

Assessing surface fluxes of CO₂ and CH₄ in urban environment: a reconnaissance study in Krakow, Southern Poland

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ABSTRACT

Regular observations of atmospheric mixing ratios of CO₂ and CH₄, combined with sodar measurements of the mixing layer height in the lower troposphere were used to assess night-time surface fluxes of these gases in the urban environment (Krakow, southern Poland). The measurements performed over the 4-yr period (May 2005–May 2009) revealed a distinct seasonality of surface night-time fluxes of CO₂, with the minimum of ca. 2 mmol m^{−2} h^{−1} during winter months and the maximum of ca. 20 mmol m^{−2} h^{−1} observed during summer months. The observed seasonality was induced by the biospheric component (soil respiration) which dominates the measured surface CO₂ fluxes during summer months. The surface fluxes of CH₄ scatter between ca. 50 and 200 μmol m^{−2} h^{−1}, without clear seasonal trend. Significant flux of CH₄ into the atmosphere (mean value over the whole observation period equal to ca. 97 μmol m^{−2} h^{−1}), indicates a presence of relatively strong methane source on the investigated area. This source is linked to methane leakages from the city gas distribution network.

1. Introduction

Quantification of surface fluxes of CO₂ and CH₄ plays a key role in assessing atmospheric budgets of these gases over continental areas. The preferred approach is a direct flux measurement on the landscape scale via eddy covariance method (Denmead, 2008). However, direct measurements of surface emissions of CO₂ and CH₄ into the atmosphere in densely populated areas using this method are complicated mostly due to large heterogeneity of urban land cover (Grimmond et al., 2002; Jarvi et al., 2009). The commonly used methodology of assessing urban fluxes of CO₂ relies on statistics of spatial and temporal distribution of fuel consumption. Reliability of this method strongly depends on the completeness and overall quality of the relevant statistical data. In order to validate the inventory data, independent methods based on atmospheric measurements have been suggested recently (Gibert et al., 2007; Casso-Torralba et al., 2008; van der Laan et al., 2009; Worthy et al., 2009).

This work presents an attempt to quantify surface fluxes of CO₂ and CH₄ in urban environment by combining the mea-

surements of atmospheric mixing ratios of these gases with measurements of the mixing layer height performed with the aid of a sodar system. The study was performed in Krakow, southern Poland (50.067°N, 19.913°E, 220 m a.s.l.), between May 2005 and May 2009. Krakow is a large urban agglomeration with about 1 million inhabitants, rapidly growing car traffic and significant industrial activities. Coal, gas and oil consumed for communal and transport purposes generate the main flux of anthropogenic carbon dioxide within the region. Another source of anthropogenic CO₂ emissions in the area are industrial plants (large metallurgic factory and three power plants localised within 50-km radius from the centre of the city). The growth in the total number of cars registered in the Krakow region, as reported by the Polish Central Statistical Office for the period from 2006 to 2008, amounts to ca. 30%. Krakow has well-developed city gas network (in parts more than 100 years old) supplying most of households in the city and its surroundings with natural gas.

2. Methodology

The presented method of assessing night-time surface fluxes of CO₂ and CH₄ is based on parallel measurements of the mixing height within the planetary boundary layer (PBL) and the

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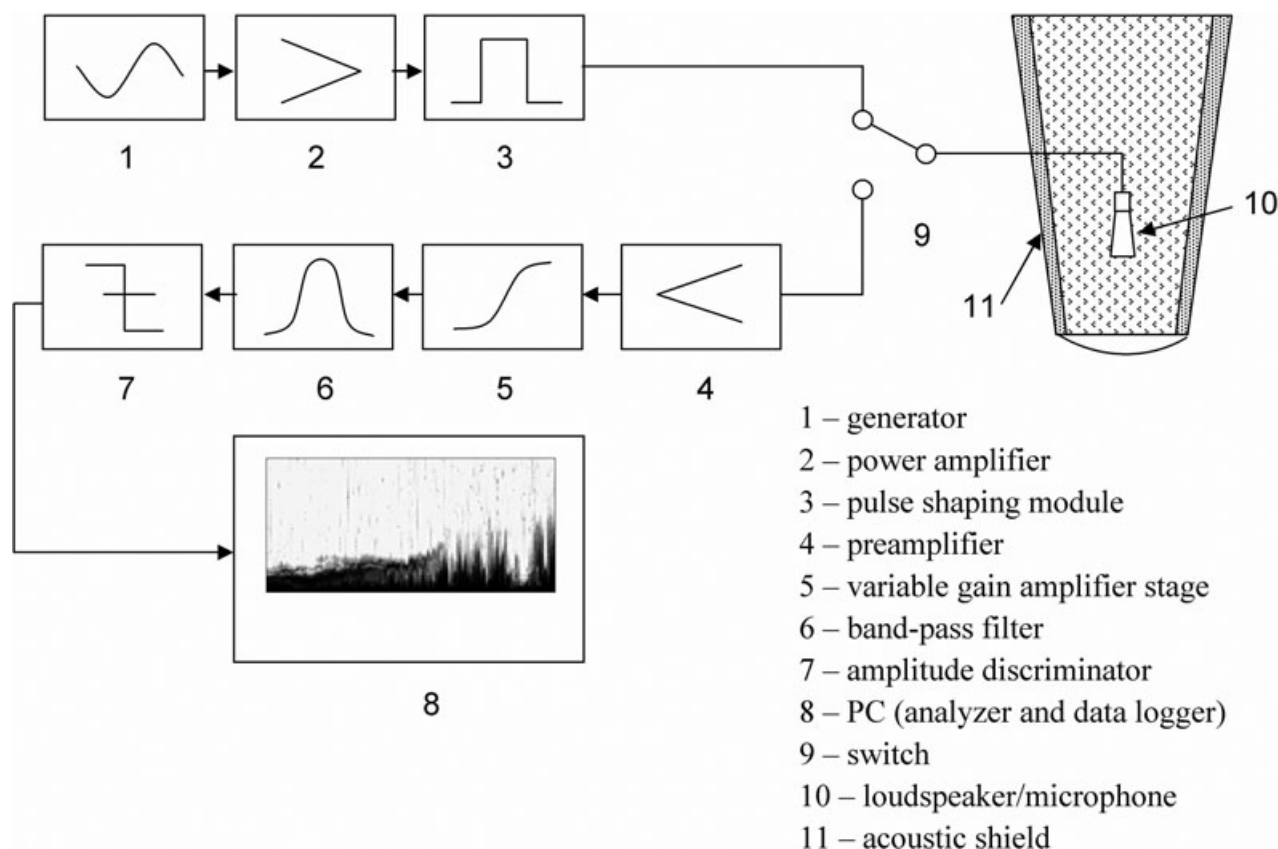


Fig. 1. Schematic diagram of the sodar system used in the study.

atmospheric mixing ratios of these gases measured at certain elevation above the local ground.

The mixing height within the PBL was monitored using VHS sodar (Version 3) built by the Krakow Branch of the Institute of Meteorology and Water Management and operated in Krakow since 1994. The block diagram of the sodar system is presented in Fig. 1. The transmitter part of the sodar consists of 1.6 kHz acoustic generator, power amplifier and pulse shaping module forming a sharp, 60-ms wide pulse emitted by the loudspeaker every 6 s. The system is switched to a receiver mode after emitting the pulse and acoustic backscatter signal returning to the antenna is registered by loudspeaker working in this mode as microphone. Then, the signal is amplified, noise is removed and signal is recorded. The power of the emitted pulse is equal 800 W. The pulse is strong enough to reach the elevation of ca. 1000 m. Detailed description of the sodar system can be found in Netzel et al. (1995).

The sodar system was located inside a park complex, between the city centre and the industrial district, at the distance of ca. 6 km east from the location where GC measurements of atmospheric mixing ratios of CO₂ and CH₄ were performed. To examine possible influence of the distance between the PBL height and the CO₂ and CH₄ mixing ratio measurement sites on the calculated flux values, two measurement campaigns were

performed. During the first campaign (August 2008) the CO₂ mixing ratio measurements were performed at the sodar location point. Then, in March 2009, the sodar system was moved to the location of the GC system and run till the end of May 2009. During both campaigns neither significant change in the mixing layer height variability nor the range of calculated fluxes were observed.

Sodar records were analysed manually. Stability of the surface layer was identified through unique features of sodar echoes and its range was defined by determining the height of the observed structures at the upper level where mixing processes still exist (Piringer and Joffre, 2005). Example of typical diurnal record of vertical sodar echoes is presented in Fig. 2.

The ground-based inversion is mainly observed during night-time. Usually, it develops after sunset and disappears ca. 1.5–2 h after sunrise. The analysis of the sodar data from 1994 to 2008 showed that the ground-based inversion in Krakow is almost always observed between 8 p.m. and 3 a.m. UTC regardless of seasons. Convection is active usually during day-time, although there are periods, especially during winter, when convection is absent during entire 24-h period.

The monthly mean values of the mixing height during the convection periods are strongly connected with season, reaching values between 200 and 800 m during the winter and summer

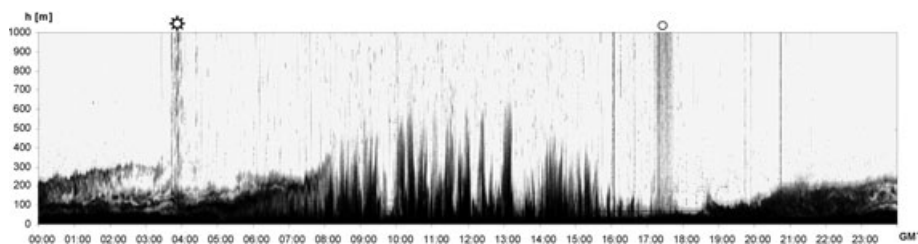


Fig. 2. An example of the acoustic backscatter of the air obtained with the VHS sodar system for 24-h period (Krakow – August 31, 2008) representing typical diurnal variability of the mixing layer height. The extent of vertical axis is from 0 to 1000 m above the local ground. The symbols on top indicate sunrise and sunset.

period, respectively. Such seasonal dependence is not observed in stable atmosphere, when mean value of the mixing height equals 250 ± 50 m, regardless of the season. The quality of the VHS sodar system used in this work and correctness of the manual analysis were checked during two experiments organised in the framework of COST-715 in August 2002 and in June 2003, using tethered balloon equipped with appropriate instrumentation for measurement of vertical profiles of wind speed, humidity and temperature (Piringer and Joffre, 2005). For 61 balloon soundings the depth of the ground-based inversion derived from the sodar data and from potential temperature profiles was compared. The mean difference between the results of both methods was only 0.7 ± 3.5 m, with the correlation coefficient r equal 0.94.

The measurements of atmospheric mixing ratios of CO₂ and CH₄ were performed inside the university campus, on the western side of the city centre, surrounded by recreation area and sport complex. Strong anthropogenic sources of CO₂ and CH₄

were absent in immediate vicinity of the measurement site, thus no filtering procedure has been applied to the mixing ratio record. The air inlet of CO₂ was installed 6 m above the roof level of the University building, ca. 20 m above the local ground level. The meteorological parameters were recorded close to the air inlet (automatic weather station). The record of available data on PBL height and CO₂ and CH₄ mixing ratios, covering the period from May 2005 to May 2009, is presented in Fig. 3.

The measurements of CO₂ and CH₄ mixing ratios were performed with the aid of automatic GC system (HP6890) equipped with Ni catalyst and FID detector. Water vapour was removed from the air stream using cryogenic trap cooled down to -70°C . After drying, the air was flushed through the stream selection valve and sample loop of the GC system. CO₂ and CH₄ were separated from the sample air using a 2 m/1 mm Shin Carbon ST column working in 60°C and analyzed with the FID detector. Each measurement cycle consisting of single analysis of air

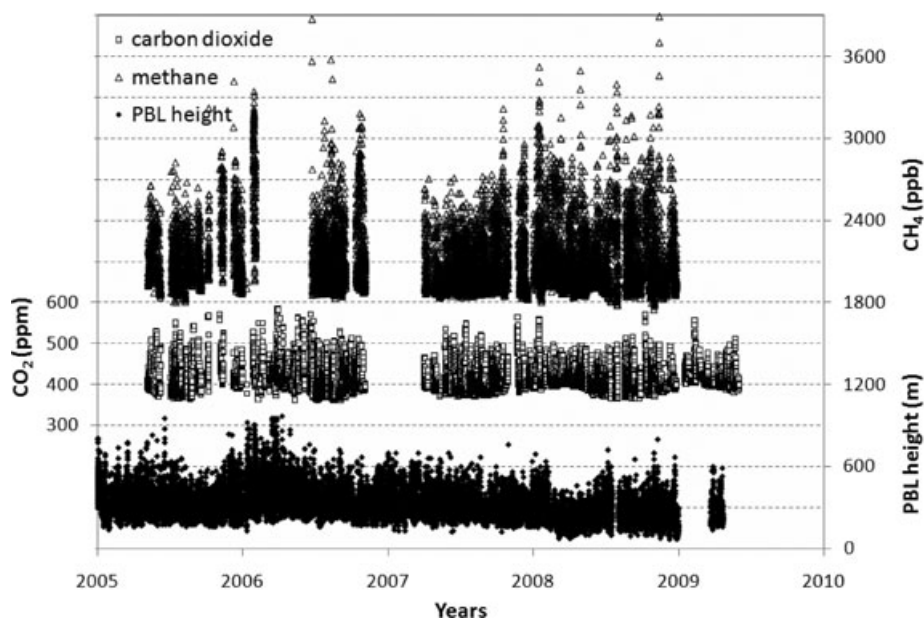


Fig. 3. Time series of PBL height and CO₂ and CH₄ mixing ratios recorded in Krakow during the period January 2005–May 2009, available for calculations of surface fluxes of these gases.

and working standard lasted between 16 and 35 min, depending on the system configuration which was modified several times during the discussed period (May 2005–May 2009). The reproducibility of single analysis calculated as a standard deviation of single measurement of the standard was equal approximately ± 0.1 ppm for CO_2 and ± 2 ppb for methane. The measured mixing ratios of CO_2 and CH_4 were expressed in NOAA04 scale and calibrated against set of NOAA tanks.

Atmospheric concentrations of trace gases within the PBL are controlled to a large extent by intensity of vertical mixing processes (Emeis, 2008). During the day, when strong thermal convection prevails, CO_2 and CH_4 emitted from the surface are diluted in a large volume of well-mixed PBL. Therefore, relatively low concentrations of these gases, close to the background values typical for the free troposphere, can be observed during the day. In late afternoon, after the sunset, the vertical temperature profile in the atmosphere is changing, largely reducing the vertical mixing. During the periods of low wind speed, when advection is small, this leads to accumulation of trace gases emitted from the surface and their concentrations within the PBL start to increase. An example of the night-time increase of CO_2 concentration associated with the reduction of the mixing layer height and the wind speed is presented in Fig. 4. While for nights between 19 and 21 of August there is a clear dependence between the mean mixing layer height and the concentration of CO_2 , for the night from 24 to 25 of August the increase of CO_2 is almost negligible, apparently due to elevated wind speed.

The rate of increase of the mean concentration of the given trace gas within the mixing layer is controlled by the actual height of the mixing layer and the net flux of this gas to this layer. The mass balance of the given trace gas within the PBL

can be described by the following relationship:

$$h \frac{d \langle c \rangle}{dt} = F_{\text{in}} - F_{\text{out}}, \quad (1)$$

where h is the actual height of the PBL, $\langle c \rangle$ is the mean concentration of the given trace gas within the PBL, t is the time, F_{in} is the total flux of the given trace gas into the PBL associated with its sources and with horizontal and vertical transport and F_{out} is the total flux of the given trace gas out of the PBL associated with its sinks (e.g. assimilation of CO_2 during photosynthesis, oxidation of methane, horizontal and vertical transport).

During the night, vertical mixing between the PLB and the free troposphere is usually very small. Also major processes removing CO_2 (assimilation) and CH_4 (oxydation) are negligible during late evening and night. Thus, for night-time, one can assume $F_{\text{out}} = 0$ and eq. (1) is simplified to

$$h \frac{d \langle c \rangle}{dt} = F_{\text{in}}. \quad (2)$$

During stable atmospheric conditions, with low wind speeds, a distinct vertical gradient of CO_2 and CH_4 concentration is usually established within the PBL. As the measurements of mixing ratios are performed close to the surface, a correction factor relating the average increase of the concentration within the PBL ($d \langle c \rangle / dt$) to the increase of the concentration observed close to the ground level (ca. 20 m) is required. This correction factor was calculated using an analytical dispersion model (Sharan and Gopalakrishnan, 2003). The calculation was performed for a distributed surface source covering an area of 1 km^2 , approximated by 10 000 point sources homogeneously distributed over the emission area. The horizontal wind speed was set to 1 m s^{-1} . The correction factor was calculated as the ratio of CO_2 (CH_4)

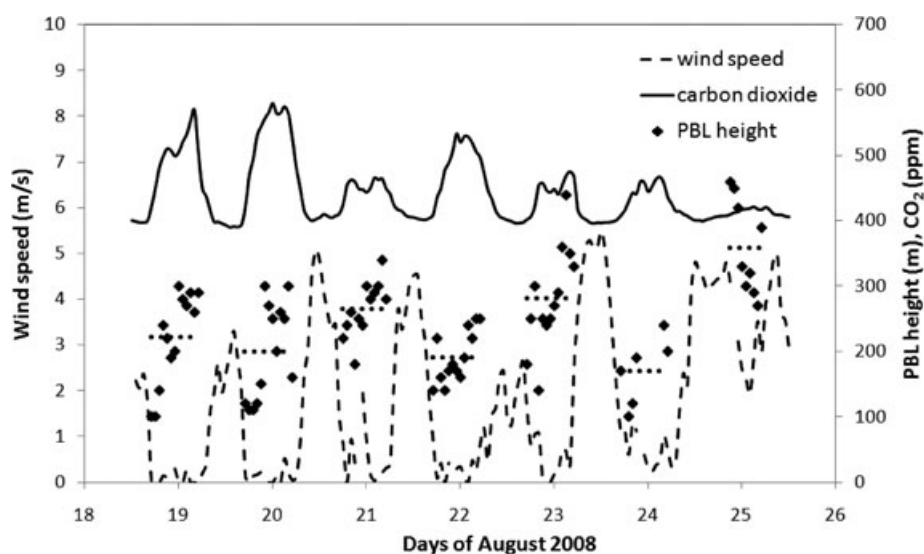


Fig. 4. Example of diurnal CO_2 mixing ratio, PBL height and horizontal wind speed variations recorded in Krakow during the period: 18–25 August, 2008. Horizontal dotted lines represent night-time mean values of PBL height.

concentration at 20 m above the surface, divided by the mean concentration for first 500 m of the atmosphere. The value of the correction factor derived for stable-stratified PBL and the aerodynamic surface roughness of a big city (one to a few metres) was equal 6.5. After applying the correction factor k , the final formula for calculating surface fluxes of CO₂ and CH₄ reads as follows:

$$\frac{h}{k} \frac{dc_{\text{surf}}}{dt} = F_{\text{in}}, \quad (3)$$

where k is the correction factor and c_{surf} is the concentration of CO₂ (CH₄) at the measurement height.

The surface fluxes of CO₂ and CH₄ were calculated using eq. (3) for late evening and night hours, when an increase of the measured mixing ratios of these gases was observed. The calculations were performed under the following assumptions: (i) the CO₂ and CH₄ emitted into the atmosphere during the periods for which calculations were performed, was accumulating within the PBL (no transport between the PBL and the free troposphere), (ii) only the nights with wind speed below 1 m s⁻¹ were chosen to fulfil the closed-system assumption (no significant advection adding or removing trace gases from the atmosphere below PBL, within the city), (iii) major removal processes of CO₂ and CH₄ are not active at that time and (iv) the mean concentration of CO₂ and CH₄ within the PBL is derived from vertical concentration profiles calculated using analytical dispersion model (Sharan and Gopalakrishanan, 2003).

3. Results and discussion

The calculations of surface night-time fluxes of CO₂ and CH₄ were performed for the period from May 2005 to May 2009, for nights with wind speed lower than 1 m s⁻¹. The upper limit of 1 m s⁻¹ for the wind speed and a typical duration of the night-time inversion equal 6 h leads to the estimated characteristic length of the footprint area equal ca. 20 km which is comparable with the extent of Krakow municipal area, making the flux estimates representative for the city scale. The growth rate of the concentration of CO₂ and CH₄ was calculated for periods starting typically at sunset and ending 6 h later, using a linear regression procedure. The correction factor derived from the dispersion model was applied to the measured mixing ratios. The average PBL height was calculated from the sodar data for the each analysed night-time period.

Extensive statistical evaluation of individual readings of the mixing layer height taken by the sodar and the mixing ratios of CO₂ and CH₄ measured close to the ground did not revealed any significant correlation between these two variables within single night-time periods. This is not surprising taking into account a very dynamic nature of the evolution of the mixing height during night and the fact the concentrations of CO₂ and CH₄ were measured close to the ground while the mixing layer was

developing on the opposite side, close to the boundary with the stratified atmosphere. Therefore, the calculations of surface fluxes of CO₂ and CH₄ were based on mean night-time values of the mixing height and the measured rate of build-up of these gases during the inversion period.

The night-time surface fluxes of CO₂ and CH₄ obtained with the procedure outlined above were subject to two-step data selection scheme. In the first step, only values representing the nights with the linear regression coefficient calculated for the increase of CO₂ and CH₄ concentration $R^2 > 0.8$ were selected. In the second step, the values of surface CO₂ and CH₄ fluxes representing the nights with standard deviation of the mean PBL height greater than 30 m were removed from the remaining dataset. Subsequently, the monthly mean values of the CO₂ and CH₄ surface fluxes were calculated. For some months, the adopted data selection procedure significantly reduced the number of available data, leading substantial increase of the uncertainty of the monthly mean value. The average number of night data used for calculating the monthly mean was 7 per month, varying between 2 and 20. Figures 5 and 6 present mean monthly fluxes of CO₂ and CH₄, respectively, calculated with the aid of the procedure outlined above.

The calculated mean monthly surface fluxes of CO₂ (Fig. 5) reveal distinct seasonality, with a minimum of ca 2 mmol m⁻² h⁻¹ occurring during winter (December to March) and a maximum of ca. 20 mmol m⁻² h⁻¹ in summer (July and August). This strong seasonality is most probably induced by seasonally modulated biospheric component, originating from soil respiration. The relative uncertainty of the calculated monthly mean CO₂ fluxes varies between ca. 1 and 87%.

The measured surface fluxes of CO₂ during summer were comparable with the soil respiration fluxes obtained from regular observations carried out in Southern Poland region between 1998 and 2000 using the enclosure method. The reported monthly mean respiration fluxes of CO₂ for summer months (MJJA) for three typical areas (grassland, mixed forest and agricultural field) were equal 11.5 ± 0.2, 19.8 ± 0.4 and 13.4 ± 0.2 mmol m⁻² h⁻¹, respectively (Gorczyca et al., 2003). The mean CO₂ flux representing summer months (MJJA) calculated using eq. (3) is equal 15.6 ± 0.9 mmol m⁻² h⁻¹. It lies within the range of respiration CO₂ fluxes quoted above. This points to a dominant role of the biospheric component in the derived night-time fluxes of CO₂ in the investigated urban setting, at least during the summer months. Similar conclusion was reached in the analysis based on measurements of isotopic composition of atmospheric CO₂ in Krakow (Zimnoch et al., 2004). The calculations based on isotopic mass balance revealed that a dominant contributor to the local CO₂ levels during summertime is the biosphere, causing the concentration of CO₂ to increase, in some cases up to 100 ppm, during night-time inversion periods.

Contrary to the CO₂ flux, the calculated surface fluxes of CH₄ (Fig. 6) do not reveal any distinct seasonality. The monthly means scatter between ca. 50 and 200 μmol m⁻² h⁻¹, with

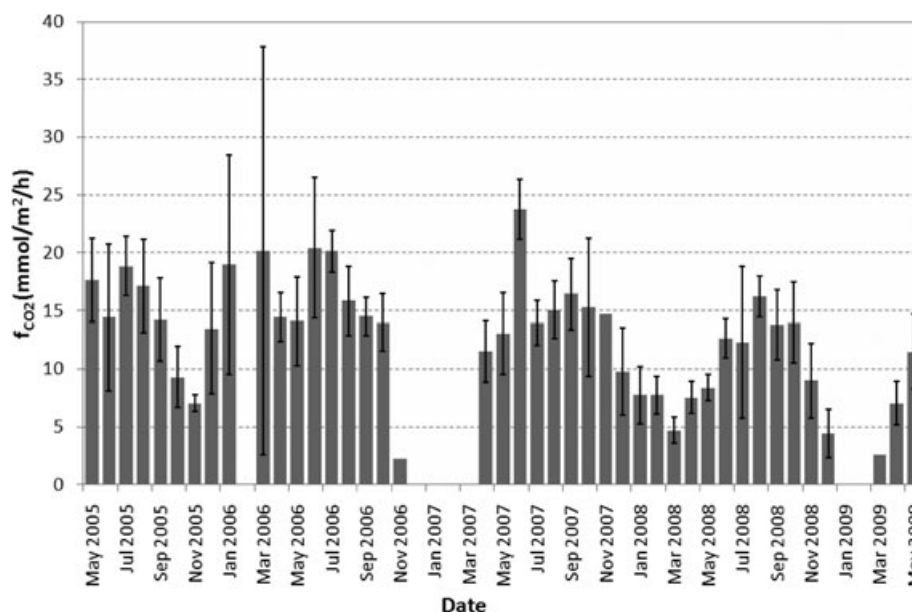


Fig. 5. The monthly means of surface night-time fluxes of CO₂ in Krakow for the period May 2005–May 2009. Dark bars represent the calculated fluxes, with the 1σ uncertainty of the mean derived from the population of the available data for the given month. The gaps in the data are due to lack of GC or sodar measurements for these periods. High uncertainties of the mean fluxes for January and March 2006 result from poor statistics of the available data.

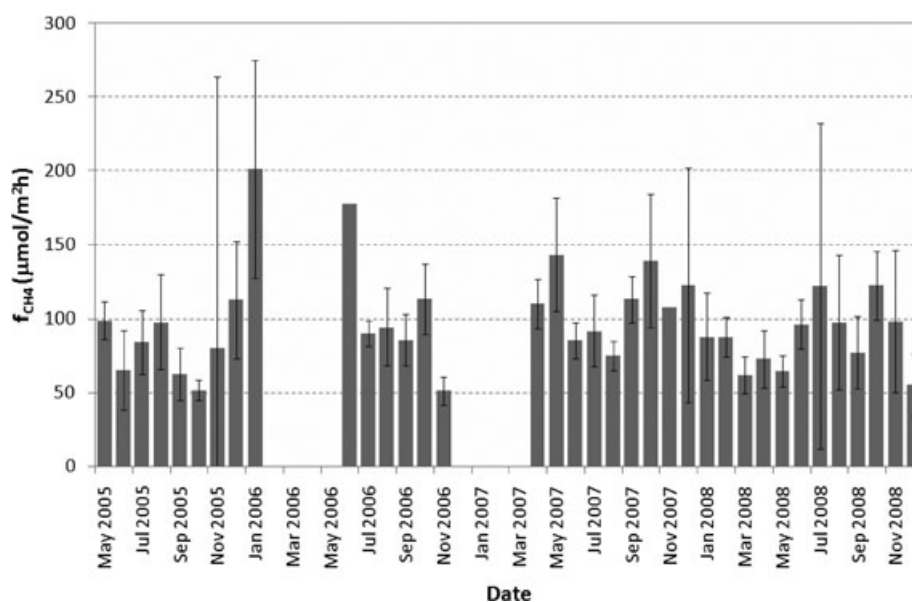


Fig. 6. The monthly means of surface night-time fluxes of CH₄ in Krakow for the period May 2005–December 2008. Error bars represent 1σ uncertainty of the mean derived from the population of the available data for the given month. The gaps in the data are due to lack of GC measurements for these periods. High uncertainties of the mean fluxes for November 2005 and July 2008 result from poor statistics of the available data.

the relative uncertainty of the mean values varying between 10 and 227%. The mean value of the CH₄ flux calculated for the whole analysed period (May 2005–December 2008) is equal $97.2 \pm 5.4 \mu\text{mol m}^{-2} \text{h}^{-1}$. The quoted uncertainty represent one standard deviation of the mean value. Multiplying the mean

CH₄ flux by the surface area of the city (326.8 km^2), one arrives at the total mean emission of methane into the atmosphere in Krakow in the order of $(6.2 \pm 0.4) \times 10^6 \text{ m}^3 \text{ yr}^{-1}$. Leakages of the city gas network are thought to be the main source of this methane. This has been confirmed by carbon isotope

analyses of atmospheric methane and the methane being distributed within the network. The carbon isotope composition of methane emitted by the hypothetical methane source in Krakow, derived from carbon isotope analyses of atmospheric methane and the two-component mixing model, is equal ca. -54.2‰ (Kuc et al., 2003). Measurements of carbon isotopic composition of methane present in the city gas yield the value of $-54.4 \pm 0.6\text{‰}$ which is virtually identical with the isotopic signature of the hypothetical methane source within the city. The leakages of CH₄ estimated by Kuc et al. (2003) for the period 1996–1997 were in the order of $2.15 \times 10^7 \text{ m}^3 \text{ yr}^{-1}$, a significantly higher value than that derived in the present study. This would imply a substantial reduction of the total CH₄ leakage in the city by a factor of 3.5, when compared to the 1996–1997 estimate. This apparent reduction of CH₄ leakages is most probably linked to major improvements of the distribution infrastructure of the city gas network in the course of the last decade, as testified by the gas operator.

4. Conclusions

Near-ground measurements of atmospheric mixing ratios of selected trace gases can be combined, under certain assumptions, with quasi-continuous measurements of the mixing layer height in the lower troposphere, yielding night-time surface fluxes of these gases averaged over the area which may reach some tens of square kilometres. The reconnaissance data obtained in the framework of this study indicate the potential of this method for assessment of surface fluxes of CO₂ and CH₄ in complex urban terrain with numerous point and distributed sources of these gases. The major weakness of the method lies in relatively large uncertainty of the adopted constant correction factor derived from assumed vertical concentration profiles of the measured gases. This factor links the mean concentrations of CO₂ and CH₄ within the PBL with the measured concentrations close to the ground.

The obtained night-time surface fluxes of CO₂ varied seasonally, with the minimum values (monthly means) of around $2 \text{ mmol m}^{-2} \text{ h}^{-1}$ during winter and up to ca. $20 \text{ mmol m}^{-2} \text{ h}^{-1}$ during summer. This seasonality is induced by strong, seasonally varying biospheric component originating from soil respiration (Gorczyca et al., 2003; Zimnoch et al., 2004).

The night-time fluxes of methane varied from ca. 50 to $200 \text{ } \mu\text{mol m}^{-2} \text{ h}^{-1}$, without clear seasonal trend. The distinct flux of CH₄ into the atmosphere, with the mean value over the whole observation period equal to ca. $97 \text{ } \mu\text{mol m}^{-2} \text{ h}^{-1}$, indicates a presence of relatively strong methane source on the investigated area. This source is linked to methane leakages from the city gas distribution network. This has been confirmed by carbon isotope analyses of atmospheric methane and the methane being distributed within the network. Comparison of the total annual leakages of this gas within the Krakow urban agglomeration estimated by Kuc et al. (2003) for the period 1996–1997

(ca. $2.15 \times 10^7 \text{ m}^3 \text{ yr}^{-1}$) with those derived in the framework of this study (ca. $6.2 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$) points to major technological improvements of the natural gas distribution infrastructure within the city in the recent years.

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