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Turbulent vertical fluxes and air quality measured in urban air in Helsinki

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Academic dissertation

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Abstract

There is a growing need to understand the exchange processes of momentum, heat and mass between an urban surface and the atmosphere as they affect our quality of life. Understanding the source/sink strengths as well as the mixing mechanisms of air pollutants is particularly important due to their effects on human health and climate. This work aims to improve our understanding of these surface-atmosphere interactions based on the analysis of measurements carried out in Helsinki, Finland. The vertical exchange of momentum, heat, carbon dioxide (CO_2) and aerosol particle number was measured with the eddy covariance technique at the urban measurement station SMEAR III, where the concentrations of ultrafine, accumulation mode and coarse particle numbers, nitrogen oxides (NO_x), carbon monoxide (CO), ozone (O_3) and sulphur dioxide (SO_2) were also measured. These measurements were carried out over varying measurement periods between 2004 and 2008. In addition, black carbon mass concentration was measured at the Helsinki Metropolitan Area Council site during three campaigns in 1996-2005. Thus, the analyzed dataset covered far, the most comprehensive long-term measurements of turbulent fluxes reported in the literature from urban areas. Moreover, simultaneously measured urban air pollution concentrations and turbulent fluxes were examined for the first time. The complex measurement surrounding enabled us to study the effect of different urban covers on the exchange processes from a single point of measurement.

The sensible and latent heat fluxes closely followed the intensity of solar radiation, and the sensible heat flux always exceeded the latent heat flux due to anthropogenic heat emissions and the conversion of solar radiation to direct heat in urban structures. This urban heat island effect was most evident during winter nights. The effect of land use cover was seen as increased sensible heat fluxes in more built-up areas than in areas with high vegetation cover. Both aerosol particle and CO_2 exchanges were largely affected by road traffic, and the highest diurnal fluxes reached 10^9 m^{-2} s^{-1} and 20 μmol m^{-2} s^{-1}, respectively, in the direction of the road. Local road traffic had the greatest effect on ultrafine particle concentrations, whereas meteorological variables were more important for accumulation mode and coarse particle concentrations. The measurement surroundings of the SMEAR III station served as a source for both particles and CO_2, except in summer, when the vegetation uptake of CO_2 exceeded the anthropogenic sources in the vegetation sector in daytime, and we observed a downward median flux of 8 μmol m^{-2} s^{-1}.

This work improved our understanding of the interactions between an urban surface and the atmosphere in a city located at high latitudes in a semi-continental climate. The results can be utilised in urban planning, as the fraction of vegetation cover and vehicular activity were found to be the major environmental drivers affecting most of the exchange processes. However, in order to understand these exchange and mixing processes on a city scale, more measurements above various urban surfaces accompanied by numerical modelling are required.

Keywords: air pollution, aerosol particles, carbon dioxide, eddy covariance technique, land use, turbulent fluxes, urban area

Abbreviations

ζ	Monin-Obukhov stability parameter
ω	dissipation of turbulent kinetic energy
ABL	atmospheric boundary layer
B	Bowen ratio
BC	black carbon
CO	carbon monoxide
CO_2	carbon dioxide
d	displacement height
d_a	aerodynamic diameter
E	turbulent kinetic energy
EC	eddy covariance
F_c	CO_2 flux
F_{CP}	closed-path CO_2 flux
F_{Fit}	open-path CO_2 flux corrected with the fitting method
F_{Lin}	open-path CO_2 flux corrected with the linear method
F_{MLR}	open-path CO_2 flux corrected with the MLR method
F_{OP}	open-path CO_2 flux
F_p	aerosol particle number flux
F_s	vertical flux of scalar
F_w	water vapour flux
H	sensible heat flux
LE	latent heat flux
LRT	long-range transport
MLR	multiple linear regression
MOS	Monin-Obukhov similarity
NO_x	nitrogen oxides ($NO + NO_2$)
NSE	net surface exchange
O_3	ozone
RSL	roughness sublayer
s	arbitrary scalar
SCADIS	numerical boundary layer model
SO_2	sulphur dioxide
u_*	friction velocity
UBL	urban boundary layer
UCL	urban canopy layer
UFP	ultrafine particles
UHI	urban heat island
w	vertical velocity
YTV	the Helsinki Metropolitan Area Council
z_0	roughness length

List of contents

List of Publications

This thesis consists of an introductory review followed by five research articles. The papers are reproduced with the kind permission of the journals concerned.

I: **Järvi L.**, Junninen H., Karppinen A., Hillamo R., Virkkula A., Mäkelä T., Pakkanen T. and Kulmala M. 2008. Temporal variations in black carbon concentrations with different time scales in Helsinki during 1996-2005. *Atmos. Chem. Phys.* 8, 1017-1027.

II: Vesala T., **Järvi L.**, Launiainen S., Sogachev A., Rannik Ü., Mammarella I., Siivola E., Keronen P., Rinne J., Riikonen A. and Nikinmaa E. 2008. Surface-atmosphere interactions over complex urban terrain in Helsinki, Finland, *Tellus B* 60: 188-199.

III: **Järvi L.**, Hannuniemi H., Hussein T., Junninen H., Aalto P. P., Hillamo R., Mäkelä T., Keronen P., Siivola E., Vesala T. and Kulmala M. 2009. The urban measurement station SMEAR III: Continuous monitoring of air pollution and surface-atmosphere interactions in Helsinki, Finland. *Boreal Env. Res.* 14 (Suppl. A), 86-109.

IV: **Järvi L.**, Mammarella I., Eugster W., Ibrom A., Siivola E., Dellwik E., Keronen P., Burba G. and Vesala T. 2009. Comparison of net CO_2 fluxes measured with open- and closed-path infrared gas analyzers in urban complex environment. *Boreal Env. Res.* 14, 499-514.

V: **Järvi L.,** Rannik Ü., Mammarella I., Sogachev A., Aalto P. P., Keronen P., Siivola E. , Kulmala M. and Vesala T. 2009. Annual particle flux observations over a heterogeneous urban area. *Atmos. Chem. Phys. Discuss.* 9, 13407-13437.

Author's contribution

I am solely responsible for the summary of this thesis. I was responsible for the quality control and post-processing of the urban flux and meteorological data, and in all papers, I participated in designing the study and in data analysis. In **Paper I**, I was responsible for the data analysis (excluding the calculations of the pre-processed meteorological variables), participated in the interpretation of the results and wrote most of the text. In **Paper II**, I performed the data analysis (excluding the footprint calculations and comparisons between the rotation angles and planar fitting), and participated in the data interpretation and writing. In **Paper III**, I had the main responsibility for the data analysis, data interpretation, and writing of the paper. In **Paper IV**, I performed the data analysis (excluding the flux calculations at the forest site), contributed to the data interpretation, and wrote most of the text. In **Paper V**, I was responsible for the data analysis (excluding the aerosol particle size distribution and footprint calculations), and contributed to the data interpretation and writing. The measurements analysed in this thesis were carried out by the technical staff of the

Department of Physics, University of Helsinki (**Papers II-V**), the Finnish Meteorological Institute (**Papers I** and **III**) and the Risø Research Centre (Paper **IV**).

1. Introduction

Today, half of Earth's population lives in urban environments, and this fraction is likely to increase in future (Elvidge *et al.* 2004). Because an increasing number of people is exposed to urban environments, there is a growing need to understand the urban climate, which strongly affects our quality of life. Urban climates result from changes in human activity and land use, which, when compared to surrounding rural areas, modify the vertical exchange of momentum, heat, moisture and air pollutants between urban surfaces and air (e.g. Oke 1982; Oke 1987; Oke 1988; Roth 2000; Arnfield 2003; Britter and Hanna 2003). The exchange of air pollutants in particular has major consequences on our environment, since they affect urban and global climates in several ways. Both gaseous and particulate pollutants adversely affect nature and human health (Nel 2005; Curtis *et al.* 2006; Hänninen *et al.* 2009), and an estimated two million premature deaths take place worldwide every year due to the effects of outdoor and indoor pollutants (WHO 2006). In addition, air pollutants, mainly aerosol particles, affect local visibility and the attenuation of solar radiation (Jáuregui and Luyando 1999; Cabada *et al.* 2004), and take part in global climate change by absorbing and reflecting solar radiation (IPCC 2007). Carbon dioxide (CO_2) has been identified as one of the main compounds that play a role in global warming, whereas particulate matter affects the climate indirectly by acting as cloud condensation nuclei, or directly by absorbing and reflecting solar and infrared radiation (Ramanathan *et al.* 2001; Panicker *et al.* 2008). Due to the variety of their effects on climate, aerosol particles are recognised to cause the greatest uncertainties in climate change predictions (IPCC 2007).

In urban areas, road traffic and other combustion processes have been found to be a major source of aerosol particles and many gaseous pollutants, including CO_2 (e.g. Shi *et al.* 2001; Dorsey *et al.* 2002; Nemitz *et al.* 2002; Hussein *et al.* 2004; Birmili *et al.* 2009). Even though the sources of urban pollution have largely been identified, much uncertainty remains regarding their source strength as well as their spatial and temporal variations. Besides their different sources, deeper knowledge is needed concerning the dispersion and mixing of air pollutants. The mixing state of the lowest level of the atmosphere is largely determined by the exchange of momentum and heat (e.g. Oke 1987; Hanna and Britter 2002), and understanding these exchange processes is important for air quality studies. Heat exchange processes are also important to understand because they can increase air temperatures and create an urban heat island (Oke 1982), where temperatures rise more easily to hazardous levels than they do in rural areas (Stone and Rodgers 2001; McMichael *et al.* 2008).

The most direct way to measure the vertical exchange of momentum, heat and mass between the surface and the air is with the eddy covariance (EC) technique (Aubinet *et al.* 2000; Baldocchi 2003). This technique has been widely utilised in natural and semi-natural ecosystems to measure sensible and latent heat, CO_2 and aerosol particle exchange (Baldocci *et al.* 2001; Pryor *et al.* 2008), whereas in urban environments, the number of studies is limited (Roth 2000; Dorsey *et al.* 2002; Grimmond *et al* 2002a; Grimmond *et al* 2002b; Nemitz *et al.* 2002; Soegaard and Møller-Jensen 2003; Grimmond *et al.* 2004; Moriwaki and Kanda 2004; Velasco *et al.* 2005; Mårtensson *et al.* 2006; Offerle *et al.* 2006; Vogt *et al.* 2006; Coutts *et al.* 2007a; Coutts *et al.* 2007b; Lemonsu *et al.* 2008; Martin *et al.* 2008; Nemitz *et al.* 2008). Urban vertical surface fluxes are strongly determined by urban design and vary between and within cities, creating a unique climate for each urban environment (Stone and Rodgers 2001; Grimmond *et al.* 2002b; Rotach *et al.* 2005; Offerle *et al.* 2006; Coutts *et al.* 2007a; Coutts *et al.* 2007b; Martin *et al.* 2008; Schmidt *et al.* 2008). In order to understand these exchange processes in urban environments and their contribution to local and global climates, more measurements and analysis are required from cities located in different climate regions and with different urban surface covers, water availability, city architecture, traffic planning and heating systems. Urban surfaces are in constant change, and exchange measurements also provide important knowledge for city planners.

The conditions of EC measurements should be statistically stationary and horizontally homogeneous in order for the measured fluxes to be representative of the net surface exchange (NSE) on a local scale (Aubinet *et al.* 2000; Baldocchi 2003). These conditions are, however, seldom met in urban areas, and the accuracy of the EC technique above urban surfaces should therefore be studied in more detail. By definition, the technique itself also includes error sources which depend on the measurement setup, the analyser used and data processing (Massman and Lee 2002). Recently, density fluctuations caused by the surface of the measuring analyser being warmer than the ambient air has gained increasing attention due to its systematic underestimation of NSE (Burba *et al.* 2006; Grelle and Burba 2007; Burba *et al.* 2008; Ono *et al.* 2008).

The aim of this work was to sharpen our understanding of the interactions between urban surfaces and the atmosphere based on the analysis of turbulent exchange and air pollution concentration measurements carried out in Helsinki, Finland. The long-term measurements of momentum, heat, CO_2 and aerosol particle number vertical exchange in a high latitude city in a semi-continental climate provided new information about the effect of different seasons, with varying emission sources and vegetation cover, on the observed exchange processes. For the first time, simultaneously measured urban turbulent exchange and air pollutant concentrations were studied in the literature. In addition, due to the complex measurement environment, the effect of different types of land use on the observed interactions could be studied with a single point of measurement. On the other hand, the complexity of the surface raised its own challenges to the measurements themselves as well as the interpretation of the results.

The more detailed objectives were:

1. to study the temporal behaviour of the turbulent vertical exchange measured with the EC technique on seasonal and diurnal scales (**Papers II**, **III** and **V**),
2. to determine the effect of different land use covers, with varying source/sink strengths, on the exchange of CO_2, sensible and latent heat, and aerosol particles (**Papers II** and **V**),
3. to examine the accuracy of the EC technique in such a non-ideal measurement environment, as well as to evaluate and to develop correction procedures for sensor heating effects causing systematic distortion in CO_2 flux estimates (**Papers II** and **IV**),

4. to determine the environmental drivers affecting the temporal behaviour of aerosol particle and gas pollutant concentrations, as well as their dependencies on land use (**Papers I** and **III**).

2. Background

2.1 Atmospheric boundary layer

The lowest level of the troposphere, which is in direct contact with Earth's surface, is known as the atmospheric boundary layer (ABL). This layer is defined as a layer where the influence of the underlying surface is directly observed and which responds to surface forcing within a period of one hour (Stull 1988; Kaimal and Finnigan 1994). Forcing due to frictional drag and heat (mechanical and thermal turbulence production, respectively) manifests in the form of turbulent transport, which is a much more efficient transport mechanism than molecular diffusion in the ABL. Turbulence itself consists of different-sized irregular swirls, called eddies, which transport momentum, energy and matter between the surface and the air. The occurrence of turbulence is also one way of defining the ABL, since in the rest of the troposphere, turbulence is observed only occasionally (Stull 1988).

The height of the ABL varies strongly according to the time of day, reaching to a few kilometres in strongly convective situations in the daytime when, in addition to frictional forcing, thermal forcing caused by solar radiation is strong. After sunset, convection in the ABL diminishes, and the nocturnal boundary layer develops, which height can drop as low as a few tens of metres (Oke 1987). The state of the whole boundary layer is governed by the turbulent exchange in the lowest level, known as the surface layer. In the presence of roughness elements on the ground, a roughness sublayer (RSL) can be separated from the surface layer (e.g. Kaimal and Finnigan 1994; Oke 1987), where the effect of individual roughness elements on the flow can be distinguished. The upper part of the surface layer is called the inertial sublayer, or constant flux layer, where the turbulent fluxes change less than 10% with height. The measurements of turbulence and its transport should be carried out above the RSL, as the standard boundary-layer formulae, such as the conventional flux-profile relationship, the Monin-Obukhov similarity (MOS) and spectral theories, apply only to the inertial sublayer (e.g. Roth 2000; Arnfield 2003). The upper part of the ABL is called the mixing layer, where turbulent fluxes decrease upward.

2.1.1 Urban boundary layer

Every surface creates an internal boundary layer in the air above, which adjusts itself according to the surface characteristics (Hanna and Britter 2002; Oke 2004). Above cities, this layer is called the urban boundary layer (UBL) and is strongly modified by the high surface roughness and thermal turbulence produced by anthropogenic heat emissions and the storage of heat in urban structures (Clarke 1969; Oke 1982; Oke 1987; Oke 1988; Roth 2000; Hanna and Britter 2002). The UBL develops downwind from the edge of the urban area so that above it, the influence of the upwind surface can still be observed (Figure 1). The growth rate of the height of the UBL from the edge of the city depends on the surface roughness and atmospheric stability (Hanna and Britter 2002; Oke 2004). In the UBL, the urban canopy layer (UCL) develops between roughness elements, extending from the ground level approximately to the height of the roughness elements (Oke 1987; Arnfield 2003; Oke 2004). Air flow in the UCL is strongly modified by building geometry.

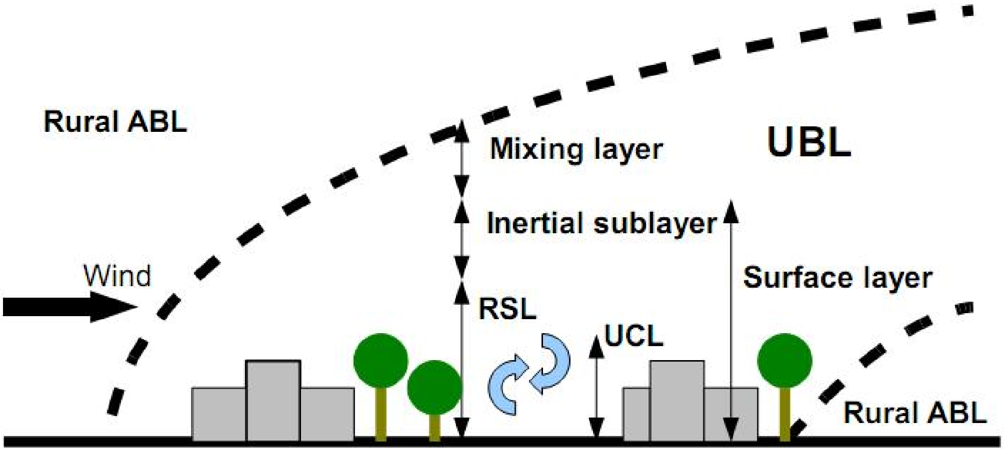

Figure 1. Schematic figure of the development and structure of the urban boundary layer (UBL). ABL, RSL and UCL stand for the atmospheric boundary layer, the roughness sublayer and the urban canopy layer, respectively. Modified from Oke (1987).

The high aerodynamic roughness of urban surfaces, often expressed with the help of parameters called the roughness length (z_0) and displacement height (d), creates frictional drag and increased turbulent intensities in the UBL (Hanna and Britter 2002; Britter and Hanna 2003; Hanna *et al.* 2007). Turbulence generated in this way is mechanical turbulence, and can be expressed as friction velocity u_*. Another primary mechanism for the generation of turbulence in the UBL is the development of the urban heat island (UHI) (Oke 1982; Oke 1987; Arnfield 2003). The UHI results from a range of factors, including anthropogenic heat emissions, the thermal properties of artificial surface materials, the changed surface albedo when compared to surrounding areas, and increased pollution levels. These affect the transport of both short- and long-wave radiation, as well as the absorption and storage of solar heat in urban structures. The strength of the UHI is not spatially homogeneous within a city, but depends on land use with lesser strength in green spaces than in more built-up areas (Spronken-Smith and Oke 1998; Ferguson and Woodbury 2007). This spatial variability can also be seen in surface energy balances, which vary according to the fraction of vegetation, anthropogenic heat emissions and storage heat fluxes (Grimmond *et al.* 2002b; Arnfield 2003; Rotach *et al.* 2005; Offerle *et al.* 2006; Coutts *et al.* 2007a; **Paper II**). Due to heat releases and induced thermal turbulence, the UBL is commonly more unstable than the surrounding rural ABL (e.g. Britter and Hanna 2003, Grimmond *et al.* 2004).

In urban areas, air pollution emissions are high due to the large number of anthropogenic sources, such as road traffic, industry and power generation. The structure and mixing conditions of the UBL strongly determine the dispersion and mixing of these pollutants and the height at which the mixing occurs (Oke 1987; Hanna and Britter 2002). It is therefore important to understand the processes creating turbulent mixing.

2.2 The eddy covariance technique

The most direct way to measure the vertical turbulent transport of momentum, heat and mass between different surfaces and the atmosphere is with the eddy covariance (EC) technique (Figure 2) (Aubinet *et al.* 2000; Baldocci 2003), which is based on the simultaneous measurement of vertical wind speed w and scalar s of interest. The average vertical flux F_s is then calculated as co-variance between w and s. The upward flux is conventionally taken to be positive. The EC measurements must be carried out at a high frequency, typically 10-20 Hz, in order to cover a wide frequency range of turbulent fluctuations. The EC technique yields the total turbulent exchange between the measurement point and some surface area upwind from the measurement point, called a footprint (Oke *et al.* 1989; Schmidt 2002). The footprint is a complex function of the measurement level, surface roughness and atmospheric stratification, and in urban areas is representative on a neighbourhood scale (Britter and Hanna 2003). Defining the footprint is especially important at complex measurements sites, where the measured flux depends strongly on what part of the landscape most influences the sensor (Schmidt 2002; Finnigan 2004). This can be done with numerical calculations, and for this purpose we used the numerical boundary layer model SCADIS (Sogachev and Lloyd 2004; Sogachev *et al.* 2004; Sogachev and Panferov 2006), which is based on a one-and-a-half-order turbulence closure applying a E-ω scheme, where E is the turbulent kinetic energy and ω is the specific dissipation of E (Sogachev *et al.* 2002; Sogachev 2009).

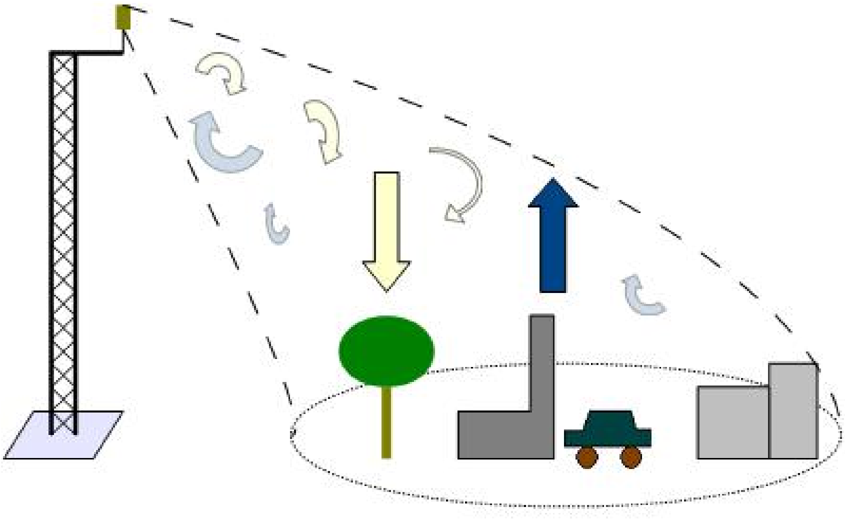

Figure 2. Schematic figure of the EC measurements. The EC system measures the integrated emissions (blue arrow) and sinks (white arrow) carried out by turbulent eddies (lighter arrows) between the footprint of the EC measurements (ellipse) and the measurement point. An example of a source is a vehicle exhaust, and of a sink, the uptake of CO_2 *by vegetation.*

In order for the turbulent flux measured with the EC technique to correspond to the net surface exchange between the surface and the air, measurements should be carried out in stationary conditions above homogeneous terrain. These conditions assure negligible horizontal and vertical advection, and zero storage of the studied scalar in the air volume below the measurement height (Aubinet *et al.* 2000; Baldocchi 2003). In reality, these assumptions are seldom met, and inaccuracies related to advection and non-zero storage term may arise. Moreover, the requirement that the EC measurements be carried out in the inertial sublayer and not in the roughness sublayer may yield errors in the fluxes at urban areas, where the height of the RSL is estimated to be 1.5-3 times the mean building height (e.g. Roth 2000; Oke 2004). Regardless of these strict assumptions, urban studies have thus far found that the basic micrometeorological theories, such as the Monin-Obukhov similarity and spectral theories, apply reasonably well (Rotach 1993; Roth 2000; Zhang *et al.* 2001; Vogt *et al.* 2006; **Paper II**).

Several possible error sources are also related to the EC technique itself and to data processing of the high frequency data. These include problems related to trend removal, co-ordinate rotation, the removal of erroneous spikes, lag-time determination and flux measurements during calm nights and low-flux situations (Aubinet *et al.* 2000; Massman and Lee 2002). EC fluxes should be corrected for losses resulting from inadequate measurement system response in the high-frequency end, and from averaging and trend removal in the low-frequency end (Moore 1986; Horst 1997). These frequency response corrections are often based on model co-spectra obtained above a flat terrain (Kaimal *et al.* 1972), and may be unsuitable to correct the fluxes in more complex terrain, where co-spectral shapes may differ. Spectral studies made in urban environments have, however, reported similar co-spectral shapes to those above flat terrain (Roth *et al.* 1989; Roth 2000, Nemitz *et al.* 2002, Mårtensson *et al.* 2006; Nemitz *et al.* 2008; **Papers II** and **IV**). Density fluctuation corrections caused by correlated heat and water vapour fluctuations should be applied to EC fluxes measured directly in ambient air (WPL correction, Webb *et al.* 1980). There is still uncertainty in how the sensor itself affects the temperature fluctuations as the sensor surface is heated by instrument electronics and solar radiation (Burba *et al.* 2006; Grelle and Burba 2007; Burba *et al.* 2008; **Paper IV**).

2.3 Air pollution in the urban environment

Air pollution, including both gaseous pollutants and aerosol particles, is linked to various health problems, such as cardiopulmonary and respiratory diseases, as well as lung cancer (Curtis *et al.* 2006; WHO 2006). These adverse health effects concern the majority of people in cities, where approximately half of the world’s population lives today (Elvidge *et al.* 2004). Curtis *et al.* (2006) listed the most important air pollutants regulated by a number of countries and organisations as particulate matter, ozone (O_3), carbon monoxide (CO), sulphur dioxide (SO_2), nitrogen oxides ($NO_x = NO + NO_2$) and lead.

2.3.1 Aerosol particles

Aerosol particles are defined as small liquid or solid particles suspended in the air (Seinfeld and Pandis 1998). Their concentrations range from a few hundreds of particles per cm^3 in remote locations to several tens of thousands of particles per cm^3 in heavily polluted urbanised areas (Koponen *et al.* 2003; Wu *et al.* 2008). These particles affect visibility and the radiation balance of urban environments, and the smallest ones are particularly likely to have severe effects on human health since they can penetrate deep into the lungs and blood circulation (Nel 2005). Aerosol particles participate in climate change by directly scattering or absorbing solar radiation, or acting as cloud condensation nuclei. Their net effect on the atmosphere is estimated to be cooling (IPCC 2007).

It is convenient to divide different-sized particles into fine and coarse particle fractions due to their differences in origin, chemical composition and physical properties. Fine particles have an aerodynamic diameter (d_a) of less than 1 µm, and in urban areas, their main source is road traffic (Morawska *et al.* 1998; Shi *et al.* 2001; Wehner and Wiedensohler 2003; Birmili *et al.* 2009; **Paper III**). In addition, stationary combustion sources have been found to be relevant to particle emissions and combustion for heating purposes has an especially well known impact on local air quality in cold regions in winter (Glasius *et al.* 2006; Saarikoski *et al.* 2008; Yttri *et al.* 2009). The smallest particles, ultrafine particles (UFP, $d_a < 0.1$ µm), are emitted primary from vehicle exhaust, or form as secondary particles in gas-to-particle conversion during the dilution and cooling of the exhaust gases. Gas-to-particle conversion also takes place without anthropogenic emission, and these particle nucleation events have been observed to occur from clean arctic to polluted urban air (Kulmala *et al.* 2004, 2005). Besides nucleation, other aerosol particle processes (dilution, condensation and coagulation) are relevant to urban road-side aerosol particle number concentrations, as has been modelled by, for example Pohjola *et al.* (2003, 2007).

Accumulation mode particles ($0.1 < d_a < 1$ µm) are mainly primary emitted from combustion sources, or grow via coagulation and condensation from smaller sizes. Contrary to UFP, which are efficiently removed from the atmosphere by coagulation and deposition mechanisms, the size of accumulation mode particles is favourable to long-range transport (LRT). The effect of LRT is small for fine particle number concentrations as they are dominated by UFP, but because accumulation mode particles are responsible for most of the mass of fine particles, approximately 50-90% of fine particle mass in Finland is due to LRT (Pakkanen *et al.* 2001; Karppinen *et al.* 2004; Kukkonen *et al.* 2008; Kauhaniemi *et al.* 2008). Urban fine particles contain substantial amounts of carbonaceous material, which is comprised of organic carbon (OC) and black carbon (BC) (Pakkanen *et al.* 2001; Sillanpää *et al.* 2005a; Yttri *et al.* 2009). BC is freshly emitted from combustion processes and can serve as a tracer for road traffic, and more precisely for the diesel vehicles (Watson *et al.* 1994; Rodríguez *et al.* 2008). BC efficiently absorbs solar radiation, and consequently plays a role in global warming (Jacobson *et al.* 2001). Coarse particles ($d_a < 1$µm), on the other hand, are mainly re-suspended material from ground and roads by natural or traffic-induced turbulence (Kupiainen *et al.* 2003; Hussein *et al.* 2008; Ketzel *et al.* 2007). These particles are removed from the atmosphere mainly by gravitational settling.

Though many aerosol particle sources have been identified in urban areas, uncertainty about the emission strength and distribution of different sources, and their contribution to measured concentrations still remain. The EC technique provides a tool to assess these uncertainties (Dorsey *et al.* 2002; Mårtensson *et al.* 2006; Martin *et al.* 2008; Nemitz *et al.* 2008; **Paper V**), and the measurements can be utilised to yield emission factors for different sources, which can then be used as input parameters in air quality and climate models or in their validation. Traditionally, the emissions factors for traffic have been determined from particle concentrations with inverse methods or directly from dynamometer measurements (e.g. Morawska *et al.* 2005), and the EC technique provides a new tool for emission factor calculations.

2.3.2 Gaseous pollutants

In the lower troposphere, O_3 forms mainly in the photo-oxidation of precursor gases emitted from fossil fuel combustion and natural processes (Seinfeld and Pandis 1998; Sillman 1999). O_3 concentrations are typically lower in city centres than in surrounding areas because in cities, O_3 is consumed rapidly in chemical reactions (Sillman 1999; Noble *et al.* 2003). NO_x play an important role in atmospheric chemistry (e.g. O_3 cycle), and their concentration is heavily influenced by fossil fuel combustion, especially road traffic (Shi *et al.* 2001; Zamboni *et al.* 2009). Similarly to NO_x, CO is emitted from road traffic, since it results from the incomplete combustion of fossil and biomass fuels (Curtis *et al.* 2006; Zamboni *et al.* 2009). SO_2 is also combustion-related, but due to the transition towards low sulphuric content fuels in road traffic, its major sources nowadays are energy production and other stationary combustion sources (Seinfeld and Pandis 1998; Shi *et al.* 2001).

Carbon dioxide (CO_2) is a gaseous compound that is not usually listed when considering air quality problems. However, because CO_2 is recognised as one of the main compounds affecting global warming, its emissions from urban areas are important to understand. Cities contribute to CO_2 emissions through changes in land use and emissions from fossil fuel combustion. Previously, estimates on anthropogenic CO_2 emissions have been based on the consumption of fossil fuels rather than direct measurements of the emissions themselves. In recent years, however, the EC technique has been utilised to obtain information about CO_2 emissions from various sources as well as the effects of different uses of land on CO_2 exchange (e.g. Grimmond *et al.* 2002b; Nemitz *et al.* 2002; Grimmond *et al.* 2004; Moriwaki and Kanda 2004; Velasco *et al.* 2005; Vogt *et al.* 2006; Coutts *et al.* 2007b; **Paper II**).

3. Measurements

The measurements in this thesis were carried out in Helsinki, Finland (60°10’N, 24°56’E), which, together with its neighbouring cities (Espoo, Vantaa and Kauniainen), forms the Helsinki metropolitan area with approximately one million inhabitants. The northern measurement location, together with a semi-continental climate, causes strong annual variations in the anthropogenic emissions of heat and pollutants, mixing conditions and the leaf area of vegetation.

3.1 The Vallila site

The measurements presented in **Paper I** were carried out at Vallila, located 2 km north-east of the Helsinki city centre. The measurement site is part of the air quality monitoring network of the Helsinki Metropolitan Area Council (YTV), and represents a typical urban area in Helsinki with an opening surrounded by five- to seven-storey block buildings. The edge of the nearest road, with a traffic rate of 14 000 vehicles per workday in 2007 (Lilleberg and Hellman 2008), is located 14 m away from the measurement site.

The BC mass concentrations were measured with aethalometers in three campaigns in November 1996 to June 1997, September 2000 to May 2001 and March 2004 to October 2005. The aethalometer is an optical instrument that measures the transmittance of aerosol particles collected on a quartz tape (Hansen *et al.* 1984). More detailed descriptions of the measurements and data handling appears in **Paper I**.

3.2 The SMEAR III station: the Kumpula site

The results presented in **Papers II-V** are based on the measurements carried out at the urban measurement station SMEAR III (*Station for Measuring Ecosystem-Atmosphere Relationships*) Kumpula site located in an urban background area about 5 km from the Helsinki city centre. The measurement site is situated around a 31-m high measurement tower (60°12.17’N, 24°57.671’E, 21 m above sea level) located on a rocky hill (Figure 3a). The surrounding area is heterogeneous, consisting of buildings, paved areas and green spaces, and was divided into urban, road and vegetation sectors according to the typical land use in each area (Figure 3b). The urban sector represents the most built-up land use with a high surface fraction of buildings (42%), roads and parking lots (51%) 250 m of the measurement tower. One of the main roads, with 45 000 vehicles per workday (Lilleberg and Hellman 2008), leading to the Helsinki city centre passes the measurement tower at a distance of 150 m in the road sector. The space between is covered with deciduous forest. The university botanical garden and allotment garden are located in the vegetation sector, where vegetation covers 85% of the area within 250 m of the tower. A more detailed description of the measurement site appears in **Papers II** and **III**.

The EC setup to measure the fluxes of momentum, sensible and latent heat, CO_2 and aerosol particle number was situated on the top boom (31 m) of the measurement tower. The setup consisted of a Metek ultrasonic anemometer (USA-1, Metek GmbH, Germany) to measure *w*, open- and closed-path infrared gas analysers (LI-7500 and LI-7000, respectively, LI-COR, Lincoln, Nebraska, USA) to measure CO_2 and H_2O densities and mixing ratios (**Paper II-IV)**, respectively, and a water-based condensation particle counter (WCPC, TSI-3781, TSI Incorporated, USA) to measure the aerosol particle number concentration starting from a size of 6 nm (**Paper V**). The measurements of momentum, sensible and latent heat and open-path CO_2 fluxes from December 2005 to June 2008 were utilised, and the data were supplemented with the closed-path CO_2 and particle number flux measurement between July 2007 and June 2008. The measurement resolution for EC measurements was 10 Hz, and for further analysis, was averaged to 30- or 60-min intervals. Commonly accepted procedures were used in the flux calculations (Aubinet *et al.* 2000).

Figure 3a. The SMEAR III station Kumpula site in Helsinki, Finland, on 26 May 2009. The photo faces the South-West, and black arrow indicates the measurement tower.

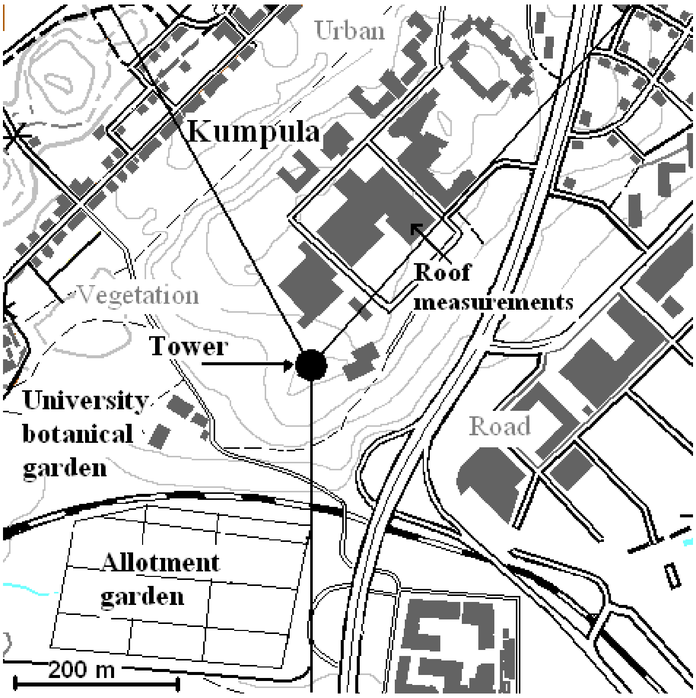

*Figure 3b. Schematic map of the SMEAR III Kumpula site. The black circle shows the place of the measurement tower and the container. The borders of the different land use sectors (urban, road and vegetation) are plotted with black lines (**Paper III)**.*

Other measurements covered air pollutant concentrations, which were sampled in a container next to the measurement tower, as well as air pressure, temperature, and relative humidity measured on top of the University of Helsinki buildings at a height of 51 m (Figure 3b). The air for the concentration measurements was drawn from a height of 4 m outside the container, and the measurements included the size-distribution of the aerosol particle number, between 3 nm and 20 µm, measured with a twin Differential Mobility Particle Sizer (DMPS, Aalto *et al.* 2001) and an

Aerodynamic Particle Sizer (APS) at a resolution of 10 min, and concentrations of ozone (O_3), nitrogen oxides (NO_x), carbon monoxide (CO) and sulphur dioxide (SO_2) at a resolution of 1 min (**Paper III**). For DMPS and meteorological measurements, data between August 2004 and June 2007 were analysed, whereas for other pollutants, the periods of analysis were shorter, as listed in **Paper III**.

4. Results

The results of this thesis can be divided into two parts. The first part covers the turbulent exchange of momentum, sensible and latent heat, CO_2 and aerosol particles measured with the EC technique, and the suitability of the EC technique for use in a complex environment. The second part covers the concentrations of different-sized aerosol particles and gaseous air pollutants.

4.1 Turbulent exchange at the SMEAR III station

4.1.1 Performance of the EC technique

In the EC technique, time series *w* and studied *s* should be rotated to certain co-ordinates in order to avoid errors related to sensor tilting relative to the ground surface. Uncertainty, about the co-ordinate system in which the calculations should be made still remains, especially at complex measurement sites (Aubinet *et al.* 2000; Kaimal and Finnigan 1994; Massman and Lee 2002). We tested the effect of two-dimensional and three-dimensional natural co-ordinate system rotations, and the planar fitting method in the calculation of momentum, sensible and latent heat, and CO_2 fluxes (**Paper II**). Deviations in each flux calculated with the different co-ordinate rotations were found to be in the order of 10%, and the largest deviations were observed in the direction of the most complex terrain, i.e. towards the direction of the highest buildings and the most sloping terrain.

The validity of the Monin-Obukhov similarity (MOS) and spectral theories were studied in order to obtain information about the suitability of the EC technique in the measurements of turbulent fluxes in such a complex environment (**Papers II** and **IV**). The accuracy of the EC technique had to be studied indirectly by using these boundary layer theories, as no self-sufficient method for verifying the functioning of the EC technique was available. According to the MOS theory, variances of atmospheric scalars and parameters normalised with the corresponding flux parameters should be a function of the atmospheric stability ζ. The normalised standard deviations of scalars (CO_2, water vapour and temperature) and *w* were plotted against ζ, and were found to follow the general equations of the MOS theory well (**Paper II**), being typical of previous urban studies (e.g. Yersel and Goble 1986; Roth 2000; Zhang *et al.* 2001). This suggests that the measured fluxes represent the neighbourhood scale without interferences from microscale perturbations. The suitability of the EC technique for the flux measurements was further supported by spectral studies, as the spectra and co-spectra of measured variables were found to follow the commonly observed spectral and co-spectral behaviours reasonably well in all areas of land use, even though the measurement point is located at only 1.5 times the mean height of the buildings in the urban sector (**Papers II and IV**). The stability dependence of the normalised co-spectral peak frequency was found to be weaker at our measurement site (**Papers IV** and **V**) than above natural surfaces (Horst 1997; Rannik *et al.* 2004). The co-spectral analysis showed that usage of the frequency response corrections seems to be justified at our measurement site also.

4.1.2 Momentum, sensible and latent heat fluxes

The transport of momentum, described as u_*, was found to be independent of season, but exhibited a diurnal dependence with higher fluxes in daytime than in night-time (Figure 4). This diurnal behaviour results from a higher production of mechanical turbulence due to the higher wind speeds in daytime, whereas annually variations in wind speeds in Helsinki are small.

Contrary to u_*, both sensible (H) and latent heat (LE) fluxes had distinguishable annual and diurnal patterns closely following the intensity of solar radiation (Figures 4 and 5). In summer, the median H and LE reached 370 W m^{-2} and 240 W m^{-2}, respectively, the latter corresponding to a water vapour flux of 4 mmol m^{-2} s^{-1}. In winter, LE was close to zero, while daytime H reached values of up to 100 W m^{-2}. H always exceeded LE, resulting in Bowen ratios ($B = H\,LE^{-1}$) larger than one, which agrees with the results of previous studies reporting ranges of B between 1 and 30, depending on the amount of vegetation cover (Grimmond *et al.* 2002b; Grimmond *et al.* 2004; Offerle *et al.* 2006; Coutts *et al.* 2007a). The effect of vegetation was also observed in our measurements, as a lower H was observed in the vegetation sector than in other land use sectors. In more built-up areas of land use, storage and anthropogenic heat emissions increased H (UHI effect). The UHI effect was most evident at the measurement point during winter nights, when upward H and unstable atmospheric stratification occurred in all areas of land use (**Papers II** and **III**). Most of this upward H likely resulted from anthropogenic heat emissions, which are typically high in cold temperatures (Taha 1997; Ichinose *et al.* 1999), as the intensity of solar radiation to be stored in urban structures is low in winter at high latitudes. In summer, the difference between H and LE decreased in the vegetation sector, as more heat is consumed in transpiration during the growing season (Figure 5).

Most of the previous studies have concentrated on summer time H and LE, and the daytime peaks have ranged from 150 to 430 W m^{-2} and from 50 to 200 W m^{-2}, respectively (Grimmond *et al.* 2004; Moriwaki and Kanda 2004; Rotach *et al.* 2005; Offerle *et al.* 2006; Vogt *et al.* 2006). These figures agree well with our results for summertime peaks ranging between 250 and 300 W m^{-2} and 50 and 150 W m^{-2}, respectively, according to the different land use covers. The large scatter between the different studies result from differences in climate zones and in urban covers, which vary from suburban to densely built-up areas. Lemonsu *et al.* (2008) was the only study reporting heat fluxes during the snow melting period in spring in Montreal, Canada, and found, as in our results, H and LE with daytime maxima of 200 and 50 W m^{-2}, respectively.

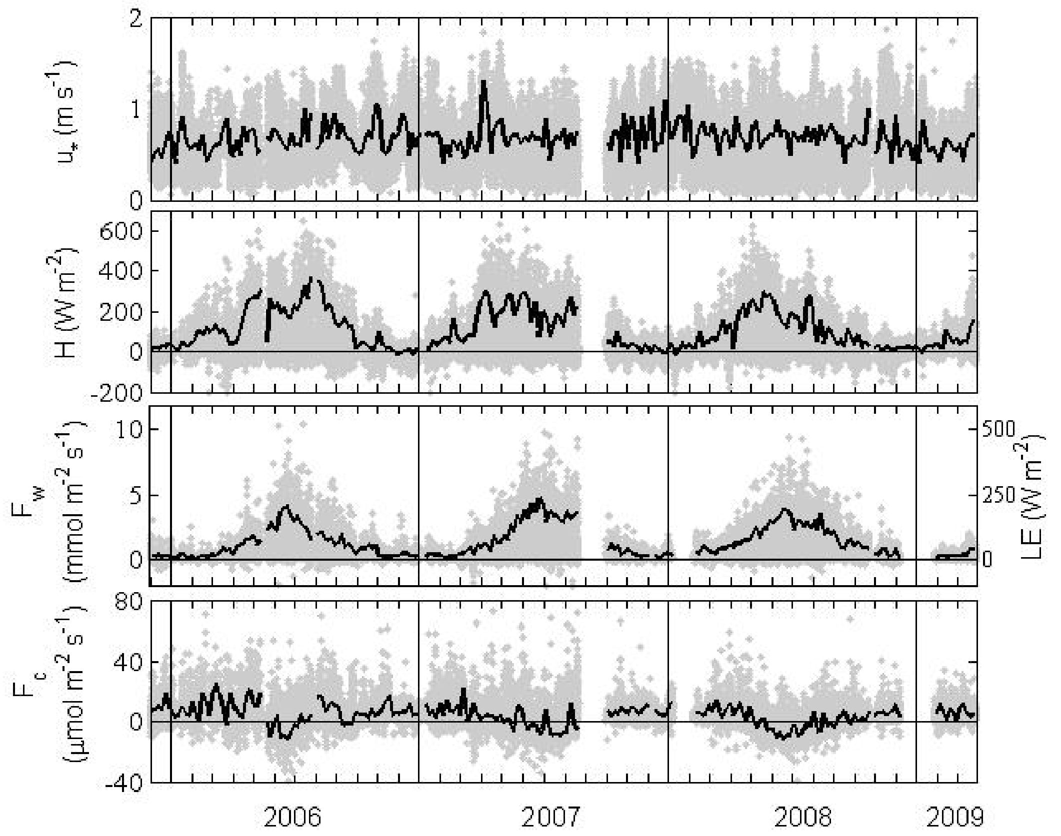

Figure 4. Time series of the vertical turbulent fluxes (friction velocity u_*, sensible heat flux H, water vapour flux F_w, latent heat flux LE, CO_2 flux F_c measured with the open-path infrared gas analyser, and particle number flux F_p) measured in Helsinki, Finland, in Dec 2005 to Mar 2009. The grey data points are half-hour averages, and the black lines show the daytime (10:00-14:00) mean fluxes calculated from five days of data. Modified from Figure 2 in ***Paper III:*** *A longer measurement period was taken into account, F_p was included, and F_c was corrected for sensor heating corrections according to the fitting method in* ***Paper IV****.*

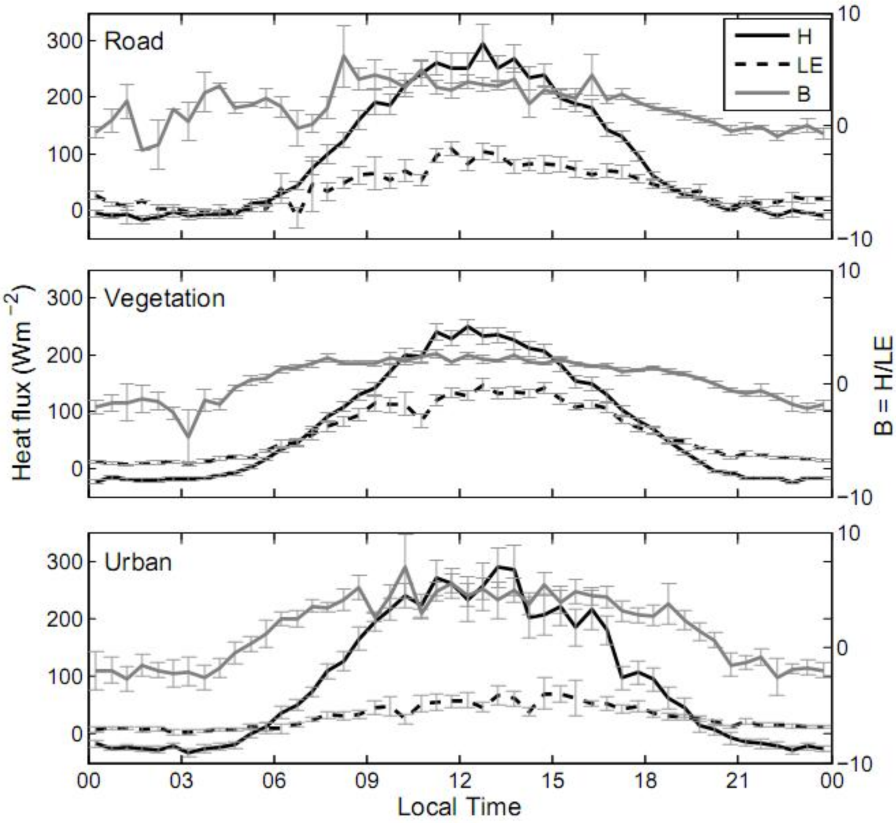

*Figure 5. The average diurnal patterns of sensible (H) and latent heat (LE) fluxes, and the Bowen ratio (B) for different land use sectors in summer 2006. Error bars show the standard errors (**Paper II**).*

4.1.3 Exchange of CO_2

The CO_2 flux (F_c) ranged between -10 and 20 µmol m^2 s^{-1} during the study period. The downward fluxes were observed during summer when, besides anthropogenic emissions, the uptake of vegetation affects the CO_2 exchange (Figure 4). Slightly higher F_c was measured in winter, likely resulting from stationary combustion processes. The highest average CO_2 emissions (20 µmol m^2 s^{-1}) were measured from the road sector, where road traffic constituted a major source of CO_2 (Figure 6), as other sources contributed only 1.1 µmol m^{-2} s^{-1} (**Paper II**). Emissions from sources other than road traffic are much lower than in Edinburgh, for example, where emissions of 11 µmol m^{-2} were observed (Nemitz *et al.* 2002), due to the widely used remote district heating in Helsinki. The surroundings of the measurement site served as a source of CO_2, except in summer, when we observed a downward flux of 8 µmol m^{-2} s^{-1} in the vegetation sector. The effect of carbon uptake was also observed as reduced fluxes in other land use sectors during the daytime, clearly showing that with more vegetation cover, we can reduce CO_2 emissions from urban environments. Nocturnal F_c in the vegetation sector was 2-3 µmol m^{-2} s^{-1} higher in summer than in other seasons due to increased vegetation respiration. This agrees with the respiration level of 1-3 µmol m^{-2} s^{-1} measured with soil chambers from ground vegetation around the measurement tower (**Paper II**).

The footprint analysis was performed separately for canopy and ground sources/sinks, and the footprint of ground sources, representative of tailpipe emissions, was found to extend further than the footprint of the canopy sources. Despite the low surface area of roads, the contribution of road traffic to the measured flux was high in the road sector. In the vegetation sector, footprint analysis showed that the vegetative areas contribute the most to F_c.

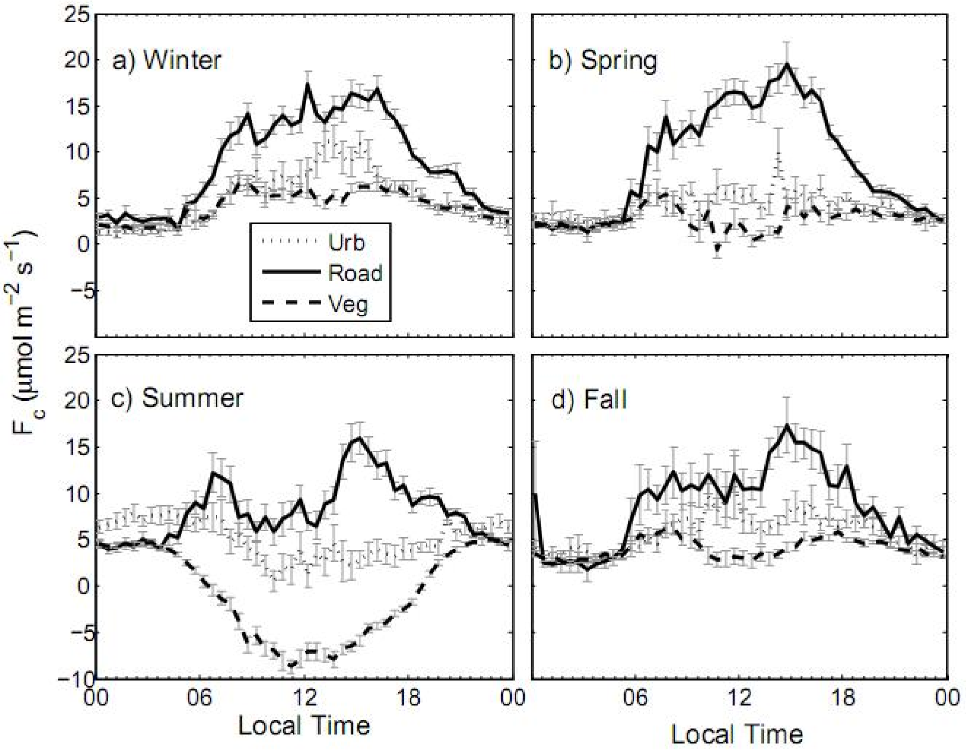

Figure 6. The average diurnal pattern of CO_2 exchange (F_c) measured with the open-path infrared gas analyser in the three land use sectors and in different seasons from Dec 2005 to Mar 2009. Error bars show standard errors. Modified from Figure 7 in ***Paper II****: A longer measurement period was taken into account, a two-dimensional co-ordinate rotation was applied to the flux calculations, and F_c was corrected for sensor heating corrections according to the fitting method in* ***Paper IV****.*

Moriwaki and Kanda (2004) collected eddy covariance CO_2 flux data from suburban Chicago (Grimmond *et al.* 2002b), the centre of Edinburgh (Nemitz *et al.* 2002) and densely built-up Basel (Vogt *et al.* 2006) in addition to their own measurements over residential Tokyo. The highest emission rate (75 µmol m^{-2} s^{-1}) was observed in Edinburgh, whereas in Chicago and Tokyo (in summer), the daily maxima remained below 10 µmol m^{-2} s^{-1}. The lowest F_c was near zero, except in Tokyo, where 5 µmol m^{-2} s^{-1} was observed. Grimmond *et al.* (2004) reported F_c from the centre of Marseille, France and found upward fluxes of up to 40 µm^{-2} s^{-1}. In Copenhagen, emission rates ranged from less than 5 µmol m^{-2} s^{-1} in residential areas to 100 µmol m^{-2} s^{-1} along major roads in the city centre (Soegaard and Møller-Jensen 2003). The city centre of Münster, Germany appeared to be a significant source of carbon as well, with average emission rate of 12 µmol m^{-2} s^{-1} (Schmidt *et al.* 2008). Velasco *et al.* (2005) and Coutts *et al.* (2007b) reported similar carbon emissions from Mexico City and Melbourne, respectively, to those observed in Europe and North America. Results from our measurement site showed similar diurnal and average flux values to those reported in previous studies. Our site was, however, found to be the largest sink for carbon in the vegetation sector in summer, where the fraction of vegetation is particularly high, and the number of anthropogenic sources is low.

Over one year, from July 2007 to June 2008, F_c was measured simultaneously with open-path and closed-path infrared analysers (F_{CP} and F_{OP}, respectively) to acquire information about the effect of open-path sensor heating on the measured flux. Correlation between the traditionally corrected fluxes was good ($R^2 = 0.93$), yielding a linear fit of $F_{OP} = 0.96F_{CP} - 0.61$, but the apparently small negative offset resulted in a difference of 17% in cumulative net ecosystem exchange (NSE), representing the effect of sensor heating (Figure 7). The underestimation of F_{OP} was greatest in warm temperatures, when solar radiation heats the analyser's surface, creating a heat flux to the ambient air. The difference in NSE was reduced to 2-11% when the effect of open-path surface heating was taken into account with the three correction procedures (fitting, linear and multiple linear regression, MLR) described in **Paper IV**. Similar measurements made above a beech forest in Denmark yielded a difference of 67% in NSE measured with the different analysers over the three-month study period from October to December 2006. This difference was high, but comparable to that in previous studies over vegetated canopies outside the growing season (Grelle and Burba 2006; Burba *et al.* 2008; Ono *et al.* 2008). With the heating correction methods, the difference in NSE was reduced to 7-50%.

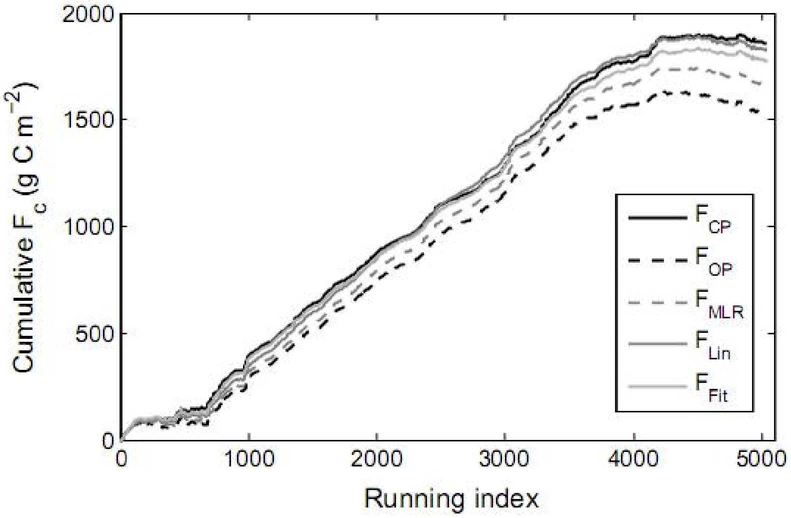

*Figure 7. Cumulative CO_2 fluxes (without gap filling) measured with the closed-path and open-path infrared gas analysers at the SMEAR III station in Helsinki, Finland, from Jul 2007 to Jun 2008. F_{CP} is the closed-path CO_2 flux; F_{OP} is the open-path CO_2 flux corrected with traditional WPL correction; F_{MLR}, F_{Lin} and F_{Fit} are the open-path CO_2 fluxes corrected with multiple linear regression (MLR), linear and fitting methods, respectively (**Paper IV**).*

From the different correction procedures, the fitting method yielded the best results at both sites, and should therefore be used in the correction. The method provides a site-specific approach to correcting F_{OP}, but the downside of the method is that it requires some period of simultaneous CO_2 flux measurements made with the open-path and closed-path infrared gas analysers, and an assumption that the closed-path analyser gives the more reliable CO_2 flux. If no simultaneous measurements are available, the linear method should be used instead of the MLR method. Ignoring the open-path sensor heating correction results in systematic error in the NSE. This would cause bias in the emission inventories on carbon at both urban and non-urban sites. As the closed-path analyser is likely to give a more correct NSE estimate than the open-path analyser, it should be used in CO_2 flux measurements instead. This is supported by the fact that quality control procedures remove more open-path flux data than closed-path flux data as periods of rain and fog always create spikes in F_{OP} (Heusinkveld *et al.* 2008; **Paper IV**).

4.1.4 Aerosol particle number fluxes

Medians of the aerosol particle number flux (F_p) ranged between 0.1-0.8·10^9 m^{-2} s^{-1}, with slightly higher fluxes in winter than in other seasons (Figure 4) (see also **Paper V**). The diurnal pattern of F_p followed the measured traffic patterns in Helsinki and reached its maximum of 1·10^9 m^{-2} s^{-1} in the road sector in the daytime. The effect of vehicular activity was observed in all areas of land use on weekdays, whereas on weekends, a distinguishable effect occurred only in the road sector. The relationship between F_p and traffic rate was found to be non-linear (Figure 8), which results from the non-linear relationship between traffic exhaust emissions and the traffic count. Moreover, the statistical correlation between traffic rate and stability, or flux dependencies on stationary emission sources and heavy duty vehicles, may affect this observed non-linear relationship (**Paper V**). Sources other than road traffic accounted only for 60·10^6 m^{-2} s^{-1} in the road sector, as was evident in the offset of the exponential fit in Figure 8. In the road sector, the highest particle fluxes correlated with the smallest particles sizes. However, in order to obtain specific information about the fluxes of different-sized particles, one should utilise measurement setups similar to those reported by Gaman *et al.* (2004) and Schmidt and Klemm (2008).

With the aid of the crosswind integrated form of the footprint function, we could estimate the emission rate for mixed fleets, yielding an average emission rate per car of 1.3·10^{13} s^{-1}, which is equivalent to 1.2·10^{15} $vehicle^{-1}$ km^{-1}. These values are slightly higher than emission rates reported in other studies where variety of methods have been used to calculate them (e.g. Gramotnev *et al.* 2003; Ketzel *et al.* 2003; Morawska *et al.* 2005; Birmili *et al.* 2009). The larger emission rates result from the lower size-detection limit of our measurement analyser, and the high amount of heavy-duty vehicles on the road next to the measurement station as their particle emissions are an order of magnitude larger than that of light-duty vehicles (Jones and Harrison 2006).

The effect of wood combustion on F_p could be observed as increased fluxes from the urban sector in winter, where an area of single-family homes with many fireplaces is located behind the University of Helsinki campus. In the urban sector, the car parks next to the measurement site also affect the particle fluxes. The surroundings only occasionally acted as a sink for aerosol particles. The measured particle number fluxes are similar to those reported in other urban studies, where the daytime maxima ranged between 0.2-2.1·10^9 m^{-2} s^{-1} (Dorsey *et al.* 2002; Mårtensson *et al.* 2006; Martin *et al.* 2008; Nemitz *et al.* 2008). The wide range as well as the difficulty of direct comparison between the studies is due to the varying lower detection limit from 3 to 11 nm. Besides, particle fluxes are highly dependent on the measurement location, the height of the measurements, and the distance from roads and other emission sources.

A comparison of particle and CO_2 fluxes showed similarity in their sources, and the highest correlation was observed in the road sector, pointing out the importance of road traffic as a source of both (**Paper V**). In summer, the correlation between the two fluxes decreased, since CO_2 exchange is affected more by vegetation cover than by particle exchange.

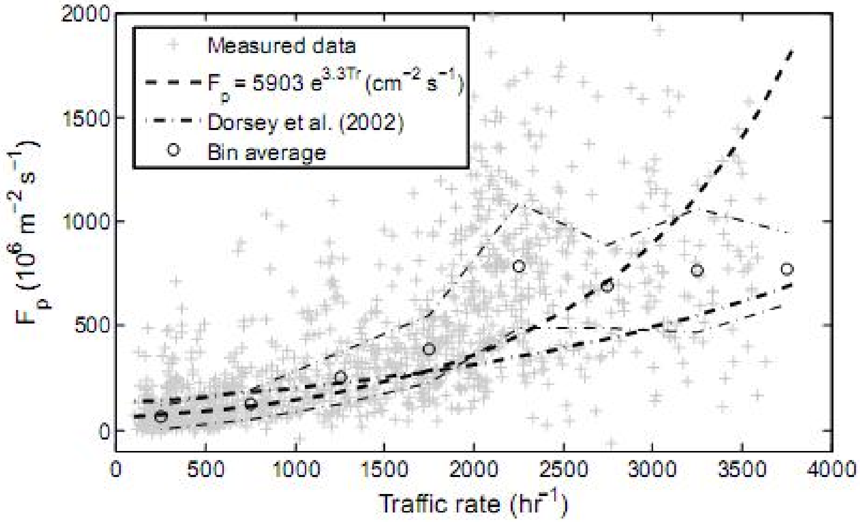

*Figure 8. The aerosol particle number flux (F_p) plotted against traffic rates in the road sector (40-180°) between Jul 2007 and May 2008. The dashed line is the exponential parameterisation made at the hourly data points, and the dash-dot line is the parameterisation obtained by Dorsey et al. (2002). The circles are averages calculated for bins of 500 vehicles per hour and the dotted lines are quartile deviations (**Paper V**).*

4.2 Concentrations of air pollutants

The combustion-related pollutants (UFP number, accumulation mode particle number, BC mass, NO_x, CO and SO_2) showed a distinct annual pattern, with the highest concentrations measured in late winter, when the largest particle emissions were also observed. In winter, emissions from stationary combustion sources are the highest, and dispersion conditions are poor, particularly during inversion situations that raise the particle level, as has also been observed in other Nordic cities (Janhäll *et al.* 2006) (**Papers I** and **III**). The stationary combustion sources refer mainly to wood combustion, since the energy production for district heating in Helsinki is well centralised, and has proper emission control, and its contribution to particle concentrations is therefore minor. In summer, on the other hand, the concentrations decreased due to more thorough mixing and lowered emissions. Accumulation mode particle number concentrations experienced a pronounced peak in late summer, when polluted air from forest fires and controlled burning in Russia and Eastern Europe is transported to Southern Finland (Sillanpää *et al.* 2005b).

At the SMEAR III station, land use cover clearly influenced traffic-related pollutants (UFP number, accumulation mode particle number, NO_x, CO), with the highest concentrations reaching 15 600 cm^{-3}, 1720 cm^{-3}, 24 ppb and 302 ppb, respectively, on weekdays in the road sector, and the lowest concentrations measured downwind from the vegetation sector. The dependence of particle number concentrations on land use was less pronounced than for particle number fluxes, since the concentration footprint is always larger than the flux footprint (Vesala *et al.* 2008). The diurnal patterns of these traffic-related pollutants were consistent with local vehicular activity, and the highest concentrations were measured during the morning rush hour, whereas afternoon peaks were diluted by turbulent mixing (**Paper III**). BC mass concentrations also followed similar diurnal patterns at the Vallila site during the measurement campaigns (**Paper I**). We observed that the importance of traffic as a source of BC decreased between 1996 and 2005, likely as a result of cleaner vehicle exhausts, since traffic rates, including the number of diesel vehicles, have increased in Helsinki during the same period.

Road traffic was a more important source of UFPs than of accumulation mode and coarse particles, thus supporting the results of previous studies (e.g. Morawska *et al.* 1998; Shi *et al.* 2001; Hussein *et al.* 2004). Accumulation mode particle concentrations are affected by long-range transport (LRT), and therefore the lower importance of local traffic as a source of these particles is reasonable to expect. LRT is responsible for the better correlation between accumulation mode particle number and CO concentrations than NO_x, since the lifetime of CO is also favourable to LRT (Seinfeld and Pandis 1998). Some effect of the local road traffic was also evident in SO_2 concentrations despite the low sulphur content of fuels in Finland, which is why the main sources of SO_2 in Helsinki are stationary combustion sources and boat traffic (Niemi *et al.* 2008). SO_2 concentrations were generally low and near the detection limits of the instrument. The maximum coarse particle concentrations were observed in spring, when the number concentration reached 1 cm^{-3}. The re-suspension of road dust by natural and traffic-induced turbulence in spring is a well known phenomenon in Nordic countries (Kukkonen *et al. 1999;* Kupiainen *et al.* 2003; Hussein *et al.* 2008). It is pronounced during dry conditions, as was evident from the inverse relationship between *LE* and coarse particle number concentration (Table 6 in **Paper III**).

Besides road traffic, mixing processes were an important factor explaining the particle concentrations at the measurement sites. Turbulent mixing had the opposite effect on different sizes of particles (Figure 9). With increasing turbulence, particles are mixed into a larger volume of air, and their concentration decreases at ground level. At the same time, the re-suspension of larger particles into the air increases (Hussein *et al.* 2006). Indications of new-particle formation events could be seen in the increased correlation between UFP and SO_2 concentrations during the spring and summer months (**Paper II**). SO_2 is considered a precursor gas for new particle formation as it oxidises to sulphuric acid, which further participates in particle formation (Kulmala 2003; Kulmala *et al.* 2004, 2005).

The behaviour of the O_3 concentration deviated from that of other pollutants, as the highest concentration of 30 ppb was measured in late spring and early summer, when O_3 is efficiently produced by the photo-oxidation of precursor vapours (Seinfeld and Pandis 1998; Sillman 1999). Higher O_3 concentrations were measured at weekends than on weekdays, when O_3 is more easily destroyed in chemical reactions (Noble *et al.* 2003).

In general, pollution concentrations at the study sites are at the lowest end of the scale, which has been measured in previous studies in Western countries (e.g. Morawska *et al.* 1998; Noble *et al.* 2003; Wehner and Wiedensohler 2003; Klumpp *et al.* 2006; Rodríguez *et al.* 2008; Yttri *et al.* 2009).

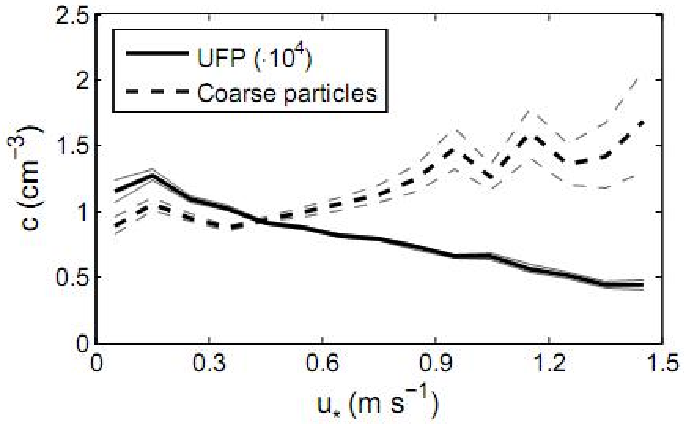

Figure 9. The bin averaged concentrations of ultrafine particles (UFP) and coarse particles as a function of friction velocity (u_*) from Dec 2005 to Jun 2007. The division was made into bins of 0.1 m s^{-1}. The grey lines show standard errors.

5. Review of papers

This thesis includes five papers examining air pollution and turbulent surface exchange measurements made in Helsinki, Finland. The turbulent fluxes calculated with the eddy covariance technique, and air pollution concentrations excluding black carbon concentration, were measured at the urban measurements station SMEAR III. The mass concentration of black carbon was measured at the Helsinki Metropolitan Area Council's measurement site.

Paper I presents the temporal variations of black carbon mass concentrations measured with an aethalometer in three campaigns between 1996 and 2005. The analysis covered comparisons between the campaigns on diurnal, weekly and seasonal scales, and the effect of road traffic and meteorological variables obtained from a meteorological pre-processor model MPP-FMI were studied by means of multiple regression analysis.

Paper II examined the long-term measurements of CO_2, sensible and latent heat fluxes made between December 2005 and August 2006. The flux data were divided according to distinguishable areas of land use, allowing us to study and to compare the fluxes between urban, road and urban vegetation covers. Footprint analysis was performed using a one-and-a-half-order closure model SCADIS to differentiate the complex topography, as well as surface and canopy sources/sinks. The nocturnal CO_2 fluxes were compared to soil fluxes measured with chambers around the measurement tower.

Paper III presents the results of the air pollution and surface flux measurements taken since August 2004. Diurnal and seasonal patterns of the ultrafine, accumulation mode and coarse particle concentrations, gas (NO_x, O_3, CO, SO_2) concentrations, fluxes of momentum, sensible and latent heat, and CO_2 were studied. In addition, dependencies between the different concentrations and basic meteorology were analysed by means of linear correlations and multiple linear regression analysis.

Paper IV studied differences in the net CO_2 exchange measured with the open- and closed-path infrared gas analysers between July 2007 and June 2008. The necessary correction procedures for each analyser, and their suitability for accurately measuring the CO_2 exchange at such a non-ideal measurement site, were examined. Three different methods were tested to correct the effect of open-path surface heating, which were compared to similar measurements made above a Danish beech forest.

Paper V examined the patterns of aerosol particle number fluxes measured from July 2007 to July 2008. Temporal variation, together with distinguishing differences between the particle exchanges on different surface covers, were analyzed, and dependencies on stability and traffic rates were studied.

6. Conclusions

The purpose of this work was to examine surface-atmosphere interactions over an urban surface based on various measurements carried out in Helsinki, Finland. Vertical exchanges of momentum, sensible and latent heat, carbon dioxide (CO_2) and aerosol particle number were measured with the eddy covariance (EC) technique at the SMEAR III station. Temporal variations of the fluxes on a seasonal and diurnal scale were analysed, and their dependencies on three distinct surface covers (urban, road and vegetation) with different source/sink contributions were examined. The accuracy of the EC technique in such a non-ideal environment was studied by examining the validity of the Monin-Obukhov and spectral theories, since no self-sufficient method was available. Systematic error in CO_2 flux resulting from open-path sensor heating was examined, and proper correction procedures were suggested. Also, the temporal behaviour of several air pollutants relevant to air quality studies was analysed, and their dependencies on environmental drivers, such as road traffic and turbulent mixing were examined. The analysed pollutants covered fine and coarse particle numbers, as well as concentrations of NO_x, CO, O_3 and SO_2 measured at the SMEAR III station, and the mass concentration of black carbon (BC) aerosol measured at the YTV measurement site.

The main conclusions of this thesis are as follows:

1. The turbulent surface fluxes, excluding the momentum flux, were affected by the high latitude measurement location in a semi-continental climate, and exhibited a distinguishable seasonal pattern. The fluxes of sensible and latent heat reached their maxima in summer, closely following the intensity of solar radiation. Solar radiation also produced a strong diurnal pattern, and the sensible heat flux always exceeded the latent heat flux due to the anthropogenic heat emissions and the efficient conversion of solar radiation to

direct heat in the urban structures (the UHI effect). The UHI was most distinguishable during winter nights, when upward *H* and unstable atmospheric stratification were observed at the measurement point. The surrounding of the measurement site was a source of both aerosol particles and CO_2, except in summer, when CO_2 uptake of the vegetation exceeded the anthropogenic sources, resulting in downward fluxes. Their diurnal behaviour was related mainly to vehicular activity and mixing conditions.

2. The sensible and latent heat, CO_2 and aerosol particle fluxes were strongly affected by the different land use covers, and the main factors influencing their exchange were the amount of vegetation and the intensity of local traffic.

   The UHI was pronounced in more built-up land use sectors (urban and road) than in the vegetation sector. In summer, the difference between the heat fluxes decreased due to heat consumed in transpiration, which was particularly evident in the vegetation sector. The highest fluxes of aerosol particle number and CO_2 were measured in the road sector, where they reached 10^9 m^{-2} s^{-1} and 20 µmol m^{-2} s^{-1}, respectively. For particles, a rough estimate of the average emission rate was $1.2 \cdot 10^{15}$ vehicles km^{-1}. Vegetation cover significantly affected the CO_2 exchange, as the vegetation uptake exceeded the anthropogenic emissions in the vegetation sector in summer, and a net downward flux of 8 µmol m^{-2} s^{-1} was observed.

3. The EC technique was found to be suitable for net surface exchange (NSE) measurements at the measurement site. Open-path sensor heating was evident in CO_2 flux, resulting in 17% lower open-path than closed-path CO_2 fluxes. From the correction procedures, the best results were obtained with the site-specific approach, and should therefore be used in the correction. However, because the sensor heating correction brings an additional source of error to the CO_2 NSE estimates, the closed-path analyser is likely to give more reliable results and should therefore be used in the EC measurements.

4. The highest combustion-related pollution concentrations were measured in winter, when reduced mixing and increased emissions from stationary combustion sources increase their concentrations. Local road traffic was found to be an important factor affecting the concentrations of UFP number, accumulation mode particle number, BC mass, NO_x and CO. Local vehicular activity was the most important environmental driver for the UFP concentration, whereas the accumulation mode and coarse particle concentrations were more affected by long-range transport and meteorological conditions. In addition, the mixing conditions of the urban boundary layer were another important factor explaining the concentrations of particles of all sizes. The type of land use had a less pronounced effect on the particle concentrations than did the particle fluxes due to its larger concentration footprint, but increased traffic-related pollutant concentrations could be observed downwind from the road sector.

This work deepened our understanding of the interactions between urban surfaces and the atmosphere with the aid of measurements carried out in a high-latitude city located in a semi-continental climate. The results of this thesis can be utilised in urban planning, as the amount of vegetation cover and vehicular activity proved to be the major environmental drivers affecting most of the exchange processes. However, these results represent only one measurement location with a footprint covering different areas of land use, and in order to understand these exchange and mixing processes on a city-scale, more measurements above various urban surfaces covering downtown areas and suburbs are required with simultaneously made numerical modelling. In future, detailed information in needed about the effects of synoptic scale meteorology on exchange processes. In particular, understanding the exchange of air pollutants and their mixing processes is vital due to their effects on the environment.

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