Characteristics of temporal variability of urban ecosystem-atmosphere CO_2, CH_4, and N_2O fluxes

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Abstract. Understanding the origin and mechanisms controlling GHGs (CO_2, CH_4 and N_2O) emission spatially and temporally is critical for evaluating future climate changes. Whether the controls on GHG dynamics in urban ecosystem are similar to those in natural ecosystems are not fully understood. In the current study, the aboveground (cover vegetation + soil) and soil (including autotrophic and heterotrophic) CO_2, N_2O and CH_4 fluxes and respective carbon stable isotopic composition ($\delta^{13}C$) of respired CO_2 at natural abundance level were simultaneously measured from a re-established grassland in the urban area of central Germany. The static chamber system (combination of transparent and opaque modes) was applied to assess the effects of intensive vegetation growth during two weeks of April 2017. The values of CO_2 fluxes obtained with both transparent and opaque chambers differed significantly due to the combined effects of the incoming photosynthetically active radiation (PAR) and temperature on vegetation and belowground processes. The average value of measured CO_2 flux with opaque chambers was 9.14 ± 1.9 (mg m^{-2} min^{-1}) vs. 2.37 ± 0.9 (mg m^{-2} min^{-1}) with transparent chambers for the re-established grassland. In contrast, soil CH_4, as well as N_2O fluxes were not different significantly for both opaque-transparent chamber measurements. Current magnitude provides the pattern of the urban ecosystem source/ sinks potential during ambient light conditions.

1 Introduction

Carbon dioxide, nitrous oxide and methane – currently the most prevalent greenhouse gases (GHG) have been increasing quite rapidly. Rising atmospheric CO_2, CH_4 and N_2O concentrations are directly affected by human activity. Thus, the fossil fuel-derived emissions (vehicle exhaust, electric and heat power plants and domestic heating), the effects of land use change and land management contribute significantly to natural processes in ecosystems (carbon balance in soil and live vegetation). Large amounts of soil C can be released as CO_2. The released CO_2 is supposed to derive from the rhizosphere

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respiration including root and microbial respiration and the remainder from organic matter decomposition [1]. Biogenic CH_4 is also produced as a result of microbial decomposition of soil organic matter under anaerobic conditions [2]. Nitrogen (N) is a one of the key elements for plant growth and development and is usually supplied through: organic matter decomposition; biological N_2 fixation from the atmosphere and in the form of N-fertilizer [3].

Studies on the land-atmosphere gas exchange have been conducted at a wide range of ecosystems including human-modified areas. Still, there is a large misbalance between information on GHG fluxes from natural and urban ecosystems [4]. The various components of the soil/atmosphere system can contribute to the complexity of the carbon, nitrogen cycle, which are especially critical and variable in highly dynamic urban areas. Urban ecosystems have more complex GHG emission source configuration because they depend on multiple human-induced factors, such as population density, human activities, and fossil fuel mix, as well as other factors including city's geospatial features, local climate, attributed soil characteristics and plant physiological processes [5-6]. Nevertheless, the certain mechanisms controlling gas fluxes from anthropogenic ecosystems are not fully understood [7].

To understand the mechanisms and factors controlling ecosystem gas fluxes over urban environment the stable C isotope signatures ($\delta^{13}C$) can be effectively applied [4]. In-situ measurements of land surface CO_2, CH_4 and N_2O fluxes combined with field manipulation studies and evaluating the drivers of land-atmosphere interactions, as well as the isotopic analyses provides the basis to assess how the urban ecosystems responding to anthropogenic pressures. According to research covering the last decade, the $\delta^{13}C$ of urban CO_2 sources is affected by two opposing factors: first, through the physiological stress caused by atmospheric and soil pollution the ratio of intercellular to ambient CO_2 concentration decreases with increasing the $\delta^{13}C$-CO_2; second, the combustion of more ^{13}C-depleted fossil fuels causes the decreasing of the $\delta^{13}C$-CO_2 in urban atmosphere [8-9]. Hence, the urban atmosphere has relatively low ($\delta^{13}C$) values of CO_2, coupled with an increase of the GHGs concentration predominately due to the fossil fuel combustion.

The urban ecosystems respiration studies are scarce as compared to studies on natural ecosystems (particularly in temperate forests and meadows) [10-11]. Understanding the magnitude and distribution of CO_2, CH_4 and N_2O emissions spatially (land surface structure) and temporally (over diurnal and seasonal time scales) is important to estimate the present and future climate impacts. The primary objective of this study is to consider the biological and physical drivers controlling the GHG exchange (CO_2, CH_4, N_2O) between the atmosphere and anthropogenic ecosystems. It is important to determine how variations in climatologic and hydrologic factors (soil temperature and water availability) affect vegetation and belowground processes, namely intensity of photosynthesis and soil respiration. The work also explores the role of intensively growing re-established grassland: how availability of aboveground vegetation (shoots), and clear cutting actually affecting the atmospheric concentrations of CO_2, CH_4 and N_2O.

2 Materials and Methods

2.1 Site Description

The study was conducted in the city of Goettingen (Lower Saxony, Germany). The selected study site, located in the Forest Botanical Garden of Georg-August-University of Goettingen in the north-eastern part of the city [12], was chosen to represent the gradient of anthropogenic influence on ecosystems in an urban area (referred to as the city grassland a

moderately polluted area – city background). The climate of the area is temperate humid: the mean annual temperature is 8.4°C, the mean annual precipitation is 628 mm, with mild winter and moderately humid summer, and the annual average wind speed is 12 km/h from South-West (SW) [13]. The air temperature, relative humidity, precipitation, photosynthetically active radiation (PAR) were recorded from an automatic meteorological station in the Botanical Garden of the University of Goettingen at 10-min intervals on 8 sampling dates within two weeks during April 2017 [14]. The mean ambient temperature range was 12–18 °C, the wind speed did not exceed 1.8 m s^{-1}, the PAR varied from 157 up to 482 μmol·m^{-2}·s^{-1} for 15 h a day at 72% relative humidity.

2.2 Field Experiment

The ecosystem respiration and CO_2 uptake by photosynthesis, CH_4 emitting and oxidizing activity and N_2O emission were measured using static (transparent and opaque) chamber method [15]. Chambers were made of acrylic glass (plexiglass, fully colorless with excellent optical properties) with a thickness of 5 mm, 25 cm in diameter and 25 cm in height (a chamber volume is ca. 16 L, area covered 0.049 m^2). Chambers were placed on the ground surface with vegetation (mixture of typical perennial grasses) using collars. Collars (lower part of a chamber - anchor) were inserted ~ 2 - 5 cm into the soil leaving ~ 5–7 cm above the soil surface two weeks before the measuring campaign. The rim of all chambers was sealed in order to isolate air in the chamber from the atmosphere. During each measurement, the gas samples were collected from the headspace at intervals of 10 min (~1; 10; 20; 30 min) in average 30 - 32 minutes after a chamber was closed. The air was pumped into aluminium foil bags by means of a mini-pump with integrated trap containing drying agent (silica gel) to remove moisture from the collected air. Before sampling, the bag was N_2-flushed and evacuated to minimize background contamination.

The contribution of vegetation to gas fluxes was explored by manipulating the vegetation cover by a clear-cut. These manipulations allowed for separating ecosystem into aboveground (removing shoots) and belowground (roots and microorganisms) compartments. This information was used to develop a model to quantify the effect of the soil temperature and moisture, and biomass on plant and soil gas dynamics.

The concentrations of CO_2, CH_4 and N_2O in samples were measured on a gas chromatograph (GC 6000 VEGASERIES 2, Carlo Erba Instruments) with an Electron Capture Detector (ECD) for CO_2, N_2O and Flame Ionization Detector (FID) for CH_4 analyses. For $\delta^{13}C$ analysis in CO_2 a Cavity Ring-Down Spectroscope (CRDS), G2131-i (Picarro Inc., Santa Clara, CA) was used. All gas measurements were conducted immediately after each sampling.

2.3 Soil Samples

Soil samples were collected from two depths 5 and 10 cm at 8 surface locations within 0.5 m of the installed chambers. Soil parameters were analysed in a laboratory to determine the initial physical characteristics (soil bulk density; soil water content/moisture; water holding capacity) and chemical properties (total nitrogen and carbon (C, N) contents; soil pH; and microbial biomass carbon (MBC). The soil pH was measured in extract with volumetric proportions of 1:3 soil:water. Soil MBC and microbial nitrogen (MBN) were determined using the chloroform fumigation-extraction method [16].

2.4 Statistical Analysis

The gas flux was calculated as a change of concentrations over time using a linear function of the slope derived from a geometric mean regression [17] and the Ideal Gas Law was used to convert the concentration from volumetric to mass units considering atmospheric pressure and temperature. Repeated measures analysis of variance (ANOVAs) was used to examine the differences in soil GHG fluxes among the treatment dates, as well as the Tukey test to identify the significance of differences between the variables.

A two-end-component mixing model, the 'Keeling plot' method [18] was used to identify the stable carbon isotope composition of the soil/ecosystem CO_2 respiration and correct for the atmospheric CO_2 admixture. As the atmospheric CO_2 concentration and its$\delta^{13}C$ the values of 400 ppm -10‰, were applied respectively [19].

3 Results and Discussion

The main characteristics of the soil were determined before the beginning of the field experiment. The values of pH, bulk density and MBC were analyzed to relate them to the fluxes of C and N. Soil on the site can be classified as Anthrosol with a bulk density equal 1.12 g/cm^3 and average soil moisture content during measuring period in April 2017 about 28–39% from the total weight. The total soil C exceeded 4.1% of the dry mass and the total N was up to 0.3% of dry mass; average soil C:N ratio was estimated as 15.3. The pH ranged from 7.4 to 7.7. The variability in MBC and MBN was substantially higher as for soil organic C (SOC) and total N, respectively. The values were estimated to be 780.7 mg C kg-1 soil and 94.5 mg N kg-1 soil in the top 0–10 cm.

Data on soil C, N content demonstrate the potential for the release or/ sink of C and N depending on current and future land management practices. On the one hand, soils contain plant-derived and/or artificially introduced organic matter, on the other hand, soils contribute with GHG release to the atmosphere. Whether soils is a source or sink for CH_4 depends on the relative rates of methanogenic and methanotrophic activity. The availability of inorganic N (nitrate or ammonium) or organic N for plants and microorganisms is a complex process that depends on soil physico-chemical properties, soil erosion, leaching, ammonia volatilization, ammonia oxidation, nitrification and denitrification activities. To assess the relationships/ differences between emitted CO_2, CH_4 and N_2O a correlation-regression analysis was performed with the soil temperature and moisture, corresponding C and N contents, MBC, MBN as affected by paired opaque-transparent chamber measurements.

The results demonstrate there was significant effect of photosynthesizing vegetation on CO_2 ($p=0.004$, $n=8$) but not on CH_4 ($p=0.2685$, $n=8$), and N_2O ($p=0.1117$, $n=8$) concentrations in headspace of transparent vs. opaque chambers (Fig. 1). The CO_2 concentrations increased three times in opaque compared to transparent chamber during 30 min exposure time. The CH_4 concentrations did not differ significantly between light conditions but demonstrated clear uptake over the time of exposure from 2000-2060 to 1930-1980 ppb (Fig. 1). In contrast to CO_2 and CH_4, N_2O concentrations did not show a clear ascending or descending pattern over time and ranged from 332 to 351 ppb and from 327 to 343 ppb in opaque and transparent chambers, respectively.

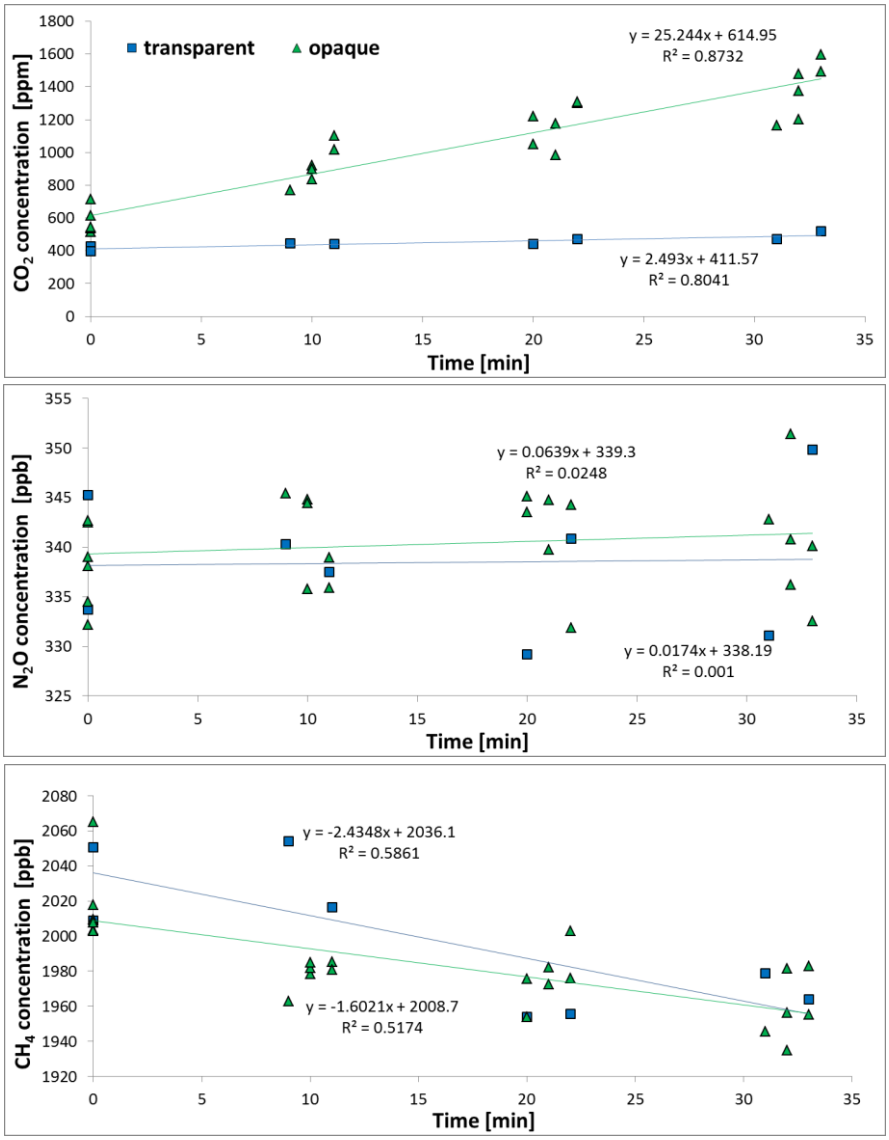

Fig. 1. The GHGs (CO_2, CH_4 and N_2O) concentrations increment during exposure time of the opaque and transparent chambers at urban grassland site in April 2017. Linear regression model and R^2 correlation coefficient are included.

The dynamics of the CO_2, CH_4 and N_2O fluxes over the period of intensive vegetation growth demonstrates the urban grasslands performed as either small sinks or small source of GHGs (Fig. 2), while both the release and uptake of C occurred. In the current study, C release was between 6.1–14.8 mg CO_2 – eq. m^{-2} min^{-1}, whereas uptake reached 0.4–1.1 mg CO_2 – eq. m^{-2} min^{-1}.This is consistent with the ranges reported in other studies [20, 21, 22]. It was expected that this grassland would be rather a small sink than a source. However, there was an important difference between experimental data set for C budgets in an experimental plot over urban locations compared to emissions from several grassland sites across Europe [23, 24]. In general, the net ecosystem CO_2 exchange (NEE, mg CO_2 m^{-2} min^{-1}) measured in urban grassland was positive what means the ecosystem was acting as a CO_2 source.

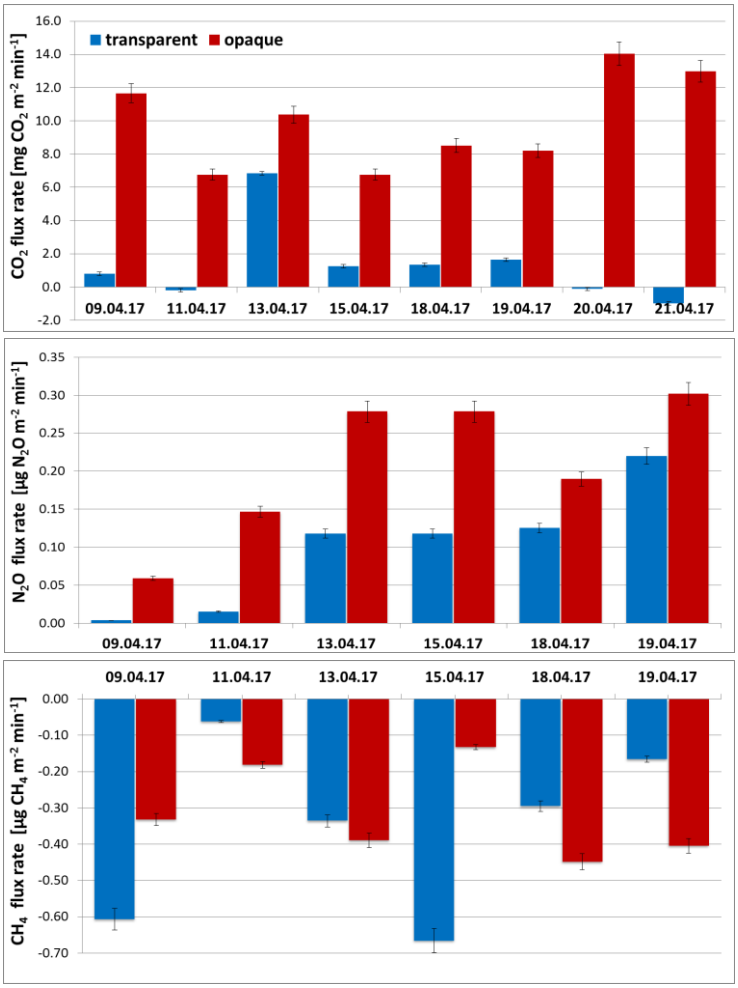

Fig. 2. The mean GHGs (CO_2, CH_4 and N_2O) fluxes with their uncertainties (standard error) observed with the opaque and transparent chambers at study site (urban grassland) during spring April 2017 sampling campaigns. The negative sign indicates a sink of GHGs.

The concentration of CO_2 in a transparent chamber did not demonstrate pronounced increase during the chamber exposure (Fig. 1), therefore the net flux was more than 3 times less as compared with dark conditions, indicating grass species assimilated up to 85% of emitted CO_2 (Fig. 2). The positive NEE may be explained by the beginning of vegetation season and weather conditions in April 2017. In particular, the grass on plots was not fully developed though experienced the intensive growth (own observations). As a result, the photosynthetic activity wasn't maximal. Also, there were cloudy days during measurement campaign, so the amount of radiation reaching the vegetation was decreased. However, on few dates (11.04.2017, 20.04.2017, 21.04.2017) a negative NEE value of -0.204 mg CO_2 m^{-2} min^{-1} was estimated (Fig. 2) representing the possibility of the urban area to sequester C. Negative emission patterns of the CH_4 fluxes with the transparent and opaque chambers showed that CH_4 oxidation has occurred in grasslands: an average uptake by soils was estimated as 0.31 µg CH_4 m^{-2} min^{-1}. The average N_2O flux was equal to 0.09 µg N_2O m^{-2} min^{-1} and 0.21 µg N_2O m^{-2} min^{-1} for transparent and opaque chambers, respectively. The significant difference in soil GHGs flux was determined between the transparent and opaque chambers during the measurement period ($P > 0.05$).

The correlation analysis revealed total soil CO_2 flux was strongly influenced by soil temperature and moisture conditions (ANOVA: temperature effect R^2=0.78; F=2.43, df=5, p>0.1411; moisture effect R^2=0.83; F=4.19, df=3, p>0.1107). In addition, CO_2 emission was strongly correlated with PAR (transparent chamber observation), R^2=0.86. The measured concentration and $\delta^{13}C$ values of CO_2 in different treatments demonstrated a strong correlation (R^2=0.89–0.95, p<0.05).

The manipulation with aboveground plant biomass showed that the concentration of CO_2 decreased (by ca. 30%) after clear-cutting of grass shoots indicating the role of vegetation in regulating ecosystem-derived CO_2 flux. The clear-cutting decreased GHGs by 1.1-1.2 times in transparent chambers compared to opaque chamber measurements. The removal of shoots slightly intensified the CH_4 oxidation (from -0.44 to -0.63 μg CH_4 m^{-2} min^{-1}) but this acceleration was insignificant. Potential increase of CH_4 oxidation with the clear-cutting may reflect the decrease of competition in the rhizosphere of plants for the C substrates – with the decrease of input of recent plant photosynthates the methanotrophic microorganisms got relative advantage demonstrating increase in the activity. This hypothesis, however, needs to be tested in further studies. Measured at the site, N_2O fluxes were small, varied in the range between ~0.12 to 0.17 μg N_2O m^{-2} min^{-1}. Many studies have shown that N_2O emission could be restricted by N availability and the conditions with relatively narrow "redox window" in soils. Neither fully dry conditions nor complete water locking promote N_2O emissions. N losses through leaching and increased C content may limit N cycling [25, 26]. The total N content of aboveground plant biomass from the study site did not exceed 0.3% of dry mass with a high C:N ratio, which may have constraints on mineralization of N. The CO_2 flux after clear-cutting correlated strongly with changes in air temperature (R^2=0.69; p>0.05). At the same time, increasing soil surface temperature after cutting could accelerate the decomposition and might also contribute to the elevation of the GHG fluxes [27]. The isotope ratios of C in CO_2 were used to distinguish between plant root and microbial respiration [28]. The $\delta^{13}C$-CO_2 decreased from -26.7±0.46‰ (isotope signature of an ecosystem (soil + vegetation) respiration) to -27.4±0.54‰ (isotope signature of heterotrophic respiration) after removal of vegetation cover and may reflect the lower discrimination of plants against heavier ^{13}C as compared with soil microorganisms.

4 Conclusions

The GHGs (CO_2, CH_4 and N_2O) fluxes from urban ecosystem during the intensive growth of re-established grassland (beginning of vegetation season) were mainly controlled by temperature and soil water content (R^2=0.81–0.87, p>0.05). The CO_2 balance between ecosystem respiration and fixation by photosynthesis shifted the flux towards positive values (ca. 2 mg CO_2 m^{-2} min^{-1} under light conditions). In contrast to CO_2, CH_4 dynamics demonstrated steady sink of C due to the oxidation (0.31 μg CH_4 m^{-2} min^{-1}). Relatively low N_2O flux (0.1 μg m^{-2} min^{-1}) revealed the re-established grassland ecosystem as not an important source of this GHG (under conditions of the study). The manipulation with the vegetation cover and meteorological factors had both direct (temperature increase) and indirect (through the decrease of recent plant photosynthates inputs) effects on the stable carbon isotope composition of CO_2. In the long-term, we conclude, the increasing anthropogenic pressure, land use changes and cities expansion may bring to a significant reduction of the C sink. To define the role of re-established grasslands as potential sources or sinks for CO_2 in urban ecosystems it is important to conduct long-term measurements of GHG fluxes and C balance with validation of existing and development of new mathematical models.

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