Thesis for the degree of doctor of philosophy

Regional and Local Surface Ozone Variations in Relation to Meteorological Conditions in Sweden

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Abstract

Air quality is strongly dependent on meteorological conditions. Atmospheric circulation encapsulates general information about local meteorological variables to some extent, and can serve as an explanatory variable for air quality at a regional or local scale. Numerical models are another useful tool for understanding the influence of meteorological factors on the chemical and physical processes involved in regional and local air quality variations. The aims of this thesis have been to: (1) investigate regional surface ozone and its correlation to atmospheric circulations by making use of synoptic weather types in southern Sweden; (2) compare numerical models performances in simulating urban meteorological conditions and apply a numerical model to urban air quality study for Gothenburg.

The study confirmed the influences of synoptic circulation on regional ozone concentrations by relating the Lamb Weather Types (LWTs) to surface ozone variations. Anticyclones, associated with atmospheric stagnation, tend to create whirling air masses and short trajectories from the European continent, which leads to effective long-range transport, enhanced local ozone photochemical production, and high-ozone levels. Cyclones, on the other hand, can also create high level ozone through frontal passages and enhanced vertical mixing. At the same time, the frequencies of cyclones and anticyclones in this region are highly anti-correlated, making cyclone frequency a skilful predictor of high ozone events. The frequency of cyclones over the past 150 years shows a high variability and showed significantly downward trend. Given the constant conditions from other factors for example emission, continuous decrease in the frequency of cyclones indicates the more occurrences of high-ozone events in southern Sweden.

A numerical model - The Air Quality Model (TAPM) - was used to simulate the complex wind system and other meteorological variables needed for air quality applications in the Gothenburg area. Compared with The PSU/NCAR fifth-generation Mesoscale Model (MM5), TAPM is able to better reproduce near-surface air temperature and wind system in Gothenburg. Both MM5 and TAPM can simulate night-time vertical temperature gradient well, but underestimate daytime vertical temperature gradient and the occurrences of low wind speed situation at night. TAPM was then used to reproduce $NO_x - O_3$ reactions and investigate the wind speed effect on spatial differences of NO_2 concentrations in the polluted urban landscape. TAPM satisfactorily simulated the relation of NO, NO_2 and ozone as well as the site differences for different wind speed categories. However, TAPM underestimated NO at certain sites due to local scale site-specific conditions and missing emissions from nearby roads and other emission sources.

Keywords: *LWTs, surface ozone, high-ozone events, long-range transport, TAPM, MM5,* $NO_x - O_3$*, Sweden.*

List of Publications

This thesis includes the following papers:

I **Tang L.**, Chen D., Karlsson P.E., Gu Y. and Ou T. 2009. Synoptic circulation and its influence on spring and summer surface ozone concentrations in Southern Sweden. *Boreal Environment Research* (in press).
(online: http://www.borenv.net/BER/pdfs/preprints/Tang721.pdf)

Tang planned and organized the article supervised by Prof. Chen and Ass. Prof. Karlsson. Tang carried out the data analysis, figure plotting and writing process.

II **Tang L.**, Karlsson P.E., Gu Y., Chen D. and Grennfelt P. 2009. Long-range transport patterns for ozone precursors during high ozone events in southern Sweden. Submitted to *Ambio*.

Tang planned and organized the article based on the discussion with other co-authors. Tang carried out the data analysis, figure plotting and writing process. Mr. Gu provided the supports in trajectory clustering analysis and GIS implication.

III Karlsson P.E., **Tang L.**, Sundberg J., Chen D., Lindskog A. and Pleijel H. 2007. Increasing risk for negative ozone impacts on the vegetation in northern Sweden. *Environmental Pollution* 150, 96–106.

Ass. Prof. Karlsson planned and wrote the article. Tang conducted the trend analysis part and took part in the related writing process. DO3SE model was conducted by Ass. Prof. Karlsson.

IV **Tang L.**, Miao J.-F. and Chen D. 2009. Performance of TAPM against MM5 at urban scale during GÖTE2001 campaign. *Boreal Environment Research* 14, 338–350.

Tang conducted modelling work for TAPM, as well as the data analysis, comparing results and the writing processes. Dr. Miao conducted MM5 and provided the simulation results.

V Klingberg J., **Tang L.**, Chen D., Karlsson G. Pihl, Bäck E. and Pleijel H. 2009. Spatial variation of modeled and measured NO, NO_2 and O_3 concentrations in the polluted urban landscape - relation to meteorology during the Göte-2005 campaign. *Atmospheric Chemical and Physics Discussion* 9, 2081–2111.

Mrs. Klingberg carried out the field measurements during GÖTE2005 and wrote the major part of article. Tang was responsible for TAPM model set-up, running and joined the discussion, result analysis and related writing process.

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Scientific publications which are not included in this thesis:

- Johansson M., Galle B., Yu T., **Tang L.** and Chen D. 2008. Quantification of total emission of air pollutions from Beijing using ground based optical remote sensing. *Atmospheric Environment* 42, 6926–6933.
- Olofson K. F. G., Andersson P. U., Hallquist M., Ljungström E., **Tang L.**, Chen D. and Pettersson J. B. C. 2009. Influence of wintertime boundary layer dynamics on aerosol properties and particle formation in Gothenburg, Sweden. *Atmospheric Environment* 43, 340–346.
- Mu H., Xu J., Ke X., **Tang L.** and Chen D. 2006. Application of High Resolution Numeric Model to Wind Energy Resources Assessment. *Journal of Meteorological Applications* 17, 152–159 (in Chinese with English abstract).

IVL (Swedish Environmental Institute) reports which are not included in this thesis:

- Haeger-Eugensson M., Jerksjö M., Fridell E., **Tang L.**, Persson K. and Svensson A. 2007. Uppbyggnad av EDB och spridningsberäkning samt mätning av luftföroreningar: För Ystad. *IVL report*.
- Sjöberg K., Haeger-Eugensson M., Forsberg B., Åström S., Hellsten S. and **Tang L.** 2007. Quantification of populaiton exposure to nitrogen dioxide in Sweden 2005. *IVL report* B-1749.
- Paulrud S., Haeger-Eugensson M. and **Tang L.** 2006. Påverkan på luftkvalitet vid användning av spannmål som bränsle-scenario för Västra Götalandsregionen. *IVL report* B-1701.
- Haeger-Eugensson M., **Tang L.**, Chen D., Axelsson J., Lönnemark A. and Stripple H. 2006. Spridning till luft från brander. *IVL report* B-1702.
- Svensson A., Haeger-Eugensson M. and **Tang L.** 2006. Spridnings och depositionsberäkningar för SSAB Oxelösund. *IVL report* U-1914.
- Haeger-Eugensson M., **Tang L.** and Moldanova J. 2006. Spridnings och depositionsberäkningar för Borealis. *IVL report* U-1925.
- Haeger-Eugensson M., **Tang L.** and Moldanova J. 2006. Spridnings och depositionsberäkningar för Hydro. *IVL report*.
- **Tang L.**, Svensson A. and Haeger-Eugensson M. 2006. Spridnings och depositionsberäkningar för Eka Chemicals AB i Ånge. *IVL report* U-1978.
- Haeger-Eugensson M. and **Tang L.** 2006. Spridnings och depositions-beräkningar för Mörrum. *IVL report*.

- Haeger-Eugensson M., Gustafson A., Flodström E., Steen E. and **Tang L.** 2005. Spridningsberäkning avseende luftkvalitet och buller vid Valhallagaten, Göteborg. *IVL report* U-1120.

- Karlsson P. E., Pleijel H., Haeger-Eugensson M., Chen D. and **Tang L.** 2004. Lokal variation av ozonexponering i jordbruks- och skogslandskap i Sverige. *IVL report.*

Tang's contributions were mainly in model (TAPM) set-up, running and result analysis.

Contents

1
Introduction

An increasing trend of background surface ozone has been reported over a large geographical scale [1], [2], [3], [4], [5]. During the last 10–15 years, +0.3–+0.5 ppb yr^{-1} is detected within the Nordic countries [3], [6]. Surface ozone is positively associated with total mortality [7] and threatens agricultural crops and forest trees (e.g. [8]). The potential annual economic loss for Sweden due to negative impacts of ozone on forest production would be in the range of 56 million Euro (2004 price) [9]. Surface ozone is also the third most important greenhouse gas after carbon dioxide (CO_2) and methane (CH_4). The total amount of tropospheric ozone is estimated to have increased by 30% globally sine 1750, which corresponds to an average positive radiative forcing of 0.35 Wm^{-2} [10].

Ozone precursors, nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs), can be emitted from both natural and anthropogenic sources. Anthropogenic precursor emissions have decreased dramatically in West Europe, central Europe and the Nordic countries since 1990s [11]. The peak ozone values in the Nordic countries have been reduced in the order of 30 $\mu g\ m^{-3}$ since 1990s due to reduced emissions of precursors in Europe [12]. However, extreme ozone episodes such as the one which occurred during the record warm summer of 2003 might occur more often in the future [13]. The effect of future climate change may gradually outweigh the benefit of emission abatement in Europe [13]. Climate change feedbacks on air pollution are becoming a new direction of policy development in Europe [14].

1.1 Chemistry of ozone

Surface ozone is produced from photochemical oxidation of CH_4, VOCs and carbon monoxide (CO) in the presence of NO_x. During daylight hours nitrogen dioxide (NO_2) is photolytically converted to nitric oxide (NO) leading to the formation of ozone:

$$NO_2 + hv(\lambda \leq 430nm) \rightarrow NO + O \tag{1.1}$$

$$O + O_2 \rightarrow O_3 \tag{1.2}$$

produces more ozone when NO_2 levels increase. NO reacts relatively rapidly with ozone and forming NO_2 under atmospheric conditions.

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1.3}$$

consumes less ozone when we decrease NO. Reactions (1.1), (1.2) and (1.3) constitute a cycle with no net chemistry which gives a steady state concentration of ozone. However, the presence of CO and VOCs can disturb this relationship by producing peroxy radicals ($HO_2^\bullet$ and $RO_2^\bullet$).

$$CO + OH^\bullet \rightarrow CO_2 + HO_2^\bullet \tag{1.4}$$

$$CH_4 + OH^\bullet(+O_2) \rightarrow CH_3O_2 + H_2O \tag{1.5}$$

$$RCH_3 + OH^\bullet(+O_2) \rightarrow RCHO + HO_2^\bullet \tag{1.6}$$

Then NO reacting with $HO_2^\bullet$ and $RO_2^\bullet$ instead of ozone result in an increased ozone concentration.

$$NO + HO_2^\bullet \rightarrow NO_2 + OH^\bullet \tag{1.7}$$

$$NO + RO_2^\bullet \rightarrow NO_2 + RO \tag{1.8}$$

Therefore, surface ozone control is generally achieved by reducing the anthropogenic emissions of both NO_x and VOCs into the atmosphere. The differences in the spatial distribution of emissions can have significant consequences in the levels of ozone exposure in Europe [11]. According to the EMEP (European Monitoring and Evaluation Programme) emission inventory in 2000 ($http://www.emep.int$), the higher levels of anthropogenic emitted NO_x and non-methane volatile organic compounds (NMVOC) were observed in the Great Britain, Netherlands, Belgium, western and eastern Germany, northwest Czech Republic, southern Poland, central Belarus, western Russia and eastern Ukraine (FIGURE 1.1). Thus, ozone gradients over Europe are most pronounced in north-west to south-east direction in summer [15]. In winter, ozone concentrations ranged from 19 to 27 ppb over the continent, compared to 39–56 ppb for summer and ozone gradients are strongest in the east-west direction [15]. This is likely because precursor emissions effectively deplete ozone by the process of NO_x titration through reaction with NO (Reaction 1.3). At night-time, there is no photolysis of NO_2 (Reaction 1.1) and reaction (Reaction 1.3) also leads to the removal of ozone.

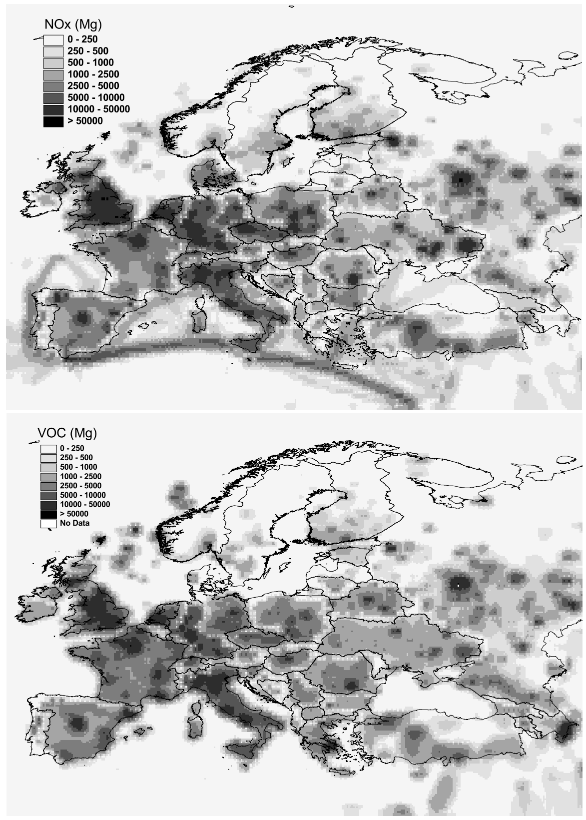

FIGURE 1.1: Spatial distribution of anthropogenic emissions over Europe in 2000: Nitrogen oxide (NO_x), and Non-Methane Volatile Organic Compounds (NMVOC) (Data sources: The EMEP Centre on Emission Inventories and Projections (CEIP), http://www.ceip.at/).

Ozone can be lost by photolysis, producing an oxygen atom in an electronically excited state.

$$O_3 + hv \rightarrow O_2 + O(^1D) \tag{1.9}$$

$$O(^1D) + H_2O \rightarrow 2OH^\bullet \tag{1.10}$$

In addition, dry deposition is a primary mechanism to cleanse the atmosphere and deliver chemical does to the surface [17]. It is one of major removal processes for surface ozone by which ozone is transferred by air motions to the surface of the Earth. Dry deposition flux of ozone is usually expressed as surface ozone concentration and deposition velocity. The deposition velocity of ozone depends strongly on land use and weather conditions [18].

1.2 Meteorological factor

Meteorological factor is dominant in leading to accumulation of ozone in the troposphere, causing large day-to-night, day-to-day, season-to-season, and year-to-year variations [16]. Ozone levels are generally increasing with increasing temperature and decreasing with increasing relative humidity [19]. The probability of ozone exceedance increases with temperature [20]. The most important explanatory meteorological variables for the daily maximum ozone concentrations were afternoon temperature, morning global radiation and number of days after a frontal passage in summer [21]. The temperature dependence of ozone is due to: (1) the temperature dependent lifetime of peroxyacetylinitrate (PAN), a major reservoir of NO_x and HO_x radicals; and (2) the temperature dependence of biogenic emission of isoprene, a major VOC precursor for ozone formation under high-NO_x conditions [23], [24]. Therefore, maximum hourly ozone concentrations occur most prevalent during mid-day to mid-afternoon attributed to local ozone formation processes. Air stagnation characterized by high ambient temperature, low wind speeds, ample sunlight is involved in most ozone episodes. The highest ozone concentrations are observed when stagnation conditions persist over several days [25], [26].

Horizontal transport and vertical transport occur under certain meteorological conditions can cause high surface ozone levels. Within the mixed layer aloft, concentrations of ozone during the day, and above the surface nocturnal layer at night, can be 20–70 ppb [27] greater than surface concentrations due to lack of NO available to react with ozone aloft and ozone deposition. This implies a potential for long-range transport of ozone and precursors. The background ozone flux over Europe show large northward fluxes in summer due to photochemically produced elevated ozone concentrations and southward fluxes in winter driven by high wind speeds [28]. The Nordic countries located on the outskirts of the main European ozone precursor emission area, long-range transport is more important than local photochemical production for elevated ozone concentrations. The typical situation of high ozone events in this area is often associated with the breaking up of an extensive high-pressure system due to the approach of a marked cold front system [12]. Ozone episode induced by long-range transport was also observed in northern Fennoscandia [29]. In addition, intercontinental transport from North America and Asia can also contribute to European ozone variations, in especially during the late summer and autumn [30].

Enhanced vertical mixing tends to increase the surface ozone concentration by bring down the ozone-rich air aloft and usually associated with nocturnal ozone maxima[31]. The reasons for enhanced vertical mixing can be valley wind, a frontal passage and low-level jets (LLJ) [32]. Stratospheric-tropospheric exchange (STE) is another important vertical transport mechanism affecting surface ozone variations. The stratospheric contribution to the observed ozone spring maximum has been widely assumed by a springtime maximum in upper level cyclogenesis and tropopause folding events [33]. The estimated cross-tropopause ozone flux within tropopause folds can reach to 10.4×10^{32} (molecules per day) for spring [34]. In Scandinavia, springtime ozone maxima has observed, coinciding with the seasonal variation of STE.

Increasing water vapour could increase ozone loss by the reactions (1.9) and (1.10). Water vapour also influences ozone dry deposition through a strong coupling with stomatal conductance. If soils are dry under warm and sunny weather, the soil water deficit leads to closure of vegetation stomatal leading to even larger surface ozone concentrations. Wind speed is generally correlated with ozone advection and deposition. A model study showed that weaker wind speeds in polluted area cause to higher ozone levels due to a longer reaction time and increased aerodynamic resistance to dry deposition [22]. In addition, the effects of mixing height, cloud cover as well as cloud liquid water content and optical depth, and precipitation on high surface ozone are appreciable [22]. Ozone dynamics are therefore sensitive to climate change. Increasing air temperatures as well as reduced cloudiness and precipitation due to climate change may promote high ozone concentrations [35]. In high latitude area, pronounced warming will accompany with increasing annual precipitation [10]. High ozone concentrations in warm climate might increase the risk of negative ozone effect on plants under wet air and soil conditions in this area.

Atmospheric circulation encapsulates general information about local meteorological variables (temperature, solar radiation, wind direction etc.) to some extent, thus can be served as an explanatory variable for air quality on a regional scale [36]. In southern Sweden, atmospheric circulation has been classified by a manual scheme developed by Lamb(1950) [37], and was automatic by Jenkinson and Collinson (1977) [38]. Lamb weather types (LWTs) has been calculated using gridded monthly and daily mean sea level pressure (MSLP) data and applied to determine local variability of meteorological variables such as temperature and extreme precipitation [39], [40], [41]. Extending the LWTs to regional surface ozone study is a significant trial to confirm its application and identify the influences of atmospheric circulation on regional air quality.

1.3 Air quality at local/urban scale

In urban areas, the inter-conversion of ozone, NO and NO_2 under atmospheric conditions is generally dominated by chemical reactions (1.1), (1.2) and (1.3). Road traffic exhaust is the dominant NO_x source in urban locations. Urban vehicle fleet and fuel type, and driving conditions determine the proportion of NO_2 in NO_x. Ozone concentrations in urban areas are relatively low due to the chemical coupling with NO_x. However, changes in the level of ozone on a global and regional scale lead to an increasing background which influences local ozone and nitrogen dioxide (NO_2) levels and the effectiveness of local emission controls [42]. The local NO_2 and ozone concentrations have significant site-to-site variations from urban background, urban kerbside, urban centre to suburban. Measurements and modelling indicate that many urban areas will have difficulty reaching the air quality standard for NO_2, especially close to major traffic routes [43], [44].

In Gothenburg, air-quality could be worsened under certain meteorological conditions, for example during winter temperature inversions [45] and simultaneously with the morning rush hour [46]. Owning to the location and topography of Gothenburg, the local- and mesoscal wind systems developed under high-pressure systems can be very complicated. Land- and sea breezes are produced when air temperature differences are strong enough [47], [48], [49]. The urban heat island circulation influences the local air flows in the city [50], [51]. The joint aligned valley landscape produces cold air drainage and shallow pools in the valley bottoms during clear and calm nights, but as the valley bottoms are flat without any inclination in the long axis direction a mountain-valley wind system develops [49]. In addition, a LLJ produced at the top of a surface inversion has also been observed in Gothenburg [53]. These local- and mesoscale wind systems dramatically influence the local air quality and the spatial distribution of air pollutants. The concentrations of gases decrease with increasing wind speed due to effect of increased dilution during higher wind speeds [52]. The NO_x peak is usually coincident with the onset of the urban heat island circulation and the second maximum of NO_x later in the evening/early morning is usually simultaneous with the start of the mesoscale wind, for example a winter land breeze or/and LLJ [53]. Summer nocturnal ozone maxima positively correlate with well-developed land breeze and vertical mixing [31]. Simultaneously, efforts in successfully simulating the complex wind system were carried out. Chen et al. (2002) [54] evaluated The Air Pollution Model (TAPM) [55] in meteorological simulations with yearly and daily time scale datasets over the Gothenburg area. Miao et al. (2006, 2007, 2008) [18], [56], [57] evaluated the advanced mesoscale model The PSU/NCAR fifth-generation Mesoscale Model (MM5) [58] in Gothenburg by comparing different boundary layer schemes and land surface schemes, and studied dry deposition velocity of ozone over the Swedish west coast. Johansson et al. (2008) [59] applied TAPM wind simulations to urban emissions study.

Therefore, surface ozone is a multi-scale phenomenon determined by interaction of chemical transformation, precursor emissions, long-range transport and dry deposition processes. Meteorological factor play a key role in causing surface ozone accumulation and variations. The thesis focused on the meteorological effects on surface ozone and its precursors at regional and local/urban scales. The study concentrated in spring (April–May) and summer (June–August) when ozone concentrations stay in a relative high level in southern Sweden.

1.4 Aim of thesis and objectives

The aims have been to: (1) better understand the influences of atmospheric circulation on regional air quality by using LWTs and reveal their relationship quantitatively; (2) simulate the urban meteorological conditions and investigate the urban air quality variation in temporal and spatial scales.

The specific objectives of the thesis have been to:

- find the links between atmospheric circulation patterns and regional surface ozone levels in southern Sweden (Paper I);
- confirm the long-range transport patterns in southern Sweden and their relation with atmospheric circulation patterns (Paper II);
- investigate the trend of ozone concentrations in northern Sweden and possible effects of future climate change on surface ozone and ozone uptake (Paper III);
- evaluate the TAPM performance in local/urban meteorological simulations by comparing with an advanced mesoscale model MM5 (Paper IV);

- evaluate the model performance in simulating $NO_x - O_3$ variations in polluted urban landscapes and study the influences of wind speed on NO_2 spatial variations (Paper V).

2

Data and Models

2.1 Ozone monitoring data

The positions of ozone monitoring sites Rörvik/Råö, Norra Kvill, Vavihill and Aspvreten in southern Sweden; Åreskutan, Esrange and Vindeln in northern Sweden are shown in FIGURE 2.1. Surface ozone data at these rural monitoring sites represent regional background levels with less contribution from local emissions and was used in Paper I and II. Hourly ozone concentrations at these sites for 1990–2006 are available from the official Swedish database hosted by the Swedish Environmental Institute (*http : //www.ivl.se/*). In addition, FIGURE 2.1 shows the location of Gothenburg studied in Paper IV and the sites locations near the heavy traffic road Olskroksmotet used in Paper V.

2.2 GÖTE2001 and GÖTE2005 campaign data

Gothenburg (57°42'N, 11°58'E), the second largest city in Sweden, is situated in a hilly landscape with steep sided joint aligned valleys over the Swedish south-western coast. The measurement campaign GÖTE2001, during 7–20 May 2001, took place in and around Gothenburg, covering the Gothenburg city centre, suburban and rural areas, including the west coastal area (FIGURE 2.2). The meteorological variables available during this campaign are temperature, wind speed, wind direction and humidity at the near-surface level. GÖTE2001 field campaign database was used to evaluate TAPM and MM5 models in Paper IV.

The GÖTE2005 campaign, from 2 February to 2 March, 2005, was carried out in Gothenburg with both meteorological and air quality measurement (http://www2.chem.gu.se/∼hallq/Gote_eng_2005.htm). As part of the GÖTE2005 campaign, passive sampler measurement near the busy traffic road Olskroksmotet was carried out at seven sites with different distances away from the road (FIGURE 2.1). The ozone and NO_x concentrations and meteorological variables were used to evaluate the air quality module of TAPM, in especially focused on the influences from wind speed (Paper V).

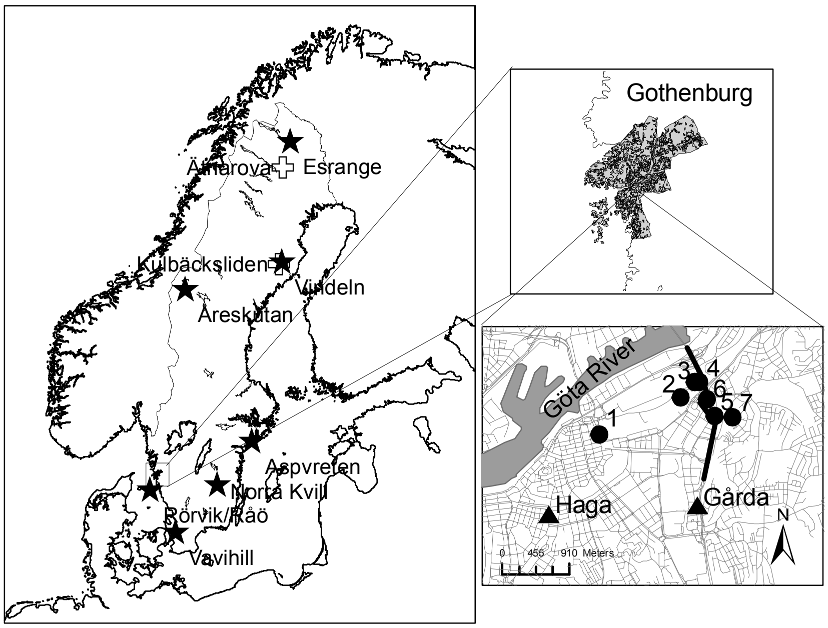

FIGURE 2.1: The stars in the left panel represent the positions of ozone monitoring sites Rörvik/Råö, Norra Kvill, Vavihill and Aspvreten in southern Sweden; Åreskutan, Esrange, Vindeln in northern Sweden. The crosses represent the positions of meteorological sites Kulbäckaliden and Ätnarova in northern Sweden. The right-up panel shows the location of Gothenburg, where the GÖTE2001 campaign was carried out. The right-down panel presents the location of Olskroksmotet and the position of the measurement sites during GÖTE2005 campaign.

2.3 The Air Pollution Model (TAPM)

Progresses in fine scale meteorological and air chemistry modelling over the last decades have made it possible to fairly realistically model urban air pollution dynamics. One such model is TAPM, a three-dimensional, nestable, prognostic meteorological and air pollution model. It includes gridded terrain height, vegetation and soil type, sea-surface temperature, and synoptic-scale meteorology databases. The global terrain height dataset, vegetation and soil-type datasets at 30-second grid spacing (approximately 1 km) are based on public domain data available from the US Geological Survey, Earth Resources Observation Systems (EROS) Data Center Distributed Active Archive Center (EDC DAAC). The monthly mean sea-surface temperatures dataset at 1.0-degree grid spacing (approximately 100 km)is based on public domain information available from the US National Center for Atmospheric Research (NCAR). A six-hourly synoptic scale analyses database at 0.75- or 1.0-degree grid spacing (approximately 75 km or 100 km) is derived from regional and global model system (LAPS or GASP) analysis data from the Bureau of Meteorology (BoM).

TAPM consists of two basic modules: a meteorology module and an air quality module. The meteorology module predicts the local scale flow, such as sea breezes and terrain-induced circulation given the larger scale synoptic meteorological fields. The mean horizontal wind components are determined from the momentum equations and the terrain-following vertical velocity from the continuity equation. The air pollution module consists of an Eulerian grid-based set of prognostic equations for pollutant concentrations. It includes variance equations representing advection, diffusion, chemical reactions and emissions. Dry and wet deposition processes are also included. The model can be run in tracer mode, chemistry mode or dust mode according to specific application. There are ten reactions for thirteen species including nitric oxide (NO), nitrogen dioxide (NO_2), ozone, sulphur dioxide, the radical pool, Rsmog (a reactivity coefficient multiplied by VOC concentration), stable gaseous products, stable non-gaseous products and particulate matter. The specific reactions and reaction rates are available in Hurley (2005) [55]. Previous studies have shown that TAPM performs well in coastal, inland and complex terrain, in sub-tropical to mid-latitude conditions [67], [68], [69].

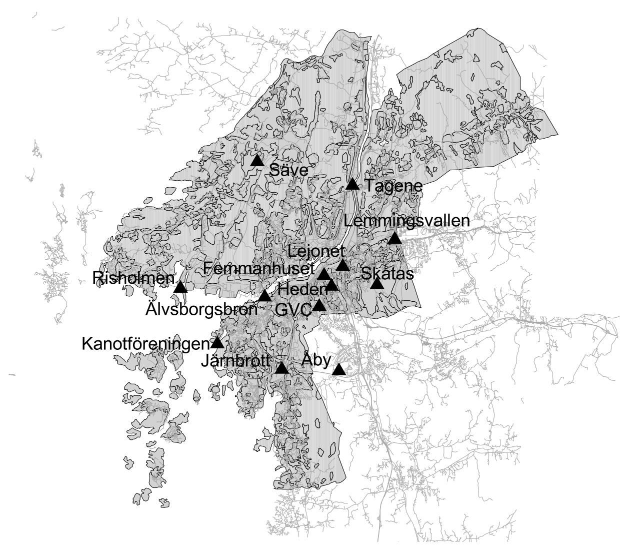

Figure 2.2: Locations of coastal sites, rural site and urban sites during GÖTE2001 campaign.

3
Methods

3.1 Statistical methods

3.1.1 Mann-Kendall test

To test the statistical significance of trends, the Mann-Kendall test was applied to a time series of surface ozone concentrations at different sites (Paper I, II, III). The Mann-Kendall test is a non-parametric test that has the advantage of robustness against outliers and can be applied to non-normally distributed data with missing values. Sen's non-parametric method was used to estimate the slope of an existing trend [60]. In addition, standard error were calculated to indicate the uncertainty around the estimated trend.

3.1.2 Stepwise regression

The stepwise regression method has been widely used in synoptic climatological and air pollution studies due to its ability to identify sequentially the optimum subset of independent variables. In Paper I, the backward stepwise method was applied to establish linear regression models between annual ozone concentrations and the three independent weather type indices.

3.1.3 Statistical measures

To evaluate the model and observations, a set of statistical measures were used to quantitatively measure the model performance. Following Willmott (1981) [61], the following measures were used in Paper IV: mean (Mean), standard deviation (SD), mean bias error (MBE), root mean square error (RMSE), correlation coefficient (R), and one skill measure index of agreement (IOA). In Paper V, the explained variance (R^2) was calculated to evaluate the model against the observations.

3.1.4 Two-stage clustering

Clustering allows large quantities of data to be processed automatically and takes account of both the curvature and length of trajectories as it groups purely in terms of the proximity at different time points (latitude, longitude coordinates). A K-means clustering algorithm using squared Euclidean distances was conducted to group the nearest trajectories geographic source regions of ozone and its precursors. By using the same methodology, two-stage clustering was implemented to achieve more specific and reasonable clusters and to capture the influence of short, slow-moving trajectories on regional air quality (Paper II).

3.2 Definition

3.2.1 Ozone episode

Ozone episodes are characterized as short periods with higher than normal ozone concentrations, which can do harm to human health and vegetation. There is no uniform definition of an “ozone episode. In Paper I, if any of the 8-h moving averages during the day was greater than or equal to 60 ppb, this day is defined as an episode day.

3.2.2 High ozone events

The WHO (World Health Organization) has recently suggested reducing the target value of ozone near the ground from 60 to 50 ppb for daily maximum 8-h average concentration to protection human health. Compared with central Europe, the mean ozone level in southern Sweden is relative low. Therefore, high-ozone events in Paper II were adjusted to 50 ppb for daily maximum 8-h moving average.

3.2.3 AOT40

Vegetation exposure to ozone in Paper III was expressed by ozone exposure index AOT40, defined as accumulated exposure over a threshold of 40 ppb. The cut-off at 40 ppb is focussed on the largely anthropogenic part of the ozone exposure and AOT40 has been considered a fair compromise between sophistication, existing experimental data and practical needs [8].

3.2.4 Growing season

There are a number of definitions for growing season of vegetation (e.g. Linderholm (2006) [62]). In Paper III, we applied the widely use definition suggested by Morèn and Perttu (1994) [63], that the start and end of the growing season are defined as when the daily mean air temperatures are above or below 5 °C during 4 consecutive days, respectively.

3.3 Objective atmospheric circulation classification

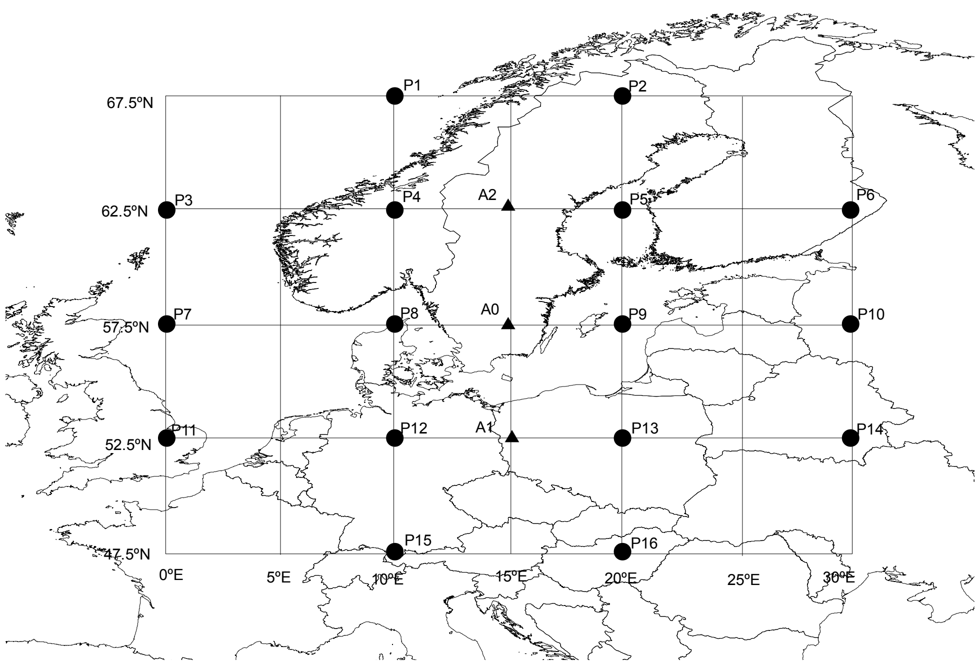

Figure 3.1: Locations of 16 grid points (circle) (P1-P16) and three points (triangles) (A0, A1, A2) used to calculate the six Lamb indices

In order to investigate the influences of atmospheric circulation, this work has applied Lamb weather types (LWTs) and their indices (Paper I, II). According to the specific rules, six indices of the geostrophic wind components and vorticity are calculated. Indices u and v represent westerly (zonal) and southerly (meridional) components of the geostrophic wind; V is the combined wind speed; ζ_u (meridional gradient of u) and ζ_v (zonal gradient of v) are westerly and southerly shear vorticity; and ζ is the total shear vorticity index. Since all pressures have the units of hecto Pascals (hPa), the indices have units of hPa per 10° longitude (hPa/10°lon) at selected central latitude. Then, the scheme defines 27 different weather types: anticyclonic (A), cyclonic (C), eight directional types (N, NE, E, SE, S, SW, W, NW), 16 hybrids (AN, ANE, CN, CNE, etc.) and one unclassified type (U). In Paper I and II, daily mean LWTs from 1990 to 2006 based on the daily mean sea level pressure (MSLP) from NCEP Reanalysis data I with 2.5° latitude by 2.5° longitude grids [64] were used to represent the character of the daily atmospheric circulation in southern Sweden (FIGURE 3.1). In Paper II, long-term LWTs from 1850 to 2003 were calculated using the daily MSLP from EMULATE (European and North Atlantic daily to MULti-decadal climATE variability) database [65].

The grouped LWTs were used in Paper I and II for reducing the number of weather types and simplifying the analysis. However, there are no established criteria for dividing the 27 types into a smaller number of main groups. Lamb (1972) [66] has indicated that hybrid types should count equally to each of their main types. Therefore, 26 LWTs (without U) were grouped into six LWTs sub-divisions based on direction: A, C, W, SEE, SWS and N+ in Paper I; three LWTs sub-divisions were obtained based on vorticity: Av, Cv and Dv in paper II (see TABLE 3.1).

TABLE 3.1: Sub-division of LWTs into categories based on direction and vorticity used in Paper I and Paper II, respectively.

Anticyclonic (A) and its hybrid types	Cyclonic (C) and its hybrid types	Directional types	
A	C		**A/C**
AW	CW	W	**W**
ASW AS	CSW CS	SW S	**SWS**
AE ASE	CE CSE	E SE	**SEE**
ANE AN ANW	CNE CN CNW	NE N NW	**N+**
Av	**Cv**	**Dv**	

4

Results

4.1 Surface ozone trend in Sweden

The increasing trend for background ozone concentrations has been observed on a large geographical scale. Mace Head, located on the Atlantic Ocean coast of Ireland, is located in clean air and regarded as a north-hemispheric baseline or background ozone monitoring site. An upwards trend in the annual mean baseline level was indicated at Mace Head for 1987–2007 of $+0.31 \pm 0.12$ ppb yr^{-1}, which is significant at the $p < 0.001$ level of confidence [5]. Trends have been highest in the spring months and lowest in the summer months. The steady increasing trend has been perturbed by dramatic and rapid increases during 1995/1996, 1998/1999 and 2002/2003 due to the large-scale boreal biomass burning during these years [70], [71], [72]. Compared with Mace Head, annual mean ozone levels at Rörvik/Råö and Vavihill have similar upwards trends of $+0.23 \pm 0.22$ ppb yr^{-1} ($p < 0.05$) and $+0.25 \pm 0.19$ ppb yr^{-1} ($p < 0.01$) during 1990 to 2006, respectively (FIGURE 4.1). For the same time period, the annual mean NO_2 significant decreased of $+2.41 \pm 0.03$ $\mu g\ m^{-3} yr^{-1}$ ($p < 0.001$) at Rörvik/Råö and $+2.15 \pm 0.02$ $\mu g\ m^{-3} yr^{-1}$ ($p < 0.001$) at Vavihill. Furthermore, the two rural sites in southern Sweden caught two of the three large-scale boreal biomass burning cases during 1995/1996 and 2003/2003, but failed to catch the largest one during 1998/1999.

Simultaneously, annual variation of NO_2 observed at the two sites responded to significant upward trend of ozone concentrations during winter (TABLE 4.1). It confirms that contribution to the increasing ozone trend during winter is a reduction in the titration by the ozone and NO reaction due to regionally reduced NO_x emissions [73]. Therefore, the variations of ozone concentrations in southern Sweden followed with those of ozone precursors through chemical reactions, sometimes can be perturbed by large-scale boreal biomass burning. The upward trends of surface ozone concentrations in southern Sweden agree well with that of the large-scale background ozone site.

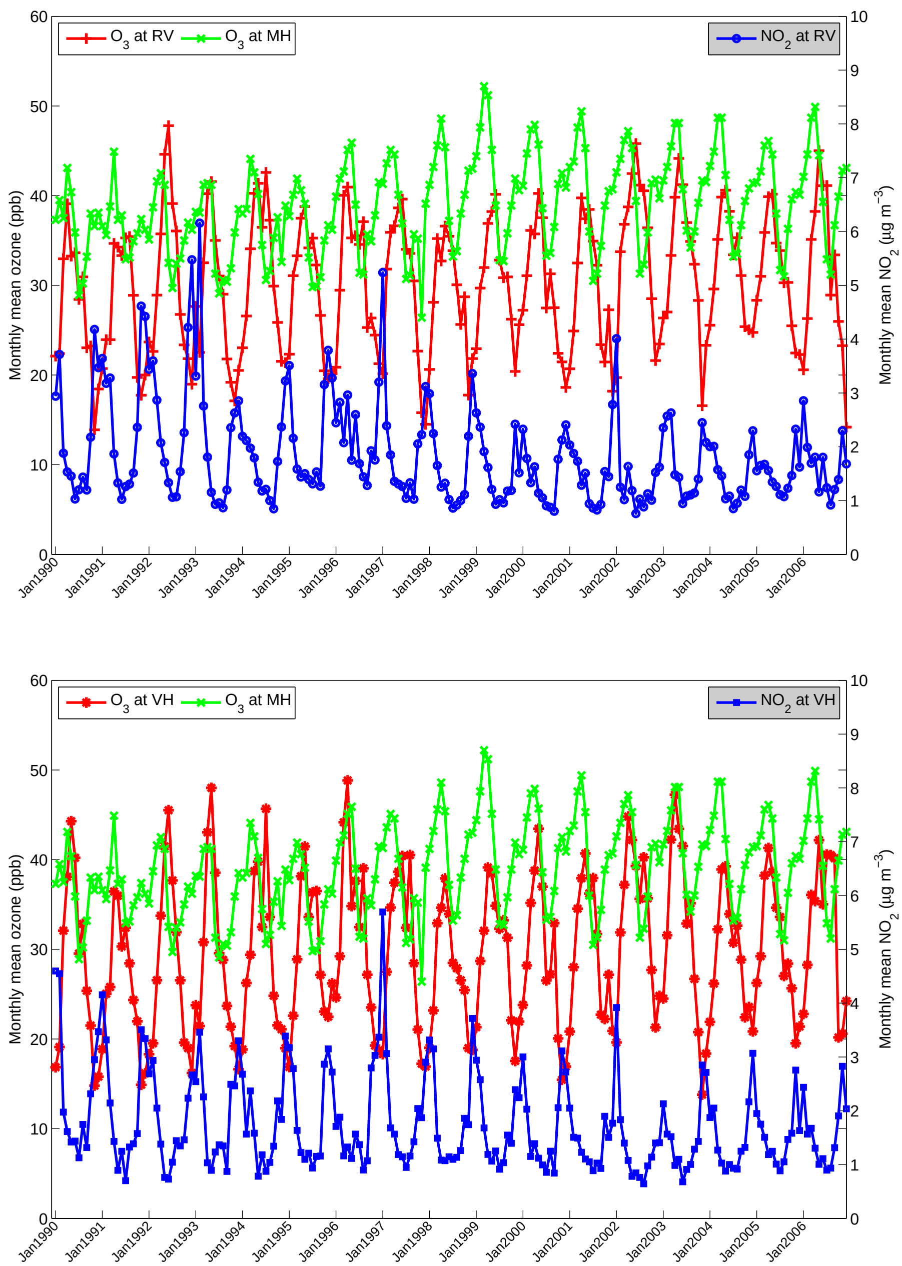

FIGURE 4.1: Time series of the monthly mean ozone concentrations at Rörvik/Råö (RV), Vavihill (VH) and Mace Head (MH) and monthly mean nitrogen dioxide (NO_2) at Rörvik/Råö (RV), Vavihill (VH) from January 1990 to December 2006.

Table 4.1: Trend analysis for annual mean concentrations of nitrogen dioxide (NO_2) (based on daily mean dataset) and ozone (based on hourly mean dataset) in each month from 1990 to 2006 at Rörvik/Råö and Vavihill. Unit for ozone: ppb yr^{-1}; for NO_2: μg $m^{-3}yr^{-1}$. *Significance: *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$, # $p < 0.1$.*

	Rörvik/Råö	Vavihill	Rörvik/Råö	Vavihill	Rörvik/Råö	Vavihill
	24-h mean NO_2		Daytime mean ozone (08:00 – 19:59 GMT+1)		Night-time mean ozone (20:00 – 07:59 GMT+1)	
Jan.	-0.09^{*}	$-0.09^{\#}$	$+0.02$	$+0.40^{**}$	-0.01	$+0.37^{*}$
Feb.	-0.12^{**}	-0.14^{**}	$+0.36^{\#}$	$+0.54^{**}$	$+0.40^{*}$	$+0.59^{**}$
Mar.	-0.05^{*}	-0.05^{*}	$+0.27^{\#}$	$+0.68^{**}$	$+0.22^{*}$	$+0.64^{**}$
Apr.	-0.02	-0.02^{*}	$+0.07$	$+0.16$	$+0.16$	$+0.14$
Maj	-0.02	$+0.003$	$+0.08$	$+0.04$	$+0.56^{\#}$	-0.01
Jun.	-0.001	-0.02^{*}	$+0.24$	-0.001	$+0.49^{*}$	$+0.04$
Jul.	-0.01	-0.01	$+0.07$	$+0.15$	$+0.25$	$+0.001$
Aug.	-0.02	-0.03^{**}	-0.11	$+0.18$	-0.07	$+0.27$
Sep.	-0.01	-0.002	$+0.37^{*}$	$+0.55^{**}$	$+0.48^{**}$	$+0.39^{*}$
Okt.	-0.07^{**}	$-0.05^{\#}$	$+0.30^{*}$	$+0.11$	$+0.36^{\#}$	$+0.04$
Nov.	-0.12^{*}	-0.03	$+0.34^{*}$	$+0.15$	$+0.40^{*}$	$+0.23$
Dec.	-0.15^{***}	-0.09^{*}	$+0.21$	$+0.39^{**}$	$+0.24$	$+0.41^{**}$

In northern Sweden, the annual mean ozone concentrations showed also upwards trends but not statistically significant (figure not present). However, the significantly increasing trends was detected for daytime (08:00 – 19:59 GMT+1) annual mean ozone concentrations ($p < 0.05$) at Vindeln during the period 1 April to 30 September, 1990–2006. In particularly, daytime mean ozone concentrations in April showed significantly upwards trends at both Esrange and Vindeln (TABLE 4.2). It is noted that ozone exposure index for vegetations AOT40 in April have increased significantly at both sites simultaneously. This result indicates a potential negative effect of surface ozone on vegetation in northern Sweden.

Table 4.2: Trends for annual daytime (08:00 – 19:59 GMT+1) mean ozone concentrations and AOT40 on April at Esrange and Vindeln during 1990 to 2006. Unit for ozone: ppb yr^{-1}; for AOT40: ppb h yr^{-1}. *Significance: ** $p < 0.01$, * $p < 0.05$. Standard errors are given.*

	Esrange	Vindeln
Daytime mean ozone	$0.50 \pm 0.44^{*}$	$0.55 \pm 0.32^{**}$
AOT40	$166.17 \pm 151.39^{**}$	$118.97 \pm 99.69^{*}$

4.2 Atmospheric circulation and surface ozone variations in southern Sweden

4.2.1 Weather type and mean ozone concentrations

Paper I showed the positive deviations of mean ozone concentrations under weather types A, SEE and SWS, with negative deviations under C, W and N+ (FIGURE 4.2). Moreover, 85.5%, 73.3% and 83.5% of ozone episode days occurred under A, SEE and SWS at Rörvik/Råö, Norra Kvill and Vavihill, respectively. These results confirm that the favourite synoptic conditions for higher ozone concentrations are associated with anticyclones and/or air masses from south-west and south-east directions.

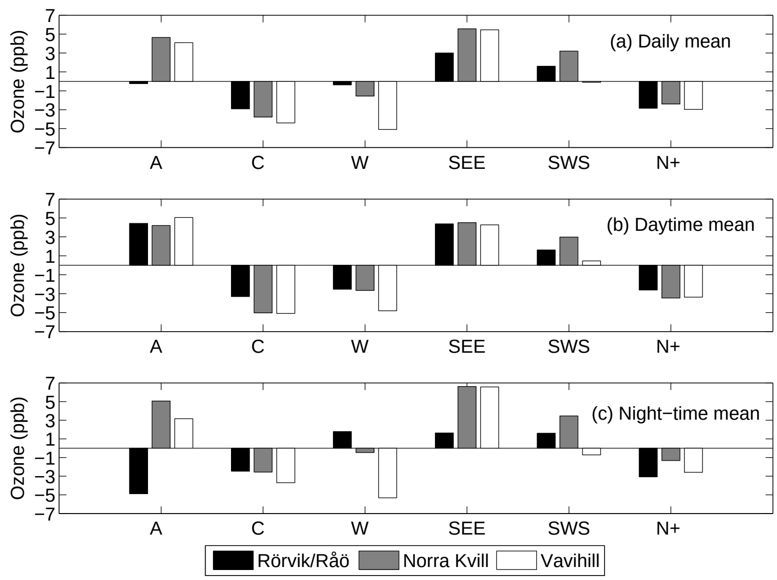

FIGURE 4.2: Mean ozone deviations from the averaged ozone concentrations at the three sites under the six LWTs from April to August over the period of 1990–2005 at Rörvik/Råö, Norra Kvill and Vavihill. a) Daily mean (24-h), b) Daytime (08:00 – 19:59 GMT+1) mean and c) Night-time (20:00 – 07:59 GMT+1) mean.

Diurnal variation patterns under major weather types at Rörvik/Råö and Norra Kvill illustrate the ozone dynamic under different synoptic conditions during daytime and night-time (FIGURE 4.3). Compared with the diurnal cycle under all types, ozone photochemical production under weather type A is apparently enhanced during daytime whilst ozone dry deposition and titration with NO as well as the restricted vertical mixing under stable boundary layer lead to lower concentration during night-time. Weather type C is usually accompanied with lower air temperature and weaker solar radiation, associated with weak ozone production during daytime. However, active vertical mixing under type C enhances the transport from ozone-rich air aloft to the surface, causing higher ozone concentrations at night. Under weather types AS and ASE, both daytime and night-time ozone concentrations are higher than those under all types. This might be associated with an extra input of ozone and its precursors from European continent due to horizontal long-range transport as well as enhanced vertical mixing.

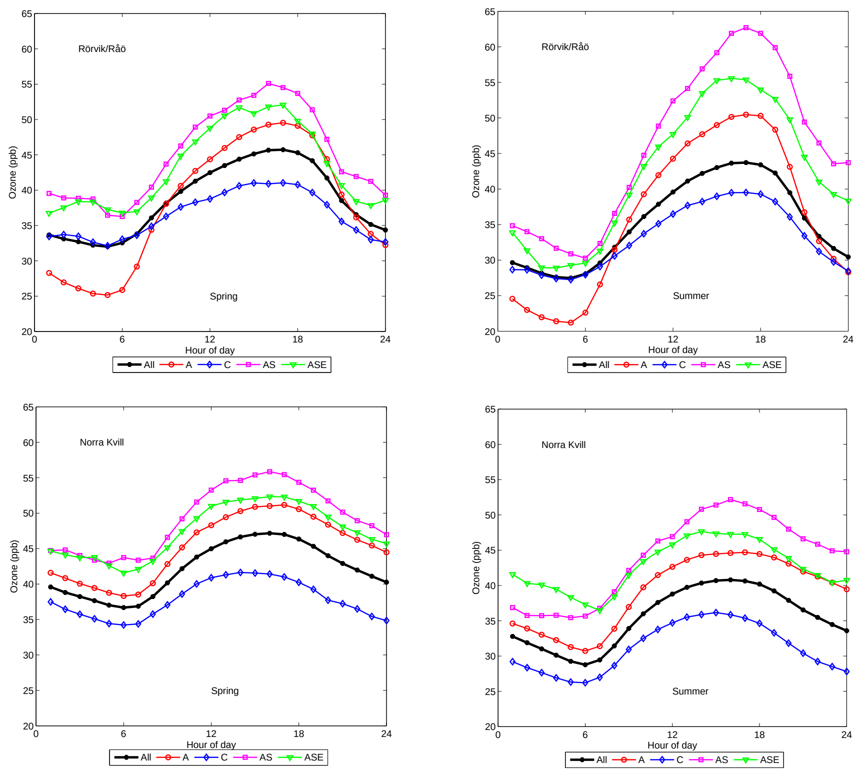

Figure 4.3: The mean hourly ozone concentrations calculated during spring (April– May) and summer (June–August) for the period 1990–2005 under all the weather types and weather type A (anticyclonic), C (cyclonic), AS (anticyclonic hybrid type from south) and ASE (anticyclonic hybrid type from south-east) at Rörvik/Råö and Norra Kvill respectively. Time is GMT+1.

The difference in the diurnal cycle of ozone concentrations between the elevated monitoring site Norra Kvill and the coastal site Rörvik/Råö might attribute to different local effects (FIGURE 4.3). Different local topographical settings and different latitudes at ozone monitoring sites imply different meteorological processes, which may have different impacts on the variations in the ozone concentrations at each site [74]. Local effects due to topography, vegetation, snow cover etc. usually contribute to the variability of ozone both diurnally and seasonally [75]. Compared with Rörvik/Råö, the ozone diurnal cycle at Norra Kvill has moderate amplitude and presents higher night ozone concentrations. Sites positioned high relative to the local topography experience less night-time ozone depletion than low-level sites under stable boundary layer when relatively ozone rich air is transported from aloft with down-slope cold air [76], [77], [74]. On the other hand, frequent night-time air temperature inversions at Rörvik/Råö prevent vertical mixing of ozone, further reducing night-time ozone concentrations near the ground. Therefore, diurnal cycles are most pronounced near the ground, while they can become insignificant above the planetary boundary layer [15]. For the same reason, ozone concentrations at the site Åreskutan, located in a mountain area, reflected the ozone variation up to heights of 4-5 km in the free troposphere, with very small mean diurnal variations (Paper III).

In summer, the diurnal cycle is much pronounced under type A. However, the mean hourly ozone concentrations in summer is apparently lower than those in spring under all types, in especially at night. This is mostly likely due to the contribution from stratosphere in spring.

4.2.2 Weather type and long-range transport during high ozone events

Except for photochemical reactions, long-range transport is another major reason causing regional high ozone concentrations in southern Sweden. Paper II focused on high-ozone events and specified the long-range transport paths when high-ozone events occurred. Three trajectory clusters were identified at the three rural sites in southern Sweden. Take Rörvik/Råö as an example, the three trajectory clusters represent the air masses from Western Europe (WE), Eastern Europe (EE) and in the vicinity of southern Sweden (VIC), respectively (FIGURE 4.4).

Trajectory cluster VIC, representing short or whirling paths trajectories in the vicinity of southern Sweden, is the most frequently occurring cluster during high-ozone events, occupying 40%, 42% and 44% at Aspvreten, Rörvik and Vavihill, respectively. Cluster VIC included more high ozone concentrations compared to other two clusters (FIGURE 4.5). Therefore, air masses transported from Western Europe or Eastern Europe usually raise regional ozone concentrations. However, those air masses characterized with short or whirling paths stay longer time in the vicinity of potential emission sources cause more effective long-range transport of ozone and its precursors, leading to more frequent and intense high-ozone events.

After related the trajectory clusters and weather types, we found the annual counts of cluster VIC was strongly correlated with the counts of anticyclone types Av and anti-correlated with counts of cyclonic types Cv, especially during summer (TABLE 4.3). This result confirms the links between atmospheric circulation and long-range transport, in especially, implying a cause-effect relationship among anticyclones, cyclones and high-ozone events. The cause-effect relationship can be summarized as: Anticyclones tend to create intensive atmospheric stagnation and benefit photochemical production and/or effective long-range transport from emission sources, thus causing high-ozone events. Cyclones, on the other hand, can also create high levels of ozone through cold-front passage and enhanced vertical mixing. At the same time, cyclones are associated with advective processes and mixing processes [78], [79], [80], causing the transport of pollution and venting the air. The annual counts of cyclones highly anti-correlated with counts of anticyclones and counts of high-ozone events in southern Sweden indicates ventilation effects due to mixing processes under cyclones, making cyclone frequency a skilful predictor for occurrences and levels of high-ozone events.

Figure 4.4: The first-stage clusters at Rörvik/Råö: EE (top panel), WE (middle panel) and VIC (bottom panel). Trajectories with different colors in each panel represent the second-stage clusters.

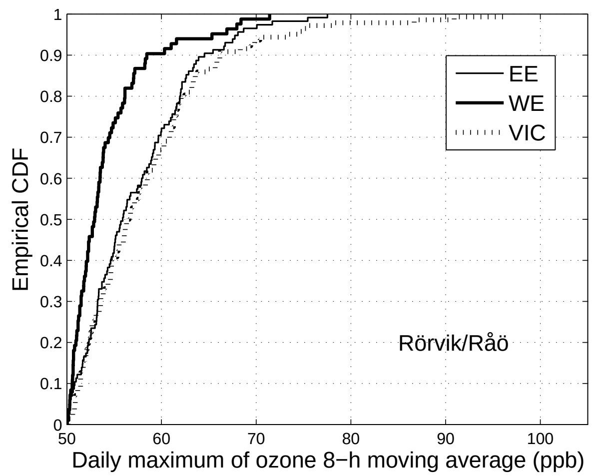

FIGURE 4.5: The empirical cumulative distribution function (CDF) plot for the mean daily maximum of 8-h moving average (ppb) under the first-stage clusters EE, WE and VIC at Rörvik/Råö.

TABLE 4.3: Correlation coefficients for detrended annual numbers of the first-stage clusters (WE (Western Europe), VIC (in the vicinity of southern Sweden) and EE (Eastern Europe)) and those of Av (anticyclonic and its hybrid types) and Cv (cyclonic and its hybrid types) at the three sites RV (Rörvik/Råö), AP (Aspvreten) and VH (Vavihill) in spring (Sp) and summer (Sm) for 1996–2005. Correlation coefficients for detrended number of Cv and Av: -0.89^{***} in spring; -0.87^{**} in summer. *Significance: *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$, # $p < 0.1$.*

	WE			VIC			EE		
Sp	RV	AP	VH	RV	AP	VH	RV	AP	VH
Cv	0.02	−0.34	0.23	−0.001	−0.31	−0.20	−0.42	−0.47	-0.73^{*}
Av	−0.02	0.18	−0.19	0.04	$0.58^{\#}$	0.18	0.30	0.39	0.64^{*}
Sm									
Cv	−0.54	−0.39	−0.47	-0.94^{***}	-0.83^{**}	-0.82^{**}	−0.51	-0.68^{*}	−0.54
Av	0.70^{*}	0.41	$0.59^{\#}$	0.82^{**}	0.82^{**}	0.83^{**}	0.41	$0.60^{\#}$	0.40

4.3 Circulation indices and surface ozone concentrations

Linking atmospheric circulation indices and regional ozone concentration is one possible way to quantitatively express the relationship between the synoptic circulation and ozone concentration. Δ C was calculated by using annual mean ozone concentration averaged the three sites at Rörvik/Råö, Norra Kvill and Vavihill. The differences from the average value during 1990–2005 represent the regional surface ozone variations (FIGURE 4.6). Larger ozone deviations occurred in 1991, 1998 and 2003 in spring; 1992, 1998 and 2002 in summer, which might be associated with large-scale biomass burning in 1998 and 2002/2003.

The total vorticity index (ζ) represents one property of atmospheric circulation, and its absolute value can indicate the intensity of atmospheric circulation. In Paper I, annual mean ozone variations were found to be significantly correlated to annual mean circulation index ζ from 1998 to 2005 during which emission reductions were slow. However, FIGURE 4.7 reproduced the good correlation between index ζ and ΔC when the analysis was extended to a longer time period for 1990–2005. The dramatic emission reduction since 1990s over Europe seems have not much perturbation on the relation between synoptic weather conditions and surface ozone variations. The correlation implies a strong influence of sea level pressure on regional ozone concentrations and helps to quantitatively estimate the synoptic circulation effects on surface ozone. However, similar with TABLE 4.3, the correlation was much better in summer.

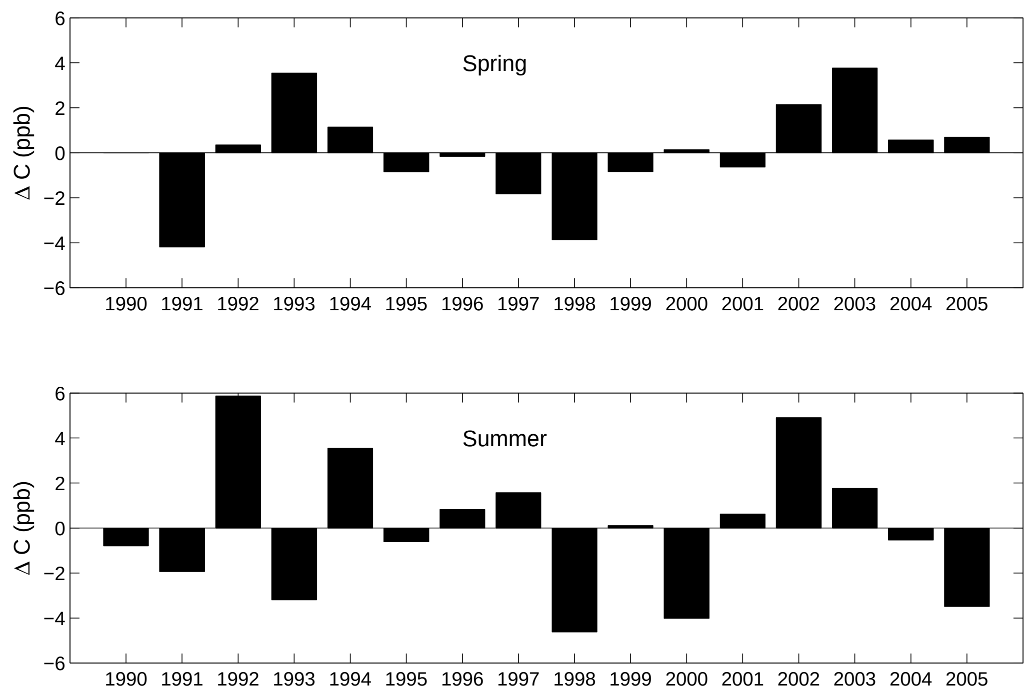

Figure 4.6: Annual variation of Δ C (ppb) (the difference between annual mean ozone concentration averaged the three sites and the corresponding 16-year average, 1990–2005) in spring and summer respectively.

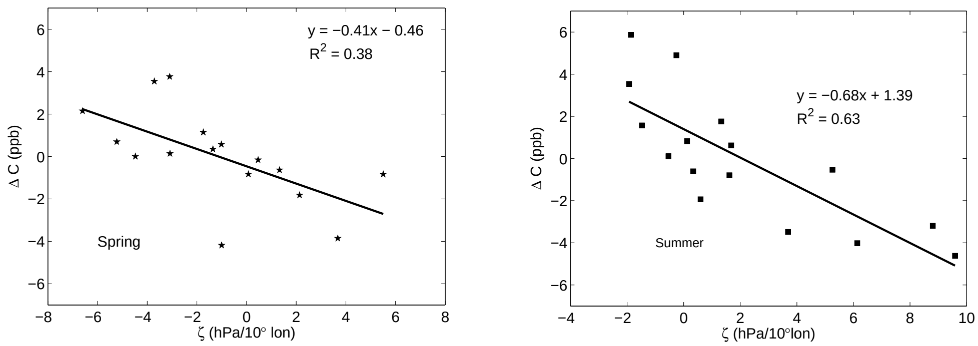

FIGURE 4.7: Scatter plot of Δ C (ppb) (the difference between annual mean ozone concentration averaged the three sites and the corresponding 16-year average, 1990–2005) versus the annual mean total vorticity index (ζ) in spring and summer. The unit of circulation index is hPa/10° longitude (hPa/10°lon). The best fit line and its expression are also shown in the figures.

4.4 Wind simulations and the $NO_x - O_3$ dynamic at local scale

4.4.1 Wind simulations by TAPM

The PSU/NCAR fifth-generation Mesoscale Model (MM5) [58] - one of the most important mesoscale dynamical models - is designed to simulate or predict mesoscale atmospheric circulation and boundary layer processes. MM5 is considered to be one of the most advanced mesoscale modelling systems and has been widely used within the air-quality community to derive meteorological boundary conditions. The comparison between MM5 and TAPM focused on those meteorological variables that are important in air quality applications, including the near–surface temperature and wind, vertical temperature gradient, low wind speed situation, diurnal cycle and diurnal heating. TAPM performance in simulating the complex wind system in Gothenburg was examined and compared with MM5. The statistical measures showed TAPM has obviously better performance in simulating 10-m wind speed and wind direction at urban, rural and coastal sites (Paper IV).

As one character of stable or very stable atmospheric conditions, low wind speed is of interest. This is partly because the simulation of airborne pollutant dispersion in these situations is rather difficult, because turbulent motions may be of the same order as the wind speed [81], [82]. In particularly, the highest ground-level concentrations of air pollutants are often encountered under low wind speeds situation ($< 2\ ms^{-1}$) [83]. Therefore, we compared the frequencies of different wind speeds during daytime and night-time at urban, coastal and rural sites (TABLE 4.4).

Table 4.4: Observed (OBS) and modelled frequencies (%) of the hourly-averaged wind speed (ms^{-1}) at 10-m a.g.l. during daytime (08:00–19:59 GMT+1) and night-time (20:00 – 07:59 GMT+1) at coastal site Kanotföreningen (Kanot), rural site Säve and urban site Heden from 7 to 20 May, 2001.

			$0-2$	$2-4$	$4-6$	$6-8$	>8
Kanot	Daytime	OBS	17.9	41.1	26.2	9.5	5.4
		TAPM	8.9	40.5	31.0	4.2	15.5
		MM5	7.1	22.0	38.1	12.5	20.2
	Night-time	OBS	57.1	23.2	6.0	7.7	6.0
		TAPM	10.7	51.2	22.0	3.6	12.5
		MM5	9.5	36.9	34.5	8.9	10.1
Säve	Daytime	OBS	21.4	35.7	21.4	17.9	3.6
		TAPM	19.6	66.1	14.3	0.0	0.0
		MM5	37.5	33.9	19.6	8.9	0.0
	Night-time	OBS	64.3	23.2	3.6	7.1	1.8
		TAPM	23.2	73.2	3.6	0.0	0.0
		MM5	23.2	69.6	7.1	0.0	0.0
Heden	Daytime	OBS	26.8	58.3	14.3	0.6	0.0
		TAPM	22.6	61.9	15.5	0.0	0.0
		MM5	39.3	29.2	22.0	9.5	0.0
	Night-time	OBS	74.4	17.9	7.7	0.0	0.0
		TAPM	40.5	50.6	8.9	0.0	0.0
		MM5	33.9	64.3	1.8	0.0	0.0

The two models performed better during daytime at all wind speeds. Compared with MM5, TAPM simulates urban sites better and gives progressively better simulation for higher wind speeds. However, the two models severely underestimate the nocturnal low wind situation ($< 2\ ms^{-1}$) at all three sites. Despite the system errors in low wind situations from measurement, the difficulties in parameterization under low wind situations still exist in dispersion models.

4.4.2 Vertical temperature gradient

Atmospheric stability, expressed by vertical temperature gradient, is an another important feature in determining local air quality. However, measurement on the atmospheric stability is limited by real world conditions and usually conducted at one site in rural area. Therefore, atmospheric stability variables from model simulation are valuable in air quality studies. Paper IV compared the performances of two models in daytime and night-time vertical temperature gradient (FIGURE 4.8). The night-time temperature gradient was well predicted by the two models with Index Of Agreement (IOA) as 0.85 for TAPM and 0.83 for MM5. However, both models failed to simulate the daytime temperature gradient. TAPM greatly underestimated the daytime temperature gradient due to the overestimation of the surface temperature and underestimation of the daytime temperature at the high altitude (105 m). It might be due to the local urban effects are not properly accounted for by the generic single-layer canopy scheme used, which indicates the necessary improvement in land-surface scheme in TAPM [84], [85].

As a result, TAPM is concluded to be able to provide comparable simulation with MM5 and can be used with confidence in describing the local-scale meteorological conditions needed for air quality application.

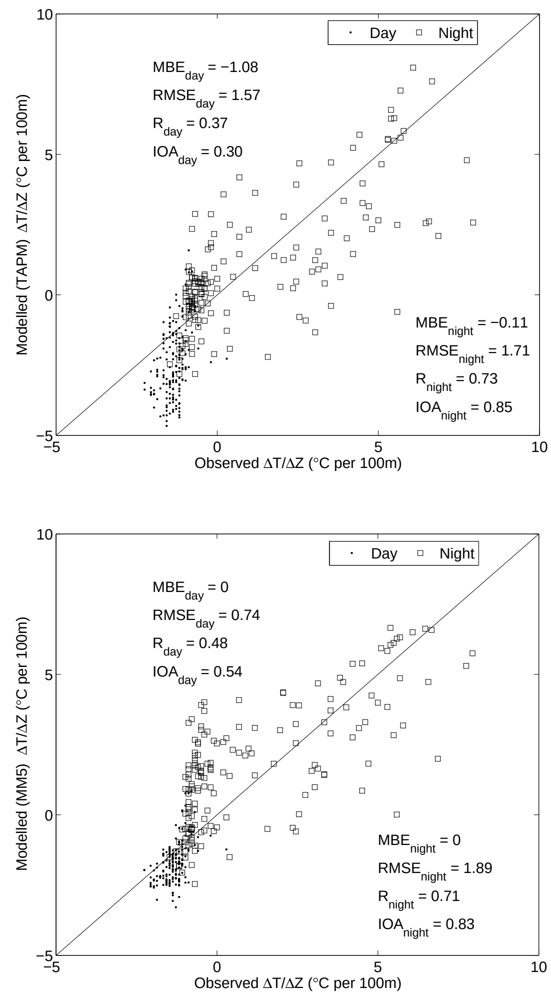

FIGURE 4.8: Observed and modelled vertical temperature gradients at the Järnbrott mast site from TAPM and MM5. The results are based on hourly data of the near-surface and 105-m measurements/simulations during the period 7–19, May 2001. The temperature gradient during night hours (20:00–07:59 GMT+1) is denoted by squares to show nocturnal temperature inversion for clarity. Statistical parameters at day and night are presented within the plot.

4.4.3 TAPM simulation for $NO_x - O_3$ dynamic in urban area

NO_x and ozone has greatly interaction in chemistry through reactions (1.3), (1.1) and (1.2). The modelled diurnal cycle of NO, NO_2 and ozone at site 6 (the most polluted site in the model, see FIGURE 2.1) was satisfactorily reproduced (FIGURE 4.9). Two peak daily values of NO and NO_2 correspond to two traffic rush hours with large emissions. The ozone concentrations were lowest at peak NO_x concentrations due to NO titration. TAPM is able to successfully reproduce the relationship between NO_x and ozone observed by the passive samplers.

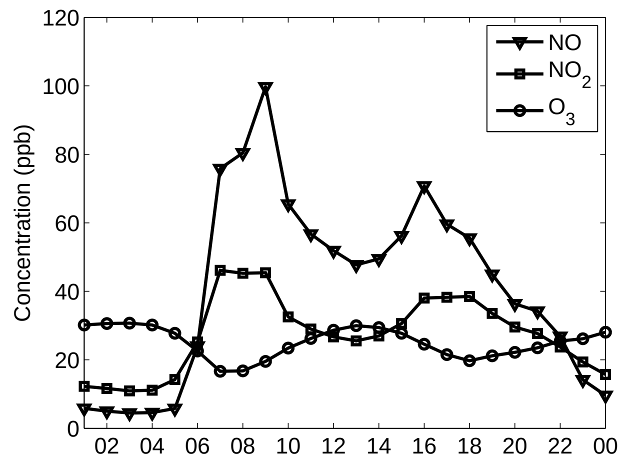

FIGURE 4.9: Diurnal cycle of NO_2, NO and ozone concentration at site 6 from 2–27, February 2005 modelled with the TAPM model. Site 6 was the most NO polluted site according to the model.

4.4.4 Wind speed and spatial variation of NO_2 in the polluted urban landscape

Wind speed is one of many factors influencing the NO_x and ozone concentrations in the urban landscape [86]. The measurements in Paper V clearly indicated that the NO_2 concentration relative to the urban background responded differently to increasing wind speed depending on the degree of pollution at the site. At the most polluted sites the NO_2 concentration ratio increased with increasing wind speed while at the least polluted sites the NO_2 concentration ratio decreased. Same pattern was shown by TAPM (FIGURE 4.10). Higher wind speeds act to dilute NO_2 due to stronger dispersion, but also lead to an enhanced vertical transport of ozone, which produces NO_2 through oxidation of NO. Two processes are of importance and in delicate balance. The results illustrate the complexity of temporal and spatial air pollution variations in the urban landscape. TAPM is helpful to understand the interaction of different processes. It suggests that TAPM has the potential to be an important tool in evaluating air quality problems in Gothenburg and other cities.

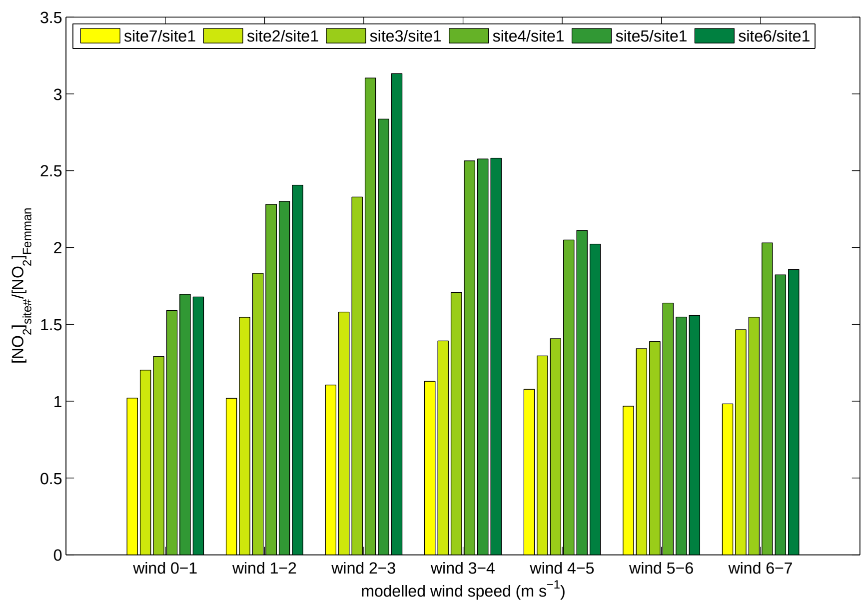

FIGURE 4.10: NO_2 concentration at site 2 to 7 averaged for different wind speed categories and divided with the rooftop site Femman. Above the bars is the percentage hours included in each wind category given. All data come from the TAPM model.

5

Discussion and Future Perspectives

5.1 Atmospheric circulation and regional air quality

Prevailing synoptic-scale circulation patterns govern variation in local climate, thus having a strong impact on surface ozone concentrations [87], [88], [89], [90], [91], [92]. Warm, dry and calm weather conditions are well-known to favourite daytime photochemical production (Paper I). In addition, anticyclones are strongly associated with high-ozone events due to effective long-range transport of ozone and its precursors for emission sources (Paper II). Atmospheric blocking, an extreme form of anticyclones, is deduced to be the leading cause of ozone episodes over Europe since it is an inherent and frequent feature of the European climate system [93], [94].

Cyclones generally represent unstable weather conditions accompanied with cool, windy, cloudy or rain. Frontal system, included in cyclones, may arouse advective processes including the warm and cold conveyor belts, and mixing processes including frontal convection [79], [80], thus becoming one of important ventilation mechanism. On the other hand, a cold-front passage can create horizontal transport of pollution and cause episode pollution on its passing way. The annual counts of cyclones highly anti-correlated with counts of anticyclones and counts of high-ozone events in southern Sweden in summer indicates dominant ventilation effect of cyclones and presents the good cause-effect relationship among cyclones, anticyclones and high-ozone events.

In spring, STE becomes more active and might cause surface ozone accumulation by dynamic processes in cyclones. FIGURE 5.1 presents the relationship between weather type index u, v, ζ and annual ozone variations from 1990 to 2005 in spring. Better linear relations presented when we excluded dataset in year 1991, 1998 and 2003 when higher ozone deviations were found (FIGURE 4.6). This indicates that the perturbations in spring can be from other factors, for example, large-scale biomass burning in year 1998 and 2003 or other events in 1991. On the other hand, weather type indies u and v have also good correlations with surface ozone variations after excluding these "perturbing years. The quantitative estimation could be extended to spring by using more indies.

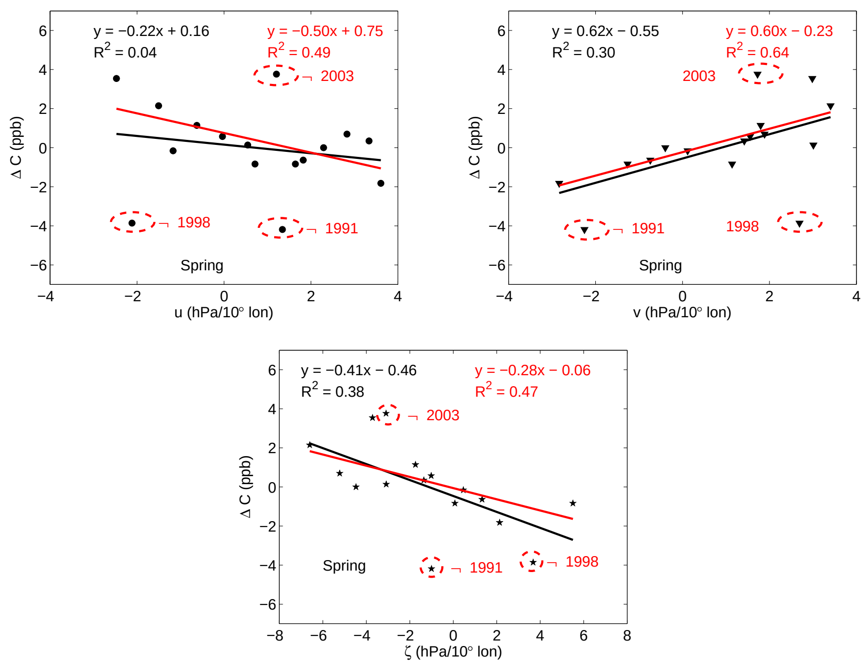

FIGURE 5.1: Scatter plot of Δ C (ppb) (the difference between annual mean ozone concentration averaged the three sites and the corresponding 16-year average, 1990–2005) versus the annual mean westerly wind index u, southerly wind index v and vorticity index ζ in spring. The unit of circulation index is hPa/10° longitude (hPa/10°lon). The best fit line and its expression are also shown in the figures. The black lines, equations and R^2 are based on dataset from 1990 to 2005; the red lines, equations and R^2 are based on the dataset without year 1991, 1998 and 2003.

Paper I and II concluded that synoptic weather types LWTs indicate well the relationships between atmospheric circulation and regional air quality, suggesting its wider practical application. For instance, LWTs can be used to study the influences of atmospheric circulation on other pollutants such as particulate matter (PM). The build-up of PM in southern Sweden is believed largely due to long-range transport [95]. The relationship between weather types and long-range transport revealed in Paper II is helpful to identify the influences of synoptic weather conditions on high PM levels as well. Moreover, six-hourly LWTs might be used to investigate the synoptic impacts on daytime and night-time ozone variations.

5.2 Climate change and surface ozone in Sweden

Future ozone trends will depend on the anthropogenic emission path of precursors and on trends in temperature, humidity and solar radiation [96]. Although anthropogenic emissions cause the largest response in ozone, a major factor influencing future trends in ozone is climate change, but the effect of both factors vary in space [97]. Recent observation and modelling studies concluded that the changing climate might have offset the regional air quality gains from reductions in anthropogenic emissions in Europe and the northeastern US [13], [36]. In Paper II, Lamb weather types Cv (cyclone and its hybrid types) over the past 150 years showed a significantly decrease in frequency during spring ($p < 0.05$) and summer ($p < 0.01$) (FIGURE 5.2). Lamb weather types Av (anticyclone and its hybrid types) increased during the same time period (FIGURE 5.3). Given constant emissions and other conditions, the decreasing frequency of Cv predicts the increasing frequency and intensity of high-ozone events over southern Sweden, especially in summer.

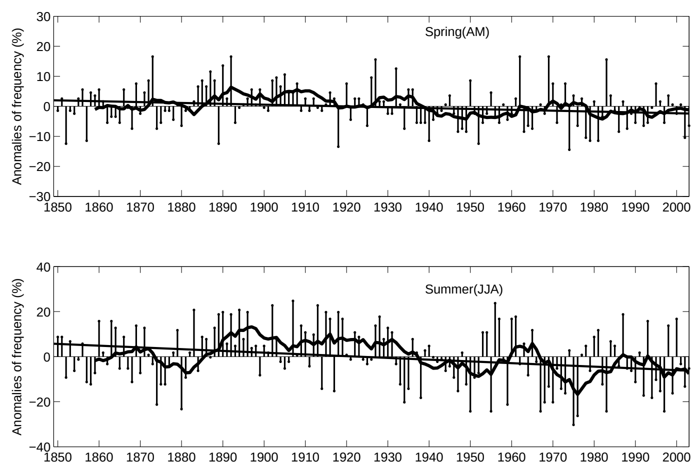

Figure 5.2: Long-term trend of circulation weather type Cv during 1850 to 2003.

IPCC [10] SRES emission scenarios consistently indicate the most pronounced warming at higher latitudes and accompanied by increasing annual precipitation. The plant's sensitivity to ozone may rise in areas where rapid warming is projected to occur in the absence of declining air and soil moisture [96]. In Paper III, trends for an earlier onset of the growing season during spring were found due to increased temperature (during the same time-period) for locations in northern Sweden. If a strong increasing trend in daytime ozone concentration simultaneously occurred in spring it might increase the negative effect of surface ozone on vegetation in the future climate.

There is a need for more evidence to identify the climate change feedbacks on air quality and the risks to human health and also to vegetation. Clear relationships between sea level pressure and pollutants provide a useful and general metric for probing the effect of climate change on air quality [36]. For example, the cause-effect relation between atmospheric circulation and regional air quality in southern Sweden can be used to probe the effect of climate change on high-ozone events since atmospheric circulation in the future climate is robustly simulated by GCMs (General Circulation Models). Such a quantitative description of climate change effects will contribute to the policy development [98].

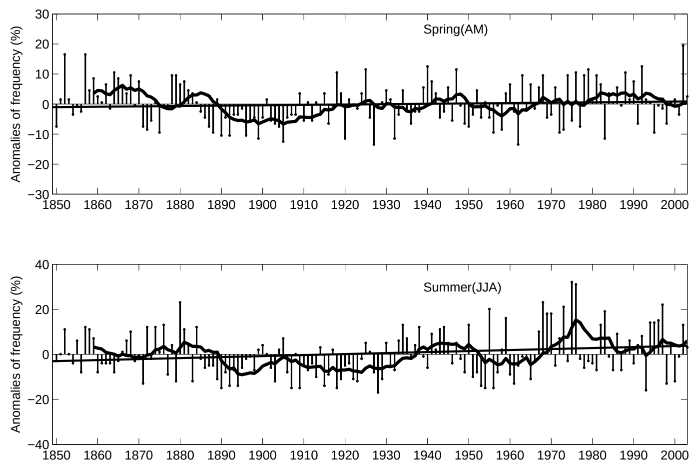

FIGURE 5.3: Long-term trend of circulation weather type Av during 1850 to 2003.

5.3 TAPM performance at local/urban scale

The urban boundary layer is usually divided into four layers [99], [85]: (1) the urban canopy layer (UCL) (from ground to about the average height of buildings); (2) the roughness sublayer (RSL) (extending to 2–5 times the height of buildings); (3) the inertial sublayer (IS) (equivalent to the surface layer over large, flat surface, where small-scale turbulence dominates transfer); and (4) the outer layer (OUBL) with mixing dominated by larger scale thermal effects. The importance of RSL has been highlighted by its role in determining the dispersion of ground-level concentrations in urban areas [100], [101]. As is well known, MOST (Monin-Obukhov Similarity Theory) is not valid within the urban RSL since turbulent fluxes are not constant with height in the RSL. The turbulent flux of momentum decreases to zero due to the drag on the flow caused by the buildings [101], [102]. However, in the practice many dispersion models still use MOST in the urban area by adjusting the roughness length or M-O length under very stable conditions [103]. The poor performance of the two models in low wind speed situations indicates the weakness of MOST under strongly stable conditions (TABLE 4.4). More intensive field campaigns are expected in investigating urban boundary layer profiles and used for parameterizing the stable conditions for the RSL.

The simulation of NO, NO_2 and ozone in the polluted urban landscape has demonstrated the abilities of TAPM at local scales. The smallest spatial resolution (100-m) in the air pollution module restricts the performance of TAPM at specific sites and lead to, for example, underestimation of NO concentrations west of the traffic road (site 1 to 3 (FIGURE 2.1)). The lack of a high-quality emission inventory is another reason cause of biases between model and measurement. The other limitations in Paper V might be the simplified ambient VOCs and omitted decomposition of PAN. However, despite the limitations found in this specific study, TAPM can be expected to provide a good ability to assess year-long average regional air quality, and this ability can be tested.

6 Conclusions

- The study confirmed the influences of different synoptic weather conditions on regional ozone concentrations. Anticyclones and synoptic wind flows from south-west and south-east are favourite situations for causing high ozone concentrations; while cyclones and synoptic wind flows from north and west are associated with low ozone concentrations. LWTs, a simple classification for atmospheric circulation, have proved to be a practical tool to examine the influences of atmospheric circulation on regional air quality. The indices of LWTs, reflecting the intensity of synoptic systems, reveal such influences and can be used to establish regression models so as to quantitatively estimate the annual variation of surface ozone concentrations in southern Sweden.
- Air masses transported from Western Europe and Eastern Europe usually tend to cause regional high-ozone events in southern Sweden. However, more effective long-range transport is associated with short and whirling air masses in vicinity of the emission sources areas in European continent. They are more frequent in leading to high-ozone events. The counts of anticyclones and this effective transport cluster showed high correlation, in especially summer. The high anti-correlation between the counts of cyclones and the effective cluster indicates a cause-effect relationship between them, making the frequencies of cyclones a skilful predictor of high-ozone events in summer. In spring, the cause-effect relationship is not as strong as in summer most likely due to the large-scale perturbations.
- Increasing trends were found for surface ozone concentrations during April–September in northern Sweden over the period 1990–2006 as well as for an earlier onset of the vegetation growing season. The earlier onset of the growing season will substantially increase the annual cumulative ozone uptake. There is a substantial and increasing risk for negative impacts of ozone on vegetation in northern Sweden under the regional/global warming background.

- Compared with MM5, the performance of TAPM in simulating hourly near-surface air temperature and wind, vertical temperature gradient and diurnal heating are satisfying and comparable. The obviously better simulation in 10-m wind speed and wind directions, comparablely acceptable reproduction in night-time vertical temperature gradient raised the confidence in TAPM applications to air quality studies for this high latitude, coastal urban area. However, the two models failed to predict the daytime vertical temperature gradient. The difficulties in correctly predicting the low-wind speed situation still exist for the two models.

- TAPM was able to simulate the interaction between NO, NO_2 and ozone in the polluted urban landscape. The spatial differences of NO_2 concentrations for different wind speed categories were satisfactorily reproduced as well. However, the underestimate of NO concentrations at certain sites might be due to local scale site-specific conditions as well as lack of emissions from nearby roads and other emission sources.

7

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8
An Appendix

Summary of the appended papers

- Paper I

  The influence of synoptic circulation patterns on surface ozone concentrations at three monitoring sites in southern Sweden was investigated for the spring (April–May) and summer (June–August) periods 1990–2005. Synoptic circulation patterns were classified into six groups based on the Lamb Weather Types (LWTs). The analyses show that the anticyclonic weather pattern (A) and the directional flows from southeast/east (SEE) and southwest/south (SWS) were most frequently associated with high ozone levels. It was estimated that 85.5%, 73.3% and 83.5% of the ozone episode days at Rörvik/Råö, Norra Kvill and Vavihill were observed under these three circulation patterns, respectively. There were apparent spatial differences in the ozone concentrations during night-time under A conditions that were related to the high altitude position of Norra Kvill and Vavihill. The wind component indices u and v, and the total vorticity index ζ for each circulation pattern reflect the intensity of synoptic circulation and they all have an impact on the variation of surface ozone concentrations. The total vorticity index seems to be the key variable in terms of synoptic influence on surface ozone. A statistic model for the relations between synoptic circulation and ozone concentrations was established based on the frequencies and intensities of the six LWTs. It is able to explain 85% and 71% of the total variances in the observed mean ozone concentrations in spring and summer over the period 1998–2005, respectively. The results demonstrated the strong impacts of synoptic circulations on surface ozone concentrations in southern Sweden.

- Paper II

High-ozone events in the Nordic countries are usually caused by long-range transport from the European continent. This study aims at identifying the long-range transport patterns on high-ozone events by applying a two-stage clustering methodology to back trajectories. The atmospheric trajectories arriving at three rural sites in southern Sweden were computed for 1996–2005 with the FLEXTRA model. The second-stage clustering splits the short or curved-path trajectories and provides more specific clusters on high-ozone events. Extreme ozone episodes in spring and summer are associated with a short trajectory or with whirling air masses close to Western Europe, while the less severe high-ozone events are linked with trajectories over Eastern Europe more often in spring. A cause-effect relation between synoptic circulation and high-ozone events was detected when relating the long-range transport patterns to synoptic weather types. Anticyclones associated with atmospheric stagnating tend to cause short trajectories with whirling air masses from the European continent, which leads to effective long-range transport for high-ozone levels and enhances local ozone photochemical production. Cyclones, on the other hand, can also create high levels of ozone through front passage and enhanced vertical mixing. At the same time, the frequencies of cyclones and anticyclones in this region are highly anti-correlated, making cyclone frequency a skilful predictor of high-ozone events. The frequency of cyclones over the past 150 years has been highly variable, demonstrating the potential of the weather type on ozone levels in a changing climate. This may have implications for future ozone levels under projected climate change.

- Paper III

  Trends were found for increasing surface ozone concentrations during April–September in northern Sweden over the period 1990–2006 as well as for an earlier onset of vegetation growing season. The highest ozone concentrations in northern Sweden occurred in April and the ozone concentrations in April showed a strong increasing trend. A model simulation of ozone flux for Norway spruce indicated that the provisional ozone flux based critical level for forests in Europe is exceeded in northern Sweden. Future climate change would have counteracting effects on the stomatal conductance and needle ozone uptake, mediated on the one hand by direct effect of increasing air temperatures and on the other through increasing water vapour pressure difference between the needles and air. Thus, there is a substantial and increasing risk for negative impacts of ozone on vegetation in northern Sweden, related mainly to increasing ozone concentrations and an earlier onset of the growing season.

- Paper IV

  In this study, the performances of two widely-used models in air quality community, The Air Pollution Model (TAPM) and the PSU/NCAR fifth-generation Mesoscale Model (MM5), were evaluated and compared at an urban scale (a few kilometres) in the greater Gothenburg (Sweden) using the GÖTE2001 campaign data. Evaluation focused on simulated meteorological variables important to air quality applications: the near-surface air temperature and wind, vertical temperature gradient, low wind speed situation, diurnal cycle and diurnal heating. The results showed that (1) TAPM performs better than MM5 in simulating near-surface air temperature and wind in urban area, (2) both models are able to reproduce nighttime vertical temperature gradient reasonably well, but underestimate daytime temperature gradient, and (3) the two models significantly underestimate the occurrences of low wind speed situation at night. These results indicate that the performance of TAPM in simulating meteorological features over the urban area is generally comparable to that of MM5. TAPM can be used with some confidence to describe the local-scale meteorology needed for air quality applications.

- Paper V

  Knowledge about temporal and spatial variations of the ozone and NO_x relationship in the urban environment are necessary to assess the exceedance of air quality standards for NO_2. Both reliable measurements and validated high-resolution air quality models are important 5 to assess the effect of traffic emission on air quality. In this study, measurements of NO, NO_2 and ozone were performed in Gothenburg, Sweden, during the Göte-2005 campaign in February 2005. The aim was to evaluate the variation of pollutant concentrations in the urban landscape in relation to urban air quality monitoring stations and wind speed. A brief description of the meteorological conditions and the air pollution situation during the Göte-2005 campaign was also given. Furthermore, the Air Pollution Model (TAPM) was used to simulate the NO_x-regime close to an urban traffic route and the simulations were compared to the measurements. Important conclusions were that the pollutant concentrations varied substantially in the urban landscape and the permanent monitoring stations were not fully representative for the most polluted environments. As expected, wind speed strongly influenced measured pollutant concentrations and gradients. Higher wind speeds dilute NO_2 due to stronger dispersion; while at the same time vertical transport of ozone is enhanced, which produces NO_2 through oxidation of NO. The oxidation effect was predominant at the more polluted sites, while the dilution effect was more important at the less polluted sites. TAPM reproduced the temporal variability in pollutant concentrations satisfactorily, but was not able to resolve the situation at the most polluted site, due to the local scale site-specific conditions.

List of Abbreviations

ABL	atmospheric boundary layer
AOT40	Accumulated exposure Over a cut-off Threshold of 40 ppb
a.s.l.	above sea level
Av	anticyclonic and its hybrid types
CDF	cumulative distribution function
CLRTAP	Convention on Long-Range Transboundary Air Pollution
Cv	cyclonic and its hybrid types
Dv	directional types
ECMWF	European Centre for Medium Range Weather Forecasts
EE	Eastern Europe
EMEP	European Monitoring and Evaluation Programme
EMULATE	European and North Atlantic daily to MULti-decadal climATE variability
etc.	and so on
h	hour
IOA	index of agreement
IS	the inertial sublayer
GCMs	General Circulation Models
GMT	Greenwich Mean Time
LLJ	low-level jet
LWTs	Lamb Weather Types
MBE	mean bias error

Mean	mean
MM5	The PSU/NCAR fifth-generation Mesoscale Model
MOST	Monin-Obukhov Similarity Theory
M-O length	Monin-Obukhov length
MSLP	mean sea level pressure
NCEP	National Centers for Environmental Prediction
NILU	Norwegian Institute for Air Research
NO	nitric oxide
NO_2	nitrogen dioxide
NO_x	nitrogen oxides
OUBL	the outer layer
PAN	peroxyacetylinitrate
PM	particular matters
ppb	parts per billion
R	correlation coefficient
R^2	the explained variance representing the proportion of the total variance attributable to the model
RMSE	root mean square error
RSL	the roughness sublayer
SD	standard deviation
STE	stratospheric−tropospheric exchange
TAPM	The Air Pollution Model
UCL	the urban canopy layer
VIC	in the vicinity of southern Sweden
VOCs	volatile organic compounds
yr	year
WE	Western Europe
WHO	World Health Organization

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