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^{14}C observations of atmospheric CO_2 at Anmyeondo GAW station, Korea: Implications for fossil fuel CO_2 and emission ratios

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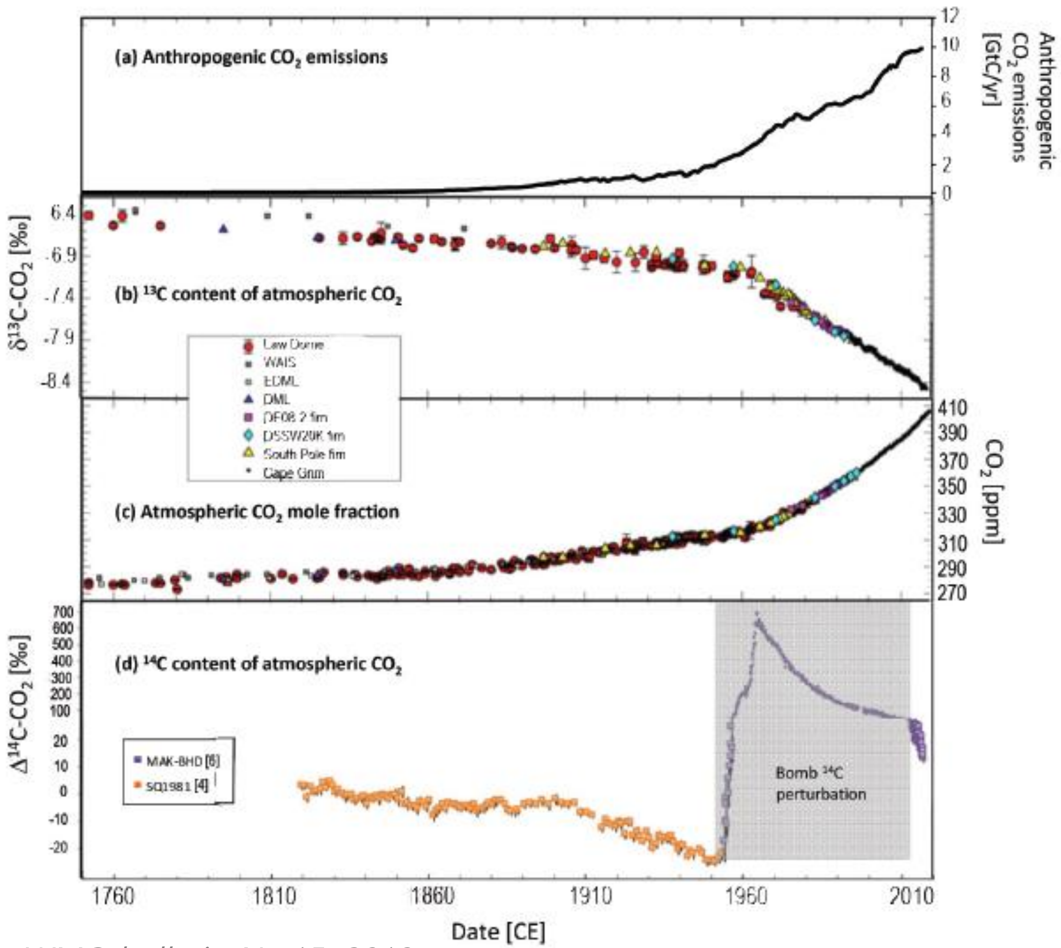
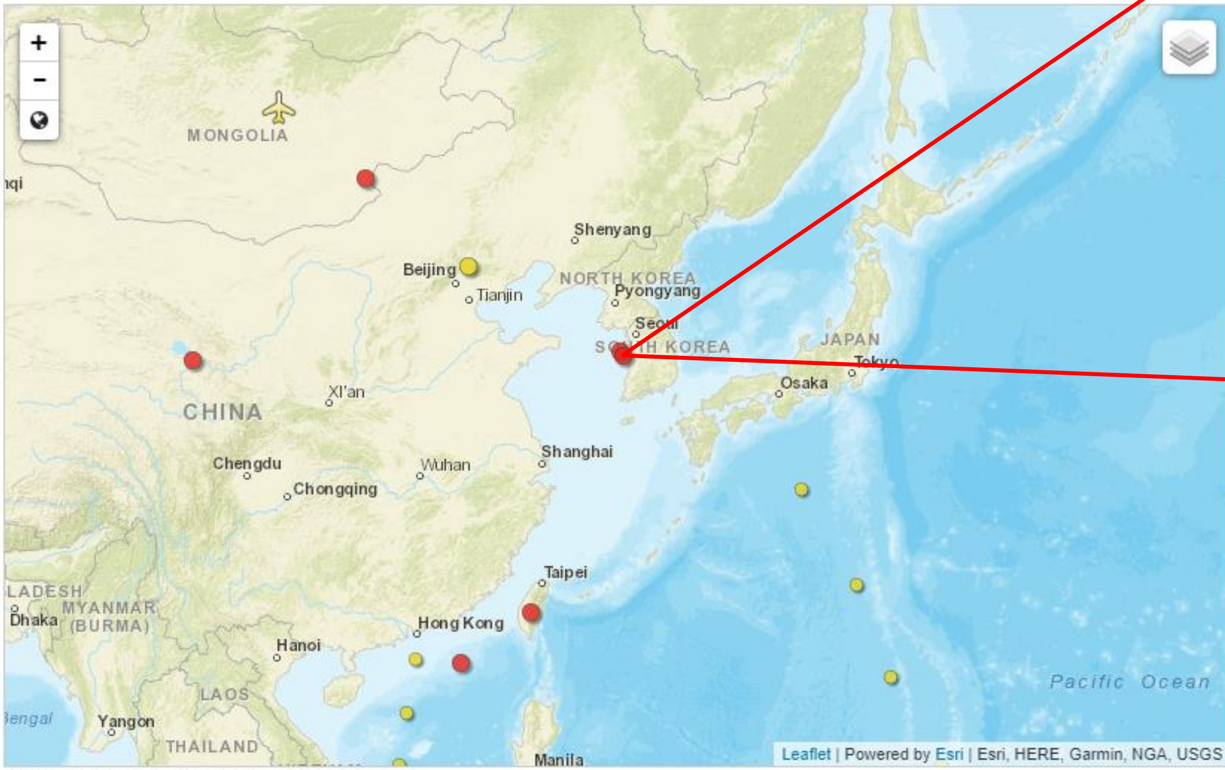
1. Radiocarbon, the good tracer of fossil fuel CO_2



WMO bulletin No.15, 2019

- ^{14}C (~1 part per trillion) produced in very small amounts in the upper atmosphere by cosmic rays.
- ^{14}C is radioactive and decays slowly with a half-life of 5 700 years, resulting in a small but measurable ^{14}C content in atmospheric CO_2 and in plant materials formed from CO_2.
- Fossil fuels were formed from plant material millions of years ago, hence any ^{14}C present when the plants were alive has since decayed during their stay in the Earth's crust.
- ^{14}C content of atmospheric CO_2 have declined, as the fossil fuel CO_2 emitted into the atmosphere has no ^{14}C.

2. Sampling site and method



Yellow markers indicate discontinued sites

- Surface Flasks
- In Situ Tall Tower
- Surface In Situ
- Airborne Flasks
- In Situ Observatory

NOAA CCGG network map: esrl.noaa.gov/gmd/dv/site/index.php?program=ccgg

- AMY: 36.53°N, 126.32°E; 46 m a.s.l.
- TAP: 36.73° N, 126.13° E, 20 m a.s.l.
- 2 pairs of flasks were collected on a weekly basis for CO_2, **SF_6, CO** (by NOAA/GML) and $^{14}CO_2$ (by Institute of Arctic and Alpine Research, INSTAAR) from 2014 to 2016 with 70 samples.

2. Data analysis: Calculation of C_{ff} and C_{bio}

$$C_{obs} = C_{bg} + C_{ff} + C_{other}$$

$$\Delta_{obs} C_{obs} = \Delta_{bg} C_{bg} + \Delta_{ff} C_{ff} + \Delta_{other} C_{other}$$

$$C_{ff} = \frac{C_{bg}(\Delta_{obs} - \Delta_{bg})}{\Delta_{ff} - \Delta_{bg}} - \frac{C_{other}(\Delta_{other} - \Delta_{bg})}{\Delta_{ff} - \Delta_{bg}}$$

$\Delta^{14}C \approx [(^{14}C/C)_{sample}/(^{14}C/C)_{standard} - 1] \times 1000‰$
$\Delta_{ff} = -1000‰$

(1) Nuclear power
(2) Ocean flux
(3) Photosynthetic contribution
(4) Heterotrophic respiration

$-0.2 \pm 0.1\ \mu mol\ mol^{-1}$ during winter
$-0.5 \pm 0.2\ \mu mol\ mol^{-1}$ during summer

Turnbull et al., 2006

*bg derived from Niwot Ridge (NWR)
*$C_{bio} = C_{obs} - C_{bg}$

3. Data analysis: The ratio of Δx to C_{ff}

- $\Delta x = x_{obs} - x_{bg}$ for SF_6 and CO

- To obtain the correlation coefficient (r) between gases and C_{ff}
- To compare the emission ratio (R_{gas}) with bottom-up inventory using RMA analysis which is known for a relatively robust method of calculating the slope of two variables.

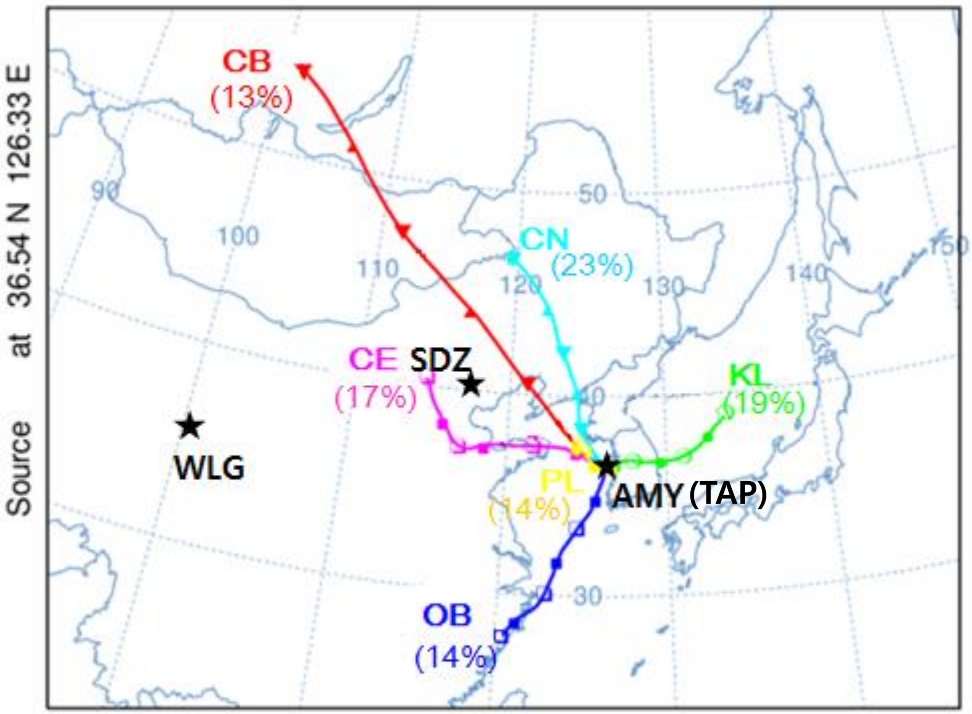
$$R_{\mathrm{gas}} = \sqrt{\frac{\sum \Delta x^2 - \left(\sum \Delta x\right)^2/n}{\sum C_{\mathrm{ff}}^{\ 2} - \left(\sum C_{\mathrm{ff}}\right)^2/n}}$$

$$r = \sqrt{\frac{\left(\sum \Delta x C_{\mathrm{ff}} - \frac{\sum \Delta x \sum C_{\mathrm{ff}}}{n}\right)^2}{\left(\sum \Delta x^2 - \frac{\left(\sum \Delta x\right)^2}{n}\right) \times \left(\sum C_{\mathrm{ff}}^{\ 2} - \frac{\left(\sum C_{\mathrm{ff}}\right)^2}{n}\right)}}$$

$$U = \sqrt{\frac{\sum(\Delta x - \Delta x')^2/n}{\sum C_{\mathrm{ff}}^{\ 2} - \left(\sum C_{\mathrm{ff}}\right)^2/n}}$$

$$\text{Here, } \Delta x' = R_{\mathrm{gas}} \times \left(C_{\mathrm{ff}} - \overline{C_{\mathrm{ff}}}\right) + \overline{\Delta x}$$

3. Data analysis: HYSPLIT



- HYSPLIT trajectories were run using Unified Model-Global Data Assimilation and Prediction System (UM-GDAPS) weather data at 25 km by 25 km horizontal resolution.

- CB: Continental Baseline
- CN: Northeast China
- CE: central Eastern China
- OB: Ocean Baseline

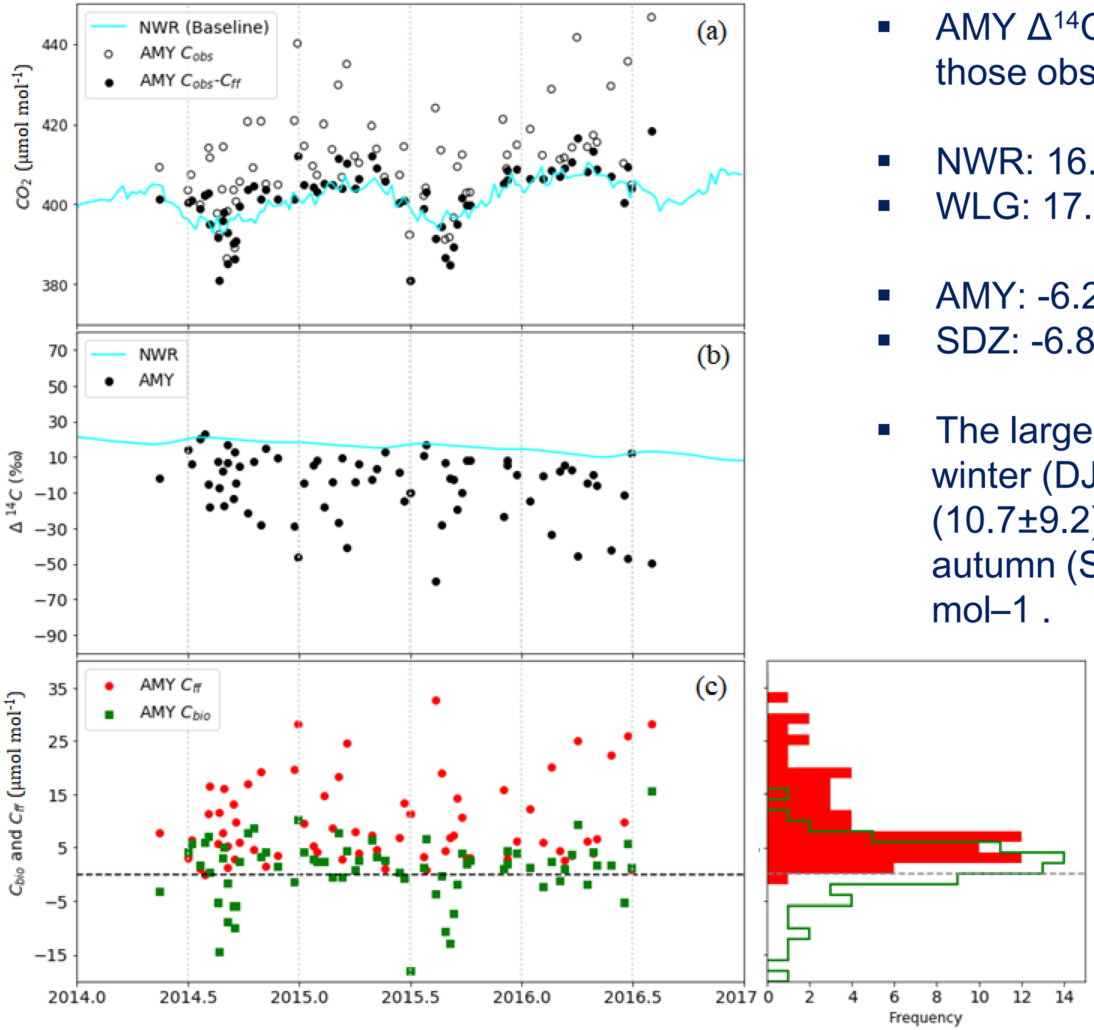
67%

- KL: Korea Local
- PL: Polluted Local

23%

- To more clearly identify samples, we removed the data when wind speed was less than 3m/s with assumption that those samples could be affected by local pollution.

4. Observed $\Delta^{14}CO_2$ at AMY



- AMY $\Delta^{14}CO_2$ values are almost always lower than those observed at NWR (of course).

- NWR: 16.6±3‰ (10 to 21.2 ‰, this study)
- WLG: 17.1±6.8 ‰ in 2015 (Niu et al., 2016)

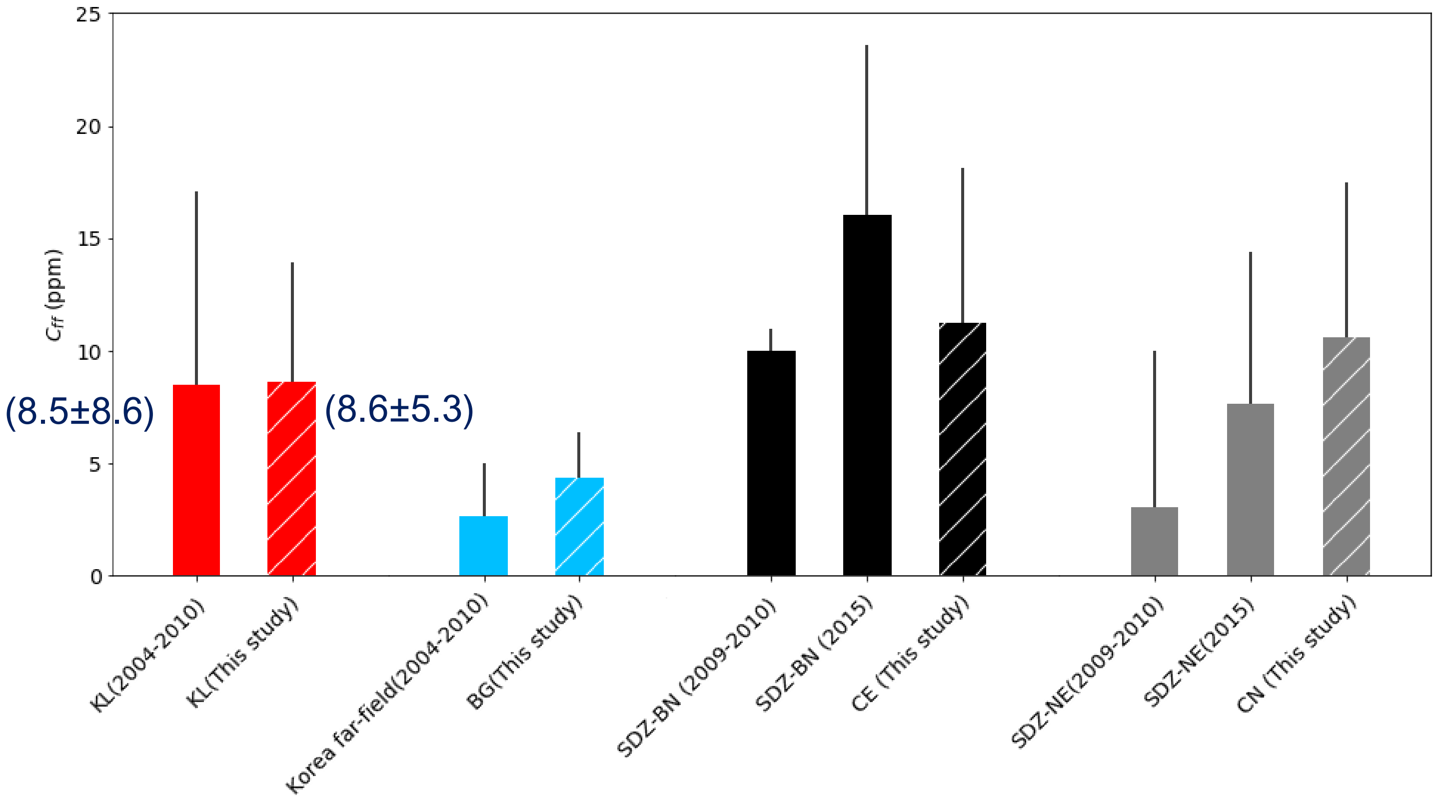
- AMY: -6.2±18.8‰ (-59.5 to 23.1‰, this study)
- SDZ: -6.8±21.1 ‰ (-53.0 to 32.6‰, Niu et al., 2016)

- The largest C_{ff} :
  winter (DJF, (11.3±7.6), n=14) > summer (JJA, (10.7±9.2), n=11) > spring (MAM, (8.6±8.0), n=22) > autumn (SON, (7.6±5.6), n=17) with a unit of μmol mol–1 .

- Only positive contributions of C_{bio}

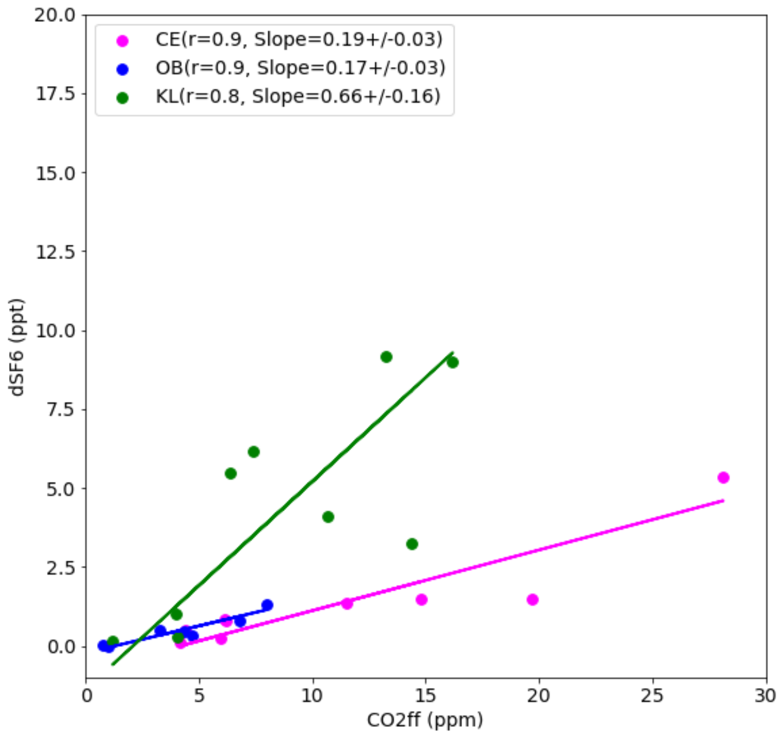
  summer ((4.6±4.0), n=14) > autumn ((4.1±2.5), n=9) > spring ((3.8±2.6), n=13) > winter 250 ((3.4±2.5), n=11)

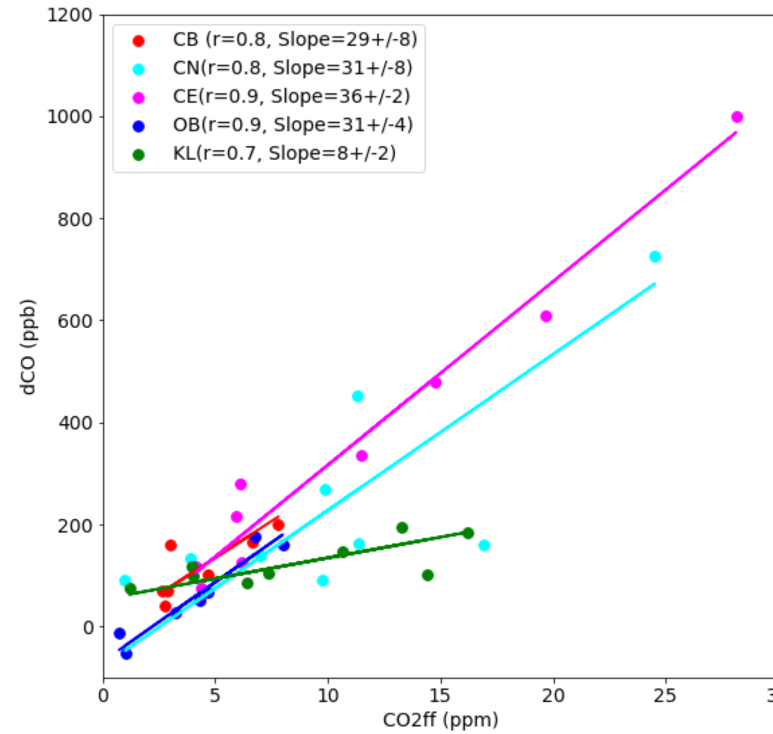
5. C_{ff} comparison between Korea Local and Asian Continent



- C_{ff} is highest in the order CE > CN > KL > CB > OB
- 2.6±2.4 (Korea far-field 2004 to 2010, Turnbull et al., 2011) → 4.3±2.1 ppm (Baseline, this study)
- 10±1 (Beijing and North China Plain, SDZ-BN, Turnbull et al., 2011) → 16±7.6 (2015, Niu et al., 2016) → 11.2 ±8.3 (CE, this study)
- 3±7 (northeast China, SDZ-NE, Turnbull et al., 2011) → 7.6±6.8 (2015, Niu et al., 2016) → 10.6±6.9 (CN, This study)

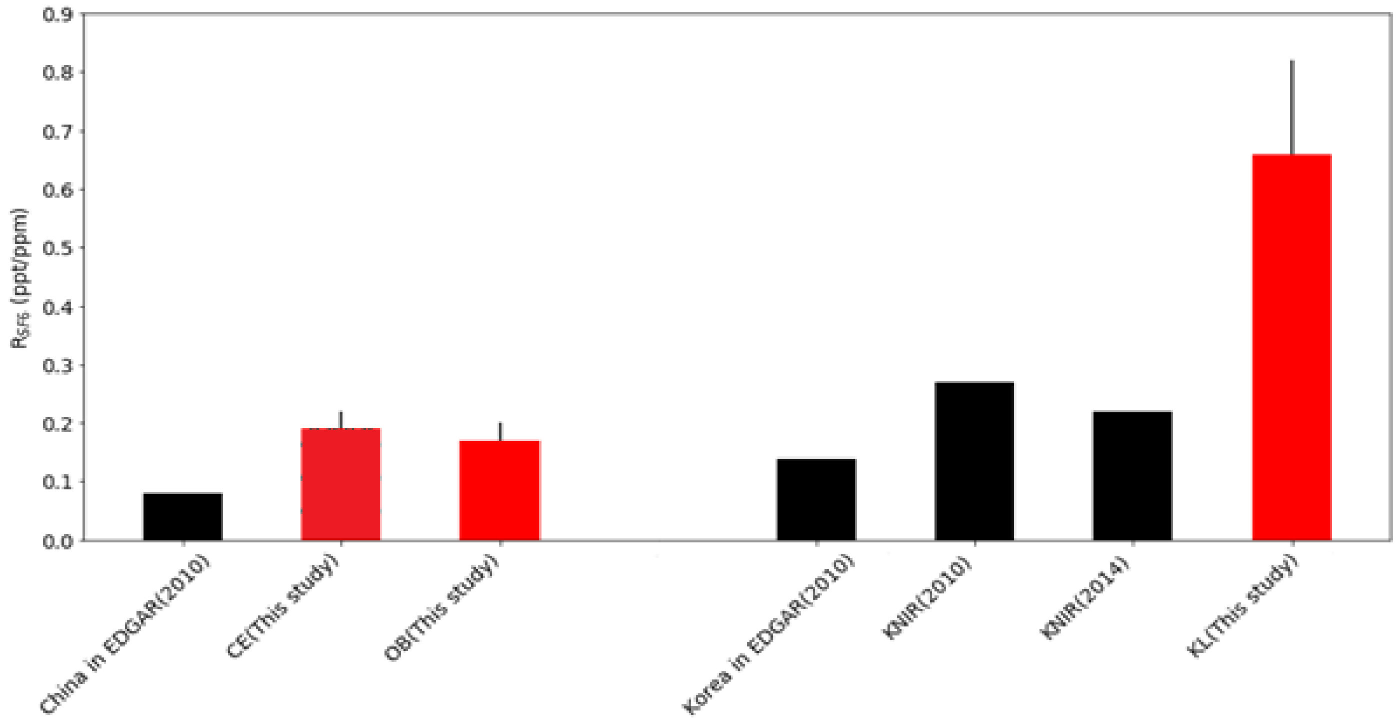
6. Correlation of C_{ff} and Δgas, observed emission ratio





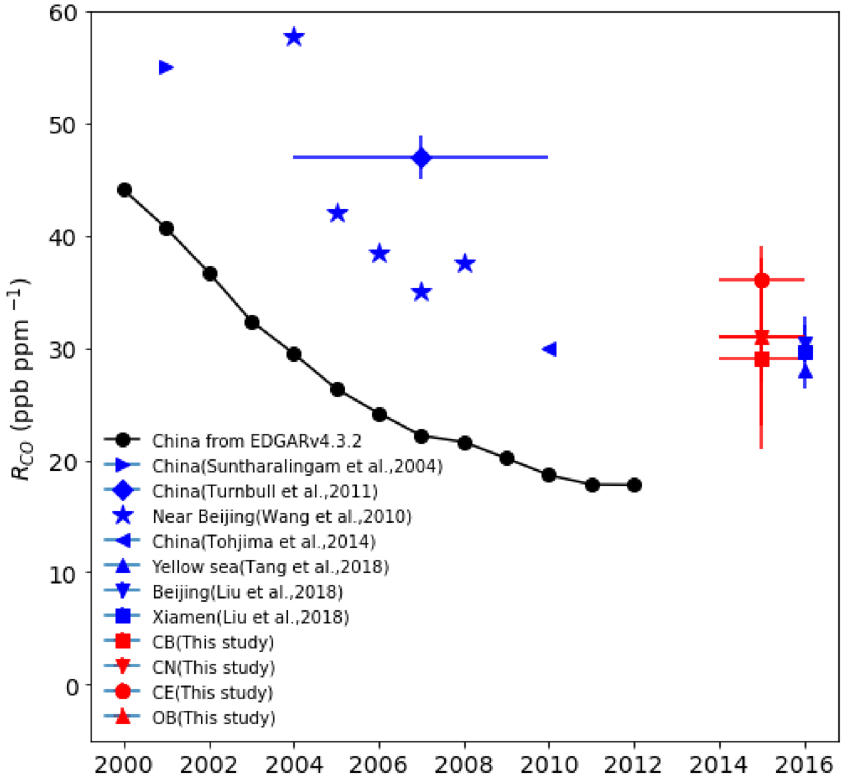
- The correlations of CO enhancements (ΔCO) with C_{ff} were strong (r > 0.7) in all sectors except PL, while SF_6 enhancements (ΔSF_6) correlated strongly with Cff (r > 0.8) for CE and OB in outflow from the Asian Continent and KL.
- KL, CE and OB showed strong correlations (r > 0.8). Those three sectors are also larger SF_6 sources compared to other regions, according to SF_6 emission estimates for Asia (Fang et al., 2014).
- CO from KL and PL is lower than from outflow from the Asian continent, except for the OB sector, indicating that high CO can be a tracer of outflow from the Asian continent

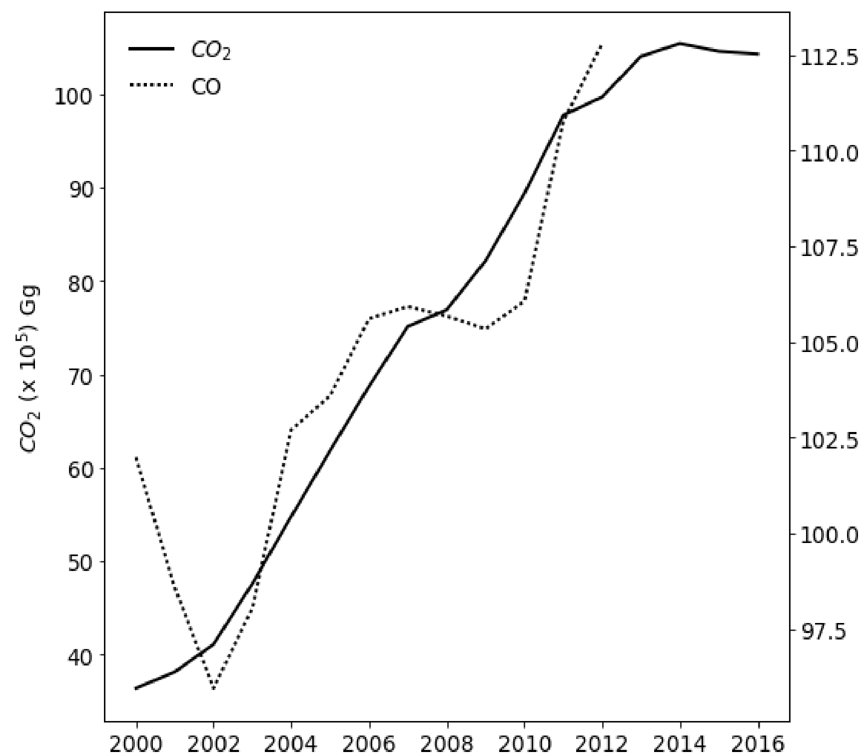
7. Comparison of emission ratio: SF_6



- R_{SF6} is different between South Korea and outflow from the Asian continent
- Here, the ratio was at (0.19±0.03) and (0.17±0.03) pmol μmol-1 for CE and OB respectively. For KL, it was (0.66±0.16) pmol μmol-1 indicating much larger ratios than in outflow from the Asian continent
- Further, observed R_{SF6} is 2 to 3 times greater for all air masses than predicted from bottom-up inventories based on national scale roughly

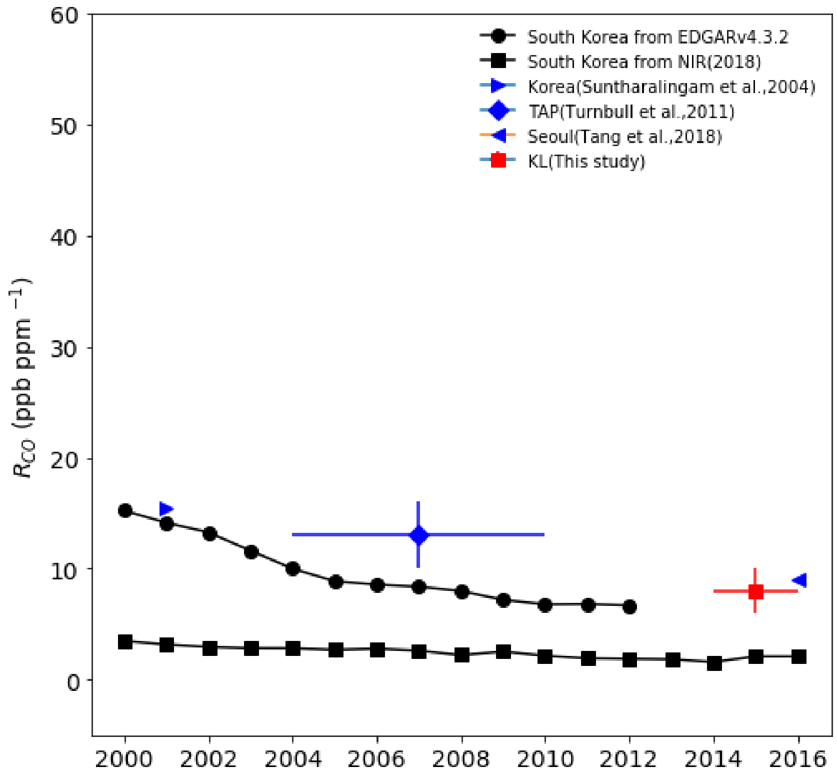
7. Comparison of emission ratio: CO for China

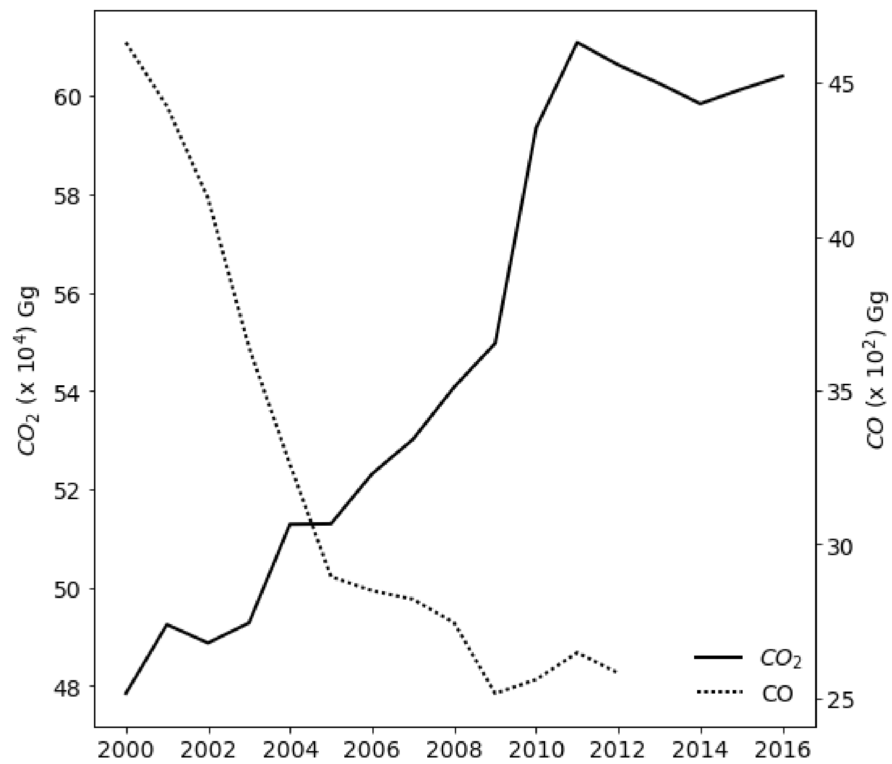




- CO to C_{ff} emission ratios (R_{CO}) derived from both observations and inventories for China decreased.
- R_{CO} is (29±8), (31±8), (36±2), and (31±4) nmol μmol-1 for CB, CN, CE and OB, respectively
- Atmosphere-based R_{CO} values calculated by this study are (1.8±0.2) times greater (with CB, CN, CE and OB) than in the inventory

7. Comparison of emission ratio: CO for South Korea





- CO to C_{ff} emission ratios (R_{CO}) derived from both observations and inventories for Korea decreased, as well.
- In South Korea, atmosphere-based R_{CO} values calculated by this study are 1.2 times (with KL) greater than inventory.

8. Summary and Conclusion

1. Observed $\Delta^{14}CO_2$ values at AMY ranged from -59.5 to 23.1‰ (a mean value of -6.2±18.8‰ (1σ)) during the study period, almost always lower than those observed at NWR. This reflects the strong imprint of fossil fuel-CO_2 emissions recorded in AMY air samples.
2. Calculated C_{ff} using $\Delta^{14}CO_2$ at AMY ranges between -0.05 and 32.7 μmol mol-1 with an average of (9.7±7.8) μmol mol-1 (1σ); this average is twice as high as in the 2004 to 2010 TAP samples (mean (4.4±5.7) μmol mol-1) (Turnbull et al., 2011).
3. Because ΔCO and ΔSF_6 agreed well with Cff, but showed different slopes for Korea and the Asian continent, those R_{gas} values can be indicators of air mass origin and those gases can be proxies for C_{ff}
4. Atmosphere-based R_{gas} values are greater than bottom-up inventories. For CO, our values are 1.2 times and (1.8±0.2) times greater than in inventory values for South Korea and China, respectively. This discrepancy may arise from several sources including the absence of atmospheric chemical CO production such as oxidation of CH_4 and non-methane VOCs.
5. We stress that because C_{bio} contributes substantially to ΔCO_2, even in winter, $\Delta^{14}C$-based C_{ff} (and not ΔCO_2) is required for accurate calculation of both R_{CO} and R_{SF6}