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Flux and concentration measurements of carbon dioxide and
ozone in a forested environment

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Helsinki, October 2017

Petri Keronen

Flux and concentration measurements of carbon dioxide and ozone in a forested environment

Petri Ilkka Rinaldo Keronen

University of Helsinki 2017

This thesis compiles the setup and characteristics of the CO₂, H₂O vapour and O₃ eddy-covariance flux and concentration profile measurement systems and the calibration arrangements at the Station for Measuring Forest Ecosystem–Atmosphere Relations (SMEAR II) of the University of Helsinki. A commercial chemiluminescence O₃ analyser operating on a liquid reagent solution was modified to improve its suitability and reliability in long term eddy-covariance measurements. Fluxes of CO₂ and O₃ were also determined with the flux-profile method relating the fluxes to the observed concentration profiles and by using the data the eddy-covariance and the flux-profile method were compared and the performances were evaluated. A separate measurement system utilising a commercial, low cost Non-dispersive Infrared-absorption analyser incorporating an automatic calibration system for measuring atmospheric CO₂ mole fraction was developed, tested and the performance of the system was evaluated.

The modifications made to the reagent liquid flow system improved the reliability of the eddy-covariance O₃ analyser. The flux-profile method was proven to be a suitable method for both CO₂ and O₃ flux measurements above forest canopy. The fluxes measured with the eddy-covariance and flux-profile method agreed during daytime under unstable conditions. At night-time the flux-profile method estimated higher respiration of CO₂ and stronger deposition of O₃, but no apparent reason for over- or underestimation by either method was identified. The night-time eddy-covariance fluxes had a spurious dependence on turbulence even after storage flux correction and for O₃ also the chemical sink strength was evaluated as negligible. Accounting for vertical advection removed the apparent dependencies. However, while accounting for the vertical advection flux seemingly resulted in invariance of CO₂ exchange and O₃ deposition rate on turbulence intensity at the SMEAR II site, the importance for estimating e.g. net ecosystem exchange (of CO₂) by different ways at flux tower sites was stressed.

The atmospheric CO₂ mole fraction measurement system had an estimated accuracy of 0.3–0.4 μmol mol⁻¹, an estimated measurement uncertainty ±0.2 μmol mol⁻¹ and its data coverage was 95 %. In a comparison between the measured atmospheric CO₂ mole fraction data and the data of MACC-II atmospheric transport model simulation for the SMEAR II site the trend and phase of the data sets were observed to generally agree and the bias of the simulation, -0.2 μmol mol⁻¹, was

within the accuracy of the measured data. Overall, the result of the comparison implied that the CO₂ mole fraction data from the SMEAR II station would clearly have the potential to be assimilated in the global inverse simulations.

Contents

List of publications	9
Definitions.....	10
Acronyms and chemical compounds.....	11
1. Introduction.....	13
2. Materials and methods.....	18
2.1 Measurement site SMEAR II.....	18
2.2 Past and current measurement systems at SMEAR II station	21
2.2.1 Eddy covariance measurement systems.....	23
2.2.2 Gas profile measurement system.....	30
2.2.3 CO ₂ mole fraction measurement system.....	36
2.2.4 Valve control, measurement timing and signal recording	39
2.3 Measurements — gas analysers, sample air conditioning, operational procedures, diagnostics monitoring and calibration arrangements.....	41
2.3.1 Eddy covariance measurements	41
2.3.1.1 Gas analysers LI-6262 and LOZ-3.....	41
2.3.1.2 Operational procedures and diagnostics monitoring of eddy-covariance instrumentation.....	46
2.3.2 Gas profile and CO ₂ mole fraction measurements	48
2.3.2.1 Gas analysers.....	48
2.3.2.2 Operational procedures and diagnostics monitoring of gas profile and CO ₂ mole fraction measurement instrumentation	52
2.3.3 Calibration arrangements	54
2.4 Accounting for vertical advection in night-time CO ₂ and O ₃ flux estimates	64
2.5 Assessment of the measured CO ₂ mole fraction data as input for modelling of regional CO ₂ exchange	66
3. Review of the papers	70

4. Author's contributions	72
5. Summary and conclusions	74
References.....	79

List of publications

This thesis consists of an introductory review and five research articles. In the thesis, these articles are cited according to their roman numerals.

- I. **P. Keronen**, A. Reissell, Ü. Rannik, T. Pohja, E. Siivola, V. Hiltunen, P. Hari, M. Kulmala and T. Vesala. 2003. Ozone flux measurements over a Scots pine forest using eddy covariance method: performance evaluation and comparison with flux-profile method. *Boreal Environment Research* 8: 425–443. Reprinted with the permission of the Boreal Environment Research Publishing Board.
- II. Ü. Rannik, **P. Keronen**, P. Hari and T. Vesala. 2004. Estimation of forest-atmosphere CO₂ exchange by eddy covariance and profile techniques. *Agricultural and forest meteorology* 126: 141–155. Reprinted with the permission of Elsevier B.V under the terms of the license number 4187601397222.
- III. **P. Keronen**, A. Reissell, F. Chevallier, E. Siivola, T. Pohja, V. Hiltunen, J. Hatakka, T. Aalto, L. Rivier, P. Ciais, A. Jordan, P. Hari, Y. Viisanen and T. Vesala. 2014. Accurate measurements of CO₂ mole fraction in the atmospheric surface layer by an affordable instrumentation. *Boreal Environment Research* 19 (suppl. B): 35–54. Reprinted with the permission of the Boreal Environment Research Publishing Board.
- IV. I. Mammarella, P. Kolari, J. Rinne, **P. Keronen**, J. Pumpanen and T. Vesala. 2007. Determining the contribution of vertical advection to the net ecosystem exchange at Hyytiälä forest, Finland. *Tellus* 59B: 900–909. Reprinted under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0/>).
- V. Ü. Rannik, I. Mammarella, **P. Keronen** and T. Vesala, 2009. Vertical advection and nocturnal deposition of ozone over a boreal pine forest. *Atmos. Chem. Phys.* 9: 2089–2095. Reprinted under the Creative Commons Attribution 3.0 License.

Definitions

accuracy — closeness of a measurement system's results for a quantity to the reference value of the quantity

bias — directed difference between the average of a measurement system's results for a quantity and the reference value of the quantity

concentration — amount a constituent in grams divided by the volume of a mixture

critical orifice — An orifice plate restricting air flow and maintaining the volumetric flow rate nearly constant when the absolute pressure ratio across the orifice plate is less than 0.53 as the flow reaches a maximum limiting condition where the velocity is the flow speed of sound (Hinds 1999).

in-situ — A phrase describing that a measurement is performed immediately on site without extracting a sample to a later analysis.

noise — random fluctuations in the measurement signal of a quantity

manifold — a pipe or chamber having multiple apertures for making connections.

mixing ratio — amount of a constituent in moles divided by the total amount of all other constituents in moles in a mixture

mole fraction — amount of a constituent in moles divided by the total amount of constituents in moles in a mixture

offset — difference between the average of a measurement system's results for a quantity and the reference value of the quantity

precision — closeness of a measurement system's results for a quantity to the average value of the results

Reynolds number (Re) — A dimensionless number indicating whether a fluid flow inside a tube is in a laminar, transitional or turbulent regime.

resolution — the smallest change in the measurement signal of a quantity that can be discriminated from the signal noise

rotameter — a device that gives the flow rate of fluid with a rotating float in a closed tube of a gradually varying cross-sectional area (Hinds 1999)

uncertainty — a parameter associated with a measurement result that characterises the dispersion of the values of quantities that are reasonably attributed to the result

Acronyms and chemical compounds

amsl — above mean sea level

VOC —volatile organic compound

BVOC — biogenic volatile organic compound

C — carbon

CFC — chlorofluorocarbon

CH₄ — methane

CO — carbon monoxide

CO₂ — carbon dioxide

CPC — condensation particle counter

EUROFLUX — A European Commission funded scientific project on Long term carbon dioxide and water vapour fluxes of European forests and interactions with the Climate System

EC — eddy covariance; a method to determine vertical turbulent fluxes by combining simultaneous records of measured fluctuations of vertical wind speed and concentration of a compound

FEP — fluorinated ethylene propylene plastic; copolymer of hexafluoropropylene and tetrafluoroethylene

FMI — Finnish Meteorological Institute

GAW — Global Atmosphere Watch (program of the World Meteorological Organization)

GC — gas chromatography; chemical separation and analysis of compounds that can be vaporized

GHG — greenhouse gas; an atmospheric gas trapping the heat in the atmosphere by absorbing infrared radiation

H₂O — water

hydrocarbons — organic compounds consisting entirely of hydrogen and carbon atoms,

ICOS — Integrated Carbon Observation System

IPCC — Intergovernmental Panel on Climate Change

isoprene (C₅H₈) — a biogenic volatile organic compound; produced and emitted by e.g. trees

MACC-II — Monitoring Atmospheric Composition and Climate – Interim Implementation

monoterpene (C₁₀H₁₆) — a biogenic volatile organic compound; a class of terpenes consisting of two isoprene units; produced and emitted by e.g. trees

MPI-BGC-GasLab — Max-Planck-Institute for Biogeochemistry-GasLab

NDIR — non-dispersive infrared

NEE — net ecosystem exchange

NNW — north-northwest

NO — nitrogen monoxide

N₂O — nitrous oxide

NO₂ — nitrogen dioxide

O₃ — ozone

PFA — perfluoroalkoxy alkane plastic; copolymer of tetrafluoroethylene and perfluoroether

PID controller — a proportional-integral-derivative controller used in (process) systems and instruments to keep a variable at a desired setpoint

PTFE — polytetrafluoroethylene plastic

sesquiterpene (C₁₅H₂₄) — a volatile organic compound; a class of terpenes consisting of three isoprene units; e.g. beta-caryophyllene

SMEAR — Station for Measuring Ecosystem-Atmosphere Relations

SO₂ — sulphur dioxide

TEI — Thermo Environmental Instruments

UEF — University of Eastern Finland

UHEI-IUP — University of Heidelberg – Institut für Umweltphysik

UHEL — University of Helsinki

URAS — Ultra-Rot-Absorptions-Schreiber (Infra-Red-Absorption-Writer)

VOC — volatile organic compound

VTT — virtual tall tower;

WMO — World Meteorological Organization

1. Introduction

Carbon dioxide (CO₂) and ozone (O₃) are both naturally occurring gas components in the atmosphere, but their concentrations are also significantly affected by human activities according to the consensus in the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC 5th AR; Cubasch et al. 2013). They both are among a group of so called Green House Gases (GHG) affecting significantly the climate through their ability to absorb the long wave (infrared) radiation emitted by the Earth's surface. This natural process, generally called as Green House Effect, contains the heat of the solar radiation in the atmosphere and keeps the global average temperature at a level favourable for living organisms. In order of decreasing atmospheric abundance the GHGs include water vapour (H₂O), carbon dioxide, methane (CH₄), nitrous oxide (N₂O), ozone and chlorofluorocarbons (CFC). While the abundance of H₂O vapour is not increased by human activities, the concentrations of the other gases have increased considerably due to anthropogenic emissions, following the industrial revolution, resulting to an amplified warming of the atmosphere due to human activities, referred to as Enhanced Greenhouse Effect (Park and Allaby 2017). The observed increase in the anthropogenic GHG concentrations is very likely the reason for most of the observed increase in global average temperatures since the mid-20th century (IPCC 4th AR; Forster et al. 2007).

CO₂ is an inert compound in the atmosphere. Plants use the carbon (C) from it, along with water from soil, to produce sugars in photosynthesis and at the same time the plants are constantly using the sugars in growth and maintaining vital functions (Hari et al. 2008). The production of the sugars is a sink while the use of sugars is a source from biosphere for the atmospheric CO₂ (plant respiration). Respiration by animals and vegetation and emission from soil following decomposition of organic matter are also natural sources of CO₂ for the atmosphere. These natural sink and source processes are oppositely directed in any ecosystem – atmosphere interface forming a continuous bi-directional flow or flux of CO₂ between e.g. forest canopy and the atmosphere. This exchange flux is crucial for the metabolism and growth of forests and other plant canopies, and increasing atmospheric CO₂ concentration in turn accelerates photosynthesis (Hari and Kulmala 2005, Farquhar and Caemmerer 1982). For the carbon, this exchange is a continuous flow of mass between the different reservoirs of atmosphere and biosphere. The sources of the most important anthropogenic CO₂, notably burning of fossil fuels, have increased its flow into the atmosphere

since pre-industrial times and as a result the global atmospheric CO₂ concentration has increased markedly (IPCC 4th AR; Forster et al. 2007).

O₃ is, contrary to CO₂, a reactive compound participating in the oxidation of many gases. It has an important role in atmospheric chemistry in troposphere (e.g. Seinfeld and Pandis 2016). O₃ is produced photo-chemically from nitrogen dioxide (NO₂), which is its only net source in troposphere (e.g. Seinfeld and Pandis 1998). Transport of the stratospheric ozone in stratosphere–troposphere exchange events are also a source of ozone for the troposphere (Holton et al. 1995; Škurlak et al. 2014). Chemical reactions involving carbon monoxide (CO), methane (CH₄), volatile organic carbons (VOCs) and nitrogen monoxide (NO) contribute to the production and gas-phase loss processes of O₃ (Atkinson 2000; Isaksen et al. 2014; Fleming et al. 2006). The production and destruction processes of O₃ are the initiation of formation of other highly reactive compounds like hydroxyl radical (OH), nitrate radical (NO₃) or peroxy radicals (HO₂+ΣRO₂) (Bonn et al. 2008). O₃ is destroyed permanently at the contact with vegetation. This process is called deposition with vegetation acting as a sink of O₃. All canopy surfaces, that is leaves, needles and bark, are sinks for O₃ (e.g. Coe et al., 1995; Rondòn et al., 1993). Soil surface, that is bare ground, is also a significant sink of O₃ while deposition rates on snow surface are generally observed to be lower than on bare ground surfaces (e.g. Stella et al. 2011; Helmig et al. 2007). In addition to this uptake by different surfaces, there is O₃ uptake also inside the foliage by the stomata in the needles and leaves (e.g. Coe et al., 1995; Fowler et al. 2001; Altimir et al. 2006). This process or rather the proceeding reactions inside the plant cause damage and injury, growth reduction and stress to the trees (Sandermann 1996, Karnosky et al. 2007). Ecosystem O₃ uptake can occur significantly also through gas phase chemical reactions with biogenic volatile organic compounds (BVOCs) in situations where the BVOC-emissions are enhanced (Goldstein et al. 2004).

Studies of the processes and phenomena occurring in any system need in principle measurements of all the quantities relevant to the system. To study the processes and phenomena in the continuum between atmosphere and any ecosystem, measurements of transport of matter and energy, storages, atmospheric concentrations of matter, meteorological quantities and solar radiation need to be considered (Hari and Kulmala 2005, Hari et al. 2009, Hari et al. 2016). In these ecophysiological measurements, three goals should be clearly recognised: a) to describe the studied ecosystem, b) to produce data sets to test models describing the ecosystem and c) to monitor all the information needed to aggregate detailed level knowledge to obtain a more comprehensive understanding of the studied ecosystem (Petäjä et al. 2008). Especially in case of a forest ecosystem the measurements of the vertical profiles of concentrations are important as there are differences in the sources and sinks

between the soil surface, air space below the tree tops, the atmospheric surface layer and the outer layer of the atmospheric boundary layer. Because the processes and phenomena depend on seasonal changes happening daily and yearly in nature, the measurements evidently need to be performed continuously. Atmospheric conditions and ecosystem state also have changes of even longer time span so it is clearly necessary to conduct long-term, inter-annual and decadal measurements.

Clearly, the data obtained from the measurements overall need to be accurate and repeatable, describing the measured quantities without bias and consistently, to facilitate a reliable analysis. And when measuring small differences either in a spatial or temporal scale the measurements also need to give precise data so that the noise of the signal does not supersede the natural variation of the measured quantity. Measuring rapid changes of any quantity requires that instruments used in the measurements have short response times. Studying seasonal and inter-annual changes requires continuous long-term measurements and there a good stability and easy maintenance of instrumentation is an additional important issue.

Initially (starting in 1930s) methods to measure fluxes of heat, momentum and moisture were developed for the needs of meteorology and agriculture (e.g. Wesely et al. 1989). Since then methods to measure fluxes of gases between the atmosphere and the canopy or soil surfaces have been extended and modified to cover more gas species of interest like CO₂, O₃, CH₄, N₂O and VOCs (e.g. Dabberdt et al. 1993 and Guenther 2002). With aerodynamic methods (Wesely et al. 1989) fluxes are quantified in air and instruments are installed on towers or in aircrafts. The measured fluxes represent the gas exchange rate of an area extending several hundred meters upwind from the measurement point. Aerodynamic methods are based on micrometeorological techniques measuring

- the concurrent turbulent fluctuations of vertical wind speed and concentration (continuous sampling eddy covariance method, e.g. Aubinet et al. 2012; disjunct sampling eddy covariance method, e.g. Rinne et al. 2001, Rinne and Ammann 2012)
- the vertical concentration profile (profile method, e.g. Wesely et al. 1989, Bocquet et al. 2011)
- the concentration difference between up- and downward directed air-drafts (relaxed eddy accumulation method, e.g. Ren et al. 2011; disjunct sampling eddy accumulation method, e.g. Rinne et al. 2000, Edwards et al. 2012)

With non-aerodynamic methods (Wesely et al. 1989) fluxes are determined by measuring the rate of change of concentration in an enclosure, i.e. by utilizing a chamber enclosing parts of a plant (or the

entire plant), soil surface or water surface (e.g. Altimir et al. 2002, Breuninger et al. 2012, Pihlatie et al. 2013, Podgrajsek et al. 2014). Specifically, in agricultural science evapotranspiration (loss of water vapour) is measured by determining the rate of mass loss of tanks filled with both soil and vegetation (so called weighing lysimeters, e.g. Fisher 2012). Obviously, in practice several enclosures are needed and the gas exchange rate observed needs to be scaled up to cover the whole ecosystem around the measurement point.

For the assessment of the combined uptake and emission of CO₂, i.e. net ecosystem exchange (NEE), and uptake of O₃ by the canopy, soil or water ecosystem additional measurements to the flux observed at the measurement level are needed. The change of the storage below the flux measurement level needs to be estimated (Aubinet et al. 1999). Also fluxes due to vertical and horizontal advection may be significant especially during stable conditions (e.g. Massmann and Lee 2002) and for O₃ chemical reactions in the air may be significant. In simplified forms the conservation equation can be written

$$F_{TURB} + F_{ST} + F_{VA} + F_{HA} = S_s + S_a \quad (1)$$

where F_{TURB} is the observed (turbulent) flux, F_{ST} is the storage change flux, F_{VA} and F_{HA} are the vertical and horizontal advection fluxes, respectively, S_s is the NEE in case of CO₂ and the ecosystem uptake in case of O₃ and S_a is the sink term due chemical reactions in the air ($S_a = 0$ for CO₂). The storage change is routinely measured at micrometeorological sites by having additional sample heights below the flux measurement level. In the assessment of O₃ deposition to a forest and any other canopy, the advection may be an important factor. And because of its chemical reactivity the aerial and surface sink terms may also have a significant effect on the observed flux at the measurement level.

At a stand or even a local scale (~1–10 km² area) the exchange of CO₂ can be assessed by using EC measurements and supplementary measurements of storage, advection and flux divergence (e.g. Baldocchi 2003). But the quantification of the Earth's carbon balance at regional scale (~10²–10⁶ km² area) is a scientific challenge as the spatial coverage of the EC measurements is not adequate to obtain estimates for regional scale flux and models utilising process studies and specific inventories are not sophisticated enough to identify sources and sinks of CO₂. Atmospheric inversion models have been shown to provide reliable estimates of the terrestrial carbon balances in the scale of subcontinental regions (e.g. Chevallier et al. 2010), but in many locations the accuracy of transport model simulations for the CO₂ mole fraction is not better than a few μmol mol⁻¹. They would

benefit from the assimilation of more measurements with accuracy a few tenths of $\mu\text{mol mol}^{-1}$, e.g., $0.5 \mu\text{mol mol}^{-1}$ (e.g. Chevallier et al. 2005; Masarie et al. 2011). In this context, usage of atmospheric CO_2 mixing ratio data from flux tower sites would provide complementary information about the fluxes for a simulation of the surface fluxes by an inversion model and reduce the uncertainty of the simulated fluxes (Butler et al. 2010).

This thesis concentrates on the measurement of fluxes, concentration profiles and concentrations of trace gases carbon dioxide (CO_2) and ozone (O_3) in a forest environment. The measurements were performed at the SMEAR II station (Station for Measuring Forest Ecosystem– Atmosphere Relations; Hari and Kulmala, 2005) of the University of Helsinki (UHEL). The fluxes were measured using both eddy-covariance (EC) and flux-profile methods (**paper I, paper II**). In the O_3 concentration measurements the focus was mainly on measurements of the vertical profile. In the case of CO_2 , the concentration was measured also at one fixed height in the surface layer to obtain data for estimation of the CO_2 concentration in the atmospheric boundary layer (**paper III**). In addition to the flux calculation the profile data was used for estimation of storage and vertical advection flux terms in the mass balance equations (e.g. Feigenwinter et al. 2004) for the net ecosystem exchange (NEE) of CO_2 and the deposition of O_3 to the forest canopy (**paper IV, paper V**).

The aims of this thesis were

- to develop and test the techniques and instruments applied in the eddy-covariance and flux-profile methods used for assessing the forest-atmosphere CO_2 exchange and deposition of O_3 to forest at the SMEAR II station,
- to construct an affordable instrumentation for measuring accurately ambient CO_2 mole fraction on top of flux towers or any tower of moderate height,
- to assess the use of the CO_2 mole fraction data from the SMEAR II station as input for inversion modelling of regional CO_2 exchange at global to continental scale.

The thesis comprises modification of a commercial fast response O_3 gas analyser to improve its suitability in long term flux measurements (**paper I**), development and testing of an automatic calibration system for a commercial CO_2 gas analyser in atmospheric mole fraction measurements (**paper III**), development of sampling and sample air conditioning instrumentation and methods to improve the use of gas analysis instruments in changing ambient conditions and development of procedures for monitoring instrumentation status to enable a more efficient allocation of the maintenance tasks. The work included laboratory and field calibrations of the instruments and inter-

comparisons with a reference CO₂ measurement system and with reference CO₂ standard gas cylinders. The measurements are used to evaluate fluxes of CO₂ and O₃ in a forest environment and to study, for example, carbon balance (Vesala et al. 2010) and O₃ deposition of a boreal forest ecosystems (Rannik et al. 2012).

2. Materials and methods

2.1 Measurement site SMEAR II

All the measurements of this work were performed at the SMEAR II station. The station is situated in southern Finland, Hyytiälä, about 220 km to the north-west from Helsinki (Fig. 1). The SMEAR II site is the central site of the ongoing SMEAR research program started in the beginning of 1990s. The SMEAR station network is designed to provide continuous and comprehensive measurements of mass flows, storages and concentrations of water vapour (H₂O), carbon dioxide (CO₂), atmospheric trace gases and atmospheric aerosols as well as momentum and energy fluxes in the land ecosystem–atmosphere continuum (Hari and Kulmala 2005).

The operation of SMEAR II station started in summer 1995 (Haataja and Vesala 1997). Other stations of the SMEAR network in Finland are SMEAR I (in operation since 1991; Hari et al. 1994) in Värriö in Finnish Lapland, SMEAR III (in operation since 2004, Järvi et al. 2009) in Helsinki and SMEAR IV (in operation since 2005, Leskinen et al 2009) in Kuopio in Eastern Finland. The SMEAR III station is co-operated by UHEL and Finnish Meteorological Institute (FMI) and the SMEAR IV station is co-operated by FMI and University of Eastern Finland (UEF). The landmark of the SMEAR II station is a micrometeorological measurement tower (Transmast VU1200, Transmast Oy, Helsinki, Finland). The tower (coordinates 61°50'50.69''N, 24°17'41.17''E in the WGS84, precisely EUREF-FIN reference frame) was erected in 1995 on a protruding bedrock surface to a height of 73 m and in autumn 2011 it was extended to its current height of 127 m. The elevation of the measurement site is 160–180 m above mean sea level (amsl) and the current highest reaching measurement level is 324 m amsl.

Hyytiälä is located in the boreal region within extended forest areas. The annual mean temperature in the area is 3.5 °C. The warmest month is July (mean temperature 10.8 °C) and the coldest is February (mean temperature of -11.5 °C). The annual mean precipitation is 711 mm. These climatological statistics are from Juupajoki-Hyytiälä meteorological station of FMI, located

about 500 m east from the SMEAR II measurement station and the data represents period 1981–2010 (Pirinen et al. 2012).

The dominant tree species in the Hyytiälä area are Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*), and in addition to them there are also broadleaved trees such as European aspen (*Populus tremula*) and birch (*Betula sp.*) to some extent. The forest around the tower was clear-cut and regenerated by a prescribed burning and sowing in 1962. Canopy height on the site was ca. 13 m in 1996 and in 2015 the height was ca. 18 m (Rantala et al. 2015). The tree population growing in a 200 m radius around the tower consists mainly of Scots pine. The stand around the tower is homogeneous for about 200 m in all directions, extending to the north for about 1 km. At longer distances, there are also other stand types and differences in age and/or composition. Towards the south-west at a distance of about 700 m there is an about 200 m wide, oblong lake (Kuivajärvi), situated at 150 m amsl, perpendicular to the south-west direction. Detailed reports on the land use categories and their respective abundancies around the SMEAR II station are given in Haapanala et al. (2009) and Williams et al. (2011), and an inventory of tree biomass stores is presented in Ilvesniemi et al. (2009).

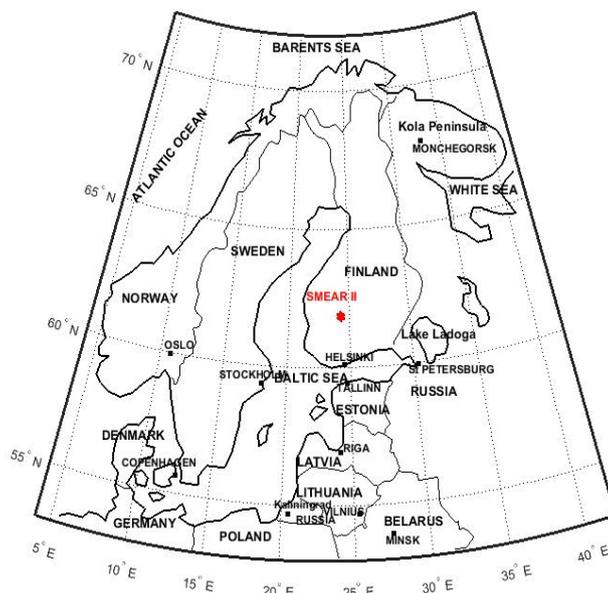


Figure 1. Location of the Smear II site.

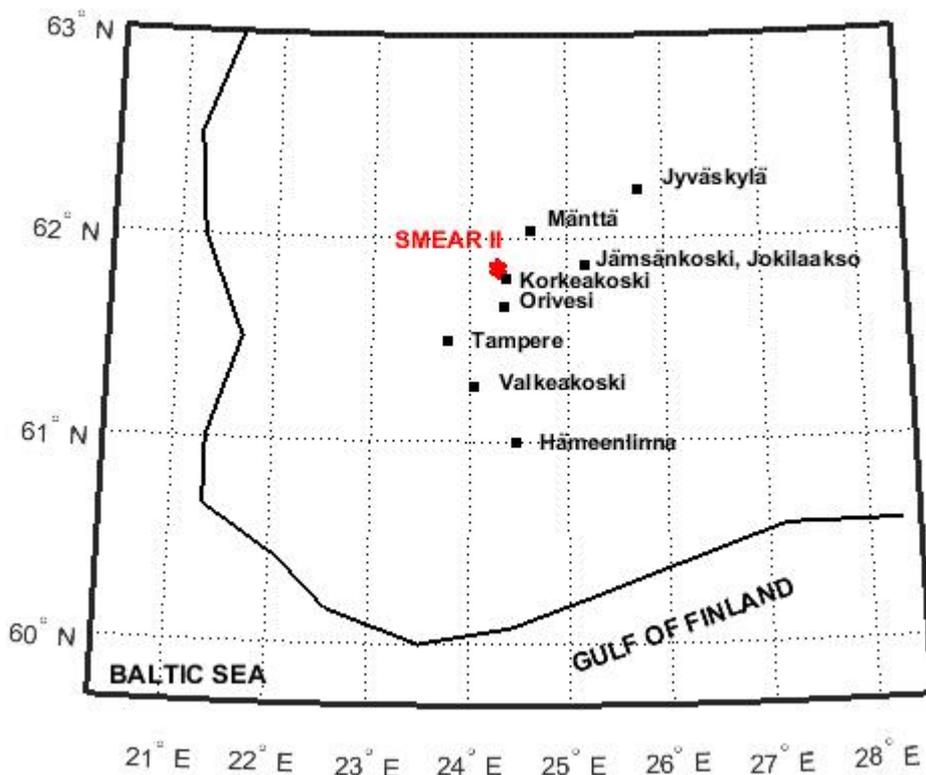


Figure 2. Location of CO₂ emission point sources within 100 km distance from the Smear II site (European Pollutant and Transfer Register; <http://prtr.ec.europa.eu/>).

The site is situated in a background area and represents a boreal coniferous forest, hence evidently natural processes are important for the CO₂ and O₃ concentrations and fluxes at the site. The main known remote source areas for pollution are continental Europe, British Isles, Eastern Europe, Southwest Russia (including St. Petersburg area) and Northern Estonia (Kulmala et al. 2000, Riuttanen et al. 2013). Nearby there are two anthropogenic sources of CO₂, namely the heating plant of the Hyytiälä Forestry Field Station situated 0.6 km in direction 245° and a saw mill and a local power plant in the village of Korkeakoski (about 2000 inhabitants) situated 7 km in direction 145°, producing some local pollution. The nearest towns are Orivesi (about 10 000 inhabitants) at a distance of 22 km in direction 165° and Mänttä-Vilppula (about 11 000 inhabitants) at a distance of about 30 km in direction 39°, respectively. In direction/distance 69°/40 km, 78°/40 km and 183°/70 km there are paper mills (Jämsänkoski, Jokilaakso and Valkeakoski, respectively). The closest bigger towns are Tampere (about 223000 inhabitants) at a distance of 40 km in direction 215°, Jyväskylä (about 68 000 inhabitants) at a distance of 100 km in direction 58° and Hämeenlinna (about 68 000 inhabitants) at a distance of 95 km in direction 178° (Fig. 2). Sectors 270°–39° and 60°–140° are relatively free from major CO₂ sources to distance up to 300 km. There are no major roads nearby, but the local emissions (of the Forestry Field Station) have been

observed to increase the wintertime CO₂ fluxes (Suni et al. 2003). The role of the remote sources and air mass trajectories is important. In case of CO₂ elevated concentrations are brought to the site from Southwest Russia and Europe in winter and spring; And in case of O₃ elevated concentrations are observed in air masses coming from those areas in spring and summertime. But also in this context the natural processes and seasonal conditions also affect the situation as e.g. in wintertime a polluted air mass acts as a sink for O₃ and in spring and summertime mainly as a source (Kulmala et al. 2000).

2.2 Past and current measurement systems at SMEAR II station

The measurement systems at the SMEAR II measuring station were planned and implemented to monitor the flows of material, energy and momentum between ecosystem and atmosphere. In the beginning the station consisted of a 73 m high tower for micrometeorological, reflected solar radiation, net radiation and trace gas concentration and flux measurements; an 18 m high scaffolding tower for shoot scale gas-exchange measurements at the top of the forest canopy and for incoming solar radiation and precipitation measurements above the canopy; soil-water and soil-atmosphere measurement setups on two water catchment areas; a measurement cottage for aerosol particle concentration and size distribution measurements and for sheltering gas analysers and measurement computers. The original description of the SMEAR II station is given in Haataja and Vesala (1997).

Over the years the measurement systems at the station have grown in number and in size and installations have been extended outside the catchment area. The measurement cottage has been enlarged and it now includes a dedicated room for instruments of central compressed air system and a place for gas cylinders. Further the station has nowadays a central vacuum system.



Figure 3. SMEAR II measurement site seen from the West over the lake Kuivajärvi. 1) 127 m high tower; 2) 18 m high scaffolding tower; 3) and 4) 16 m and 17 m scaffolding towers; 5) SMEAR cottage; 6) 35 m high tower; 7) Forestry field station; 8) floating platform. (Photo courtesy of Katri Leino).

Currently basic operation units (Fig. 3) are the 127 m high micro-meteorological tower (1) for micrometeorological, solar reflected radiation, net radiation, long wave incoming and outgoing radiation, and trace gas concentration and flux measurements; an 18 m high scaffolding tower (2) with a small hut underneath for trace gas flux measurements; two additional scaffolding towers of heights 16 m and 17 m for tree physiology measurements (3 and 4, respectively); SMEAR cottage (5) for computers controlling the measurements and recording the data. The 127 m high tower also incorporates sample lines of a separate measurement unit for greenhouse gas concentration measurements, instrumentation for flux measurements and meteorological sensors of Integrated Carbon Observation System (ICOS; <https://www.icos-ri.eu/>). In the vicinity of the catchment areas there is a locus for aerosol particle, solar incoming radiation, additional trace gas and precipitation measurements with several instrument containers and a 35 m high walk-up tower (6) for extending the measurements above the canopy. Instruments for measuring solar radiance spectrum and the atmospheric boundary layer height and vertical wind profile are installed on a roof of the Forestry

Field Station building (7). On the nearby lake Kuivajärvi there is a floating platform (8) for measurements of forest-lake-atmosphere carbon cycle, lake-atmosphere energy and gas exchange and nutrient cycling (Heiskanen 2015).

2.2.1 Eddy covariance measurement systems

In eddy-covariance method turbulent fluctuations (eddies) of wind velocity components (u , v and w) and concentration (c) of a substance are measured (Aubinet et al. 2012). The measuring instruments or sensors should have response times less than 0.1 s to capture the all eddies contributing to the flux (e.g. Kaimal and Finnigan 1994). The vertical mass flux density of a substance (F_c) is then obtained as the time average of the product of the concurrent w and c (e.g. Baldocchi 2003). The calculation makes use of the Reynolds decomposition where instantaneous values of w and c are decomposed into a mean and a fluctuating part. The time averaged (such as 30 min or 60 min) F_c of the substance at the measurement height is then

$$F_c = \overline{w \cdot c} = \overline{(w + w') \cdot (c + c')} = \overline{w \cdot c} + \overline{w' \cdot c'}, \quad (2),$$

where the over-bars denote the time-average parts and primes the fluctuating parts. By definition the time averages of the fluctuating parts (w' and c') are zero.

All in all, two eddy covariance (EC) measurement systems were utilized in this work to measure gas (CO_2 , H_2O and O_3), momentum and energy (sensible heat and latent heat) fluxes. CO_2 and H_2O fluxes were measured both in the micrometeorological tower (Eddy233) and in the scaffolding tower (EddyTow). O_3 fluxes were measured only in the scaffolding tower. EC measurements in the micrometeorological tower were started in April 1996 and EC measurements in the scaffolding tower were started in August 2001. Details of the original set-up of the Eddy233 measurement system including the data collecting/processing software and analysis of the quality of the measurements are given in Rannik (1998a) and Rannik (1998b). The EddyTow measurement system is described in detail and especially its suitability for O_3 flux measurements is analysed thoroughly including estimates of the systematic and random errors in **paper I**. Main points and changes made to the instrumentations after those early years are described in the introductory part of this thesis in the sections below.

Micrometeorological tower (Eddy233)

The Eddy233 measurement system included a sonic anemometer (Solent Research 1012R2; Gill Instruments Ltd., Lymington, Hampshire, England) to measure the three wind speed components and sonic temperature and a CO₂ & H₂O gas analyser (LI-6262; Li-Cor Inc., Lincoln, NE, USA) measuring both CO₂ and H₂O concentration simultaneously. A separate air temperature sensor was not in use. The anemometer outputs the sonic temperature as a result of its speed of sound data. By applying established procedures, the sonic temperature can be used to calculate sensible heat flux and no separate air temperature sensor is generally not needed (e.g. Aubinet et al. 2000). These instruments were chosen to be the ones in use in EC flux measurement systems of EUROFLUX project (European Commission, Programme Environment and Climate 1994–1998, contract ENV4-CT95-0078) and SMEAR II was one of the 14 measurement stations of the EUROFLUX network. The common methodologies for the operation of the instruments and for the correction and treatment of the data of an EC-measurement system in the EUROFLUX network were described in Aubinet et al. (1999).

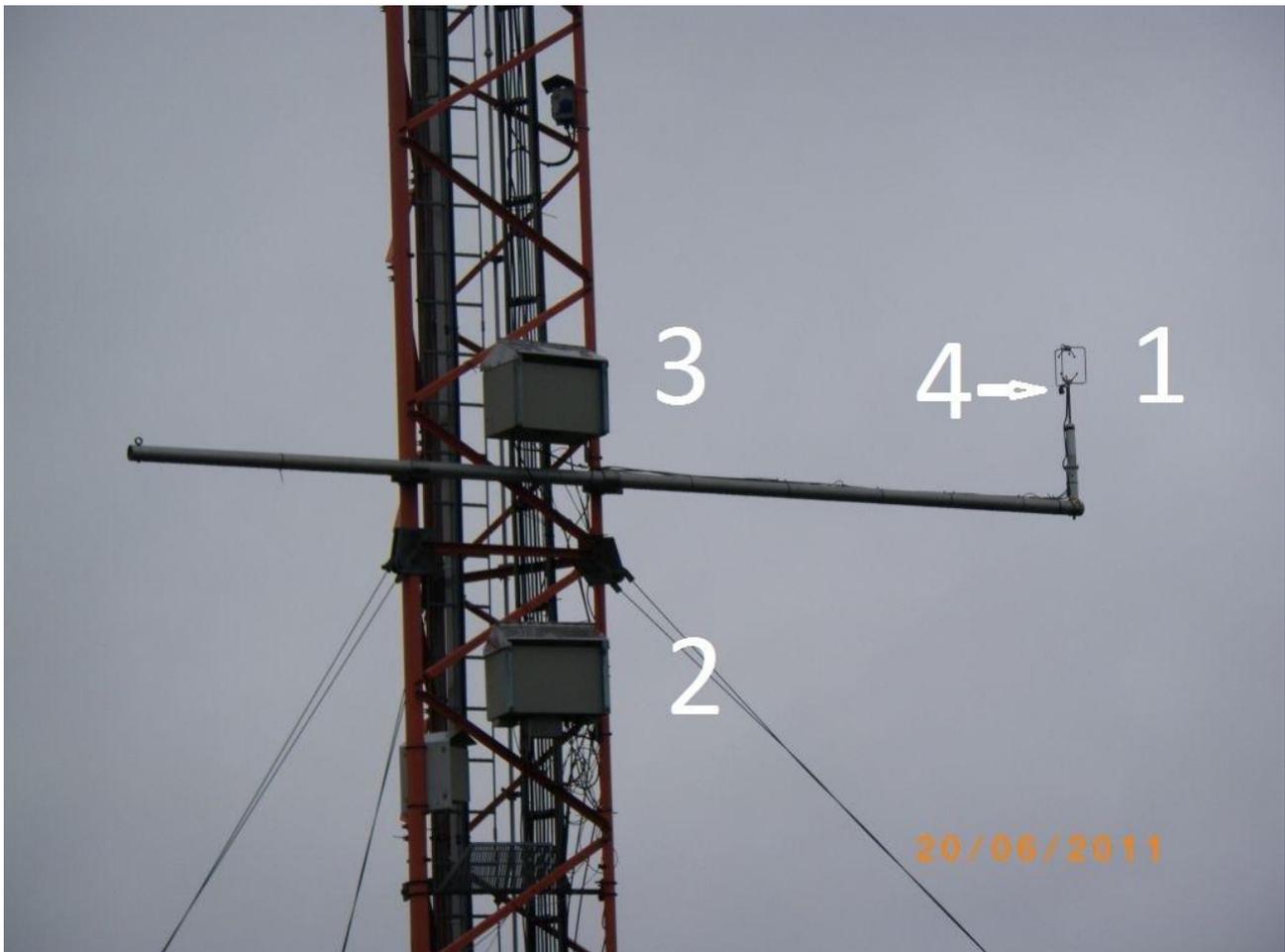


Figure 4. Eddy co-variance measurement instruments in the high tower, 1) sonic anemometer; 2) enclosure of CO₂ & H₂O gas analyser; 3) enclosure of aerosol particle counter; 4) sample air inlet.

The Eddy233 measurement system was installed at 23.3 m height in the high tower (Fig. 4). The anemometer (1) is attached at the end of a north-northwest (NNW) pointing boom (of a circular cross-section) at a distance of 3.5 m from the tower structures. The gas analyser (Licor233) was placed in a heated (controlled by a thermostat) and ventilated enclosure (2) installed on the outer side of the tower below the boom attachment point. The intake of the sample line was fixed below the sensor probe head of the anemometer at about 15 cm distance from the centre of the sensing volume formed by the probes. The dimensions of the sample line tube were: length 7 m and diameter 6x4 mm (outer x inner). At the intake, there was an inlet structure kept on purpose as small as possible to avoid unnecessary structures causing flow distortions near the sensing volume, but as a necessity the inlet comprised of a simple plastic rain cover big enough to fit inside it the sample tube with a coarse dust filter (sintered brass compressed air filter/silencer) to prevent water and larger (diameter over ~50 µm) particles, mainly pollen, from entering the tube. And the filter also prevented insect intrusion into the line. The flow rate of the sample air was 6.3 l min⁻¹, and it was set and controlled with a mass flow controller (Model 5850E; Brooks Instrument, Veenendaal, The Netherlands) placed in the vacuum line. The flow rate was considered as high enough to ensure turbulent flow in the tube. At the end of the line, at the Licor233 sample inlet, a 1 µm pore size PTFE membrane filter in a polypropylene housing (Gelman Acro 50 Vent Filter; Pall Corporation, Port Washington, NY, USA) was in use to protect the measurement chamber from dust contamination. The sample line and the inlet were slightly heated (power 5 W m⁻¹) to prevent condensation inside the line and frost formation/build-up of snow obstruction on the inlet.

Originally there was also a separate, parallel stainless steel (SS) sample line connected to an aerosol particle concentration measuring instrument (CPC 3010; TSI Inc., Shoreview, MN, USA; 3) used for corresponding flux measurements utilising the same anemometer. In May 2002, the Licor233 sample line was removed and the separate sample lines combined to a single line. This resulted to two changes in the construction of the gas analyser sample line: a) the tube material was changed from PTFE to SS (electro-polished, seamless). The last 0.5 m length of the line before the Licor233 was, however, left to be PTFE-tube to provide necessary flexibility. b) The filter was left out from the combined sample line's inlet construction because of the measurement of aerosol particles that would have been trapped in the filter. However, as the inlet (height 45 mm, diameter 16 mm, with a 6x4 mm opening in the lower rim) of the aerosol instrument's sample line was recycled in the new sample line, also the simple steel insect net (sieve size 0.5 mm) at its opening was

left in place. Then later, in September 2003, the inlet construction was changed with improvements to the efficiency of the heating and prevention of water intrusion into the tube. This improved sample air inlet (item No. 4 in Fig. 4) was 28 mm high and the total diameter was 40 mm with the heating cable wrapped around it. The sieve size of the insect net was 1 mm.

Scaffolding tower (EddyTow)

The sonic anemometer of the EddyTow measurement system was another model of Gill Instruments' sonic anemometers, namely HS1199 Research. The CO₂ & H₂O gas analyser in the EddyTow measurement system was a similar LI-6262 instrument as was in use in the Eddy233 measurement system. A separate air temperature sensor was not in use in the EddyTow measurement system either. The EddyTow measurement system was from the very beginning constructed for O₃ flux measurements also (**paper I**). The fast response O₃ analyser installed in it was a model LOZ-3 Ozone analyser (Unisearch Associates Inc., Concord, Ontario, Canada). Its operation is based on chemiluminescence technique (e.g. Heard 2006). A diagram of the EddyTow measurement system is shown in Fig. 5.

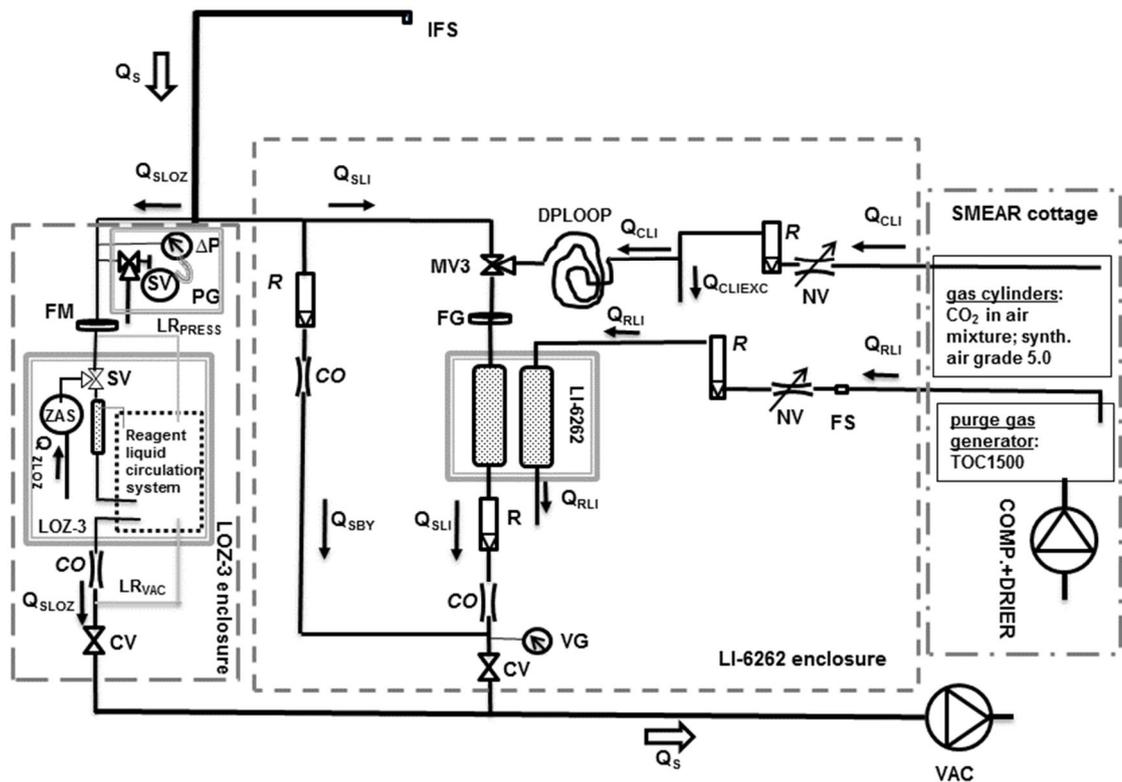


Figure 5. IFS inlet filter (SwageLok); Q_s total sample flow; Q_{SLOZ} sample flow of LOZ-3 analyser; Q_{ZLOZ} zero air sample flow of LOZ-3 analyser; Q_{SLI} sample flow of LI-6262 analyser; Q_{SBY} by-pass flow; Q_{CLI} calibration gas flow of LI-6262 analyser; Q_{CLIEXC} excess flow of calibration gas; TOC1500 reference gas generator for LI-6262 analyser; Q_{RLI} reference gas flow of LI-6262 analyser; FM dust filter (Mitex); FG dust filter (Gelman Acro); FS dust filter (SwageLok); PG pressure guard system; ΔP pressure sensor; SV solenoid valve; CO critical orifice; NV needle valve; CV shut-off valve (manual operation); R rotameter; MV3 3-way valve (manually operated); VG vacuum gauge; VAC central vacuum pump and COMP + DRIER compressed air system of the station; DPLOOP loop for decreasing pressure of calibration gas flow.

The anemometer (Solent HS) was installed at a height of 23.0 m by means of the 18 m high tower and a 6 m long rectangular installation mast (Fig. 6). In addition to the installation mast the sample line structure of a Relaxed Eddy Accumulation system (item 2 in Fig. 6) also extends above the tower structures, but all in all the tower is relatively unobstructed above 16 m height with a ratio of obstructed-to-unobstructed area of about 10 %. The Solent HS is of a horizontal mount design

and the supporting rod for the sensor head is 1.25 m long. The heated, temperature controlled by a thermostat, and ventilated enclosures sheltering the gas analysers were installed in the tower at a height of 15 m. The intake of the sample line was fixed along the Solent HS's supporting rod at a distance of about 25 cm from the centre point of the sensing volume. The CO₂ and H₂O (LicorTow) and O₃ (LOZ-3) analysers had a common main sample line (tube material PTFE, diameter 10x8 mm). The LOZ-3 was connected to the main sample line at about 10 m distance from the intake with a 0.5 m long branch line (tube material FEP, diameter 1/8x1/16 in). The LicorTow was in turn connected with a 0.5 m long PTFE tube to the end of the main sample line. The inlet protecting the intake against rain was machined from a plastic rod and had a 5x15 mm in size opening directed downwards.

There were no aerosol particle measurements in the EddyTow system and so a coarse particulate filter (IFS in Fig. 5) of stainless steel material (FW series SS-316 pleated mesh element, mesh size range 5–10 µm; Swagelok Company, Solon, Ohio, USA) could be placed at the sample line inlet (item 3 in Fig. 6) as a protection against dust, pollen and insects. The size of the inlet was evidently bigger than supporting rod (diameter 25.4 mm) of the Solent HS, but as in the direction of the rod there was already the installation mast of the Solent HS (see Fig. .6), the size of the inlet was not considered to cause any excessive disturbances. The flow rate of the sample air in the main line was 14 l min⁻¹ for the first 10 m and 13 l min⁻¹ for the last 2 m, which were considered to be high enough to maintain a turbulent flow (Reynolds number Re ~2100) while keeping the pressure drop along the sample line at its minimum (~50 hPa). The sample flow rates of the LicorTow and LOZ-3 analysers were 6.5 min⁻¹ and 1 min⁻¹, respectively. The flow rates were set with so called critical orifices (see definitions) placed inside the respective vacuum lines. To reach the full flow rate in the main line an additional flow (by-pass flow) of 6.5 min⁻¹ was in use and set also with a critical orifice. The LicorTow sample flow rate and the by-pass flow rate were controlled with rotameters (see definitions) placed inside the LicorTow enclosure (R in Fig. 7). The sample line, the filter and the inlet were slightly heated (power 3.5 W m⁻¹) to avoid condensation inside the line and to minimize the risk of frost formation/build-up of snow obstruction on the inlet. At the LicorTow analyser's sample inlet there was a µm pore size PTFE membrane dust filter (FG in Fig. 5) in a polypropylene housing (Gelman Acro 50 Vent Filter; Pall Corporation, Port Washington, NY, USA). The dust filter (FM in Fig. 5) at the LOZ-3 sample inlet was a 5.0 µm pore size PTFE membrane filter (Mitex; Millipore Corporation, Bedford, MA, USA).



Figure 6. 1) Solent HS sonic anemometer;
 2) sample lines of Relaxed Eddy accumulation;
 3) sample air inlet.

Figure 7. 1) LI-6262 CO₂ & H₂O analyser
 2) sample air/calibration gas switching valve

The usage and characteristics of the Solent R2 and Solent HS are described in Rannik (1998) and in **paper I**, respectively. During the first years, 1996 and beginning of 1997, a program developed at the University of Edinburgh, namely EdiSol version V 0.36, was used for the data recording. But all the data was post-processed and fluxes calculated with a program SMEARSol, developed by Dr. Rannik (Rannik 1998). In 1997 also the data recording was started to be performed by that program. The data collection and post-processing procedures are presented in Rannik (1998) for the Eddy233 system and in **paper I** for the EddyTow system. The post-processing of the Smear II EC-data has been developed rigorously later on and currently all the processing is performed with a program EddyUH developed in the Micrometeorological group of the Division of Atmospheric Sciences of University of Helsinki (Peltola and Mammarella 2015).

2.2.2 Gas profile measurement system

In flux-profile method the vertical (z axis) concentration profile $\frac{\partial c}{\partial z}$ of a substance is measured. The response times of the instruments can be several seconds or even tens of seconds. The concentration differences to be measured are small and so instruments need to have a high resolution (e.g., Wesely et al. 1989). The time averaged F_c is then calculated using a formula for mass transport analogous to molecular diffusion (Fick's first law) as

$$F_c = -K_c \frac{\partial \bar{c}}{\partial z}, \quad (3),$$

where K_c is turbulent exchange coefficient and the over-bar again denotes time average. The averaging interval is usually 30 or 60 min. The basis for the calculation of the flux from the measured profile is the Monin-Obukhov similarity theory (e.g. Foken 2006). The turbulent exchange coefficient depends on atmospheric stability, surface roughness and observation height above the surface.

For substances which don't have any sources but only sinks a frequently used formulation is that the F_c is directly proportional to the c at the measurement height

$$F_c = -v_d c, \quad (4)$$

where v_d is a proportionality constant called deposition velocity (e.g. Seinfeld and Pandis 2016). By convention flux downwards has a negative sign giving a positive deposition velocity.

The measurements of vertical profiles of gas concentrations were started gradually by the end of year 1995. During the year 1996 the gas analysers were intermittently used in other applications so that the continuous profile measurements began in January 1997. Description of the original profile method sample lines, valve system, air pump and blower installation, recording of instrument signals and computer system for controlling the measurements is given in Haataja and Vesala (1997). The main architecture has worked well over the years. The applicability of the profile method for estimation of vertical fluxes at the site was demonstrated in Rannik (1998a) and Rannik (1998b). The flux-profile method was shown to be a suitable method for the flux measurements for

both CO₂ (**paper II**) and O₃ (**paper I**). Technical details related especially to the measurement of CO₂, H₂O and O₃ profiles are described in this work.

The concentration profile measurement system includes (main) sample lines equal in length and diameter from the measurement levels up in the high tower down into the main cottage, manifolds for diverting the sample air flows to the analysers from the main flows, solenoid valves for switching the sample levels, pumps and blowers for transferring sample air along the lines and one analyser for each of the gas species (O₃, NO & NO_x, SO₂, CO, CO₂, H₂O, VOC). For O₃ measurements a TEI 49 series analyser (Thermo Fisher Scientific, Waltham, MA, USA) is in use. For CO₂ and H₂O measurements two separate single component URAS 4 analysers (Hartmann & Braun, Frankfurt am Main, Germany) were in use during the first 15 and 16 years, respectively. Since July 2010 a two component LI-840 (Li-Cor Inc., Lincoln, NE, USA) analyser is in use for the CO₂ measurements. The H₂O measurements are performed with the LI-840 analyser since September 2011.

After the main sample lines the measurement system is divided into three parts: CO₂ & H₂O system, O₃, NO & NO_x, SO₂ & CO system and a VOC system (Fig. 8). Profiles of NO & NO_x, SO₂ and CO are measured using the same sample lines, valve control, signal logging and data recording instrumentation as is used for O₃ measurements and only the actual gas analysers are separate and different ones. For reasons of simplicity and clarity the O₃, NO & NO_x, SO₂ & CO system will from now on be referred to as O₃ system. The VOC system for measuring the profiles and further fluxes of VOCs with flux/gradient method is described in Rantala et al. (2014). In this work measurements with the CO₂ & H₂O and O₃ systems are considered.

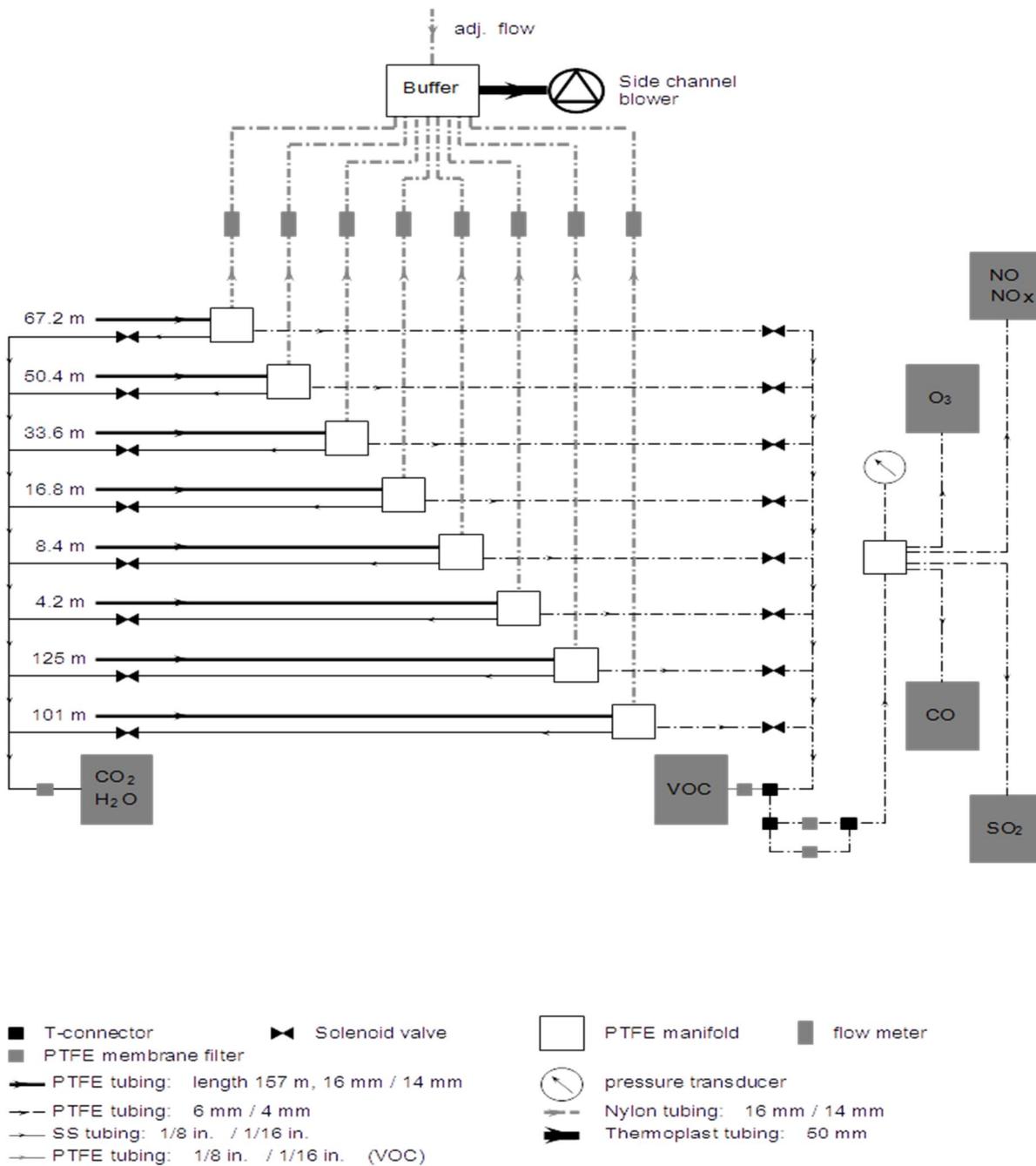


Figure 8. A diagram of the gas concentration profile measurement system at SMEAR II station updated and modified after Fig. 1 in Rantala et al. 2014 (courtesy of Pekka Rantala).

Until June 2012 the sample line configuration for concentration profile measurements consisted of six sample lines from levels at 4.2, 8.4, 16.8, 33.6, 50.4 and 67.2 m heights above the base of the high tower. During July 2012, the sample lines were completely renewed and also two more lines were installed at heights 101 and 125 m. The actual deployment of these two lines was postponed to February–March 2013. Chemically pure, i.e. without any additives, PTFE plastic was chosen to be the material of the sample line tubes to minimize the potential losses or emissions of gases inside them due to adsorption and desorption, respectively. PTFE is hydrophobic and non-reactive towards the normal atmospheric constituents and it has an intrinsically smooth non-stick surface. PTFE is also resistant to microbiological growth, maintains elasticity even at winter time freezing temperatures and withstands UV-radiation and subsequently aging. The sample air inlets (Fig. 9) in the tower protecting the lines and ultimately the analysers against intrusion of water are also made of PTFE material (machined from a PTFE rod by T. Pohja, Juupajoki, Finland). Otherwise the inlets are freely open without any dust filters.



Figure 9. Sample air inlet in the high tower (photo courtesy of Janne Levula).

In measurements of rapid fluctuations of H_2O vapour concentration there exists considerable attenuation and delay of the signal due to adsorption and desorption processes even when using PTFE tubes as sample lines (e.g. Nordbo et al. 2013). But in the profile measurements, where significantly longer averaging times are used, the signal dispersion caused by these processes is not a disturbing factor. Successful measurements of H_2O vapour profiles using long sample lines of

plastic tubes have been reported e.g. by Mölder et al. (2000), who had 140 m long lines of HD-polyethylene.

Initially the main lines were constructed of 100 m long and 16x14 mm in diameter PTFE tubes (Laborex Oy, Helsinki, Finland). With the extension of the tower the lengths of the sample lines were increased to 157 m, but the diameter of the tubes was kept the same. Until the renewal of the sample lines there were also water separators (material laboratory glass), where the air flows inside made a 180° degree turn, installed in the lines at the base of the tower. These separators were not reinstalled to the renewed sample lines as they were observed to be unnecessary. The distance between the main cottage and the tower is about 30 m. The excess lengths of the tubes are kept coiled inside a separate shelter built ca. 0.3 m above the ground. The inlets, tubes and water separators are slightly heated (5.5–7.4 W m⁻¹) by heating cables (Deviflex-84-9DSIG, Devi A/S, Veijle, Denmark) attached separately to each of them all the length. In the tower section, the heating cables are taped without gaps onto the tubes with the heating power of 5.5 W m⁻¹ on average. In the ground section the tubes are placed inside a wooden covered channel, leading to and from the shelter, and likewise lifted ca. 0.3 m above the ground. In this section, a single heating cable is installed loosely inside the channel while the heating power is 7.4 W m⁻¹. The temperature inside the tube channel has been checked to be about 3°C above the ambient temperature, which means that the relative humidity is 75–85 %.

The air flow rates, generated with a side channel blower (Gast R3105 regenerative blower; Gast Group Ltd., Redditch, UK), in the main lines have been at two different levels over the years, ca. 35 l min⁻¹ and 45 l min⁻¹, due to technical reasons related to other scientific activities at the station. There are no air flow controllers in use for the main lines, but rather the flow rate per line depends on the number of lines connected, length and other dimensions of the lines and adjustable by-flow in a 100 l volume buffer chamber located in the line (Buffer in Fig. 8). The actual flow rates are manually monitored with rotameters (Dwyer RMB-53; Dwyer Instruments, Inc., Michigan City, IN, USA). Because of this the lag time for the transport of sample air inside the main lines was 25 s in period 1995–August 10th 1997, 20 s in period August 11th 1997–October 19th 1998, again 25 s in period October 20th 1998–June 10th 2002 and then again 20 s in period June 11th 2002–June 2012. With the extension of the sample lines on July 27th 2012 the lag time lengthened to 35 s. The pressure drop in the main sample lines, currently about 55 hPa, is monitored with a differential pressure transmitter (Dwyer series 604A; Dwyer Instruments, Inc., Michigan City, IN, USA) installed at the 16.8 m level manifold.

A detailed diagram of the concentration profile measurement system is depicted in Fig. 10 of chapter 2.2.3. The length of the main sample lines indoors is about 0.5 m each and the sample air flows are taken as side flows from the main lines at manifolds made of a PTFE rod (machined by T. Pohja, Juupajoki, Finland). Until September 2006, CO₂ & H₂O and O₃ & NO, NO_x, SO₂ and CO analysers had common solenoid valves (SV_{O3} in Fig. 10; type 0211-A-03-F, wetted parts SS, viton™ gasket, orifice size 3.0 mm; Christian Bürkert GmbH & Co. KG, Ingelfingen, Germany) for switching between the main lines from the sample heights and the sample lines leading to the valves and further to the analysers were 6 x 4 mm diameter PTFE tubes. Starting September 2006, the CO₂ & H₂O analyser sample flows are taken via dedicated solenoid operated valves (SV in Fig. 10; type 6011-A-F, wetted parts SS, viton™ gasket, orifice size 2.0 mm; Christian Bürkert GmbH & Co. KG, Ingelfingen, Germany) installed to a common anodised aluminium plate. Coincident with this change the CO₂ & H₂O sample lines from the manifolds were changed to 3.18x2.1 mm diameter stainless steel tubes (Supelco™ 20526U, sleek electro-polished, grade AISI304 SS, Sigma-Aldrich, St. Louis, MO, USA) and the sample line from the valve assembly was changed to stainless steel tube also being partly of 6x4 mm size due to technical/practical reasons. Between September 2006 and August, 2011 the sample air of the CO₂ analyser was dried as the analyser was connected also to the concentration measurement system (see chapter 2.2.3). In case of the O₃ & NO, NO_x, SO₂ and CO analysers the sample level switching valves are still the original ones and the sample line indoors have remained as 6x4 mm diameter PTFE tubes. In case of both CO₂ & H₂O and O₃ & NO, NO_x, SO₂ and CO analysers the lengths of sample lines indoors are 2–3 m. The differences in the lengths are ± 0.5 m due to the differences between the mutual placement of the manifolds and valves. Single gas analysers were used to avoid variations in calibration between instruments especially as the concentration profiles were expected to be small at the site during daytime when turbulent mixing usually is the strongest.

Gas concentrations are measured successively at 60 s intervals from the sample levels. With the eight sample levels, the arrangement nowadays is such that levels 67.2 m, 33.6 m, 16.8 m, 8.4 m and 4.2 m are measured five times during a ½ h averaging period while the levels 125 m, 101 m and 50.4 m are measured by turns two times per the same period. The response times of the CO₂ and O₃ measurement systems (analyser + sample lines inside the cottage) was experimentally determined to be 30 and 40 s, respectively. These times were assigned for flushing after each measurement level change before starting to record the concentration signals. The configuration of the profile measurement system enables to set these times separately for every analyser. The use of any averaging, so called buffer, volumes to smooth real concentration fluctuations caused by

atmospheric turbulence (e.g. Mölder et al. 2000) from the signals would not have been a reasonable nor a working solution in the profile measurement system because of the common sample line and valve system for both the CO₂ and H₂O samples and the samples of reactive O₃, NO & NO_x and SO₂ gas species. Instead the filtering of the concentration fluctuations is accomplished with the profile measurement program by taking e.g. the CO₂ and O₃ concentration signals at five second intervals after the flushing times for the remaining 30 and 20 s, respectively, and calculating the averages before recording the signals in the data file. For the CO₂ and O₃ analysers a recording interval of 10 s would of course be a relevant one taking into account their time constants, but the set time interval is a feature of the measuring program serving also other purposes. The standard deviations of the CO₂ and O₃ analyser signals for calibration gases were found to be on the order of 0.1 μmol mol⁻¹ and 0.5 nmol mol⁻¹ setting the precisions of 30 min average concentration detection at about 0.03 μmol mol⁻¹ and 0.2 nmol mol⁻¹, respectively.

The strategy of sampling the profile levels successively using the same analyser for all the levels assures there are no systematic differences between the levels due to instrumentation. But without the buffer volumes the chosen strategy obviously introduces an error because the sampling of the concentration profiles is not done simultaneously (Meyers et al., 1996). However, because this error is random in nature it was not assumed to lead to any systematic biases in the results.

2.2.3 CO₂ mole fraction measurement system

During the first (10) years the CO₂ & H₂O system and O₃ system had a common main sample line switching valves so that only after the valves the sample lines were divided into the respective systems. In September 2006, a dedicated CO₂ mole fraction measurement system incorporating instrumentation for automatic calibration was taken into use. The CO₂ & H₂O profile measuring system was equipped with a new separate (from the O₃ system) unit for sample line switching valves as well as calibration gas line switching valves and a sample air dryer (Nafion® membrane, 12" PD™-200T-KA, Perma Pure LLC, Toms River, NJ, USA) for the CO₂ analyser was added to the system (SVs and PD-200T in Fig. 2, respectively, in **paper III**). The technical design and the construction of the new valve unit was accomplished by Dr. h.c. T. Pohja.

The make and model of the analyser in the dedicated CO₂ mole fraction measurements has been changed several times since the start in October 2006. Until March 2008 the URAS 4 CO₂ analyser of the profile measurement system was in use for the CO₂ mole fraction measurements also. First, in March 2008, a separate analyser, namely the LI-840 CO₂ & H₂O analyser was installed in the

system. Between June 2010 and August 2011, the profile and mole fraction measurement systems again had the LI-840 as the common analyser. In September 2011 an LI-820 CO₂ analyser (Li-Cor Inc., Lincoln, NE, USA) was installed in the CO₂ mole fraction measurement system as a separate analyser. The use of the LI-820 analyser continued until the end of year 2012. In year 2013 the measurements were transferred to a separate system distinct from the SMEAR II profile measurement system and a new type of an analyser, at first Picarro G1301 and later on Picarro G2401 (Picarro Inc., Santa Clara, CA, USA) was taken into use (illustrated as Picarro system in Fig. 10).

In the CO₂ & H₂O system the total sample air flow rate is 1 l min⁻¹ set with needle valves (S series metering valve; SwageLok, Solon, OH, USA) and monitored with mass flow meters (PFM7 series flow switch; SMC Corporation, Tokyo, Japan) installed in the pump line after the analysers. In the O₃ system the total combined sample air flow rate is 5 l min⁻¹ set with needle valves, critical orifices or capillary tubes installed inside the individual analysers.

As a protection against soiling of the gas analysers' measurement chambers and other internal parts hydrophobic PTFE membrane particulate filters (F and F_{O₃} in Fig. 10; Merck Millipore, Merck KGaA, Darmstadt, Germany) are in use at the analysers' sample inlets. In the CO₂ & H₂O system the filter of choice is 47 mm in diameter, 1 µm in pore size Fluoropore™ FALP04700 bonded to polyethylene support grid. As the sample air flow rate in the O₃ system is higher two Mitex™ LSWP04700 filters with larger diameter (47 mm) and pore size (5 µm) are installed parallel to reduce the pressure decrease in the filters. There is no supporting grid on these membranes but instead they consist of the plain PTFE membrane. The filter holders are made of PTFE coated aluminium with a glass window (Teledyne Advanced Pollution Instrumentation, San Diego, CA, USA). Previously filter holders made completely of perfluoroalkoxy alkane (PFA) (e.g. Savillex, Eden Prairie, MN, USA) were in use in the O₃ system.

A diagram of the concentration measurement system is illustrated in Fig. 10, where VOC system and Picarro system stand for the VOC measurements (Rantala et al. 2014) and greenhouse gas measurements with a Picarro CO₂, CH₄, CO and H₂O analyser (Peltola et al. 2014), respectively.

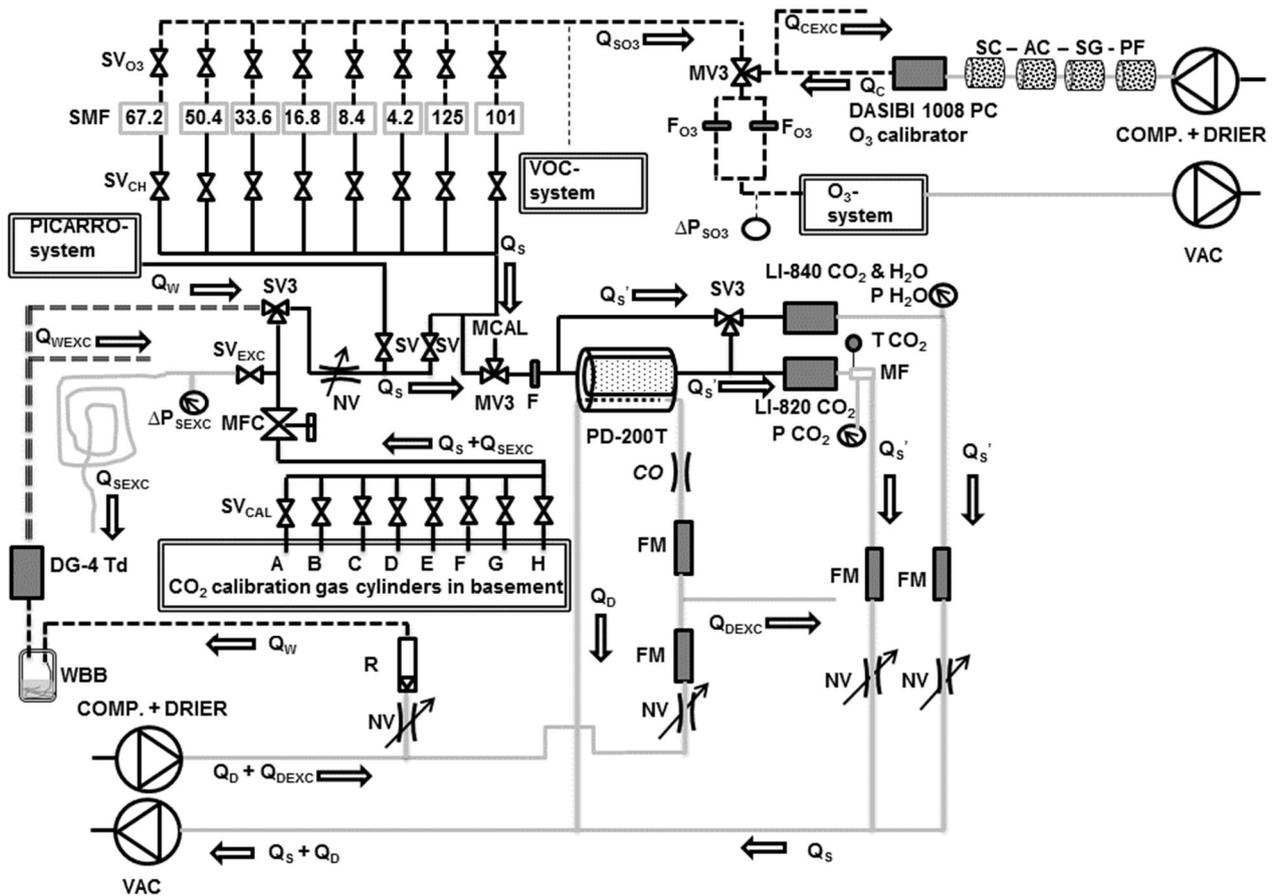


Figure 10. Diagram of the instrumentation for the measurement of the ambient gas concentrations. The system consists of the following parts: SMF manifolds in the main sample lines; $Q_S (=Q_S' + Q_S')$ sample air flow; PD-200T sample air drier; F and F_{O_3} particulate filter; P H_2O and P CO_2 pressure transducers; T CO_2 temperature sensor; R rotameter; FM mass flow sensor; MFC mass flow controller (Brooks 5850E; Brooks Instrument, Hatfield, PA, USA); Q_D drier purge air flow; MV3 (manual) 3-way valve (40 series ball valve; Swagelok Company, Solon, OH, USA); SV3 solenoid 3-way valve (Bürkert 0330T; Christian Bürkert GmbH & Co. KG, Ingelfingen, Germany); SV solenoid valve; SV_{CAL} solenoid valve (type 6011-A-F; Christian Bürkert GmbH & Co. KG, Ingelfingen, Germany); SV_{EXC} solenoid valve (type 6011-A-F; Christian Bürkert GmbH & Co. KG, Ingelfingen, Germany); ΔP_{SEXC} pressure difference transducer for excess flow of the calibration gas; SV_{CH} and SV_{O_3} solenoid valve; NV needle valve (M series metering valve; SwageLok, Solon OH, USA); CO critical orifice; cylinders (not drawn) of the (five) CO_2 calibration gas mixtures connected to ports A, B, C, D and E; a cylinder of compressed air connected to port G; (port F not in use; port H reserved for leak tests etc.); VAC and COMP. + DRIER central vacuum pump and compressed air system of the station, respectively; Q_W flow of the H_2O span air; Q_{WEXC} excess flow

of the H₂O span air; Q_{SEXC} excess flow of calibration gas; Q_{DEXC} excess flow of the compressed air; Q_{SO3} sample air flow; F_{O3} particulate filter; ΔP_{O3} pressure difference transducer; ZA zero air generation system; Q_{ZAEXC} excess flow of the zero air. DG-4 Td dew point generator; WBB water bubbler bottle; R rotameter (Kytölä Oy, Muurame, Finland).

2.2.4 Valve control, measurement timing and signal recording

The solenoid valves of the profile and concentration measurement systems are controlled by a serially connected digital valve interface (Grayhill Promux® 72-PMO-3, Grayhill Inc., IL, USA). The valve sequencing and data recording is defined by timing table lists and operating system command scripts. The sequence timing resolution is 1 s with an uncertainty of approximately 0.1s. Both valve sequencer and signal recorder are C (programming language) -coded programs and are run in conjunction and partly synchronously with other continuous measuring activities of the station. The measuring programs and the data transfer electronics of the profile measurement systems were planned, programmed and constructed by Dr. T. Lahti and M.Sc. (Tech.) E. Siivola, respectively. (Haataja and Vesala 1997). The dedicated calibration gas line valve control and a separate signal logging system including data recording program for the CO₂ mole fraction measurements was designed, constructed and coded by M.Sc. (Tech.) E. Siivola. The control of the separate sample line valves of the CO₂ & H₂O and O₃ profile measurement system are synchronised.

The signals from the various sample line pressure difference, sample flow, sample temperature sensors and pressure sensors and gas concentration signals from the analysers are connected to analogue interfaces. In CO₂ and H₂O profile system there is an analog-to-digital (A/D) converter (PA-AD12-H; Acqutek Corporation, Inc., Taipei, R.O.C., Taiwan) in use for the concentration and sample pressure signals and in O₃ profile system a serial transmitter (Nokeval 5020; Nokeval Oy, Nokia, Finland) is utilised. A Nokeval 5020 serial transmitter was in use in CO₂ and H₂O concentration system, too. The (older) model 5020 transmitters are gradually being changed to model RMD680. The A/D-converter has differential input channels while the Nokeval transmitters are of single-ended type having a common ground for all the input channels.

The PA-AD12-H has an A/D conversion time of 10 μs. During initial tests, it was observed that by filtering out rapid signal oscillations of the URAS 4 analysers at the A/D-converter the electronic processing noise could be reduced effectively. This reduction is accomplished by taking 200 readings and calculating the average value of those for each channel in one second. The Nokeval

serial transmitters are serially controlled 16 channel multiplexing ad-converters. The maximum measuring rate of the Nokeval 5020 is 1.6 s. This was utilised in the CO₂ and H₂O concentration measurement system where the signals were read at 2 s intervals. From the A/D-converter all the channels could also be read in less than 2 s intervals, but the response times of analysers set the reasonable overall logging interval to 5 s. The stability of the ½ h concentration data for each sample level is increased by averaging the concentration signals for the time remaining after the flushing time set separately for each gas species.

Summarizing the sampling procedure, the precision of the data was maximised by reducing the influence of real concentration fluctuations caused by atmospheric turbulence by maximising the sampling flow to the analysers and by reducing the short-term fluctuation of the concentration signal by optimizing the data averaging. The measurement program also has as an option to convert the signals to physical units, but otherwise are stored as recorded in daily files without any further processing.

In the both EC systems, the integrated loggers of the anemometers were used to log the CO₂, H₂O, O₃ and aerosol particle concentrations as analog mV-signals. The loggers integrated the wind and analog input data and output the combined data as a digital signal utilizing RS-422 standard. It was considered reasonable to log the analog signals directly with the loggers instead of having separate data cables from the instruments connected to the measuring computer placed in the main cottage. The analog inputs of the Solent R2 logger are of single-ended type and the A/D-conversion is 11 bits. The Solent HS is a newer and enhanced model and has differential analog inputs with a 14 bit A/D conversion. To avoid electromagnetic interferences and grounding errors in the long cable lines and especially for lightning protection, optical fibre was taken in use as the data line between both the Solent R2 and Solent HS and the measurement computer in the main cottage. This required modifications inside the anemometers as the original bi-directional RS-422 signal was replaced with separate input and output signals.

The diagnostic signals (e.g. sample pressure, analysis lamp intensity, detector temperature) of the first set of gas analysers were monitored and recorded manually from time-to-time. For some analysers, a digital output was an optional, separate feature and some of the analysers were not equipped at all with digital outputs. Over the years new additional analysers or replacements for the broken ones have a digital output of the diagnostic values as a standard feature and so the recording of the diagnostic signals is nowadays done automatically.

2.3 Measurements — gas analysers, sample air conditioning, operational procedures, diagnostics monitoring and calibration arrangements

2.3.1 Eddy covariance measurements

2.3.1.1 Gas analysers LI-6262 and LOZ-3

CO₂ and H₂O analyser LI-6262

Two component LI-6262 analysers have been in use in the CO₂ and H₂O eddy covariance measurements since April 1995 (Eddy233 system) and since August 2001 (EddyTow system). Actually the LI-6262 analyser of the EddyTow system has been in use since February 1998. It was utilised until June 2000 in another EC-measurement setup at 46 m height in the high tower.

An LI-6262 is an NDIR instrument where the detection is based on infrared radiation absorption technique (e.g. Heard 2006). The degree of absorption is related to the CO₂ or H₂O concentration as described by the Beer-Lambert Law of light attenuation, which states that the attenuation of light along a path depends on the concentrations of the attenuating species, their optical properties and the length of the path. The optical properties further depend on the frequencies of the light. A simplified mathematical expression of the Beer-Lambert Law relating those parameters to the measured intensities is given as

$$I = I_0 e^{-SP\chi Nl}, \quad (5),$$

where I is transmitted intensity (W m^{-2}), I_0 is incident intensity (W m^{-2}) from a light source, S is absorption cross section per molecule ($\text{cm}^2 \text{ molecule}^{-1}$), P is sample pressure (atm), χ is volume mixing ratio of the species; N is total molecule number density of the sample ($\text{molecule cm}^{-3} \text{ atm}^{-1}$) and l is sample path length (cm).

The LI-6262 is a differential analyser with two separate absorption chambers in its optical bench. One chamber is for the sample air and the other is for a reference gas and the measurements are based on the difference in absorption of the radiation passing through the chambers. The source of the infrared radiation is a (heated) metal filament and the intensity of the radiation is measured with pyroelectric solid state detectors. Inside the measurement enclosure there in the optical path

between the source and optical bench there is, a chopping shutter disk rotating at 500 Hz to modulate the radiation and subsequently the signal. The reference chamber is open and user can choose the type and the composition of the reference gas. A continuous flow of the reference gas is needed. The enclosure housing the chopper disk needs to be continuously purged of CO₂ and H₂O vapour. There is also a bottle filled with scrubber chemicals inside the detector housing to keep it free from CO₂ and H₂O vapours. The selectivity is based on the use of narrow band optical filters placed in front of the detectors. For the CO₂ channel the optical band pass filter is centred at 4.26 μm . In the H₂O channel the optical filter is centred at 2.59 μm (LI-6262 CO₂/H₂O Analyzer operating and service manual, 9003-59, 1996). The embedded software of an LI-6262 analyser compensates the direct effects of temperature and pressure on the concentrations of CO₂ and H₂O in the sample chamber. The software also calculates a dilution correction to the CO₂ concentration that is due to presence of H₂O vapour. The pressure has an effect also on the absorption characteristics of the molecules. The LI-6262 analysers used in the studies were equipped with pressure transducers and this effect of pressure on the absorbance was also taken into account by the analyser's software. No additional pressure and temperature sensors were in use, but the pressure and temperature correction of the CO₂ and H₂O signals by the embedded software was assumed to be adequate.

The LI-6262 analysers of the Eddy233 and EddyTow systems are operated in so called absolute mode, in which the CO₂ concentration of the reference gas needs to be zero and the reference gas needs to be dry. In tests preceding the start of the EC measurements it was determined that a flow of 200 ml min⁻¹ was the minimum to purge the reference chamber free of CO₂ without any noticeable effect, higher than 0.1 $\mu\text{mol mol}^{-1}$ in the signal. In the beginning of the measurements the chopper disk enclosure was purged using an external bottle filled scrubber chemicals attached to the in- and out-port of the enclosure as is instructed in the instrument manual. But the eddy covariance systems were reconstructed (already in 1999), following the recommendation by Li-Cor, Inc. (McDermitt, 1997), so that the reference gas was directed to flow through the chopper enclosure after purging the reference chamber. This modification was found to work well, and especially it reduced the amount of maintenance work.

O₃ analyser LOZ-3

Measurements of O₃ concentration were performed with a closed path LOZ-3 Ozone analyser (Unisearch Associates Inc., Concord, Ontario, Canada) from August 2001 until September 2013. It operates on chemiluminescence principle (e.g. Heard et al. 2006). Inside a measurement chamber

the sample air flows across a fabric wick saturated with a continuously flowing reagent liquid solution containing chemical Eosin-Y dissolved in ethylene glycol. The reaction between O_3 and Eosin-Y then produces light by chemiluminescence in proportion to the O_3 concentration and the light is measured with a photomultiplier tube. The wick area of the measurement chamber is thermostatically controlled to $35\text{ }^\circ\text{C}$ as the reaction rate coefficient is temperature dependent. The temperature is also measured and subsequently compensated for by the analyser's internal software. The sample pressure is also measured and compensated for by the software (LOZ-3 Operator's manual 1998). There is no separate liquid pump but instead the reagent solution is drawn from a reservoir vessel to the wick by a slight pressure difference ($\sim 100\text{ hPa}$) against the ambient pressure created by a short capillary tube inside the sample air inlet of the reaction chamber. The inside of the reservoir vessel is normally at ambient pressure. The reagent solution is re-circulated by removing it from the exhaust sample air in a form of droplets inside a separation vessel. The collected liquid is then automatically, at 5 s intervals for less than 1 s at a time, drained to the reservoir vessel by a valve operation connecting the reservoir vessel volume to the pump vacuum (Fig. 11).

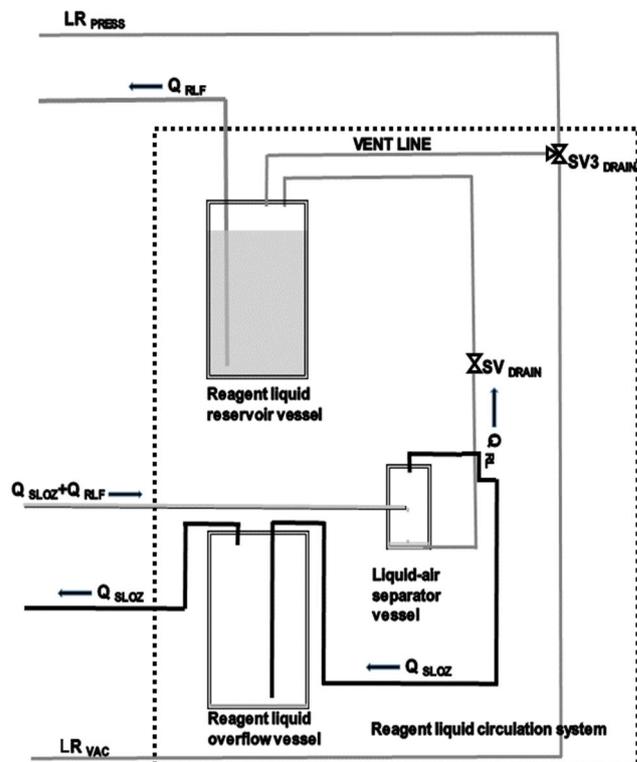


Figure 11. Diagram of the liquid flow of LOZ-3 analyser. LR_{press} pressure line for reagent liquid reservoir vessel; LR_{vac} vacuum line for reagent liquid vessel; Q_{RLF} reagent liquid feed line;

SV_{3DRAIN} and SV_{DRAIN} 3-way and 2-way solenoid valve, respectively, for drainage of Liquid-air-separator vessel; Q_{RL} flow of reagent liquid; $Q_{SLOZ} + Q_{RLF}$ sample air flow + reagent liquid feed flow; Q_{SLOZ} sample air flow.

Rather significant modifications to the arrangements of the control of the sample air flow, to the structure of the sample air lines, to the placement of the reagent liquid reservoir vessel and separation vessel were necessary already before the deployment and further during the first years of use of the LOZ-3 analyser.



Figure 12. 1) LOZ-3 analyser, 2) reservoir vessel for reagent liquid, 3) sample line.

As the LOZ-3 analyser was installed outdoors (Fig. 12), the reagent liquid reservoir vessel was relocated outside the analyser chassis (item 2 in Fig. 12) to enable an easier or in winter conditions altogether possible replenishment or change of the reagent liquid. Additionally, the original reservoir vessel, a plastic 100 cm³ bottle with brittle tube connectors in the lid, was replaced by a more robust glass bottle with a more sturdy lid facilitating the use of dedicated tube connectors. The new reservoir vessel had also a bigger volume of 250 cm³.

Also, the separator and the liquid trap placed after the separator were soon after the deployment of the analyser relocated outside its chassis. Failures of the automatic draining, resulting in an up to top filling of the separator and the trap with the reagent liquid, turned out to happen to quite

frequently. In those cases a manual emptying of the separator and the trap was necessary and by having these components placed outside the chassis rendered the maintenance crucially easier. After some time the original trap vessel was taken out of use and in its place a larger overflow vessel for the liquid was installed in the system as the control of the liquid flow turned out to be unreliable quite frequently. The overflowed and collected liquid could then be reused.

The original sample air pump, located inside the chassis, was taken out of use and instead the analyser was connected to the central vacuum system of the station (in October 2003). In practice not all reagent liquid was recycled, but some of it was continuously removed out of the circulation in the exhaust air flow. And sometimes the amount of removed liquid was for some reason bigger than normal. As a result the empty volume inside the reservoir vessel could un-noticed grow considerably. After some pondering it was concluded that this chain of events eventually resulted to a drainage failure, as the factory installed sample pump was not powerful enough to create an adequate vacuum inside the vessel with a bigger than expected air space. The original coil of capillary tube controlling the air flow rate was also in this connection changed to a critical orifice to control the flow.

A separate actuator system (pressure guard) to monitor the pressure drop inside the main sample line and to disconnect the analyser inlet from the main sample line was taken in use in December 2006 (PG in Fig. 5). As the analyser was obviously designed for a certain liquid flow rate combined with a certain time-lapsed valve operation for draining the separation vessel, an increase of the liquid flow rate to the measurement chamber combined with a decrease of the liquid suction rate from the separation vessel resulted in the end to an overflow situation inside the separation vessel where the liquid level reached the air exhaust opening at the vessel's top. At this point the operation of the liquid recirculation system collapsed and all the reagent liquid was subsequently sucked out of the reservoir vessel. In winter time clogging of the filter at the sample line inlet due to a build-up of an ice/snow obstruction was the reason for an increase of the pressure difference between the measurement chamber and the reservoir vessel. In summer time (small) insects could clog the filter. Dust, e.g. pollen, in the filter was also a cause to an increased pressure difference. Especially the build up of the ice/snow obstruction could happen quickly and somewhat unpredictably. These malfunction situations were of course unwanted. The pressure guard system consisted of a pressure sensor, 3-way solenoid valve + microcontroller unit (engineering and construction by B. Eng. H. Laakso). It was installed to monitor the pressure drop inside the main sample line and to turn the 3-way valve to direct the LOZ-3 sample intake away from the main sample line to the free air instead whenever the pressure drop reached a pre-set trigger level (50 hPa). In a case the pressure drop

decreased below the trigger level, the sample intake was directed back to the sample line, but with a delay function to prevent oscillation.

2.3.1.2 Operational procedures and diagnostics monitoring of eddy-covariance instrumentation

During the first years of operation, when there were two EC measurement setups in use, bottled nitrogen gas (purity grade 5.0) was used as the reference gas for the LI-6262 analysers. The amount of CO₂ impurity is not specified for that grade, but as an estimate CO₂ concentration $\leq 1 \mu\text{mol mol}^{-1}$ can be used (pers. comm. Aga Oy/Special gases, Espoo, Finland). This impurity level doesn't degrade remarkably the accuracy of the CO₂ flux measurement. The specified amount of H₂O impurity in the nitrogen gas is $\leq 3 \mu\text{mol mol}^{-1}$. During the first years of operation the tube material of the reference gas line (6x4 mm diameter tube) was nylon. As a tube material nylon is from a practical, installation point of view a good choice for tens of meters long gas lines up in a tower. It has a combination of lightness, strength, elasticity and resistance to abrasion, mold and fungi. But as a disadvantage it is hygroscopic and susceptible to permeation of H₂O vapour and CO₂ through the tube wall in to the line which would contaminate the reference gas. Especially there was concern of the possible contamination by ambient H₂O vapour, which naturally has highly variable concentrations in the air. The H₂O vapour concentration in the reference chamber of the Eddy233 system's LI6262 analyser was estimated in a test setup (in Nov. 1999), where the dew point of the reference gas was measured after it had passed through the reference chamber and the chopper enclosure. The H₂O vapour concentration was observed to be about $0.4 \text{ mmol mol}^{-1}$ while the ambient H₂O vapour concentration was about 8 mmol mol^{-1} . It was recognized that a portion of the H₂O vapour may also have leaked into the reference gas through the sealing of the analyser's chopper housing, but nevertheless to prevent any diffusion of H₂O vapour and also CO₂ in to the reference gas line the nylon tube was changed to a stainless steel tube (6x4 mm in diameter) in May 2002 in a major modification of the Eddy233 system.

By the end of year 2003 there were four EC measurement setups in use at the station, which all had a Li-Cor gas analyser needing reference gas. To supply them all with cylinder gas was considered to be a too cumbersome maintenance task, especially in the long run. Instead a dedicated reference gas generator (TOC1500, Peak Scientific Instruments Ltd., Inchinnan, Scotland, UK) was taken into use (see Fig. 5). Its operation is based on the principle of Pressure Swing Adsorption method, where gas and moisture are selectively adsorbed from compressed air into a special molecular sieve material (TOC1500 User Manual 2014). It has two adsorbent columns used

alternatively which allows for a self-regenerative operation. In its factory setup, the TOC1500 is specified to output CO₂ free and dry air at 14 l min⁻¹ while taking 28 l min⁻¹ as input air flow rate. To reduce its consumption of the station's compressed air, the TOC1500 was modified to operate on a smaller flow rate of input air (4 l min⁻¹). On the basis of test results this modification limited the output gas flow rate at max. 1.5 l min⁻¹ in order to keep the impurity levels of the reference gas still comparable to bottled nitrogen gas or synthetic air. The operation of the TOC1500 has proven to be accurate and stable and the use of it reduced the amount of maintenance work considerably.

The dust filters at the gas analyser inlets were not changed at regular pre-set intervals. Instead the pressure drops over the filters were monitored and a change of a filter was set to be necessary when dust build-up had caused a two-fold increase to the pressure drop. Here the internal pressure sensors of the LI-6262 analysers combined with the ambient pressure data of the station was utilised. As the sample air flow controllers, mass flow controller in Eddy233 system and critical orifice in EddyTow system, were installed after the gas analysers they were protected against soiling by airborne dust. And then by changing the inlet filters on the basis of the pressure drop the sample air flow rates could be kept sufficiently constant. While the mass flow controller in the Eddy233 system provided an electronic signal of the sample flow rate, the sample and by-pass flow rates of the EddyTow system were monitored with rotameters. As the by-pass flow line of the EddyTow system didn't have any dust filter it was necessary to clean the critical orifice from time to time in order to keep the by-pass flow rate at the set level. The filter of the LOZ-3 analyser was changed at the same time as the filter of the LicorTow was changed. The reference gas flows of the LI-6262 analysers were set with needle valves and monitored with rotameters.

The LOZ-3 analyser required special maintenance due to its need of constant, steady and sufficient reagent liquid flow (**paper I**). After every few months, it was necessary to add liquid to keep the reservoir vessel full. Without this preventive measure, the function of emptying the separator failed. And as a result, the all the liquid was sucked out of the circulation system stopping the instrument's operation completely. It was necessary to monitor the pressure difference driving the liquid flow from the reservoir vessel to avoid situations of the flow rate exceeding the emptying rate of the separator vessel. Should this happen the result was an overflow situation at the separator and subsequent failure of re-circulation function. During the first years this monitoring was performed manually by comparing the sample pressure inside the LOZ-3 measurement chamber to the ambient pressure. After a major break in the O₃ flux measurements during year 2005, this monitoring and ultimately the protection against these unwanted situations was automated in December 2006 with the pressure guard system described in chapter 2.3.1.1. A failure of the re-

circulation function wasn't immediately discernible in O₃ concentration signal. But with the separation vessel full of liquid the measurement chamber pressure signal went totally noisy making it easy to detect the malfunction situation. The flow rate of the reagent liquid also needed to be sufficient to preserve the sensitivity of the detection. The chemical Eosin-Y is powder and so it was prone to get accumulated over time in the narrow channel under the fabric wick inside the measurement chamber. The accumulated powder then slowed down the flow and could choke it completely. The LOZ-3 analyser was equipped with a flow sensor to electronically monitor the liquid flow rate, but the sensor didn't withstand the solution and ceased to function quite shortly. As no alternative, practical sensor could be found the malfunctioning sensor was removed. A complete cleaning of the measurement chamber from the accumulated powder block once year was found to be a working service practice for maintaining an adequate flow rate. As a check measure of the flow rate the formation rate of liquid droplets at the tip of the tube inside the separation vessel was utilised.

2.3.2 Gas profile and CO₂ mole fraction measurements

2.3.2.1 Gas analysers

URAS 4 CO₂ and H₂O analysers

Between 1995 and February 2008 two single component URAS 4 analysers (see Fig. 2 in **paper III**) were in use for the measurements CO₂ and H₂O, respectively. The aging of the URAS 4 analysers initiated a search of new CO₂ and H₂O analysers. The relatively large size, weight and power consumption of the URAS 4 analysers then led to a choice of a more compact sized analyser, namely the two component LI-840 CO₂/H₂O-analyser. It was added to the measurement system in March 2008. It measures both CO₂ and H₂O simultaneously from the same sample air, but at first it was installed after the URAS 4 CO₂ analyser, which was left in the system as a backup instrument and also the simultaneous use of two analysers with different type of detectors allowed a chance to compare the performance of the two analysers (**paper III**). The addition of the LI-840 analyser didn't cause any significant changes to the system as it was installed after the outlet of the URAS 4 measurement chamber. The comparison between the two CO₂ analysers went on for 26 months. In May 2010, the URAS 4 CO₂ analyser started to malfunction severely and it was subsequently removed from the system. In September 2011, the URAS 4 H₂O analyser was removed from the system. The CO₂ and H₂O profile measurements were continued with the LI-840 analyser and in the

CO₂ mole fraction measurements an LI-820 CO₂ analyser was taken into use (see Fig. 10). The LI-820 CO₂ analyser that replaced the LI-840 analyser is basically a similar instrument with a same type of (CO₂) detector.

The measurement of CO₂ or H₂O concentration of an URAS 4 analyser is based on absorption of infrared (IR) radiation. The infrared radiation is emitted from a heated metal coil. The measurement bench has two chambers, one for a sample gas and one for a reference gas. The concentration in the sample gas is determined against the respective concentration in the reference gas. A rotating shutter disk modulates the radiation and subsequently the signal. The analysers in use had closed reference chambers filled with CO₂-free and dry nitrogen gas. There are no filter volumes in the light path and the broad band infrared radiation enters the chambers without cutting/dispersion and so the analysers can be considered as NDIR instruments. The detection in an URAS 4 analyser is based on photo-acoustic technique (e.g. Harren et al. 2000), where the absorbed radiation is determined via heat and subsequently pressure pulse generated and then detected with a sensitive microphone. Selectivity is achieved by using a detector filled with the gas component to be measured. Technically, the detector is filled with ammonia in the H₂O analyser (URAS 4 operating manual 42/20-29-3 EN, 1994).

As was already previously discussed in the chapter 2.3.1.1 temperature and pressure affect directly the concentrations of the sample air components inside the measurement chamber of an analyser. Differences in these factors between the calibration and measurement situations, and also between different measurement situations need to be taken into account in order to get accurate results. In addition to the direct effect, pressure also has an indirect effect via affecting the shape of the absorption lines. The widths of the absorption bands increase and so the total absorption per mole of an absorber increases as pressure increases (Burch *et al.* 1962). Moreover, gas species affect the pressure broadening differently. In ambient air measurements with NDIR instruments H₂O vapour has a noticeable effect on the pressure broadening of the CO₂ signal. The URAS 4 analysers were not equipped with pressure correction modules, so we used separate pressure sensors (P CO₂ and P H₂O in Fig. 2 in **paper III**; Barocap® PTB100A, Vaisala Oyj, Helsinki, Finland) to allow for the pressure correction of the concentration signals during post-processing of the data. The sensors were installed externally at the outlet of the measurement chamber.

The variation of the absorption band widths with temperature is not significant at the typical temperatures prevalent in the atmosphere (Jamieson *et al.* 1963), and so the effect of the sample temperature on the absorption line shape can be neglected. But its effect on the concentrations can

be significant. The optical bench of an URAS 4 analyser is in its entirety including measurement and reference chambers, IR-source, chopper disk and detector enclosed to a temperature controlled enclosure set to 60 °C temperature and the signals are not corrected for temperature dependence by the software of the instruments. In the measurements of the CO₂ and H₂O profiles the sample temperature was assumed to be sufficiently stable and equal between the measurements from the different heights and so not to distort the measured concentration profile. But in the measurements of CO₂ mole fraction, we used a separate thermistor (T CO₂ in Fig. 10; type PT100, accuracy ±0.1 °C) to monitor the sample temperature and facilitate a temperature correction in the data post-processing in order to improve and secure data quality.

H₂O vapour is the major interfering compound in measurements of atmospheric trace gas concentrations with the NDIR method. Compared to trace gases, like CO₂, the concentration of H₂O vapour in the atmosphere is high and considerably variable. H₂O vapour has multiple strong absorption peaks overlapping the absorption peaks of other components, and the broad tails of the H₂O absorption peaks cause background to the absorption signal (Heard 2006). The dilution effect of H₂O vapour on the partial pressure of CO₂ is also significant amounting in mole fraction units to ~4–6 μmol mol⁻¹ in typical summer time conditions of 10–15 mmol mol⁻¹ concentrations of H₂O vapour. The URAS 4 CO₂ analysers are equipped with CO₂-filled detectors which reduce the interference effect of H₂O vapour (URAS 4 operating manual 42/20-29-3 EN, 1994), but the sensitivity to H₂O vapour is not specified. Separate test measurements were performed to examine and determine the interference of H₂O vapour on the CO₂ mole fraction signal. The analysis of the data revealed the interference effect in the CO₂ signal (of the URAS 4 analyser in use) to be equal to 3 μmol mol⁻¹ CO₂ per 1 mmol mol⁻¹ of H₂O vapour (**paper III**). This interference was subsequently corrected for during post-processing of the data.

LI-820 CO₂ and LI-840 CO₂ & H₂O analysers

The LI-840 and LI-820 analysers are also based on NDIR absorption technique. They both have a single sample chamber in the measurement bench. The source of the infrared radiation is a (heated) metal filament and the intensity of the radiation is measured with pyroelectric solid state detectors. The determination of concentration and the selectivity is based on the use of narrow band optical filters placed in front of the detectors. For the CO₂ channel the optical band filters are centred at 4.26 μm, corresponding to the absorption band for CO₂, and at 3.95 μm (outside absorption band), which has no absorption due to CO₂. In the H₂O channel the optical filters are centred at 2.595 μm (absorption band) and at 2.35 μm (outside absorption band). The absorptions

measured at the absorption band and outside the absorption band called the sample and reference signals, respectively. The concentrations are determined from the difference ratio in the IR absorption between the reference and sample signals (LI-840 CO₂/H₂O Instruction manual 2003; LI-820 CO₂ analyser 2002).

An LI-840 (and LI-820) analyser is as standard equipped with a pressure sensor to measure the pressure of the sample gas inside the sample cell and the effect of the sample pressure on the signal is taken into account by the instrument's embedded software. However, the LI-840 and LI-820 analysers were observed also to have a distinct, although relatively small, approximately $-0.0082 \mu\text{mol mol}^{-1} \text{ hPa}^{-1}$, dependence of CO₂ signal on the sample pressure even after the pressure correction implemented by the instrument's correction algorithm. Therefore, the use of the external pressure sensors (P CO₂ and P H₂O in Fig. 10) was continued even with the LI-840 and LI-820 analysers to facilitate a correction for the remaining effect.

The housings of the radiation source and the detector in an LI-840 analyser are thermostatically heated and regulated at a constant operating temperature of about 50 °C. In addition, the both housings are equipped with temperature sensors and the software performs a temperature correction as a part of the signal processing. Like in the case of URAS 4 analyser the sample temperature was assumed to sufficiently constant and stable and the measurements of the concentration profiles were not assumed to be affected. But in the measurements of atmospheric CO₂ mole fraction, the use of a separate thermistor (T CO₂ in Fig. 10) was continued.

The optical band filter in use in LI-840 analysers reduce the interference effect of H₂O vapour on the CO₂ absorption signal, and a correction algorithm in the analysers compensates for the direct cross sensitivity of H₂O vapour on the signal and also takes into account H₂O concentration in the band broadening correction (LI-840 CO₂/H₂O Instruction manual 2003; LI-820 CO₂ analyser 2002). According to the specifications the CO₂ signal has remaining sensitivity of less than $0.1 \mu\text{mol mol}^{-1}$ CO₂ per 1 mmol mol^{-1} of H₂O vapour. With separate measurements, the specification of the interference was found to be correct.

TEI 49C O₃ analyser

The measurement of O₃ concentration inside the TEI 49C analyser is based on the absorption of ultraviolet (UV) light of wavelength 254 nm, and the degree of the absorption is related to the O₃ concentration according to the Beer-Lambert Law of light attenuation (see Eq. 5). The measurement bench has two similar tubular cells which both act as a sample and reference cell alternately at 10 s

intervals. The air sample is split in to two equal streams, sample and reference gas flow, by two 3-way valves. Reference gas is generated from the sample air by selectively removing O₃ from it in a scrubber element containing manganese dioxide (MnO₂). The UV light is generated in a low pressure mercury lamp and the light beam is directed by mirrors into the cells. The windows at the both ends of the tubes are of specific material transparent to the wavelength of 254 nm and the detectors are also specific to that wavelength so that no other optical filtering is used. After passing through the cells the intensities of the two light beams are measured with vacuum photo diode detectors. The ozone concentration is calculated for both cells and the average of the readings is then output as the measured concentration. The effect of sample pressure and temperature are taken into account by the embedded software of the analyser.

2.3.2.2 Operational procedures and diagnostics monitoring of gas profile and CO₂ mole fraction measurement instrumentation

It was necessary to compensate for the effect of sample pressure on the CO₂ concentration signal in both profile and mole fraction measurement system (**paper II** and **paper III**, respectively). The changing atmospheric pressure and a changing pressure drop in the sample lines due to different number of analysers connected and due to clogging of the inlet filter resulted to differences in the sample pressure between calibration and measurement situations. The degree of the pressure correction between the calibration and measurement situations was minimised by setting the pressure decrease in the sample lines during a calibration to approximately equal to the pressure decrease during ambient air measurement. This was accomplished by a pressure-decreasing needle valve installed in the calibration gas feed line (NV in Fig. 10). Furthermore, all calibration adjustments were performed at the same consistent pressure. In the profile measurements, it was important to compensate for the differences in sample pressures between the measurement heights. Slightly different sample line lengths inside the cottage and differences between internal dimensions of the magnetic valves resulted to differences of 0.05–0.6% in the sample pressures between the sample heights. Especially in the case of the URAS 4 CO₂ analyser this would have resulted to considerable errors, 0.3–3.3 μmol mol⁻¹, between the signals observed at the different heights for a nominal mole fraction of 400 μmol mol⁻¹. Errors of this magnitude would have rendered the profile measurements useless unless a correction was applied.

The dependence of the signal on the sample pressure inside the URAS 4 CO₂ analyser was quantified in dedicated test measurements (**paper III**). The basis of the correction equation for the

pressure dependence were (i) the Beer-Lambert absorption law and (ii) the method presented by Jamieson *et al.* (1963) for scaling the absorption measured in one pressure to another pressure condition. This method is in use e.g. in the internal algorithms of LI-COR CO₂ analysers (McDermitt *et al.*). For the scaling to work most accurately the raw data of the absorbance as measured by the analyser is needed. In the case of the URAS 4 analyser the raw data was not available but instead the fully processed concentration data was scaled to a reference pressure using a semi-empirical equation. The equation correcting for the effect of sample pressure on the mole fraction signal was determined over a pressure range of 835 – 980 hPa covering well the encountered sample pressures in both the profile and mole fraction measurement system. Typically, the sample pressure was around 900 hPa. The dependence of the URAS 4 CO₂ mole fraction signal on the sample pressure was found to be adequately described with a second order polynomial determined by fitting pressure ratios to measured mole fractions

$$\frac{c}{c_{ref}} = a \left(\frac{p}{p_{ref}} \right)^2 + b \left(\frac{p}{p_{ref}} \right) + c, \quad (6)$$

where C is the measured mole fraction, C_{ref} is the reference mole fraction, p_{ref} is the reference pressure and a , b and c are empirical coefficients determined by the regression. The reference pressure was chosen to be equal to the pressure at which calibration of the URAS 4 analyser was adjusted and checked. The precision of the pressure correction was estimated to be $0.1 \mu\text{mol mol}^{-1}$.

The magnitude of the pressure correction to the CO₂ signal of the URAS 4 analyser due 1) to the difference in the sample pressures between the calibration and ambient air sample was variable, 2) because the pressure decreases in the sample line and 3) also the throttle effect of the pressure decreasing needle valve in the calibration gas sample line were variable. The pressure ratio (p/p_{ref} in Eq. 6) ranged from ~ 0.998 to ~ 1.005 , and as a result the correction factor applied to the measured mole fraction CO₂ signal ranged from about 0.9972 to 1.0070. Expressed in concentration scale, the correction ranged from about 1 to $-3 \mu\text{mol mol}^{-1}$. Because the sample pressure during the ambient air measurements varied in the same interval as during the test measurements, the precision of the pressure correction to the ambient signal in case of the URAS 4 analyser was assumed to be likewise $0.1 \mu\text{mol mol}^{-1}$. In case of the LI-840 and LI-820 analysers the remaining error after the internal pressure correction was about $0.04 \mu\text{mol mol}^{-1}$. By applying a similar pressure correction algorithm that was used for the URAS 4 analyser the precision of the pressure correction could be improved further to $0.02 \mu\text{mol mol}^{-1}$.

The temperature equilibration features of the analysers helped to minimize the degree of temperature correction needed to the signals. The sample temperature during the measurements of the calibration gases and during the measurements of the ambient air samples were found to differ by less than 0.1 °C, which resulted in a correction of 0.1 $\mu\text{mol mol}^{-1}$ or less to the CO₂ mole fraction signals based on calculations using the ideal gas law. On average, the temperature difference was slightly negative (about -0.02 °C), and this resulted in about 0.03 $\mu\text{mol mol}^{-1}$ (positive) correction to the CO₂ signal. Considering the precision of the temperature signal of about 0.05 °C, the precision of the correction due to the temperature difference was about 0.07 $\mu\text{mol mol}^{-1}$.

The correction for the interference of H₂O vapour on the CO₂ signal was estimated to have an accuracy of 0.3 $\mu\text{mol mol}^{-1}$ (in case of URAS 4 analyser). For the profile measurements, this was considered adequate. But for the mole fraction measurements a more accurate and reliable H₂O interference correction equation would have been needed. It was considered that it would not be reasonable to make an effort to newly determine the interference and formulate a more accurate correction equation. The correction equation was specific to the analyser it was formulated for and the degree of the correction would depend on the analyser's current calibration or sensitivity. Instead it was decided to reduce the amount of interference by H₂O vapour in the first place by drying the sample air. And then later on, the change to the LI-820 CO₂ analyser after the LI-840 CO₂ & H₂O analyser in practice necessitated the use of a sample air drier (PD-200T in Fig. 10). Also it was considered beneficial to direct the calibration gas sample through the sample air drier where it was in effect humidified to essentially the same humidity as the ambient air sample was dried to. The observed difference the H₂O mole fractions between the samples was less than 0.01 mmol mol^{-1} and the corresponding bias in the CO₂ signal was not relevant for any of the analysers.

2.3.3 Calibration arrangements

Expressed shortly calibration of a gas analyser is a procedure where gas samples of known concentration, that is reference concentrations, are introduced to the analyser's sample inlet and the responses are measured (e.g. Heard 2006). The reference concentrations should cover the range of the typical prevalent concentrations at the measurement site. In its simplest form calibration includes measuring the analyser's responses to a zero reference gas and to a single reference mixture of a desired upper range concentration. The zero and upper range concentration reference define the calibration range where zero is the lower end and span is the difference between the

upper range value and the zero. The non-zero reference mixture is often called ‘span’ gas. In addition to rectifying the analyser’s response so that it gives accurate concentration data, a calibration gives data about the analyser’s measuring precision as the reference gases are stable measurands and any noise in the signals can be taken to be due to the analyser, at least for the most part. By calibration hidden malfunction situations can also be detected when unusual or exceptionally large, but still not readily detectable in the measurement data, deviation in the response is observed.

At first calibration includes also adjusting the responses to the reference concentrations. The adjustment of the responses is then often necessary also later if and when the zero offset and response to the upper range concentration drift too far away from the set points. The calibration procedure involving only measuring of the responses will be referred to as a calibration check and the procedure where the responses are adjusted will be referred to as calibration hereafter. Evidently in a calibration check, calibration correction parameters are determined in order to correct the measured concentration values during data processing. For an analyser with a linear response over the calibration range a linear fit between the measured and the reference values is naturally what is needed and at minimum only the zero and the span reference points are needed. Any significant non-linearity in the response then increases the number of the reference points needed. For a linear response, the correction parameters would ideally be exactly 0 for offset correction and 1 for span coefficient after calibration adjustment. However, generally it is not reasonable to try to adjust the calibration exactly, but instead calculate the calibration correction parameters from the calibration measurement data. This is especially so for the offset parameter as the level of noise in the analyser signal in practice can be comparable to the lowest ambient concentrations. The correction parameters are assumed to change linearly with time between the calibrations. Gradual soiling of the analyser’s sample chamber and line, aging of the light source, detector and other optical components and changes in composition of the reference gas and concentration of the reagent liquid can cause changes both in offset and span.

Eddy-covariance CO₂ and H₂O analyser LI-6262

The calibration check of the Eddy233 and EddyTow measurement systems’ LI-6262 CO₂ & H₂O analysers is regularly performed four times per year. The zero offsets of the CO₂ and H₂O channels and the span calibration of the CO₂ channel are checked using reference gases from compressed gas cylinders. To avoid any extra structures in the sample line at the inlet near the measuring volume of the sonic anemometer, the reference gases are fed via 6x4 mm nylon tubes from inside the main

cottage into the instrument enclosures. The switch from ambient sample air to a calibration gas sample is accomplished via (manually operated) a 3-way valve located inside the instrument enclosures (item 2 in Fig. 7). The sample flow rate of the analyser is not changed for the calibration. And to keep the sample pressure similar to the measurement conditions there is a coil of 6x4 mm PTFE tube (DPLOOP in Fig. 5) inside the enclosures attached to the branch of a T-connector in the calibration gas feed line. The length of the coil is cut so that pressure drop inside it is more or less equal to the pressure drop in the ambient air sample line.

Each calibration check of the CO₂ channel includes a zero reference gas (grade 5.0 synthetic air) and a span reference gas (a mixture of CO₂ in synthetic air) using compressed gas cylinders supplied by a gas company (AGA Oy, Espoo, Finland). Reference gas mixtures analysed to 1 % relative accuracy (in CO₂ mole fraction) are regularly used. This accuracy class is considered adequate for the purposes of the eddy covariance measurements and also it is a standard product for gas companies setting the compromise between the accuracy, price and delivery time is reasonable. Because the range of CO₂ mole fraction at the eddy-covariance measurement height is rather narrow ($\sim 40 \mu\text{mol mol}^{-1}$) it was considered unnecessary to use multiple span gas mixtures as the LI-6262 analyser's specified accuracy of $1 \mu\text{mol mol}^{-1}$ for the interval from zero up to $1000 \mu\text{mol mol}^{-1}$ (LI-6262 CO₂/H₂O Analyzer operating and service manual, 9003-59, 1996) is better than the accuracy of the regular reference gases. Leaving out the actual sample line from the calibration is not considered to affect the CO₂ span calibration.

In the calibration check of the H₂O channel the zero reference gas is the same that is used for the CO₂ calibration, but in case of span check the procedure includes the use of a separate reference analyser or sensor, because there is no practical way to introduce a generated reference H₂O vapour span concentration to the analyser of either eddy covariance measurement systems. From the practical point of view the procedure is essentially rather simple as no separate preparations are needed and the reference concentration is continuously available. Furthermore, it is also advantageous that the actual, whole sample line is included in the calibration. During the first years of operation the H₂O vapour concentration measured with the URAS 4 analyser of the profile measurement system was used as the span reference. Starting April 1998, the reference H₂O vapour span concentration is calculated from a dedicated dew point measurement at the SMEAR II station. Those measurements were started with a chilled mirror dew point sensor (M4 Dew point monitor; General Eastern Instruments, Woburn, MA, USA) installed at 23 m height in the high tower. In July 2011, the dew point measurements were moved to the 18 m high scaffolding tower, where the

sensor is installed at 16 m height. The instrument was changed at the same time to a different make (DewTrak Model 200M Meteorological Humidity System; EdgeTech, Marlborough, MA, USA).

The relative accuracy of the URAS 4 H₂O analyser was on the average $\pm 10\%$. During freeze in winter time when ambient air is dry with H₂O concentration decreasing down to 1 mmol mol⁻¹ or even below the accuracy was rather poor for the span reference concentration as the detection limit was 0.5 mmol mol⁻¹. With the start of the dew point measurements the quality of the H₂O channel calibration was improved considerably as the accuracy of the dew point sensors is 0.3 °C, corresponding to about 3 % accuracy in H₂O concentration. However, in weather conditions with air temperature around 0 °C and relative humidity approaching 100 % the dew point sensors have turned out to malfunction repeatedly. Air temperatures of -25 °C or below have also rendered the dew point sensors un-operational. These instrumental shortcomings limit somewhat their usefulness as H₂O concentration span reference as in wintertime there can be several occasions with no valid data available.

Although the factory calibration of an LI-6262 analyser evidently is accurate the offset of the CO₂ and H₂O channel zero signals turned out to change considerably between the calibration checks, that is several $\mu\text{mol mol}^{-1}$ and mmol mol⁻¹, respectively. Changes exceeding 10 $\mu\text{mol mol}^{-1}$ in CO₂ channel and 0.5 mmol mol⁻¹ in H₂O channel were observed many times. According to the manufacturer temperature changes are a major cause for zero drift, but the observed zero drifts were observed to be larger than are given in specifications. As the LI-6262 analysers were equipped with pressure sensors the span calibrations normally didn't drift noticeably. Large changes in the analysers' calibration were usually connected to gradual soiling of the sample cell, which was observed to be inevitable despite the use of dust filters at the analyser inlets. Abrupt changes in the calibration could also occur, and so especially during winter time. These cases could usually be associated with contamination by liquid water due to melting of an ice/snow obstruction at the sample line inlet. In practice, the calibration adjustments had to be performed by instruments' front panel zero and span adjustment potentiometers.

Taking into account the work load of the maintenance personnel and the knowledge that mere zero offsets don't cause errors in the fluctuation measurements, it was not considered worth the effort to try to keep the analysers' zero offsets at exactly zero. But by the time the zero drifts had developed to $\pm 20 \mu\text{mol mol}^{-1}$ in CO₂ channel and 1 mmol mol⁻¹ in H₂O channel the linearity of the calibration started to fail deteriorating the accuracy of the (CO₂) span calibration and it was necessary to adjust the calibrations. Often adjustment of just the offset calibration was enough to re-

achieve the 1 % accuracy of the CO₂ span calibration. By the time zero drift of an analyser had developed so large that any of the potentiometers had reached its limit, the analyser had to be sent to manufacturer's service location for a change of the sample cell and re-calibration.

Eddy-covariance O₃ analyser LOZ-3

During initial tests the calibration of the eddy-covariance O₃ analyser LOZ-3 was observed to be drifting considerably and so it was obvious that the calibration should be checked regularly and frequently. Generally, the sensitivity of the analyser was expected to decrease with aging reagent liquid. According to the manual 100 cm³ of reagent liquid should maintain its calibration for at least one month. That amount seemed to cover a considerably longer time evidently because of the rather low general ambient O₃ concentration level at the site. The sensitivity was observed not only to decrease with time, but it could also increase. This behaviour was assumed to be due to the reagent becoming more concentrated. This increase in concentration was concluded to happen as the solvent ethylene glycol was drawn out of the solution in the re-circulation system as small droplets to the exhaust line. And breaks in the analyser's operation, that is power off periods and sample flow off periods quite often lead to a suddenly increased sensitivity followed by a several days long period of decreasing sensitivity. The calibration correction factor ranged between 0.5 and 1.5.

The LOZ-3 analyser has a built-in automatic zero correction function in which the sample air is periodically, for 30 s time at 10 min interval, diverted through a scrubber tube filled (ZAS in Fig. 5) with activated carbon removing O₃ from it. During this zeroing operation, the analyser software holds the most recent concentration signal. But as this was considered to cause considerable complexities in the flux processing software the LOZ-3 was operated during the first years in a so called 'MEAS mode' in which the automatic zero correction function is not in use. Then in practice a manual operation was performed weekly for determining the zero offset using the internal activated carbon containing scrubber (**paper I**). And for determining the span correction coefficient for the LOZ-3 ozone concentration reading the continuously measuring O₃ profile analyser (TEI 49) was utilised as the reference analyser. As the sample height of the LOZ-3 ozone analyser was 23 m and there wasn't a profile measurement level at exactly 23 m, the geometric mean of the 30 min average concentrations measured at heights 16.8 and 33.6 m was calculated and used as the reference concentration.

In effect, the stability of the span correction coefficient could be kept within ± 10 % precision range. In December 2006, after a major break in O₃ eddy-covariance measurements for in practice

the whole year of 2006, the built-in automatic zeroing function was taken into use. This enabled a more or less continuous calibration correction against the reference analyser without any need to approximate drift in the calibration. Also, this diminished the work load of the maintenance personnel. The internal scrubber tube containing activated carbon was in this connection changed to a catalytic MnO₂ scrubber element that are customary used in UV-absorption based O₃ analysers. This modification was considered to improve the quality and reliability of the zeroing function as due to constructional limitations the size of the internal scrubber tube containing activated carbon was considerably small and so its scrubbing efficiency was a matter of concern.

URAS 4 and LI-840 CO₂ and H₂O analysers of the profile measurement system

The calibration check of the profile measurement systems' URAS 4 CO₂ and H₂O analysers was regularly performed (manually) once a month until September 2006 (**paper II**). The switch from ambient sample air to a calibration gas sample was accomplished via a 3-way valve (40 series ball valve; SwageLok, Solon OH, USA) installed in the sample line. The sample flow rate was not changed for the calibration. To keep the sample pressure similar to the measurement conditions there was a needle valve (M series metering valve; SwageLok, Solon OH, USA) acting as a pressure reducing throttle in the calibration gas feed line. The zero offsets and the span calibration of both the URAS 4 CO₂ and URAS 4 H₂O analyser were checked using reference gases from compressed gas cylinders. Between the calibration checks the offset and span correction parameters were assumed to have drifted linearly with time unless an abrupt change in the signal level was observed. In the calibrations two compressed gas CO₂ mixtures of mole fractions on the order of 300 $\mu\text{mol mol}^{-1}$ and 400 $\mu\text{mol mol}^{-1}$ with grade 5.0 nitrogen as the base gas were used for the CO₂ analyser. The mole fractions of the gas mixtures were analysed by the gas company (AGA, Sunbyberg, Sweden) to a relative accuracy of 1 %. The 300 $\mu\text{mol mol}^{-1}$ mixture was at the lower end of the analyser's measuring range and the 400 $\mu\text{mol mol}^{-1}$ mixture was close to the upper range of the ambient air CO₂ mole fraction. For the H₂O analyser either of the CO₂ mixtures could be used as the zero reference gas. And as the H₂O span reference gas a mixture of sulphur hexafluoride (SF₆) in nitrogen gas could be used as a H₂O vapour surrogate. The equivalency data between the SF₆ and H₂O concentrations was supplied by the URAS 4 manufacturer Hartmann & Braun. As an example, a concentration of 6 % of SF₆ was equivalent to a H₂O vapour concentration of 17.8 g m⁻³.

On the average, the offset correction of the CO₂ signal varied by $\pm 9 \mu\text{mol mol}^{-1}$ and the span correction by about 2 % between calibrations. In case of the H₂O signal the average offset correction varied by $\pm 0.5 \text{ g m}^{-3}$ and the span correction by about 4 % between calibrations. As the

offset and span correction parameters are interdependent an estimate for the calibration accuracy is obtained by evaluating the distribution of the difference in calibration correction between successive calibration checks using a constant un-calibrated concentration signal. During this time period of monthly calibration checks the estimated measurement uncertainties of CO₂ and H₂O between the calibration checks were $\pm 4 \mu\text{mol mol}^{-1}$ and $\pm 0.6 \text{ g m}^{-3}$, respectively.

The deployment of the automated calibration system in October 2006 (**paper III**) then made it possible in practice to check the calibrations frequently and also to use multiple gas mixtures. In the automatic calibrations five ‘CO₂ in synthetic air’ gas mixtures with mole fractions evenly distributed between about $350 \mu\text{mol mol}^{-1}$ and $430 \mu\text{mol mol}^{-1}$ were in use (see Fig. 2 in **paper III**). The use of the SF₆ mixture in the calibration of the URAS 4 H₂O analyser was continued. The use of multiple CO₂ gas mixtures in the calibration of the profile measurement system continued until mid-November 2013. During the time when multiple gas mixtures were in use the offset correction of the CO₂ analyser varied by $\pm 8 \mu\text{mol mol}^{-1}$ and the span correction by about 1.5 % between calibrations. And the estimated calibration accuracy of the CO₂ signal between the calibration checks was $\pm 0.8 \mu\text{mol mol}^{-1}$. The change of the CO₂ analyser from the URAS 4 to an LI-840 in June 2010 wasn’t discernible in the variation of the calibration parameters, but while the measurement uncertainty was $\pm 1.0 \mu\text{mol mol}^{-1}$ for the URAS 4 it was better for the LI-840, that is $\pm 0.5 \mu\text{mol mol}^{-1}$.

Since the mid-November 2013 the calibration of the profile measurements system’s CO₂ analyser is performed with a zero reference gas (grade 5.0 synthetic air; supplier AGA, Riihimäki, Finland) and one span reference gas of about $600 \mu\text{mol mol}^{-1}$ mole fraction (supplier AGA, Sundbyberg, Sweden). The number of the calibration gases was reduced in order to dedicate the rest of the valve positions to the new separate CO₂ mole fraction measurement system. The relatively high mole fraction of the span reference gas is because of the use of the same gas for calibration of the CO₂ analyser in another measurement system where sample air is taken from ground level where CO₂ mole fraction often approaches the $600 \mu\text{mol mol}^{-1}$ m.

Since the return to a two point calibration the offset correction of the CO₂ signal varies by $\pm 6 \mu\text{mol mol}^{-1}$ and the span correction by about 1.5 % between calibrations. And the estimated measurement uncertainty of CO₂ concentration between the calibration checks in the profile measurement system is $\pm 1.0 \mu\text{mol mol}^{-1}$.

The number of the calibration gas mixtures for the profile measurement system’s H₂O analyser was not increased in connection with the deployment of the automatic calibration system. The zero

reference gas has all the time been compressed gas from a cylinder. But the span reference gas was changed from the (surrogate) SF₆ mixture to a real H₂O vapour-in-air mixture in September 2011 in the connection with the change of the H₂O analyser from the URAS 4 analyser to an LI-840 analyser, because the wavelength band that is used for the H₂O measurement in the LI-840 analyser is not absorbed by the SF₆ gas. For the generation of the H₂O vapour span reference a dew point generator (DG-4 Dew point generator, Sable Systems Europe GmbH, Berlin, Germany) was added into the gas concentration profile and concentration measurement system (DG-4 Td in Fig. 10). The dew point controlled H₂O vapour-in-air mixture is continuously generated from a flow of air saturated with water vapour in the condenser unit of the DG-4 dew point generator. The water-saturated air is produced in a bubbler bottle filled with de-ionized water (WBB in Fig. 10) through which compressed air flows. The temperature of the condenser is set to 10 °C, which corresponds to 12.1 mmol mol⁻¹ H₂O mole fraction at ambient pressure of 1013 hPa. The condensate, that is the excess of water vapour in the air flow, is periodically removed with an integral pump. The specified accuracy of the dew point is 0.25 C°. This corresponds to about 0.2 mmol mol⁻¹ accuracy in H₂O mole fraction at the set dew point. The DG-4 dew point generator is not designed to be operated pressurized and so its integration to the calibration system required modifications to the valve configuration and sample inlet of the automatic calibration system, e.g. the feed line of the H₂O vapour-in-air mixture is separated from the pressurized reference gas feed lines by a 3-way valve (see Fig. 10). In effect, the automatic calibration with the H₂O vapour span reference mixture was operative in July 2012. The use of the DG-4 dew point generator in a continuous rather than in a periodic way turned out to cause malfunction situations and even breakdowns. To ensure an uninterrupted operation an improvement of the moisture insulation of its internal thermal probes was needed. Furthermore, modification of the settings of its Peltier element's PID controller (proportional-integrative-derivative controller) making the Peltier-element to operate only as a cooler were required. The set dew point temperature does not correspond to the upper range of ambient dew point temperatures appearing at the site, but it is chosen to minimize the risk of condensate formation in the feed line during the cold season.

In the automatic daily calibrations, the offset correction of the URAS 4 H₂O analyser varied by ±0.4 g m⁻³ and the span correction by about 1 % between calibrations. And the estimated calibration accuracy of H₂O concentration between the calibration checks was ±0.1 g m⁻³. The offset correction of the LI-840 analyser's H₂O signal varies by ±0.3 g m⁻³ and the span correction by about 2.5 %. The estimated measurement uncertainty of H₂O concentration is ±0.1 g m⁻³.

TEI 49 O₃ analyser of the profile measurement system

The calibration of the profile measurement system's O₃ analyser is performed against the reference O₃ photometer of the SMEAR-stations (Dasibi 1008 PC, s/n 7152; Dasibi Environmental Corp., Glendale, CA, USA). The Dasibi 1008 PC is equipped with a photolytic ozone generator producing concentrations at nominally 1 nmol mol⁻¹ steps from about 10 up to 1000 nmol mol⁻¹. This reference O₃ photometer is yearly calibrated at the national calibration laboratory K043 of Finnish Meteorological Institute against the national primary ozone photometer (SRP-37) traceable to the Standard Reference Photometer (SRP-27) of the International Bureau of Weights and Measures (BIPM). The reported measurement uncertainty of the SMEAR reference O₃ photometer is on the average ±1.5 nmol mol⁻¹ for concentration range 0 – 50 nmol mol⁻¹.

The calibration frequency of the profile measurement system's O₃ analyser is once or twice per year. The calibration is performed (generally) with four to five reference span mixtures and zero air. The range of the span mixtures is from near 10 nmol mol⁻¹ to 80 nmol mol⁻¹. Purified compressed air of the station is used as the zero reference air and as the dilution air for the span reference concentrations, not only for the O₃ analyser but also for the other gas analysers of the profile measurement system. For the purification of the compressed air from contaminants like O₃, NO, NO₂, SO₂, CO, VOC's a series of (dry) chemicals in pellet form packed inside tubular cartridges is used (SC, AC, SG and PF in Fig. 10). The first cartridge in line (PF) contains Chemisorbant (Purafil Inc., Doraville, GA, USA). It is a combination of porous media impregnated with an effective oxidant, namely activated alumina and potassium permanganate, respectively. The contaminants, including hydrocarbons, are trapped irreversibly within the pellets by adsorption, absorption and oxidation. The second cartridge in line contains silica gel, a drying chemical. The third cartridge in line contains activated carbon effective in removing O₃ from the air, but it also removes other contaminants. The last cartridge in line contains Sofnocat (Molecular Products Ltd., Essex, UK) and it is dedicated to the removal of CO. The switch from ambient sample air to a calibration gas sample is accomplished via a 3-way valve (MV3 in Fig. 10) installed in the sample line between the measurement level switching valves and the dust filters. The sample flow rate is not changed for the calibration. Between the calibration checks the offset and span correction parameters are assumed to have drifted linearly with time.

The continuous measurement of the reference signal in the operation of the analyser obviously keeps the calibration offset stable and at zero. The utilisation of a dust filter at the analyser's sample

inlet and evidently also the relatively clean ambient air at the SMEAR II site helps to keep also the span correction coefficient rather constant. During the years 1996 – 2003 large changes in the span correction, i.e. exceeding 10 % and causing considerable inaccuracy of the calibration, were observed twice. The reason for the large changes were gradually developing leaks in the sample and reference solenoid valves. The leaks are rather concealed as they are not routinely detectable during the operation of the analyser. In fact, those malfunction situations are best detected during calibrations. Depending on the reason/type of the leak the repair measure was either a cleaning of the leaking valve or a change to a new one.

On the average, the offset correction of the O₃ signal varies by $\pm 0.4 \text{ nmol mol}^{-1}$. Due to the malfunction situations of analyser the span correction varied on the average by about 8 % between calibrations during years 1996 – 2003. With more frequent, that is twice a year, calibrations starting 2004 the variation of the span correction coefficient is observed to be $\pm 4 \%$. Combined these observed variations of the calibration correction parameters set the estimated measurement uncertainty of O₃ between the calibration checks to $\pm 4 \text{ nmol mol}^{-3}$ and $\pm 2 \text{ nmol mol}^{-3}$, respectively.

Automatic calibration in the CO₂ mole fraction measurement system

The calibration of the CO₂ (and H₂O) analyser and the measurement of the ambient CO₂ mole fraction were performed using a dedicated arrangement (**paper III**) where the daily measurements of the ambient mole fraction were accompanied with the calibration in one 30 min time frame between 13:00 and 13:30 (UTC + 2 h). While in **paper III** the setup is depicted for the time period between March 2008 and May 2010 (Fig. 2 in **paper III**), in the Fig.10 of this work is depicted the setup in December 2012 when the URAS 4 analysers were already replaced by the LI-820 CO₂ and LI-840 CO₂&H₂O analysers and the reference dew point generator (DG-4 Td in Fig. 10) was in use for the H₂O calibration.

Five ‘CO₂ in synthetic air’ gas mixtures (see Fig. 10) with concentrations evenly, in steps of 20 $\mu\text{mol mol}^{-1}$, distributed between about 350 $\mu\text{mol mol}^{-1}$ and 430 $\mu\text{mol mol}^{-1}$ were in use. Initially these gas mixtures were analysed to an accuracy of 1 % by the supplier (Deuste Steininger GmbH, Mühlhausen, Germany), but for the atmospheric CO₂ mole fraction measurements they were analysed to an accuracy of 0.05 $\mu\text{mol mol}^{-1}$ by Finnish Meteorological Institute (FMI) against World Meteorological Organization/Central Calibration Laboratory standards (WMO/CCL). All in all, four sets of the five calibration gases were in use between October 2006 and December 2012: the 1st set October 2006 – September 2009; the 2nd set September 2009 – January 2012; the 3rd set

January 2012 – June 2012; the 4th set June 2012 – June 2013. In the switch-overs to the 2nd and 3rd set all five gases were changed, but of the gases of the 4th set the lowest and the highest mole fraction cylinder were not changed. The three new gases had more or less the same mole fractions as the ones they replaced, but as a new feature they were mixtures of CO₂, CH₄ and CO in natural air. The new mixtures were in addition to the analysis also filled by FMI. The CO₂ mole fractions of the gases of the first and second set were re-analysed after the use later-on to determine possible drifts in the mole fractions (table 1 in **paper III**).

The estimated calibration accuracy was generally 0.2 $\mu\text{mol mol}^{-1}$ considering the signal noise of the analysers, precision of the calibrations, stability of the analyser responses, and short term (12 hours) repeatability of the instrumentation. However, between October 2006 and October 2007 the calibration accuracy was 0.4 $\mu\text{mol mol}^{-1}$ due to the erroneous use of only three calibration gases which impaired the precision of the calibrations (**paper III**).

2.4 Accounting for vertical advection in night-time CO₂ and O₃ flux estimates

The fluxes obtained with the flux-profile and eddy-covariance systems generally showed good correspondence during daytime under unstable conditions for both CO₂ and O₃ (**paper I** and **paper II**). But at night and especially in early morning during the transition period in atmospheric turbulence and stability the profile method predicted stronger respiration (of CO₂) and larger deposition of O₃ than the EC method. In effect, the EC method underestimated both the CO₂ and O₃ night-time fluxes and the fluxes had an apparent dependence on intensity of the turbulent mixing (**paper IV** and **paper V**). This dependence on the turbulence intensity is a well-known night-time measurement problem and in general EC-measurements at night-time are known to have several limitations (e.g. Massman and Lee 2002) which can cause underestimation of the fluxes. In **paper I**, the discrepancy between the flux results from the two methods for O₃ was suspected to originate from the impact of chemistry which was not taken into account in the calculations. Also, it was recognized that the applicability of the Monin-Obukhov similarity theory might not hold in such conditions. In case of CO₂ there was obviously no chemistry involved and no clear reason for the discrepancy was identified in **paper II**.

The contribution of the horizontal and vertical advection fluxes of CO₂ (F_{HA} and F_{VA} , respectively, in Eq. 1) to the NEE at night-time at the SMEAR II site was studied in **paper IV**. There are typically no direct measurements available for the F_{HA} and F_{VA} but instead they are estimated using in-direct methods. Following the principle set by Lee (1998) and using the

measured CO₂ concentration profiles and an estimation of the mean vertical wind velocity during each half an hour averaging period the F_{VA} was determined (in **paper IV**) according to

$$F_{VA} = \bar{w}_{EC}(\bar{c}_{EC} - \langle \bar{c} \rangle) \quad (7),$$

where \bar{w}_{EC} and \bar{c}_{EC} are the mean vertical velocity and CO₂ concentration at the EC measurement height and $\langle \bar{c} \rangle$ is the average concentration between the ground and the EC measurement height (**paper IV**). The planar fit method by Wilczak et al. (2001) was applied to estimate the \bar{w}_{EC} for each half an hour averaging period (**paper IV**). For the estimation of F_{HA} there were no horizontal concentration gradient data available. In **paper IV** it was hypothesized that at the SMEAR II site the F_{HA} should be negligible because the area around the site is mainly dominated by conifer forest and it can be assumed the sources and sinks are rather homogeneously distributed. The hypothesis of the negligible F_{HA} was tested by estimating the F_{HA} as a residual between two NEE estimates. One estimate was based on independent measurements of the forest floor CO₂ efflux, wood respiration and foliage respiration with flux chambers and an up-scaling model (**paper IV**). The other estimate for the NEE was the measured flux combined with storage change flux and the vertical advection flux (F_{TURB}, F_{ST} and F_{VA} in Eq. 1, respectively). For the estimation of the F_{ST} the measured concentration profile was utilized (**paper IV**).

In case of O₃ the contribution of the vertical advection flux (F_{VA} in Eq. 1) to the deposition at night-time at the SMEAR II site was studied in **paper V**. Similarly to night-time flux of CO₂, the measured flux of O₃ (F_{TURB} in Eq. 1) was found to have a specious dependence on turbulence intensity, i.e. it was decreasing with the turbulence intensity even after compensation with the storage change flux (F_{ST} in Eq. 1). In **paper V** the specious dependence of F_{TURB} on the turbulence intensity was analysed by evaluating the F_{ST}, the F_{VA}, the horizontal advection flux (F_{HA} in Eq. 1), the ecosystem uptake and the sink term due to gas-phase chemical reactions in the air (S_s and S_a in Eq. 1, respectively). The F_{ST} was estimated from the measured concentration profile and the F_{VA} was estimated using Eq. 7. There were no measurements available for the determination of the F_{HA}, but as the significance of the horizontal advection flux for CO₂ was evaluated as negligible the F_{HA} for O₃ was subsequently neglected (**paper V**). While CO₂ can be considered as a non-reactive gas, O₃ is a reactive gas and so chemical reactions in gas-phase in the air (S_a) and also on the canopy surface (non-stomatal component of S_s) in addition to stomatal uptake can act as a sink (e.g. Altimir et al. 2006; Rinne et al. 2012). The components of the S_s, stomatal and canopy surface uptake, are not affected by turbulent mixing. Thus turbulence intensity dependent resistances and turbulent

transport times, relevant to O₃ transport and/or chemical reactions, were considered in **paper V**. Following Rannik et al. (2003a) the deposition model by Slinn (1982) was repeated in **paper V** and the resistances included the resistance through the air layer from the EC measurement level to the canopy surface (aerodynamic resistance) and the resistance through the laminar boundary layer adjacent to the needle surfaces (canopy resistance). The estimates of the turbulent transport time, i.e. the time available for chemical reactions, were performed with Lagrangian trajectory simulations according to Rannik et al. (2003b) in **paper V**. Furthermore, the sink strengths of the chemical compounds with life-times about equal to the turbulent transport time of O₃ were estimated and compared with the observed O₃ deposition rates in **paper V**.

2.5 Assessment of the measured CO₂ mole fraction data as input for modelling of regional CO₂ exchange

The development of the instrumentation for measuring ambient CO₂ mole fraction was performed with a set goal of accuracy of 0.5 μmol mol⁻¹. This followed the guidelines assigned to the EC flux tower sites of the CarboEurope-IP Integrated Project 505572: Assessment of the European Terrestrial Carbon Balance (*see for reference* <http://www.carboeurope.org/>; http://cordis.europa.eu/project/rcn/74277_en.html; Schulze et al. 2009) for obtaining accurately and consistently calibrated CO₂ mole fraction data on the EC towers in Activity 2.7 of the Atmosphere Component for subsequent assimilation in atmospheric inversion models used to quantify carbon fluxes (*see for reference* <http://carboeurope.org/ceip/about/activities.htm#calibrated>; <http://carboeurope.org/ceip/about/atmosphere.htm>).

The measured CO₂ mole fraction data from period October 2006–December 2011 were compared with the results of a large scale atmospheric transport model simulation covering years 1979–2011 (**paper III**). The overall difference between the data sets, expressed as measured – simulated data, was -0.2 ± 3.3 μmol mol⁻¹. The modelled CO₂ mole fraction data corresponded to the version 11.2 inversion product from the Monitoring Atmospheric Composition and Climate – Interim Implementation (MACC-II) service (*see for reference* <http://www.gmes-atmosphere.eu/services/esf/>) using measured CO₂ mole fraction data from a series of global databases as constraints. For a description of (an earlier version) of the product see Chevalier et al. 2010. The trend and phase between the measured and modelled data agreed generally well (Fig. 8a in **paper III**). The observed discrepancies (Fig. 8b in **paper III**) were considered to be due to a lack of local measurement constraints. The data from the Pallas-Sammaltunturi GAW station (Hatakka

et al. 2003) located 700 km north of SMEAR II site was included in the inversion, but e.g. the region to the east of the SMEAR II site including the western part of Russia was void of stations (*see for reference* Chevallier et al. 2010), which was anticipated to induce uncertainty in the CO₂ flux estimates and further in the modelled CO₂ mole fraction data.

The CO₂ mole fraction data from the simulation was for the 200 m thick first layer. For constraining land carbon sinks in transport and process models the measurements of the CO₂ mole fraction should concentrate on the afternoon hours during conditions of well mixed atmospheric boundary layer (e.g. Karstens et al. 2006). Following a virtual tall tower (VTT) approach CO₂ mole fraction measured in the surface layer has been successfully extrapolated, using a mixed layer gradient correction, to estimate the mixed layer CO₂ mole fraction (Davis 2005). However, in **paper III** the measured mole fraction at 67.2 m was utilized directly without the gradient correction because there was no data from a higher layer to corroborate the estimation. To justify the use of the at 67.2 m height measured surface layer CO₂ mole fraction data as an estimate of the atmospheric boundary layer CO₂ mole fraction, only afternoon results when the atmospheric boundary layer generally is well mixed were selected. Furthermore, the gradient in the CO₂ mole fraction between the 67.2 and 33.6 m levels observed in the profile measurements was used as a filter to select the well-mixed conditions. The selection criterion was set to use data only from situations in which the gradient was $\leq \pm 0.2 \mu\text{mol mol}^{-1}$. In effect about 25 % of the potential data points were rejected because of too large gradients. The use of the filtered measurement data was observed to improve the comparison on average by about $0.2 \mu\text{mol mol}^{-1}$ (**paper III**).

In **paper II** it was shown that the observed CO₂ mole fraction profile could be used for an accurate estimation of the CO₂ flux. This is considered an indication that there are no significant, i.e. $> 0.1 \mu\text{mol mol}^{-1}$, offsets between the sample lines. In case of CO₂ offsets could arise due to the combination of the sampling arrangement, where the main (PTFE) sample lines extend for different lengths just about 0.3 m above the soil surface in an air layer where CO₂ mole fractions can exceed $500 \mu\text{mol mol}^{-1}$ in summer, and the generally recognized susceptibility of PTFE material to permeation of gas molecules including CO₂. As a further indication of the validity of the air sample from the 67.2 m height an insignificant increase of $0.001 \mu\text{mol mol}^{-1}$ at maximum in the CO₂ mole fraction of the sample air due to possible permeation through the sample tube wall was obtained in a semi-empirical model calculation (**paper III**).

The SMEAR II CO₂ mole fraction measuring instrumentation was also checked as a whole in August 2007 in an inter-comparison experiment (**paper III**) where air samples were simultaneously

collected with a reference instrumentation (flask sample), connected directly to the PTFE manifold of the 67.2 m sample line and so not exposed to possible leaks through the pneumatic connections between the manifold and the analyser, and analysed afterwards with gas chromatography (GC). The reference sampling instrumentation and GC-analysis were provided by MPI-BGC-GasLab of Max-Planck Institute for Biogeochemistry, Jena, Germany. The CO₂ mole fraction data obtained with the SMEAR II instrumentation were systematically $0.3 \pm 0.2 \mu\text{mol mol}^{-1}$ lower than the data from the reference instrumentation (*see for reference* Table 2 in **paper III**). The offset could partly be explained by the concurrent $-0.1 \mu\text{mol mol}^{-1}$ residual of the fit to the calibration data at $370.31 \mu\text{mol mol}^{-1}$ in the situation where the average CO₂ mole fraction was $372.16 \mu\text{mol mol}^{-1}$. Also, it was speculated that in the August 2007 the calibration scale of the SMEAR II instrumentation might have had an offset of $-0.1 \mu\text{mol mol}^{-1}$ resulting in the SMEAR II instrumentation to give lower CO₂ mole fraction (*see for reference* Table 1. in **paper III**). However, the negative offset was considered as an indication that the SMEAR II instrumentation was not affected by any leaks inside the measurement cabin causing positive bias in the signal, but nevertheless no evident reason for the negative bias was found.

Participation in the CarboEurope-Atmosphere Cucumber Inter-comparison program (*see* <http://cucumbers/uea.ac.uk/>) enabled an independent assessment of possible offsets in the calibration of the CO₂ mole fraction measuring system. As part of the program the SMEAR II CO₂ measurement system was inter-compared regularly (July 2008, May 2010, January 2011, December 2011 and October 2012) against the University of Heidelberg-Institute of Physics (Heidelberg, Germany) reference laboratory UHEI-IUP (**paper III**) by analysing a set gas cylinders, called as ‘Cucumber’ cylinders, filled with CO₂/air mixtures to (previously) unknown concentrations. Any difference in the analysis results was obviously regarded as a calibration offset of the SMEAR II CO₂ system. The differences between the SMEAR II analyses and UHEI-IUP reference CO₂ mole fractions of the three ‘Cucumber’ cylinders are shown in Fig. 13 plotted with error estimates based on the concurrent analyser signal noise. The compiled data are from June 2014 (provided by CarboEurope Cucumber Intercomparison Programme/ Dr. Andrew Manning, University of East Anglia, United Kingdom). The SMEAR II data from years 2014 and 2015 are from a different measuring system (Picarro system in Fig. 10) and the data is not addressed in this work.

The average offsets of the combined three ‘Cucumber’ cylinder analyses were $0.04 \mu\text{mol mol}^{-1}$, $-0.04 \mu\text{mol mol}^{-1}$, $0.02 \mu\text{mol mol}^{-1}$, $-0.04 \mu\text{mol mol}^{-1}$ and $-0.11 \mu\text{mol mol}^{-1}$ in the successive inter-comparisons, respectively. Averaged over the inter-comparisons the observed offset was $-0.03 \pm 0.06 \mu\text{mol mol}^{-1}$. Examining the time period of the simulation experiment only (until end of 2011)

the average offsets were even within the WMO goal of $\pm 0.1 \mu\text{mol mol}^{-1}$ compatibility among laboratories and central facilities for Northern Hemisphere (GAW Report #206 2012). Coincident with the May 2010 Cucumber inter-comparison the LI-840 analyser was inoperative and the URAS 4 analyser (from the gas profile measurement system) was used as a replacement. Unfortunately, the URAS 4 analyser was not working satisfactory at the time but rather its calibration was unstable and it had unusually high signal noise rendering the precision of the May 2010 analyses rather poor ($\pm 0.2 \mu\text{mol mol}^{-1}$). Noteworthy in the results is that the offsets depend significantly and clearly on the mole fraction in the January 2011 and December 2011 inter-comparisons even when considering the estimated calibration accuracy of $0.2 \mu\text{mol mol}^{-1}$ (Fig. 13). Cylinder specific drifts were observed in the mole fractions of the SMEAR II calibration gases (*see for reference* table 1 in **paper III**). However, the data has not been revised on the basis of the later-on performed re-analyses of the SMEAR II calibration gases, because it was reasoned rather uncertain to determine the mole fractions of the calibration gases at the dates of the inter-comparisons by interpolation between the analysis dates of the calibration gases. Nevertheless, it is speculated that the drifts of the 2nd set of calibration gases could possibly explain the mole fraction dependent offsets observed in the results in January and December 2011. While the mole fractions of the gases of the 1st set of cylinders were observed to have drifted to the same direction and in more or less equal amounts between the analyses, the differences between the analyses of the 2nd set of cylinders ranged from -0.09 to $0.18 \mu\text{mol mol}^{-1}$. Deviations of that amount in the mole fractions of the calibration gases might well have caused the offsets of $\pm 0.1 \mu\text{mol mol}^{-1}$ in the inter-comparison results. There was an evident change in the SMEAR II CO₂ data during the December 2012 inter-comparison when compared to the data of the previous inter-comparisons. The about $-0.1 \mu\text{mol mol}^{-1}$ offset was observed consistently with all three Cucumber cylinders (Fig. 13). It was likely due to the change of the calibration gases in June 2012 (*see chapter* Automatic calibration in the CO₂ mole fraction measurement system in 2.3.3 Calibration arrangements).

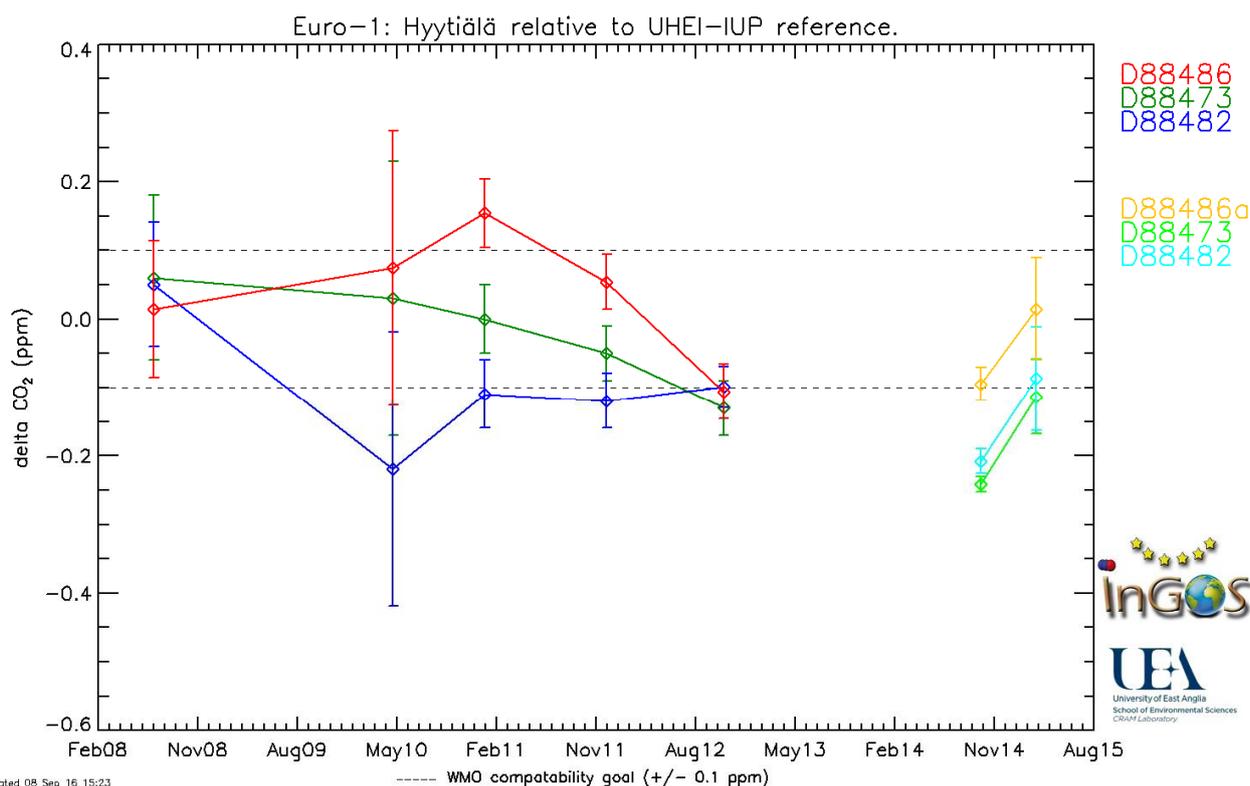


Figure 13. Time series of CO₂ mole fraction differences ‘SMEAR II – UHEI-IUP reference’ in the analyses of gas cylinders D88486, D88473 and D 88482. Error bars are based on the SMEAR II analyser signal noise. ‘Hyttiälä’ in the figure stands for SMEAR II. Reference CO₂ mixing ratios (as given in June 2014) of the cylinders were D88486: 408.45 $\mu\text{mol mol}^{-1}$, D88473: 379.28 $\mu\text{mol mol}^{-1}$ and D 88482: 359.97 $\mu\text{mol mol}^{-1}$. (Figure and reference CO₂ data courtesy of CarboEurope Cucumber Intercomparison Programme/ Dr. Andrew Manning, University of East Anglia, United Kingdom).

Summing up the accuracies from the inter-comparison experiments, the overall estimate for the accuracy of the measured atmospheric CO₂ mole fraction data during the simulation experiment period was between 0.3–0.4 $\mu\text{mol mol}^{-1}$ setting the relative accuracy at about 0.09 % level.

3. Review of the papers

Paper I (Keronen et al. 2003) presents the construction of a system to continuously measure O₃ flux above a forest utilizing eddy-covariance method at SMEAR II station. The instrumentation and measurement setup of the system is described in detail. The diurnal and seasonal variation of the observed flux is discussed. The flux was also determined using simultaneous measurements of concentration profiles (flux-profile method) for comparison between the two methods. The

systematic errors due to flux attenuation caused by imperfect frequency response and random errors due to stochastic nature of turbulence were evaluated. The results from the eddy-variance and flux-profile method agreed well particularly during daytime. At night and towards morning the flux results were found to be significantly different. The influence of chemistry on the concentration profiles and flux ignored by the flux-profile method was believed to cause the discrepancy but the need of further studies to improve the application of either or both methods was acknowledged.

Paper II (Rannik et al. 2004) describes the system to accurately measure CO₂ concentration profiles at SMEAR II station and presents the characteristics of the flux-profile method for estimation of CO₂ flux, the simultaneous results of the eddy-covariance measurement system and a comparison between the observed fluxes. Also, the characteristics of the corrections for the underestimation of the fluxes due to imperfect frequency response of the eddy-covariance system at high and low frequencies are discussed and evaluated. The profile measurement system was proved to meet the demanding requirements of the flux-profile method and there was generally a good correspondence between the CO₂ flux results of the eddy-covariance and flux-profile method. During day-time the observed fluxes were on the average equal. In early morning hours, during the transition period of atmospheric stability and turbulence, there was observed to be a distinct difference between the results, but no obvious reason was identified.

Paper III (Keronen et al. 2014) assesses the technical feasibility of the instrumentation constructed at SMEAR II station to obtain accurate and continuous atmospheric CO₂ mole fraction data for inversion modelling of regional CO₂ exchange at the SMEAR II station. The instrumentation, calibration, measurements and data processing are described in detail. A comparison between two different analysers, inter-comparisons with a flask sampling system and with reference gas cylinders and a comparison with an independent inversion model are presented. The obtained accuracy was found to be better than 0.5 $\mu\text{mol mol}^{-1}$. The agreement between the measured and reference data ranged between -0.3 and 0.06 $\mu\text{mol mol}^{-1}$. Between the analysers the difference in the results was 0.1 $\mu\text{mol mol}^{-1}$. The instrumentation was found to fulfil the set two requirements — accurate results and continuous operation. The study highlighted the importance of quantifying all sources of uncertainty in the measurements.

Paper IV (Mammarella et al. 2007) presents a test on the utilization of a planar-fitting based vertical advection correction for carbon balance using the long-term CO₂ flux and concentration gradient data measured at SMEAR II station. The planar-fitting algorithm (Wilczak et al. 2001) was applied to estimate the real vertical wind velocity for use in the calculation of the vertical advection

flux for subsequent use in an estimation of the night-time net ecosystem exchange (NEE) based on CO₂ flux measured with EC method, CO₂ storage change flux obtained from concentration profile measurements and the calculated CO₂ vertical advection flux. An independent estimate of the NEE was calculated with an ecosystem model using chamber measurements data including forest floor efflux and respiration of tree trunks and foliage for parameterization. The aim was to estimate the significance of the horizontal advection flux of CO₂ at the SMEAR II site based on the possible imbalance between the two NEE estimates. Also, the vertical advection flux was used in the estimation of the annual carbon balance at the SMEAR II site without any filtering due to low turbulence conditions nor subsequent gap-filling for a comparison with the NEE obtained with a standard procedure where low friction velocity periods are filtered and gap-filled by regressions (e.g. Moffat et al. 2007). The inclusion of the vertical flux estimate in the NEE removed the (usual) apparent dependence of the EC flux of CO₂ on the turbulent mixing and the results indicated that the horizontal flux of CO₂ was marginal. The vertical-advection corrected carbon balance was found to agree well with the other two estimates.

Paper V (Rannik et al. 2009) studies the night-time deposition of O₃ to the forest at the SMEAR II site in relation to turbulence intensity by evaluating the turbulent eddy-covariance, storage change and vertical advection fluxes, the aerodynamic and canopy resistances, the turbulent transport time and the sink term due to gas-phase chemical reactions in the air. The horizontal advection flux was assumed to be negligible. The eddy-covariance flux was measured with the system described in the **paper I**. The storage change flux was estimated using measurements of concentration profiles. For the estimate of the vertical advection flux the measured concentration profiles were used and the average vertical wind speed was estimated using the planar fit method of Wilczak et al. (2011). The resistances were estimated with the deposition model by Slinn (1982) following Rannik et al. (2003a). The turbulent transport time was estimated by Lagrangian trajectory simulations according to Rannik et al. (2003b). The chemical sink strengths of O₃ by known fast enough chemical reactions, i.e. with sesquiterpenes and NO, were evaluated using reported reaction rates and estimated emission rates. The eddy-covariance fluxes were observed to decrease with decreasing turbulence intensity. Analysis of the resistances and the chemical sink strength indicated the invariance of the deposition on the turbulence intensity. Accounting for the vertical advection resulted in invariance of the O₃ deposition rate on the turbulence intensity.

4. Author's contributions

I am solely responsible for the summary part of this thesis.

In **paper I** (Keronen et al. 2003) I carried out the ozone flux and concentration profile measurements. I participated in the experimental planning, designed the gas analysis part of the instrumental set-up, tested and modified the gas analyser for continuous use in field conditions, planned and organised the maintenance and calibration procedures. I pre-treated the measurement data, performed part of the data analysis and wrote most part of the paper.

In **paper II** (Rannik et al. 2004) I carried out the flux and concentration profile measurements and pre-treated the measurement data. I participated in the experimental planning, tested the gas analyser for the requirements of the experiment, designed the gas analysis part of the instrumental set-up, planned and organised the maintenance and calibration procedures. I wrote the instrumental section of the Material and methods part of the paper.

In **paper III** (Keronen et al. 2014) I was responsible for the design and building of the sampling and analysis section of the instrumentation and I participated in the design of the automatic calibration set-up and procedures. I took care of the measurements and analyser calibrations and planned and organised the maintenance procedures. I processed the data, performed most part of the data analysis and wrote main part of the paper.

In **paper IV** (Mammarella et al. 2007) I carried out the CO₂ flux and concentration profile measurements, was responsible for the maintenance and calibration procedures and pre-treated the measurement data. I planned and organised the maintenance and calibration procedures of the gas analysis part of the chamber measurements of carbon dioxide flux. I wrote part of the Material and methods section of the paper and commented the manuscript.

In **paper V** (Rannik et al. 2009) I carried out the ozone and carbon dioxide flux and concentration profile measurements and pre-treated the measurement data. I was responsible for the maintenance and calibration procedures of the gas analysis instrumentation. I wrote part of the Material and methods section of the paper.

5. Summary and conclusions

This thesis compiles the setup and measurement characteristics of the eddy-covariance (EC), concentration and concentration profile measurement systems and the calibration arrangements for CO₂, H₂O vapour and O₃ analysers at the SMEAR II station. The details are presented for 1) of the eddy-covariance measurement setup with a modified commercial chemiluminescence O₃ gas analyser operating on liquid reagent solution, 2) of the flux-profile measurement systems for CO₂ and O₃, 3) of the sampling and sample air conditioning instrumentation and methods in the measurement systems, 4) of the procedures for monitoring status of the instrumentation in the measurement systems, 5) of the laboratory and field calibrations, 6) of the automatic calibration system developed for an atmospheric CO₂ mole fraction measurement system as well as 7) inter-comparisons of the CO₂ mole fraction measurement system with a reference measurement system and with reference CO₂ standard gas cylinders.

The EC instrumentation and measurement setup for the measurement of O₃ fluxes was observed to work well and gave results comparable to other studies (**paper I**). The correction factors for flux underestimation in conditions of unstable atmospheric stratification were 1.03–1.19 which is within reasonable limits. With weekly manual calibrations, the span stability of the O₃ analyser (LOZ-3) of the EC instrumentation could be kept within $\pm 10\%$. Starting 2007, the use of the internal, automatic zeroing function of the LOZ-3, enabled a more or less continuous calibration correction against the O₃ analyser (TEI 49) of the concentration profile measurement system without any need to approximate drift in the calibration of the LOZ-3 analyser. The original arrangements and technical structures for the control of the reagent liquid flow in the LOZ-3 O₃ analyser were found to be susceptible to malfunctions, especially in situations of excessive pressure drop in the sample line, rendering the analyser un-operative and requiring time-consuming or even tedious service. Consequently, rather significant technical modifications to the flow control were undertaken and finally a separate actuator system, triggered by the pressure drop, was adopted to prevent analyser malfunctions by disconnecting the analyser inlet from the main sample line. The modifications improved the reliability of the analyser, but nevertheless occasional, inexplicable, malfunctions still occurred.

The fluxes obtained with the flux-profile method were observed to have good correspondence with the fluxes obtained by the EC method during daytime for both CO₂ and O₃ (**paper I and paper II**), which proved the flux-profile method to be suitable for flux measurements above forest canopy. As the CO₂ and O₃ concentration profiles above a forest are small during daytime unstable

conditions minimisation of systematic and random errors and maximisation of the precision of the concentration signals was necessary. A strategy of successive sampling using the same analyser for all sample levels was utilised to minimise any systematic error due to instrumentation. The influence of real concentration fluctuations caused by atmospheric turbulence was reduced with a carefully planned sampling over the 30 min averaging periods where the switching frequency between the sample lines enabled sampling from each level with 6-min intervals to average over the turbulent fluctuations. The precision of the measured average concentrations was maximised by reducing the noise of the analyser concentration signals by averaging over the ~30 s sampling period from each level. The compensation for the different pressures in the sample lines from the different levels was especially important in case of the CO₂ profile measurements with the URAS 4 analyser. As the sample pressures differed by 0.05–0.6 % with each other the biases between the CO₂ signals would have been 0.3–3.3 μmol mol⁻¹ if not corrected for. With the pressure compensation developed (**paper III**), the signals could be corrected to a precision of 0.1 μmol mol⁻¹. The CO₂ and O₃ fluxes observed with both the EC and flux-profile method agreed well during daytime under unstable conditions. The average daily patterns of the daytime fluxes were similar and differences between the flux estimates were within ±1 μmol m⁻²s⁻¹ and ±1 nmol m⁻²s⁻¹ during summer time conditions in June–July, where the fluxes ranged from -10 μmol m⁻²s⁻¹ to 5 μmol m⁻²s⁻¹ and from -9 nmol m⁻²s⁻¹ to -3 nmol m⁻²s⁻¹ for CO₂ and O₃, respectively (**paper II** and **paper I**). At night and especially in the early morning hours, during a transition period of atmospheric stability and turbulence, the flux estimates of the two methods were significantly different. In case of CO₂ the flux-profile method estimated higher respiration (**paper II**) and in case of O₃ it estimated stronger deposition (**paper I**) than the EC method. No apparent reasons for flux over- or underestimation by any one of the methods was identified.

The night-time fluxes measured with EC method for both CO₂ and O₃ had a specious dependence on intensity of the turbulent mixing even after storage flux correction (**paper IV** and **paper V**). For CO₂ the exchange between atmosphere and canopy should not depend on the efficiency of turbulent transport. Also for O₃ the aerodynamic and boundary layer resistances were not limiting the deposition rate as was estimated by model calculations (**paper V**) while surface uptake of O₃ by canopy both in stomatal and non-stomatal parts are not dependent on turbulence intensity. The evaluation of possible chemical sink strengths of O₃ was conducted for the reactions with BVOCs (sesquiterpenes and monoterpenes) and NO (**paper V**). Among the BVOCs with emissions detected at the SMEAR II site (Hakola et al. 2006) only the most abundant sesquiterpene (beta-caryophyllene) was known to have fast enough reaction rate constant with O₃ to result in a

fast enough reaction time scale (~ 2 min) comparable to the turbulent transport time of O_3 (**paper V**). For NO the reaction time scale was estimated to be in the order of 1 min (**paper V**). The turbulent transport time, estimated to be from a few minutes to 20 min, would have been long enough for these chemical reactions (**paper V**). But the known emission rates of sesquiterpene and NO at the SMEAR II site (Hakola et al. 2006 and Pilegaard et al. 2006, respectively) site limited the corresponding O_3 destruction rates as negligible to explain the deposition flux un-detected by the EC method. Thus, it was expected that the night-time O_3 deposition was not controlled by turbulence. Estimating the vertical wind velocity for each 30 min averaging period and using the measured concentration profiles the vertical advection could be estimated. Accounting for the vertical advection the short-term carbon balance estimated by the EC method was improved which could be verified by comparison to an independent NEE estimate based on chamber measurements and models for respiration (**paper IV**). Also, the inclusion of vertical advection removed the apparent dependence on turbulent mixing. There were no measurements for horizontal advection available, but the results indicated that the horizontal advection of CO_2 had only a minor significance (**paper IV**). Following the same procedure to estimate the vertical advection flux of O_3 and taking it into account in night-time EC O_3 flux measurements resulted to an invariance of O_3 deposition rate on turbulent mixing (**paper V**). Although the results showed that the estimated vertical velocities were reliable for estimating the vertical advection of CO_2 at the SMEAR II site, the importance for estimating NEE by different ways at flux tower sites was stressed. Also, it is recognised that generally the improvement of EC measurements by advection correction to the measured CO_2 fluxes is not considered be reliable in practice (Aubinet et al. 2010).

The SMEAR II CO_2 measurement system developed and constructed for accurate measurements of atmospheric CO_2 mole fraction utilising a commercial, low cost NDIR-absorption analyser fulfilled the two basic requirements — accurate results and reliable, continuous operation (**paper III**). Summing up the precisions of the pressure and temperature correction, analyser signal noise and precision, stability and repeatability of the calibration, the estimate of the measurement uncertainty of the ambient CO_2 mole fraction data was $\pm 0.2 \mu\text{mol mol}^{-1}$ regardless of the analyser in use. However, between October 2006 and October 2007 the estimated measurement uncertainty was $\pm 0.4 \mu\text{mol mol}^{-1}$ because of an impaired calibration precision (**paper III**). The fraction of unsuccessful measurements due to technical problems directly related to the CO_2 instrumentation was about 1 %. Various technical malfunctions at the SMEAR II site affecting the CO_2 measurement system accounted for about 2 % of the missing data while about 2 % of the

measurements were cancelled on purpose, e.g. in April 2008 due to the intermediate check of calibration gases at FMI. All in all the data coverage was 95 % (**paper III**).

In a comparison experiment between two different CO₂ analysers utilised in the SMEAR II CO₂ measurement system (URAS 4 and LI-840, respectively) the analysers were observed to give consistent results for the ambient CO₂ mole fraction data. On average the URAS 4 analyser indicated $0.1 \pm 0.4 \mu\text{mol mol}^{-1}$ higher CO₂ mole fraction, but the difference could be considered consistent throughout the continuous 26 months long experiment. While the effective pressure correction (of the URAS 4 analyser) ranged between 0 and $2 \mu\text{mol mol}^{-1}$ changes in it were not correlated with the observed CO₂ mole fraction differences (**paper III**).

The instrumentation of the SMEAR II CO₂ measurement system was assessed as a whole in August 2007 in an inter-comparison experiment where air samples were simultaneously measured with a reference instrumentation in which flask samples were collected and analysed afterwards with gas chromatography (GC). The reference sampling instrumentation and GC-analysis were provided by MPI-BGC-GasLab (Germany). The CO₂ mole fraction data obtained with the SMEAR II instrumentation were systematically $0.3 \pm 0.2 \mu\text{mol mol}^{-1}$ lower than the data from the reference instrumentation (**paper III**). Possible calibration offsets of the SMEAR II system were assessed in five occasions (July 2008, May 2010, January 2011, December 2011 and October 2012) where the measurement system was inter-compared against the University of Heidelberg-Institute of Physics (Heidelberg, Germany) reference laboratory UHEI-IUP by analysing the CO₂ mole fractions in a set of gas cylinders. Averaged over the inter-comparisons the observed offset was $-0.01 \pm 0.06 \mu\text{mol mol}^{-1}$. As a conclusion the estimated overall accuracy was $0.3\text{--}0.4 \mu\text{mol mol}^{-1}$ and with it the set goal of accuracy of $0.5 \mu\text{mol mol}^{-1}$ was achieved.

The measured atmospheric CO₂ mole fraction data were compared with an atmospheric transport model simulation data (MACC-II) over the years 1979–2011 (**paper III**). Both the trend and phase of the measured and the simulated data for the SMEAR II site were observed to agree generally well and the overall bias of the simulation, $-0.2 \mu\text{mol mol}^{-1}$, was well within the accuracy of the measured data. During some periods, the model underestimated the (summer time) uptake for longer continuous time periods, i.e. for 2–3 months. Specifically, in years 2007 and 2008 the underestimation was obvious and the simulated CO₂ mole fraction data was showing $3\text{--}4 \mu\text{mol mol}^{-1}$ higher values than the measured data. On the other hand, in May–July 2010 the simulation clearly overestimated the uptake and the measured CO₂ mole fraction data exceeded the simulated one by up to $7 \mu\text{mol mol}^{-1}$. Because the simulated CO₂ data was driven by (for the SMEAR II site) remote

measurements and by prior flux data, the main contributor to the discrepancies was considered to be the lack of local measurement constraints (**paper III**). Overall, the result of the comparison nevertheless implied that after flux correction the observed variability of the atmospheric CO₂ mole fraction at the SMEAR II site could be modelled and the CO₂ mole fraction data from the SMEAR II station would clearly have the potential to be assimilated in the global inverse simulations (**paper III**).

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