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

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Abstract

In the period between July 2013 and August 2015, continuous measurements of turbulent methane exchange between an urbanised area and the atmosphere were carried out in Łódź. Such long, continuous measurement series of turbulent methane exchange between the city and the atmosphere are still a rarity. The measurement station was located in the centre of the city, where fluxes of energy (sensible and latent heat) and fluxes of mass (carbon dioxide) have been continuously measured since 2000 and 2007, respectively. In the immediate vicinity of the measurement station there are potential sources of methane, such as streets with vehicle traffic or dense sewerage and natural gas networks. To determine the fluxes, the eddy covariance technique was used; the measurement station was equipped with instruments for recording fluctuations in the vertical component of the wind speed (an ultrasonic 3D anemometer, RM Young 81000, RM Young, USA) as well as the concentration of methane in the air (an open path Li 7700 CH4 Analyzer, Li-cor, USA). The devices were mounted on a mast at a height of 37 metres above ground level and, on average, 20 metres over the roofs of the surrounding buildings. The results were therefore averaged for an area with a diameter of approximately 1 kilometre. Our aim was to investigate the temporal variability of the turbulent exchange of methane in the city-atmosphere system. The results show in the first place that positive methane fluxes (turbulent gas transport from the surface to the atmosphere) definitely dominate compared with negative fluxes. This indicates that the study area of the centre of Łódź is a net source of methane to the troposphere. The measurements also indicated the existence of a clear annual rhythm of the turbulent flux of methane in the centre of Łódź (on average, the values observed in winter amounted to ~40-60 $nmol \cdot m^{-2} \cdot s^{-1}$ and were significantly larger than in summer). The daily variability of the flux of CH_4 (FCH_4) is faintly

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visible throughout the year. The studied area of the centre of Łódź is also characterised by a cycle of methane exchange – the values measured on working days were higher by 6.6% (winter) to 5.6% (summer) than those observed at weekends. The largest monthly exchange was characteristic of 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 FCH_4 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 analyses the covariability of methane and carbon dioxide fluxes.

1 Introduction

The temporal and spatial exchangeability of the concentration of greenhouse gases in the atmosphere is at present one of the most widely discussed climatological problems. Methane, despite its trace presence in the air (ca 1.8 ppm, Hartman et al., 2013), plays an important role in the energy exchange between the biosphere, the atmosphere, the lithosphere and the hydrosphere. In the first place, it participates in the global carbon cycle; furthermore, besides water vapour, carbon dioxide, nitrous oxide, and CFCs, it is considered one of the greenhouse gases whose concentration in the atmosphere affects the formation of the radiation balance of the Earth's surface. An increase in the concentration of methane contributes to an enhancement of the greenhouse effect; therefore, the emissions of this gas to the 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 farming (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, the emissions of methane accompany forest fires and grass vegetation, and methane is also the main component of natural gas. 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 course of 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). On the other hand, certain soil bacteria consume methane, which is one of the processes of its removal from the air (Goldman et al., 1995; Kaye et al., 2004; Groffman et al., 2006; Groffman and Pouyat, 2009). Furthermore, 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).

Research into the methane content in the air is now a priority, not only from the point of view of the natural sciences, but also that of the economic and social sciences (Hartmann et al., 2013), and, as it follows from the literature on the problem, the city may 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 classical measurements of changes in CH_4 concentrations have been carried out for decades (Ciais et al., 2013; Hartmann et al., 2013), while the analyses of its exchange, especially in urban areas, are extremely rare. The process of the exchange of methane and other greenhouse gases between the ground and the atmosphere is closely related to the turbulent air movement in the atmospheric boundary layer, and therefore such measurement techniques should be used in the research which allow the determination of vertical turbulent mass, energy and momentum fluxes, and which have been developed for decades (Stull, 1988; Lee et al., 2005; Foken, 2008; Aubinet et al., 2013). Unfortunately, the lack of suitable instruments resulted in the fact that it was initially only possible to use indirect methods employing empirical coefficients selected arbitrarily by the researchers, or not allowing for the turbulent mixing of air in the boundary layer, such as the gradient method or the chamber method (Nicolini et al., 2013). The instruments to measure the turbulent fluxes of greenhouse gases such as water vapour and carbon dioxide became more widely available several years ago and since then (the first half of the 1990s) the research has intensified (Aubinet et al. 2012). Unfortunately, the measurements of the turbulent exchange of methane were severely limited due to the lack of suitable sensors, which did not begin to appear until a few years ago (Pattey et al. 2006;

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Hendricks et al., 2008; Eugster and Pluss, 2010; Dengel et al., 2011; Detto et al., 2011; Sakabe et al., 2012). At present, the most widely used instrument is believed to be the LI 7700 Open Path CH_4 Analyzer (Burba and Anderson, 2010; McDermitt et al., 2011). The number of publications describing the results of measurements of the turbulent flux of the gas is therefore relatively small, in contrast to the turbulent process of carbon dioxide exchange which has been described fairly specifically for more than a decade; however, it should be noted that this kind of research in urbanised areas is still relatively rare (Nordbo et al., 2012; Oliphant, 2012). In recent years, there have been approximately 500 stations measuring the turbulent exchange of CO_2 around the world, of which only ca 20 are located in cities (Nordbo et al., 2012; Oliphant, 2012; Christen, 2014). The complicated methodology resulting from the heterogeneity of urban areas and the necessity to hang the sensors at least several tens of metres above the ground, as well as considerable funds necessary to launch a measurement station have meant that measurements of turbulent fluxes are still poorly widespread. Worldwide, there are only a few long-term, continuous measurement series of turbulent fluxes of water vapour and carbon dioxide recorded in urban areas (Christen, 2014). In the case of methane flux, such series are probably at the implementation phase, since 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, only has a limited relevance in the city: it makes it possible to take punctual measurements (Baciu et al., 2008); however, it cannot be used in the case of larger urban areas. The few published results of measurements of methane fluxes in urbanised areas indicate their positive values, i.e. the emissions of methane into the atmosphere. In Germany, based on various kinds of indirect methods, the existence of a flux of methane into the atmosphere was demonstrated, comparable to those observed in wetlands. The leakage of gas from the natural gas system is suggested as the main reason for the existence of the flux (Shorter et al., 1996). Morizumi (1996), in turn, suggested the occurrence of covariability of Rn-222 radon and the methane flux concentrations, which, based on this, were estimated to be 20 $mg \cdot m^{-2} \cdot 24h^{-1}$. In recent years, there have been studies showing the results of measurements performed in Florence (Gioli et al. 2012) and London (O'Shea et al., 2012). The measurements taken in Columbus, USA, enabled the estimation of methane exchange between wetlands located in the city and the troposphere (Morin et al., 2015). In Poland, the issue of exchange of greenhouse gases in an urban area is studied, besides Łódź, in Cracow, where, based on the measurements of CH_4 concentrations and the height of the atmospheric boundary layer, the average monthly nocturnal flux of methane has been estimated to be 0.8 to 3 mg·m^{-2}·h^{-1} (Kuc et al., 2003; Zimnoch et al., 2010). The question of determining the features of diurnal and seasonal variability of the vertical turbulent exchange of methane in the city and the assessment of the impact of meteorological conditions on the exchange intensity of the gas should be regarded as still open. The measurements described so far, despite having contributed valuable information, at the same time hinder an estimate of the annual flux of methane emitted by urban areas.

The measurements of turbulent fluxes of mass and energy have been taken in the centre of Łódź since the autumn of 2000 (Offerle et al., 2006a; 2006b, Fortuniak et al., 2013, Fortuniak and Pawlak, 2014). At present, the continuous series of measurements of greenhouse gas fluxes cover 15 years (water vapour, with an interval in the years 2004-2005), and 9 years in the case of carbon dioxide (Pawlak et al., 2011). In July 2013, the measurement kit was equipped with a methane gas analyzer (Li 7700 open-path CH4 Analyzer, Li-cor, USA).

The aim of this study is to analyse the temporal variability of a turbulent flux of methane (FCH_4) based on a long-term series of measurements recorded for over two years in the centre of Łódź between July 2013 and August 2015. Furthermore, the diurnal variability of FCH_4 was analysed in the following months, the monthly values of the flux were determined and an attempt was undertaken to assess the cumulative annual exchange of methane between an urban area and the troposphere in order to determine whether the centre of Łódź 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 values of fluxes on weekdays and at weekends were compared. Due to the impossibility to obtain relevant data, there was no comparison made with the values of fluxes using specific inventory methods.

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 km^2, and its population is estimated at about 706 thousand residents. The city is located in central Poland, on a relatively flat terrain sloping south-westwards (its altitude varying from ~280 to ~160 m.a.s.l.). The most densely built-up city centre covers an area of 80 km^2 and the altitude differences in this part of town do not exceed 60 m. In the immediate vicinity of Łódź, there are no large bodies of water, rivers or orographic obstacles, which definitely facilitates investigating the climate of the city. Another factor making it easier to take measurements of turbulent fluxes of mass and energy in Łódź is that the city, unlike other large cities in Poland, does not have a standard central sector of tall buildings, clearly towering over the urban canopy layer. The measurements of turbulent fluxes of methane are conducted in the western part of the city centre (51°47'N, 19°28'E, Fig. 1), in an area with the highest population density, reaching 17.2 thousand persons per km^2. The average percentage of artificial surfaces (buildings, sidewalks, streets, squares, etc.) in this part of town reaches 62%, the remaining part being covered with vegetation, of which only 10% are trees (Kłysik, 1998). The vegetation is distributed unevenly in the form of lawns and trees growing along the street canyons. In the immediate vicinity of the measurement point, 3-5 storey 15-20 m high buildings dominate, built mostly in the 20th century. Most of them are characterised by flat roofs covered with black tar paper or sheet metal. 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 trees growing in the area are mostly deciduous and their height usually does not exceed the height of the buildings, which results in a well-formed roof surface with an average height of 11 m. The height of displacement 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 centre is surrounded by industrial and residential areas with tall 10-12 storey buildings or loosely built-up with single-family houses. 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 local climate conditions can be found, e.g. 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 station for measurements of turbulent exchange 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), but methane fluxes have been studied since July 2013, when the existing station for measuring sensible heat flux as well as water vapour and carbon dioxide was equipped with a fast response sensor for methane concentration fluctuations in the atmospheric air. The measurement kit 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). Based on the data obtained during the study period, the source area of turbulent fluxes was estimated (Fig. 1). To this end, Schmid's method (Schmid, 1994) was used, and all available data were used for the analysis. The analysis was performed for unstable stratification conditions ($(z - z_d)/L < -0.05$) at the noon hours (from 10 a.m. to 2 p.m.). The significant height at which the measurement sensors were installed resulted in a large area of the source fluxes, which, depending on the wind direction, ranged from 250 to 750 m away from the measurement station during the study period (Fig. 1). The investigated sector of the city centre is a dense network of street canyons made available for motor traffic, i.e. one of the most important sources of greenhouse gases to the troposphere. The combustion of fossil fuels in vehicle engines produces water vapour, carbon dioxide and methane (when combustion is incomplete), which may also come from another source, i.e. leakage from vehicle natural gas tanks. Moreover, the measurement point is surrounded by a dense natural gas pipeline distribution network whose leaks lead to methane emissions into the troposphere (Fig. 1, bottom left). The dense sewerage system is another source of methane (Fig. 2, bottom, right).

2.2 Instrumentation and data processing

The measurements of the turbulent fluxes of methane were carried out using a standard measurement kit. Its main unit was an ultrasonic anemometer RM Young model 81000 (RMYoung, Traverse City, Michigan, USA), enabling the measurement of vertical wind velocity fluctuations. The station was equipped with a methane fluctuation sensor with an open measurement path LI 7700 (Li-cor, Lincoln, Nebraska, USA). As the final calculation of methane flux also requires the values of sensible heat flux and water vapour in the place of observation (LI 7700 instruction manual), the measurement kit also included a sensor of the fluctuations of water vapour and carbon dioxide LI 7500 Infra-Red CO_2/H_2O open path analyser (Li-cor, Lincoln, Nebraska, USA). The fluctuations of air temperature necessary for the calculation of sensible heat flux were measured using the aforementioned ultrasonic anemometer RM Young. The whole measurement system was attached ca 1 m below the top of the mast (Fig. 2, middle). On the horizontal arm, on the south-eastern side of the mast at a distance of about 60 cm from the mast, the LI 7500 head was placed, and the ultrasonic anemometer was then installed at a distance of 20 cm. The LI 7700 methane sensor was installed on an additional arm, slightly lower, so that the centre of its measurement path, which is about 4 times longer than the paths of LI 7500 and ultrasonic anemometer, was at a similar level. As follows from earlier analyses, the influence of the mast whose diameter is about 0.15 m is negligible and does not generate a flow distortion (for details, see Fortuniak et al., 2013). All of the aforementioned sensors measured the fluctuations of parameters with a frequency of 10 Hz. Immediately before starting the measurements in July 2013, the sensor for measuring H_2O and CO_2 fluctuations 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, with the methane sensor needing it in the first place, as its mirrors proved to be highly susceptible to grime (air impurities, bird droppings, atmospheric deposits, drying raindrops or melting snowflakes). Although the manufacturer had equipped the instrument with a mirror heating and condensation anti-freezing system as well as a cleaning system which, by means of a pump, applied the cleaning liquid to the lower mirror; in practice, however, especially in autumn and winter, this turned out to be insufficient. There were situations, for example 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 (RSSI - Relative Signal Strength Indicator) is less than 10%, this means that the measurement path was blocked by external factors. During the measurements, however, it was decided to tighten this criterion, and in order to calculate the fluxes, the methane fluctuation values observed at RSSI >20% were chosen. The signal strength of the instrument when measuring the concentration of methane only in about 8% of cases exceeded 70% (Fig. 2, right), while observations at 20%<RSSI<70% had a much greater share, and most often, in 20% of cases, the signal strength value 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

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together with fast changing data archived on a PC. The turbulent fluxes of methane were calculated using software written by the authors in Fortran 77.

The methane flux (FCH_4) was determined directly from the definition as the covariability 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):

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

The w' and $\rho CH4'$ 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 intake by the urban surface. In the calculations, block averaging was used, with 1 hour being 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 covariability 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 LI 7700 manufacturer's recommendations, the correction terms related to air density fluctuations affecting both the spectroscopic response and the mass density retrieval were applied (LI 7700 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 the purpose, and 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, which classified the data as suitable for further analysis when and only when all the three tests confirmed that the condition of stationarity was met. A milder criterion, indicating good data quality if at least one test suggested stationarity, did not meet the expectations because it accepted a number of data with unrealistically high positive values and a substantial number of fluxes with high negative values whose existence is physically difficult to explain. On the one hand, the restrictive evaluation of the data reduced the number of data suitable for further analysis by 23.8%, but on the other hand, uncertainty regarding their quality was kept to a minimum. Earlier, about 10% of the data were not registered due to problems with electricity and the computer 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 LI 7700 sensor to measure the concentration of methane properly (precipitation and atmospheric deposits, saturation of air with water vapour, impurities, etc.). This problem used to occur particularly in autumn and winter (Table. 1) when frequently cleaning the sensor placed on the mast was impossible. As a result, the percentage of good data was 36.4% (Table. 1).

3 Results

3.1 Climate background

The climate of central Poland where Łódź is situated is a typical transitional climate of moderate latitudes, formed 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 years were hot, with heatwaves occurring, and 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 average 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-year. The maximum solar radiation totals were observed in July (688 $MJ \cdot month^{-1}$ in 2014 and 697 $MJ \cdot month^{-1}$ in 2015), while the minimum totals occurred in the winter months when they fell below 100 $MJ \cdot month^{-1}$. The monthly radiation balance totals were almost 400 $MJ \cdot month^{-1}$ in July, while in the winter months they became negative and reached even -56 $MJ \cdot month^{-1}$ (December 2013). The average wind speed in the period was 3.1 $m \cdot s^{-1}$, with slightly higher values in winter (3.4 $m \cdot s^{-1}$) and lower in the summer (2.8 $m \cdot s^{-1}$ on average). The study area of the city is dominated by air flow from the west (for details, see Fortuniak et al., 2013). Generally, it can be noted that during the measurement period, atmospheric instability or neutrality conditions prevailed in the city centre. A stable air stratification could rarely be observed in the centre of Łódź, only in 7.6% of cases (from 2.9% in winter to 10.4% in summer). The frequency of neutral and unstable stratification was very similar and was, respectively, 46.0% and 46.4%. Instability prevailed in summer (51.6% of cases), while neutrality was 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 equilibrium appeared in the daytime in 19.7% (neutral) and in 80% (unstable) of cases. At night, atmospheric neutrality prevailed (67.0% of cases), while instability was 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 $MJ \cdot month^{-1}$ and 120-150 $MJ \cdot month^{-1}$, respectively). The values of the Bowen ratio $B=Q_H/Q_E$ were typically urban, i.e. greater than 1 (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 (vehicle traffic, domestic heating, etc.), were the largest. The typical values exceeded 20 $\mu mol \cdot m^{-2} \cdot s^{-1}$ and had a maximum of ~55 $\mu mol \cdot m^{-2} \cdot s^{-1}$. In summer, when the consumption of carbon dioxide by urban vegetation and reduced emissions of this gas due to the lack of need to heat homes contribute to a decrease in the intensity of net exchange, the minimum values of FCO_2 were observed, from -10 to 10 $\mu mol \cdot m^{-2} \cdot s^{-1}$.

3.2 Annual variability of FCH_4

The two-year measurements of turbulent methane flux (FCH_4) revealed a number of characteristics of the exchange of methane in the city-troposphere system. First of all, regardless of the season, there was a definite domination of positive values of FCH_4 (Fig. 3). On average, the percentage of positive values over the study period was 93.7%, being slightly greater in the cold season (94.6%) than in the warm season (93.2% of cases). 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 clearly 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. 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 occurs an increase in methane emissions associated with the combustion of fossil fuels, which results from the increased discharge of motor vehicle exhaust gas, being a significant source of methane in the city. (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 during the use of domestic gas burners. Certain amounts of methane are also produced by heating ovens (Ciais et al., 2013). The absence of inventory data makes it difficult to verify these dependencies in the case of Łódź; however, the increased values of the flux of methane are clearly visible in the periods of rapid drops in air temperature, e.g. in late October or late November and December 2014 (Fig. 3). A pronounced annual cycle can also be seen in the time 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, 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 as compared to the previous one. 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 measurement, 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 about 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 turbulent exchange of methane (Table 3). 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 twice greater. An exception is the aforementioned summer of 2013.

3.3 Diurnal variability of FCH_4

Figure 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). Most importantly, the average daily variability in the successive months confirms the above described annual variability: higher values of FCH_4 occurred in the cold season. Furthermore, the average daily variability, regardless of month and time of day, is always

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positive, which means that the emissions of methane definitely dominate over its uptake by the urban surface. In the case of the daily pattern, averaged for the entire measurement period, it certainly represents 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 afternoon (19.00 - 20.00 UTC + 1). During the maxima, the values of FCH_4 reached almost 40 nmol·m^{-2}·s^{-1}, whereas during the noon hours and at night they dropped to 26-28 nmol·m^{-2}·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·m^{-2}·s^{-1}, and its source may be the sewerage system or the natural gas distribution system. Before noon and in the afternoon, additional sources of methane (vehicle traffic, combustion of natural gas, leaks from gas network, associated with the distribution increasing during the day) are activated, increasing the flux by 10-12 nmol·m^{-2}·s^{-1}. Due to the lack of inventory data, the above considerations are only hypothetical. In the following months, the average daily variability was not so clear. 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 24 hours. 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}. At that time, the double daily maximum was easier to identify, and in November, December, January and February the afternoon peak seemed to be by a few nmol·m^{-2}·s^{-1} 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 (cooking, heating homes) and the diurnal variability of motor vehicle traffic, which is often accompanied by traffic jams in winter. In the warm season of the year (and especially during the holiday 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 FCH4 in this season is even up to 50 nmol·m^{-2}·s^{-1}, while in the warm season it rarely exceeds 20 nmol·m^{-2}·s^{-1}.

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3.4 Monthly and annual exchange of FCH_4

Based on the average daily patterns of FCH_4 calculated for each month, the exchange of methane in the successive months of the study period was determined (Fig. 5). The highest values occurred in winter when they were up to 2.0 $g \cdot m^{-2} \cdot month^{-1}$, and in January and February 2014 they exceeded 2.5 $g \cdot m^{-2} \cdot month^{-1}$. The summer values were more than twice lower and dropped to 0.7-0.8 $g \cdot m^{-2} \cdot month^{-1}$. The autumn of 2013 was characterised 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). Therefore, 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 $g \cdot m^{-2} \cdot month^{-1}$). The next winter, the monthly exchange of methane between November and March differed only slightly, 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 the mean January temperature in the previous winter season 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 gas in the air.

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 supplementing the long-term data series of turbulent fluxes of methane in urbanised 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) are required 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 ~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·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 differences in the exchange of methane described in section 3.4, from the point of view of 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 9.2% lower than in 2015.

3.5 Weekly differences of FCH$_4$

Since the turbulent exchange of methane in the city is associated with anthropogenic sources of this gas, a weekly cycle of FCH$_4$ should be expected, similar that that seen in the case of carbon dioxide exchange (Pawlak et al., 2011). Based the on 1-hour data for FCH$_4$ recorded in the period from July 2013 to August 2015, an average daily flux of 44.3 mg·m^{-2}·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. it was 45.2 mg·m^{-2}·day^{-1}. On the other hand, the average daily exchange of methane during weekends (Saturday and Sunday) amounted to 42.3 mg·m^{-2}·day^{-1} and was therefore lower by 4.5%. Thus, it can be concluded that, on average, in the study period, anthropogenic sources of methane were less active at weekends compared with working days. 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) mg·m^{-2}·day^{-1} when compared with the average for the whole week. The average daily exchange at weekends was, in turn, lower by respectively 4.0% and 4.7%. 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

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to be higher and amounted to +1.6% (spring) and 3.8% (autumn). Without the inventory data, it is difficult to explain such values of the fluxes, especially because in the case of carbon dioxide fluxes, higher values are observed on working days compared to weekends throughout the year (Pawlak et al., 2011).

3.6 Methane turbulent exchange and wind direction

The centre of Łódź is the most densely built-up area of the city. The measurement point is located in an area of uniform similar building density parameters, 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 CH_4 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·m^{-2}·s^{-1} (Fig. 8, left). However, it is difficult to regard the relationship urban design-FCH_4 as certain, due to the increased values of FCH_4 coming also from the south-western sector (approximately 40 nmol·m^{-2}·s^{-1}). Of course, such a relationship cannot be ruled out; however, the local point sources of methane may play an important role, but are difficult to identify. In the case of the south-western sector, the LPG station located approximately 800 m from the measurement station may be such a source. The distribution of average values of FCH_4 depending on the wind direction, calculated for the cold half of the year (Fig. 8, middle), suggests that in this season of the year the 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 nmol·m^{-2}·s^{-1}. Therefore, the sources could be, e.g., 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, regardless of the wind direction, were significantly lower (less than 30 nmol·m^{-2}·s^{-1}, Fig. 8, right), and contrasts between the sectors were not too clear. An exception is the clearly visible elevated value of FCH_4, associated with the airflow from the south-western sector.

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3.7 Methane turbulent exchange in relation with carbon dioxide fluxes

The measurements of turbulent mass fluxes in urban areas are performed relatively rarely (Aubinet et al., 2012). This applies to the fluxes of carbon dioxide, but in the first place to the fluxes of methane. While the measurements of FCO_2 in cities have been carried out for more than a decade and the results summarising such long-term measurements in at least a dozen cities around the world have been published to date, similar results concerning the fluxes of methane are still lacking. During more than two years of measurements in Łódź, both FCO_2 and FCH_4 were measured and therefore the question about the temporal covariability of both fluxes should be asked, and, consequently, whether the exchange of methane can be estimated based on the knowledge of the flux of CO_2. To this end, 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 - bigger fluxes of CH_4 are accompanied by larger fluxes of CO_2. Unfortunately, the values of the coefficient of determination of 0.57 and 0.56, which were not very high, leave no illusions about the possibility of using FCO_2 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. It is therefore difficult to talk about covariability of the fluxes of CO_2 and CH_4 in the centre of Łódź, which could, for example, facilitate the process of filling gaps in the series of methane fluxes based on the FCO_2 data.

4 Summary and conclusions

The measurements of methane flux (FCH_4) carried out in the centre of Łódź for more than two years provided information on the time variability of turbulent exchanges of methane 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 carbon dioxide (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: the city centre to the 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 in the case FCO_2 (Pawlak et al., 2011). The annual exchange of methane in

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terms of pure carbon in the centre of Łódź was estimated at 13.2 gC·m^{-2}·year^{-1}, which, compared to the exchange of carbon dioxide estimated in Łódź at 2.93 kgC·m^{-2}·year^{-1}, does not seem too large a quantity. However, it should be kept in mind that the greenhouse potential of methane is much higher, which is one reason why the measurements of this gas exchange should not be marginalised in favour of carbon dioxide. At the same time, it must be noted that the centre of Łódź, in terms of intensity, is a source of methane comparable to natural areas considered to be the most productive, i.e. wetlands. The annual exchange of methane in Łódź was estimated to be 17.6 g·m^{-2}·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·m^{-2}·year^{-1} (Fortuniak and Pawlak, 2015, paper in preparation). Comparable values for the annual exchange of methane were also observed at other stations located in wetlands: approx. 16.5 g·m^{-2}·year^{-1} (Finland, Rinne et al., 2007), or 14.0 - 18.5 g·m^{-2}·year^{-1} (Sweden Nilsson et al., 2008).

Unfortunately, currently, the possibility of comparing the results obtained with those from other cities is severely limited. The only longer-term measurements of the CH_4 flux were performed in Florence (March - May 2011, Gioli et al., 2012) and in London (summer 2012, O'Shea et al., 2014). The mean values of the CH_4 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·m^{-2}·s^{-1}, while the average FCH_4 in Łódź in the same season was 4 times lower, equal to 31 nmol·m^{-2}·s^{-1}. In London, in turn, the average exchange during the summer was also several times higher than that observed in Łódź (140 and 21 nmol·m^{-2}·s^{-1}, respectively). The results of this type, however, allow only a very general comparison, and the brief periods of research prevent further 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 at the same time: before and after noon. The measurements in Florence showed no correlation between FCH_4 and air temperature (R^2=-0.04, Gioli et al., 2012), while in Łódź, such a relation 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 characterising the study area of the city in a general way. In the case of carbon dioxide 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

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flux of methane. 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).

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Table 1. Data capture of 1-hour values recorded for FCH_4 in the centre of Łódź in the period July2013 – August 2015

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

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Table 2. Monthly values of mean, median and standard deviation values of FCH_4 in the centre of Łódź in the period July2013 – August 2015 (all fluxes in $nmol \cdot m^{-2} \cdot s^{-1}$).

		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 centre of Łódź (top). Solid white lines indicate the source area with *P* = 25, 50, 75 and 90%, calculated for the turbulent fluxes measured at 10-14 hours 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. 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 Centre of Łódź (www.mapa.lodz.pl). Photo source: www.google.com

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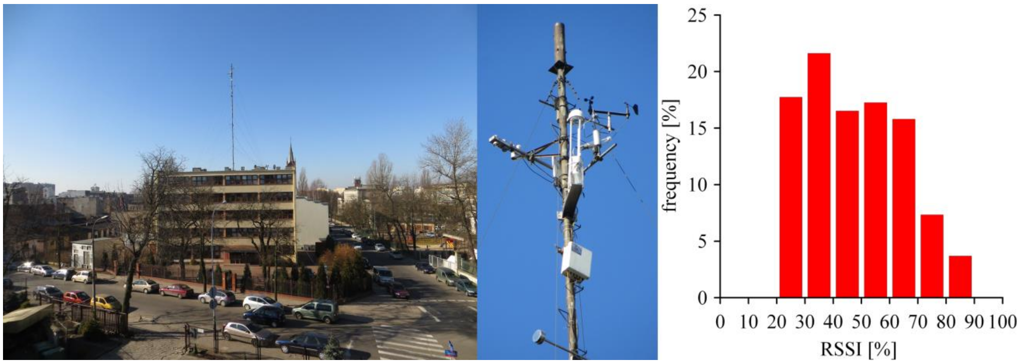

Figure 2. FCH_4 measurement site in Łódź (left) and instrumentation set (middle). Right figure shows the frequency of measured 1-hour blocks of raw data in relation with RSSI (Received Signal Strength Indicator) of Li7700 methane open path analyzer.

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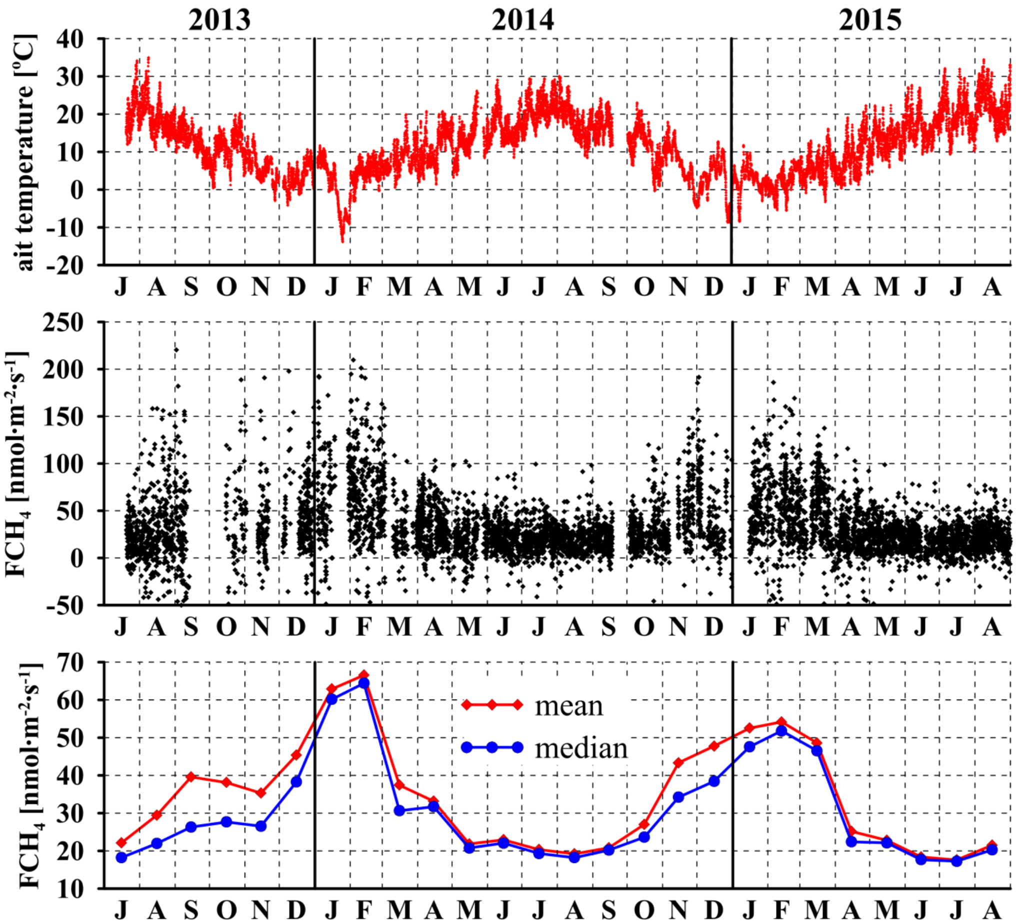

Figure 3. One hour means of air temperature, one hour net turbulent FCH_4 flux (approved by three stationarity tests), mean and median of FCH_4 measured in the Łódź centre in the period July 2013 – August 2015.

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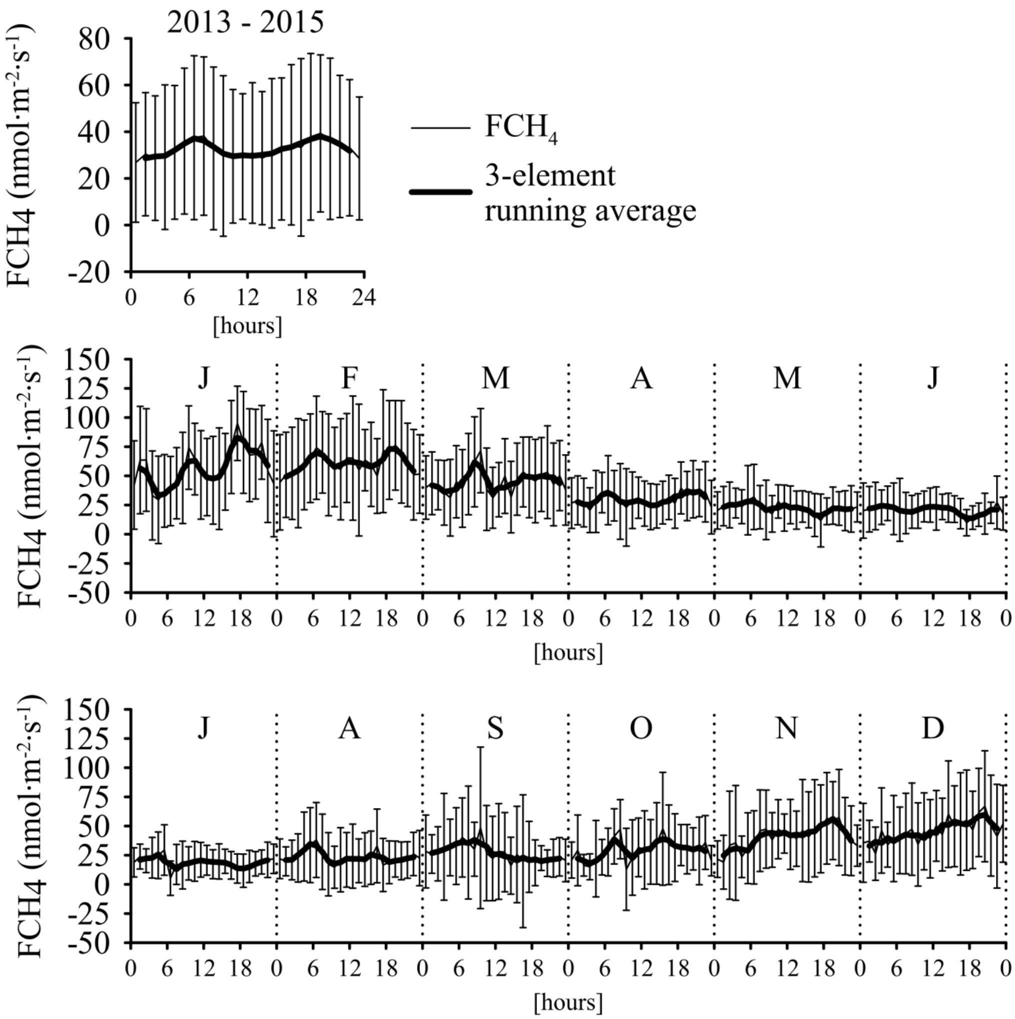

Figure 4. Mean diurnal variability of FCH_4 flux in the Łódź centre in the period July 2013 – August 2015 (top left figure) and for months. Thin and thick black lines indicate, respectively, variability of FCH_4 and 3-element running average of FCH_4. Thin vertical lines indicate standard deviation of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

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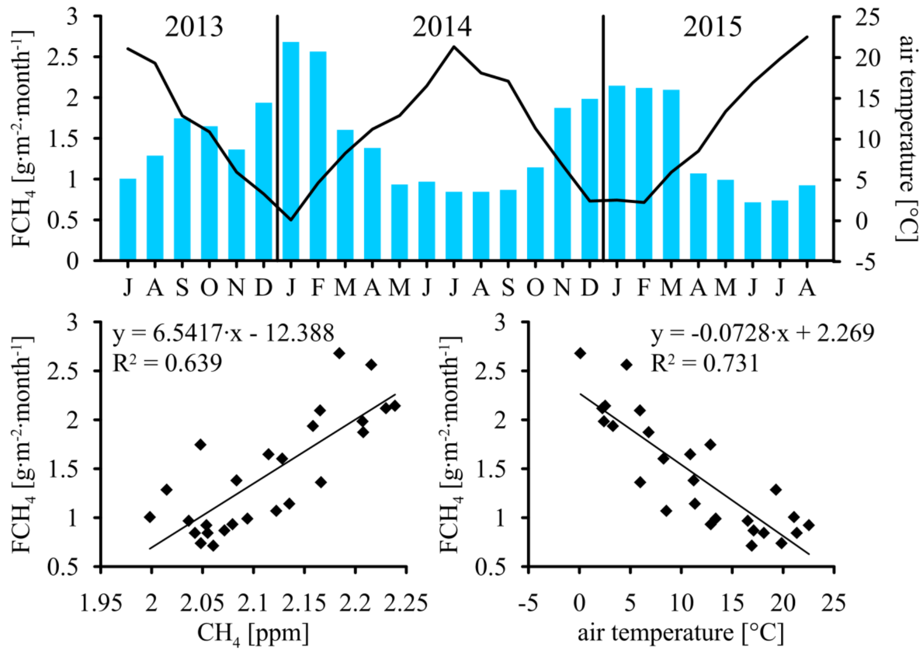

Figure 5. Monthly totals of FCH_4 (top) in relation with mean monthly CH_4 concentration (bottom left) and mean monthly air temperature (bottom right) in the Łódź centre in the period July 2013 – August 2015.

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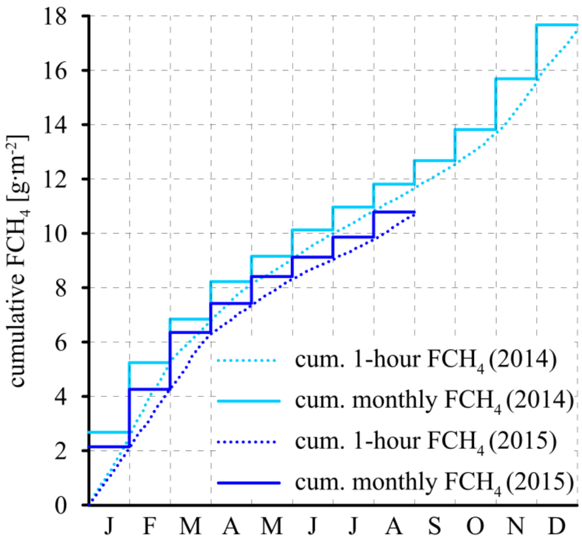

Figure 6. Cumulative fluxes of FCH_4 in the centre of Łódź in the period January – December 2014 (blues lines) and January – August 2015 (navy blue lines). Dotted and solid lines indicate, respectively, cumulative annual FCH_4 calculated on the basis of all 1-hour data and on the basis of integrated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

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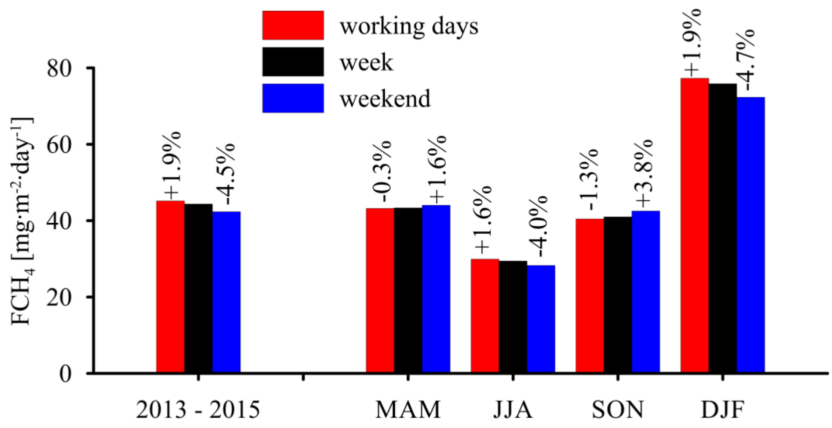

Figure. 7. Mean daily values of FCH_4 in the centre of Łódź in the period July 2013 – June 2015 calculated for study period and seasons. Red, black and blue bars indicate, respectively, mean daily exchange during working days (Monday to Friday), weeks (Monday to Sunday) and weekends (Saturday and Sunday).

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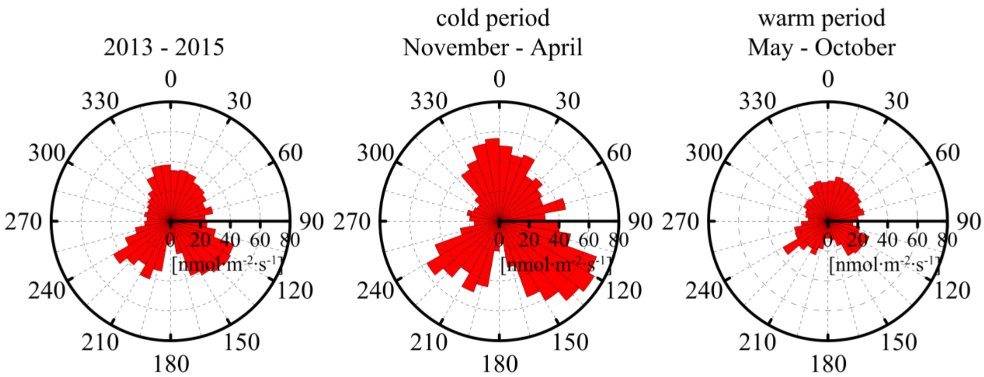

Figure 8. Mean FCH_4 calculated for all data (left), cold (middle) and warm period (right) in relation with wind direction in the centre of Łódź in the period July 2013 – August 2015.

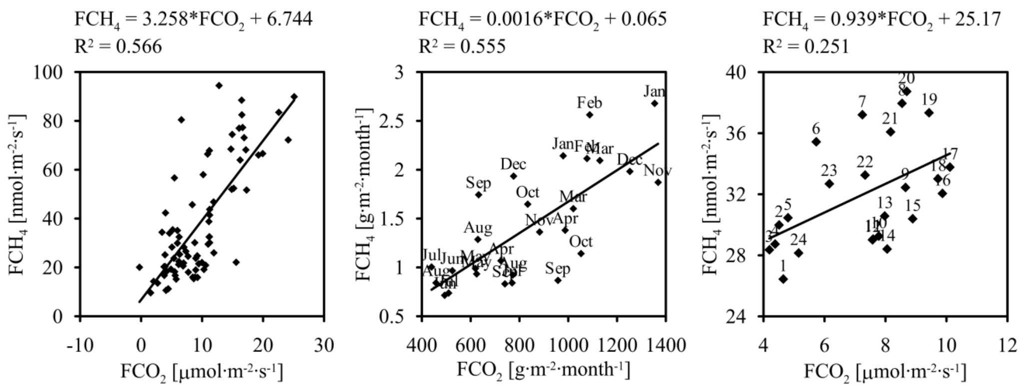

Figure 9. Mean daily (left), monthly (middle) and hourly FCH_4 fluxes against FCO_2 in the Łódź centre in the period July 2013 – June 2015.