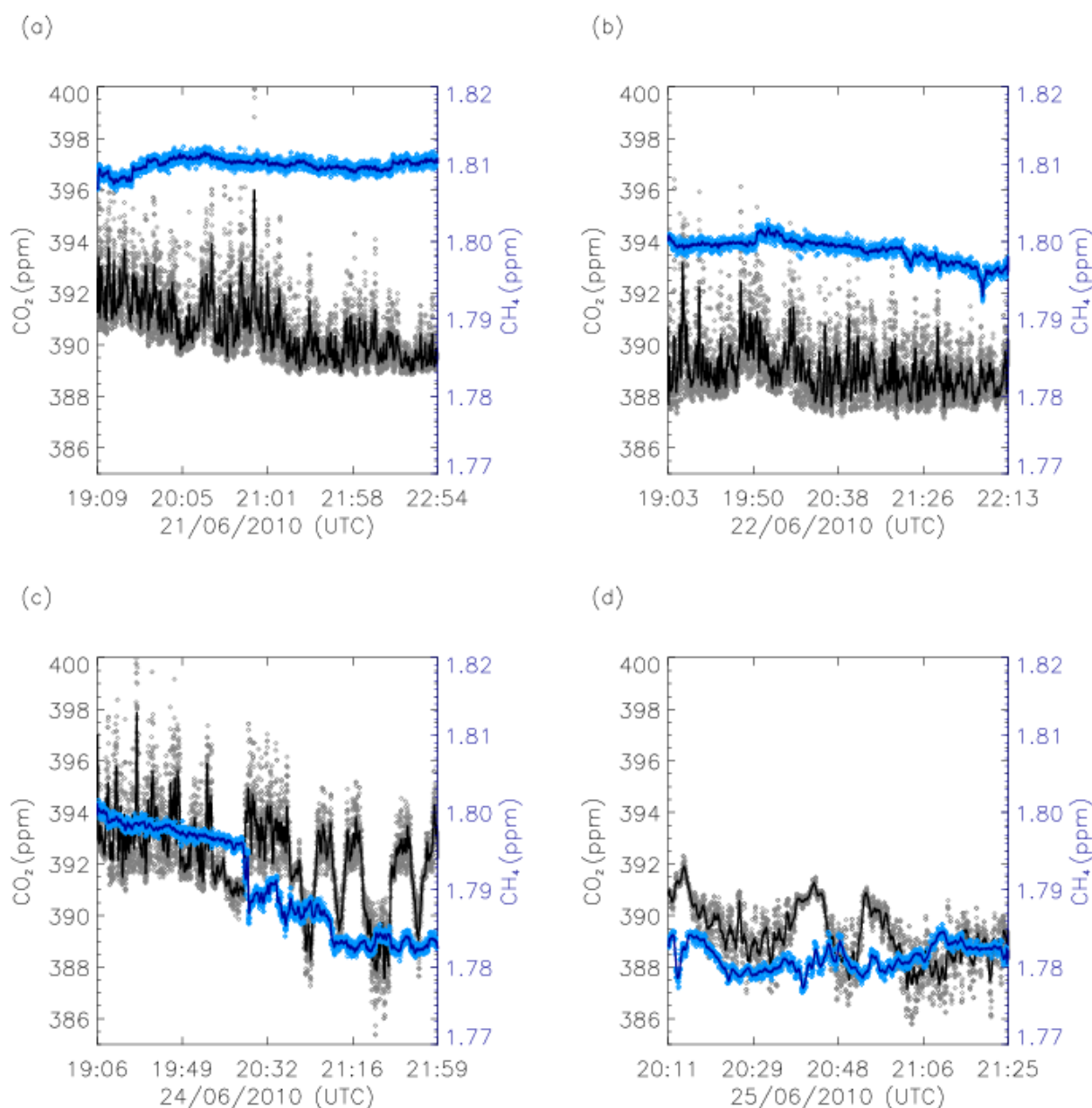
Laboratory analyzer tests were performed with a synthetic standard to calibrate the analyzer before and after deployment at RRV (Scott-Marrin, Inc. 420 ppm CO₂, 1.997 ppm CH₄ (±1% NIST) balance in ultrapure air). Instrument precision was calculated from the average 1-sigma standard deviation during standard sampling and was below 0.17 ppm for CO₂ and 0.56 ppb for CH₄, with no outliers greater than ±0.20 and 0.001 ppm from the standard mean for CO₂ and CH₄ respectively. Applying least-squares linear fit to the measured standard values analyzed before and after the deployment gave an estimation of the analyzer drift. Drift was estimated to be −1.9 ppb/day for CO₂ and −0.002 ppb/day for CH₄. A flow mixing system was used to dilute the standard with pure nitrogen to determine instrument linearity over a wide concentration range (100–400 ppm), the instrument proved to be extremely linear (slope = 1.04, $r^2 = 1.00$).

The field deployment was conducted in support of GOSAT overpasses which occurred on 21 (20:44 UTC), 22 (21:16 UTC), 24 (20:44 UTC) and 26 (21:16 UTC) June 2010. The analyzer operated a minimum of 1.5 h either side of the GOSAT overpasses. The analyzer was located upwind of the base-camp and to prevent the use of a generator, the instrument was powered using two marine batteries wired in parallel and connected to an inverter which provided 110 VAC. The instrument inlet was approximately 3 m above the ground. During measurements, all generators were switched off and human interaction was prevented. The location of the analyzer was approximately 10 m from a ground-based meteorological station (R.M. Young Company, MI, USA) which reported wind direction and speed, temperature, humidity and pressure every second for the entire duration of the campaign.

3. Results and Discussion

The RRV field campaign bracketed the summer solstice, from 20–25 June 2010, and coincided with the decreasing phases of the seasonal cycles of the CO₂ and CH₄. Data from the closest NOAA station at Wendover, Utah show that the CO₂ and CH₄ seasonal minima occur in August/September and July/August respectively (www.esrl.noaa.gov/gmd/dv/iadv). The 2 s temporal resolution ground-based datasets of CO₂ and CH₄ are presented in Figure 1 for each GOSAT overpass day.

Figure 1. Mixing ratios of CO₂ (gray) and CH₄ (blue) on (a) 21 June, (b) 22 June, (c) 24 June, (d) 25 June, 2010. For each species the one minute boxcar average (darker colored line) is overlaid with the raw data (lighter colored symbols) and is plotted against Coordinated Universal Time, UTC, (local time plus 7 h).



The minimum and maximum concentrations during the measurement campaign were 385.39–404.25 ppm for CO₂ and 1.777–1.812 ppm for CH₄. As expected the overall mean CO₂ and

CH₄ concentrations on each measurement day were close to (although, always higher than for CO₂) the global average of 386.8 ppm and 1.803 ppm respectively, see Table 1. Differences from these mean concentrations are discussed more in the following sections. Day-to-day variations in the average CO₂ and CH₄ values result primarily from large scale mixing and variations on a time-scale of 2–5 days due to changes in emission sources and synoptic variability [23] which mixes background, oceanic air with continental signals. The small time-scales of the daily CO₂ fluctuations, defined as lasting <1 min in duration and consisting of >10 data points, are seen in the raw data in Figure 1. The speed and magnitude of these fluctuations (most fluctuations are approximately 5 ppm (which is 30 times the instrument 1 σ standard deviation)) were not observed in pre-deployment laboratory calibration testing. Given the location of the field instrument (removed from base-camp emissions and limited human interaction) we believe these fluctuations indicate local sources and/or sinks influence observations at this remote site.

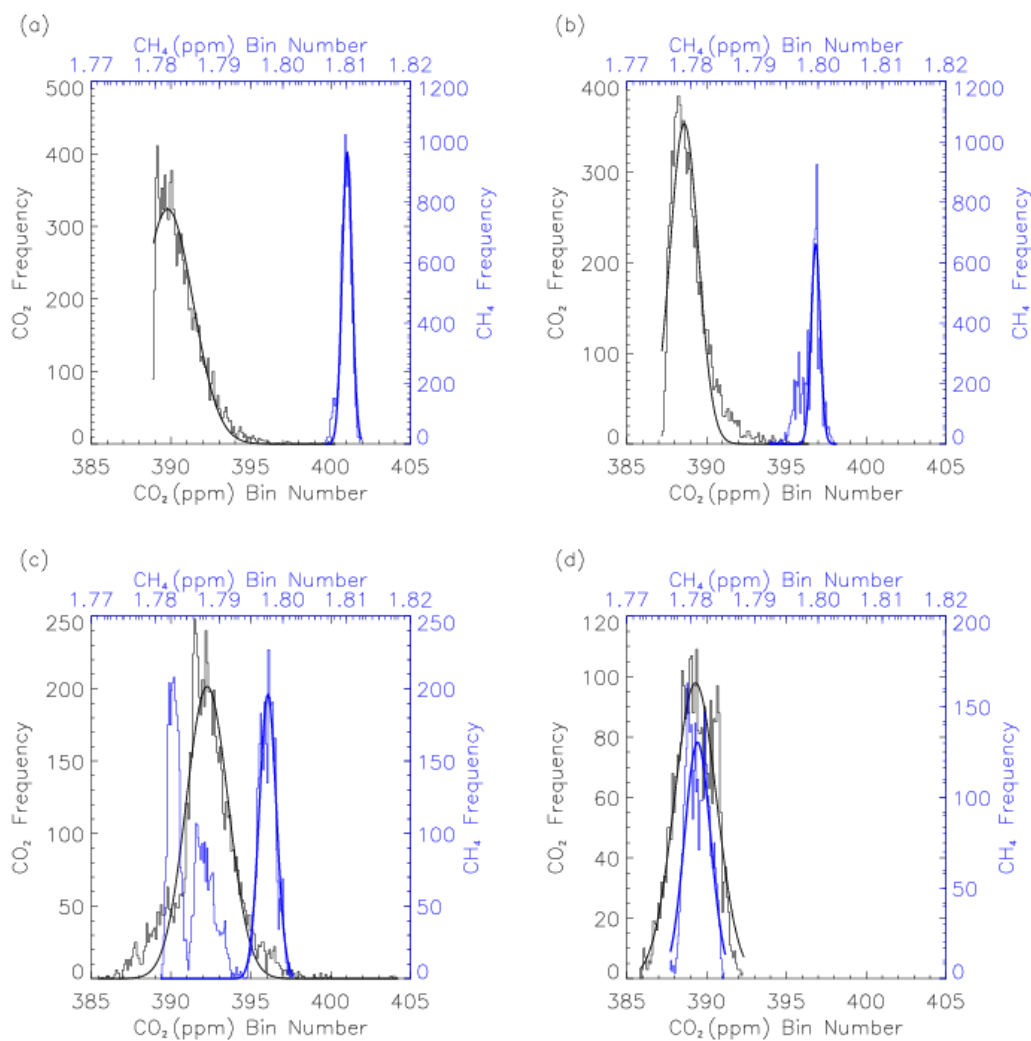
Table 1. Statistics table for 0.5 Hz *in-situ* CO₂ and CH₄ mixing ratios during the ~3 h measurement period on each overpass day. Data reported: minimum, median, standard deviation, maximum, histogram, skewness and kurtosis. (* Values reported in ppm, ** Stdev = standard deviation in ppm).

	21 June 2010		22 June 2010		24 June 2010		25 June 2010	
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
Minimum *	388.84	1.806	387.15	1.792	385.39	1.781	385.78	1.777
Mean *	390.66	1.809	389.01	1.799	392.23	1.791	389.26	1.781
Median *	390.37	1.810	388.75	1.799	392.22	1.789	389.26	1.781
Stdev **	1.34	8.70e ⁻⁴	1.17	1.53e ⁻⁴	1.85	6.55e ⁻³	1.19	1.72e ⁻³
Maximum *	400.34	1.812	396.41	1.803	404.25	1.802	392.31	1.786
Skewness	1.27	0.719	1.24	1.938	1.86	0.796	0.14	0.002
Kurtosis	0.18	-1.096	0.04	3.569	2.48	-0.697	-1.522	-1.322

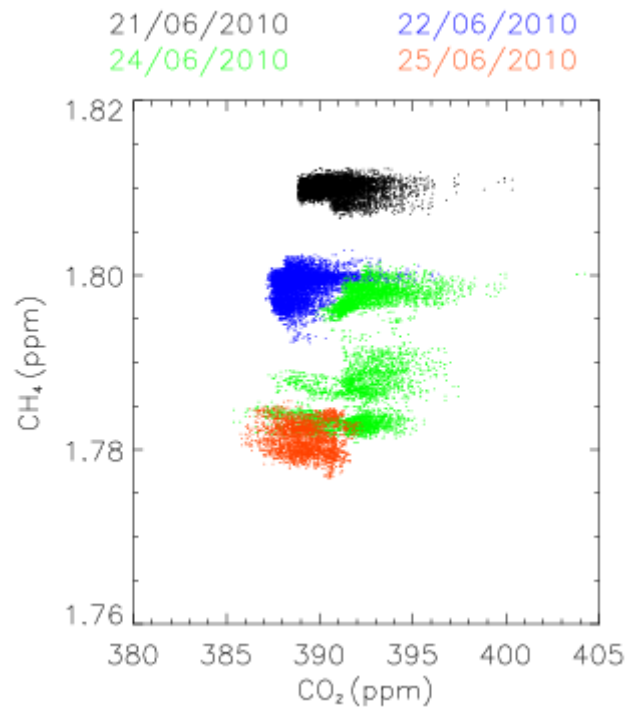
3.1. Investigating Emission Sources

The measured CO₂ and CH₄ probability distributions during each GOSAT overpass day are shown in Figure 2. Superimposed on the Figure 2 histograms is a Gaussian probability distribution. The comparison of the actual and the Gaussian probability distributions, along with the statistical summary provided in Table 1, informs us that each histogram is positively skewed (with varying extents), with more data points lying to the right of the centre. The non-symmetric, positive skew of the histograms suggests there are more fluctuations of CO₂ and CH₄ concentration values above the mean concentration than below, indicative of potential local sources influencing the observations at this remote site.

Figure 2. Probabilistic histograms of CO₂ (black) and CH₄ (blue) mixing ratios during each overpass day. Superimposed is the Gaussian distribution. (a) 21 June, (b) 22 June, (c) 24 June, (d) 25 June, 2010.



The histogram plot of CH₄ on 24 June 2010 is bi-modal in shape, with two apparent peaks of similar occurrence frequency. This suggests that the data is from two separate processes or distinct sources, providing further evidence towards a local emission source. To investigate this possibility further a scatter plot of CH₄ *versus* CO₂ is presented in Figure 3. Excluding 24 June, it can be deduced from Figure 3 that the CH₄ values on each day vary by less than 0.02 ppm (~1% variation compared with background concentration value). Because, the day-to-day differences are larger than 0.02 ppm, each day's data falls into a distinct group bracketed by these small changes (0.02 ppm) in CH₄ concentration. CO₂, on the other hand shows much more daily variation, in the order of 20 ppm. This is a ~5% variation when compared with the background CO₂ value. On 24 June the CH₄ measurements span a wider range of concentrations (2 ppm) and appear to have several distinct groups. The scatter plot further confirms that measurements on 24 June 2010 were influenced by two or more distinct sources with differing CH₄/CO₂ emission ratios.

Figure 3. Scatter plot of CH₄ versus CO₂ on each GOSAT overpass day.

The CH₄/CO₂ ratio does not appear to have a very robust relationship, as represented by the variation in the r^2 values (r^2 values: 0.008, 0.06, 0.2, and 0.02 on 21, 22, 24, 25 June 2010 respectively). Using the reported, average background concentrations of CO₂ (386.8 ppm) and CH₄ (1.803 ppm) [4] the expected CH₄/CO₂ ratio is 0.0047. However, these are averaged concentrations, and in reality concentrations of CO₂ and CH₄ vary in time and space depending on the magnitude of local (or large regional and global) sources and sinks. The absence of a direct link between CH₄ and CO₂ concentrations can be expected when considering their independent and varying emission sources.

The fluctuations of CO₂ (up to 10 ppm) during each measurement period was unexpected given that the measurement period occurred at the same time on each day (late-morning to mid-afternoon) and considering the playa was virtually free from all vegetation. Further research is needed to investigate possible CO₂ fluxes. The Great Basin area (including RRV) is considered to have a minimal carbon emission, however due to the sparse measurement data of carbon fluxes in the desert region of United States Midwest the possibility of a local source/sink must also be considered. Further investigation is required to identify CO₂ (and CH₄) sources and sinks including RRV oil fields and the role of soil-atmosphere interactions.

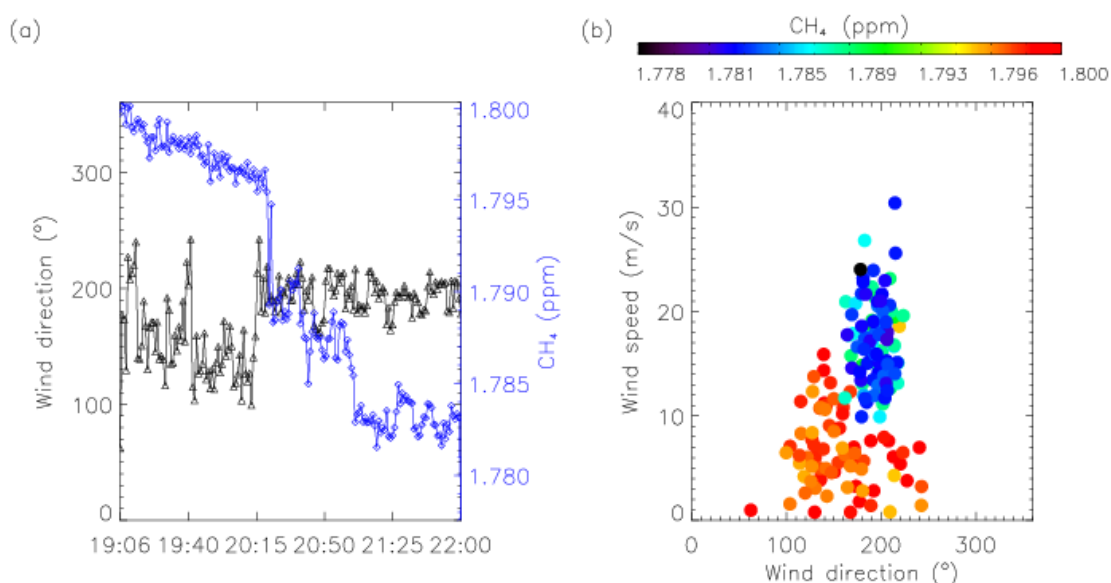
3.2. Comparisons with Meteorological Data

During the CO₂ and CH₄ measurement period, the first two GOSAT overpass days wind speeds were low (~5 m/s) and the wind direction was highly variable. Temperatures on 21 and 22 June 2010 remained below 30 °C, skies were clear and mean humidity was 9–13%. Radiosonde data launched at GOSAT overpass time (20:44 and 21:16 UTC) on 21 and 22 June 2010 show a well-mixed planetary boundary layer (PBL) to 4000 m (above sea level) as indicated by the base of the temperature inversion and the level of minimum vertical gradient of relative humidity. Hence we expect the CO₂

and CH₄ mixing ratios within the PBL to be fairly constant during the measurement time and during the well-mixed PBL case. Indeed, evidence presented in Figures 1 and 2 and Table 1 does show that the CO₂ and CH₄ observations are well-mixed, with fluctuations around the mean values.

In contrast, the final two measurement days were characterized by increasing wind speeds in the afternoon (average wind speed: 12.64 m/s and 19.08 m/s on 24 and 25 June 2010 respectively, with gusts up to 30 m/s) from a more sustained and less variable, (100–250°) direction, particularly during the afternoon winds. Temperatures on these final measurement days remained above 30 °C, cloud cover was present, and humidity decreased (mean: 7.69% and 4.90% on 24 and 25 June respectively). Comparing wind data with CH₄ mixing ratios on 24 June 2010 does indicate a relationship between CH₄ mixing ratios and wind direction/speed. The decrease in CH₄ concentration at 20:23 UTC on 24 June 2010 presented in Figures 1 and 2 coincides with a change in wind direction from SW (higher CH₄ concentrations) to SE (lower CH₄ concentrations) with wind speeds from the SW direction being lower than those from the SE. Figure 4 shows the relationship between CH₄ and wind speed/direction (CH₄ has been interpolated to the same temporal resolution as the wind data: once per minute) and points towards a local CH₄ source in the SW region. The origins of the source are inconclusive. Small oil fields are located in RRV, however most appear to be towards the north and east of RRV playa. Other potential sources could include biogenic emissions from the soil or thermal springs; all possibilities, and the subsequent effects on the local environment, require further investigation. The same behavior was not observed for CO₂; fluctuations in CO₂ did not depend on wind direction/speed.

Figure 4. Relationship between wind speed and direction and CH₄ concentration on 24 June 2010 (a) time series of wind direction and CH₄ (b) 3D plot of wind speed, direction, and (interpolated) CH₄ concentration.



The effects of temperature and humidity on CO₂ and CH₄ concentrations have been investigated to help determine the role of biosphere interactions on the atmospheric levels of these carbon species. The area is not vegetated and hence evidence of photosynthesis as a key role in controlling CO₂ is not expected. However, there are local hot and cold springs which could potentially result in biogenic emissions of CH₄ and as such would be temperature dependent. Temperature and humidity would also

determine the potential role of the playa soil itself, in terms of decomposition of organic matter. When CO₂ and CH₄ time series data is over-plotted with temperature and humidity there does appear to be a general degree of correlation; for example as temperature increases CO₂ appears to decrease. However, a scatter-plot of meteorological parameters (1 min resolution) *versus* (1 min average) CO₂ data shows little correlation, in terms of r^2 values, due to the large variability in CO₂ concentration on each day. Given the general observations of decreasing CO₂ concentrations throughout each afternoon (as temperature increases) and the short time-frame of each day's measurements, no definite conclusion can be drawn regarding the effects of temperature on CO₂ mixing ratios. Comparisons of temperature and humidity with the less-variable CH₄ data result in a better degree of correlation, but r^2 values vary dramatically from day-to-day. For example, the r^2 values for temperature/CH₄ are 0.066, 0.50, 0.63, and 0.0043 on 21, 22, 24 and 25 June respectively. The lack of correlation between meteorological data and the carbon species leads us to deduce that in this instance local temperature and humidity conditions observed on the playa had little influence on the measured CO₂ and CH₄ concentrations, at least under the limited temperature and humidity range observed here. To better assess the role of temperature and humidity diurnal cycles would be required over larger temperature and humidity ranges.

3.3. GOSAT Comparisons

The X_{CO₂} and X_{CH₄} GOSAT retrievals were derived using a method described elsewhere [24-26]. Briefly the data analysis method consists of three steps: (a) data is filtered by several cloud-detection methods to determine cloud-free observations, (b) determination of X_{CO₂} and X_{CH₄}, and (c) examination of retrieval quality. X_{CH₄} are obtained from the Japanese National Institute for Environmental Studies (NIES) products, whereas X_{CO₂} is retrieved with two different algorithms; X_{CO₂} from NIES products and from the NASA-sponsored Atmospheric CO₂ Observations from Space (ACOS) team. NIES X_{CO₂} and X_{CH₄} products V01.39 are retrieved as requested from L1 V110 data with NIES V01 algorithm and corrected the lower bias (8.9 ppm for X_{CO₂} and 0.02 ppm for X_{CH₄}). ACOS X_{CO₂} products are retrieved from L1 V130 data with ACOS b2.9 algorithm. GOSAT's onboard Thermal and Near infrared Sensor for carbon Observation Fourier Transform Spectrometer (TANSO-FTS) pointing mechanism has image motion compensation capability, this mechanism can view the same surface target for up to 20 s. The RRV GOSAT overpasses were approximately 13 s in total, comprising of up to three data points for each GOSAT overpass.

The ground based *in-situ* measurements of CO₂ and CH₄, averaged over 30 min (15 min either side of the GOSAT overpass), were compared with the X_{CO₂} and X_{CH₄} retrievals by NIES and by ACOS from GOSAT overpasses on 21 and 22 June 2010. Comparisons of the GOSAT overpasses on 24 and 25 June 2010 could not be made due to large cloud cover fraction during these days, preventing X_{CO₂} and X_{CH₄} retrievals. The data is presented in Table 2. Note that on 22 June NIES rejected two and ACOS rejected one of the possible three data points.

Table 2. Summary of the comparisons of GOSAT column-averaged dry air mole fractions of CO₂ and CH₄ with *in-situ* surface level mixing ratios averaged for 30 min centered on the overpass time (values reported in ppm).

Date/time of GOSAT overpass	X _{CO2} NIES	X _{CO2} ACOS	<i>In-situ</i> CO ₂	X _{CH4} NIES	<i>In-situ</i> CH ₄
21/06/2010 20:44	392.7	390.0	393.60	1.814	1.810
	389.9	389.3		1.816	
	390.3	390.2		1.806	
22/06/2010 21:16	-	391.4	388.01	-	1.798
	390.7	391.3		1.805	
	-	-		-	

The differences in the measurements of *in-situ* CO₂ and CH₄ mixing ratios and X_{CO2} and X_{CH4} can be understood when considering the nature of the measurements. Ground-based, surface CO₂ mixing ratios are largely influenced by their diurnal cycle (which in turn is driven by synoptic-scale weather patterns which affect boundary layer mixing, photosynthesis and ecosystem respiration [27]). In contrast, in order for there to be large-scale replacement of air within the column, column CO₂ is largely linked to events that have timescales in the order of 2 to 6 days [28]. Despite these differences there appears to be a good agreement between *in-situ* CO₂ and X_{CO2} and between *in-situ* CH₄ and X_{CH4}. It has been previously concluded that the varying amplitude of the CO₂ seasonal cycle with altitude is responsible for column average CO₂ being greater than surface CO₂ in summer and fall and lower in winter and spring in the Northern Hemisphere mid-latitudes [28]. However, during this summer study the NIES and ACOS X_{CO2} values are less than the surface CO₂ mixing ratio on the 21 June and greater than on 22 June 2010. The reason for this discrepancy on 21 June 2010 may be due to the “rectifier effect”: interactions between biosphere emissions (here effects of photosynthesis rates are limited but other biogenic sources have not been accounted for) and boundary layer dynamics and/or local sources and sinks, and further investigation is required to better address these roles.

4. Conclusions

Ground based *in-situ* measurements of CO₂ and CH₄ at RRV playa were carried out during June 2010. The measurements were in support of the vicarious calibration experiment which in turn helps validate GOSAT X_{CO2} and X_{CH4} retrievals. This work focuses on the analysis of the ground-based *in-situ* measurements of CO₂ and CH₄. The daily mean CO₂ and CH₄ concentrations are close to the reported global average values. However, fluctuations were observed, which were greater than expected given the remoteness of the RRV site. Further investigation is required in order to analyze the cause of these fluctuations and their influence on satellite validations.

Comparisons of *in-situ* CO₂ and CH₄ measurements with X_{CO2} and X_{CH4} from GOSAT show a general good-approximation of boundary layer mixing ratios. However, due to the spatially limited coverage of the *in-situ* data and the reliance on cloud-free measurement days, the results presented should be regarded as a first attempt at comparison. Further validation including a more comprehensive study of the boundary layer is needed.

Planned improvements for future calibration campaigns include increased power availability to measure CO₂ and CH₄ for longer periods of time, including the analysis of diurnal cycles which would help identify the role of local sources/sinks. A detailed analysis of local emission sources/sinks would be advantageous, allowing the assessment of the role of the oil fields, identification of potential biogenic sources/sinks, and assessment of the potential influence of these on satellite measurements. Measurement of ground based CO₂ and CH₄ mixing ratios coincident with *in-situ* analysis of CO₂ and CH₄ in the free troposphere would allow for the investigation of CO₂ and CH₄ vertical profiles and provide a method of calculating column averages from aircraft profiles to directly compare with GOSAT column X_{CO₂} and X_{CH₄}, which is a method routinely used for satellite validation [9,29].

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