Cities as Net Sources of CO₂: Review of Atmospheric CO₂ Exchange in Urban Environments Measured by Eddy Covariance Technique

Erik Velasco and Matthias Roth* Department of Geography, National University of Singapore

Abstract

Cities are main contributors to the CO_2 rise in the atmosphere. It is clear that accurate estimates of the magnitude of anthropogenic and natural urban emissions are needed to assess their influence on the carbon balance. Increasingly the eddy covariance (EC) method is applied in urban environments to quantify CO_2 fluxes. The technique has many advantages over other methods. It is a direct measure of the flux that includes all major and minor natural and anthropogenic sources and sinks, is *in situ*, non-intrusive, quasi-continuous and with proper selection of the footprint can represent a large upwind extent similar to the size of a complete urban neighborhood. This article reviews the basic principles and requirements of the EC technique, discusses its application in the urban context and summarizes observations from over 30 EC systems, primarily deployed in midlatitude cities. The results show that the urban surface is a net source of CO_2 , with vehicle exhaust and domestic heating as the major contributors while urban vegetation is not capable to completely offset the anthropogenic emissions. The largest CO_2 fluxes have been observed in densely built up locations in city centers, followed by sites within urban core, while the lowest fluxes are found in suburban neighborhoods. The daily net CO_2 exchange depicts a strong relationship with vegetation fraction, but not with population density.

Introduction

Cities are the most visible physical sign of anthropogenic global change. Due to their dense population, settlement structure, transportation networks, energy use and altered surface characteristics, they fundamentally change the carbon cycle, as well as the state of the atmosphere and climate (Mills 2007). Cities have an intensive metabolism requiring a significant inflow of artificial energy, and energy consumption per unit area is orders of magnitude higher than the same for rural, vegetated or less developed surfaces. Although cities take up only $\sim 2\%$ of the global land area, they release more than 70% of the total emissions of carbon dioxide (CO₂) of anthropogenic origin (Canadell et al. 2009). CO₂ is the greenhouse gas (GHG) of most concern due to its rapidly increasing concentration in the atmosphere (from ~ 280 ppm about 150 years ago to the present concentration of \sim 388 ppm). Fossil fuel combustion (including urban and non-urban sources) together with small contributions from cement manufacturing is responsible for 88% of the anthropogenic CO₂ emissions while land-use change, primarily deforestation, is accountable for the remaining 12% (Le Quéré et al. 2009). CO2 emissions now represent 77% of the total anthropogenic GHG emissions and account for 63% of the direct radiative forcing responsible for global climate change (Hofmann et al. 2006).

In cities, CO_2 is emitted by the burning of fossil fuel associated with transport, energy use in households and public buildings, as well as manufacturing and industry. In the

transport sector, the often dominant and fastest growing CO_2 sector, the burning of gasoline or diesel fuel results in direct emission of CO_2 [each liter of gasoline burned produces ~2.3 kg CO_2 (~1.3 m³)]. CO_2 emissions from households, public buildings and industry have a direct local contribution from combustion processes (e.g. use of natural gas or biomass for cooking and heating), as well as an emission component at the site of the electricity generation (assuming electricity is generated from burning fossil fuel) which may be located some distance away from the city. Similarly, the emissions from incinerators, airports, maritime ports, etc. do not always occur within the urban boundaries, but contribute to the total emissions from cities.

The urban CO_2 flux is also influenced by natural sources and sinks. Vegetation (urban parks, scattered trees, vegetated rooftops) removes CO_2 from the atmosphere through photosynthesis during daytime and releases a fraction of it through respiration at night, with additional uptake from soils and corresponding belowground activity. Finally, the metabolic release of CO_2 by human respiration is an important and growing component that has not yet been considered in current strategies to mitigate GHG emissions (Prairie and Duarte 2007; West et al. 2009).

The relative strength of each of the aforementioned sources and sinks of the urban carbon flux varies widely as a function of population density, industrial activity, climatic region, local meteorology, amount of vegetation, land use distribution, and socioeconomic and cultural factors that vary from country to country. It is clear that accurate estimates of the CO_2 flux are needed to understand how urban emissions and land modifications are affecting the regional carbon exchange and explore how these impacts may change with urban growth and development patterns across the full range of city diversity. Figure 1 illustrates the range of city form and structure across a sample of cities from which direct CO_2 flux measurements are available.

This article presents a review of currently available results from urban CO_2 flux measurements using the eddy covariance (EC) technique, which is the only existing method to measure directly CO_2 fluxes that include all major and minor natural and anthropogenic sources and sinks. Given the relatively recent nature of such research this review also considers work not yet published in the peer-reviewed literature (e.g. conference proceedings, articles in newsletters and research reports) but which is original and meets a set of guidelines regarding, e.g. methodological rigor. A small number of studies were excluded because they clearly did not meet basic requirements for the application of the EC technique. An overview of the methods most commonly used to estimate CO_2 fluxes in urban environments and the basic principles and requirements of the EC technique in the urban context are introduced first. A summary of urban CO_2 flux measurements is used to assess the role of cities in the carbon exchange and provides the basis for some concluding remarks and suggestions for future research.

Measuring Urban CO₂ Exchange

A number of methods exist to estimate the carbon exchange from cities. The CO_2 released from the various emission sources is typically quantified by a bottom-up aggregation process that accounts for emission factors and fossil fuel consumption data. Since CO_2 emissions are primarily dependent on the carbon content of the fuel, the emissions are calculated by multiplying the amount of fuel burned by emission factors expressed as mass of CO_2 per unit of consumed fuel (e.g. IPCC 1997). However, this simple approach does not consider the heterogeneity and variability of the emission sources. Accurate estimations require specific emission rates for each type of source, as well as



Fig. 1. Sample of CO_2 flux measurement sites (indicated by purple dot) illustrating the possible diversity across cities in terms of morphology and vegetation fraction (North is top on all images). Source: Google-Maps[®] and IAUC Urban Flux Network (http://www.urban-climate.org/).

detailed information of fuel composition, operation conditions, technology, activity levels and emission regulations. Emission rates are often derived from laboratory or specific field measurements. Fossil fuel consumption and activity levels can be obtained from local authorities or specific surveys, such as traffic counts. Complete inventories must include emissions from mobile (e.g. vehicles), area (e.g. residences) and point (e.g. industries) sources plus the natural contributions from vegetation, soil and human breathing. A complete emissions inventory also needs to account for diurnal variations in activity levels and source distribution. The latter may be obtained from maps, aerial photographs or from population density estimates. The propagation of errors associated with this bottom-up process can result in large uncertainties (e.g. Marland 2008). In many cities, particularly in developing nations, the required data to quantify the CO_2 emissions are not always available, and the emission factors may not be representative.

Other attempts to quantify and characterize CO_2 emissions from urbanized land areas include measurements of ambient concentration of CO_2 describing spatial patterns across cities (e.g. Henninger and Kuttler 2007; Idso et al. 2001), downwind and upwind CO_2 concentration measurements which are directly assimilated into transport models to obtain regional surface fluxes (e.g. Geels et al. 2007; Mays et al. 2009; Rigby et al. 2008) and isotopic analysis to partition anthropogenic and biogenic contributions (e.g. Clark-Thorne and Yapp 2003; Pataki et al. 2003).

Large uncertainties are associated with estimating CO_2 emissions using the indirect methods above. Direct measurements of CO_2 fluxes that include all anthropogenic and natural sources and sinks from a specific region can be used to evaluate emission inventories.

Such direct flux measurements are now increasingly performed in cities using the EC technique and fast-response analytical sensors. The EC technique has been widely employed to investigate the surface–atmosphere exchange of CO_2 and other trace gases over natural ecosystems, including forests, grasslands and wetlands, often as part of long-term programs such as AmeriFlux (Baldocchi et al. 2001), AsiaFlux (Mizoguchi et al. 2009) and EuroFlux (Valentini et al. 2000). The application of this technique in the urban case, however, is particularly challenging.

Methodological Considerations when Using the Eddy Covariance Method in the Urban Environment

Eddy covariance has become the method of choice to measure CO_2 fluxes over a range of land covers, including urban environments. Its application, however, is complex and careful attention has to be given to the selection of measurement sites, positioning and operation of instruments as well as data processing to obtain meaningful and representative results. For an introduction to micrometeorological theory, the reader is referred to textbooks such as Arya (2001), Kaimal and Finnigan (1994) and Stull (1988). Information on measuring turbulence statistics and CO_2 fluxes in the urban environment is available in e.g. Roth (2000) and Grimmond et al. (2002a) and about the EC technique in Moncrieff et al. (1997), Aubinet et al. (2000), Baldocchi (2003), Lee et al. (2004) and Burba and Anderson (2007).

OVERVIEW OF THEORY

The vertical transport in the atmospheric layer near the ground, known as surface layer, is dominated by turbulent motions generated by surface friction or drag on the flow and surface heating due to absorption of energy from the sun. These turbulent motions (eddies or swirls of different sizes) are embedded in the mean flow and move air containing CO_2 (and other scalar entities such as heat, moisture and pollutants) upward and downward. Figure 2 is a conceptual diagram of the atmospheric eddy transport and its application to the EC technique. Choosing as a reference the top of an instrumented tower for example, at one moment one eddy will be moving an air parcel downward with a specific vertical velocity while at the next moment another eddy will be moving a new air parcel upward with a different vertical velocity. Knowing the CO_2 concentration of each air parcel and the speed of the vertical air movement, the vertical upward or downward flux of CO_2 can be calculated. The turbulent vertical flux (F) equals the covariance (product) between the instantaneous deviations or fluctuations of the vertical wind velocity (w_i) and CO_2 mass density (c_i) averaged over a specific time interval:

$$F = \overline{c'w'} = \frac{1}{N} \sum_{i=1}^{N} w'_i c'_i, \tag{1}$$

where N is the number of samples during the averaging time, and the fluctuations are the differences between the instantaneous readings and their respective means (e.g. $c'_i = c_i - \overline{c}$). If the net flux is away from the surface, the surface is a source and the flux may be called *emission*. If the opposite is true, the surface is a sink and the flux may be called *deposition*.

From eqn (1), it follows that the CO_2 flux is expressed in units of mass per area and time (e.g. g m⁻² s⁻¹). The mass can be given in micromoles (µmol), grams of CO_2 (g) or

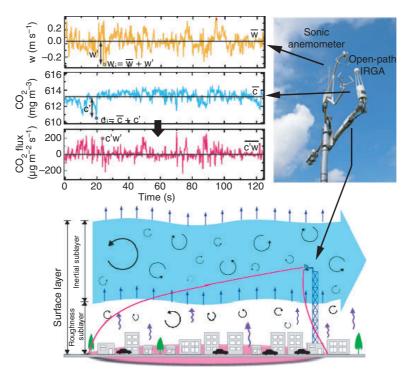


Fig. 2. Cross-section through the surface layer which forms the lowest part of the urban boundary layer (lower panel). Emissions from different sources (indicated by blue wavy and straight arrows) distributed across the threedimensional city surface are blended by turbulent eddies (black circular arrows) to produce a net exchange (positive upward flux in this example) across the surface–atmosphere interface. The flux is measured by an EC system (top right; here consisting of a sonic anemometer and an open-path IRGA) which must be mounted within the inertial sublayer to produce values representative of the general characteristics of the underlying surface within the sensor footprint (pink ellipse). Reynolds decomposition is used to derive time series of vertical wind velocity and CO_2 concentration fluctuations which yield the flux (top left).

grams of carbon (gC), the area in m^2 , ha or km^2 , and the time in seconds, hours, days or years. To convert from moles to grams, the flux is multiplied by the molecular weight of CO₂ (44 g mol⁻¹). To convert from g to gC the flux is multiplied by 3/11 (the fraction of carbon in the CO₂ molecule). The units are selected depending on the study purpose, flux magnitude, and spatial and temporal scales.

INSTRUMENTATION AND FIELD IMPLEMENTATION

An EC system to measure fluxes of CO_2 consists of a sonic anemometer and a CO_2 analytical sensor (Figure 2). Fast-response CO_2 analyzers are based on the principle of absorption of infrared radiation by trace gases, and often measure CO_2 and water vapor at the same time. They are known as Infrared Gas Analyzers (IRGA) and the sensing path can be either closed or open. For urban setups, the open-path IRGA is usually chosen. It measures *in situ* next to the anemometer (Figure 2), and does not require a sampling line and external pump to collect samples as is the case for a closed-path IRGA. Both open-and closed-path sensors respond to changes in density (mass_{gas}/volume_{air}) rather than mixing ratio (volume_{gas}/volume_{air}) of CO_2 and H_2O with respect to dry air. The measured fluxes therefore need to be corrected for fluctuations in the air density produced by fluctuations of

temperature and moisture in the air. This is usually done by applying the Webb–Pearman– Leuning (WPL) correction, which requires measurements of temperature and water vapor fluctuations (Webb et al. 1980).

Open-path IRGAs do not require frequent calibration for measuring fluxes but periodic setting of zero and span (e.g. every 15 days) using two standard concentrations below and above the monitored CO_2 range (e.g. at 350 and 500 ppm) are recommended to make accurate measurements of absolute values (Auble and Meyers 1992). The instrument response to water vapor can be verified using a dew point generator or by comparisons with data from a regular (slow-response) humidity sensor.

Turbulent motions responsible for the flux span across a wide range of eddy sizes. EC sensors have to be capable of measuring wind velocity and scalar concentration at very high sampling rates (10–20 Hz) and with high accuracy (low noise level) to capture the smallest eddies which occur very fast and are of small magnitude. The length of the averaging interval determines the size of the largest eddies that will be included in the calculation. For low measurement heights, 15 min may be adequate, but the averaging period has to be increased with increasing height because the proportion of large eddies contributing to the flux is also increasing with height above the surface (the peak of the energy spectrum is shifting toward lower frequencies, i.e. larger eddies) (Wyngaard 1973). An averaging period of 30 min or longer is therefore recommended for most applications.

To obtain representative and meaningful results, it is essential to conduct measurements at sufficient height above surfaces which are uniform in terms of topography (i.e. flat), urban morphology (i.e. buildings of similar height) and distribution of emission sources and sinks (i.e. no large factories, parking lots or urban parks). To avoid the microscale variability introduced by individual buildings, trees or emission sources and sinks characteristic of the roughness sublayer (RSL), the EC sensors need to be located above the blending height in the inertial sublayer (ISL) (also called constant flux layer). Here, flow divergence or convergence is reduced, emissions (of CO₂, H₂O, heat, etc.) have become completely blended (individual plumes have merged) by the turbulence generated at the surface and fluxes are expected to vary little with height and space and are considered representative of a well-defined neighborhood (Figure 2). The lower boundary of the ISL is about 15-40 m above ground for residential areas and higher for central city sites (Grimmond and Oke 1999); in practice, this works out to 2-4 times the mean height of buildings. The upper extent of the ISL layer is determined by the development of an internal boundary layer which responds to regional-scale land use changes in an upwind region 100-300 times the measurement height (Grimmond and Oke 1999). Bottema (1997) suggests that measurement heights should be <0.25 the height of the urban boundary layer. It is possible that under certain conditions, in particular when land-cover changes at scales of only a few kilometers, the depth of the RSL exceeds the potential depth of the ISL and no such layer exists (Oke et al. 1989). Fluxes obtained from very tall towers (>100 m) may therefore not be representative of the urban ecosystem. Tall towers may also reach above the top of the collapsing boundary layer at night, causing additional difficulties in interpreting such data.

Neither the instruments nor the tower should interfere with the turbulent motions carrying the flux, and their shape and installation must be as aerodynamic as possible. A large and solid structure as instrument platform for example will obstruct the flow and introduce additional turbulence upwind, which may be sensed by the instrument as a flux contribution (Griessbaum and Schmidt 2009; Mennen et al. 1996; Wyngaard 1988). The distance between the turbulence sensors should be small enough to allow the measurement of the smallest energy-carrying eddies but care has to be taken to prevent flow interference by the sensors themselves (Figure 2).

FOOTPRINT ANALYSIS

The height of the tower, together with the surface roughness length, turbulence intensity, wind speed and direction, and atmospheric thermal stability determine the footprint (also called source area) of the measured flux. The footprint is the fraction of the surface containing the sources and sinks that contribute to the vertical flux measured at the sensor platform (Figure 2). In the case of an extensive, homogeneous surface, the size or location of the footprint is not a major issue. However, over an inhomogeneous surface such as a city, it becomes imperative to ensure that the measured signal includes a representative sample of all sources and sinks of a certain neighborhood, without being biased toward unusual features such as e.g. a major traffic intersection or urban park.

An initial estimation of the source area of the flux measurements during daytime is to assume a footprint extending between 100 and 300 times the effective measurement height (Grimmond and Oke 1999). Since the early 1990s many footprint models have been developed using different approaches including analytical, Lagrangian stochastic particle dispersion, large-eddy and ensemble-averaged closure models. Vesala et al. (2008) review the advantages and disadvantages of these approaches. Analytical model such as those based on parameterization of Lagrangian dispersion modeling and dimensional analysis (e.g. Hsieh et al. 2000; Kljun et al. 2004; Schmid 1994) are often suitable to evaluate footprints. It is important to remember that none of these approaches have been developed exclusively for flux measurements over urbanized land areas and that their performance is still under evaluation.

The size of the footprint and location of the peak flux contribution strongly depend on atmospheric stability. With increasingly convective conditions, the former extends less in the upwind direction and the latter moves closer to the tower (Figure 3), i.e. during unstable conditions the upward transport of CO₂, or any other trace gas, originates from an area relatively close to the tower. The location of the footprint peak is typically

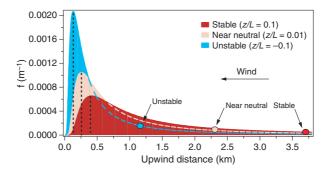


Fig. 3. Crosswind-integrated footprint evaluated for three different atmospheric stabilities (z and L are measurement height and Obukhov length, repsectively) for a hypothetical EC system mounted at 42 m above the surface in a residential neighborhood with average building height of 12 m. The area below the curve represents the flux proportion in the upwind direction (tower is located at 0.0). The upwind extent of the footprints encompassing 80% of the measured fluxes and locations of peak fluxes are indicated by filled circles and vertical dashed lines, respectively. Both move closer to the base of the tower with increasing instability (smaller z/L). Calculations are made with the analytical model of Hsieh et al. (2000) assuming a roughness height of 1 m which is a typical value for a suburban surface (Stull 1988).

between a few times the measurement height (unstable) to a few dozen times (stable) from the tower base. Mathematically, the surface area influencing the flux goes to infinity and it is necessary to define the fraction of the source area considered. Often a footprint encompassing from 70% to 90% of the total source area is acceptable (Vesala et al. 2008). The calculations in Figure 3 yield maximum footprints of \sim 3.7 km during stable conditions, which may prevail at nighttime, and \sim 1.2 km during unstable conditions. Lowering the sensor height will result in shorter footprints but increases the possibility that the observations are no longer located in the ISL (Figure 2). The footprint analysis is ideally carried out before the actual measurements to evaluate the micrometeorological suitability of a flux site and again afterwards to determine the exact location and characteristics of the sources and sinks contributing to the measurements within the monitored neighborhood to help in the interpretation of the results.

DATA PROCESSING AND QUALITY CONTROL

Data post-processing software is often included when buying turbulence sensors and a few open source codes are available on the web at no charge. However, they can only be used to compute on-line or preliminary estimates. It is necessary to adapt available software packages or design new ones to accommodate a specific sensor set-up and data acquisition systems and to calculate the turbulent fluxes of interest. Table 1 summarizes the steps that should be followed during the processing of EC data from an urban measurement program. A more in-depth discussion of each step in Table 1 is available in McMillen (1988) and Aubinet et al. (2000).

The quality of flux measurements is difficult to assess because there are various sources of possible errors, such as badly chosen sites, failure to satisfy the theoretical assumptions underlying the EC approach and inappropriate sensor installation. These effects cannot be quantified solely from the EC data and a classical error analysis and propagation will remain incomplete. Instead, Aubinet et al. (2000) suggest an empirical approach to determine whether the fluxes meet certain plausibility criteria. Besides the statistical and stationarity characteristics of the raw measurements, the frequency resolution of the EC system needs to be verified through inspection of the (co)spectra of the measured variables. An EC system attenuates the true turbulent signal at low and high frequencies, which correspond to large and small eddy sizes, respectively. This can occur due to limitations imposed by the physical size of the instruments, finite distance between co-located sensors, inherent time response limitations and any signal processing associated with de-trending or removal of the mean (Massman and Lee 2002). Inspection of the (co)spectra of the measured variables helps to determine the influence of these attenuations. For example, a logarithmic plot of the power density (co)spectra should be free of distortions (such as e.g. a -1 slope) at the low-frequency end (Chapter 2 in Kaimal and Finnigan 1994) and exhibit the characteristic -5/3 (-7/3) slope in the inertial subrange at the high-frequency end.

Applicability of the EC method and the derivation of the fluxes requires stationary conditions, i.e. statistical properties of the flow do not change with time, which permits the introduction of time averages and hence Reynolds decomposition (Kaimal and Finnigan 1994). Non-stationary conditions may occur during sunrise and sunset, during periods with changing wind direction or those affected by short-term horizontal advection of plumes from unusual local sources. Periods that do not fulfill the stationarity requirements also do not meet the (co)spectral low-frequency criteria mentioned above. They can therefore be discarded from further analysis based on the stationarity test, which is easier

Table 1. Guidelines for processing eddy covariance flux data measured in urban environment.

Step	Action	References
1	Conversion of raw data to scientific units by applying calibration factors; removal of hard spikes (i.e. unreasonable values; e.g. $CO_2 > 800$ ppm, $T > 60$ °C); identification and flagging of data gaps – if gaps represent >25% of readings in a period, then calculated fluxes need to be treated with suspicion	
2	Computation of mean values and standard deviations. Removal of soft spikes (large, short-lived, e.g. <0.4-s departures from the mean values)	Schmid et al. (2000)
3	Three-dimensional coordinate rotation for alignment of axes to the local mean streamlines. Removes the vertical advective from the total flux and eliminates errors due to sensor tilt relative to the terrain surface or aerodynamic shadow due to sensor or tower structure	Aubinet et al. (2000), Lee et al. (2004)
4	Apply Reynolds decomposition to remove mean values and obtain turbulent fluctuations ('primed' quantities). Apply a filter to remove trends (recursive digital filter is recommended for complex terrains and places where rapid changes in CO_2 concentrations are expected as is the case in a city)	McMillen (1988), Kaimal and Finnigan (1994)
5	Calculate vertical fluxes (e.g. CO_2 , momentum, sensible heat, latent heat) and other turbulence statistics over chosen averaging interval. If the CO_2 and H_2O densities were measured by a closed-path IRGA, lag time correction needs to be applied first. The lag time may be determined empirically by running a circular correlation and shifting the delay scan-by-scan until a maximum flux is found	Schmid et al. (2000)
6	Account for the effects of air density fluctuations (due to fluctuations in temperature and water vapor) on the CO ₂ and H ₂ O fluxes by applying the Webb–Pearman–Leuning (WPL) correction. This is particularly important for impervious and dry surfaces which can generate large heat but small CO ₂ and H ₂ O fluxes	Webb et al. (1980), Ham and Heilman (2003), Kondo and Tsukamoto (2008)
7	Flux correction for high-frequency loss due to sensor separation. If a closed-path IRGA was used, correction for loss due to damping of fluctuations within the sampling tube and limited instrument response time is necessary	Massman and Lee (2002)
8	Check for stationarity. If the difference between the flux obtained from an averaging period (i.e. 30 min) and the average of fluxes from six continuous sub-periods (i.e. 5 min) during the same averaging period is <60%, the data are acceptable	Aubinet et al. (2000)
9	Apply second phase of quality control to see if calculated turbulence statistics are reasonable and within pre-defined limits, otherwise they will have to be rejected. Inspect shape of (co)spectra	

to apply in an objective manner than (co)spectral shape criteria. Nevertheless, it is always recommended to evaluate (co)spectra of a number of sampling periods to verify the capability of the EC system to measure the entire range of energy-carrying eddies.

Eddy Covariance Flux Measurements of CO₂ in Urban Environments

The first urban CO_2 flux measurements by EC were carried out over a residential district of Chicago in 1995 (Grimmond et al. 2002a). Since then, the number of EC sites has grown and now includes locations representing a wide range of urban land uses (Figure 4 and Table 2). The earliest observations were restricted to short campaigns (e.g.

ux measurements reported in the peer-reviewed literature.
D ₂ fl
8
Ĕ
urbar
of
summary
Chronological
Table 2.

		Sensor				Pop.		
City, country	Deriod	neignt (z) and z/z _H	۲CZ	Land use	LCF (%) ²	density (km ⁻²)	Sonic, IRGA ³	References
Chicago – Dunning, USA	June–August 1995	27 m 4.29	House and garden	Residential	Bldg: 36 Veg: 39 IG: 25	4342	ATI SAT-211/3k, LICOR-6262 ^c	Grimmond et al. (2002a)
Edinburgh – Calton Hill, UK	November 2000	65 m 6	Old core	Commercial Residential Recreational	Bldg: NA Veg: NA IG: NA	1724	Gill Solent R1012, LICOR-6262 ^c	Nemitz et al. (2002)
Copenhagen – Frederiksberg, Denmark	2001	40 m 1.78	AN	Residential Commercial	Bldg: NA Veg: 9 IG: NA	10,923	Gill Solent, LICOR-6262 ^c	Soegaard and Møller-Jensen (2003) ⁴
Marseille – CAA, France	June–July 2001	43.9 m 2.81	Old core	Residential Commercial	Bldg: 59 Veg: 14 IG: 27	AN	RM Young-81000, LICOR-7500°	Grimmond et al. (2004)
Tokyo – Kugahara, Japan	2001-2007	29 m 3.97	Compact housing	Residential	Bldg: 33 Veg: 29 IG: 38	11,800	Metek USA-1, LICOR-7500°	Moriwaki and Kanda (2004)
Basel – Sperrstrasse, Switzerland	June–July 2002	31 m 2.07	Old core	Residential Commercial	Bldg: 54 Veg: 16 IG: 30	25,000	Gill R2, LICOR-7500°	Vogt et al. (2006a)
Mexico City – Iztapalapa, Mexico	April 2003	37 m 3.08	Compact housing	Institutional Residential Industrial	Bldg: 50 Veg: 12 IG: 38	12,000	ATI SATI-3K, NOAA-IRGA°	Velasco et al. (2005a)
Melbourne – Preston, Australia	February 2004– June 2005	40 m 3.33	House and garden	Residential	Bldg: 45 Veg: 37 IG: 18	2939	CS CSAT3, LICOR-7500°	Coutts et al. (2007)
Melbourne – Surrey Hill, Australia	February–July 2004	40 m 2	House and garden	Residential	Bldg: NA Veg: 47 IG: NA	NA	CS CSAT3, LICOR-7500°	Coutts et al. (2007)
Firenze – Ximeniano, Italy	September 2005–	33 m 1.32	Old core	Residential Commercial	Bldg: 69 Veg: 2 IG: 29	3561	RM Young-81000V, LICOR-7500°	Matese et al. (2009)
Helsinki – SMEAR III, Finland	December 2005–	31 m 1.55	NA	Institutional	Bldg: 10 Veg: 30 IG: 60	NA	Metek USA-1, LICOR-7500°	Vesala et al. (2007)

© 2010 The Authors Geography Compass © 2010 Blackwell Publishing Ltd

\sim
σ
CD.
ž.
2
2
÷20
2
-
0
U.
-
\sim
-
Ð
0
B

City, country	Observation period	Sensor height (z) and z⁄z _H	۲CZ	Land use	LCF (%) ²	Pop. density (km ⁻²)	Sonic, IRGA ³	References
Mexico City – Escandon, Mexico	March 2006, February 2009–	42 m 3.5	Compact housing	Residential Commercial	Bldg: 57 Veg: 6 IG: 37	7412	ATI SATI-3K, ADC OP2°	Velasco et al. (2009)
Münster – near city center, Germany	August 2006–	65 m 4.33	House and garden	Residential Commercial Recreational	Bldg: 40 Veg: 35 IG: 23 ⁵	NA	RM Young-81000V, LICOR-7500°	Schmidt et al. (2008)
² H, average building height. ¹ Local climate zone classification proposed by Stewart and Oke (2009).	ht. sification proposed k	y Stewart and	Oke (2009).					

² Land-cover fraction: Bldg., buildings; Veg., vegetation; IG, impervious ground. Data from original references and IAUC Urban Flux Network (http:// www.urban-climate.org). ³ (c) – Closed-path IRGA, (o) – open-path IRGA.

⁴ Study included additional short-term measurements with a mobile 10-m tower in six urban sites.

⁵ The remaining 2% correspond to open water.

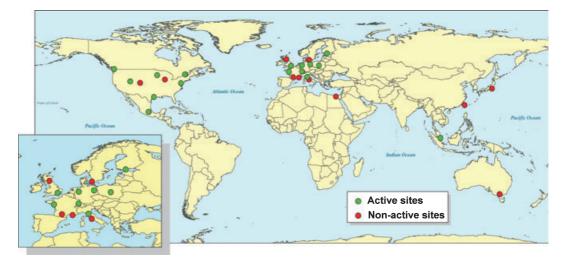


Fig. 4. Cities with current (active) or past (non-active) EC CO₂ flux measurement sites. An updated list of urban flux sites and bibliography is available at the Urban Flux Network website (http://www.urban-climate.org).

Grimmond et al. 2002a; Nemitz et al. 2002) and even more recent research published in peer-reviewed literature often lacks long-term (>1 year) measurements with the notable exceptions of Copenhagen-Frederiksberg (Soegaard and Møller-Jensen 2003), Tokyo-Kugahara (Moriwaki and Kanda 2004) and Melbourne-Preston (Coutts et al. 2007). Another long-term program has recently been initiated in Vancouver and Montréal (Canada) by the Environmental Prediction in Canadian Cities program (http://www.epicc.uwo.ca).

The majority of CO_2 flux measurements by EC in urban environments have been carried out in residential and commercial neighborhoods. Some sites have been located in city core areas, e.g. in Edinburgh-Calton Hill (Nemitz et al. 2002), Marseille-CCA (Grimmond et al. 2004) and Firenze-Ximeniano (Matese et al. 2009) or densely populated districts in Tokyo-Kugahara (Moriwaki and Kanda 2004), Basel-Sperrstrasse (Vogt et al. 2006a) and Mexico City-Escandon (Velasco et al. 2009). Both types of sites are characterized by high population density, compact housing, intense vehicular traffic and scarce vegetation. Other flux systems have been deployed in residential suburbs of Chicago-Dunning (Grimmond et al. 2002a) and Melbourne-Preston (Coutts et al. 2007), where population density is relatively low, vehicular traffic is reduced and vegetation cover is quite extensive. A fourth category of sites represents university environments, e.g. Mexico City-Iztapalapa (Velasco et al. 2005a) and Helsinki-SMEAR III (Vesala et al. 2007). Table 2 summarizes experimental and site information of EC CO₂ flux measurement projects reported in the peer-reviewed literature.

To date, more than 30 EC systems have been deployed with the majority in midlatitude cities of Europe and North America. Only one tropical (Singapore: Roth and Jansson 2008) and four subtropical sites (two in Mexico City: Velasco et al. 2005a, 2009; Houston: Schade 2009; Cairo: Burri et al. 2009) have been studied to date. Similar to investigations into other aspects of the urban climate most studies have been carried out in developed countries with the exception of Mexico City and Cairo. This is unfortunate because much of the current and projected urban growth is occurring in countries with developing economies.

DIURNAL AND SEASONAL PATTERNS

The most striking feature reported is the positive (i.e. directed away from the surface) flux values observed during most hours of the day at the vast majority of sites (Figures 5 and 6). This indicates that cities are generally a source of CO_2 . The diurnal patterns reveal the importance of vehicular traffic as the main emission source in urban environments. In most locations, the CO_2 flux and the traffic volume increase during the morning

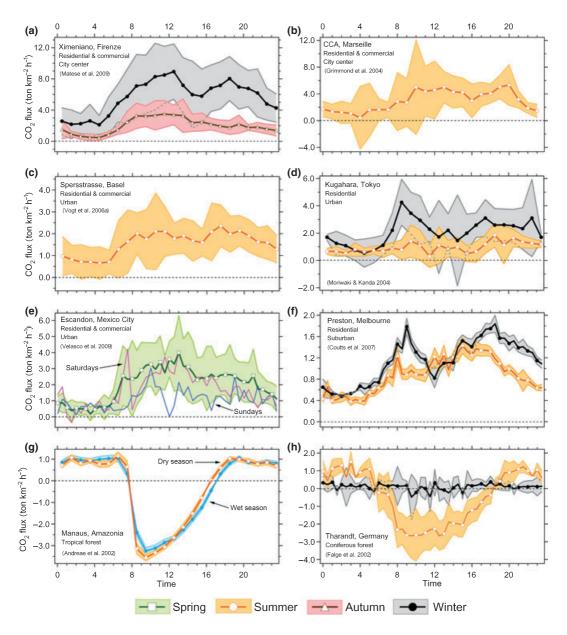


Fig. 5. Average diurnal variation of CO_2 fluxes from selected urban and forested sites for different seasons. The shaded regions are ±1 standard deviation and give an indication of the day-to-day variability at every hour of the day. Note different flux scales for individual panels.

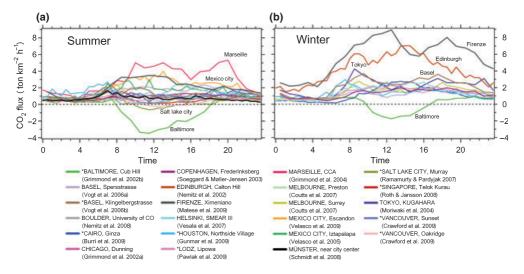


Fig. 6. Average diurnal variation of CO_2 fluxes from a range of urban sites during (a) summer and (b) winter. Sites marked with * have not been reported in the peer-reviewed literature. Sites reported in peer-reviewed literature are also listed in Table 2.

rush hour. In busy districts with heavy traffic and scarce vegetation, the CO₂ flux tends to stay constant and high throughout the day, decreasing in phase with the traffic load in the evening (e.g. Mexico City-Escandon, Figure 5e). Many places exhibit strong early morning and late afternoon traffic peaks (e.g. Basel-Sperrstrasse and Melbourne-Preston, Figure 5c and f, respectively), whereas at other sites only minor peaks are observed during the rush hours (e.g. Marseille-CCA; Figure 5b). Usually, the correlation coefficient obtained from linear regression between traffic volume and CO₂ flux for busy districts is high (r > 0.7) (e.g. Nemitz et al. 2002; Soegaard and Møller-Jensen 2003; Velasco et al. 2009). In suburban neighborhoods, the magnitude of the fluxes in the middle of the day is modulated by the amount of vegetation, particularly during the summer growing season. For example, the measurement site Cub Hill in Baltimore is heavily treed and hence capable of significant daytime uptake exceeding the anthropogenic emissions (Figures 1 and 6).

The morning and late afternoon peaks are also related to domestic activities such as cooking and household heating or cooling. The impact of domestic heating on the CO_2 flux increases as the ambient temperature drops in winter as demonstrated by Firenze-Ximeniano where the CO_2 flux correlates negatively with ambient temperature (Matese et al. 2009). They found that household heating increases the wintertime CO_2 flux by 2.8 times compared to that measured in autumn (Figure 5a). In Tokyo-Kugahara, Moriwaki and Kanda (2004) found that domestic heating contributes 62% to the total CO_2 flux in winter. In contrast to vegetated areas, the lowest CO_2 fluxes in urban locations occur at night when human activities are at a minimum. The positive fluxes are supported by the remaining traffic, plant respiration mainly during summer and heating in winter.

The diurnal variability of the fluxes shown in Figure 5 is primarily the result of the flux strengths of the anthropogenic and natural sources and sinks but modulated by other factors. The vegetation uptake depends on meteorological variables as well as on the plants' phenology and environmental stress conditions (e.g. pollution, dryness).

Some anthropogenic emissions, such as household heating, also depend on meteorological variables, but others merely on social patterns. For example, the traffic emissions on weekends are usually lower than on weekdays as shown in Figure 5e for the Escandon site in Mexico City. Similarly, in Cairo, the *Jumu'ah* (Muslim prayer day) is held on Friday, and because it is a rest day the traffic emissions are much reduced (Burri et al. 2009).

The generally large urban fluxes during daytime, with the exceptions of Baltimore-Calton Hill, Salt Lake City-Murray and Vancouver-Oakridge (all sites with surface vegetation fractions >50%), illustrate the anthropogenic contribution cities have on the atmospheric CO₂ exchange. Forested ecosystems, in contrast, have negative fluxes during daytime (Figure 5g,h) due to photosynthesis, while at night plant respiration produces positive fluxes of similar magnitude to those observed in urban environments. Hourly average fluxes from densely built-up sites in Marseille-CCA and Mexico City-Escandon, which have surface vegetation fractions <14% exceed 4 tons km⁻² h⁻¹ (Figure 6a) during summer and spring, respectively. In wintertime, the average fluxes from sites in city centers such as Firenze-Ximeniano and Edinburgh-Calton Hill exceed 6 tons km⁻² h⁻¹ (Figure 6b). In general, daytime CO₂ fluxes shown in Figure 6 range from about 0 to 1.5 tons km⁻² h⁻¹ in summer and from 1 to 3 tons km⁻² h⁻¹ in winter. In comparison CO₂ fluxes observed in the rainforest of Manaus (Brazil) and the coniferous forest of Tharandt (Germany) reach daytime values below -3 tons km⁻² h⁻¹ (i.e. uptake) during the entire year and summer, respectively (Figure 5g,h).

Figure 7 summarizes the daily net CO₂ exchanges in winter and summer for urban sites with available flux data. In mid-latitude locations wintertime fluxes can be more than two times those measured during the summer (e.g. Firenze-Ximeniano, Tokyo-Kugahara, Lodz-Lipowa, Copenhagen-Frederiksberg). In cities with mild winters, such as Houston and Melbourne, the cold season increase is 1.2-2 times. Such seasonal differences are primarily due to space heating patterns and reductions in vegetation and biological activity during the cold season which constrain the CO_2 uptake. In sites like SMEAR III in Helsinki where the heating is provided by a central station and emissions are therefore non-local and produced outside the measurement footprint, the seasonal difference is only due to reduction in vegetation. Traffic load has little influence on seasonal differences since it is nearly constant throughout the year as shown by data from Copenhagen-Frederiksberg, Tokyo-Kugahara and Firenze-Ximeniano. Little seasonal variation is observed in low-latitude cities based on preliminary results from Singapore (Roth and Jansson 2008) where temperature, cooling needs and vegetation cover (growing season) are relatively constant throughout the year. In case of tropical locations with substantial green-spaces and dense vegetation, small variations may be expected in the carbon uptake between the dry and wet seasons, similar to the small variations observed in the tropical forest of Manaus, Brazil (Figure 5g).

IMPACT OF URBAN CHARACTERISTICS ON THE CO2 FLUX

The largest CO_2 fluxes are found in densely built-up locations and city centers (Figure 7). Their CO_2 emissions are two to five times larger compared to residential sites in suburban districts, where vehicular traffic is usually lower and vegetation fraction is larger. There is a strong relationship between the daily net CO_2 exchange and vegetation fraction fraction during summer (Figure 8). Including autumn and spring fluxes from Firenze and Mexico City where vegetation influence is negligible, a correlation coefficient of 0.70 is obtained. Removing the two more distant points from the correlation line (Copenhagen-

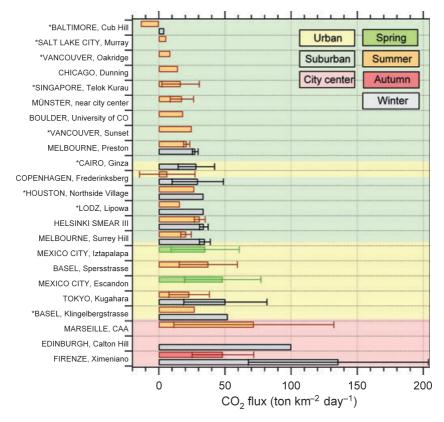


Fig. 7. Net daily CO_2 fluxes for a range of urban sites for different seasons and land uses. Length of solid bars correspond to the seasonal average, thin lines indicate ± 1 standard deviation. Sites marked with * have not been reported in peer-reviewed literature. The flux for Singapore–Telok Kurau is the annual average.

Frederiksberg and Marseille-CCA), the correlation coefficient improves to 0.87. No correlation was found between population density and daily CO₂ flux, as well as vegetation fraction and CO_2 flux per capita. Urban cores generally have higher daily CO_2 emissions compared to suburban neighborhoods, but not in terms of per capita emissions. Comparing daily fluxes with population density, it is found that many suburban sites have higher per capita emissions despite the larger abundance of vegetation and lower population densities. This surprising result may be due to differences in traffic patterns, domestic activities and contributions from suburban vegetation. However, these results may not be fully representative given the limited sample available and parameters considered. For example, the fraction of area covered by vegetation is not a good indicator of available biomass and density of trees by species may be more representative. Additional environmental factors such as atmospheric pollution and water availability may also bias the relationship between CO_2 flux and vegetation, and explain some of the variability seen in Figure 8. Further, population density values given usually only consider permanent residents, neglecting the daytime working population which can be significant in downtown and commercial districts. It is obvious that the large diversity of urban morphology, climatology, level of activity, and economic and social factors complicate a comprehensive comparison between urban areas.

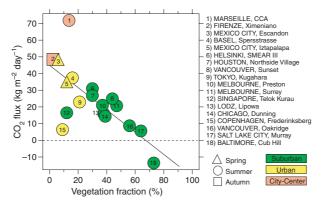


Fig. 8. Net daily CO_2 flux versus vegetation fraction for different urban land covers. Black line is regression through all data points.

ANNUAL CO2 EXCHANGE

The few available long-term studies provide a first indication of annual CO₂ budgets. Moriwaki and Kanda (2004) measured an annual CO_2 emission of 12.3 kg m⁻² for the densely populated residential neighborhood of Kugahara in Tokyo. Coutts et al. (2007) obtained an annual emission of 8.5 kg m⁻² for the residential district of Preston in Melbourne. Combining remote sensing and EC flux measurements from various neighborhoods, Soegaard and Møller-Jensen (2003) computed an average annual CO₂ flux of 12.8 kg m⁻², representative of the entire metropolitan area of Copenhagen. Finally, based on short-term studies assuming little seasonal variation, Velasco et al. (2005a, 2009) determined annual fluxes of 12.8 and 17.6 kg m^{-2} for two different districts in Mexico City. These annual fluxes can be compared to typical net CO₂ ecosystem exchanges in nearby forests. For example, the average CO_2 emission per unit area from Copenhagen is 20–28 times the total CO₂ sequestered by a Danish beech forest (Pilegaard et al. 2001). Similarly, the CO₂ emission from Kugahara in Tokyo is \sim 27 times the CO₂ absorbed by a broadleaf deciduous forest in Japan (Yamamoto et al. 1999). Comparing the two districts in Mexico City with the absorption rate from an evergreen oak forest (Baldocchi et al. 2001), forest areas which are five to seven times larger than those neighborhoods are needed to absorb their emissions. Tropical and subtropical forests are usually evergreen and therefore have a larger potential for CO₂ assimilation than boreal and temperate forests (Falge et al. 2002). Considering two hypothetical urban neighborhoods of equal size and CO_2 emission rate, one in a mid-latitude location and the other in the tropics, a larger temperate forest is needed to counterbalance the CO₂ emissions from the former neighborhood in comparison to a tropical forest to counterbalance the emissions from the second neighborhood.

EVALUATION OF EMISSION INVENTORIES BY EC FLUX MEASUREMENTS

An important purpose of the EC flux measurements of CO_2 in urban environments is to evaluate the accuracy of local emission inventories which are usually based on the indirect methods described earlier. The CO_2 fluxes measured by EC can be compared directly to the estimated emissions within the monitored neighborhood if these are available. Only few such comparisons have been carried out to date (Matese et al. 2009; Moriwaki and Kanda 2004; Nemitz et al. 2002; Soegaard and Møller-Jensen 2003; Velasco et al. 2009).

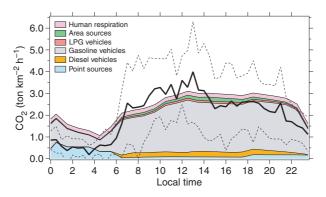


Fig. 9. Diurnal CO₂ emission profiles by source types for the Escandon district in Mexico City extracted from a local CO₂ emissions inventory (SMAGDF 2008). The CO₂ released by human breathing was estimated as the product of per capita rate of respiration, average CO₂ concentration of the air expired and population density (West et al. 2009). Under normal breathing conditions and considering the average weight of Mexico City inhabitants, a per capita metabolic emission of 0.6 kg day⁻¹ was determined. The solid black line corresponds to the average flux measured by EC, while the dashed lines indicate ±1 standard deviation from the measured flux (Velasco et al. 2009).

In general, the agreement between directly measured fluxes and indirectly estimated emissions has been good. An example is shown in Figure 9, which includes CO_2 emissions from anthropogenic sources, including human respiration, together with the measured CO_2 flux for the Escandon district in Mexico City. With the exception of the early morning period, the indirect estimates were generally within 10% of the measured flux. In this particular example, the transport sector contributes 87% to the total CO_2 emissions. The benign weather eliminates the need for household heating or cooling, but the high population density makes human respiration a significant source of CO_2 (~6%). In contrast, the biogenic CO_2 uptake or release is negligible due to the scarce presence of trees (25 ha⁻¹) and soils for respiration, respectively.

Summary and Conclusion

The majority of the monitored urban sites exhibit clear diurnal patterns with significant contributions from vehicular traffic and domestic heating, particularly in winter in the northern hemisphere. During daytime, the CO_2 uptake by urban vegetation is generally not strong enough to offset the anthropogenic CO_2 emissions. The maximum daily CO_2 fluxes are observed during winter. Summer values show a distinct minimum due to the benign weather which reduces emissions associated with fossil fuel consumption for heating and trees are in full leaf which increases the potential for CO_2 sequestration. In spring, the flux gradually changes from winter to summer levels and the opposite is found in autumn.

The CO₂ flux data presented in this review indicate that it is possible to obtain meaningful and representative results from city surfaces if careful attention is given to the selection of measurement sites, positioning and operation of instruments as well as data processing. EC observations provide an integrated measurement from all potential anthropogenic and natural CO₂ sources and sinks, including those not usually accounted for in typical emission inventories, such as emissions from food street sellers, human respiration and CO₂ uptake by photosynthesis. EC observations can also be used to evaluate CO₂ emissions inventories, whose spatial resolution is similar to the size of flux footprints (10^2-10^4 m).

The number of measurement sites is still insufficient to assess the potential spatial and temporal variability of the CO_2 exchange produced by the full diversity (in terms of

economic development, transport, amount of vegetation, heat/cooling needs, etc.) of cities. Many more studies of urban areas are needed to produce reliable city-wide emission budgets. Since the analytical sensors to measure CO_2 require only limited maintenance and calibration, permanent CO_2 flux monitoring programs using the EC technique may become part of meteorological and air quality networks in cities. EC observations provide continuous CO_2 flux data that may be used in the development of environmental policies intended to reduce GHG emissions.

The EC technique has also been used to measure urban fluxes of other species of concern for climate change and public health, such as volatile organic compounds (e.g. Langford et al. 2009, 2010; Velasco et al. 2005b, 2009) and aerosols (e.g. Dorsey et al. 2002; Mårtensson et al. 2006; Nemitz et al. 2008). Results of these measurements have contributed to improve emission inventories used for air quality and GHG assessment. Simultaneous EC flux measurements of selected trace gases strongly associated with particular emission sources and CO_2 fluxes may be conducted to determine the CO_2 apportionment from individual sources. For example, benzene is a good tracer of vehicle exhaust and knowing the ratio of benzene emitted per mass of CO_2 by traffic (Zavala et al. 2006) the vehicular contribution to the observed CO_2 fluxes may be found. Similarly, acetonitrile and hydrogen cyanide may be used as indicators of biomass burning (Crounse et al. 2009; de Gouw et al. 2009). Further, analysis of CO_2 isotopes in conjunction with EC measurements can be used to separate the anthropogenic and biogenic contributions to the total CO_2 flux (Pataki et al. 2003).

Acknowledgement

Matthias Roth would like to acknowledge funding from National University Research grant R-109-000-091-112. Erik Velasco acknowledges the postdoctoral funding provided by the Faculty of Arts and Social Sciences of the National University of Singapore. The authors acknowledge the assistance provided by Elvagris Segovia for the digitization of the diurnal profiles of CO_2 flux shown in Figures 5 and 6, and Reuben Li for the preparation of Figure 4.

Short Biographies

Erik Velasco is an environmental engineer involved in research concerning urban air pollution and climatology. His research focus is on the evaluation of emission inventories by direct and indirect methods (i.e. micrometeorological techniques and modeling comparison). He is also interested in the interactions between the urban surface and the low boundary layer in terms of mass and energy exchange and pollution dispersion. He is currently a postdoctoral fellow at the National University of Singapore. He holds BS and MS degrees from the National Autonomous University of Mexico, and a PhD from Washington State University.

Matthias Roth is an Associate Professor in the Department of Geography at the National University of Singapore. He holds a PhD degree from the University of British Columbia in Vancouver (Canada) and is the immediate Past-President of the *International Association for Urban Climate* (IAUC). His main academic interest is to understand how land-cover changes affect local climates with a particular focus on the climate of cities and the role they play in climate change. As an experimental researcher he has conducted observations of the energy balance, carbon dioxide fluxes and fundamental turbulence properties in North American, European and Asian cities.

Note

* Correspondence address: Matthias Roth, Department of Geography, National University of Singapore, 1 Arts Link, Kent Ridge, Singapore 117570, Singapore. E-mail: geomr@nus.edu.sg.

References

- Andreae, M. O., et al. (2002). Biogeochemical cycling of carbon, water, energy, trace gases, and aerosols in Amazonia: the LBA-EUSTACH experiments. *Journal of Geophysical Research* 107 (D20), 8066 pp., doi:10.1029/ 2001JD000524.
- Arya, S. P. (2001). Introduction to micrometeorology. 2nd ed. New York, USA: Academic Press.
- Aubinet, M., et al. (2000). Estimates of the annual net carbon and water exchange of forests: the EUROFLUX methodology. *Advances in Ecological Research* 30, pp. 113–175.
- Auble, D. L. and Meyers, T. P. (1992). An open path, fast response infrared absorption gas analyzer for H₂O and CO₂. *Boundary-Layer Meteorology* 59, pp. 243–256.
- Baldocchi, D. B. (2003). Assessing the eddy covariance technique for evaluating carbon dioxide rates of ecosystems: past, present and future. *Global Change Biology* 9, pp. 479–492.
- Baldocchi, D., et al. (2001). FLUXNET: a new tool to study the temporal and spatial variability of ecosystem scale carbon dioxide, water vapor and energy flux densities. *Bulletin of the American Meteorological Society* 82, pp. 2415–2434.
- Bottema, M. (1997). Urban roughness modelling in relation to pollutant dispersion. *Atmospheric Environment* 31, pp. 3059–3075.
- Burba, G. and Anderson, D. (2007). Introduction to the eddy covariance method: general guidelines, and conventional workflow. Lincoln, NE, USA: Li-COR Biosciences.
- Burri, S., Frey, C., Parlow, E. and Vogt, R. (2009). CO_2 fluxes and concentrations over an urban surface in Cairo/Egypt. Paper presented at the Seventh International Conference on Urban Climate organized by the IAUC, Yokohama, 29 June–3 July.
- Canadell, J. G., et al. (2009). The human perturbation of the carbon cycle. Paris, France: UNESCO-SCOPE-UNEP.
- Clark-Thorne, S. T. and Yapp, C. J. (2003). Stable carbon isotope constraints on mixing and mass balance of CO₂ in an urban atmosphere: Dallas metropolitan area, Texas, USA. *Applied Geochemistry* 18 (1), pp. 75–95.
- Coutts, A. M., Beringer, J. and Tapper, N. J. (2007). Characteristics influencing the variability of urban CO₂ fluxes in Melbourne, Australia. *Atmospheric Environment* 41, pp. 51–62.
- Crawford, B., et al. (2009). Observations of carbon dioxide fluxes in two suburban neighborhoods in Vancouver, Canada. Paper presented at the Eighth Symposium on the Urban Environment organized by the American Meteorological Society, Phoenix, 10–16 January.
- Crounse, J. D., et al. (2009). Biomass burning and urban pollution over the Central Mexican Plateau. Atmospheric Chemistry and Physics 9, pp. 4929–4944.
- Dorsey, J. R., et al. (2002). Direct measurements and parameterisation of aerosol flux, concentration and emission velocity above a city. *Atmospheric Environment* 36, pp. 791–800.
- Falge, E., et al. (2002). Phase and amplitude of ecosystem carbon release and uptake potential as derived from FLUXNET measurements. *Agricultural and Forest Meteorology* 113, pp. 75–95.
- Geels, C., et al. (2007). Comparing atmospheric transport models for future regional inversions over Europe Part 1: mapping the atmospheric CO₂ signals. *Atmospheric Chemistry and Physics* 7, pp. 3461–3479.
- de Gouw, J. A., et al. (2009). Emission and chemistry of organic carbon in the gas and aerosol phase at a sub-urban site near Mexico City in March 2006 during the MILAGRO study. *Atmospheric Chemistry and Physics* 9, pp. 3425–3442.
- Griessbaum, F. and Schmidt, A. (2009). Advanced tilt correction from flow distortion effects on turbulent CO₂ fluxes in complex environments using large eddy simulation. *Quarterly Journal of the Royal Meteorological Society* 135, pp. 1603–1613.
- Grimmond, C. S. B. and Oke, T. R. (1999). Aerodynamic properties of urban areas derived from analysis of surface form. *Journal of Applied Meteorology* 38, pp. 1262–1292.
- Grimmond, C. S. B., et al. (2002a). Local-scale fluxes of carbon dioxide in urban environments: methodological challenges and results from Chicago. *Environmental Pollution* 116, pp. S243–S254.
- Grimmond, C. S. B., Offerle, B. D., Hom, J. and Golub, D. (2002b). Observations of local- scale heat, water, momentum and CO₂ fluxes at Cub Hill. Paper presented at the Fourth Symposium on the Urban Environment organized by the American Meteorological Society, Norfolk, 20–24 May.
- Grimmond, C. S. B., et al. (2004). Flux and turbulence measurements at a densely built-up site in Marseille: heat, mass (water and carbon dioxide), and momentum. *Journal of Geophysical Research* 109, D24101 pp.
- Ham, J. M. and Heilman, J. L. (2003). Experimental test of density and energy-balance corrections on carbon-dioxide flux as measured using open-path eddy covariance. *Agronomy Journal* 95, pp. 1363–1403.

- Henninger, S. and Kuttler, W. (2007). Methodology for mobile measurements of carbon dioxide within the urban canopy layer. *Climate Research* 34 (2), pp. 161–167.
- Hofmann, D. J., et al. (2006). The role of carbon dioxide in climate forcing from 1979 to 2004: introduction of the annual greenhouse gas index. *Tellus* 58B (5), pp. 614–619.
- Hsieh, C. I., Katul, G. and Chi, T. (2000). An approximate analytical model for footprint estimation of scalar fluxes in thermally stratified atmospheric flows. *Advances in Water Resources* 23, pp. 765–772.
- Idso, C. D., Idso, S. B. and Balling, R. C., Jr (2001). An intensive two-week study of an urban CO₂ dome in Phoenix, Arizona, USA. *Atmospheric Environment* 35 (6), pp. 995–1000.
- Intergovernmental Panel on Climate Change (1997). Revised 1996 IPCC guidelines for national greenhouse gas inventories. Paris: IPCC/OECD/IEA.
- Kaimal, J. C. and Finnigan, J. J. (1994). Atmospheric boundary layer flows: their structure and measurement. New York: Oxford University Press.
- Kljun, N., Calanca, P., Rotach, M. W. and Schmid, H. P. (2004). A simple parameterization for flux footprint predictions. *Boundary-Layer Meteorology* 112, pp. 503–523.
- Kondo, F. and Tsukamoto, O. (2008). Evaluation of Webb correction on CO₂ flux by eddy covariance technique using open-path gas analyzer over asphalt surface. *Journal of Agricultural Meteorology* 64 (1), pp. 1–8.
- Langford, B., Davison, B., Nemitz, E. and Hewitt, C. N. (2009). Mixing ratios and eddy covariance flux measurements of volatile organic compounds from an urban canopy (Manchester, UK). *Atmospheric Chemistry and Physics* 9, pp. 1971–1987.
- Langford, B., et al. (2010). Fluxes and concentrations of volatile organic compounds above central London, UK. Atmospheric Chemistry and Physics 10, pp. 627–645.
- Le Quéré, C., et al. (2009). Trends in the sources and sinks of carbon dioxide. Nature Geosciences 2 (12), pp. 831-836.
- Lee, X., Massman, W. and Law, B. (2004). Handbook of micrometeorology: a guide for surface flux measurements and analysis. Dordrecht, The Netherlands: Kluwer Academic Publishers.
- Marland, G. (2008). Uncertainties in accounting for CO₂ from fossil fuels. *Journal of Industrial Ecology* 12 (2), pp. 136–139.
- Mårtensson, E. M., Nilsson, E. D., Buzorius, G. and Johansson, C. (2006). Eddy covariance measurements and parameterization of traffic related particle emissions in an urban environment. *Atmospheric Chemistry and Physics* 6, pp. 769–785.
- Massman, W. J. and Lee, X. (2002). Eddy covariance flux corrections and uncertainties in long-term studies of carbon and energy exchanges. Agricultural and Forest Meteorology 113, pp. 121–144.
- Matese, A., et al. (2009). CO₂ emissions of the city center of Firenze, Italy: measurement, evaluation and source partitioning. *Journal of Applied Meteorology and Climatology* 48, pp. 1940–1947.
- Mays, K. L., et al. (2009). Aircraft-based measurements of the carbon footprint of Indianapolis. Environmental Science and Technology 43 (20), pp. 7816–7823.
- McMillen, R. (1988). An eddy correlation technique with extended applicability to non-simple terrain. *Boundary-Layer Meteorology* 43, pp. 231–245.
- Mennen, M. G., Zwart, H. J. M. A., Hogenkamp, J. E. M. and Erisman, J. W. (1996). Flow distortion errors caused by rigid obstacles in dry deposition measurement systems. *Boundary-Layer Meteorology* 81, pp. 353–371.
- Mills, G. (2007). Cities as agents of global change. International Journal of Climatology 27, pp. 1849–1857.
- Mizoguchi, Y., et al. (2009). A review of tower flux observation sites in Asia. Journal of Forest Research 14, pp. 1-9.
- Moncrieff, J. B., et al. (1997). A system to measure surface fluxes of momentum, sensible heat, water vapour and carbon dioxide. *Journal of Hydrology* 188–189, pp. 589–611.
- Moriwaki, R. and Kanda, M. (2004). Seasonal and diurnal fluxes of radiation, heat, water vapor and CO₂ over a suburban area. *Journal of Applied Meteorology* 43, pp. 1700–1710.
- Nemitz, E., et al. (2002). Micrometeorological measurements of the urban heat budget and CO₂ emissions on a city scale. *Environmental Science and Technology* 36, pp. 3139–3146.
- Nemitz, E., et al. (2008). An eddy-covariance system for the measurement of surface/atmosphere exchange fluxes of submicron aerosol chemical species – first application above an urban area. *Aerosol Science and Technology* 42, pp. 636–657.
- Oke, T. R., et al. (1989). Evaluation of spatially-averaged fluxes of heat, mass and momentum in the urban boundary layer. *Weather and Climate* 9, pp. 14–21.
- Pataki, D. E., Bowling, D. R., Jr and Ehleringer, J. R. (2003). Seasonal cycle of carbon dioxide and its isotopic composition in an urban atmosphere: anthropogenic and biogenic effects. *Journal of Geophysical Research* 108 (D23), 4735 pp., doi:10.1029/2003JD003865.
- Pawlak, W., Fortuniak, K. and Siedlecki, M. (2009). Carbon dioxide flux in the center of Łódź, Poland Analysis of two years eddy covariance measurements data set. Paper presented at the Seventh International Conference on Urban Climate organized by the IAUC, Yokohama, 29 June–3 July.
- Pilegaard, K., Hunnelshøj, P., Jensen, N. O. and Chen, Z. (2001). Two years of continuous CO₂ eddy-flux measurements over a Danish beech forest. Agricultural and Forest Meteorology 107, pp. 29–41.

- Prairie, Y. T. and Duarte, C. M. (2007). Direct and indirect metabolic CO₂ release by humanity. *Biogeosciences* 4, pp. 215–217.
- Ramamurty, P. and Pardyjak, E. R. (2007). A comparison of CO₂ fluxes at two sites within the urbanized Salt Lake Valley. Paper presented at the Seventh Symposium on the Urban Environment organized by the American Meteorological Society, San Diego, 10–13 September.
- Rigby, M., et al. (2008). First continuous measurements of CO₂ mixing ratio in central London using a compact diffusion probe. *Atmospheric Environment* 42, pp. 8943–8953.
- Roth, M. (2000). Review of atmospheric turbulence over cities. *Quarterly Journal of the Royal Meteorological Society* 126, pp. 941–990.
- Roth, M. and Jansson, C. (2008). Energy balance and carbon dioxide fluxes in Singapore. Newsletter of the International Association for Urban Climate 28, pp. 6–10.
- Schade, G. W. (2009). Relating urban turbulence and trace gas flux measurements from a tall tower to surface characteristics and anthropogenic activities. Texas Air Research Center (TARC), Lamar University. [Online]. Retrieved on 30 December 2009 from: http://atmo.tamu.edu/yellowcabtower/index_files/TARCreport09.pdf.
- Schmid, H. P. (1994). Source areas for scalar and scalar fluxes. Boundary-Layer Meteorology 67, pp. 293-318.
- Schmid, H. P., et al. (2000). Measurements of CO₂ and energy fluxes over a mixed hardwood forest in the midwestern United States. Agricultural and Forest Meteorology 103, pp. 357–374.
- Schmidt, A., Wrzesinsky, T. and Klemm, O. (2008). Gap filling and quality assessment of CO₂ and water vapour fluxes above and urban area with radial basis function neural networks. *Boundary-Layer Meteorology* 126, pp. 389–413.
- SMAGDF (2008). Inventario de emisiones de contaminantes criterio de la Zona Metropolitana del Valle de México. México: Secretaria del Medio Ambiente del Gobierno del Distrito Federal.
- Soegaard, H. and Møller-Jensen, L. (2003). Towards a spatial CO₂ budget of a metropolitan region based on textural image classification and flux measurements. *Remote Sensing of Environment* 87, pp. 283–294.
- Stewart, I. and Oke, T. R. (2009). Newly developed thermal climate zones for defining and measuring urban heat island magnitude in the canopy layer. Paper presented at the Eighth Symposium on the Urban Environment organized by the American Meteorological Society, Phoenix, 10–16 January.
- Stull, R. B. (1988). An introduction to boundary layer meteorology. Dordrecht, The Netherlands: Kluwer Academic Publishers.
- Valentini, R., et al. (2000). Respiration as the main determinant of carbon balance in European forests. *Nature* 404, pp. 861–865.
- Velasco, E., et al. (2005a). Measurements of CO₂ fluxes from the Mexico City urban landscape. *Atmospheric Environment* 39, pp. 7433–7446.
- Velasco, E., et al. (2005b). Flux measurements of volatile organic compounds from an urban landscape. Geophysical Research Letters 32, L20802 pp., doi:10.1029/2005GL023356.
- Velasco, E., et al. (2009). Eddy covariance flux measurements of pollutant gases in urban Mexico City. Atmospheric Chemistry and Physics 9, pp. 7325–7342.
- Vesala, T., et al. (2007). Surface-atmosphere interactions over complex urban terrain in Helsinki, Finland. *Tellus* 60B, pp. 188–199.
- Vesala, T., et al. (2008). Flux concentration footprint modeling: state of the art. *Environmental Pollution* 152, pp. 653-666.
- Vogt, R., et al. (2006a). Temporal dynamics of CO₂ fluxes and profiles over a Central European city. *Theoretical and Applied Climatology* 84, pp. 117–126.
- Vogt, R., Eitel, J. and Parlow, E. (2006b). CO₂ flux measurements in a heterogeneous urban environment. Paper presented at the Sixth International Conference on Urban Climate organized by the IAUC, Goteborg, 12–16 June.
- Webb, E. K., Pearman, G. I. and Leuning, R. (1980). Correction of flux measurements for density effects due to heat and water vapour transfer. *Quarterly Journal of the Royal Meteorological Society* 106, pp. 85–100.
- West, T. O., et al. (2009). The human carbon budget: an estimate of the spatial distribution of metabolic carbon consumption and release in the United States. *Biogeochemistry* 94, pp. 29–41.
- Wyngaard, J. C. (1973). On surface-layer turbulence. In: Haugen, D. A. (ed.) Workshop on micrometeorology. Boston: American Meteorological Society, pp. 101–149.
- Wyngaard, J. C. (1988). Flow-distorsion effects on scalar flux measurements in the surface-layer: implications for sensor design. *Boundary-Layer Meteorology* 42, pp. 19–26.
- Yamamoto, S., Murayama, S., Saigusa, N. and Kondo, H. (1999). Seasonal and inter-annual variation of CO₂ flux between a temperate forest and the atmosphere in Japan. *Tellus* 51B, pp. 402–413.
- Zavala, M., et al. (2006). Characterization of on-road vehicle emissions in the Mexico City Metropolitan Area using a mobile laboratory in chase and fleet average measurement modes during the MCMA-2003 field campaign. *Atmospheric Chemistry and Physics* 6, pp. 5129–5142.