Eddy covariance measurements of the net turbulent methane flux in the city centre – results of 2 year campaign in Łódź, Poland.

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Abstract

In the period July 2013 to August 2015, continuous measurements of turbulent methane exchange between an urbanised area and the atmosphere were carried out in Łódź. Long-term continuous measurements of CH_4 fluxes from cities are still relatively rare. The measurement station was located in the centre of the city, where since 2000 fluxes of energy (sensible and latent heat) and since 2007 fluxes of mass (carbon dioxide) have been continuously measured. In the immediate vicinity of the measurement station there are potential sources of methane, such as vehicle traffic, dense sewerage infrastructure and natural gas networks. To assess fluxes, the eddy covariance technique was used. The study aim was to investigate the temporal variability of methane fluxes in the city-atmosphere system.

The results show that positive methane fluxes dominate which indicates that the centre of Łódź is a net source of methane to the troposphere. The measurements also indicate the existence of an annual rhythm in the turbulent flux of methane. On average, the values observed in winter amounted to ~40-60 nmol·m-2·s-1 and were significantly larger than in summer (~20 nmol·m^{-2}·s^{-1}). The daily variability in the methane flux is also just visible throughout the year. Values measured on working days were higher (6.6% (winter) to 5.6% (summer)) than those observed at weekends. The largest monthly exchange occurred in the winter months (from 2.0 to 2.7 g·m^{-2}·month^{-1}) and the lowest occurred in summer (from 0.8 to 1.0 g·m^{-2}·month^{-1}).

The mean daily patterns of methane fluxes in consecutive months were used to determine the cumulative annual exchange. In 2014, the centre of Łódź emitted a net quantity of almost 18

g·m^{-2}. Furthermore, the study assessed the co-variability of methane and carbon dioxide fluxes.

1 Introduction

The temporal and spatial variability of greenhouse gas fluxes in the atmosphere is currently one of the most widely discussed climatological problems in the scientific community. Methane, despite its trace presence in the air (ca 1.8 ppm, Hartman et al., 2013), plays an important role in the environment. It participates in the global carbon cycle and is one of the greenhouse gases whose concentration in the atmosphere affects the radiation balance of the earth's surface. An increase in the concentration of methane contributes to an enhancement of the greenhouse effect (Ciais et al., 2013). Therefore, emissions of this gas to atmosphere should be carefully monitored.

Methane is produced during the process of methanogenesis under anaerobic conditions, from the decay of organic plant debris in water. The most important source of methane in the world is wetlands (Shurpali et al., 1998; Rinne et al., 2007; Baldocchi et al., 2012; Hatalaa eta al., 2012), but paddy fields (Miyata et al., 2000), cattle farms (Laubach and Kelliher, 2005; Dengel et al., 2011; Hartmann et al., 2013; Nicollini et al., 2013) and emissions from the soil are all important sources (Smeets et al., 2009; Denmead et al., 2010; Wang et al., 2013). Moreover, emissions of methane accompany forest fires and grass vegetation. The effect of the combustion of natural gas (which contains at least 80% methane) is mainly water vapour and carbon dioxide. The combustion of fossil fuels is, however, predominantly incomplete, and is therefore an important factor causing anthropogenic methane emissions. This happens in the case of combustion of both natural gas and hydrocarbons contained in petrol and other fuels (Nam, 2004; Nakagawa et al., 2005; Wennberg et al., 2012). Another important source of methane in urbanised areas is leakage from urban gas pipelines (Lowry, et al., 2001; Gioli et al., 2012; Wennberg et al., 2012; Phillips et al., 2013). Methane may also be emitted during the anaerobic respiration of bacteria in urban soils (Bogner and Matthews, 2003) and in the decomposition of solid waste and wastewater in sewage systems and at landfill sites (Bogner and Matthews, 2003; Laurila et al., 2005; Lohila etal., 2007; Wennberg et al., 2012; Jha etal., 2014). In contrast, methane is removed from the air by consumption by soil bacteria (Goldman et al., 1995; Kaye et al., 2004; Groffman et al., 2006; Groffman and Pouyat, 2009). Methane is involved in some of the reactions leading to photochemical smog formation

(Seinfeld and Pandis, 2006). The disintegration of methane also results from its reacting with the hydroxyl group in the atmosphere (Whalen, 2005). Annual global emissions of methane to the atmosphere have been estimated as ~5000 Tg. Emissions from landfills and waste (87-94 TG) or fossil fuels (85-105 Tg) are 2-3 times lower than estimated emission from wetlands (177-284 Tg) (Ciais et al, 2013).

Research into the methane content in the air is now a priority because the literature indicates that cities could be a significant source of this gas (Elliot et al., 2000; Gioli et al. 2012; O'Shea et al., 2012; Nicolini et al., 2013; Phillips et al., 2013; Christen, 2014; Kumar and Sharma, 2014). The measurements of changes in methane concentration have been carried out for decades (Ciais et al., 2013; Hartmann et al., 2013). However, the analysis of its flux in urban areas is extremely rare. In recent years, there have been approximately 500 stations measuring the fluxes of carbon dioxide (CO_2) around the world of which approximately 20 are located in cities and only a few are able to measure methane flux (Nordbo et al., 2012; Oliphant, 2012; Christen, 2014; Helfter et al., 2016). It can be concluded that the measurement of methane flux in cities is in its infancy and challenges like the need for long term measurements (beyond a month) and the relationship between methane fluxes and land use are yet to be overcome.

The development of the theory and measurement techniques of turbulent exchange of mass, energy and momentum fluxes have been progressing for decades (Stull, 1988; Lee et al., 2005; Foken, 2008; Aubinet et al., 2013). Historical measurements of methane flux have been severely limited due to the lack of suitable sensors which have only recently become available (Pattey et al. 2006; Hendricks et al., 2008; Eugster and Pluss, 2010; Dengel et al., 2011; Detto et al., 2011; Sakabe et al., 2012). At present, one of the most widely used instruments is the LI7700 Open Path CH_4 Analyser (Burba and Anderson, 2010; McDermitt et al., 2011) which uses eddy-covariance as a measurement technique (Aubinet et al., 2012). Worldwide, there are only a few long-term, continuous measurement stations measuring turbulent fluxes of water vapour and carbon dioxide in urban areas (Christen, 2014; Helfter et al., 2016). For methane flux in urban areas, such data are probably at the implementation phase because previous studies focused on areas which are the largest source of methane i.e. natural wetlands (Shurpali et al., 1998; Rinne et al., 2007; Baldocchi eta al., 2012; Hatalaa eta al., 2012; Aubinet et al., 2013), agricultural land (paddy fields, Miyata et al., 2000) or forests (Smeets et al., 2009; Wang et al., 2013). The chamber method, widely used in rural areas, has only a limited relevance in the city. This method makes it possible to take measurements of methane emissions from specific areas like urban lawns (Baciu et al., 2008), however, it cannot be used in larger urban areas. A variety of techniques have recently been applied to provide independent estimates of urban methane emissions such as airborne observations (O'Shea et al., 2014; Mays et al., 2009), Fourier Transform Spectrometry (Wunch et al., 2009) or isotopic source apportionment studies (Lowry et al., 2001). Morizumi (1996) suggested the occurrence of covariability of radon Rn-222 and methane flux concentrations which he estimated to be 20 $mg \cdot m^{-2} \cdot day^{-1}$. In Poland, the issue of exchange of greenhouse gases in an urban area is studied has also been studies in Cracow where, based on the measurements of methane concentrations and the height of the atmospheric boundary layer, the average monthly nocturnal flux of methane has been estimated to be 0.8 do 3 $mg \cdot m^{-2} \cdot h^{-1}$ (Kuc et al., 2003; Zimnoch et al., 2010).

The aim of this study is to analyse the temporal variability of the turbulent flux of methane (FCH_4) based on a long-term series of measurements recorded for over two years in the centre of Łódź (July 2013 to August 2015). The diurnal variability of FCH_4 was analysed and monthly values of the flux were determined. An assessment of the cumulative annual exchange of methane between urban Łódź and the troposphere was completed to determine whether it was an equally efficient source of methane to the troposphere as of carbon dioxide. The measurement results were compared to the variability of selected meteorological elements. As the methane emissions in the city are determined mainly by anthropogenic factors, the value of fluxes on weekdays and at weekends were compared. No comparison was made to the fluxes estimated using specific inventory methods because of a lack of data.

2 Measurement site and instrumentation

2.1 Study area and site location

Łódź is one of the largest cities in Poland. The area of the city is about 295 square kilometres (km^2), and its population is estimated at 706,000 residents. The city is located in central Poland on relatively flat terrain which slopes south-westwards. Its altitude varies from 280 to 160 m above mean sea level. The most densely built-up city centre area covers 80 km^2 and the altitude difference in this part of the city does not exceed 60 m. In the immediate vicinity of Łódź, there are no large bodies of water, rivers or orographic obstacles impacting on the climate of the city which are worthy of investigation. Another factor making it easier to take measurements of turbulent fluxes of mass and energy in Łódź, is that the city, does not have a standard central sector of tall buildings, towering over an urban canopy layer unlike other large cities in Poland.

The measurements of turbulent fluxes of methane are conducted in the western part of the city centre (51°47'N, 19°28'E) as shown in Fig. 1). This part of the city has the highest population density which reaches 17.2 thousand people per km^2. The station for measurements of fluxes of mass, energy and momentum has been operating in the western part of Łódź since 2000 (Offerle et al., 2006a; 2006b, Pawlak et al., 2011; Fortuniak et al., 2013, Fortuniak and Pawlak, 2014), however, methane fluxes have been studied since July 2013. The measurement set is mounted on top of a mast at a height of $z = 37$ m (Fig. 2, left) which given the average height of buildings of 11 m, enables the assumption that the measurements are taken above the blending height in the inertial sub-layer (Fig. 2). The source area of turbulent fluxes was estimated (Fig. 1) for data collected during unstable stratification $((z-z_d)/L < -0.05)$ around midday (10.00–14.00) following the method of Schmid (1994) and ranged from 250 to 750 m away from the measurement station (Fig. 1).

The percentage of artificial surface coverage from buildings, pavements, streets and squares in this part of the city is 62%. The remaining part of the area is covered in vegetation of only 10% is by trees (Kłysik, 1998). The vegetation is distributed unevenly in the form of lawns and trees growing along street canyons. In the immediate vicinity of the measurement location, 3-5 storey buildings which range from 15 to 20 m in height dominate. Most of the buildings have flat roofs covered with black tar paper or sheet metal. The trees growing in the area are mostly deciduous and their height usually does not exceed the height of the buildings. Thisresults in a well-formed roof surface with an average height of 11 m. The density of built-up areas north and east of the measurement point, compared to the southern and western sectors, is 10-20% greater (Fig. 1). The displacement height z_d is estimated at 7.7 m. According to the classification by Stewart and Oke (2012), the local climate zone can be described as compact low rise. The roughness coefficient z_{0m} estimated for the neutral stratification surrounding the measurement point was 2.5 m on average. More information on the city's structure and the local climate conditions can be found in Kłysik (1996), Kłysik and Fortuniak (1999), Fortuniak et al. (2006, 2013), Offerle, (2006a, 2006b), Pawlak et al. (2011)

and Zieliński et al. (2013). The gas distribution network and sewerage system around the flux tower are shown in Fig. 1.

2.2 Instrumentation and data processing

Measurements of turbulent fluxes of methane were carried out using a standard measurement set consisting of the ultrasonic anemometer RMYoung model 81000 (RMYoung, Traverse City, Michigan, USA) and a fast response methane concentration sensor with an open measurement path LI7700 (Li-cor, Lincoln, Nebraska, USA). The measurements were carried out with a precision of 0.001 $m \cdot s^{-1}$ and 1 ppb respectively. As the final calculation of methane flux also requires values of sensible heat and water vapour fluxes in the place of observation (LI 7700 instruction manual), the measurement set also included a sensor measuring the concentrations of water vapour and carbon dioxide. This was a LI7500 Infra-Red CO_2/H_2O open path analyser (Li-cor, Lincoln, Nebraska, USA).

The whole measurement system was attached approximately 1 m below the top of the mast (Fig. 2, middle). The LI7500 head was placed on the horizontal arm on the south-eastern side of the mast at a distance of about 60 cm from the mast. The ultrasonic anemometer was then installed at a distance of 20 cm. The LI7700 methane sensor was installed on an additional arm, 30 cm lower, so that the centre of its measurement path, which is about four times longer than the paths of LI7500 and ultrasonic anemometer, was at a similar level. Previous studies have shown that the influence of a mast of diameter 0.15 m is negligible and does not generate flow distortion (Fortuniak et al., 2013).

All the aforementioned sensors sampled with a frequency of 10 Hz. Immediately before starting the measurements in July 2013, the sensor for measuring H_2O and CO_2 mole fractions was calibrated (the zero and span values were set). The methane concentration analyser was installed directly after purchase, so the zero and span had been set by the manufacturer. The two sensors and the ultrasonic anemometer were cleaned approximately once a month. This was pertinent to the methane sensor because its mirrors proved to be highly susceptible to grime (air impurities, bird droppings, atmospheric deposits, drying raindrops or melting snowflakes). The manufacturer equipped the instrument with a mirror heating and condensation anti-freezing system and a cleaning system. Using a pump, this applied cleaning liquid to the lower mirror. However, in practice and particularly in autumn and winter this was insufficient particularly on days with humidity of up to 100% when the signal strength dropped by several tens of percent in just a few hours. According to the manufacturer of the instrument, if the signal strength Relative Signal Strength Indicator (RSSI) is less than 10%, this means that the measurement path is blocked by external factors. However, it was decided to tighten this criterion. In order to calculate the fluxes, the methane mole fraction values observed at RSSI >20% were chosen. Of these, the RSSI exceeded 70% in only 8% of cases (Fig. 2, right), while observations at 20% < RSSI < 70% had a much greater share. Most often and in 20% of cases the signal strength was between 30% and 40% (Fig. 2, right).

The 10 Hz fluctuation data for the vertical wind velocity and the concentrations of water vapour and methane were recorded by a CR21X datalogger (Campbell Scientific, Logan, Utah, USA) so that all parameters could be recorded at the same time. The measurement station was also equipped with sensors recording the general weather conditions (air temperature and humidity, atmospheric pressure, wind direction and velocity, radiation balance components, precipitation). These data were recorded every 10 minutes by a CR10 datalogger (Campbell Scientific, Logan, Utah, USA) and were archived together with the 10 Hz data on a PC.

The FCH_4 was determined directly from the definition as the covariance of the vertical wind velocity fluctuations and the methane concentration fluctuations in the air (Lee et al., 2005; Foken, 2008; Burba and Anderson, 2010; Aubinet et al., 2012):

$$FCH_4 = \overline{w'\rho CH_4'} = \frac{1}{N}\sum_{N}^{i=1}\left(w-\overline{w}\right)\left(\rho CH_4 - \overline{\rho CH_4}\right). \qquad (1)$$

The *w’* and *ρCH4’* parameters are, respectively, the fluctuations of vertical wind velocity and the concentration of methane in the air, while $\overline{w}$ and $\overline{\rho CH_4}$ are their averaged values. A positive flux means the turbulent transport of methane into the troposphere, a negative flux is its uptake by the urban surface. 1 hour block averaging was used as an averaging period. Since the measurements were carried out at a considerable height, a shorter averaging period could lead to underestimating the fluxes (Pawlak et al., 2011). During the calculations, all necessary procedures and corrections were applied. Any data with non-real values were rejected, the spike detection procedure was performed (Vickers and Mahrt, 1997), the double rotation of the wind coordinate system was applied (Kaimal and Finnigan, 1994) and the impact of separation of the sensors was eliminated by maximizing the covariance in the interval +/-2 s. Furthermore, sonic temperature was corrected for humidity in the air

(Schotanus et al., 1983) and the WPL correction was added (Webb et al., 1980). According to LI7700 manufacturer's recommendations, the correction terms related to air density fluctuations affecting both the spectroscopic response and the mass density retrieval were applied (LI7700 instruction manual).

A detailed control of the quality of the calculated fluxes was also carried out which focused primarily on the assessment of data stationarity. The most commonly used Foken's test (Foken and Wichura, 1996) is not always fit for purpose. Therefore two other tests were used as proposed by Mahrt (1998) and Dutaur et al. (1999) modified by Affre et al., (2000). During the data quality assessment, a very strict criterion was adopted to classify the data as suitable for further analysis when three tests confirmed that stationarity was met. A milder criterion, indicating good data quality if at least one test suggested stationarity did not meet the expectations. This criterion accepted data with unrealistically high positive values and a substantial number of fluxes with high negative values whose existence cannot be explained. However, the restrictive evaluation of the data reduced the amount of data suitable for further analysis by 23.8%. Uncertainty regarding their quality was kept to a minimum. Approximately 10% of the data were not registered due to problems with power supply in autumn 2013, and 29.8% of the recorded data were rejected because the measurements had been taken in weather conditions which made it impossible for the LI7700 sensor to measure the concentration of methane properly. This was a result of such factors as precipitation and atmospheric deposits, saturation of air with water vapour and impurities. This problem occurred particularly in autumn and winter (Table. 1) when frequent cleaning of the sensor placed on the mast was impossible. As a result the percentage of acceptable data was 36.4% as shown in Table. 1.

3 Results

3.1 Climate background

The climate of central Poland is a typical transitional climate of moderate latitudes. It is characterised by marine air masses flowing from the west and by continental air from the east. The mean monthly air temperature in the study period varied from 0.1°C in winter (January 2014) to 22.8°C in summer (August 2015). The study period was considered to be hot with heat waves occurring and the winters were relatively warm with mean temperatures in 2014 and 2015 of 2.7°C and 2.4°C respectively. The average temperature in 2014 was 10.9°C. The total precipitation in the same year was 584 mm, with a greater amount of precipitation of 360 mm (61.6% of the annual total) recorded in the warm half of the year. The maximum solar radiation was observed in July (688 MJ·month^{-1} in 2014 and 697 MJ·month^{-1} in 2015) while the minimum occurred in the winter months when they fell below 80 MJ·month^{-1}. The monthly radiation balance totals were almost 400 MJ·month^{-1} in July, while in the winter months they became negative and reached even -56 MJ·month^{-1} (December 2013). The average wind speed in the period was 3.1 m·s^{-1}, with slightly higher values in winter (3.4 m·s^{-1}) and lower values in the summer (2.8 m·s^{-1} on average). The study area of the city is dominated by air flow from the west (Fortuniak et al., 2013).

During the measurement period, atmospheric instability or neutral conditions prevailed in the city centre. Stable air stratification was observed in the centre of Łódź in only 7.6% of cases (from 2.9% in winter to 10.4% in summer). The frequency of neutral and unstable stratification was similar and was 46.0% and 46.4% respectively. Unstable conditions prevailed in summer (51.6% of cases), while neutral conditions were observed in 61.7% of cases in winter. In the diurnal cycle, stable stratification was also a rarity. In the daytime (10.00 a.m. to 2.00 p.m.), this type of stratification was observed in only 0.3% of cases on average throughout the year, while at night the condition $\xi > 0$ was met by 15.0% of the data. Other types of atmospheric stability appeared in the daytime in 19.7% (neutral) and in 80% (unstable) of cases. At night, neutral conditions prevailed (67.0% of cases), while unstable conditions were observed in 18.0% of cases on average throughout the year.

Clear annual and diurnal cycles characterized the fluxes of energy and mass. Both the sensible heat flux Q_H and the latent heat flux Q_E were largest in summer (about 190 MJ·month^{-1}and 120-150 MJ·month^{-1}, respectively) The Bowen ratio $B=Q_H/Q_E$ was typically urban i.e. greater than 1 and up to 2.25 in May 2015). The annual variability of carbon dioxide flux (FCO_2) was also marked by an annual cycle. The maximum values occurred in winter when anthropogenic CO_2 emissions, being a result of burning fossil fuels for vehicle traffic and domestic heating were the largest. The typical values exceeded 20 μmol·m^{-2}·s^{-1} and had a maximum of ~55 μmol·m^{-2}·s^{-1}. In summer, the consumption of CO_2 by urban vegetation and lack of domestic house heating contribute to a decrease in the intensity of net exchange. The minimum values of FCO_2 were observed as-10 to 10 μmol·m^{-2}·s^{-1}.

3.2 Annual variability of FCH_4

The two-year measurements of FCH_4 revealed a number of characteristics of the exchange of methane in the city-troposphere system. Irrespective of the season mainly positive of FCH_4 were observed (Fig. 3). On average, the percentage of positive values over the study period was 93.7% which was slightly greater in the cold season (94.6%) than in the warm season (93.2%). This means that regardless of the season the centre of Łódź is a source of methane to the atmosphere. In addition, the time variability of FCH_4 shows a clear annual cycle with a maximum in the cold season and a minimum in the warm season (Fig. 3). The highest recorded values exceeded 100 $nmol \cdot m^{-2} \cdot s^{-1}$ and were observed in November, December, January and February. The least intense exchange of methane was observed from May to September, when FCH_4 was rarely greater than 50 $nmol \cdot m^{-2} \cdot s^{-1}$. The exception was the summer of 2013 when the recorded values of FCH_4 were close to winter values in July and August. However, only average values were elevated, while the median values are similar to those of July and August 2014 and 2015. It can be assumed that in the summer of 2013 additional sources of methane were present which could be the result of damages to the gas network. It is likely that this occurred south-east of the station where the deep excavations associated with the construction of a tunnel for one of the main streets of the city centre was completed (Fig. 2).

It seems that the annual cycle of turbulent methane exchange should be attributed to the anthropogenic origin of this gas in the centre of the city. In the cold season, there is an increase in methane emissions associated with the combustion of fossil fuels, which results from the increased discharge of motor vehicle exhaust gas (Heeb et al., 2003; Nakagawa et al., 2005). Another important factor is the increased natural gas consumption in winter, its leakage from distribution networks and its use in domestic gas burners. Methane is also produced by heating ovens (Ciais et al., 2013). The absence of inventory data makes it difficult to verify these dependencies for Łódź. However, the increased values of the flux of methane are clearly visible where there are rapid drops in air temperature i.e. in late October or late November and December 2014 (Fig. 3). A pronounced annual cycle can also be seen in the temporal variability of the mean monthly values of FCH_4 (Fig. 3, Table 2). The highest monthly averages of FCH_4 were recorded in January and February 2014 when the average exchange exceeded 60 $nmol \cdot m^{-2} \cdot s^{-1}$. In the same months of 2015, the FCH_4 values were lower and slightly exceeded 50 $nmol \cdot m^{-2} \cdot s^{-1}$, which was a consequence of winter 2014/2015 being warmer than 2013/2014. The mean monthly values of FCH_4 in summer rarely exceeded 20 $nmol \cdot m^{-2} \cdot s^{-1}$. The median values in the warm half of the year were very similar to the average values. In the cold season, the median was lower due to the sporadically occurring elevated levels of FCH_4. Regardless of the measurements, some differences in the time variability of methane flux in transitional seasons can also be observed. In late winter and early spring, a rapid drop in FCH_4 by approximately 30 $nmol \cdot m^{-2} \cdot s^{-1}$ can be observed, while FCH_4 starts to increase at the end of summer and slowly continues until winter. The cold half of the year is also characterised by a greater variability of the fluxes of methane (Table 2). In the summer months, the standard deviation of FCH_4 did not exceed 20 $nmol \cdot m^{-2} \cdot s^{-1}$, whereas during the winter months it was more than two times greater. An exception is the aforementioned summer of 2013.

3.3 Diurnal variability of FCH_4

Fig. 4 shows the average daily flux of methane in the centre of Łódź calculated for the entire study period (top graph) and for the successive months of the year (middle and bottom graphs). The average daily variability in the successive months confirms the above described annual variability i.e. higher values of FCH_4 occurred in the cold season. Furthermore, the average daily variability, regardless of month and time of day, is always positive. This means that the emissions of methane dominate over its uptake by the urban surface. The daily pattern, averaged for the entire measurement period, show a clear diurnal cycle with two maxima and two minima. The maximum values occurred in the morning (7.00 - 8.00 UTC + 1) and in the evening (19.00 - 20.00 UTC + 1). During the maxima, the values of FCH_4 reached almost 40 $nmol \cdot m^{-2} \cdot s^{-1}$, whereas during the noon hours and at night they dropped to 26-28 $nmol \cdot m^{-2} \cdot s^{-1}$. Such a daily pattern suggests that the average flux of methane can be divided into two components. One has an approximately constant value of up to 26-28 $nmol \cdot m^{-2} \cdot s^{-1}$ and its source may be the sewerage system and the natural gas distribution system. In the morning and in the afternoon, additional sources of methane (vehicle traffic, combustion of natural gas, leaks from gas network associated with the increasing gas consumption) are activate, increasing the flux by 10-12 $nmol \cdot m^{-2} \cdot s^{-1}$. However, it should be noted that due to the lack of inventory data, the above considerations are only hypothetical.

In the warm half of the year (May-October), the average daily variability was low and from April to September it ranged between 10 and 40 nmol·m^{-2}·s^{-1}. In May, June and July it was difficult to see clear maxima during a 24–hour period. In August, September and October there was a maximum in the morning. In the cold half of the year (November-April), the average daily variability of FCH_4 was characterised by distinctly higher values from 20 to 90 nmol·m^{-2}·s^{-1}. In this period, the double daily maximum was easier to identify and in November, December, January and February the afternoon peak seemed to be greater than in the mornings. In March and April, the maximum values were comparable. The presence of two maxima in the variability of FCH_4 in the cold season could be explained by the increased consumption of natural gas, the combustion of fossil fuels in the morning and afternoon hours from cooking and domestic heating and the diurnal variability of motor vehicle traffic which can cause road congestion in winter. In the warmer seasons and particularly during the holidays periods, motor vehicle traffic became less intense and the city's inhabitants stopped heating their homes. In the cold season, FCH_4 is also characterised by greater variability throughout the day. The standard deviation of FCH_4 in this season can reach 50 nmol·m^{-2}·s^{-1} while in the warm season it rarely exceeds 20 nmol·m^{-2}·s^{-1}.

3.4 Monthly and annual exchange of FCH_4

Based on the average daily patterns of FCH_4 calculated for each month (the sum of the average hourly FCH_4 multiplied by the number of days in the month), the exchange of methane in the successive months of the study period was determined (Fig. 5). The highest values occurred in winter where in January and February 2014 they exceeded 2.5 g·m^{-2}·month^{-1}. The summer values were more than two times lower and dropped to 0.7-0.8 g·m^{-2}·month^{-1}. The autumn of 2013 was characterized by elevated values of FCH_4. A comparison between the monthly exchange of methane and the mean monthly air temperature reveals a clear link between these parameters (coefficient of determination = 0.731, Fig. 5, bottom right). So, the anthropogenic sources of methane gain intensity at low air temperatures, which can be seen by comparing the results of FCH_4 measurements in winter 2013/14 and 2014/15 (Fig. 5). In the first case, an increase of the monthly values of the flux was recorded starting from November, with a maximum in January and then a decrease until April-May. Between November 2013 and January 2014, the exchange almost doubled (from 1.36 to 2.67 g·m^{-2}·month^{-1}). The next winter, the monthly exchange of methane between November and March differed little, and FCH_4 increased from November 2014 to January 2015 only by ca 0.27 $g \cdot m^{-2} \cdot month^{-1}$. The differences were associated with thermal contrasts during the two winters. In winter 2014/2015, the monthly average temperature remained at 2.2-2.5°C, while in the previous winter season the mean January temperature dropped to 0.1°C. The greater activity of the anthropogenic sources of methane in the centre of the city is also confirmed by the measurements of methane concentrations (Fig. 5, bottom left). The high winter values of the flux of methane are accompanied by higher concentrations of the gas in the air and seasonal changes in OH concentration.

Based on the data on the exchange of methane in Łódź obtained between January 2014 and August 2015, an attempt was made to assess the cumulative annual exchange of this gas in the centre of Łódź between the city centre and the atmosphere (Fig. 6). To date, there have been no standard methods for filling gaps in the long-term data series of turbulent fluxes of methane in urbanized areas. Difficulties with their development arise primarily from the fact that the continuous measurements of FCH_4 in cities are still rare. Furthermore, as in the case of carbon dioxide fluxes, data on anthropogenic sources of the gas and the parameters of natural processes (e.g. air temperature) may be useful for the data gap filling procedures (Aubinet et al., 2012). The annual exchange of methane in the city centre was therefore estimated using two simple methods. Firstly, on the basis of the average daily patterns of FCH_4, the monthly exchange in the successive months was determined and then the accumulation was made (Fig. 6, solid step plots). Secondly, the gaps were filled in a series of 1-hour values of FCH_4 in two ways. If a data gap was not longer than 3 hours, interpolation was used, while for longer gaps data were inserted from the average daily pattern in the respective month for the respective hour. Both methods yielded very similar results (the difference was approximately 1%), although it is obvious that the cumulative fluxes obtained in this manner should be regarded as an approximation. Therefore it can be stated that the annual exchange of methane in the centre of Łódź in 2014 was equal to about 17.6 $g \cdot m^{-2}$ (Fig. 6). The graph shows the impact of the annual variability of methane flux: the cumulative flux grows fastest in the cold half of the year. Due to the differences in the exchange of methane described in Section 3.4, with reference to changes in air temperature in the study period, the cumulative exchange in the period January-August 2015 was calculated in a similar manner. The relatively warmer beginning of 2015 caused the exchange to be less intense and the cumulative flux of FCH_4 in August 2015 was by 9.2% lower than in 2015.

3.5 Weekly differences of FCH_4

Since fluxes of methane in the city are associated with anthropogenic sources, a weekly cycle of FCH_4 should be expected which is similar to that seen for CO_2 exchange (Pawlak et al., 2011). Based the on 1-hour data for FCH_4 recorded in the period July 2013 to August 2015, an average daily flux of 44.3 $mg{\cdot}m^{-2}{\cdot}day^{-1}$ was determined (Fig. 7). Having taken only working days for the calculation (Monday to Friday), it was found that the exchange was higher i.e. 45.2 $mg{\cdot}m^{-2}{\cdot}day^{-1}$. In contrast, the average daily exchange of methane during weekends (Saturday and Sunday) amounted to 42.3 $mg{\cdot}m^{-2}{\cdot}day^{-1}$ and was therefore lower by 4.5%. These results suggest that, on average, in the study period anthropogenic sources of methane are likely to be less at weekends compared to working days. It should be emphasized that on Saturday, the average flux was lower by 6.9% in comparison with working days, while on Sunday it was lower by 12%. The difference is a result of significantly lower peak on Sunday morning, which can be attributed to less intensive human activity on Sunday morning and lower traffic load in comparison to the same time of day on Saturday. Similar results were observed in summer and winter, when the average daily exchange on working days was higher by 1.6% (summer) and 1.9% (winter) compared with the average for the whole week. The average daily exchange at weekends was lower by 4.0% and 4.7% respectively. An exception is the transitional seasons when the average daily exchange of methane on working days was comparable (spring, -0.3%) or slightly lower (autumn, -1.6%) than the average for the entire week (Fig. 7). On the other hand, the average daily exchange during the weekend turned out to be higher and amounted to +1.6% (spring) and +3.8% (autumn). Without the inventory data, it is difficult to explain why the fluxes vary, particularly in the case of CO_2 fluxes where higher values are observed on working days as compared to weekends throughout the year (Pawlak et al., 2011).

3.6 Methane fluxes and wind direction

As mentioned in Section 2.1, the centre of Łódź is the most densely built-up area of the city. The measurement point is located in an area of uniform building density while, as mentioned in Section 2.1, this density is slightly greater to the east and north of the station. An analysis of the average value of FCH_4 depending on the wind direction confirms, at least in part, the impact of building density on the value of methane turbulent exchange (Fig. 8). The fluxes of methane recorded during airflow from the north, and especially from the south-east, were by far the largest in the study period and reached 35-45 $nmol \cdot m^{-2} \cdot s^{-1}$ (Fig. 8, left). However, it is difficult to be confident in the direct relationship between urban design and FCH_4 because of the increased values of FCH_4 from the south-western sector (approximately 40 $nmol \cdot m^{-2} \cdot s^{-1}$). Such a relationship cannot be ruled out, however the local point sources of methane may play an important role even though they are difficult to identify. In the case of the south-western sector, the liquid petroleum gas (LPG) station located approximately 800 m from the measurement station may be such a source. It lies approximately 200 m to the west of the large intersection where traffic load is usually larger than the surrounding streets. Significantly lower values of FCH_4 (less than 20 $nmol \cdot m^{-2} \cdot s^{-1}$) observed with airflow from the south and west may be due to the presence of large urban parks (Fig. 1).Heavy traffic does not run through these streets and the density of the gas network and sewage system is also significantly smaller in comparison with other sectors (Fig. 1). The distribution of average FCH_4 depending on the wind direction, calculated for the cold half of the year (Fig. 8, middle) suggests that in this season local anthropogenic methane sources were more intense. The relationship between FCH_4 and the wind direction was much the same throughout the study period, while the average values of fluxes were higher and amounted to 55-70 $nmol \cdot m^{-2} \cdot s^{-1}$. Therefore, the sources could be clusters of houses with leaks from gas installations or vehicles at nearby intersections which are heavily jammed in the cold half of the year. In summer, the average fluxes of CH_4 were significantly lower (less than 30 $nmol \cdot m^{-2} \cdot s^{-1}$, Fig. 8, right) regardless of the wind direction. The contrast between the sectors was not clear. An exception is the clearly visible elevated value of FCH_4, associated with the airflow from the south-western sector.

3.7 Methane fluxes in relation with carbon dioxide fluxes

During more than two years of measurements in Łódź, both FCO_2 and FCH_4 were measured and therefore the question about temporal covariability of both fluxes can be addressed, and, consequently, whether the exchange of methane can be estimated based on the knowledge of the flux of CO_2. The average daily variability (Fig. 9, left) and the average monthly variability (Fig. 9, middle) of the value of methane flux were compared to the fluxes of CO_2. As the figure indicates, such covariability exists and bigger fluxes of CH_4 are accompanied by larger fluxes of CO_2. Unfortunately, the low coefficients of determination (0.57 and 0.56)mean FCO_2 cannot be used as a proxy for FCH_4 in the centre of Łódź. An even weaker relationship was observed between the average daily patterns of FCH_4 and FCO_2 (Fig. 9, right). Although the two fluxes have a characteristic pattern with two maxima in a 24-hour period, the coefficient of determination is only 0.25. We therefore conclude that FCO_2 data cannot be used to facilitate gap-filling of FCH_4 data in the centre of Łódź.

The comparison of FCH_4 and FCO_2 fluxes allow analysis of the relative contribution of each of the fluxes to total emissions to atmosphere. The average value of the FCH_4/FCO_2 ratio in 2013-2015 was $3.71*10^{-3}$ (Fig. 10, top). Rather stable values of the ratio in months (minimum $2.41*10^{-3}$, maximum $5.3*10^{-3}$) and the lack of a clear annual course suggest rather comparable magnitude of both fluxes. However, a clear diurnal course in the ratio has been observed (Fig. 10, bottom) with reduced values in the day and elevated values at night. On average, over the study period and in the transitional seasons, the daily variation of FCH_4/FCO_2 was similar. Between the hours of 9 a.m. and 5 p.m. FCH_4/FCO_2 was approximately constant of the order 2.5 to $3.5*10^{-3}$. At night, these values grow to about $5\text{-}7*10^{-3}$ which can be explained by relatively constant methane emissions related to leaks from pipelines, and reduced emission of CO_2 which is the result of minimum of traffic load. In winter, the average daily variability of the FCH_4/FCO_2 ratio can be characterised by slightly higher values during the day (about $4.4*10^{-3}$) and significantly higher at night reaching $12*10^{-3}$ between the hours of 2 a.m. and 6 a.m. (Fig. 10, bottom). The causes again are clear: a minimum traffic load giving reduced fluxes of FCO_2 but also increased methane leaks from pipelines associated with higher gas consumption for heating of the surrounding buildings. The exception was the daily course FCH_4/FCO_2 in the summer which is reversed. The minimum (of the order of $3\text{-}5*10^{-3}$) was observed at night and the maximum (more than $8*10^{-3}$) around noon (Fig. 10, bottom). Elevated values of the ratio during the day are the result photosynthesis reducing FCO_2 flux.

4 Summary and conclusions

The measurements of the methane flux (FCH_4) carried out in the centre of Łódź for more than two years provided information on the time variability of methane exchange between the urban surface and the atmosphere. The measurement results showed that, as in the case of other greenhouse gases, i.e. water vapour (Offerle et al., 2006a, 2006b) and CO_2 (Pawlak et al., 2011), the centre of Łódź is a source of methane to the atmosphere. Another feature indicating the similarity in the time variability of greenhouse gases is the annual cycle of the exchange of methane in the system: city centre/atmosphere, which seems to result from an annual cycle of anthropogenic methane emissions. Other characteristics such as diurnal variability, and notably weekly variability, are not as pronounced as for FCO_2 (Pawlak et al., 2011). The annual exchange of methane in terms of pure carbon in the centre of Łódź was estimated at 13.2 $gC \cdot m^{-2} \cdot year^{-1}$, which, compared to the exchange of CO_2 estimated in Łódź at 2.93 $kgC \cdot m^{-2} \cdot year^{-1}$, does not seem too large. At the same time, it must be noted that the centre of Łódź is a source of methane comparable in intensity to the most productive natural areas , i.e. wetlands. The annual exchange of methane in Łódź was estimated to be 17.6 $g \cdot m^{-2} \cdot year^{-1}$, while at the same time (2014) the exchange in the wetlands of the Biebrza National Park (north-eastern Poland) was approximately 18 $g \cdot m^{-2} \cdot year^{-1}$ (Fortuniak and Pawlak, 2015). Comparable values of the annual exchange of methane were also observed at other stations located in wetlands: approximately 16.5 $g \cdot m^{-2} \cdot year^{-1}$ (Finland, Rinne et al., 2007) or 14.0 - 18.5 $g \cdot m^{-2} \cdot year^{-1}$ (Sweden, Nilsson et al., 2008).

Unfortunately, possibility of comparing the results obtained with those from other cities is limited at this time. The only longer-term measurements of methane flux were performed in Florence (March - May 2011, Gioli et al., 2012) and in London (3-year campaign, Helfter et al., 2016). The mean values of the methane fluxes obtained in these cities were higher than in Łódź. In Florence, the average methane exchange in the spring of 2011 was estimated to be 135 $nmol \cdot m^{-2} \cdot s^{-1}$. The average FCH_4 in Łódź in the same season was four times lower and equal to 31 $nmol \cdot m^{-2} \cdot s^{-1}$. On the other hand, a comparison of the obtained results of FCH_4 measurements with inventory research does not necessarily yield a positive outcome (Gioli et al., 2012). In London, the average exchange was also several times higher than that observed in Łódź (142 and 32 $nmol \cdot m^{-2} \cdot s^{-1}$, respectively). The results of this type, however, allow only a very general comparison and the limited sampling period prevents analysis. For example, the mean variability of daily FCH_4 in Florence in spring was characterised by one maximum during the day, while two maxima were observed in Łódź for the same period: morning and evening. The measurements in Florence showed no correlation between FCH_4 and air temperature (R^2=-0.04, Gioli et al., 2012), while in Łódź a strong relationship occurs (R^2=0.71). It is also impossible to compare the annual exchange and in the absence of measurements in other cities, it is difficult to determine the relationship between the intensity of annual methane exchange and a parameter characterizing the study area of the city in general. In the case of CO_2 flux, a clear relationship between the annual FCO_2 and the percentage of artificial surfaces in the vicinity of the measurement point (Nordbo et al., 2012; Oliphant, 2012) was observed. Based on the existing measurements, it is difficult to attempt to seek a similar dependence for the flux of methane since only in London a relationship between FCH_4 and population has been found (Helfter et al., 2016). There are also several published results of urban methane emissions obtained using eddy-covariance techniques such as using alkanes (Los Angeles, Pieschl et al., 2013), aircraft measurements (Indianapolis, Mays et al., 2009) or a ground-based Fourier transform spectrometer (Los Angeles, Wunch et al., 2009). All of them reports existence of higher FCH_4 fluxes than measured in Łódź.

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Table 1. Data capture of 1-hour values recorded for FCH_4 in the center of Łódź in the period July 2013 – August 2015

Spring MAM	39.1%
Summer JJA	47.4%
Autumn SON	26.5%
Winter DJF	31.1%
July 2013 – August 2015	36.4%

Table 2. Monthly values of mean, median and standard deviation values of FCH_4 in the centre of Łódź in the period July 2013 – August 2015 (all fluxes in nmol·m^{-2}·s^{-1}).

		J	F	M	A	M	J	J	A	S	O	N	D
2013	Mean	-	-	-	-	-	-	22.1	29.5	39.6	38.1	35.3	45.3
2013	Median	-	-	-	-	-	-	18.2	22.0	26.3	27.7	26.6	38.6
2013	St. dev.	-	-	-	-	-	-	27.1	35.7	56.2	43.7	39.3	35.9
2014	Mean	62.9	66.6	37.4	33.1	21.8	22.9	20.3	19.2	20.8	27.0	43.4	47.8
2014	Median	60.2	64.4	30.6	31.7	20.8	22.1	19.3	18.2	20.2	23.6	34.2	38.4
2014	St. dev.	46.7	42.6	32.9	21.8	20.8	16.8	14.7	15.2	11.3	20.9	31.9	39.3
2015	Mean	52.5	54.2	48.6	25.2	22.8	18.4	17.6	21.5	-	-	-	-
2015	Median	47.6	51.8	46.5	22.4	22.1	17.7	17.3	20.3	-	-	-	-
2015	St. dev.	34.5	39.4	32.4	23.7	16.2	14.9	12.9	14.6	-	-	-	-

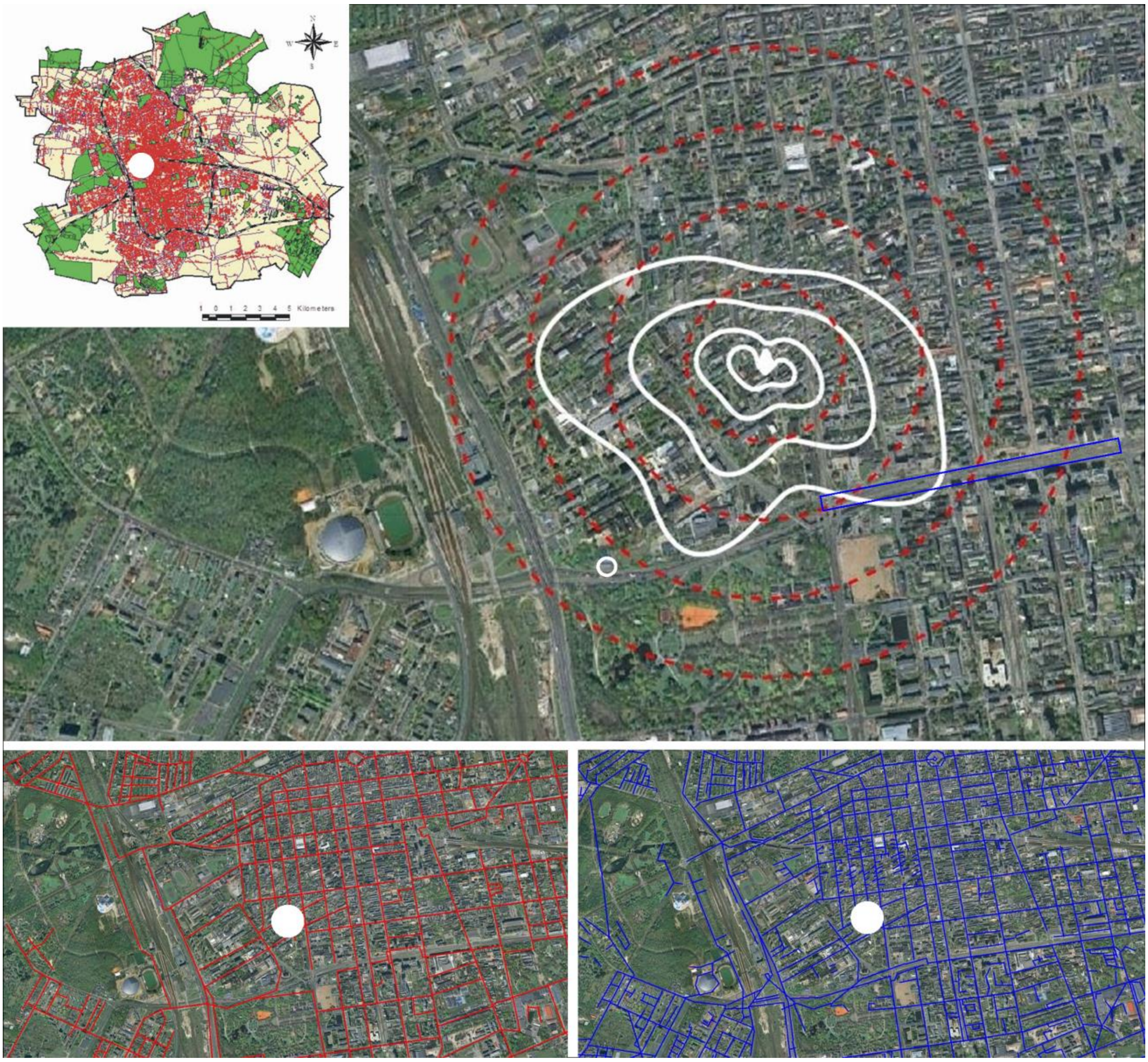

Figure 1. The western part of the center of Łódź (top). Solid white lines indicate the source area with P = 25, 50, 75 and 90%, calculated for the turbulent fluxes measured at 10 a.m. to 2 p.m. during unstable stratification (all available data from the period July 2013 - August 2015). The dashed red lines represent the 250, 500, 750 and 1000 m distance from the measurement point. White circle indicates LPG station and blue rectangle indicates area of road tunnel construction. Bottom figures show spatial distribution of gas network (bottom left) and sewage system (bottom right) in the neighbourhood of the measurement site (white dots). Schemes are based on data from Geodesy Center of Łódź (www.mapa.lodz.pl). Photo source: www.google.com

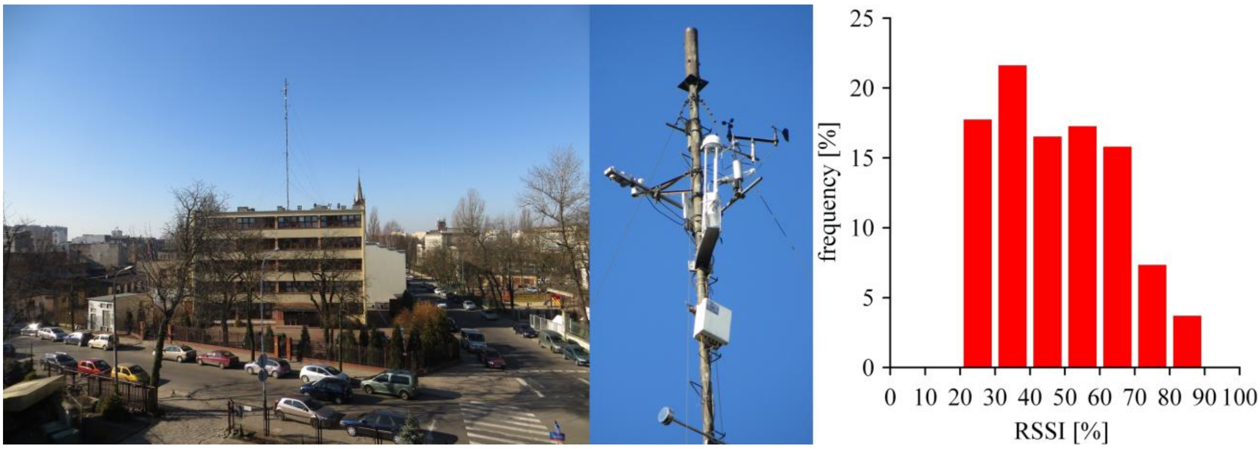

Figure 2. A FCH$_4$ measurement site in Łódź (left) and instrumentation (middle). The right figure shows the frequency of measured 1-hour blocks of raw data in relation to the RSSI (Received Signal Strength Indicator) of Li7700 methane open path analyser. Data recorded only in the case RSSI>20% were taken into account.

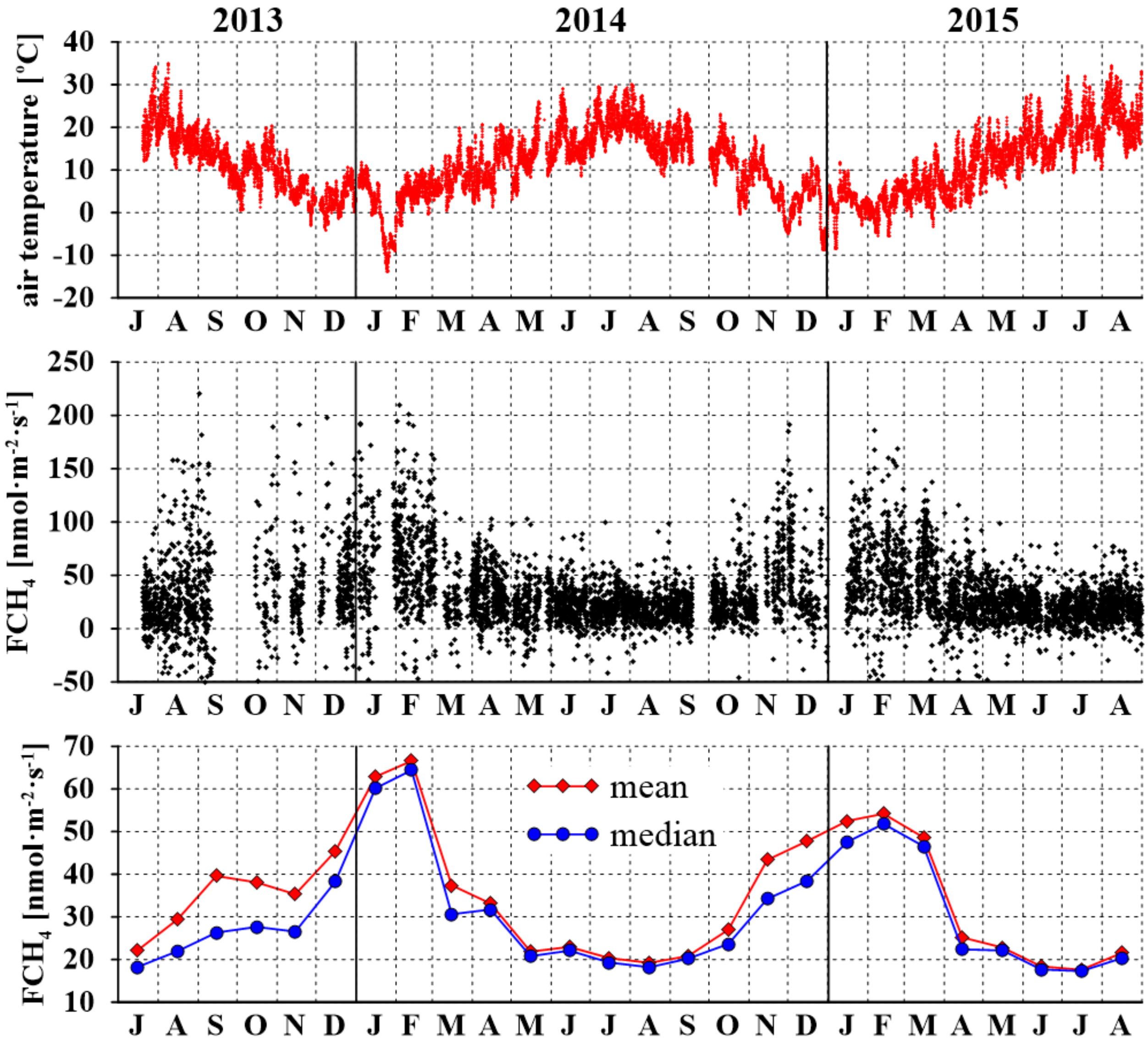

Figure 3. One hour means of air temperature, one hour net turbulent FCH_4 flux (approved by three stationarity tests), mean and median of FCH_4 measured in the period July 2013 – August 2015.

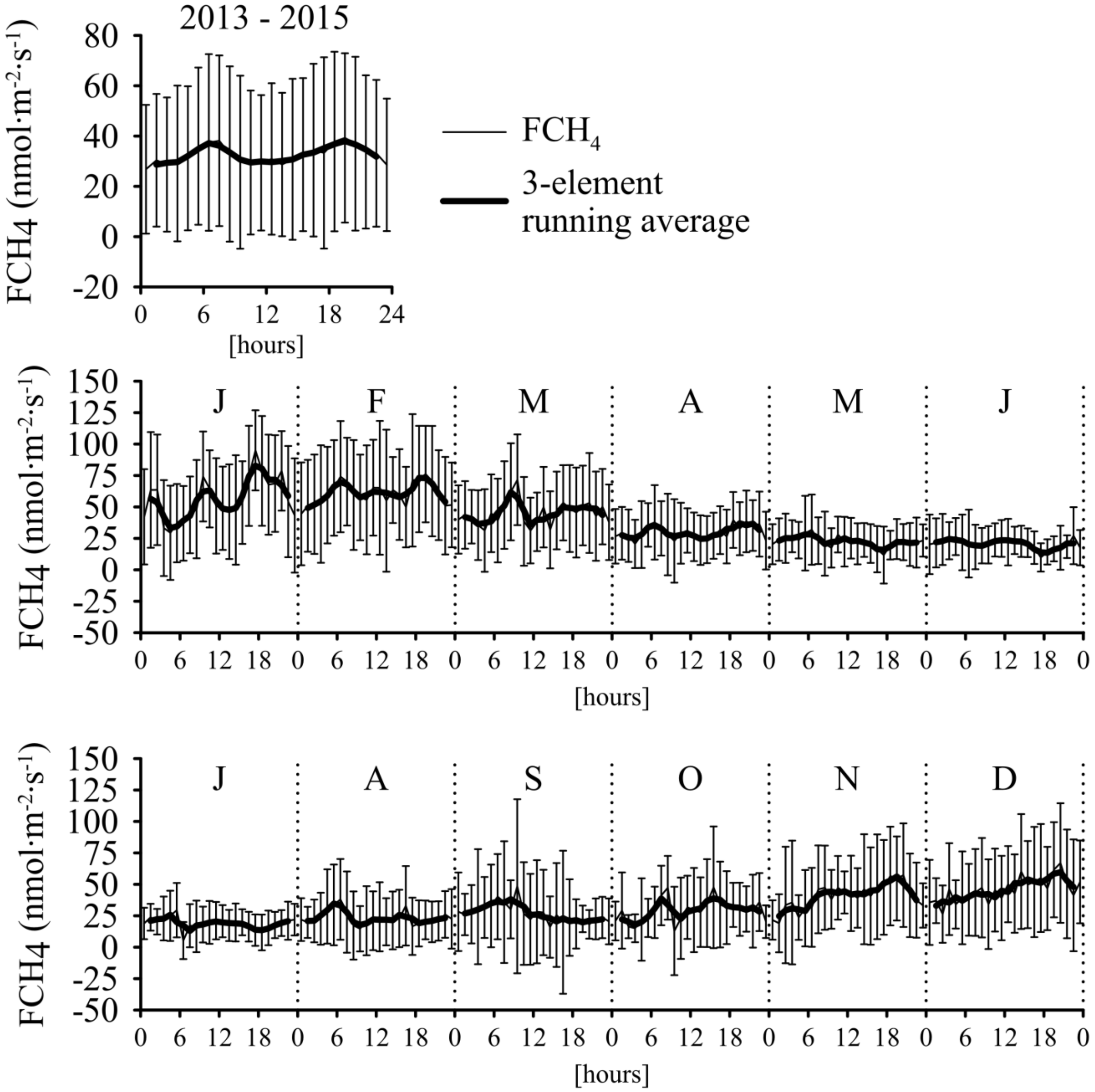

Figure 4. Mean diurnal variability of FCH_4 flux in the period July 2013 – August 2015 (top left figure) and for months. Thin and thick black lines indicate, respectively, variability of FCH_4 and 3-element running average of FCH_4. Thin vertical lines indicate standard deviation of FCH_4.

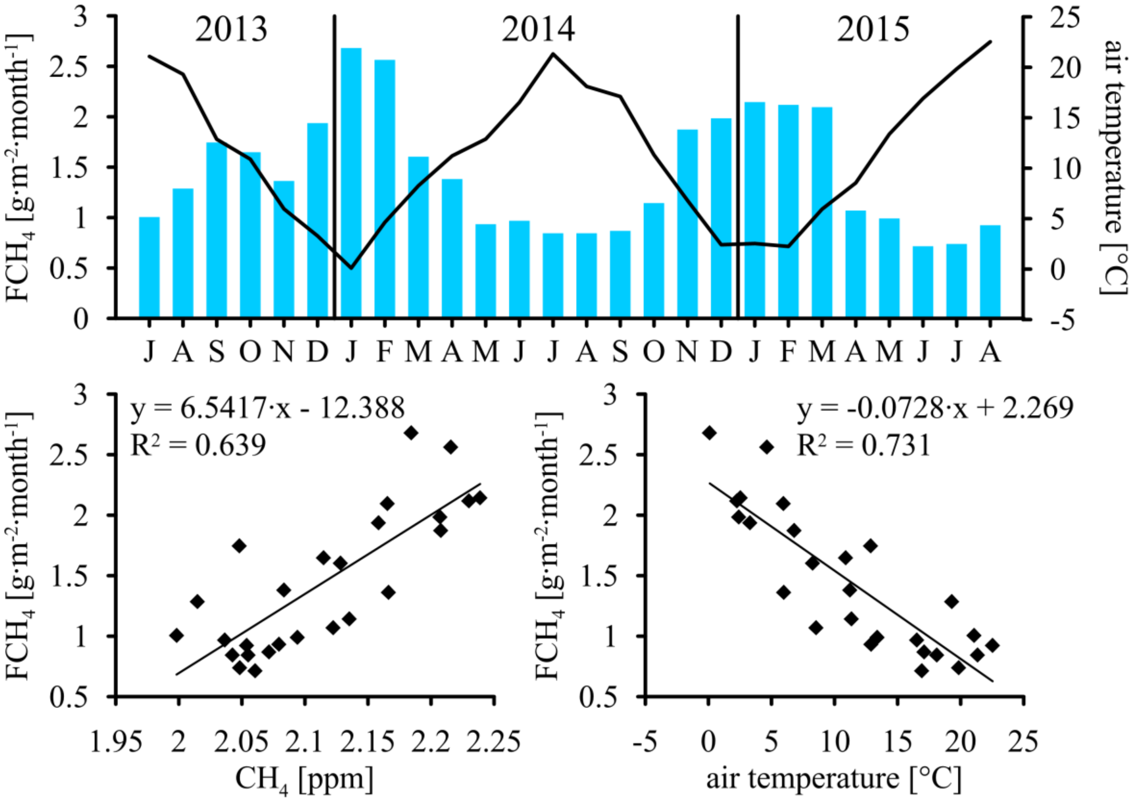

Figure 5. Monthly totals of FCH_4 (top) in relation with mean monthly CH_4 concentration (bottom left) and mean monthly air temperature (bottom right) in the period July 2013 – August 2015.

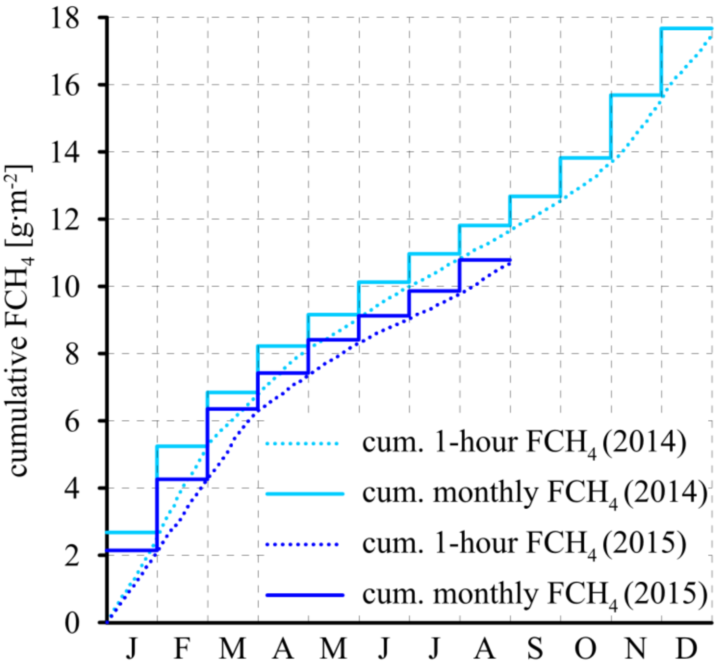

Figure 6. Cumulative fluxes of FCH_4 in the period January – December 2014 (light blue lines) and January – August 2015 (dark blue lines). Dotted and solid lines indicate, respectively, cumulative annual FCH_4 calculated on the basis of all 1-hour data and on the basis of integrated mean daily courses of consecutive months.

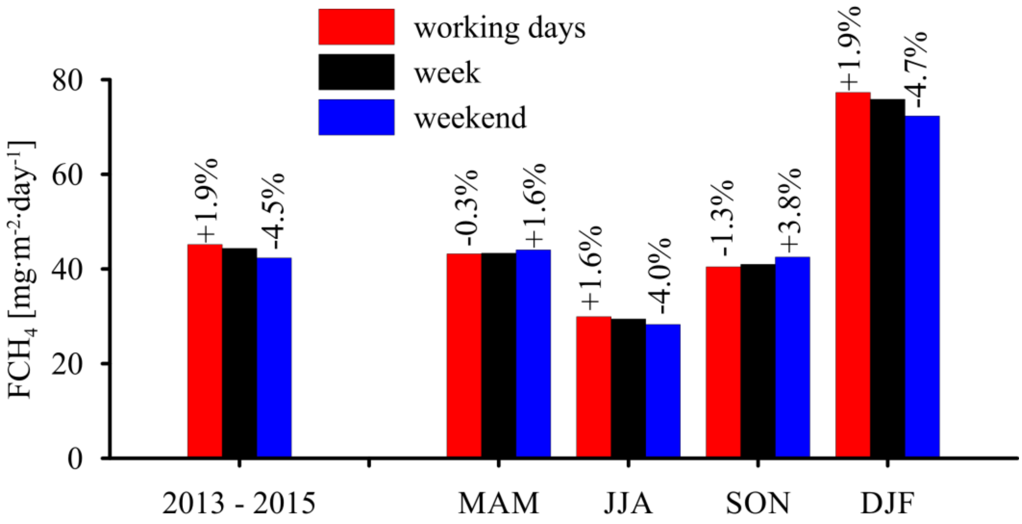

Figure. 7. Mean daily values of FCH_4 in the period July 2013 – June 2015 calculated for study period and seasons. Red, black and blue bars indicate, respectively, mean daily exchange during working days (Monday to Friday), weeks (Monday to Sunday) and weekends (Saturday and Sunday).

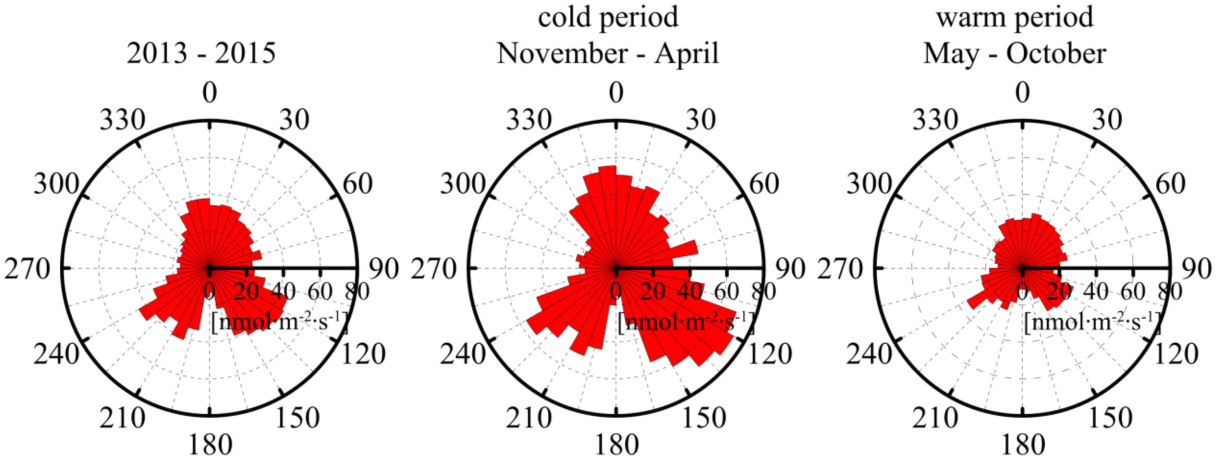

Figure 8. Mean FCH_4 calculated for all data (left), cold (middle) and warm period (right) in relation with wind direction in the period July 2013 – August 2015.

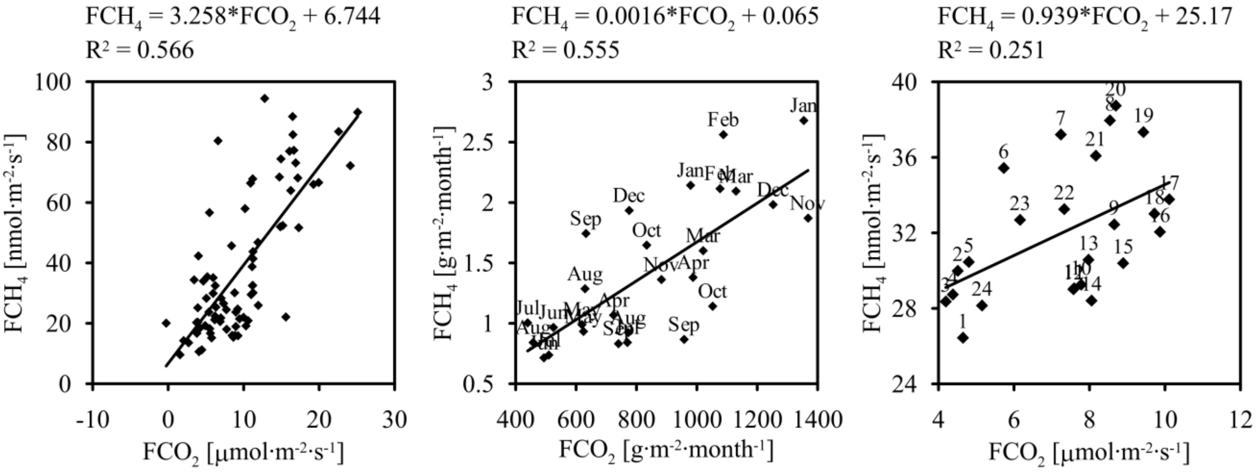

Figure 9. Mean daily (left), monthly (middle) and hourly FCH_4 fluxes against FCO_2 in the period July 2013 – June 2015.

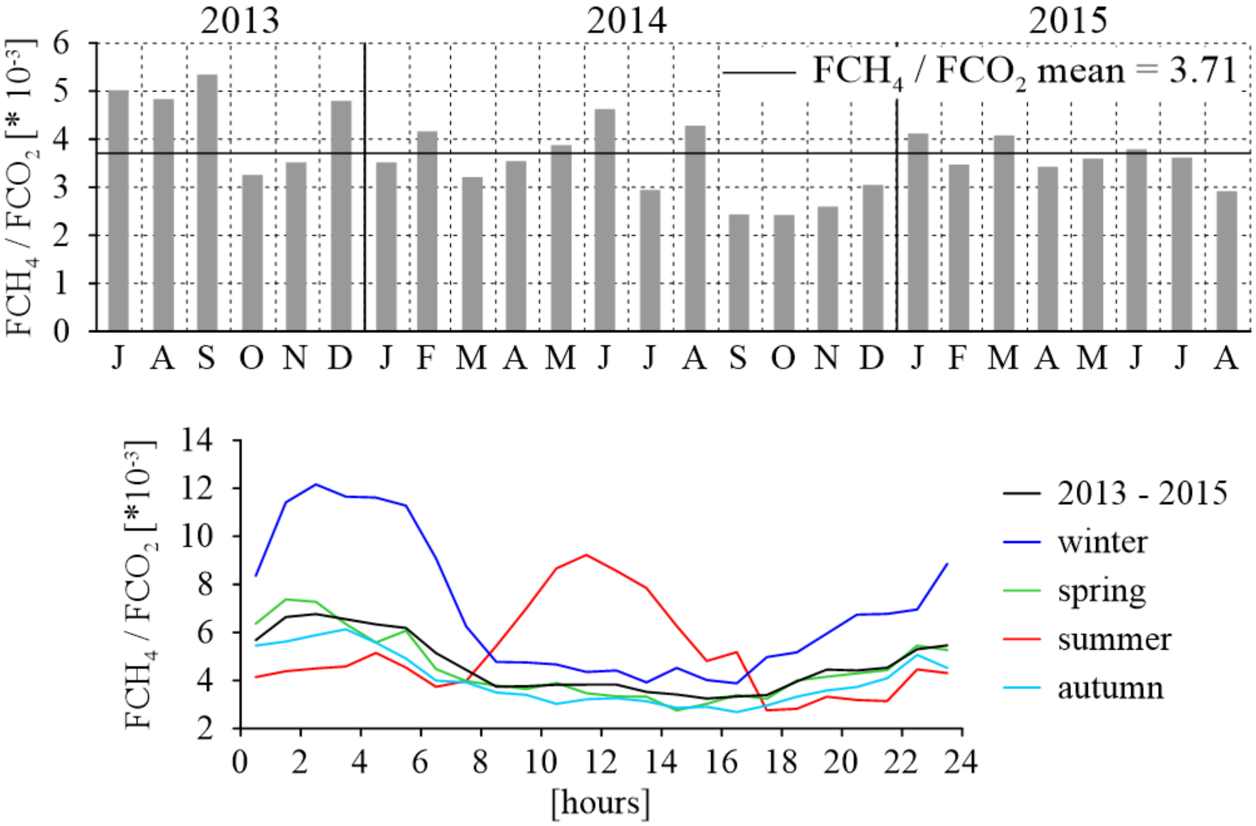

Fig. 10. Monthly FCH_4 to FCO_2 ratio (up) and mean diurnal courses of FCH_4 to FCO_2 ratio in the period July 2013 – August 2015 and for seasons.