



Supplement of

Revised methodology for CO₂ and CH₄ measurements at remote sites using a working standard-gas-saving system

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Supplement

1. Evaluation of the fourth term in equation 23-1 related to methane standard gases

In 1994, we prepared methane standard gases at various mole fractions using a gravimetric method involving four-step dilution of pure methane with purified air. These gases have been maintained as primary standard gases for the NIES 94 CH₄ scale.

The mole fraction (f) of each primary standard gas is calculated using the following equation:

$$f = \frac{a \cdot m_1}{a \cdot m_1 + b \cdot m_2}$$

where m_1 is the mass of pure methane [g], m_2 is the mass of purified air [g], a is the reciprocal of the molecular weight of methane [mol/g], and b is the reciprocal of the mean molecular weight of purified air [mol/g]. The mass of purified air was determined as $m_2 = m_t - m_1$, where m_t is the total mass of the mixed gas [g].

The combined standard uncertainty ($u_c(f)$) of each f is given by the positive square root of the combined variance, following eq. 10 in section 5.1.2 of the GUM (JCGM, 2008):

$$u_c^2(f) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) = \left\{ \frac{abm_2}{(am_1 + bm_2)^2} \right\}^2 \cdot u^2(m_1) + \left\{ \frac{-abm_1}{(am_1 + bm_2)^2} \right\}^2 \cdot u^2(m_2)$$

The mass of methane (m_1) after n-step dilution is determined as follows:

$$m_1 = com(n) \times \frac{com(n-1)}{tot(n-1)} \times \dots \times \frac{com(1)}{tot(1)}$$

where com represents the mass [g] taken from the previous step's mixed gas (pure methane in the first step), and tot represents the total mass of mixed gas [g] in that step. For variables expressed as products, the relative combined variance of m_1 can be evaluated from individual relative variances according to eq. 12 in section 5.1.6 of the GUM (JCGM, 2008), as follows. Denoting the balance uncertainty as u_b [g]:

$$\left[\frac{u(m_1)}{m_1} \right]^2 = \sum_{i=1}^N [u(x_i)/x_i]^2 = \left[\frac{u_b}{com(n)} \right]^2 + \sum_{i=1}^{n-1} \left\{ \left[\frac{u_b}{com(n-i)} \right]^2 + \left[\frac{u_b}{tot(n-i)} \right]^2 \right\}$$

Meanwhile, $u(m_2)$ is evaluated as:

$$u^2(m_2) = u^2(m_t) + u^2(m_1) = u_b^2 + u^2(m_1)$$

At each dilution step, 13-107 g of pure methane or mixed gas from the previous step was combined with 1087-1383 g of purified air. The combined standard uncertainty (u_b) for the weighing process was estimated to be 20 mg. The combined standard uncertainty calculated from actual weighing values was 2.5 ppb for the 1511 ppb primary gas, 2.9 ppb for the 1763 ppb primary gas, 3.3 ppb for the 2013 ppb primary gas, and 4.1 ppb for the 2512 ppb primary gas. The scale propagation uncertainty by our gas chromatograph calibration was 0.3 ppb, 0.4 ppb, and 0.4 ppb for secondary standards at 1713 ppb, 2097 ppb, and 2486 ppb, respectively. For the calibration of the WS-gas used in Siberia using secondary gases, the propagation uncertainty was 0.4 ppb (0.5 ppb) for the WS-gas at 1755 ppb (2479 ppb). The uncertainty of the WS-gas

is calculated as the square root of the sum of squares of $u_c(f)$ and the scale propagation uncertainty at each step. However, since the standard gases were manufactured by dividing the necessary amount from the same mixture diluted up to three stages, they cannot be considered independent. The correlation coefficients between primary gases were 0.98-0.99. Using the correlation coefficients between primary gases and following eq. 13 in section 5.2.2 of the GUM (JCGM, 2008), the square root of the fourth term in equation 23-1 can be evaluated as 3.2 ppb.

Given that the purity of pure methane is greater than 99.999%, the uncertainty dependent on methane impurity is at most 0.025 ppb for 2500 ppb. While other factors, such as errors in the molecular mass of methane, also contribute to uncertainty, they are more than an order of magnitude smaller than the uncertainty of mass measurement (Tohjima et al., 2006) and are therefore not included in the calculation.

References

JCGM 100, 2008: *Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement* (ISO GUM 1995 with minor corrections), Joint Committee for Guides in Metrology (2008); http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf.

Tohjima, Y., Machida, T., Mukai, H., Maruyama, M., Nishino, T., Akama, I., Amari, T., and Watai, T.: Preparation of gravimetric CO₂ standards by one-step dilution method, In: John B. Miller eds. 13th IAEA/WMO Meeting of CO₂ Experts, Vol WMO-GAW Report 168. Boulder, 2005, 26-32, 2006.

2. Figures

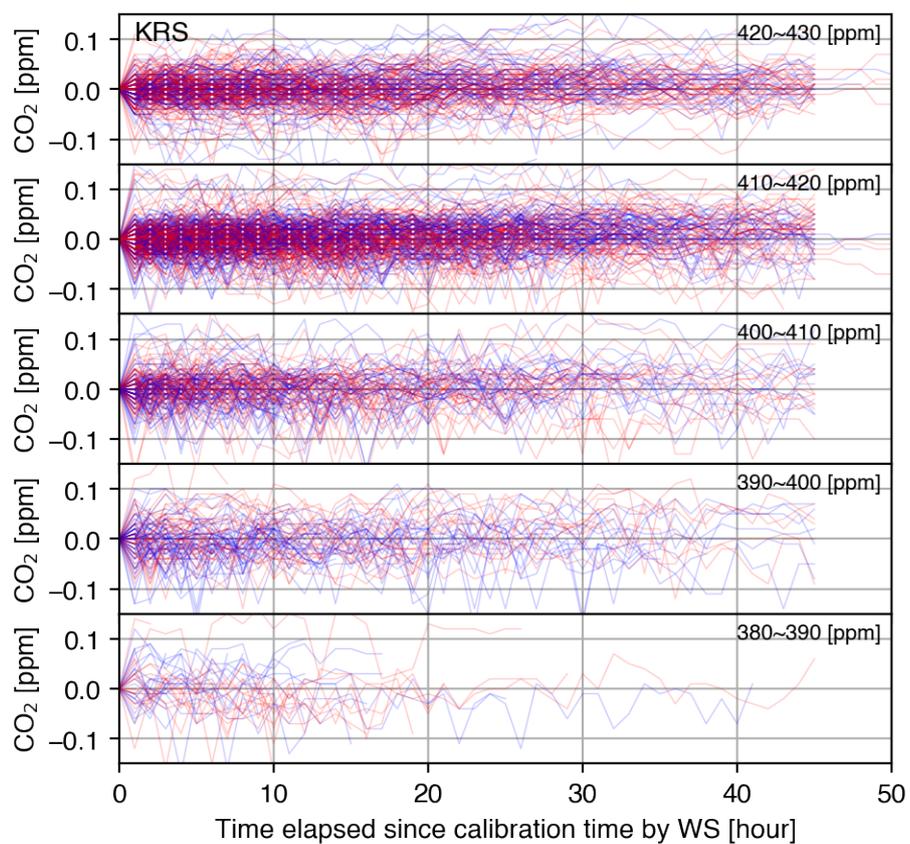


Figure S1. Variation from the CO₂ value of SWS immediately after the WS measurement. Each data is a 3-minute average of the CRDS. The values are divided according to the mole fraction range of the value immediately after the WS measurement. The blue line indicates values for cylinder A, and the red line for cylinder B.

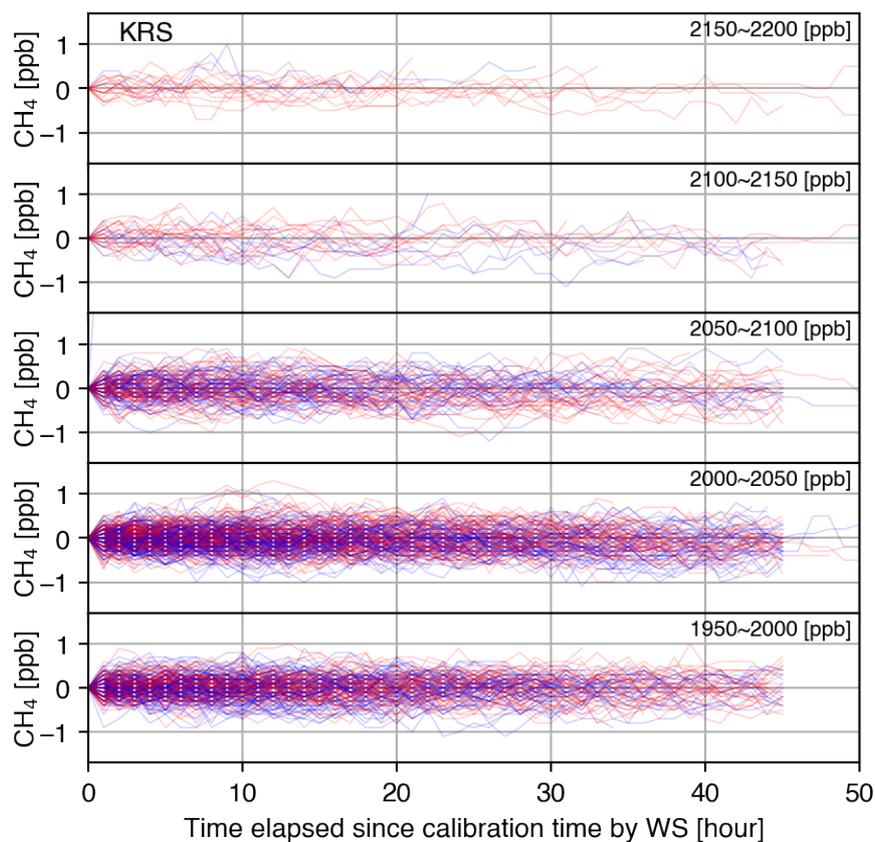


Figure S2. Variation from the CH₄ value of SWS immediately after the WS measurement. Each data is a 3-minute average of the CRDS. The values are divided according to the mole fraction range of the value immediately after the WS measurement. The blue line indicates values for cylinder A, and the red line for cylinder B.

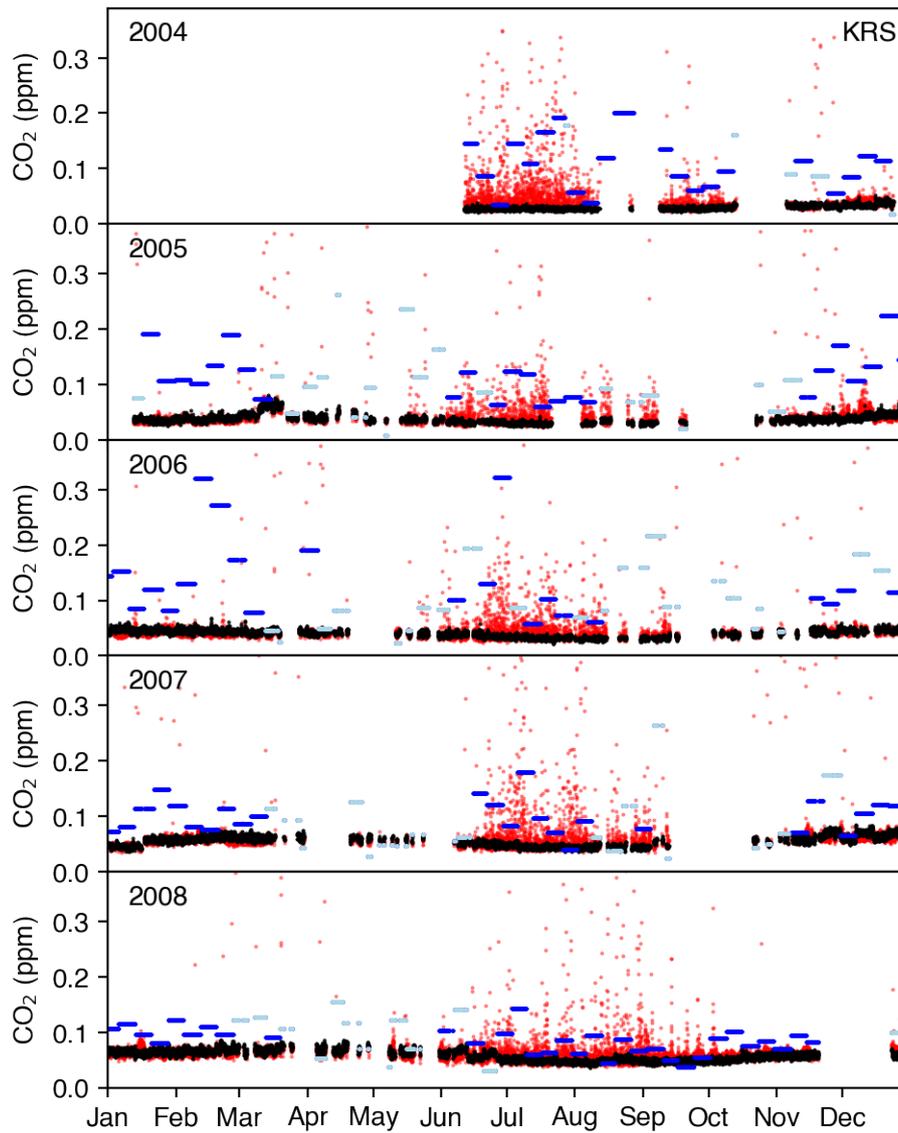


Figure S3. Time series of combined standard uncertainty ($u_c(x)$) for the ambient air CO₂ mole fraction (red dot) and the sensor repeatability (u_r) (black dot) at KRS from 2004 to 2008. A blue dot indicates the reproducibility of the measurement system (σ_{sps}) for about one week. Note that a light blue dot is used when the number of measurements is less than 10.

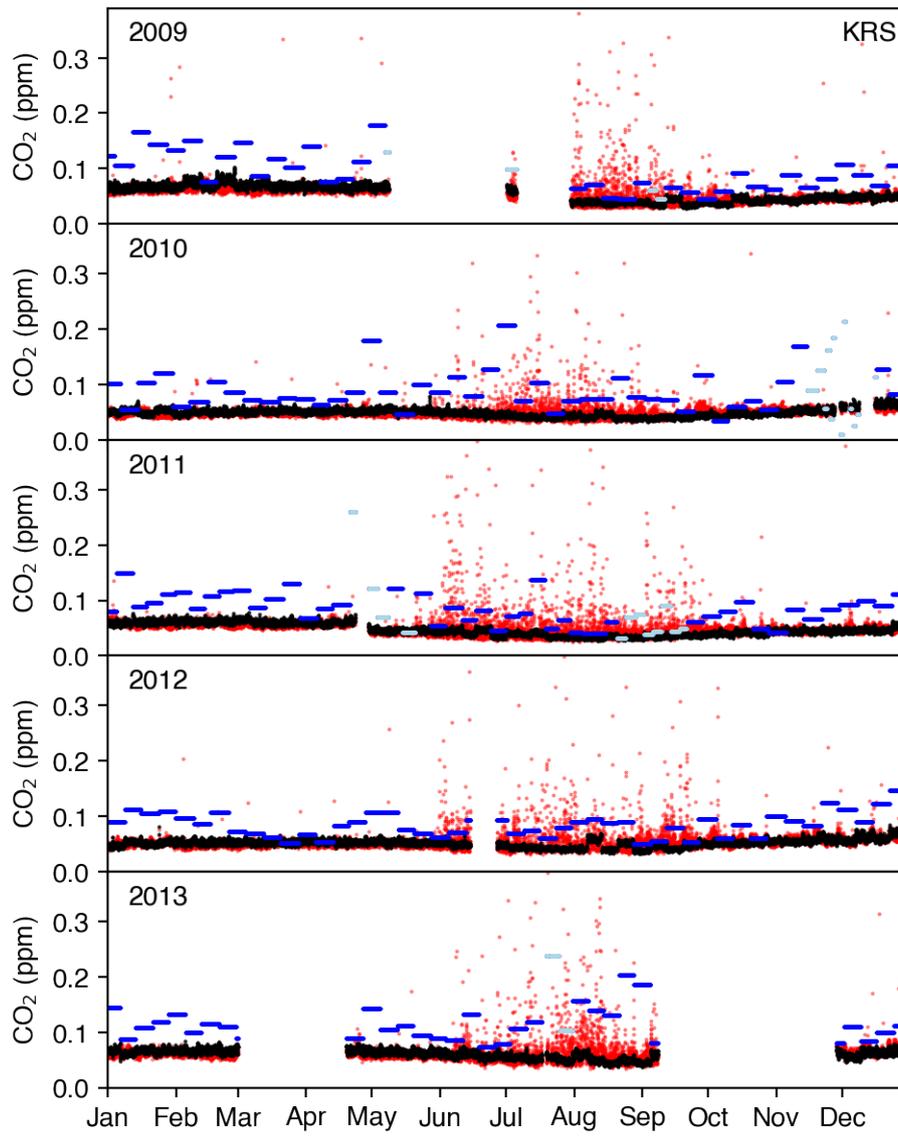


Figure S4. The same as Figure S3 but from 2009 to 2013.

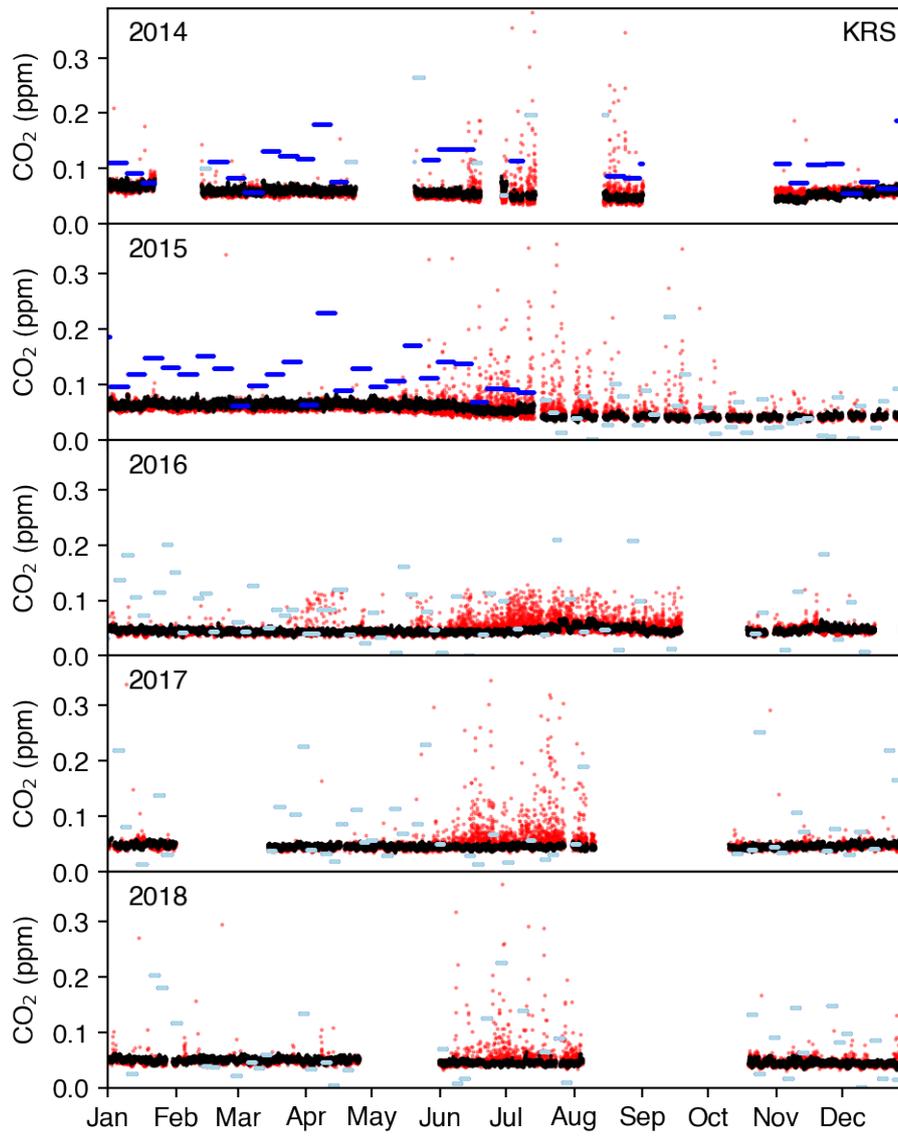


Figure S5. The same as Figure S3 but from 2014 to 2018. Since the CRDS was installed at KRS in July 2015, the consumption flow rate has doubled, and the SWS-gas changeover time has decreased.

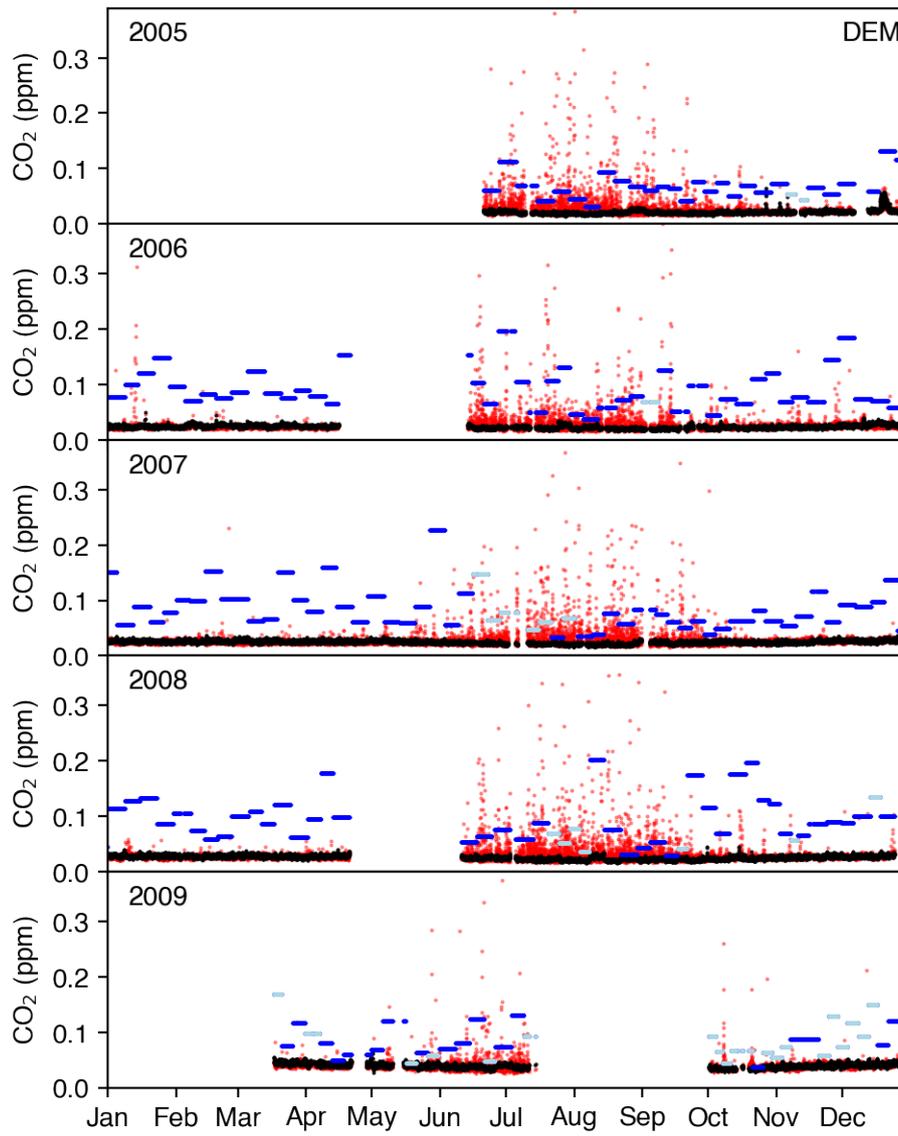


Figure S6. The same as Figure S3 but at DEM from 2005 to 2009.

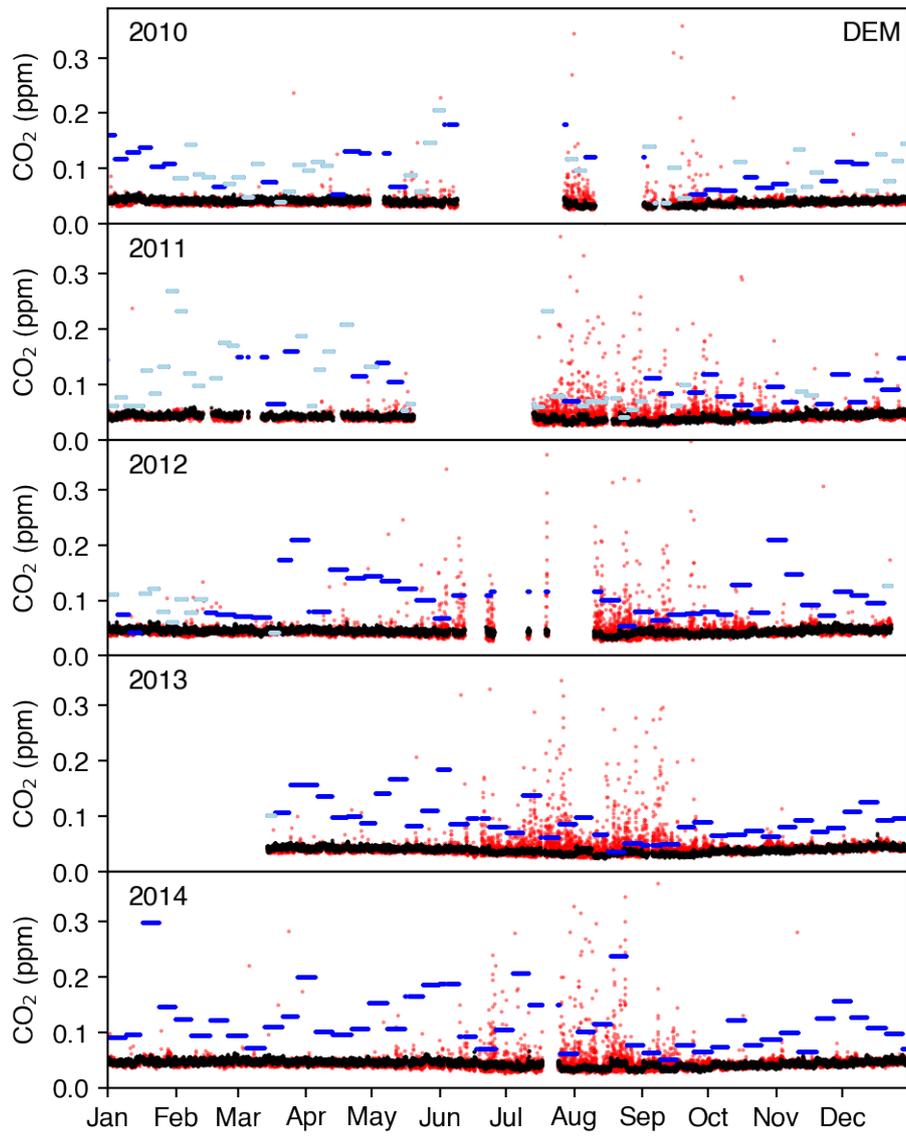


Figure S7. The same as Figure S6 but from 2010 to 2014.

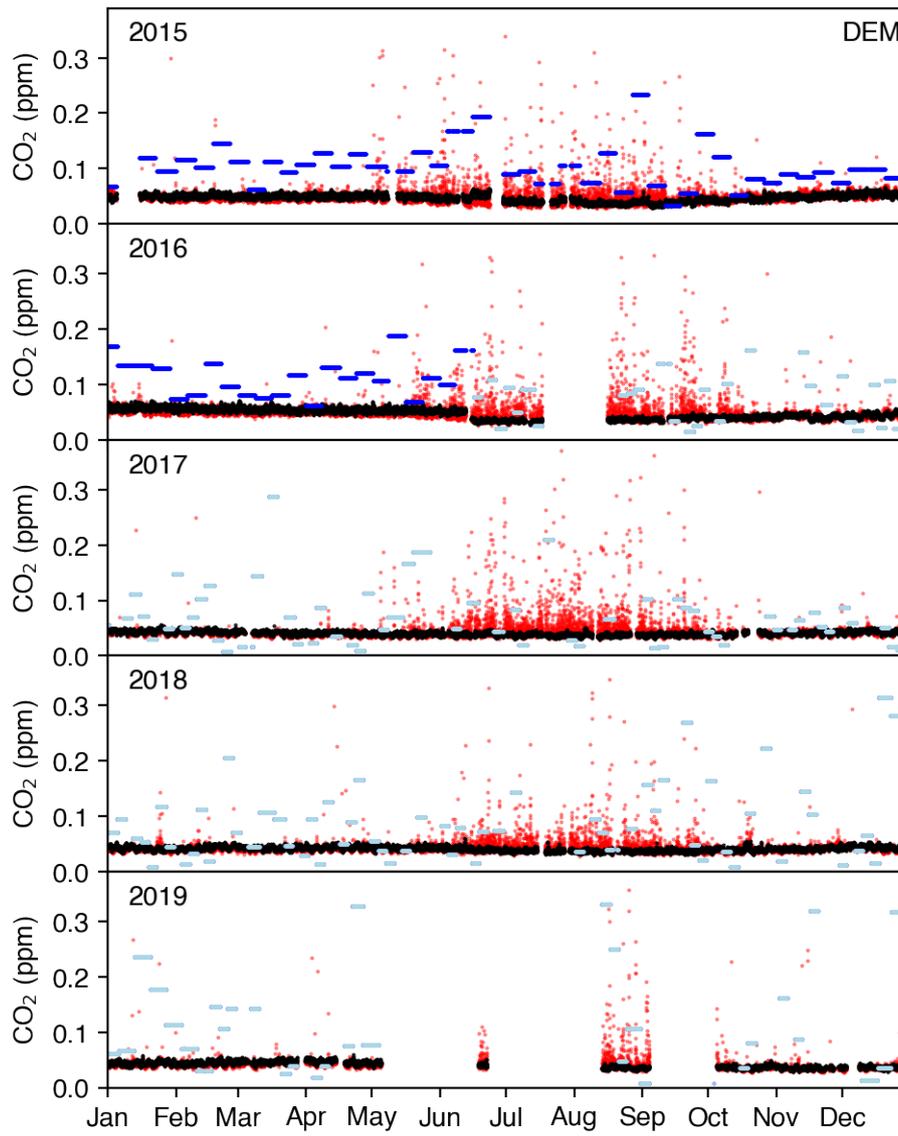


Figure S8. The same as Figure S6 but from 2015 to 2019. Since the CRDS was installed at DEM in June 2016, the consumption flow rate has doubled, and the SWS-gas changeover time has decreased.

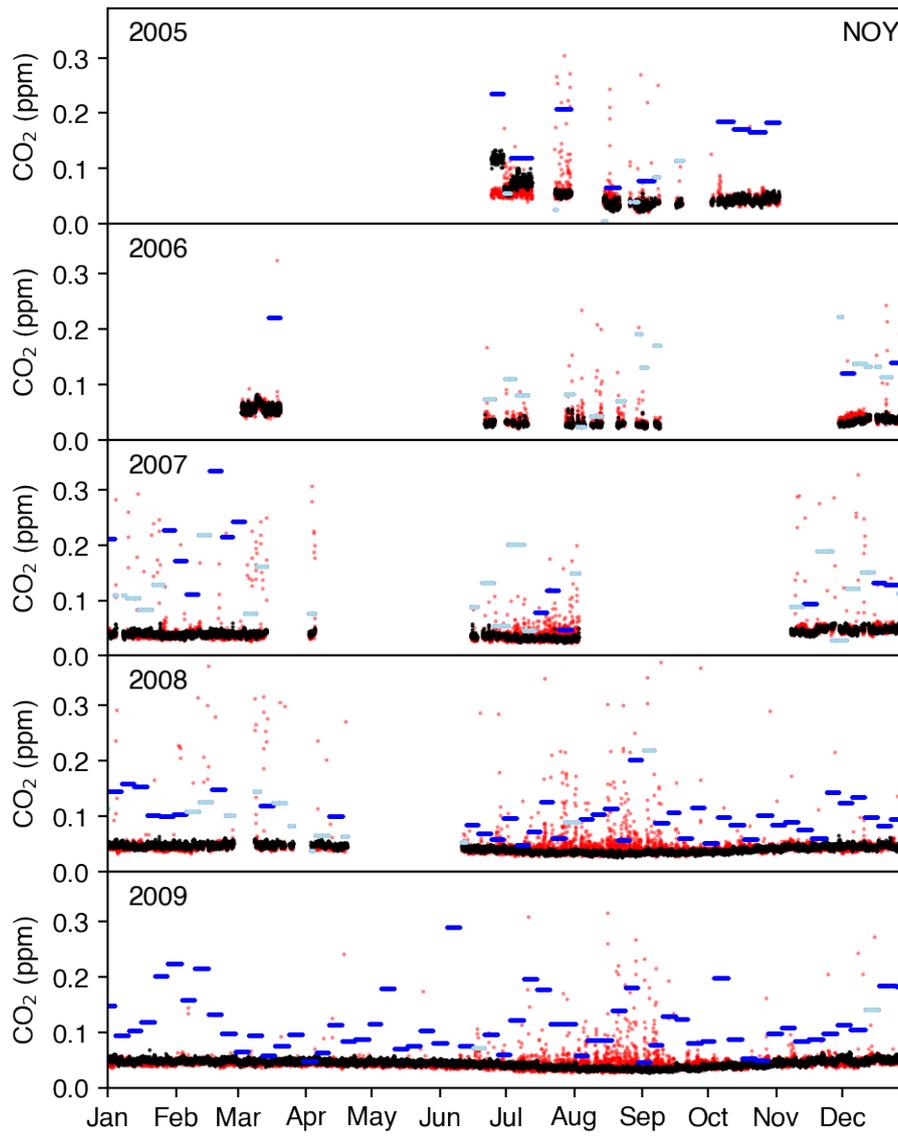


Figure S9. The same as Figure S3 but at NOY from 2005 to 2009.

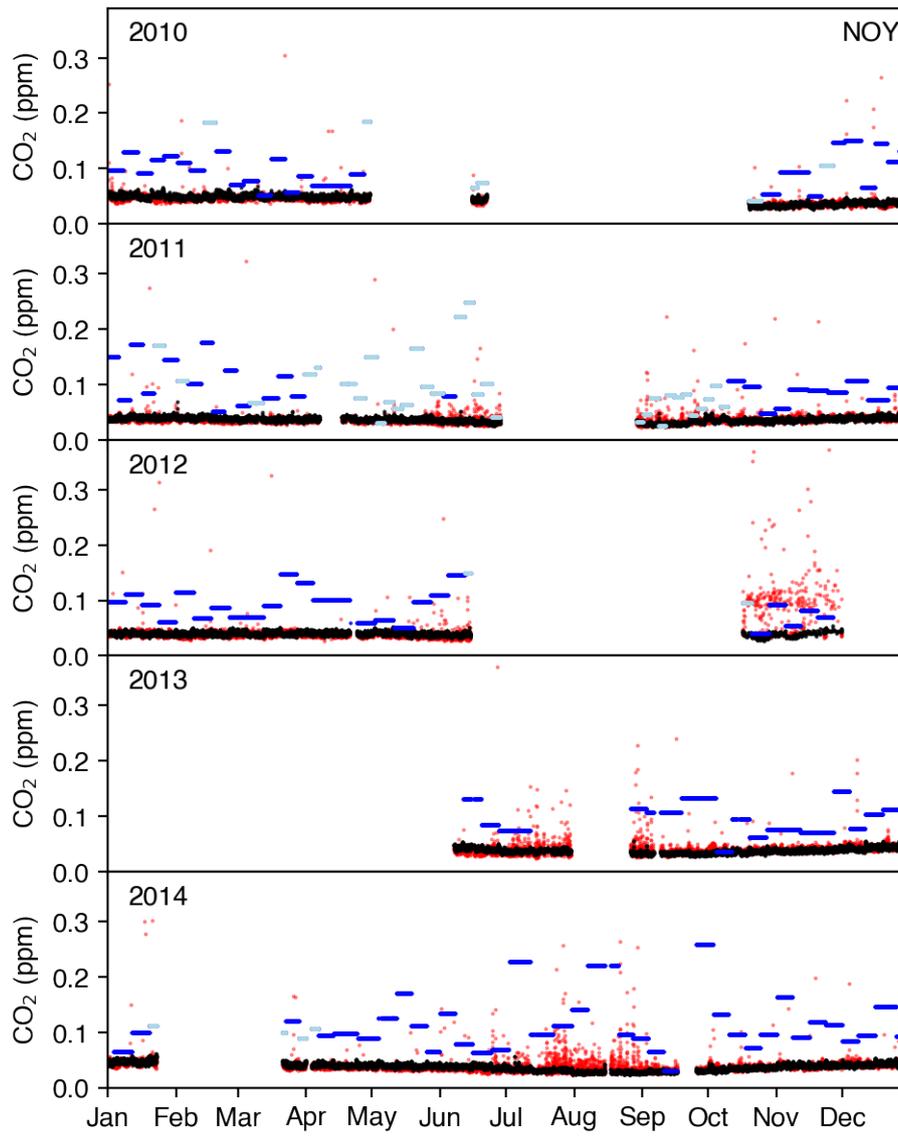


Figure S10. The same as Figure S9 but from 2010 to 2014.

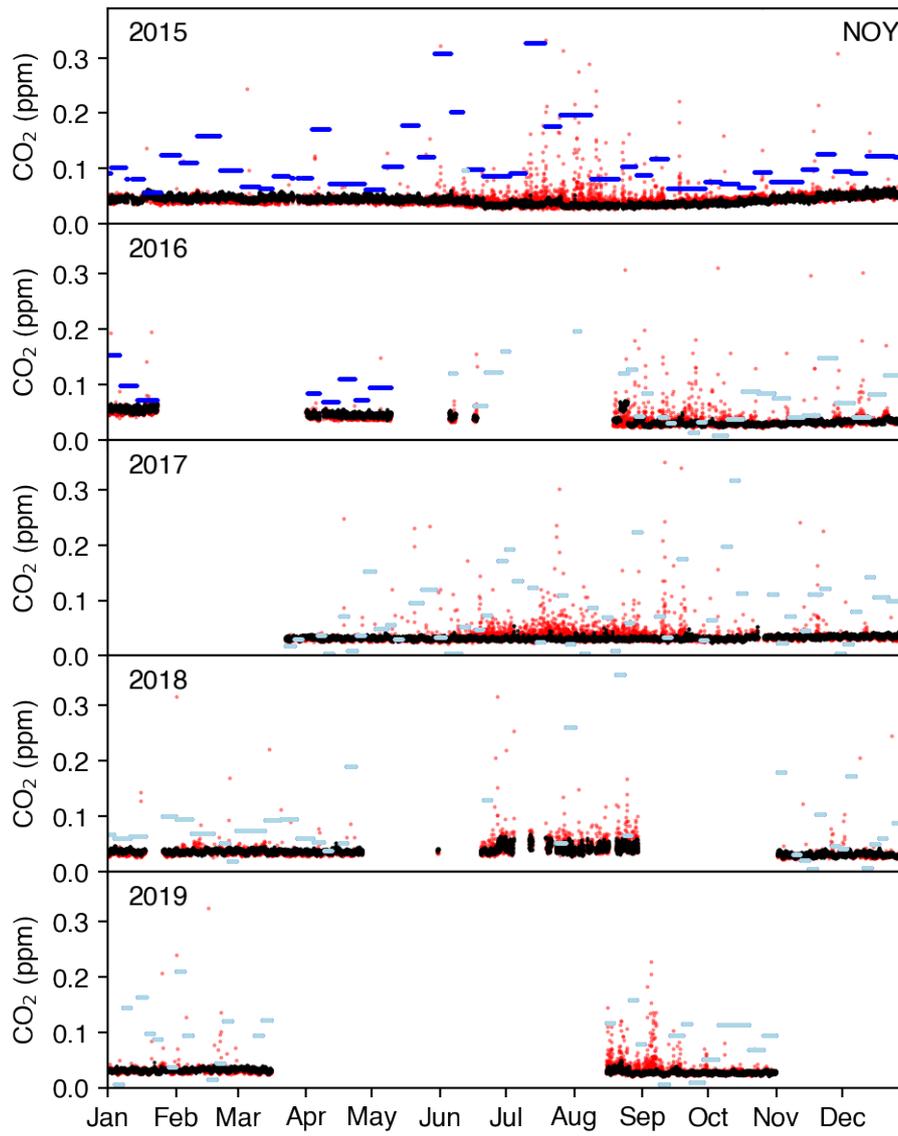


Figure S11. The same as Figure S9 but from 2015 to 2019. Since the CRDS was installed at NOY in August 2016, the consumption flow rate has doubled, and the SWS-gas changeover time has decreased.

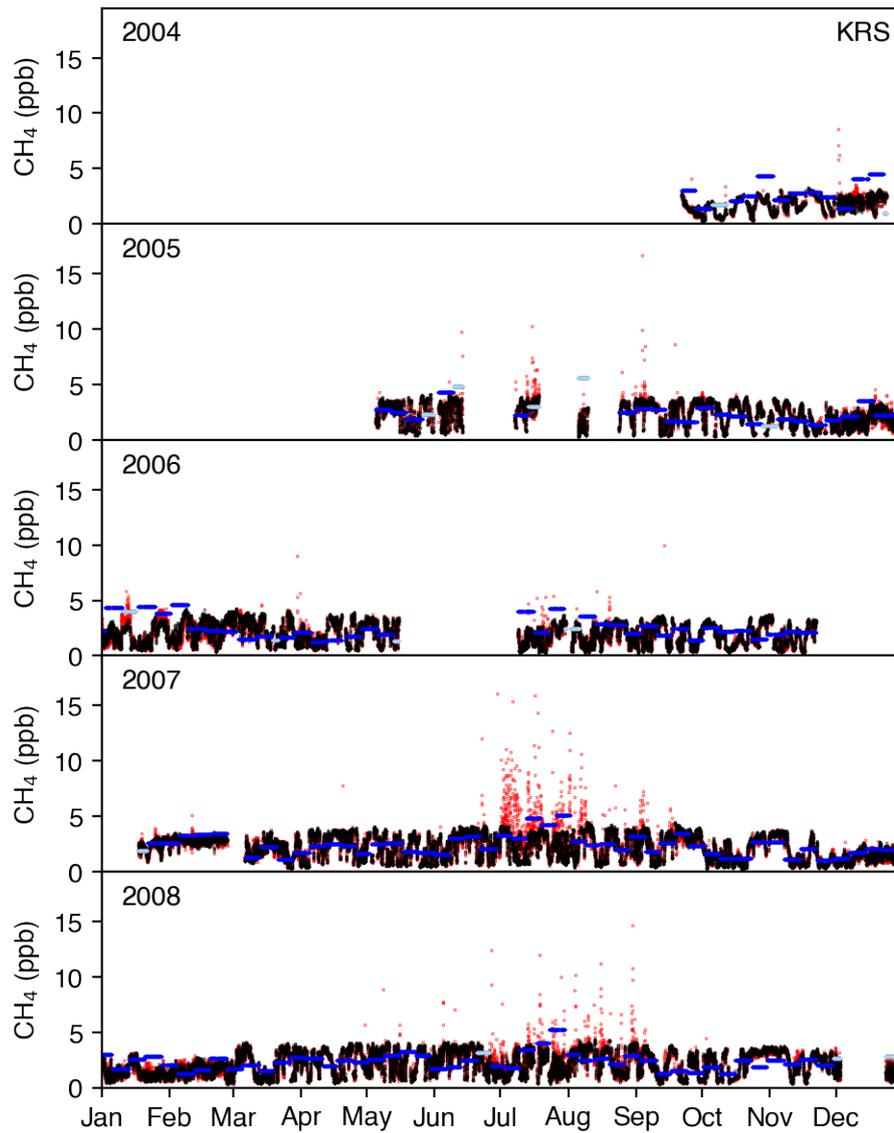


Figure S12. Time series of combined standard uncertainty ($u_c(x)$) for the ambient air CH₄ mole fraction (red dot) and the sensor repeatability (u_r) (black dot) at KRS from 2004 to 2008. A blue dot indicates the reproducibility of the measurement system (σ_{sys}) for about one week. Note that a light blue dot is used when the number of measurements is less than 10.

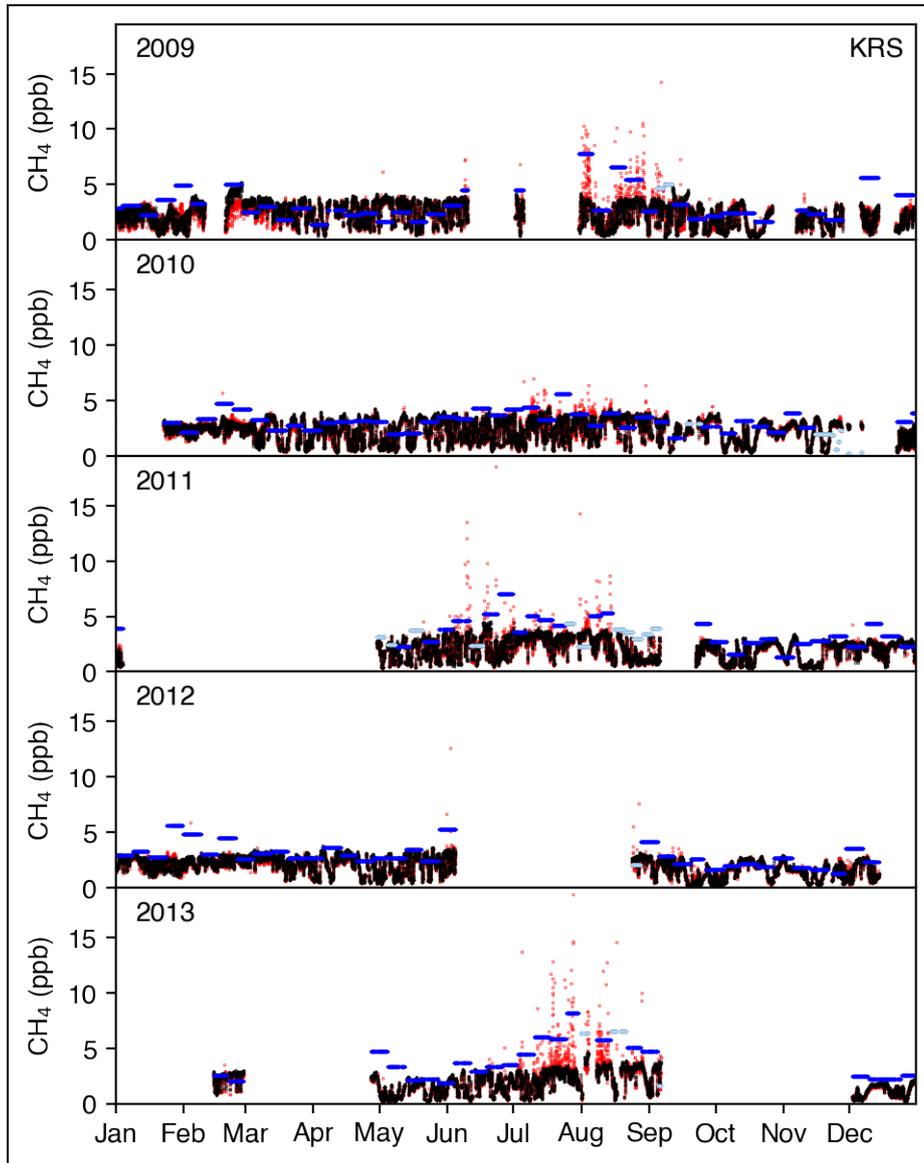


Figure S13. The same as Figure S12 but from 2009 to 2013.

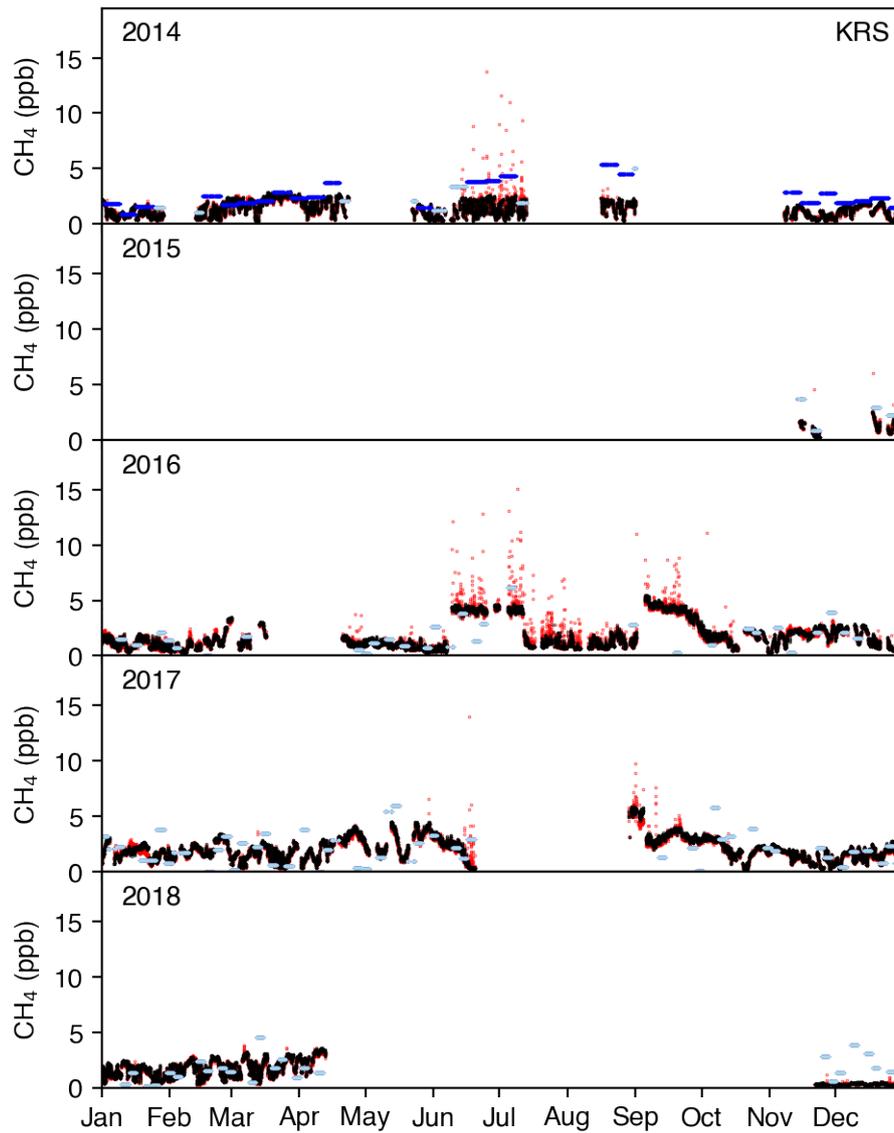


Figure S14. The same as Figure S12 but from 2014 to 2018. Since the CRDS was installed at KRS in July 2015, the consumption flow rate has doubled, and the SWS-gas changeover time has decreased.

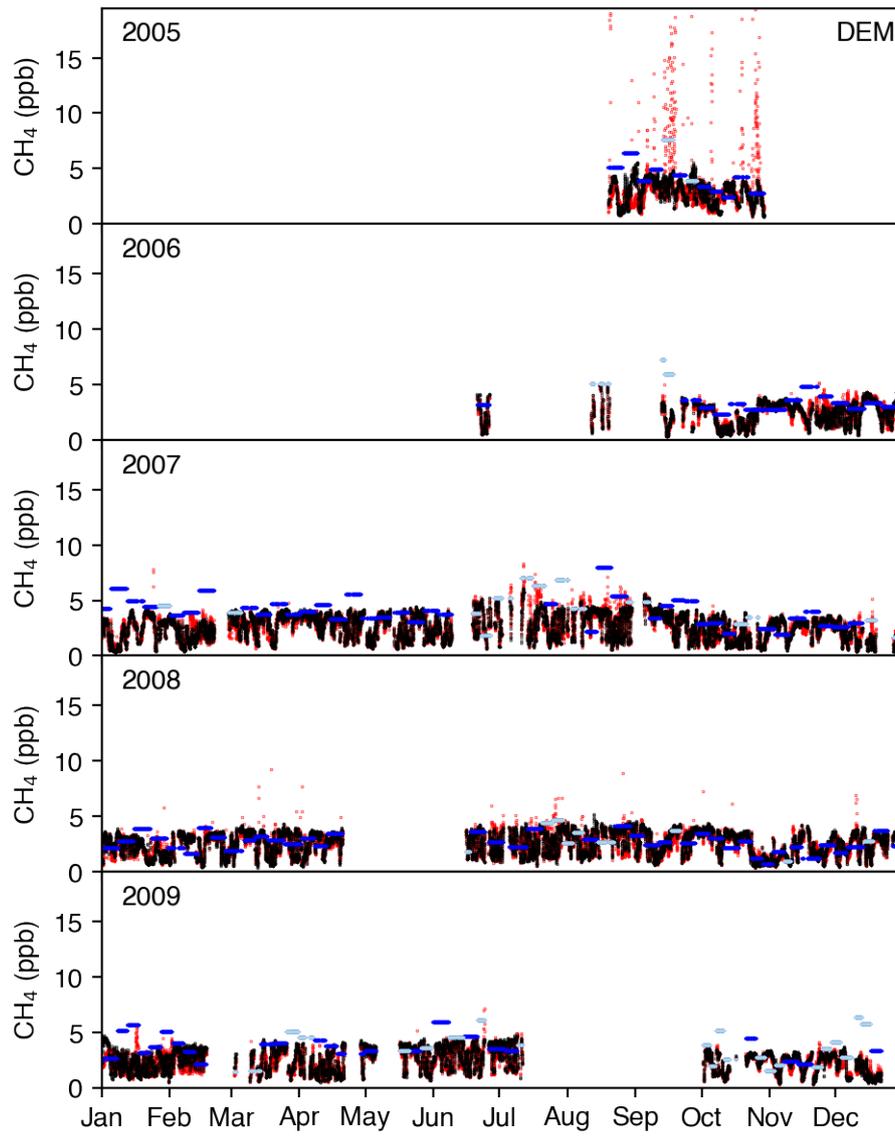


Figure S15. The same as Figure S12 but at DEM from 2005 to 2009.

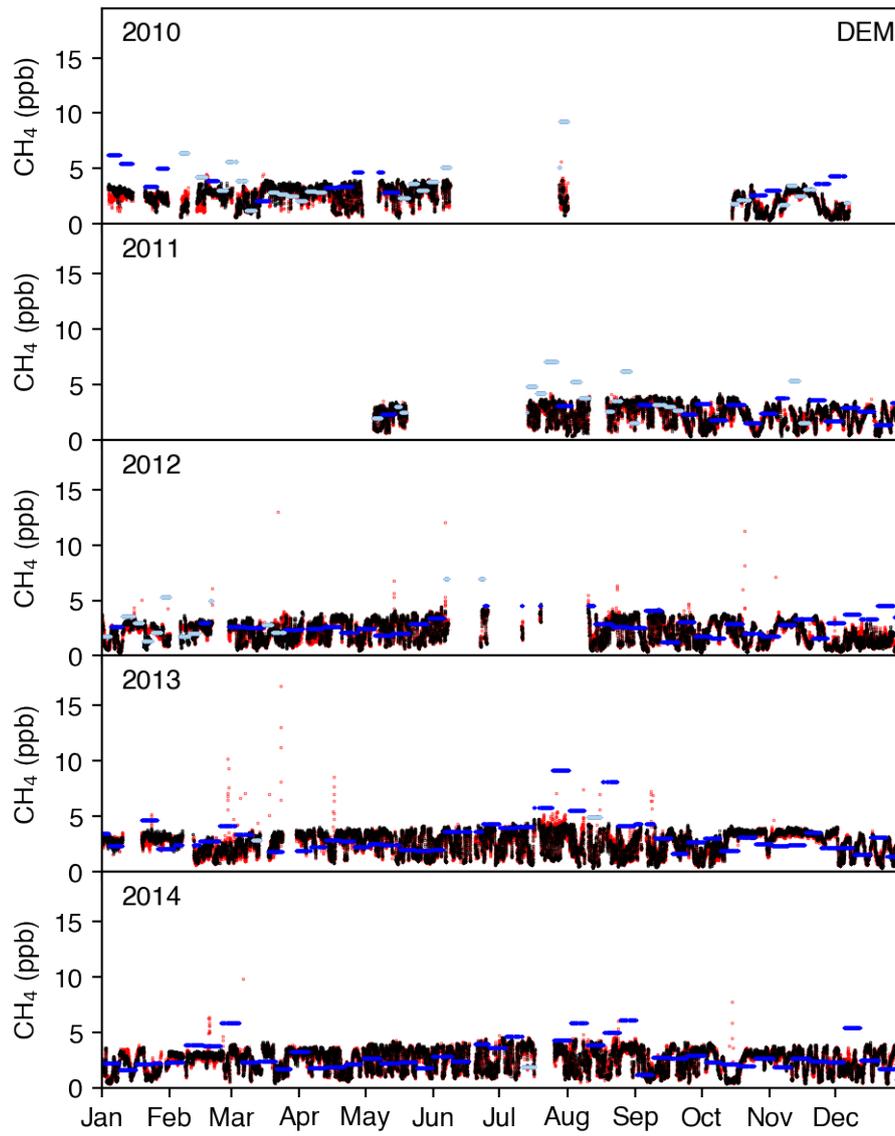


Figure S16. The same as Figure S15 but from 2010 to 2014.

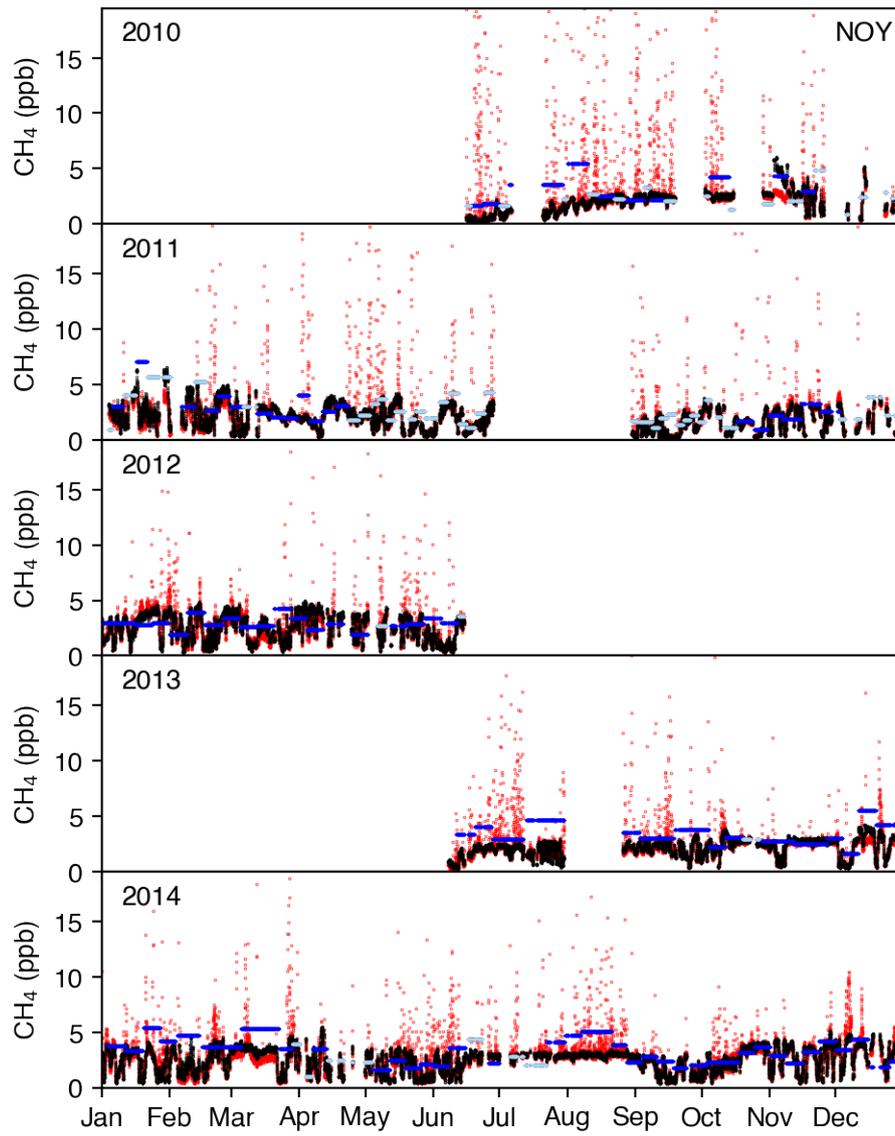


Figure S17. The same as Figure S12 but at NOY from 2010 to 2014.

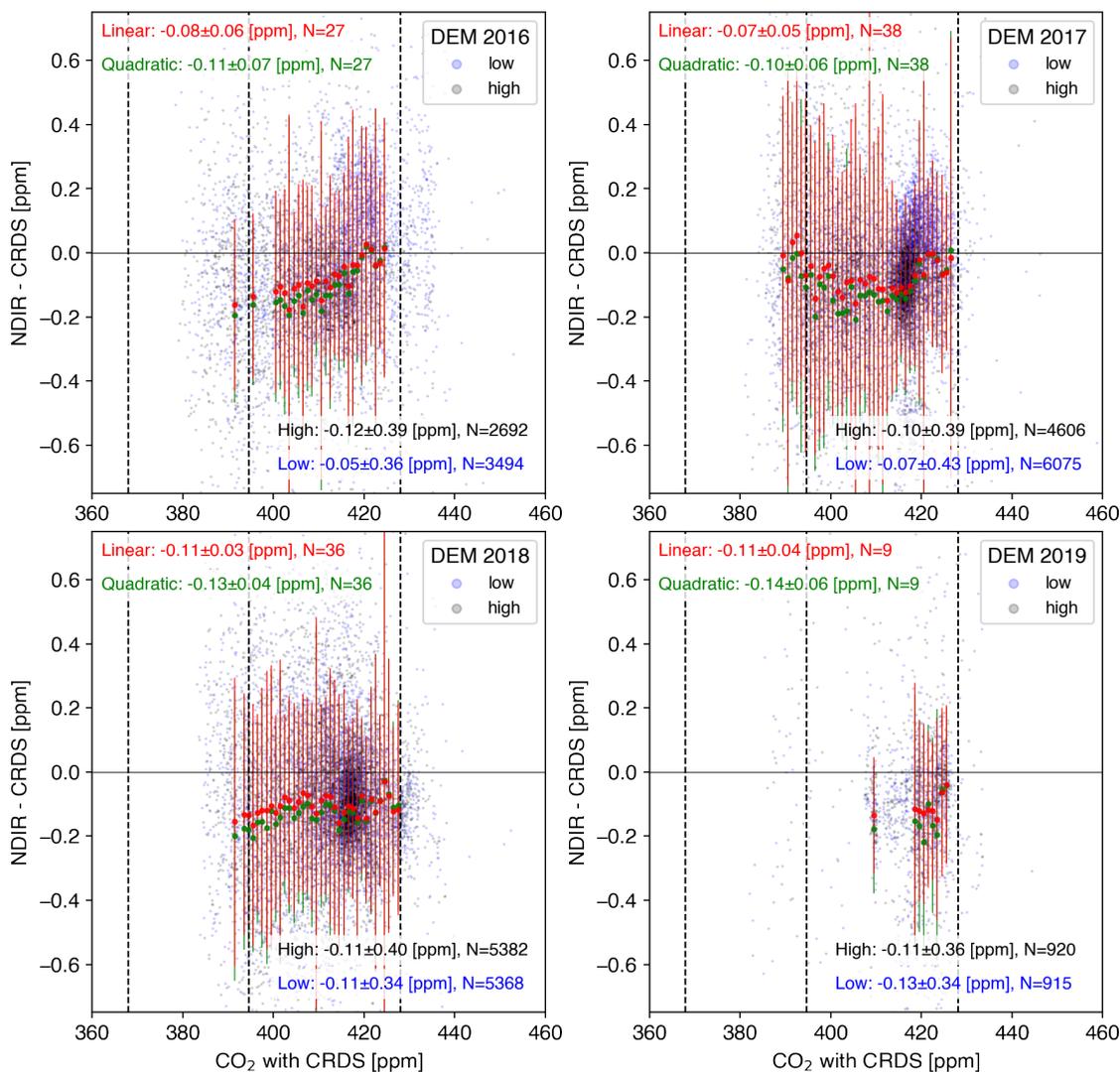


Figure S18. Relationship between the CO₂ mole fraction by the CRDS at DEM and the difference in respective CO₂ mole fractions measured by the NDIR and the CRDS (NDIR-CRDS): The CRDS values were averaged over the corresponding 3-minute period. The light blue (gray) circle shows the difference from a low (high) altitude inlet. The dotted lines indicate the mole fraction of standard gases. The figure (mean \pm SD) in the right bottom represents the average difference for each inlet. Only data that were within the standard gas mole fraction range were used. The red dots indicate the values averaged every one ppm for the combined high-altitude and low-altitude data. However, calculations were only made when the number of data points used was 100 or more. The results from the calibration curve using the quadratic equation are shown as green dots. Error bars indicate the SD. These annual averages are marked by their respective colors in the upper left.

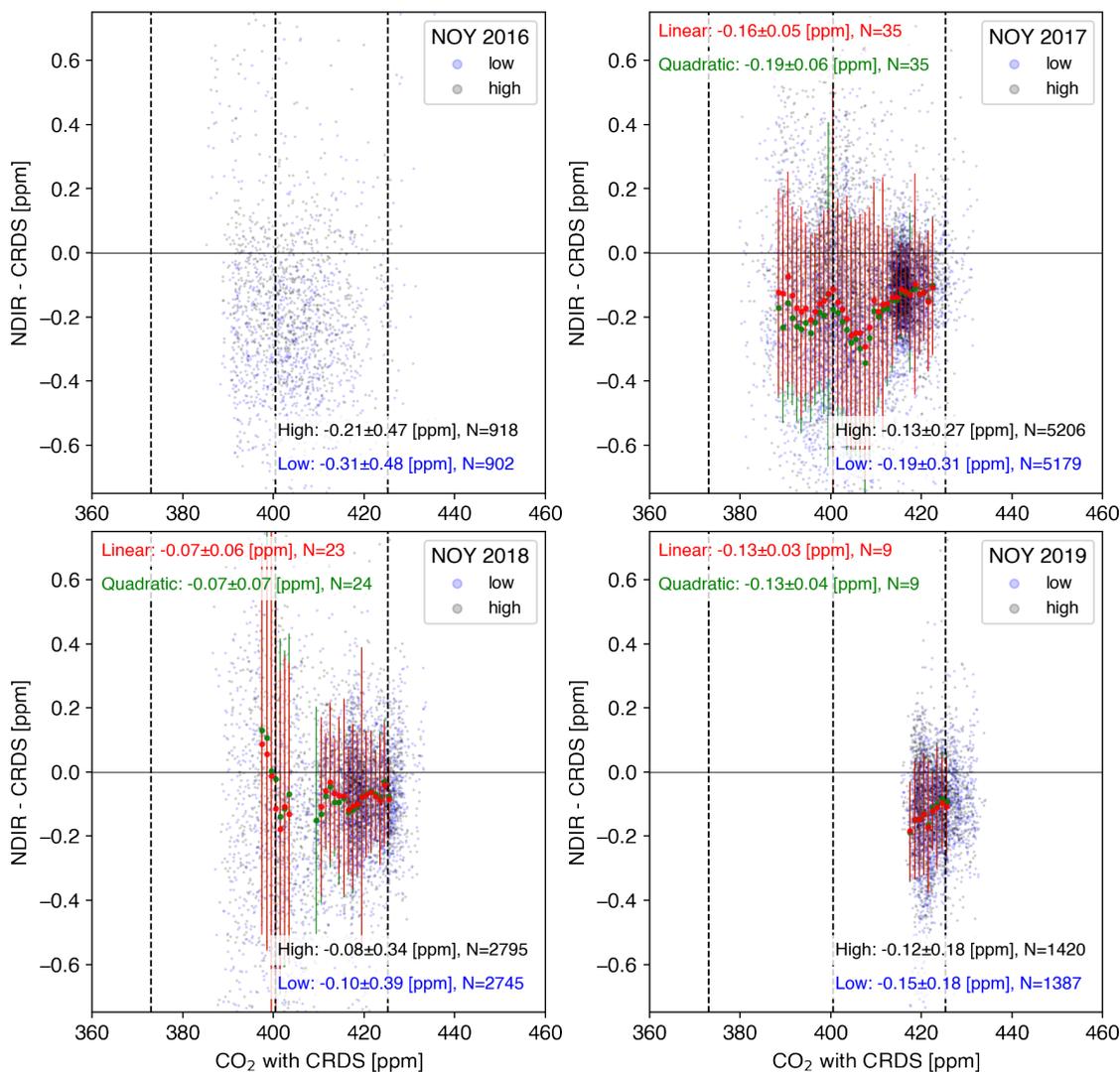


Figure S19. Relationship between the CO₂ mole fraction by the CRDS at NOY and the difference in respective CO₂ mole fractions measured by the NDIR and the CRDS (NDIR-CRDS): The CRDS values were averaged over the corresponding 3-minute period. The light blue (gray) circle shows the difference from a low (high) altitude inlet. The dotted lines indicate the mole fraction of standard gases. The figure (mean ± SD) in the right bottom represents the average difference for each inlet. Only data that were within the standard gas mole fraction range were used. The red dots indicate the values averaged every one ppm for the combined high-altitude and low-altitude data. However, calculations were only made when the number of data points used was 100 or more. The results from the calibration curve using the quadratic equation are shown as green dots. Error bars indicate the SD. These annual averages are marked by their respective colors in the upper left.

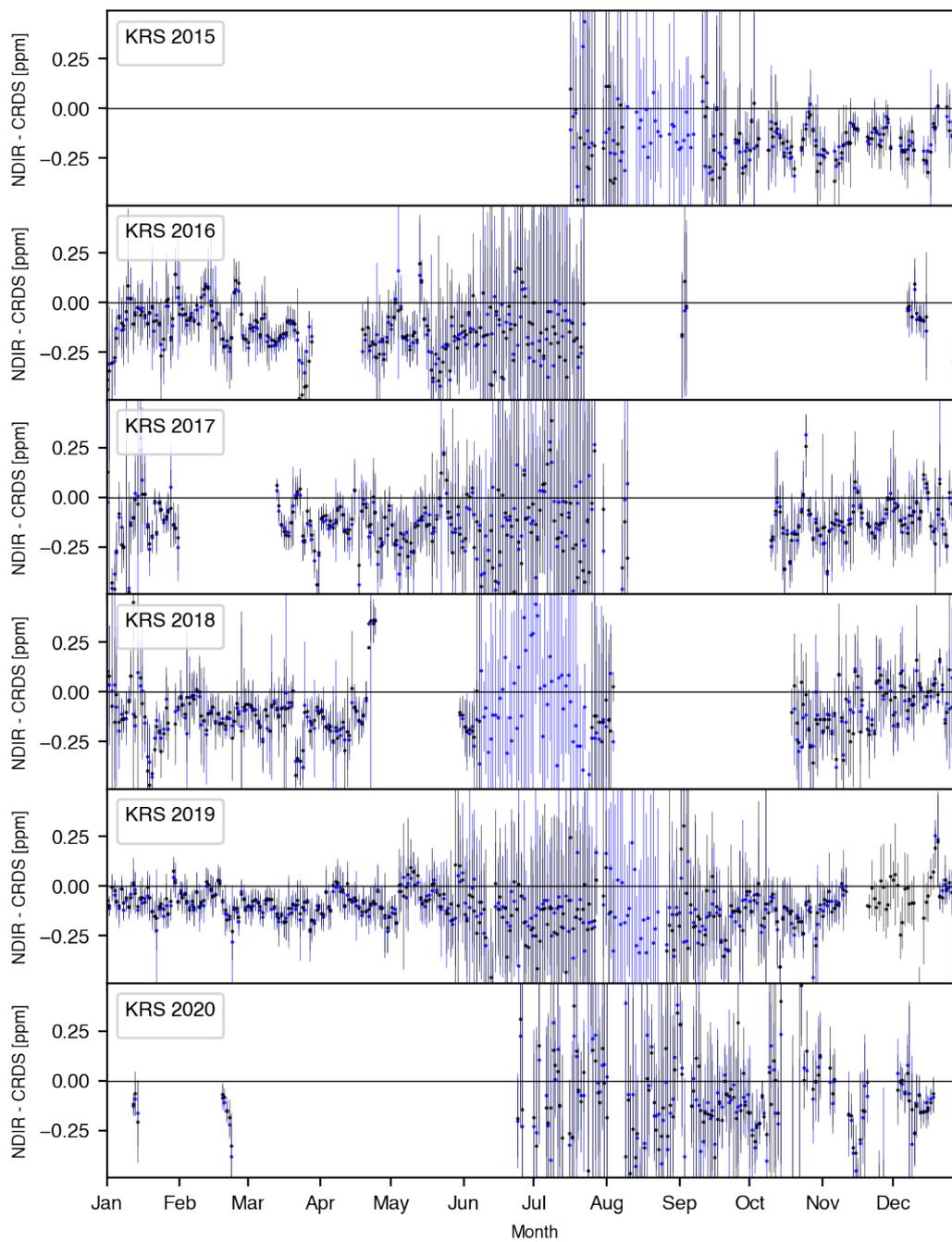


Figure S20. Time series of daily mean of the difference in respective CO_2 mole fractions measured by the NDIR and the CRDS (NDIR-CRDS) at KRS: The CRDS values were averaged over the corresponding 3-minute period. The blue (black) circle shows the daily mean from a low (high) altitude inlet. Error bars are the SD.

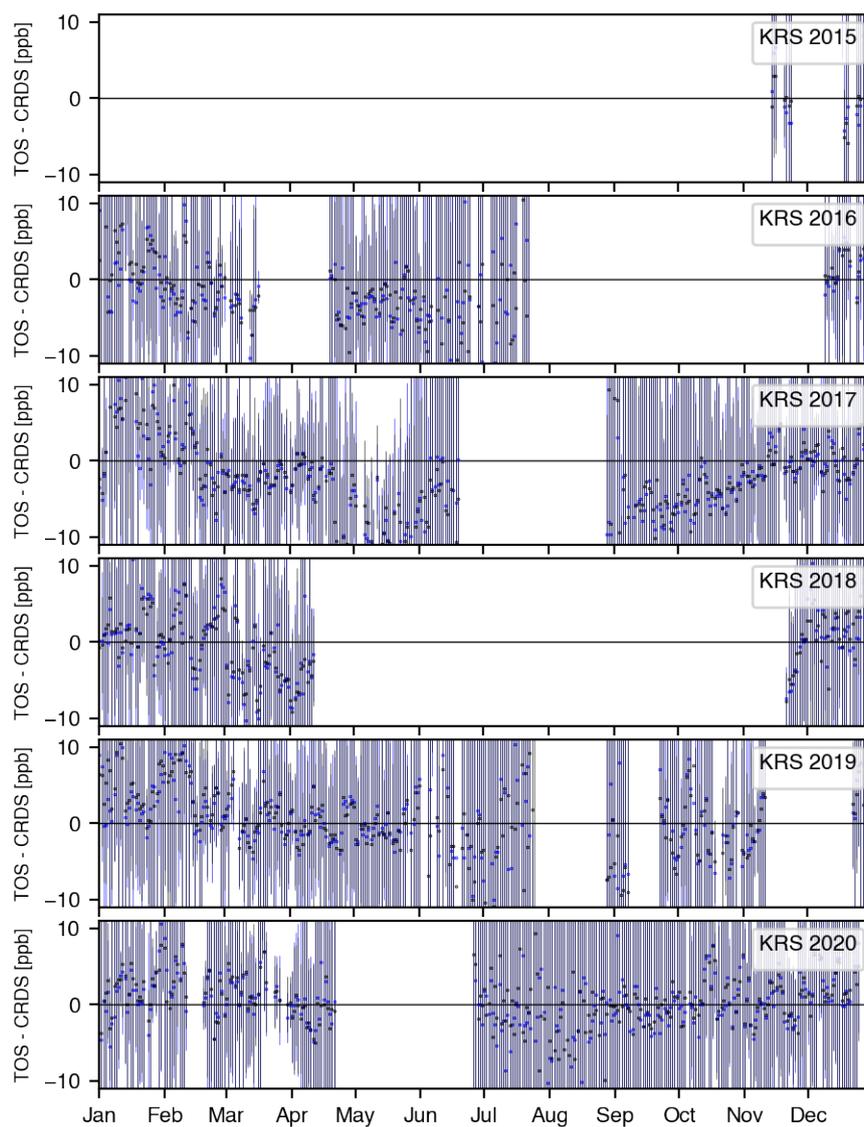


Figure S21. Time series of daily mean of the difference in respective CH_4 mole fractions measured by the TOS and the CRDS (TOS-CRDS) at KRS: The CRDS values were averaged over the corresponding 3-minute period. The blue (black) circle shows the daily mean from a low (high) altitude inlet. Error bars are the SD.