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Constraining Anthropogenic CH_4 Emissions in Nanjing and the Yangtze River Delta, China, Using Atmospheric CO_2 and CH_4 Mixing Ratios

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ABSTRACT

Methane (CH_4) emissions estimated with the Intergovernmental Panel on Climate Change (IPCC) inventory method at the city and regional scale are subject to large uncertainties. In this study, we determined the CH_4:CO_2 emissions ratio for both Nanjing and the Yangtze River Delta (YRD), using the atmospheric CH_4 and CO_2 concentrations measured at a suburban site in Nanjing in the winter. The atmospheric estimate of the CH_4:CO_2 emissions ratio was in reasonable agreement with that calculated using the IPCC method for the YRD (within 20%), but was 200% greater for the municipality of Nanjing. The most likely reason for the discrepancy is that emissions from unmanaged landfills are omitted from the official statistics on garbage production.

Key words: methane, IPCC inventory, atmospheric mixing ratio, city, region

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1. Introduction

Cities are greenhouse gas (GHG) emission hotspots, and are responsible for 70%–80% of global anthropogenic GHG emissions (e.g., O'Meara and Peterson, 1999; Koerner and Klopatek, 2002; Satterthwaite, 2008; Canadell et al., 2009). In many countries, strategies for controlling GHG emissions are shifting from the national level to the city scale. In order to verify the effectiveness of these strategies, GHG inventories have been established in New York, Tokyo, and London (e.g., Baldasano et al., 1999; Mayor of London, 2007; Vande Weghe and Kennedy, 2007; City of New York, 2012). In China, cities play a disproportionately large part in the national GHG emission totals: in 2006 they accounted for 75% of the national economy but 84% of the GHG emissions (e.g., Dhakal, 2009). In China's 12th five-year plan, reducing GHG emissions has become an important goal of sustainable development (e.g., Geng, 2011). Even though GHG inventories are useful indicators of low-carbon city development, we are only aware of a few published studies on emissions inventories for municipalities in China (e.g., Geng et al., 2011; Liu et al., 2012).

In China, CH_4 emissions account for 11% to 13% of the total global warming potential associated with anthropogenic activities (e.g., Chen and Zhang, 2010; Leggett et al., 2011). At the city scale, this proportion has a tenfold variation: from 2% in Shanghai to 19.5% in Chongqing (e.g., Zhu, 2009; Yang et al., 2011, 2012; Zhao et al., 2011). The most common method used to calculate the CH_4 emissions inventory is the Intergovernmental Panel on Climate Change (IPCC) method. This method was originally intended for establishing national estimates. At the urban or regional scale, large uncertainties exist because in many applications local emission factors are not known (e.g., Bun et al., 2010). Moreover, official energy consumption and pollution discharge statistics often have large uncertainties. Therefore, it is important that IPCC-based estimates are verified against other independent methods.

The goal of this study was to evaluate the inventory CH_4 emission rates, using measurements of atmospheric CH_4 and CO_2 concentrations for the city of Nanjing and the Yangtze River Delta (YRD; encompassing the provinces of Jiangsu, Zhejiang, Anhui and the city of Shanghai). The YRD is one of the most developed economic regions in China and has one of the highest concentrations of urbanized land of

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any region in the world, with a total land area of 3.5×10^5 km^2, and an urban fraction of 2.4%. After Shanghai, Nanjing is the second-largest city in the YRD, with an area of 6.6×10^3 km^2. Specifically, in this study we aimed to compare the CH_4:CO_2 emissions ratio derived from the atmospheric method and the emissions ratio determined with the IPCC inventory method.

The atmospheric method assumes that the correlation between the concentrations of two inert and passive scalars in the atmosphere preserves the source emission signals. This method is frequently used to determine local and regional emission rates of air pollutants (e.g., Lee et al., 2001; Widory and Javoy, 2003; Yamada et al., 2005; Tarasova et al., 2006; Greally et al., 2007; Warneke et al., 2007). In recent years, it has been increasingly used in the investigation of GHG cycling in urban airsheds. Hsu et al. (2010) used the correlation between CH_4 and CO to calculate the CH_4 emissions in the airshed of Los Angles, USA. Suntharalingam et al. (2004) used the CO_2:CO concentrations ratio correlations in the Asian outflow from the TRACE-P aircraft campaign to improve the quantification of CO_2 flux in eastern China. Wang et al. (2010) analyzed the observed CO_2:CO concentrations ratio at a rural site near Beijing, China, and compared it to the bottom-up CO_2:CO emissions ratio to investigate the combustion efficiency of urban sources. The research presented in this paper is one of the few studies that uses CO_2 as a tracer to investigate CH_4 emission rates (e.g., Conway and Steele, 1989; Wunch et al., 2009). As shown by Bakwin et al. (1997), Lee et al. (2001), Pataki et al. (2005) and others, the CO_2 mixing ratio can be used as a tracer of wintertime atmospheric transport and mixing at midlatitudes. In this study, the method was refined by dividing the observations into daytime and nighttime periods, before linking them to emission patterns on two different spatial scales (the YRD versus Nanjing).

2. Methods

2.1. *CO_2 and CH_4 observations*

We measured the mixing ratios of CO_2 and CH_4 continuously on the campus of Nanjing University of Information Science and Technology (NUIST; 32°12'N, 118°43'E) in Nanjing from June 2010 to April 2011. This is a suburban site situated 18 km northwest of the city center, surrounded by residential housing. The prevailing wind direction in 2011 was southeasterly. Except for vehicles, there were no significant CO_2 or CH_4 emission sources within 5 km of the site.

The CO_2 and CH_4 mixing ratios were measured with an infrared gas analyzer based on wavelength-scanned cavity ring-down spectroscopy (model G1301, Picarro, Inc, Sunnyvale, California). The measurement precision was better than 50 ppbv for CO_2 and 0.7 ppbv for CH_4 (5 min average). The analyzer was installed on the ninth floor of an office building with a total of 13 floors. Ambient air was drawn in at a height of 25 m above the ground into the analyzer for analysis. At the end of the experiment, the analyzer was calibrated against both a CO_2 and a CH_4 standard (mixing ratios: 390 ppm and 3.05 ppm, balance gas: synthetic air), both of which had a 1% uncertainty in concentration.

2.2. *Inventory estimates*

The International Council for Local Environmental Initiatives have classified carbon accounting into three categories (ICLEI, 2008): the first includes direct emissions from sources within the geographic boundary of investigation; the second comprises indirect emissions associated with electricity, steam and heating generated outside the boundary; while the third category covers other lifecycle emissions excluded from the first and second categories. In this paper, only the direct GHG emissions of the first category are considered.

In both Nanjing and the YRD, the direct sources of CO_2 include both energy consumption sectors (industry, transport, service and household) and non-energy consumption industrial processes. The main sources of CH_4 are rice cultivation, landfill, coal mining, wastewater, livestock, and combustion of fossil fuel and biomass. The CH_4 emissions from rice cultivation were not included in the anthropogenic CH_4 emissions calculated using the atmospheric method, as the emissions in winter are negligible for Nanjing and the YRD. The CH_4 emissions from natural wetland were included. The anthropogenic emissions of CO_2 and CH_4 were calculated using the IPCC methodology by assigning an emission factor for each of the source categories. Energy consumption and other data were obtained from official sources (Energy Statistics Division of the National Bureau of Statistics, 2010; Agricultural Social and Economic Survey Office of the State Statistics Bureau, 2010; National Bureau of Statistics of China, 2010; Nanjing Municipal Bureau of Statistics, 2010).

For the purpose of comparison with the atmospheric method, the total CH_4 emission was divided by the total CO_2 emission in Nanjing and in the YRD as molar ratios. Expressing the results as an emissions ratio has the advantage of canceling out some of the errors in the official statistics on energy consumption.

We used the Monte Carlo method to investigate how errors in the emission factors propagated through the inventory calculations (e.g., Reilly et al., 1987; Winiwarter and Rypdal, 2001; Kumar et al., 2004; Brown et al., 2012). This method involved four steps (e.g., Morgan and Henrion, 1990; Bevington and Robinson, 1992). First, a uniform probability distribution was assigned to each of the emission factors, which were bounded by the limits suggested by the IPCC guidelines. Second, an ensemble of emission estimates was obtained, with combinations of the emission factor values randomly generated according to the probability distribution. Third, a probability distribution function was determined from the ensemble. Fourth, the 2.5% and 97.5% probability values were used as the lower and upper bounds of the estimates of the total CH_4 and CO_2 emissions and their emissions ratio. In the following, the inventory data are reported as the mean of the ensemble generated by the Monte Carlo method, with the 2.5%–97.5% uncertainty range noted.

2.3. *Atmospheric method*

In this study, we used CO_2 as a tracer to constrain the anthropogenic CH_4 emission rate. Because CH_4 and CO_2 have long lifetimes, they can be considered non-reactive passive scalars on the spatial scale of diffusion considered in this study. Following the method of studies conducted in Krakow, Poland (Zimnoch et al., 2010), the South Coast Air Basin in California, USA (Wunch et al., 2009), and Barrow, Alaska, USA (Conway et al., 1993), the slope of the linear correlation of the CH_4 mixing ratio against the CO_2 mixing ratio was taken as being equivalent to their emissions ratio. This method is based on the principle that atmospheric transport and diffusion do not discriminate the passive scalars and therefore the slope of the regression line preserves their source information. The geometric linear regression (Ricker, 1973) was adopted to derive the correlation slope between the CH_4 and CO_2 mixing ratios.

The source area of air concentration in the atmospheric boundary layer is variable from day to night because of changes in air stability. The measurements were divided into midday [1000–1700 local standard time (LST)] and midnight (2300–0500 LST) periods. The midday measurements were assumed to be influenced by anthropogenic emissions in the YRD, while the midnight boundary layer was assumed to be sensitive to local sources in the city of Nanjing. The rationale for this assumption will be discussed in section 3.2.

Even though the measurements were continuous, the correlation analysis was restricted mostly to the winter (December–February), when the biological fluxes were negligible compared to the anthropogenic fluxes. The main driver of seasonal variation in fuel consumption is residential heating. Unlike in northern China, residents in the YRD generally do not heat their homes in the winter. Consequently, while at the national level fuel consumption shows slight variations between the four seasons (winter 29%, spring 25%, summer 22%, autumn 24%; Rotty, 1987), the CO_2 emissions in Nanjing and in the YRD region should have negligible seasonal variations. Therefore, the emission intensity of CO_2 was regarded as a constant all year round.

3. Results and discussion

3.1. *Atmospheric CH_4 and CO_2 mixing ratios*

Nearly a year of observations at the NUIST and Mauna Loa monitoring stations were used to analyze the characteristics of the atmospheric CO_2 and CH_4 (Fig. 1). The measurements at Mauna Loa were regared as the atmospheric background values. Comparision between the two sites allowed assessment of the impact of anthropogenic sources on the atmospheric CO_2 and CH_4 mixing ratios. The annual mean CO_2 and CH_4 mixing ratios at NUIST were, respectively, 11.5 ppm (1 ppm = 1 μmol mol^{-1}) and 0.30 ppm higher than the background values. For CO_2, the largest difference occurred in November (20.99 ppm) and the smallest difference in July (3.77 ppm). In the case of CH_4, the largest difference occurred in July (0.46 ppm) and the smallest difference in January (0.21 ppm).

The seasonal variations of CO_2 and CH_4 at NUIST were controlled by several factors. Due to the prescence of growing vegetation, low CO_2 mixing ratios were observed in the summer and autumn months. In comparison, higher CO_2 concentrations were maintained in winter months. The maximum monthly mean concentration was observed in November for both CO_2 and CH_4, mainly due to field burning of crop straw at that time of the year (e.g., Su and Zhu, 2011; Su et al., 2012). Seasonal variation of CH_4 concentrations is controlled by biological activities and chemical reactions in the atmosphere (e.g., Robbins et al., 1973; Dlugokencky et al., 1994). Although the primary chemical sink of CH_4 has a maximum concentration in the summer, biological emission sources of CH_4 increase too and in fact dominate, resulting in higher concentrations in the summer.

Numerous studies have demonstrated enhanced CO_2 concentration in urban areas. Idso et al. (1998) refer to this phenomenon as the urban CO_2 dome. They found that the maximum mean winter CO_2 mixing ratio at the center of Phoenix, USA, was 619 ppm, or 67% greater than that of the rural background value. George et al. (2007) found that the annual mean difference between the urban and background sites in

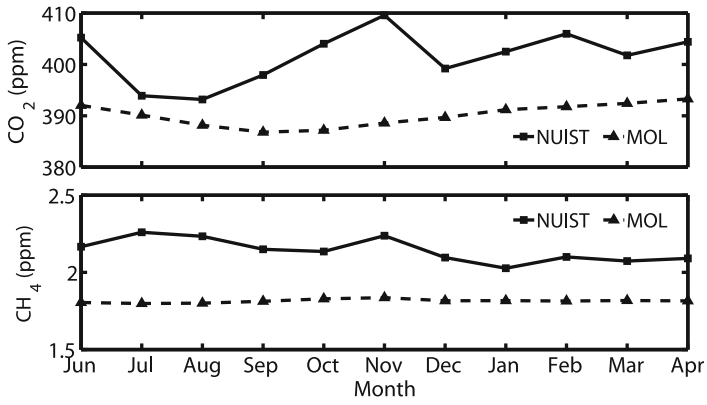

Fig. 1. Monthly mean value of the CO_2 and CH_4 concentrations measured between June 2010 to April 2011 at NUIST and the background Mauna Loa site in Hawaii, USA. (http://www.esrl.noaa.gov/gmd/dv/data/?site=MLO.)

Baltimore, USA, was 66 ppm. While in Nottingham, UK, Berry and Colls (1990) found the difference between urban and rural sites was small (5 ppm) during an 8 month study, due to the fact that both sites were close to power stations.

Significant differences have also been observed between urban and background atmospheric CH_4 mixing ratios. Anthropogenic emissions have been seen to cause higher CH_4 concentrations (by 0.2 ppm, annual mean) in Moscow, Russia, when compared with the background value (Vinogradova et al., 2007). Similarly, the annual mean CH_4 concentration in Krakow, Poland, was found to be 0.5 ppm higher than the regional background level (Kuc et al., 2003). The annual mean CH_4 concentration enhancement in Nanjing was comparable to the values reported in these studies.

3.2. *Relationship between the CH_4 and CO_2 mixing ratio*

Figure 2 shows the relationship between the CH_4 and CO_2 mixing ratios measured in the winter (December–February). In this plot, each data point represents the mean value of a midday (1000–1700 LST) or midnight (2300–0500 LST) period. Regression analysis was used to determine the CH_4:CO_2 emissions ratio. The regression slope for midnight periods is (0.011 ± 0.002) ppm CH_4 : 1 ppm CO_2, where the error bound represents the 95% confidence interval of the parameter estimate, and is about twice that of the midday slope of (0.0043 ± 0.0007) ppm CH_4 : 1 ppm CO_2. These two slopes are significantly different at the confidence level of $p < 0.05$, according to the Student's t-test.

The significantly different slope values imply that a large difference existed in the relative emissions intensity of CH_4 and CO_2 between the Nanjing municipality and the YRD. This interpretation is based on the consideration that the source area for scalar concentrations in the boundary layer is different during the day and at night. During the midday period, the surface measurements are representative of the full mixed layer (e.g., Conway and Steele, 1989; Lee et al., 2001), as the atmospheric boundary layer is well mixed. Consequently, scalar concentrations are indicative of regional scale influences, with a source area size on the order of 100 to 1000 km (e.g., Potosnak et al., 1999; Gloor et al., 2001; Lee et al., 2001; Wunch et al., 2009). To quantify the source area size, we carried out a 2 day backward trajectory analysis following the procedure of Sigler and Lee (2006). One air parcel was released every hour from 1000 to 1700 LST at a height of 500 m above the ground, within the estimates of the midday boundary layer height in winter for the region of Nanjing (e.g., Zhang et al., 2009). This result indicated that the source area was about 3.94×10^5 km^2 (Fig. 3), with the area boundary determined using the end-point probability threshold of 0.1. Of this area, 77% was found to lie on land with the remainder over the oceans. Within the land source area, 73% was in the YRD and the rest in neighboring provinces that have similar GHG emission structures. The likeliest source region, as measured by the potential source contribution functions PSCF > 0.5, almost overlapped with the YRD.

Compared to its daytime counterpart, the nighttime tracer correlation had a much smaller source area. Several other studies have agreed with this conclusion. According to the measurement campaign carried out by Guha and Ghosh (2010) in Bangalore, India, the δ^{13}C of atmospheric CO_2 was much more depleted in the early morning than in the afternoon. This indicated that a greater proportion of the nighttime CO_2 in the city originated locally from fossil fuel combustion whose δ^{13}C signal was lower than the regional background value. Kelliher et al. (2002) used the nighttime tracer method to determine the flux of N_2O from a pasture land with a size of roughly 9 km^2. Pattey et al. (2002) used profile measurements in the nocturnal boundary layer to obtain the CO_2 flux of a boreal forest over several square kilometers. Obrist et al. (2006) carried out a ^{222}Rn and Hg^0 tracer correlation analysis in Basel, Switzerland, and found that the source area of the resulting emissions ratio represented an area of ~ 80 km^2. Similarly, Zimnoch et al. (2010) calculated the nighttime surface fluxes of CO_2 and CH_4, using atmospheric concentrations of CO_2 and CH_4, and found that the source area was about 20 km^2, roughly the size of the city of Krakow.

The winter CH_4:CO_2 correlation slope was different from those found for the other seasons (Fig. 4). Because CO_2 is removed by biological activity in the summer, and CH_4

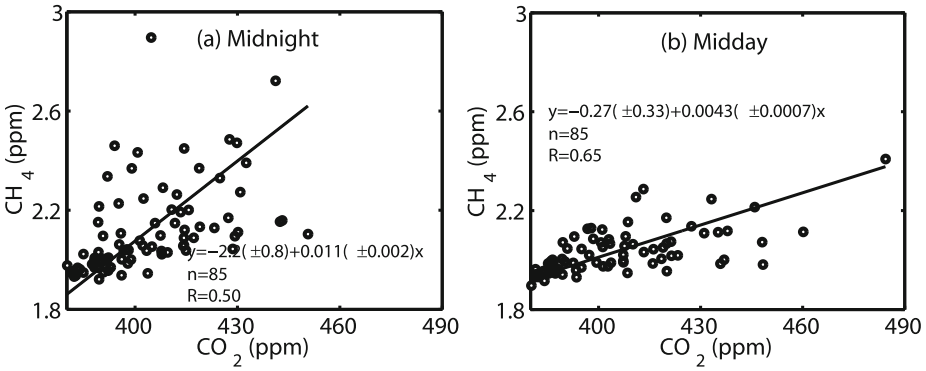

Fig. 2. Scatter plots of winter (December–February) CH_4 and CO_2 concentrations at NUIST. Lines represent the regression equation shown. The 95% confidence bound (numbers in parentheses), the number of observations (n) and the regression coefficient (R) are also shown.

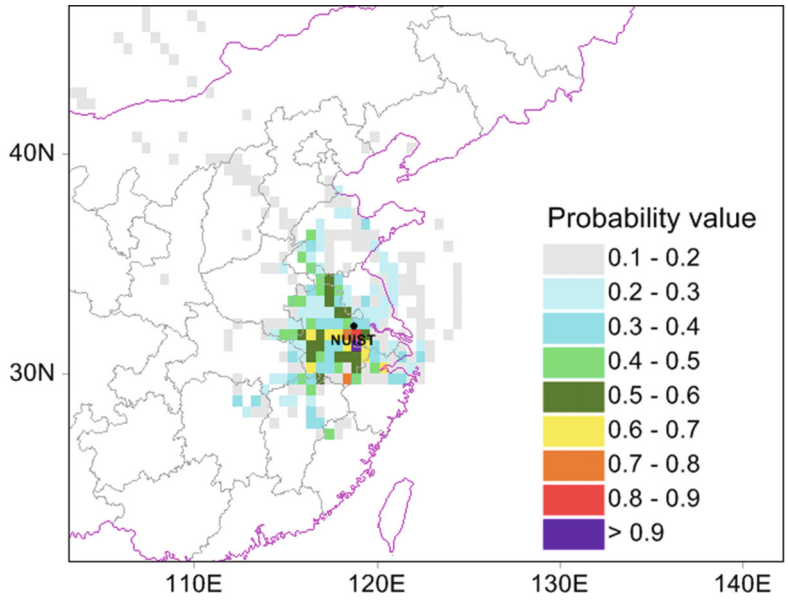

Fig. 3. The potential source contribution function (PSCF) grid values during winter 2010–11. The solid point marks the location of NUIST.

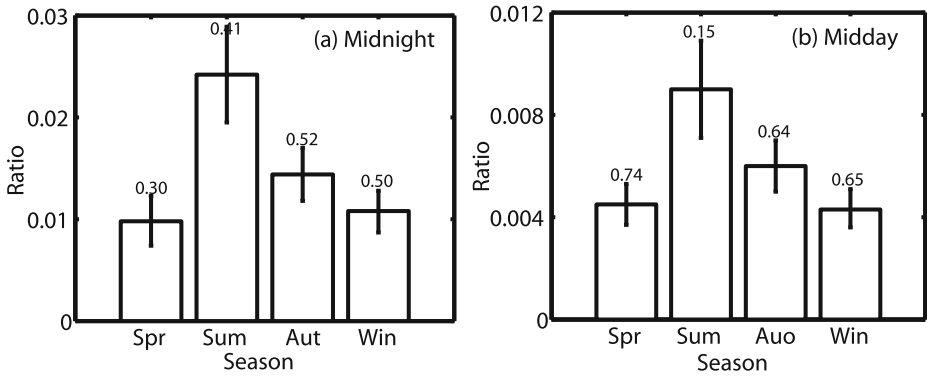

Fig. 4. (a) Midnight and (b) midday correlation slopes (with the 95% confidence interval indicated) for the four seasons (Spr: Spring; Sum: Summer; Aut: Autumn; Win: Winter). The value above each bar is the linear correlation coefficient.

is emitted by rice paddies, the midday CH_4:CO_2 correlation had a slope value [(0.009 ± 0.002) ppm CH_4 : 1 ppm CO_2] in the summer (June–August) that was higher than that in the spring [March–May; (0.0045 ± 0.0008) ppm CH_4 : 1 ppm CO_2], autumn [September–November; (0.006 ± 0.001) ppm CH_4 : 1 ppm CO_2] and winter (December–February; (0.0043 ± 0.0007) ppm CH_4 : 1 ppm CO_2). The midnight slope was (0.0098 ± 0.0024), (0.024 ± 0.005), (0.014 ± 0.003) and (0.011 ± 0.002) ppm CH_4 : 1 ppm CO_2 in the spring, summer, autumn and winter, respectively.

The CH_4:CO_2 flux ratio for Nanjing, as determined using nighttime measurements in the winter [(0.011 ± 0.002) ppm CH_4 : 1 ppm CO_2; Fig. 2], appears high compared to some results in the published literature. This ratio was (0.0028 ± 0.0003) CH_4 : 1 ppm CO_2 in Florence, Italy, from late winter to late spring according to the eddy covariance measurements carried out by Gioli et al. (2012). The simultaneous measurements of CO_2 and CH_4 concentrations made by Conway and Steele (1989) revealed a flux ratio of (0.0076 ± 0.0007) ppm CH_4 : 1 ppm CO_2 for Boulder, USA. Mays et al. (2009) reported a ratio of (0.0089 ± 0.0079) ppm CH_4 : 1 ppm CO_2 for Indianapolis, USA, based on aircraft eddy covariance measurements in the winter to early spring. The tracer correlation analysis by Wunch et al. (2009) yielded a flux ratio of (0.0078 ± 0.0008) ppm CH_4 : 1 ppm CO_2 for the Los Angeles air basin, USA. There are two possible reasons why the CH_4:CO_2 flux ratio for Nanjing was found to be larger than those in the European and American cities mentioned above. First, the proportion of the sources with high CH_4:CO_2 flux ratios, such as landfill and wastewater, is larger in Nanjing (Table 2). Second, the management standards for landfills and wastewater in Nanjing are weak in comparison to those of the cities mentioned above. On the other hand, Zimnoch et al. (2010) reported a flux ratio [(0.011 ± 0.0036) ppm CH_4 : 1 ppm CO_2] for Krakow, Poland, similar to this study.

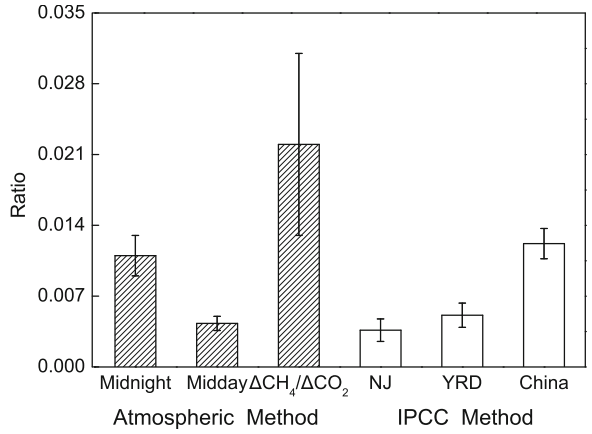

Fig. 5. CH_4:CO_2 emissions ratio estimated with the two different methods. Error bars represent the 95% confidence bound on the midday and midnight correlation slopes, the 1% uncertainty on the concentration measurement for ΔCH_4:ΔCO_2, and the 95% confidence interval calculated with the Monte Carlo method for the IPCC estimates (uncertainty associated with emission factors).

The CH_4:CO_2 correlation pattern differed from those reported for other chemical species. Wang et al. (2010) found that the slope of the CO_2:CO correlation measured near Beijing, China, was similar in both the summer and the winter, although the slope showed diurnal variations in the summer and remained nearly constant throughout the diurnal cycle in the winter. Hsu et al. (2010) studied CH_4 emissions in southern California, USA, and showed that the CH_4:CO correlation slope was a conserved property independent of time of the day or season, suggesting that combustion was the dominant emission source for both species. In this study, the CH_4:CO_2 correlation slope varied seasonally, due to changes in the biological CO_2 and CH_4 fluxes, and diurnally, due to changes in the size of source area.

The CH_4:CO_2 correlation slope can also be compared with the concentration enhancement ratio ΔCH_4:ΔCO_2. Greenberg et al. (1984) and Cofer et al. (1988) have used this ratio to approximate the CH_4:CO_2 emissions ratio of biomass burning events. The flux enhancement was calculated in this study as the difference in the winter concentrations in Nanjing and Mauna Loa. This method gives a flux ratio of (0.022 ± 0.009) ppm CH_4 : 1 ppm CO_2, with the error bound representing a 1% uncertainty on the concentration measurements. The value of ΔCH_4:ΔCO_2 was much higher than the CH_4:CO_2 slope derived from the midday and midnight measurements and the emissions ratio derived from the inventory estimates (Fig. 5). It appears that this enhancement ratio is not suitable for assessing urban GHG emissions.

3.3. *CH_4 and CO_2 emissions based on the IPCC method*

Table 1 and table 2 summarize the anthropogenic CO_2 and CH_4 emissions calculated using the IPCC inventory method. There were large differences in the relative contributions of the source categories of CH_4 between Nanjing and the YRD. Rice cultivation, landfill and wastewater were the main sources of CH_4 in Nanjing, while fugitive emissions from coal mining played the most important role in the YRD. Compared to CH_4, there were smaller relative differences of the source categories of CO_2 between Nanjing and the YRD. The CO_2 emissions were mainly from the industrial burning of fossil fuels and other processes both for Nanjing and the YRD. Nanjing has advanced chemical and metal industries, and the CO_2 from industrial processes accounted for 42% of its total anthropogenic CO_2 emissions, compared to 21% for the same category in the YRD.

The inventory estimates presented in this paper are in broad agreement with those published by other researchers. The estimate of the CO_2 emission of Nanjing in 2009 was 9% to 14% higher than that in 2007–08 (Bi et al., 2011; Wang et al., 2012), and is approximately equal to the direct emission in 2009 (6.71×10^{10} kg) given by Xu (2011). For the YRD region, the emission of CO_2 increased by 26% when compared to that (1.22×10^{12} kg) in 2007 (Liu et al., 2010).

The CH_4 and CO_2 emissions of China were also calculated using the same methodology as for Nanjing and the YRD. Excluding rice cultivation, the national CO_2 and CH_4 emissions were $7.41 \pm 0.45 \times 10^{12}$ kg and $3.29 \pm 0.32 \times 10^{10}$ kg, respectively. The CO_2 emission in 2009 increased by 12% to 14%, when compared with the CO_2 emissions in 2007 (CDIAC, 2010; Chen and Zhang, 2010), and is 8% and 2% higher than that for the year 2009 estimated by IEA (2011) and Guan et al. (2012), respectively. Excluding the rice field emissions in the growing season, the CH_4 emission (3.12×10^{10} kg) given by Zhang and Chen (2010) is equal to the estimate presented here.

3.4. *Comparison between the two methods*

Figure 5 shows the comparison of the emissions ratio derived from the atmospheric data with the inventory emission ratios at the three different scales (Nanjing, the YRD, China) calculated with the IPCC methodology. Using the IPCC inventory methodology, there was a gradually increasing trend with scale in the CH_4:CO_2 emissions ratio. The ratio was lowest for Nanjing [(0.0036 ± 0.0011) ppm CH_4 : 1 ppm CO_2], intermediate for the YRD [(0.0051 ± 0.0012) ppm CH_4 : 1 ppm CO_2] and highest for the whole of China [(0.012 ± 0.0015) ppm CH_4 : 1 ppm CO_2]. By comparison, China's CH_4:CO_2 emissions ratio was 29% lower than that of the USA (EPA, 2011), mostly due to a lower proportion of natural gas in China's fuel mix. The disparity among the three scales is associated with differences in source type and intensity.

The atmospheric data reveal an opposite trend. The midnight data, which correspond to a source area size similar to the scale of Nanjing, yielded an emissions ratio of (0.011 ± 0.002) ppm CH_4 : 1 ppm CO_2, whereas the midday data, having a source in the order of the size of the YRD, produced an emissions ratio of (0.0043 ± 0.0007) ppm CH_4 : 1 ppm CO_2. The midday estimate was within 20% of the inventory estimate for the YRD, but the midnight estimate was 200% greater than the inventory estimate for Nanjing.

Table 1. CO_2 emissions estimated with the IPCC inventory method for Nanjing and the Yangtze River Delta in 2009 (units: kg). The uncertainty range represents the 95% confidence interval.

	Nanjing		YRD	
	Emission ($\times 10^9$ kg)	Percent of total (%)	Emission ($\times 10^{11}$ kg)	Percent of total (%)
Industrial energy Consumption	30.18 (±7%)	45.4	10.81 (±5%)	70.4
Industrial processes	28.01 (±20%)	42.1	3.26 (±16%)	21.2
Transportation	7.82 (±2%)	11.8	0.94 (±2%)	6.1
Household	0.48 (±3%)	0.9	0.34 (±3%)	2.2
Commercial	—	—	—	—
Total	66.49 (±8%)	100	15.35 (±10%)	100

Table 2. CH_4 emissions estimated with the IPCC inventory method for Nanjing and the Yangtze River Delta in 2009 (units: kg). The uncertainty range represents the 95% confidence interval.

	Nanjing		YRD	
	Emission ($\times 10^7$ kg)	Percent of total (%)	Emission ($\times 10^8$ kg)	Percent of total (%)
Landfill	6.16 (±32%)	40.8	5.71 (±31%)	10.8
Wastewater	1.40 (±30%)	9.3	1.76 (±30%)	3.3
Livestock	0.51 (±29%)	3.4	3.70 (±30%)	7.0
Fuel and biomass	0.52 (±33%)	3.4	3.46 (±37%)	6.6
Coal mining	—	—	13.89 (±20%)	26.4
Rice cultivation	6.22 (±14%)	41.2	22.20 (±11%)	42.1
Natural wetland	0.27 (±25%)	1.9	1.98 (±20%)	3.8
Anthropogenic total[a]	8.59 (±29%)	56.9	28.52 (±22%)	54.1
Total	15.08 (±20%)	100	52.70 (±15%)	100

[a]Anthropogenic total consists of the CH_4 emissions from landfill, wastewater, livestock, coal mining, fuel and biomass. CH_4 emissions from rice cultivation were not included in the anthropogenic total as the analysis was limited to wintertime measurements.

Several possible reasons may explain the large difference between the top-down atmospheric and the bottom-up inventory estimate for Nanjing:

(1) As landfill was the most important CH_4 source in Nanjing, the uncertainties in this source category could have had a large impact on the total emission estimate. There are two sources of uncertainty. First, the default IPCC emission factor may not be appropriate for Nanjing. Toward that end, the models of Gardner and Probert (1993) and Marticorena et al. (1993) were also used to calculate the landfill CH_4 emission. These two models are also dynamic models but, unlike the IPCC method, they either separate the garbage input into different age layers or biomass groups of different decay rates. The CH_4 emission calculated with the Gardner and Probert model (6.22×10^7 kg) was nearly equal to the inventory estimate, and that with the Marticorena model (5.74×10^7 kg) was only 7% lower than the inventory estimate. Second, the data on landfills from official sources may be inaccurate. Using remote sensing image analysis, Dai et al. (2012) found that the area actually covered by landfill (6.35×10^5 m^2) is larger than the area (2.85×10^5 m^2) reported to be so by the government source for Nanjing. This finding was confirmed through site visits to the predicted landfills. Using the area measured by Dai et al. (2012) as a correction factor, the inventory CH_4:CO_2 emissions ratio would increase to (0.0068 ± 0.002) ppm CH_4 : 1 ppm CO_2. A further increase is possible because some unreported landfills may have evaded remote sensing detection, owing to the fact that they are smaller than the resolution (30 m) of the Landsat TM image used by Dai et al. (2012), and because these unmanaged landfills may be emitting CH_4 at rates much higher than the managed landfills.

(2) The source area size in the nocturnal boundary layer is another source of uncertainty. Estimating the nocturnal concentration footprint and source area remains challenging (Sogachev and Leclerc, 2011). In this paper, as an order of magnitude estimate, the source area of the nocturnal concentration was assumed to be about the size of the city of Nanjing, and the value of CH_4:CO_2 was assumed to be influenced by the local sources in Nanjing. However, as the administrative region of Nanjing has a larger north–south than east–west span, the nocturnal concentration source area and the geographic area of Nanjing may not overlap precisely. As a result, the CH_4:CO_2 value may have been influenced by the anthropogenic emissions from the neighboring province, Anhui, which has a CH_4:CO_2 flux ratio of 0.015 ppm CH_4 : 1 ppm CO_2—significantly higher than that of Nanjing. As the anthropogenic sources of CH_4 and CO_2 are distributed unevenly, and because the CH_4:CO_2 flux ratio may well vary significantly on a local scale, detailed statistics for the cities and counties around Nanjing are needed in order to further improve the comparison of the two methodologies.

(3) The atmospheric concentrations of CO_2 and CH_4 were measured in 2010 and 2011, while the statistical data for the

IPCC estimates were for 2009. However, uncertainty arising from this mismatch is negligible, as according to the statistical data for Nanjing, the interannual variations in the sources of CO_2 and CH_4 were very small. For example, the coal consumption change from 2005 to 2009 was less than 3%, and the change in garbage volume during this period was less than 2%.

(4) The atmospheric emissions ratio may have been inflated by the CH_4 emissions from natural wetlands (total area: 4.4×10^2 km^2) and rice paddies (total area: 9.7×10^2 km^2) in the Nanjing municipality. According to Chen et al. (2007), the emissions of CH_4 from winter wetlands (1.56×10^5 kg) is negligible when compared to anthropogenic emissions (Table 2). Using the CH_4 flux intensity observed in the rice paddies in the YRD in the winter (0.18–0.65mg m^{-2} h^{-1}; Huang et al., 2001; Zhang et al., 2012), it was estimated that the total emission from the rice paddies in Nanjing was 3.77×10^5 to 1.36×10^6 kg, which is also negligible when compared to the anthropogenic emissions (Table 2).

(5) CH_4 can escape from leaky natural gas distribution networks. Kuc et al. (2003) used a carbon isotope tracer method to assess CH_4 sources, and found that network leakage is an important source of CH_4 in Krakow, Poland. Zimnoch et al. (2010) also found a strong source of CH_4 in Krakow, Poland, linked to the leakage of natural gas from the city's network. In the city center of Florence, the gas network leakage accounts for 86% of the observed CH_4 flux (Gioli et al., 2012). While in the USA, the natural gas system emissions accounted for nearly 30% of the total CH_4 emission in 2009 (EPA, 2011). However, the leakage problem was probably insignificant in Nanjing, because CH_4 emission from natural gas consumption was less than 0.1% of the total anthropogenic CH_4 emission. To put it in another way, if the disparity between the atmospheric and the inventory emissions ratio were to be attributed solely to distribution line leakage, the amount leaked would be huge (11.5% of the supplied CH_4).

4. Conclusions

In this study, the CH_4:CO_2 emissions ratios calculated from atmospheric concentration measurements and from the IPCC inventory method were compared for the city of Nanjing and for the YRD. The midday and midnight atmospheric measurement data revealed emissions ratios of (0.0043 ± 0.0007) and (0.011 ± 0.002) ppm CH_4 : 1 ppm CO_2, corresponding to source areas comparable to the size of the YRD and the city of Nanjing, respectively. The midday CH_4:CO_2 emissions ratio was approximately 20% smaller than that calculated with the IPCC method for the YRD, but the midnight value was nearly 200% greater than the inventory estimate for Nanjing. The most likely reason for this discrepancy was that a large number of unmanaged landfills were omitted from the official statistics. Finally, it is suggested that the atmospheric tracer correlation method provides a useful approach to constrain the CH_4 emission rate at the municipality scale where the IPCC method is uncertain.

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