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Atmospheric Chemistry and Physics Discussions

^{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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Abstract. To understand Korea's carbon dioxide (CO_2) emissions and sinks as well as those of the surrounding region, we used 70 flask-air samples collected during May 2014 to August 2016 at Anmyeondo (AMY, 36.53° N, 126.32° E; 46 m a.s.l) World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) station, located on the west coast of South Korea, for analysis of observed ^{14}C in atmospheric CO_2 as a tracer of fossil fuel CO_2 contribution (C_{ff}). Observed $^{14}C/C$ ratios in CO_2 at AMY varied from -59.5 to 23.1‰ with the measurement uncertainty of ±1.8‰. The derived mean value C_{ff} of (9.7±7.8) μmol mol^{-1} (1σ) is greater than that found in earlier observations from Tae-Ahn Peninsula (TAP, 36.73° N, 126.13° E, 20 m a.s.l., 24 km away from AMY) of (4.4±5.7) μmol mol^{-1} from 2004 to 2010. The enhancement above background of sulfur hexafluoride ($\Delta x(SF_6)$) and carbon monoxide ($\Delta x(CO)$) correlate strongly with C_{ff} ($r > 0.7$) and appear to be good proxies for fossil fuel CO_2 at regional and

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continental scales. Samples originating from the Asian continent had greater Δx(CO):C_{ff} (R_{CO}) values, (29±8) to (36±2) nmol μmol^{-1}, than in Korean local air ((8±2) nmol μmol^{-1}). Air masses originating in China showed (1.8±0.2) times greater R_{CO} than a bottom-up inventory suggesting that China's CO emissions are underestimated in the inventory. However, both R_{CO} derived from inventories and observations have decreased relative to previous studies, indicating that combustion efficiency is increasing in both China and South Korea.

1 Introduction

Carbon Dioxide (CO_2) is the principle cause of climate change in the industrial era, and is increasing in the atmosphere at (2.4±0.5) μmol mol^{-1} a^{-1} in a recent decade globally (www.esrl.noaa.gov/gmd/ccgg/trends/, last access: 6 December 2019). This increase is in fact predominantly an anthropogenic disturbance that has been demonstrated through ^{14}C analysis of tree rings from the last two centuries (Stuiver and Quay, 1981; Suess, 1955; Tans et al., 1979), caused by accelerated release of CO_2 from fossil fuel burning. Atmospheric measurement program for the ratio $^{14}C/C$ in CO_2 was initiated in the 1950s and 1960s (Rafter and Fergusson, 1957; Nydal, 1996). Observed $^{14}C/C$ ratios are reported in Delta notation ($\Delta(^{14}CO_2)$) as fractionation-corrected permil (or ‰) deviations from the absolute radiocarbon standard (Stuiver and Polach, 1977). Many studies show that the variation of $\Delta(^{14}CO_2)$ is an unbiased and now widely used tracer for CO_2 emitted from fossil-fuel combustion (Levin et al., 2003; Turnbull et al., 2006; Graven et al., 2009; Miller et al., 2012). Therefore measurements of $\Delta(^{14}CO_2)$ are important to test the effectiveness of emission reduction strategies to mitigate the rapid

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atmospheric CO_2 increase, since they can partition observed CO_2 enhancements, $\Delta x(CO_2)$, into fossil fuel CO_2 (C_{ff}) and biological CO_2 (C_{bio}) components with high confidence (Turnbull et al., 2006).

When trace gases are co-emitted with C_{ff}, correlations of their enhancements with C_{ff} improve understanding of the emission sources of both C_{ff} and the co-emitted tracers. For example, CO and CH_4 emission inventories are typically more uncertain than the fossil fuel CO_2 emission inventory, since those emissions related to complete combustion are generally well estimated while emissions related to incomplete combustion and agricultural activities are poorly constrained (Kurokawa et al., 2013). Temporal changes in the observed emission ratio of a trace gas to C_{ff} can be used to examine emission trends in the trace gas (Tohijima et al., 2014). Therefore the observed emission ratios of trace gases to C_{ff} can be used to evaluate bottom-up inventories of various trace gases (e.g., Miller et al., 2012). Here, we used two trace gases, carbon monoxide (CO) and sulfur hexafluoride (SF_6) for this analysis. CO is produced along with CO_2 during incomplete combustion of fossil fuels and biomass. CO enhancements above background ($\Delta x(CO_2)$) correlate well with C_{ff} and have been used as a fossil fuel tracer (Gamnitzer et al., 2006; Turnbull et al., 2011a; Turnbull et al., 2011b; Tohijima et al., 2014). SF_6 is an entirely anthropogenic gas and is widely used as an arc quencher in high-voltage electrical equipment (Geller et al., 1997). At regional to continental scales, persistent small leaks to the atmosphere of SF_6 are typically co-located with fossil fuel CO_2 sources and allow SF_6 to be used as an indirect C_{ff} tracer, if the leaks are co-located with C_{ff} emissions at the location and scale of interest (Turnbull et al., 2006; Rivier et al., 2006).

South Korea is a rapidly developing country with fast economic growth, and it is located next to China, which is the world's largest emitter of anthropogenic CO_2, according to the Emissions

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Database for Global Atmospheric Research EDGAR (Janssens-Maenhout et al., 2017). The first $\Delta(^{14}CO_2)$ measurements in South Korea were reported by Turnbull et al. (2011a) based on air samples collected during October 2004 to March 2010 at Tae-Ahn Peninsula (TAP, 36.73° N, 126.13° E, 20 m a.s.l.). This study showed that observed CO_2 at this site was often influenced by Chinese emissions and the observed ratio of Δx(CO):C_{ff} (R_{CO}) was greater than expected from bottom-up inventories. However South Korean $\Delta(^{14}CO_2)$ data are still limited and the ratio of the other trace gases to C_{ff} barely discussed.

Here we use whole-air samples collected in glass flasks during May 2014 to August 2016 at Anmyeondo (AMY, 36.53° N, 126.32° E; 46 m a.s.l.) World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) station, located on the west coast of South Korea and about 28 km SSE of TAP, where the first study was conducted. We decompose observed CO_2 enhancements into their fossil fuel and biological components at AMY to understand sources and sinks of CO_2. We also implemented cluster analysis using the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) to calculate back-trajectories for sample times and dates. Based on clusters of trajectories from specific regions, trace gas enhancement: C_{ff} ratios and correlation coefficients were analyzed, especially focused on SF_6 and CO, to determine the potential of alternative proxies to $\Delta(^{14}CO_2)$. Finally we compared our Δx(CO):C_{ff} ratio with ratios determined from bottom-up inventories (EDGARv4.3.2) to evaluate reported CO emissions and how they've changed since 2010.

2. Materials and Method

2.1 Sampling site and methods

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The AMY GAW station is managed by the National Institute of Meteorological Sciences (NIMS) in the Korea Meteorological Administration (KMA). It has the longest record of continuous CO_2 measurement in South Korea, beginning in 1999. It is located on the west coast of Korea about 130 km southwest of the megacity of Seoul, whose population was 9.8 million in 2017. Semiconductor and other industries exist within a 100 km radius of the station. Also, the largest thermal power plants fired by coal and heavy oil in South Korea are within 35 km to the northeast and southeast of the station. The closest town, around 30 km to the east of AMY, is well known for its livestock industries. Local economic activities are related to agriculture, e.g., production of rice paddies, sweet potatoes, and onions, and the area is also known for its leisure opportunities that increase traffic and tourists in summer, indicating the complexity of greenhouse gas sources around AMY. On the other hand, air masses often arrive at AMY from the west and south, which is open to the Yellow Sea. Therefore AMY observes enhanced CO_2 compared to many other East Asian stations due not only to numerous local sources but also long-range transport of air-masses from the Asian continent (Lee et al., 2019).

Two pairs of flask-air samples (4 flasks total, 2 L, borosilicate glass with Teflon O-ring sealed stopcocks) were collected about weekly from a 40 m tall tower at AMY, regardless of wind direction and speed from May 2014 to August 2016, generally between 1400 to 1600 local time (Table S1). A total of 70 sets were collected and analyzed at the National Oceanic and Atmospheric Administration/Earth System Research Laboratory/Global Monitoring Division (NOAA/ESRL/GMD) for CO_2, CO, and SF_6 and for $\Delta(^{14}CO_2)$ by University of Colorado Boulder, Institute of Arctic and Alpine Research (INSTAAR). NOAA/ESRL/GMD analyzed CO_2 using a non-dispersive infrared analyzer, SF_6 using gas chromatography (GC) with electron capture detection, and CO by vacuum UV, resonance fluorescence. All analyzers were calibrated

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with the appropriate WMO mole fraction scales (WMO-X2007 scale for CO_2, WMO-X2014A scale for CO, and WMO-X2014 for SF_6; https://www.esrl.noaa.gov/gmd/ccl/, last access: 4 December 2019). The measurement and analysis methods for those gases are described in detail (http://www.esrl.noaa.gov/gmd/ccgg/behind_the_scenes/measurementlab.html, last access: 4 December 2019). Measurement uncertainties for CO_2 and SF_6 are reported as 68% confidential intervals. For CO_2, it is 0.07 μmol mol^{-1} for all measurements used here. For SF_6, it is 0.04 up to 12 pmol mol^{-1}, and undefined above that. For CO, measurement uncertainty has not yet been formally evaluated, but is estimated at 1 nmol mol^{-1} (68% confidence interval). All CO_2, SF_6 and CO data at AMY can be downloaded through ftp://aftp.cmdl.noaa.gov/data/trace_gases/.

The analysis methods for $\Delta(^{14}CO_2)$ are described by Lehman et al.(2013). Measurement repeatability of $\Delta(^{14}CO_2)$ in aliquots of whole air extracted from surveillance cylinders is 1.8‰ (1 σ), roughly equating to 1 μmol mol^{-1} C_{ff} detection capability from the measurement uncertainty alone. The $\Delta(^{14}CO_2)$ data at AMY was suggested in Table S1.

2.2 Data analysis method using $\Delta(^{14}CO_2)$ data

2.2.1 Calculation of C_{ff} and C_{bio}

As Turnbull et al. (2009) suggested the observed CO_2 (C_{obs}) at AMY can be defined as:

$$C_{\mathrm{obs}} = C_{\mathrm{bg}} + C_{\mathrm{ff}} + C_{\mathrm{other}} \quad (1)$$

where C_{bg}, C_{ff} and C_{other} are the background, recently added fossil fuel CO_2 and the CO_2 derived from the other sources.

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According to Tans et al. (1993), the product of CO_2 abundance and its isotopic ratio is conserved; the isotopic mass balance can be described as below:

$$\Delta_{\mathrm{obs}} C_{\mathrm{obs}} = \Delta_{\mathrm{bg}} C_{\mathrm{bg}} + \Delta_{\mathrm{ff}} C_{\mathrm{ff}} + \Delta_{\mathrm{other}} C_{\mathrm{other}} \quad (2)$$

where Δ is the $\Delta^{14}C$ of each CO_2 component of Equ. (1).

Therefore we can calculate fossil fuel CO_2 by combining equations (1) and (2) as:

$$C_{\mathrm{ff}} = \frac{C_{\mathrm{bg}}(\Delta_{\mathrm{obs}} - \Delta_{\mathrm{bg}})}{\Delta_{\mathrm{ff}} - \Delta_{\mathrm{bg}}} - \frac{C_{\mathrm{other}}(\Delta_{\mathrm{other}} - \Delta_{\mathrm{bg}})}{\Delta_{\mathrm{ff}} - \Delta_{\mathrm{bg}}} \quad (3)$$

Fossil fuel derived CO_2 contains no ^{14}C because the half–life of ^{14}C is (5700±30) years (Godwin, 1962) while these fuels are hundreds of millions of years old. As we mentioned in the section 1, $\Delta(^{14}CO_2)$ is reported as a per mil (‰) deviation from the absolute radiocarbon reference standard corrected for fractionation and decay with a simplified form; $\Delta(^{14}C) \approx [(^{14}C/C)\mathrm{sample}/(^{14}C/C)\mathrm{standard} - 1]1000‰$. Therefore Δ_{ff} is set at -1000‰ (Stuiver and Pollach, 1977). Background values (Δ_{bg}) in equations (1) to (3) are determined from measurements from background air collected at Niwot Ridge, Colorado, a high altitude site at a similar latitude as AMY (NWR, 40.05° N, 105.58° W, 3,526 m a.s.l.). Turnbull et al. (2011a) showed that the choice of background values did not significantly influence derived enhancements due to the large regional and local signal at TAP, 28 km from AMY. NWR $\Delta(^{14}CO_2)$ and other trace gas background values are selected using a flagging system to exclude polluted samples (Turnbull et al., 2007), and then fitted with a smooth curve following Thoning et al. (1989).

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The second term of equation (3) is typically a small correction for the effect of other sources of CO_2 that have a $\Delta^{14}C$ differing by a small amount that of the atmospheric background, such as CO_2 from 1) nuclear power industry, 2) oceans, 3) photosynthesis and 4) heterotrophic respiration.

1) The nuclear power industry produces ^{14}C that can influence the C_{ff} calculation. South Korea has nuclear power plants along the east coast that may influence AMY air samples when air-masses originated from the eastern part of Korea (Figure 1). It is also possible that Chinese nuclear plants could influence some samples. Here we did not make any correction for this since most nuclear installations in this region are pressurized water reactors, which produce mainly ^{14}C in CH_4 rather than CO_2 (Graven and Gruber, 2011). 2) For the ocean, although there may also be a small contribution from oceanic carbon exchange across the Yellow Sea, we consider this effect small enough to ignore (Turnbull et al., 2011a). Larger scale ocean exchange and also stratospheric exchange affect both background and observed samples equally, so they can be ignored in the calculations. 3) For the photosynthetic terms, ^{14}C in CO_2 accounts for natural fractionation during uptake, so we also set this observed value the same as the background value. 4) Therefore we only consider heterotrophic respiration. For land regions, where most fossil fuel emissions occur, heterotrophic respiration could be a main contributor to the second term of equation (3) due to large ^{14}C disequilibrium potentially. When this value is ignored, C_{ff} would be consistently underestimated (Palstra et al., 2008; Riley et al., 2008; Hsueh et al., 2007; Turnbull et al., 2006). For this, corrections were estimated as (-0.2±0.1) μmol mol^{-1} during winter and (-0.5±0.2) μmol mol^{-1} during summer (Turnbull et al., 2009; Turnbull et al., 2006).

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CO_2 enhancements relative to baseline CO_2 are defined as $\Delta x(CO_2)$, with the excess signal of C_{obs} minus C_{bg} in Equ.(1). Partitioning of $\Delta x(CO_2)$ into C_{ff} and C_{bio} is calculated simply from the residual of the difference between observed $\Delta x(CO_2)$ and C_{ff}.

2.2.2 The ratio of trace gas enhancement to C_{ff} and its correlation

To obtain the correlation coefficient (r) between C_{ff} and other trace gas enhancements ($\Delta x(x) = x_{obs} - x_{bg}$) and the ratio of any trace gas to C_{ff} (R_{gas}), we use reduced major axis (RMA) regression analysis. The distributions of R_{gas} are normally broad and non-Gaussian and RMA analysis is a relatively robust method of calculating the slope of two variables that show some causative relationship. Here, x_{bg} was derived from NWR with the same method described in section 2.2.1.

Therefore, the slope of the linear regression of the RMA fit can be expressed as

$$R_{gas} = \sqrt{\frac{\sum \Delta x(x)^2 - (\sum \Delta x(x))^2/n}{\sum C_{ff}^2 - (\sum C_{ff})^2/n}} \quad (4)$$

And the uncertainty of R_{gas} is defined as

$$U = \sqrt{\frac{\sum (\Delta x(x) - \Delta x(x)')^2/n}{\sum C_{ff}^2 - (\sum C_{ff})^2/n}} \quad (5)$$

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

The correlation coefficient is expressed,

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$$r = \sqrt{\frac{(\sum \Delta x(\mathrm{x}) C_{\mathrm{ff}} - \frac{\sum \Delta x(\mathrm{x}) \sum C_{\mathrm{ff}}}{n})^2}{(\sum \Delta x(\mathrm{x})^2 - \frac{(\sum \Delta x(\mathrm{x}))^2}{n}) \times (\sum C_{\mathrm{ff}}{}^2 - \frac{(\sum C_{\mathrm{ff}})^2}{n})}} \quad (6)$$

Results for each species are given in Table 1.

2.3 HYSPLIT cluster analysis

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 to determine the regions that influence air mass transport to AMY. A total of 70 air-parcel back-trajectories were calculated for 72-h periods at 3-h intervals matching the time of each flask-air sample taken at AMY from May 2014 to August 2016. We assign the sampling altitude as 500 m, since it was demonstrated that HYSPLIT and other particle dispersion back-trajectory models (e.g., FLEXPART) are consistent at 500 m altitude (Li et al., 2014). Cluster analysis of the resulting 70 back-trajectories categorized six pathways through which air parcels arrive at AMY during the time period of interest.

Among the calculated back-trajectories, 67% indicate air masses originating from the Asian continent. Back-trajectories of continental background air (CB) originating in Russia and Mongolia occurred 13% of the time. 23% of the trajectories originated and travelled through northeast China (CN). The CN region includes Inner Mongolia and Liaoning, one of the most populated regions in China with 43.9 million people in 2012. These CN air masses arrive in South Korea after crossing through western North Korea. 17% of the trajectories are derived from central eastern China around the Shandong area (CE). The CE region contains Shandianzi (SDZ, 40.65° N, 117.12° E, 287 m a.s.l.) located next to the megacities of Beijing and Tianjin, which are some of China's highest CO_2 emitting regions (Gregg et al., 2008). 14% are Ocean

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Background (OB) derived from the East China Sea, which passed over the eastern part of China such as Shanghai. Flow from South Korea also travels through heavily industrialized and/or metropolitan regions in South Korea (Korea Local, KL, 19%) and under stagnant conditions (Polluted Local region, PL, 14%). Some of the KL air-masses have also passed over the East Sea and Japan.

3. Results and discussions

3.1 Observed $\Delta(^{14}CO_2)$ and portioning of CO_2 into C_{ff} and C_{bio}

AMY $\Delta(^{14}CO_2)$ values are almost always lower than those observed at NWR, which we consider to be broadly representative of background values for the mid-latitude Northern Hemisphere (Figure 2). NWR $\Delta(^{14}CO_2)$, which is based on weekly air samples, was in the range 10.0 to 21.2 ‰, with an average (16.6±3)‰ (1σ) from May 2014 to August 2016. Waliguan (WLG, 36.28° N, 100.9° E, 3816 m a.s.l.), an Asian background GAW station in China, also showed similar $\Delta(^{14}CO_2)$ levels to NWR with an average of (17.1 ± 6.8) ‰ in 2015 (Niu et al., 2016, measurement uncertainty ±3‰). $\Delta(^{14}CO_2)$ at AMY varied from -59.5 to 23.1‰ and had a mean value of (-6.2±18.8)‰ (1σ) during the experiment period (Table S1). This was similar to results from observations at SDZ, which is located about 100 km northeast of Beijing, in the range of -53.0 to 32.6‰ with an average (-6.8±21.1)‰ during Sep 2014 to Dec 2015 (Niu et al., 2016).

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Calculated C_{ff} at AMY ranges between -0.05 and 32.7 μmol mol^{-1} with an average of (9.7±7.8) μmol mol^{-1} (1σ); high C_{ff} was observed regardless of season (Figure 2 (a)). One negative C_{ff} value of -0.05 μmol mol^{-1} was estimated due to greater AMY $\Delta(^{14}CO_2)$ than NWR on July 30, 2014. Although negative C_{ff} values are non-physical, this value is not significantly different from zero, and is reasonable given that this air originated from the OB sector. The range of C_{ff} in the AMY samples is similar to that observed at TAP from 2004 to 2010 (-1.6 to 42.9 μmol mol^{-1} C_{ff}), but C_{ff} is on average about twice as high at AMY as in the 2004 to 2010 TAP samples (mean (4.4±5.7) μmol mol^{-1}) (Turnbull et al., 2011a). A more detailed comparison of results based on differences between samples derived from the Asian continent and Korea local air is provided in section 3.2.

Estimated C_{bio}, as defined in section 2.2.1, varied from -18.1 to 15.7 μmol mol^{-1} (mean (0.9±5.8) μmol mol^{-1}) at AMY (Figure 2 (c)). C_{bio} showed a strong seasonal cycle with the lowest values from July to September when photosynthetic drawdown is expected to be strongest, in good agreement with the previous TAP study (Turnbull et al., 2011a). Even though C_{bio} was at times negative, mainly due to photosynthesis during summer, the largest positive C_{bio} was also observed in summer.

The largest C_{ff} by season was observed in order of 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}. When we consider only positive contributions of C_{bio} samples, the order was summer ((4.6±4.0), n=14) > autumn ((4.1±2.5), n=9) > spring ((3.8±2.6), n=13) > winter ((3.4±2.5), n=11) with a unit of μmol mol^{-1}.

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C_{ff} in summer was nearly as high as in winter. This is because lower wind speeds are observed at AMY during summer (Lee et al., 2019), suggesting that these summer high values may reflect emission from local activities, which were described in section 2.1, more than in other seasons. The highest C_{bio} value was also observed in summer. PL sector showed that positive C_{bio} correlates with CH_4, which is a tracer for agriculture when observed in TAP local air masses. Turnbull et al.(2011a) also showed similar results.

In winter, C_{bio} was relatively lower than in other seasons while C_{ff} was highest. During winter, AMY is mainly affected by long-range transport of air-masses from China due to the Siberian high (Lee et al., 2019). Therefore air samples were less affected by local activities in winter but C_{bio} still contributed almost 23% to $\Delta x(CO_2)$. In the dry season (from October to March), forest fires, which contribute the largest portion of total CO_2 emissions from open fires at the national scale, are concentrated in northeastern and southern China (Yin et al., 2019). The highest CO was observed in winter ((449.1±244.1) nmol mol^{-1} (1σ) in winter while (236.8±124.4) nmol mol^{-1} (1σ) in summer), which also supports biomass burning and bio fuels as large contributors to observed CO_2 enhancements in winter. Turnbull et al. (2011a) also showed that 20-30% of winter CO_2 enhancements at TAP were likely contributed by biofuel combustion, along with plant, soil, human, and animal respiration.

Regardless of the source, we find that C_{bio} contributes substantially to atmospheric CO_2 enhancements at AMY in air masses affected by local and long-range transport, so CO_2 enhancements above background cannot be reliably interpreted as entirely due to C_{ff}.

3.2 C_{ff} comparison between Korea Local and Asian Continent samples

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To more clearly identify samples originating from the Asian continent (trajectory clusters CB, CN, CE, and OB) and Korea Local (trajectory cluster KL) after cluster analysis of the 70 sets of measurements, we use wind speed data from the Automatic Weather System (AWS) installed at the same level as the air sample inlet at AMY. Among the data from CB, CN, CE, OB, and KL, when wind speed was less than 3 m/s, we assumed that those samples could be affected by local pollution. PL was also ruled out since it was affected by local pollutions under the stagnant condition. Therefore we use only 41 sets of observations for this analysis (Table 1).

C_{ff} is highest in the order CE > CN > KL > CB > OB (Table 1). During the experimental period, the averages from Asian continent (sectors CE and CN) were higher than KL without the baseline level. The calculated mean C_{ff} using only CE, CN, CB and OB, which sample substantial outflow from the Asian Continent, was (7.6±3.9) μmol mol^{-1}.

When we compared the KL samples ((8.6±5.3) μmol mol^{-1}) with those from Korea Local air-masses observed at TAP ((8.5±8.6) μmol mol^{-1}, Turnbull et al., 2011a), mean C_{ff} was quite similar (Figure 3). However, when comparing the C_{ff} values from CB air masses in this study and TAP far-field (from China) samples (Turnbull et al., 2011a), C_{ff} almost doubled from (2.6±2.4) to (4.3±2.1) μmol mol^{-1}, even though they might be expected to have had similar air mass back-trajectories. We also compared the values at SDZ from 2009 to 2010 (Turnbull et al., 2011a) and in 2015 (Niu et al., 2016); they also increased, not only in the samples that were affected by Beijing and North China Plain (SDZ-BN), which are comparably polluted, but also in the samples that were affected by northeast China (SDZ-NE). For SDZ-BN samples, C_{ff} increased

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from (10±1) to (16±7.6) μmol mol^{-1} from 2009/2010 to 2015. The AMY samples from CE, which flow over Beijing, showed (11.2±8.3) μmol mol^{-1} of C_{ff} and were also slightly greater than the 2009 – 2010 SDZ-BN samples (Turnbull et al., 2011a). For SDZ-NE samples, C_{ff} was (3±7) μmol mol^{-1} in 2009 to 2010 and increased to (7.6±6.8) μmol mol^{-1} in 2015. Since the SDZ-NE samples are affected by northeast China according to Turnbull et al. (2011a) and Niu et al. (2016), we also see CN originated from northeast China and it was around (10.6±6.9) μmol mol^{-1}.

It has been suggested that inter-annual variability in observed mean C_{ff} in South Korea could reflect changing fossil fuel CO_2 emissions, or could indicate inter-annual variability in the air mass trajectories of the (small) dataset of flask-air samples (Turnbull et al., 2011a). Even though the growth rate of C_{ff} emission has been decreasing slowly in East Asia since 2010 due to emission reduction policies (Labzovskii et al., 2019), reported emissions increased 16.7% in China and 1.8% in South Korea from 2010 to 2016 (Janssens-Maenhout et al., 2017). This is broadly consistent with the flat trend in observed C_{ff} in Korea Local air masses, and in the upward trend in C_{ff} observed in air-masses flowing out from Asia. Therefore it is possible that AMY mean C_{ff} increased relative to the earlier TAP observations due to increased fossil fuel emissions from the Asian continent. It is also likely that the proximity of local emission sources to AMY is causing higher observed C_{ff} under some synoptic conditions.

On the other hand, those values from this study showed large variability with small sample numbers, further study will be necessary.

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3.3. Correlation of C_{ff} with SF_6 and CO, and their emission ratios

We calculated correlation coefficients (r from Equ. (6)) between SF_6 and CO enhancements with C_{ff} and their ratios from Equ. (4) with the 50 samples that were described in section 3.2 including PL sector (n=9) and whose values are tabulated in Table 1.

The correlations of CO enhancements (Δx(CO)) with C_{ff} were strong (r > 0.7) in all sectors except PL, while SF_6 enhancements ($\Delta x(SF_6)$) correlated strongly with C_{ff} (r > 0.8) for CE and OB in outflow from the Asian Continent and KL. R_{CO} and R_{SF6} were different between Korea Local and outflows from the Asian Continent.

For SF_6, observed mean levels were high in order of KL > PL > CN and CE > OB > CB (Table 1). SF_6 in KL and PL were higher than from the Asian Continent, since South Korea has larger SF_6 emissions than most countries (ranked at 4th as of 2010 according to the EDGAR4.2.) because of liquid-crystal display (LCD) and electrical equipment production (Fang et al., 2014). Even though South Korea showed higher SF_6, the correlation is different between KL and PL. Under stagnant conditions, emitted SF_6 is less diluted by mixing, so that in PL, $\Delta x(SF_6)$ correlated weakly with C_{ff}. On the other hand, 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). Because long-range transport allows time for mixing, SF_6 and C_{ff} emissions are effectively co-located at not only continental scales but also regional scales. Thus SF_6 can be a good tracer of fossil fuel CO_2.

Even though the correlation between $\Delta x(SF_6)$ and C_{ff} was strong in CE, OB and KL, R_{SF6} is different between South Korea and outflow from the Asian continent (Figure S2). In a previous study, observed R_{SF6} was 0.02 to 0.03 pmol μmol^{-1} at NWR in 2004 (Turnbull et al., 2006). Here,

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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. For this calculation, we use EDGAR4.3.2 for CO_2 and EDGAR4.2 for SF_6. We repeat the calculations for both CO_2 and SF_6 with Korea's National Inventory Report (KNIR, Greenhouse Gas Inventory and Research Center, 2018). Using SF_6 for 2010 from EDGAR4.2, we obtain R_{SF6} of 0.08 pmol μmol^{-1} for China while for South Korea it was 0.14 pmol μmol^{-1}. Especially for South Korea, this is much lower than the observed $R_{SF6.}$ When KL R_{SF6} was compared to ratios calculated from the KNIR inventory (0.27 pmol μmol^{-1} for 2010 and 0.22 pmol μmol^{-1} for 2014), it was closer to observed R_{SF6} than EDGAR, but still underestimated (Figure S3 and S2). This result suggests that the observed ratio could be used to re-evaluate the bottom-up inventories (Rivier et al., 2006), especially targeting the Asian continent. Since KL R_{SF6} showed greater uncertainty than CE and OB, it would be useful to get more data to try and derive a more robust estimate to evaluate SF_6 emissions in Korea.

High CO was mainly observed in outflow from the Asian continent in order of CE > CN > PL > CB > KL > OB (Table 1). The order of CO is quite different to that of SF_6. 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. Since CO is produced during incomplete combustion, it is more closely related to fossil fuel CO_2 emissions than the other trace gases. Therefore in most cases the correlation between CO and C_{ff} was strong. R_{CO} was very different between air masses originating from South Korea Local ((8±2) nmol μmol^{-1}) and

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the Asian continent ((29±8) to (36±2) nmol μmol^{-1}), likely due to differences in combustion efficiencies. The higher continental emission ratios may also result from some contribution of biofuel combustion and agricultural burning in the Asian continent, which have significantly higher CO emission than fossil-fuel combustion (Akagi et al., 2011).

Typically CO shows seasonal variations with lower values in summer due to the photochemical sink. Among the samples, the samples collected in summer were mainly rejected through wind speed cut-off (less than 3 m/s) since AMY has lower wind speed in summer (Lee et al., 2019). Only OB sector includes 4 summer samples (of 7), because summer air masses are mainly from the southern part of the Yellow Sea (Lee et al., 2019). However, we assumed R_{CO} is less affected by the summer sink, since only two Δx(CO) samples were negative for OB (Figure S2) and R_{CO} was consistent whether or not the negative Δx(CO) values were considered. We compare our R_{CO} to results from previous studies in section 3.4.

3.4 Comparison of measured emission ratios to CO inventory data

To compare emission ratios derived from atmospheric observations with those from inventories for 2000 to 2012, we calculated inventory emission ratio ($I_{CO/CO2}$) as:

$$I_{CO/CO2} = E_{CO}/E_{CO2} \times M_{CO2}/M_{CO} \quad (7)$$

Where, E_{CO} and E_{CO2} are total CO and fossil fuel CO_2 emissions in gigagrams (Gg, 10^9 g) from the bottom-up national inventory. M_X are the molar masses of CO and CO_2 in g mol^{-1}.

We use EDGAR4.3.2 (Janssens-Maenhout et al., 2017) and KNIR (Greenhouse Gas Inventory and Research Center, 2018) for inventory information for both CO and CO_2.

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The uncertainty of EDGAR4.3.2 emissions was reported as a 95% confidence interval (Janssens-Maenhout et al., 2019), ±5.4% for China and ±3.6% for South Korea (personal communication with Dr. Efisio Solazzo). The uncertainties of CO and SF_6 emissions were not reported by EDGAR. For KNIR, the CO_2 2016 emission uncertainty in the energy sector was ±3% (Greenhouse Gas Inventory and Research Center, 2018). KNIR does not provide uncertainties for other emission sectors of CO_2, nor from emissions of CO and SF_6.

In Fig. 4 we confirm that the CO to C_{ff} emission ratios (R_{CO}) derived from both observations and inventories for China and South Korea are decreasing. Since C_{ff} emissions appear to be flat (South Korea) or slightly increasing (China), this indicates that combustion efficiency and/or scrubbing of CO is improving.

For South Korea, EDGAR4.3.2 indicated that CO emissions from the energy sector (98% to 99% of total emission) decreased by 47% between the 1997 and 2012. South Korean fossil fuel CO_2 emissions increased until 2011 and remained mostly constant from 2011 to 2016 ((603,901±4,315) Gg CO_2) (Figure S4). Therefore the decreased trend in the emission ratio seems to reflect recent decreases in CO emissions in South Korea. Turnbull et al. (2011a) determined an observed mean R_{CO} of (13±3) nmol μmol^{-1} during 2004 to 2010. Suntharalingam et al. (2004) estimated R_{CO} 15.4 nmol μmol^{-1} for South Korea in 2001 from CO_2 and CO airborne observations (C_{ff} was not determined). Recently, the KORUS-AQ campaign, which was conducted over Seoul from May to June in 2016, estimated R_{CO} as 9 nmol μmol^{-1} (Tang et al., 2018) based on CO_2 and CO observations (C_{ff} was not determined). Our study gives R_{CO} of (8±2)

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nmol μmol^{-1} for South Korea, slightly but not significantly lower than the KORUS-AQ result for Seoul. This difference could be due to different source regions (Seoul vs the larger Korean region) and different experimental periods (two months vs two years). Different contributions of C_{bio} and C_{ff} to total CO_2 may bias the R_{CO} calculation when total CO_2 was used in the KORUS-AQ study (e.g., Miller et al., 2012). The South Korean national R_{CO} from EDGAR4.3.2 in 2012 was 6.7 nmol μmol^{-1}, consistent with our observations. Using KNIR for 2016, we obtain R_{CO} of 2.1 nmol μmol^{-1}. KNIR seems to have uncounted CO emissions, since it is unreasonably low during all comparison periods (Figure S5). For example, CO emissions recently derived from fugitive emissions and residential/other sectors increased to 14% and 11.5% of total emission respectively in EDGAR but were not reported in KNIR.

For China the inventories estimate that CO emissions from the energy sector, (96.5±0.2)%, were almost constant through the 1990s, and then increased during the early-2000s from industrial processes (8.8% of total emissions in 2012). Fossil fuel CO_2 emission in China also increased until 2013 and then stayed roughly constant at (10,461,890±60,571) Gg according to EDGAR4.3.2. Thus even though both emissions show an increase from 2000 to 2016 for fossil fuel CO_2 and to 2012 for CO, the emission ratio decreased (Figure S4 and Figure 4) seeming to indicate that combustion efficiency is improving. Many studies observed decreasing R_{CO} in China from 2000 to 2010 (Turnbull et al., 2011a; Wang et al., 2010). Suntharalingam et al. (2004) reported R_{CO} was 55 nmol μmol^{-1} in 2001 (C_{ff} was not determined). In the Beijing region, R_{CO} decreased from 57.80 to 37.59 nmol μmol^{-1} during 2004 to 2008 (Wang et al., 2010). The overall R_{CO} was (47±2) nmol μmol^{-1} at SDZ for 2009-2010 and (44±3) nmol μmol^{-1} in air-masses that originated from the Asian continent from 2005 to 2009 (Turnbull et al., 2011a). Tohjima et al.

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(2014) explained that surface based R_{CO} decreased from 45 to 30 nmol μmol^{-1} in outflow air masses from China from 1998 to 2010. Fu et al. (2015) also observed R_{CO} of 29 nmol μmol^{-1} over mainland China in 2009. In Beijing, which is located along the path of CE, it was (30.4±1.6) nmol μmol^{-1} and (29.6±3.2) nmol μmol^{-1} for Xiamen in 2016, which is in the OB sector (Niu et al., 2018). During KORUS-AQ in 2016, R_{CO} of 28 nmol μmol^{-1} was observed over the Yellow Sea. Some of those studies did not differentiate C_{ff} from the total CO_2 enhancement, so, although R_{CO} still includes uncertainties, it is continually decreasing.

In this study R_{CO} is (29±8), (31±8), (36±2), and (31±4) nmol μmol^{-1} for CB, CN, CE and OB, consistent with Tang et al.(2018) and Liu et al.(2018). On the other hand, R_{CO} in CE is higher than in other sectors in this study. The Shandong area, which is located in the path of CE, has been plagued with problems of combustion inefficiency and ranked as the largest consumer of fossil fuels in all of China (Chen and Li, 2009). The uncertainties in our observed R_{CO} for this region overlap with other sectors such as CB, CN and OB, so further monitoring of the ratios will help to get more detailed information.

In South Korea and China, atmosphere-based R_{CO} values are 1.2 times and (1.8±0.2) times greater than in the inventory, respectively. This is in agreement with previous studies (Turnbull et al., 2011a; Kurokawa et al., 2013; Tohjima et al., 2014). One explanation is that EDGAR does not reflect secondary CO production, which can be a significant contributor to CO (Kurokawa et al., 2013). Also, CO derived from biomass burning and biofuels was not included in this inventory. Therefore, this indicates that top-down observations are necessary to evaluate and improve bottom-up emission products.

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4. Summary and conclusion

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, which we consider to be broadly representative of background values for the mid-latitude Northern Hemisphere. This reflects the strong imprint of fossil fuel-CO_2 emissions recorded in AMY air samples. 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., 2011a). We also observed high C_{ff} regardless of the season or source region. After separately identifying samples originating from the Asian continent and the Korean peninsula, we determined that the mean C_{ff} increased relative to the earlier observations due to increased fossil fuel emissions from the Asian continent. Note, however, that our data span a relatively limited time period, so a longer time-series would increase confidence in tracking this change.

Because Δx(CO) and $\Delta x(SF_6)$ agreed well with C_{ff}, 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}. Overall, we have confirmed that both R_{CO} derived from inventory and observation have decreased relative to previous studies, indicating that combustion efficiency is increasing in both China and South Korea. Atmosphere-based R_{CO} 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

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production such as oxidation of CH_4 and non-methane VOCs. Therefore those values can be used for improving bottom-up inventory in the future. Finally, we stress that because C_{bio} contributes substantially to $\Delta x(CO_2)$, even in winter, $\Delta^{14}C$-based C_{ff} (and not $\Delta x(CO_2)$) is required for accurate calculation of both R_{CO} and R_{SF6}.

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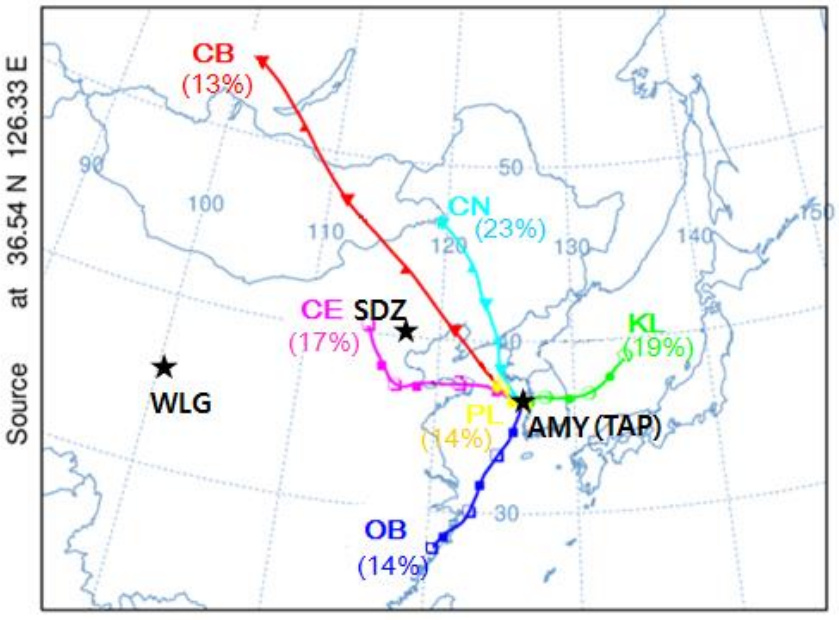

Figure 1. A total of 70 air-parcel back-trajectories were calculated for 72-h periods at 3-h intervals from May 2014 to August 2016 using the HYSPLIT model in conjunction with KMA UM GDAPS data at 25 km by 25 km resolution. Station locations are: WLG (Waliguan, 36.28° N, 100.9° E, 3816 m a.s.l.), SDZ (Shandianzi, 40.65° N, 117.12° E, 287 m a.s.l.), and AMY (Anmyeondo, 36.53° N, 126.32° E, 86 m a.s.l.). TAP (Tae-Ahn Peninsula, 36.73° N, 126.13° E, 20 m a.s.l.) is around 28 km northeast from AMY.

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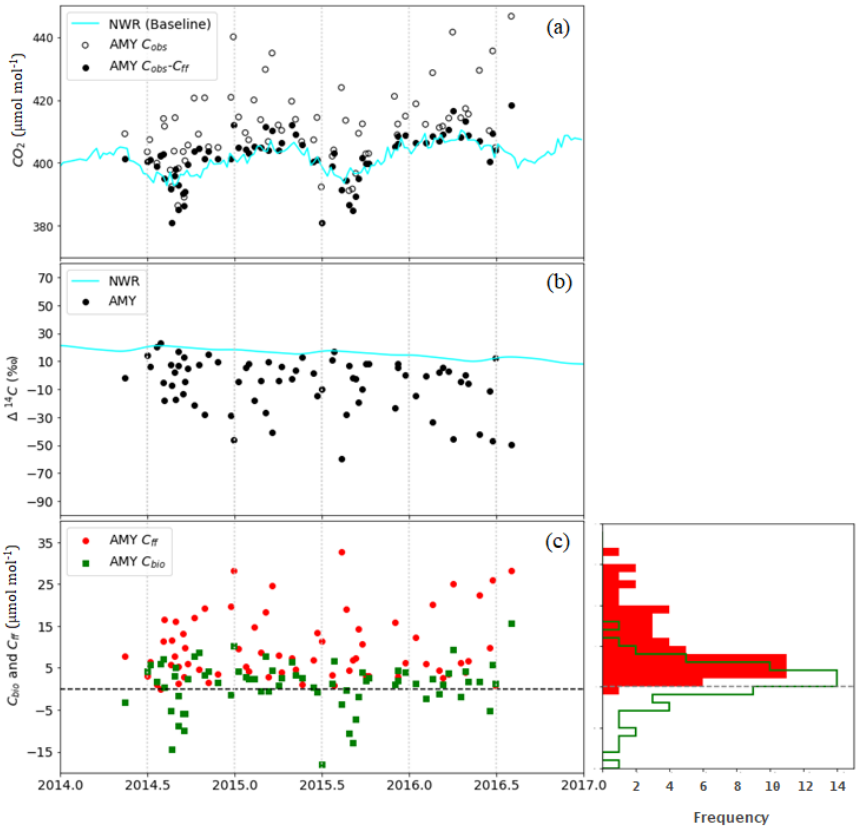

Figure 2. Time series of (a) observed CO_2 dry air mole fraction (open circles) and observed CO_2 (C_{obs}) minus C_{ff} calculated from $\Delta(^{14}CO_2)$ (closed circles). (b) $\Delta(^{14}CO_2)$ at AMY (black circles) and at NWR (Niwot Ridge, line), baseline data. (c) Time series of C_{ff} and C_{bio} calculated from $\Delta(^{14}CO_2)$ at AMY.

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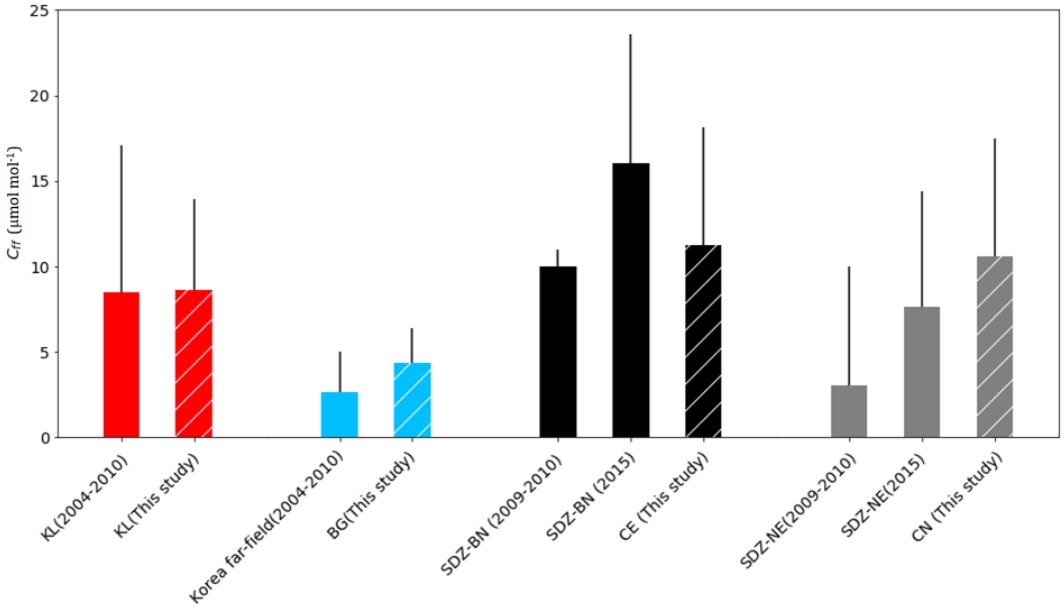

Figure 3. Calculated C_{ff} (μmol mol^{-1}). Red bars are for KL and blue bars are for Korea far-field (China) (2004-2010 from Turnbull et al. (2011a)). Black bars are for SDZ-BN samples that were affected by Beijing and North China plain. Gray bars for SDZ-NE indicate samples that were affected by regions northeast of SDZ. SDZ (2009-2010) is from Turnbull et al. (2011a) and SDZ (2015) is from Niu et al. (2016). Hatched red, blue, black and grey bars are derived from this study during 2014 to 2016.

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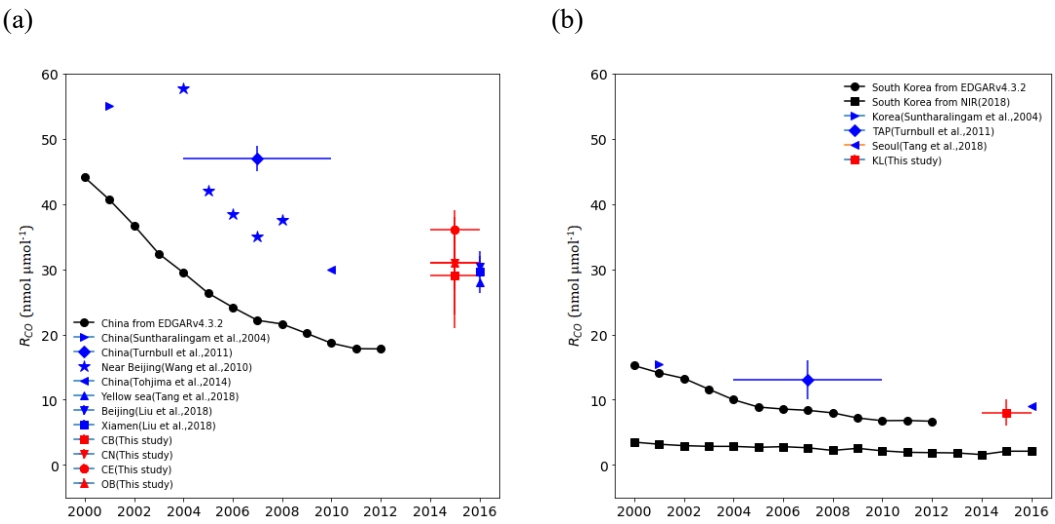

Figure 4. R_{CO} for China (a) and for South Korea (b). Black circles: EDGARv.4.3.2 emission inventory. Black squares: National Inventory Report, Korea (2018). Blue symbols are from other studies (Suntharalingam et al., 2004; Wang et al., 2010; Turnbull et al., 2011a; Tohjima et al., 2014; Liu et al., 2018; Tang et al., 2018). Red symbols: This study. Y-error bars: uncertainty according to equation (5). X-error bars: the period for the mean value.

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Table 1. Means and standard deviations of C_{ff} (μmol mol^{-1}), CO (nmol mol^{-1}) and SF_6 (pmol mol^{-1}) (total N=50, without PL N=41). The correlations (r) and the ratio (R_{gas}) of enhancement between C_{ff} were determined by Reduced Major Axis (RMA) regression analysis on each scatter plot to obtain regression slopes. The uncertainty of R_{gas} refers to equation (5). When r is less than 0.7, R_{gas} was not included here. N is the number of data. The unit of R_{CO} is nmol μmol^{-1} and for R_{SF6} it is pmol μmol^{-1}. A plot of R_{CO} and R_{SF6} is shown in Figure S1.

	Outflow from the Asia continent				South Korea	
	CB (N=7)	CN (N =9)	CE (N =9)	OB (N =7)	KL (N =9)	PL (N =9)
C_{ff}	4.3±2.1	10.6±6.9	11.2±8.3	4.1±2.7	8.6±5.3	15.6±11.6
CO	233±59	353±219	473±293	169±90	228±40	259±100
SF_6	9.0±0.4	10.1±1.2	10.1±1.5	9.2±0.5	13.0±3.3	12.7±6.2
R_{CO} (r)	29±8 (0.80)	31±8 (0.76)	36±2 (0.98)	31±4 (0.96)	8±2 (0.74)	- (0.44)
R_{SF6} (r)	- (0.63)	- (0.48)	0.19±0.03 (0.91)	0.17±0.03 (0.94)	0.66±0.16 (0.76)	- (0.38)

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Data availability

Our CO_2, CO, SF_6 data from AMY and NWR can be downloaded from ftp://aftp.cmdl.noaa.gov/data/trace_gases. $\Delta(^{14}CO_2)$ data are provided in the supplementary material of this paper.

Author contributions

HL wrote this paper and analyzed all data. HL and GWL designed this study. EJD and JCT guided and reviewed this paper. SL collected samples and gave the information of the data at AMY. EJD, JCT, SJL, JBM, GP, and JL provided data and reviewed the manuscript. SSL and YSP reviewed this paper. All authors contributed this work.

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