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Estimation of Potential Source Region in Northeast Asia through Continuous In-Situ Measurement of Atmospheric CO_2 at Gosan, Jeju Island, Korea

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ABSTRACT

High-Precision (0.1 ppm), high-frequency (hourly averaged) measurement of atmospheric carbon dioxide (CO_2) was made at Gosan Station on Jeju Island, Korea, using a Non-dispersive Infrared (NDIR) analyzer calibrated with National Oceanic and Atmospheric Administration/Earth System Research Laboratory standards. This paper presents the one-year results from these measurements, including discussions on data quality control and data selection, data characteristics through comparing with other regional data and on the techniques for estimating potential source regions of pollution emissions in Northeast Asia with pollution events in the record.

Comparisons of the continuous monitoring data with independent flask measurements at Gosan show good correlation in overall trend. In addition, the continuous monitoring data show signals of extreme pollution and sink episodes which are difficult to monitor in discrete flask measurements, showing the importance of continuous measurements.

The CO_2 concentrations of “representative data” at Gosan, derived by the statistical pollution identification procedure, show strong seasonality similar to those of other background observatories in the middle-to-high Northern Hemisphere. The amplitude of the seasonal variation at Gosan is approximately 16 ppm, similar to high-latitude Northern Hemisphere marine sites such as Ryori and Point Barrow stations.

A hybrid receptor model was applied to the “regional pollution events”, a statistically extracted subset of the data with a high probability of being influenced by regional pollution for understanding the distribution and strengths of the major CO_2 pollution sources in the Northeast Asia region. Results indicate strong potential source areas around the Yangtze River region including Shanghai and the Huabei plain including Beijing of China, as well as the Korean peninsula including Seoul contributing to pollution events observed at Gosan.

The methodologies and results describe our continuing efforts in establishing a “top-down” estimation of greenhouse gas emissions in the Northeast Asia region, important for scientific validation and monitoring of anthropogenic CO_2 emissions from the active industrial development in this region.

Key words: Carbon dioxide, Continuous *in-situ* monitoring, Gosan, Northeast Asia, Pollution emission, Top-down model

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1. INTRODUCTION

Atmospheric carbon dioxide (CO_2) is a widely studied species, the importance of which has been well documented in the scientific reports of the Intergovernmental Panel on Climate Change (IPCC 2007), including its role as a dominant greenhouse gas leading to the increase of radiative forcing in the climate system since the Industrial Revolution. Atmospheric CO_2 concentrations have increased steeply from a pre-industrial value of about 280 to 383 ppm in 2007, the reasons for which have been attributed to anthropogenic emissions of CO_2, including fossil fuel burning, deforestation, and cement production (IPCC 2007).

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Understanding and quantifying the sources and sinks of carbon has become a key focus of scientific research, even more so as inter-governmental efforts such as the Kyoto protocol attempt to address the issue of controlling the year-to-year increase of atmospheric CO_2 concentrations. The Northeast Asia region is of special interest in terms of the source emission area in which the developed economies of Japan and Korea and the emerging economy of China are situated. Thus Northeast Asia could constitute an important part of the global anthropogenic CO_2 budget.

Research at Gosan station (126 9'E, 33 17'N, 72 m asl; Fig. 1), located on the western tip of Jeju Island and south of the Korean peninsula, has made important contributions in understanding the pollution emissions of Northeast Asia. Notable studies at Gosan station include ACE-Asia (Bush and Valero 2003; Kim et al. 2005a) and ABC (Kim et al. 2005b; Zahorowski et al. 2005), aiming to understand the outflow of various aerosol species from the Northeast Asia region.

One of the longest research activities at Gosan, however, is the CO_2 flask measurements (Park 1997, 2005; Park and Kim 2003; Cho et al. 2005) for identifying long-term changes in CO_2 concentrations such as annual, seasonal and interannual variation in the ambient levels of CO_2. Weekly flask samples have been carried out since the summer of 1990 for measuring atmospheric CO_2 as well as ^{13}C and ^{14}C (since 1992). The flask samples are analyzed at the Keeling laboratory in Scripps Institute of Oceanography (UC San Diego) and the data from these flask measurements are being used in major global analysis program such as GLOBALVIEW.

The need to further understand the emissions of anthropogenic CO_2 in the Northeast Asia region has been one of the principle motivations to begin our continuous CO_2 monitoring research in 2004 at Gosan station. Namely, we strived to identify pollution occurrences from high-quality and high-frequency measurements (not feasible from previous flask measurements), then combine them with air mass trajectory models to derive a "top-down" model to estimate regional anthropogenic CO_2 emissions.

Various trajectory-modeling techniques (Stohl 1996) have been used to estimate the potential source regions of pollution emissions. One method first used by Ashbaugh (1983) and Ashbaugh et al. (1985) utilizes residence time analysis to estimate the source region. This method evolved into the hybrid receptor model (Seibert et al. 1994; Stohl 1996). The hybrid receptor model is driven by three-dimensional synoptic meteorology models such as the Hybrid Single-Particle Lagrange Integrated Trajectory (HYSPLIT) model (Draxler and Rolph 2005), which is combined with observation data to estimate potential source regions of pollution occurrences in observation data. This method was applied to many atmospheric components such as halogenated gases, aerosol, sulfur compounds (Stohl 1996; Reimann et al. 2004), carbon monoxide, CO_2 (Charron et al. 2000; Ferrarese et al. 2002; Apadula et al. 2003) and ozone. These previous studies indicate that a hybrid receptor model can be applied to a long-lived CO_2 component.

This article will explain the methodologies in our CO_2 continuous monitoring program at Gosan station, and discuss the monitoring results spanning the period of April 2003 to March 2004. Our discussion will include comparisons with the weekly flask measurements at Gosan, as well as comparisons with other global baseline stations and regional stations in the Northern Hemisphere (NH). In addition, we describe the methodology for a systematic identification of so-called "representative data" and "regional pollution events", and the development of a hybrid receptor model to describe possible sources and relative strengths of the regional pollution events. The results of the hybrid receptor model presented here are the first application of this model in the Northeast Asia region and its results and performance are discussed.

2. METHODOLOGY

2.1 Description of Measurement System and Data Quality Control Procedures

Precision, high-frequency (30 sec interval) atmospheric CO_2 concentration was measured using a system built around a Seimens Ultramat5F non-dispersive infrared (NDIR) analyzer (Fig. 2). The overall design of the system closely follows well-established procedures in the CO_2 measurement community (Komhyr et al. 1989; WMO 1999). The specifics of our system are as follows.

Ambient air is supplied via 10 mm o.d. Dekoron tubing 40 meters up to an intake tower (5 m height, 70 m asl) to reduce sample contamination in the sampling process while minimizing the effects of local contamination from the measurement facility itself. Air is drawn in via a vacuum pump and transferred to a back-pressure regulator set at 6 psi to

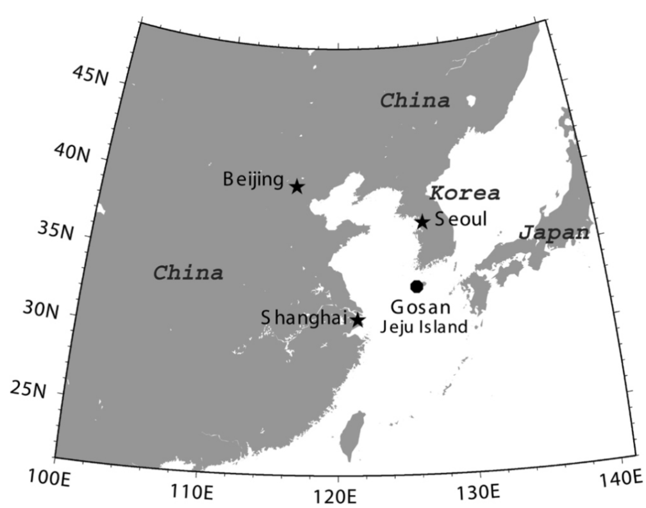

Fig. 1. Geographical situation of the Gosan/Jeju island station (dot) accompanied by the major cities (star) in Northeast Asia.

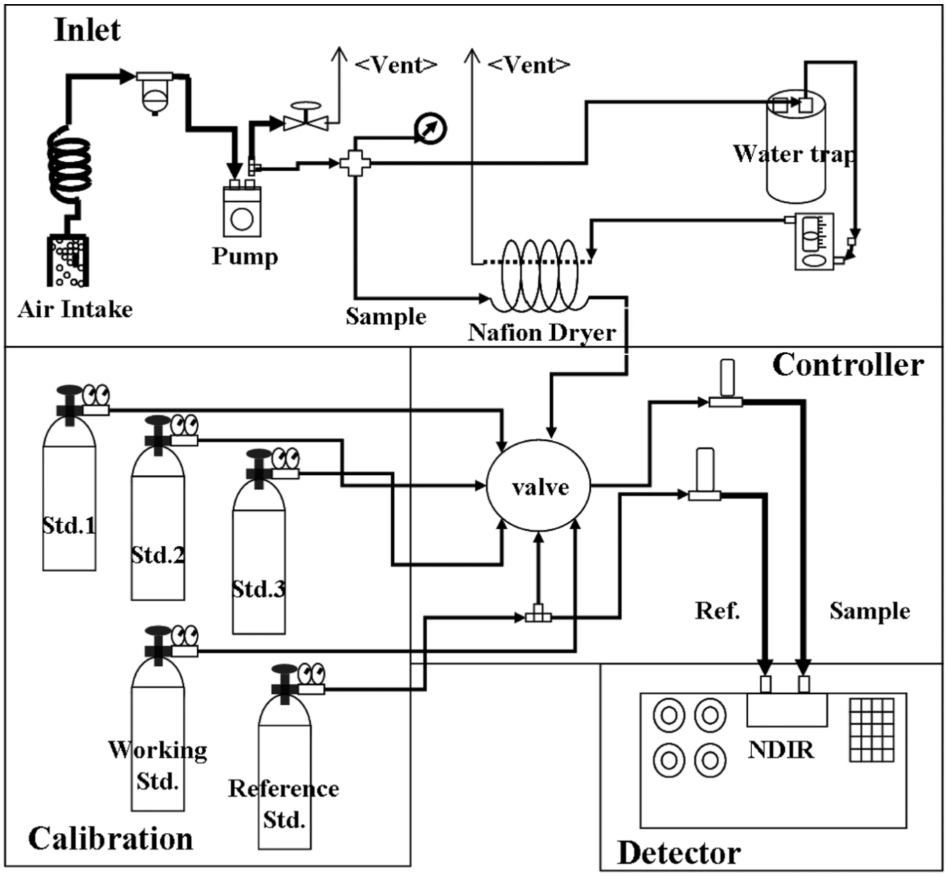

Fig. 2. Continuous CO_2 monitoring system made by the Environmental Chemistry lab in Seoul National University.

remove excess air while allowing adequate continuous flow through the main sample pathway. This is followed by a 7 m in-line filter to remove particles and a Nafion dryer to remove the effects of moisture from the sample. A selection valve from VICI/Valco is used to facilitate automatic switching between different gas processes and two mass flow controllers are used to ensure stable and proper air flow into the two cells of the NDIR analyzer (60 mL min^{-1} for sample gas; 10 mL min^{-1} for reference gas). The complete system is automated using a custom computer program to monitor, control and log the system operation status and measurement results.

NDIR analyzer is operated in a "differential mode", in which the sample air measurements through the sample cell are made relative to a reference air standard (purchased from Daesung gas Co. LTD, Korea) through the reference cell. In this way, any analyzer-induced noise in the sample measurement is effectively canceled out.

NDIR sensors are known to be sensitive to changes in the monitoring environment, such as changes in the laboratory temperature. To correct for these effects, a working standard gas (also from Daesung gas Co. LTD in Korea) was injected hourly and used in the data correction process.

For globally traceable calibration of the measurement data, a suite of three National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL) CO_2-in-air secondary standards was used as the calibrating standard gases.

A regular 1-day measurement sequence is as follows. A calibration curve of the NDIR analyzer is derived at the start of each day's measurement from a calibration sequence starting with a working standard measurement, following by the measurement of "zero" gas (reference air standard inserted into both cells) and three calibration standards and ending with a working standard measurement again (10 minutes measurements each). For the remainder of the day, 1-hour cycles with 10 minutes flow from the working standard gas followed by 50 minutes of flow from the ambient air is repeated until 1 day has passed since the last calibration sequence.

Whenever a change occurs in the measuremet sequence, the first 9 minutes of the measurements are flagged out. This allows the previously measured gas to completely flush out of the sample cell and insures proper measurement of the current gas. The remaining measurements from the measurement sequence are then averaged to represent the value of that sequence 1 min mean for the standard gas measurement sequences, and 41 min mean for the ambient air measurement sequence.

Employing the methodology of sampling, calibration and correction described above, measurement precisions have been shown to be below 0.1 at 370 ppm, within the recommended data quality for WMO background monitoring stations (WMO 2004).

Measurements with worse precision affected by instrument malfunctions or power failures and other factors have been flagged out. Observational data during the summer monsoon season are especially sparse, as normal station operation was difficult to maintain during the severe weather conditions.

2.2 Data Selection

Systematic and sound criteria for dividing the data by their characteristics are essential to analyzing the measurements at Gosan. Namely, we attempted to separate the "representative data" and "regional pollution events" from the complete data set. The "representative data" in this study refer to the non-pollution data assumed to be the representative value of normal conditions at Gosan, while "regional pollution events" refer to the exceptionally high concentration events noticed in the measurement events, with a high probability of being caused by regional transport of pollution, as opposed to an effect of local pollution influences near the vicinity of the measurement site. The following criteria have been established to distinguish the representative data and regional pollution events data from the observation dataset.

First, a statistical pollution identification procedure is used to determine abnormally high concentration (i.e., pollution) values, separating the non-pollution data with the "preliminary pollution events". This statistical pollution identification procedure determines the pollution events of a given day by examining the trends from 60 days before to 60 days after it. Events that deviate positively from the median (thought to be a more representative value than the mean) of the distribution by more than a certain factor (typically 2 ~ 3) are labeled as preliminary pollution events, while the remainder are assumed to be non-pollution data with a Gaussian distribution and labeled as representative data. A similar statistical procedure has been employed successfully in O'Doherty et al. (2001). The characteristics of the representative data are further discussed in section 3.2.

This statistical methodology was used in this study because traditional methods of local wind sector based pollution identification (Gras 2001; Zhou et al. 2003) are not as effective under the air conditions at Gosan. The dominant local wind direction at Gosan during the winter months is northerly, the direction from which both pollution and non-pollution periods occur. In these conditions, local surface wind direction becomes a less meaningful factor in determining the characteristics of different CO_2 patterns, hence some other criteria was necessary for separating the pollution events.

The second step involves selecting regional pollution event data from the statistically determined preliminary pollution events, which can also be described as removing events with a high probability of local influence. Specifically, pollution events that occur during periods when the mean mixed depth was below 300 m (derived using the HYSPLIT meteorological model), and pollution events when surface wind speed (provided by Gosan weather station) was lower than 3 m s^{-1} were all excluded as pollution events possibly affected by local sources (local pollution data). Such procedures to remove local influence have previously been used in Simmonds et al. (2000) and Derwent et al. (2002).

The end result of above two procedures yield the pollution events data expected to show influence of regional transport of pollution into Gosan and will be combined with air mass back trajectory analysis to estimate source regions.

2.3 Air Mass Back Trajectory Analysis

Three-day back trajectories from Gosan (from April 2004 to March 2005) for every hour were calculated by the HYSPLIT model (Draxler and Rolph 2005) with 6-hourly archived meteorological data provided from the final run (FNL) data of US National Centers for Environmental Prediction (NCEP) Global Data Assimilation System (GDAS). The altitude of the starting point of the trajectory was set to the value of the tropospheric atmospheric mean mixed depth (Gosan, 800 m) derived from HYSPLIT model with NCEP meteorological data during the sampling period. This altitude was adopted to reflect more realistic movement of air masses in the planetary boundary layer. A three-dimensional vertical velocity field was used to calculate the vertical motion of the air parcel.

The uncertainty of the hybrid receptor model (section 2.4) is directly expressed by that of the back-trajectory data, therefore reducing errors in the back-trajectory analysis is critical to reducing overall model errors. In this study, an ensemble technique (Scheele and Siegmund 2001; Draxler 2003) was applied to reduce possible errors in initial conditions, in which the starting point of the trajectory model was set to five points (one at the exact starting location and four at the corner of the grids (0.5 0.5 for our study) in which the starting location was situated) at each respective altitude (800, 800 200 m).

2.4 Hybrid Receptor Model

Air-mass back trajectories have often been used in combination with observational data to identify potential source areas of air pollutants and determine their respective contribution at receptor sites (Stohl 1996; Ferrarese et al. 2002; Reimann et al. 2004). To investigate potential CO_2 source regions in this study, we combined back-trajectories diagnosed by HYPLIT model with the measured value at station.

We have used a hybrid receptor model method (Reimann et al. 2004), which computes the mean concentration for each grid cell after superimposing a grid on the domain of the trajectory by the following formula:

$$\overline{C_{ij}} = \frac{1}{\sum_{i=1}^{M} \tau_{ijl}} \sum_{i=1}^{M} (C_l)\tau_{ijl} \quad (1)$$

In Eq. (1), $\overline{C_{ij}}$ is a relative measure of potential source region strength, *i, j* are the indices of the horizontal grid, *l* is the index of the trajectory, *M* is the total number of trajectories, C_l is the magnitude (minus the background concentration) measured during the arrival of trajectory *l* and τ_{ijl} is the residence time of the trajectory *l* spent over grid cell *i, j*. Regional pollution events selected by the methods in section 2.2 during the sampling period have been combined with their appropriate trajectories.

The domain of the calculated trajectories was superimposed with a 0.5 0.5 grid. For the calculation of residence time, we used the method of Poirot and Wishinski (1986), with adjustments applied for geometry.

A high value of $\overline{C_{ij}}$ means that, on average, air parcels passing over the cells (*i, j*) result in high concentrations at the receptor site. But as this model assumes measured concentrations are distributed equally to all grid cells passed by the appropriate trajectory, the approach used is susceptible to underestimation of spatial gradients of the true emission field (Stohl 1996).

In order to eliminate low confidence level areas, a point filter was applied to the model results, removing grids where the counts of trajectory were less than 12. This increases the confidence level of the results but also reduces the area of the model results.

3. RESULTS AND DISCUSSION

3.1 General Observations

Figure 3 shows the continuous monitoring data from Gosan in the periods from April 2004 to March 2005, collected and analyzed using methods described earlier in section 2.2. Figure 3 shows hourly averaged representative data (dot), regional pollution data (open diamond), and local pollution data (open triangle). The hourly averaged CO_2 concentrations from continuous monitoring show large variability from 360 to 410 ppm during the measurement period with minimum in summer and maximum in early spring.

Of all the measurement data used in this study, 75% (4064 hourly means) were statistically determined to be representative data. Of the remaining 25% of the data, 64% (16% of all data, 837 hourly means) were determined to be possible influences from regional pollution sources.

3.2 Comparisons with Flask Measurements

As mentioned earlier in the introduction, flask measurements of ambient CO_2 have been performed at Gosan since 1990. Since the flask measurements are calibrated independently from a well-established laboratory (Keeling laboratory, SIO, UC San Diego), comparisons between the continuous *in-situ* observation and the flask sampling measurements can help verify the accuracy of the newer continuous measurements.

Figure 4 also shows the flask measurements plotted over the continuous data. Overall agreement between the two data sets is very good in seasonal trends. In addition,

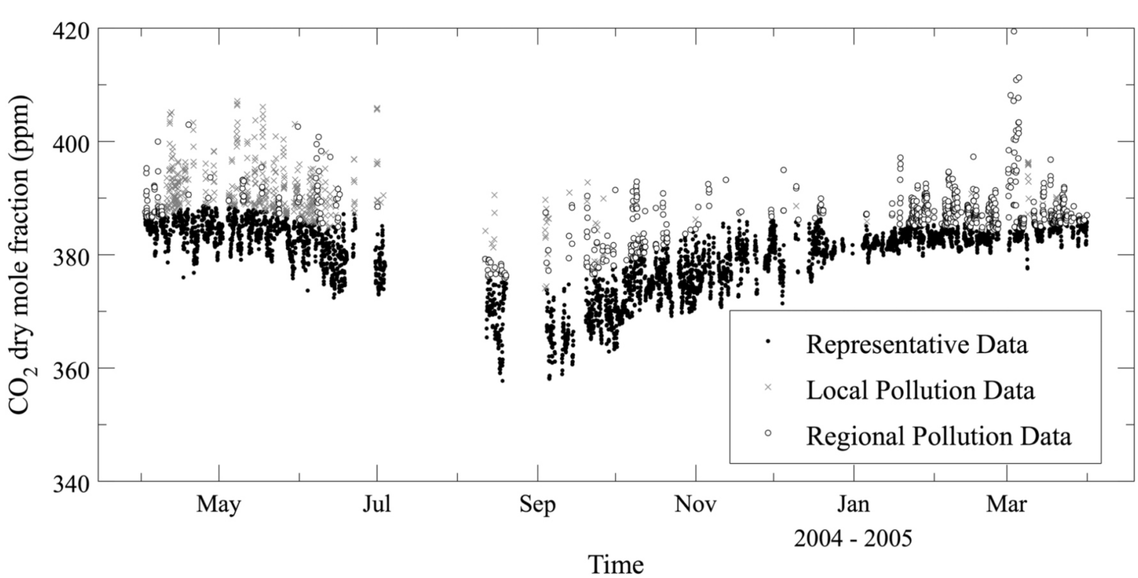

Fig. 3. Continuous monitoring data from Gosan in the periods from April 2004 to March 2005, also show representative data (dot), regional pollution data (open diamond), and local pollution data (open triangle) collected and analyzed using methods described in sections 2.2 and 2.3.

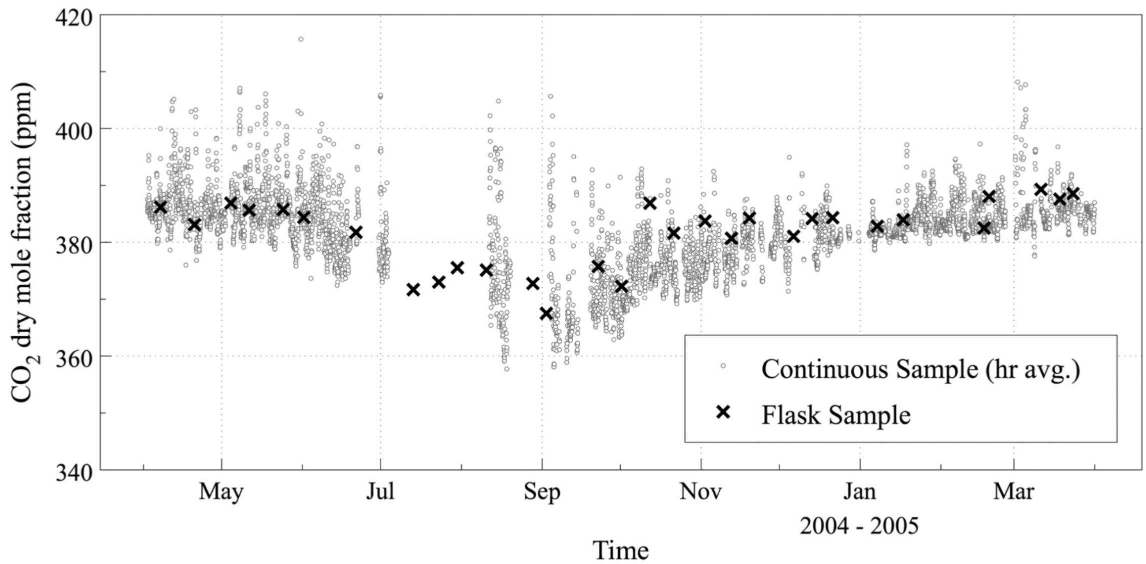

Fig. 4. Comparison continuous measurement data with flask sampling data. ×'s represents flask sampling data, dot represents *in-situ* continuous measurement data.

the yearly average value of continuous measurement data (381.06 4.98 ppm) is similar to that of discrete measurement data (381.38 5.45 ppm), indicating overall excellent agreement between the two independent measurements. Average difference between continuous measurements and flask is about -0.17 ppm within the general atmospheric fluctuations and close to measurement precisions.

An important observation is that the flask record clearly underestimates the actual seasonal variations that are observed in the continuous data, which is to be expected from the nature of the flask sampling frequency. This highlights the importance of high frequency measurements in understanding true atmospheric variability of CO_2, despite the fact that flask measurements have been very effective in establishing the yearly increase and the general seasonal patterns of ambient CO_2 levels.

Also interesting is the flask record on October 12 which seems to be higher than expected from the overall trends. Continuous monitoring results help explain this anomaly, showing that a pollution event occurred during that time. Therefore the high value by flask sampling is likely to be reasonable, in the sense that it represents the true atmospheric concentrations during that time, which should be discussed with caution as the concentrations are more likely to be biased compared to the general trends. Thus, continuous measurements can be a useful tool in verifying discrete flask measurements.

3.3 Representative Data and Comparison with Other Background Observatory Data

The monthly-averaged CO_2 seasonal variation for the representative data of our observation is shown in Fig. 5, with the standard deviation of the hourly mean indicated as an error bar. The yearly mean representative data at Gosan is about 378.89 5.63 ppm. There was an obvious seasonal variation at Gosan, with a maximum occurring in April and a minimum is September. The atmospheric CO_2 concentration declined during the period April - August, and climbed during the period September - March. The CO_2 seasonal amplitude was up to about 16 ppm at Gosan. The strong seasonal variation reflects the annual variability of terrestrial vegetation growth in the middle of NH (Keeling et al. 1989; Heimann et al. 1989).

In an attempt to put our continuous monitoring results in context, we compare the representative data from *in-situ* continuous measurement with other well-established moni-

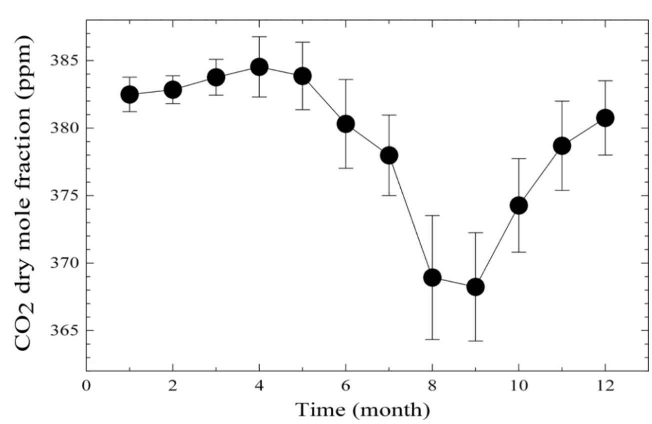

Fig. 5. Monthly-averaged CO_2 seasonal variation for the representative data of our observation with the standard deviation of the hourly mean indicated as an error bar.

toring stations in the NH, namely Mauna Loa (MLO), Point Barrows (BRW) and Ryori (Ryori), detailed in Table 1. Data for this comparison was obtained from the WDCGG database (http://gaw.kishou.go.jp/cgi-bin/wdcgg/catalogue.cgi)

Due to its remote location, the seasonal variation at Gosan is in close agreement with the variations at the comparison sites located in the middle-to-high latitude NH. Strong seasonality is apparent in all sites. Comparing the seasonal amplitude from April 2004 to March 2005, the value at Gosan (16.29 ppm) is larger than that at MLO (6.73 ppm), while being close to that at BRW (17.96 ppm), and Ryori (16.79 ppm) (Table 1). The enhanced seasonality in the middle-to-high latitude NH stations is due to photosynthesis and respiration of the terrestrial biosphere. The higher latitude of Gosan station with closer location at the eastern end of the Eurasia continent would result stronger influence by the biogenic flux in the NH compared to that at MLO, which reflects larger seasonal variability at Gosan. Overall comparisons are well matched with previous modeling studies on global CO_2 transport, including the overall agreement in concentrations between Gosan and BRW (Heimann et al. 1989).

3.4 Variation in Trajectory Trends and Definition of the "Cold Semester"

Figure 6 shows the monthly residence time map of the air masses reaching Gosan, drawn from analysis of the HYSPLIT back trajectories using techniques described in section 2.4. Residence time analysis analyzing trajectories reaching Gosan station provides a way to infer the dominant pathways of air masses traveling into Gosan, from which could the general pattern of regional influence at Gosan can be understood.

As is well know for the region, Fig. 6 reflects the typical monsoon wind patterns at Gosan, with north to northwesterly trajectories dominant during the colder months, and increased southern influence in the warmer months.

For the purpose of modeling the likely regional sources of pollution events, a selection process was needed for separating the periods most likely to be affected by anthropogenic sources in the north. Therefore time periods throughout the year when the probability of northern influence is expected to be dominant were selected and labeled as "cold semester" months, the process for which is detailed in the following criteria.

First, the months of June - September were removed from consideration, as trajectory residence time maps clearly show influence of dominant southern air masses, thus unsuitable for monitoring northern pollution.

Second, the month of October was removed from consideration, as drastic changes in the air mass flow pattern occur at this time period, and therefore model results from October were shown to be unreliable.

Third, the months of March and April, although traditionally not thought of as cold months, were included with the cold months from November to February, because fossil fuel burning from heating continues through April in the colder northern regions of China, and model results were able to show signals of these pollution sources in early spring.

These selected months (November - April) will hereafter be referred to as the cold semester, reflecting the time periods when anthropogenic pollution from the northern regions is most likely to reach Gosan station. The modeling of major pollution emission sources in the next section will be based on regional pollution data during this cold semester, when model results have the highest probability for accuracy.

The occurrence of regional pollution events in the cold semester occupied about 75% (630 hours) in total regional pollution events. Therefore the majority of regional pollution events occurred in the cold semester, further evidence that defining the cold semester is important in obtaining statistically meaningful results.

3.5 Estimations of Major Source Regions in Northeast Asia

On the basis of regional pollution data in the cold semester (section 3.4), we applied a hybrid receptor model (section 2.4) to estimate the potential source regions of pollution events at Gosan. High potential source strength for a specific grid means that air masses passing over the grid are on average associated with high concentration at the measur-

Table 1. Station information and amplitude of the monthly averaged atmospheric CO_2 concentrations data from selected NH sites during April 2004 - March 2005.

Site	Latitude, Longitude, deg	Altitude, m asl	Site General description	Amplitude CO_2
BRW	71.32°N, 156.60°W	11	High NH (Global site)	17.96
Ryori	39.03°N, 141.82°E	260	Middle NH coastal (regional site)	16.76
Gosan	33.29°N, 126.17°E	72	Middle NH Island	16.29
MLO	19.53°N, 155.58°W	3397	Low NH island (Global site)	6.73

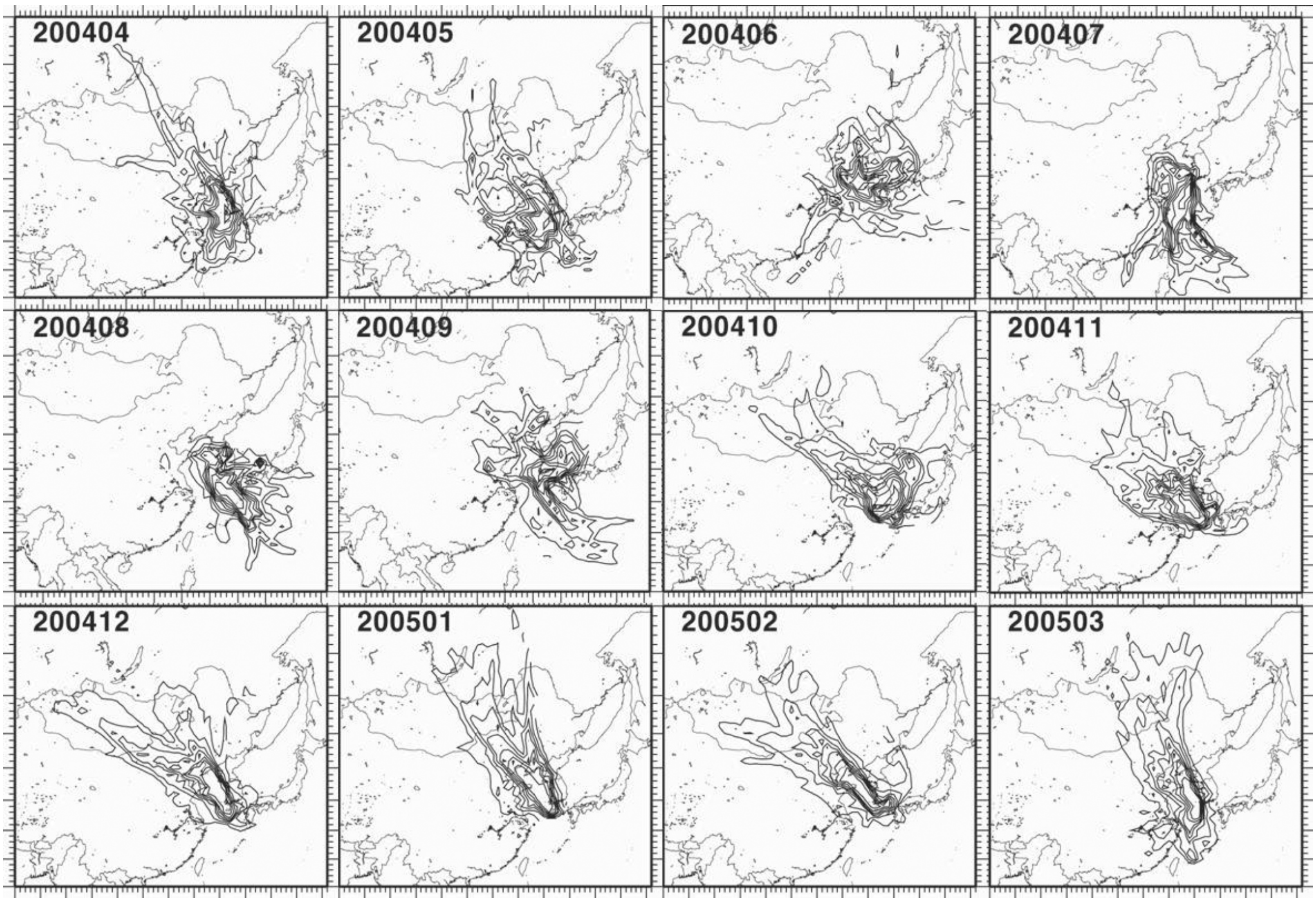

Fig. 6. Contour plot of the residence time (total counts of trajectory in respective grid) analysis using trajectories arriving at Gosan. The ridges in the contour pattern indicate the predominant transport pathways of air mass to Gosan.

ing site. The scale refers to the increased concentration above the representative data.

Model results show three main potential source regions in: (1) the Yangzte River region including Shanghai in China; (2) Huabei plain including Beijing in China; and (3) the Korean peninsula around Seoul in Korea (Fig. 7).

One of the main concerns in the development of the hybrid receptor model was the need for meaningful separation in the various pollution source regions. Ideally the model would be able to pin-point various pollution sources exactly, but mixing within the air mass en route to Gosan as well as modeling errors introduced in calculating this air mass movement all reduce the spatial precision of the emissions model result.

Hybrid receptor model results were successful in showing the pollution signals of three major cities in Northeast Asia: Shanghai, Beijing, and Seoul. This is a positive indication that the model is capable of analyzing actual pollution patterns in the region.

However, there are signs that the model isn't completely successful. For example, the regions in Beijing and especially Shanghai are not clearly defined but smeared into large regions. There's uncertainty as to whether this is an actual phenomenon or an artifact of model deficiencies. Also questionable are the relatively large pollution sources in the oceans in general. The cooler temperatures in winter should in theory make the oceans a sink of atmospheric CO_2 rather than a source. Even if the oceans were acting as a source indeed, it seems unlikely that the size of the net emission would be within or of greater magnitude than emissions from Seoul.

One key factor in understanding these errors is the fact that the hybrid receptor model is ultimately driven by the trajectory pathways during a regional pollution episode. For example, a trajectory coming from Beijing to Gosan will show itself as pollution from somewhere along the trajectory pathway but not necessarily at Beijing precisely. Ideally, trajectories that come through Beijing will come to Gosan through various different pathways, so that the compilation of all the trajectory analysis will point out the common denominator in Beijing while the non-pollution grids in the pathways are averaged out. This ideal mechanism may not be working very well for the results in our model, because air mass trajectories from each of the pollution sources could

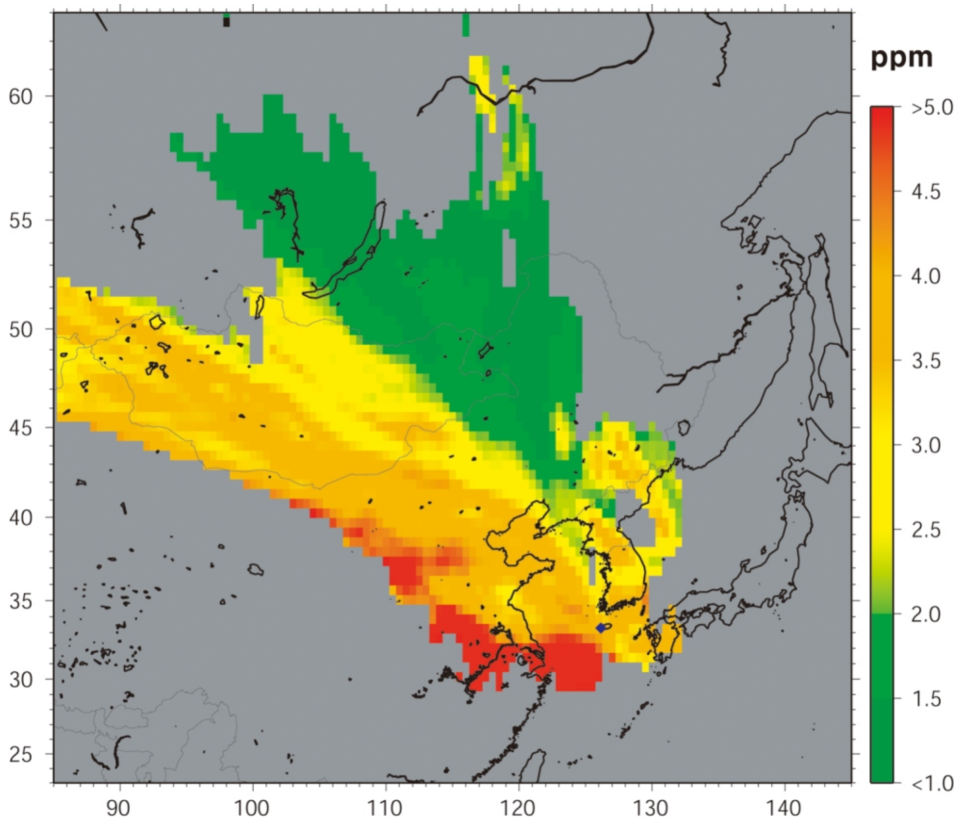

Fig. 7. Concentration field of CO_2 using 630 trajectories starting at Gosan in the cold semester from April 2004 to March 2005. The position of Gosan is shown by a black point, the trajectory length is 3 days. Those grids that have been crossed by less than 12 trajectories are left blank. The unit shows above the non-pollution data.

have relatively uniform trajectory pathways, and therefore the separation of the actual pollution source from the trajectory pathway becomes more difficult. The large, high pollution source region in and around Shanghai could be a good example of this problem.

One way to improve upon the hybrid receptor model results is to use data from multiple stations with reasonable spatial separation. In this case, trajectory pathways of a polluted air mass reaching one station would be very different from the trajectory pathway of another station, making statistical analysis of the real pollution source more viable.

Another way to improve the modeling results would be to have a larger data set spanning multiple years. A larger initial data set would help improve the statistical accuracy of the results, plus yearly variation in the model results could lead to clues in pointing to the real pollution sources.

The hybrid receptor model results described here are generally referred to as "top-down" modeling of emissions, as opposed to "bottom-up" modeling of emissions calculated through emissions inventory databases. Although "bottom-up" techniques are used widely in many emissions modeling studies, there are large uncertainties to its credibility, mostly due to difficulties in compiling and maintaining an accurate inventory database. "Top-down" methods, although much harder to implement accurately, could help validate and support the "bottom-up" results, in the overall process of defining the detailed anthropogenic emissions of greenhouse gases on regional spatial scales.

The results of the hybrid receptor model presented here indicate that although the monsoon wind patterns play an important part in increasing modeling errors in the hybrid receptor model technique, broad definition of the overall emission patterns are quite capable, and show promise that further refinement in the model techniques could make accurate regional "top-town" emissions estimates possible in the Northeast Asia region. Such efforts could have important scientific and political implications.

4. SUMMARY AND CONCLUSION

Results of continuous atmospheric CO_2 measurements conducted in the period from April 2004 to March 2005 at Gosan station are presented and discussed. Measurement techniques closely followed the schemes recognized internationally such as those from GAW and care was taken to calibrate the system on the NOAA/ESRL calibration scale. The achieved precisions were better than the WMO-recommended 0.1 at about 370 ppm.

The general trend of the measurement dataset shows very good correlation with that of independent, globally-recognized flask sampling data at Gosan.

The representative data occupied 75% of total valid data, which was separated by a statistical pollution identification procedure. The seasonal variation of the representative data was about 16 ppm, within the boundaries of variations observed at other background stations in the NH and previous modeling studies on global CO_2 transport.

The regional pollution events distributed 16% of all valid data and were selected by a combination of a statistical pollution identification procedure with meteorological data analysis. Three quarters of the regional pollution events occurred in the cold semester, which was further studied for estimating potential source regions using a hybrid receptor model.

Model results identify three dominant potential source regions for Gosan in the cold semester, namely: (1) the Yangzte River region including Shanghai in China; (2) Huabei plain including Beijing in China; and (3) the Korea peninsula including Seoul.

However, the deficiencies of the current model can clearly be seen in the results with the wide spread of high emission source regions nearby dominant sources, especially around Shanghai. The reasons for these errors are thought to be due to the uniformity of the air trajectories reaching Gosan, as the hybrid receptor model relies on the higher statistical probability of pollution trajectory pathways passing over the actual pollution source to distinguish the actual pollution emitting grids. Improvements such as employing a multi-site driven model and using a larger dataset could help raise the accuracy of the current model results.

The modeling results and implementation challenges presented in this study show some important considerations in establishing a "top-down" emission model scheme for validating and monitoring anthropogenic emissions in the Northeast Asia region, where such efforts could be especially important both scientifically and politically, due to heavily concentrated industrialization in this region.

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REFERENCES

Apadula, F., A. Gotti, A. Pigini, F. Rocchetti, C. Cassardo, S. Ferrarese, and R. Forza, 2003: Localization of source and sink regions of carbon dioxide through the method of the synoptic air trajectory statistics. *Atmos. Environon*., **37**, 3757-3770, doi: 10.1016/S1352-2310(03)00505-3. [Link]

Ashbaugh, L. L., 1983: A statistical trajectory technique for determining air pollution source regions. *J. Air pollut. Control Assoc*., **33**, 1096-1098.

Ashbaugh, L. L., W. C. Malm, and W. Z .Sadeh, 1985: A residence time probability analysis of sulfur concentrations at Grand Canyon National Park. *Atmos. Environ*., **19**, 1263-1270.

Bush, B. C. and F. Valero, 2003: Surface aerosol radiative forcing at Gosan during the ACE-Asia Campaign. *J. Geophys. Res*., **108**, 8660, doi: 10.1029/2002JD003233. [Link]

Charron, A., H. Plaisance, S. Sauvage, P. Coddeville, J. C. Gallo, and R. Guillermo, 2000: A study of the source-receptor relationships influencing the acidity of precipitation collected at a rural site in France. *Atmos. Environ*., **34**, 3665-3674, doi: 10.1016/S1352-2310(00)00096-0. [Link]

Cho, C. B., S. N. Oh, K. J. Park, B. C. Choi, M. K. Park, and K. R. Kim, 2005: The distribution characteristics of atmospheric CO_2 in the Korean Peninsula and the expectations on its annual growth trend by the year 2015. *J. Korean Meteor. Soc*., **41**, 371-385.

Derwent, R. G., D. B. Ryall, A. J. Manning, P. G. Simmonds, S. O'Doherty, S. Biraud, P. Ciais, M. Ramonnet, and S. G. Jennings, 2002: Continuous observations of carbon dioxide at Mace Head Ireland from 1995 to 1999 and its net European ecosystem exchange. *Atmos. Environ*., **36**, 2799-2807, doi: 10.1016/S1352-2310(02)00203-0. [Link]

Draxler, R. R., 2003: Evaluation of an Ensemble Dispersion calculation. *J. Appl. Meteorol*., **42**, 308-317.

Draxler, R. R. and G. D. Rohph, 2005: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD.

Ferrarese, S., A. Longhetto, C. Cassrdo, F. Apadula, D. Bertoni, C. Giraud, and A. Gotti, 2002: A study of seasonal and yearly modulation of carbon dioxide sources and sinks, with a particular attention to the Boreal Atlantic Ocean. *Atmos. Environ*., **36**, 5517-5526, doi: 10.1016/S1352-2310(02)00669-6. [Link]

Gras, J. L., 2001: Aerosol black carbon at Cape Grim, by light absorption. Baseline Atmospheric program (Australia), 1997-98, 20-26.

Heimann, M., C. D. Keeling, and C. J. Tucker, 1989: A three-dimensional model of atmospheric CO_2 transport based on observed winds: 3. Seasonal cycle and synoptic time scale variations. In: Peterson, D. H. (Ed.), Aspects of Climate Variability in the Pacific and the Western Americas, Washington, D. C., AGU, *Geophys. Monogr*., **55**, 277-303.

IPCC, 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel On Climate Change In: Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, and H. L. Miller (Eds.), Cambridge

University Press, Cambridge, United Kingdom and New York, NY, USA.

Keeling, C. D., R. B. Bacastow, A. F. Carter, S. C. Piper, T. P. Whorf, M. Heimann, W. G. Mook, and H. Roeloffzen, 1989: A three-dimensional model of atmospheric CO_2 transport based on observed winds: 1. Analysis of observational data. In: Peterson, D. H. (Ed.), Aspects of Climate Variability in the Pacific and the Western Americas, Washington, D. C., AGU, *Geophys. Monogr.*, **55**, 165-236.

Kim, J. Y., S. C. Yoon, A. Jefferson, W. Zahorowski, and C. H. Kang, 2005a: Air mass characterization and source region analysis for the Gosan super-site, Korea, during the ACE-Asia 2001 field campaign. *Atmos. Environ*., **39**, 6513-6523, doi: 10.1016/j.atmosenv.2005.07.021. [Link]

Kim, S. W., S. C. Yoon, A. Jefferson, J. A. Ogren, E. G. Dutton, A. John, J. G. Won, Y. S. Ghim, B. I. Lee, and J. S. Han, 2005b: Aerosol optical, chemical and physical properties at Gosan, Korea during Asian dust and pollution episodes in 2001. *Atmos. Environ*., **39**, 39-50, doi: 10.1016/j.atmosenv.2004.09.056. [Link]

Komhyr, W. D., T. B. Harris, L. S. Waterman, J. F. S. Chin, and K. W. Thoning, 1989: Atmospheric carbon dioxide at Mauna Loa observatory 1. NOAA Global Monitoring for Climatic Measurements with a Nondispersive Infrared Analyzer, 1974-1985. *J. Geophys, Res*., **94**, 8533-8547. [Link]

O'Doherty, S., P. G. Simmonds, D. M. Cunnold, H. J. Wang, G. A. Sturrock, P. J. Fraser, D. Ryall, R. G. Derwent, R. F. Weiss, P. Salamech, B. R. Miller, and R. G. Prinn, 2001: In situ chloroform measurements at Advanced Global Atmospheric Gases Experiment atmospheric research stations from 1994 to 1998. *J. Geophys, Res*., **106**, 21429-20444.

Park, M. K., 1997: A study on the atmospheric CO_2 (carbon dioxide) in Korea. Master Thesis, Seoul National University, Korea.

Park, M. K., 2005: A study on the atmospheric CO_2 and its carbon isotopes at Gosan, Korea, Ph.D. Thesis, Seoul National University, Korea.

Park, M. K. and K. R. Kim, 2003: A Study on the atmosphere CO_2 and its carbon isotopes at Gosan. *Atmosphere*, **13**, 308-309.

Poirot, R. L. and P. R. Wishinski, 1986: Visibility, sulfate and air mass history associated with the summertime aerosol in northern Vermont. *Atmos. Environ*., **20**, 1457-1469.

Reimann, S., D. Schaub, K. Stemmler, D. Folini, M. Hill, P. Hofer, B. Buchmann, P. G. Simmonds, B. R. Greally, and S. O'Doherty, 2004: Halogenated greenhouse gases at the Swiss High Alpine Site of Jungfraujoch (3580 m asl): Continuous measurements and their use for regional European source allocation. *J. Geophys. Res*., **109**, D05307, doi: 10.1029/2003JD003923. [Link]

Scheele, M. P. and P. C. Siegmund, 2001: Estimating errors in trajectory forecasts using ensemble predictions. *J. Appl. Meteorol*., **40**, 1223-1232.

Seibert, P., H. Kromp-Kolb, U. Baltensperger, D. T. Jost, M. Schwikowdki, A. Kasper, and H. Pusbaum, 1994: Trajectory analysis of aerosol measurements at high Alpine sites. *Eurotrac Symposium*, 689-693.

Simmonds, P. G., R. G. Derwent, S. O'Doherty, D. B. Ryall, L. P. Steele, R. L. Langenfelds, P. Salameh, H. J. Wang, C. H. Dimmer, and L. E. Hudson, 2000: Continuous high-frequency observations of hydrogen at the Mace Head baseline atmospheric monitoring station over the 1994-1998 period. *J. Geophys. Res*., **105**, 12105-12121.

Stohl, A., 1996: Trajectory statistics-A new method to establish source-receptor relationships of air pollutants and its application to the transport of particulate sulfate in Europe. *Atmos. Environ*., **30**, 579-587, doi: 10.1016/1352-2310(95)00314-2. [Link]

WMO, 1999: Guide on sampling and analysis techniques for chemical constituents and physical properties in air and Precipitation as Applied at stations of the global atmospheric watch, Part1: Carbon dioxide, **134**, TD-No.980.

WMO, 2004: 12th WMO/IAEA Meeting of Experts on carbon dioxide concentration and related tracers measurement techniques. **161**, TD-No.1275, Toronto, Canada, 15-18 September, 2003.

Zahorowski, W., S. Chambers, T. Wang, C. H. Kang, I. Uno, S. Poon, S. N. Oh, S. Werczynski, J. Kim, and A. Henderson-Sellers, 2005: Radon-222 in boundary layer and free tropospheric continental outflow events at three ACE-Asia sites. *Tellus*, **57B**, 124-140, doi: 10.1111/j.1600-0889.2005.00133.x. [Link]

Zhou, L. X., J. Tang, Y. P. Wen, J. L. Li, P. Yan, and X. C. Zhang, 2003: The impact of local winds and long-range transport on the continuous carbon dioxide record at Mount Waliguan, China. *Tellus*, **55B**, 145-158, doi: 10.1034/j.1600-0889.2003.00064.x. [Link]