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Title: Mechanisms responsible for the build-up of ozone over South East England during the August 2003 heatwave

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Abstract: The Community Multiscale Air Quality (CMAQ) model is used in order to quantify reasons for the build-up of ozone over South East England during the August 2003 heatwave. Unlike previous studies, the effects of individual meteorological and chemical processes on the temporal evolution of the episode are assessed quantitatively in the present work. The performance of the modelling system was briefly evaluated. The modelling system was able to capture the evolution of the episode, with increasing ozone levels during the period 1-4 August 2003, and maximum values afterwards. Analysis of the results of the CMAQ model indicates that three mechanisms were mainly responsible for the episode: (i) horizontal transport from mainland Europe in the presence of a long-lived high-pressure system, (ii) convergence of westerly and easterly near-surface winds, and (iii) downward entrainment of ozone-rich air from residual layers in the free troposphere. The downward entrainment of ozone from residual layers in the morning is found to be key to enhancing ozone levels during the day. The relevance of this mechanism is supported by the good agreement of the model vertical ozone distribution with that derived from Light detection and ranging (Lidar) measurements. The process analysis of the rate of change of ozone concentration shows that both horizontal transport and vertical transport were equally important in explaining the variability of ozone. The contribution of chemical processes to the increase of ozone concentration as simulated by the modelling system is relatively small close to the surface. However, its contribution to the decrease of ozone concentration there becomes as important as that of meteorological processes. By investigating the role of separate meteorological and chemical mechanisms, this study hopes to add to the current understanding of the evolution of air pollution episode.

Ms. Ref. No.: ATMENV-D-10-01569
Response to Reviewer #1

We thank the anonymous reviewer for his enlightened review of our manuscript. Below is our response point by point and wherever necessary an indication of the changes that have been made to the original manuscript. Note that the page numbers that are 'given' in our response refer to those of the revised manuscript, unless otherwise indicated.

- The paper is well written and provides a relevant insight on mechanisms underlying the growth of ozone concentrations during an episode associated to a summer heat wave.

  Just a few points should be further clarified, see the following notes.

  Line 181-183:
  18 monitoring stations data have been averaged. Please provide details on the kind of stations used. Are all selected stations background monitors or they include roadside stations?

  > → The 18 monitoring sites are all background sites. We have added 'background' before 'sites' on line 160, page 6 of the revised manuscript.

- Line 189-191:
  The formulated hypothesis are interesting but they should be better specified. How can soil dryness affect ozone concentrations? It is not obvious by my point of view. Weak effects on max O3 concentrations are usually expected from an increase of model resolution, while it can cause an increase of titration effects due to higher local emissions. Which effects of higher resolution are expected to increase ozone production?

  > → Thanks for this. We have changed the last sentence of Section 3.1 to 'The source of this underestimation has not yet been identified. However, the possible reasons for this underestimation are extreme dryness of the soil, resulting in a decrease in dry deposition during that period, an underestimation of emissions of VOCs (including isoprene) as suggested by Utembe et al. (2005), and inadequate model resolution to properly represent the spatial distribution of ozone precursors.' in the revised version of the manuscript (see lines 190-194, pages 7-8). The mention of the underestimation of emissions of VOCs has been suggested by Reviewer #2.

- Line 238-239:
  The sentence "This clearly supports...", commenting Figure 5, is not convincing. The important role of vertical transport of ozone from the upper layers to the surface is well described by Figure 6 but it is not evident from Figure 5, where it can be argued only from Fig. 5j.

  > → Agreed. This sentence should not been linked to Fig. 5. Hence it is removed in the revised version of the manuscript.

- Line 258-260:
  It should be better specified that model concentrations underestimate lidar measurements while the vertical distribution and its change in time is correctly described. Please see the following comment about Figure 7.

  > → Point taken. We have changed the sentence 'The model successfully simulated the overall features of the observed vertical cross-section of ozone concentration on 10 August 2003.' to 'While the model underestimated ozone levels, it successfully reproduced the observed vertical distribution of ozone concentration and its evolution in time on 10 August 2003.' in the revised version of the manuscript (see lines 260-261, page 10).

- Line 287:
  What is the origin of the relevant VADV observed? Surface flow convergence? Coastal uprise originated by breeze flow? or other phenomena ?

  > → Thanks for this. We have added 'This finding may be explained by the convergence of westerly and easterly flows on that day (see Section 3.2).' in the revised version of the manuscript (see lines 291-292, page 11).

- Figure 5 caption should mention that x axis represents latitude.

  > → Fixed.

- Figure 6 caption:
  scales used for model and lidar concentration fields are different. If it has been done to make figures mode readable and fields more easily comparable, it should be reminded that scales are different, otherwise the use of the same scale should be preferred.

  > → Fixed. We have used the same scale in the revised version of the manuscript.

Ms. Ref. No.: ATMENV-D-10-01569
Response to Reviewer #2

We thank the anonymous reviewer for his enlightened review of our manuscript. Below is our response point by point and wherever necessary an indication of the changes that have been made to the original manuscript. Note that the page numbers that are 'given' in our response refer to those of the revised manuscript, unless otherwise indicated.

- This paper presents modelling results looking at UK ozone during the heatwave of August 2003. It attempts to quantify the source of the high levels of ozone seen over the UK during this period by use of the CMAQ model. It shows that downward entrainment of ozone from residual layers in the morning is the key to enhancing ozone levels during the day. It is an interesting and well written paper and provides key insights into how high ozone levels during heatwaves in the UK come about. I would recommend it for publication in Atmospheric Environment subject to the minor comments below.

  The paragraph of lines 74-81 does not give a full picture of the work in the Lee et al. paper. The authors state that no clear evidence was provided to support the fact that ozone was produced locally due to enhance isoprene levels. However in the Lee et al paper there are descriptions of a series of measurements that do support this hypothesis (albeit with no modelling study). For example the measurement of high levels of peroxy radicals (which the authors here incorrectly state are emitted (line 78)) would show a high level of local photochemical activity. The authors should change this paragraph to reflect this. More evidence to suggest that local ozone production may be important is given in a paper by Utembe et al (Faraday Discussions, 2005, 130, 311-326). This paper shows that a photochemical trajectory model underestimates the observed ozone concentrations at the Writtle site during the heatwave period, something that is attributed to poorly constrained biogenic and long chain VOC emissions in the model. The authors should comment on this paper in relation to their current publication.

  → Thanks for this. We have changed the sentence 'Nevertheless, because of lack of observation data, no clear evidence was provided to support this suggestion.' to 'The high levels of peroxy radicals observed during the episode indicated a high level of local photochemical activity.' (see lines 78-79, page 3). Also, we have added the reference, Utembe et al., 2005, in the revised version of the manuscript (page 8, line 193).

- Line 190. The authors state that there is an underestimation of the high ozone peaks but they have not indentified the source. Could they comment on whether the source of the underestimation is in fact missing isoprene in the chemistry scheme. It is likely that the emissions for isoprene used will be an underestimate so the authors should comment on how increased isoprene in the model may affect the chemistry and therefore modelled ozone.

  → Thanks for this. We have changed the last sentence of Section 3.1 to The source of this underestimation has not yet been identified. However, the possible reasons for this underestimation are extreme dryness of the soil, resulting in a decrease in dry deposition during that period, an underestimation of emissions of VOCs (including isoprene) as suggested by Utembe et al. (2005), and inadequate model resolution to properly represent the spatial distribution of ozone precursors.' in the revised version of the manuscript (see

lines 190-194, pages 7-8).

- Paragraph beginning line 233. The authors state that Figures 5f and 5g clearly support the contribution of vertical transport to the enhancement of ground-level ozone on 6th and 7th August. It is not clear to me how the figure does show this. How do high ozone concentrations in the boundary layer (as stated on line 237) show that vertical transport contributes to ground level ozone. The authors should expand this section to make their argument clearer.

  → Agreed. Point raised by Reviewer #1 as well. This sentence should not been linked to Fig. 5. Hence it is removed in the revised version of the manuscript.

- Lines 244-247. The authors state that the predicted boundary layer height agrees 'well' with the observation. This appears to be true for some times but not for others. What is the authors justification for saying that they agree well? Are there statistics to back this up. The authors should comment further on the comparison between modelled and measured BL height and why the agreement is better at some times than others.

  → Thanks for this. We have changed the sentence 'The simulated boundary-layer height compares well with observations at Writtle, although it is lower in the afternoon and decays more rapidly on 6 August 2003.' to 'The simulated boundary-layer height is comparable to that of observations at Writtle, although it is lower in the afternoon and decays more rapidly on 6 August 2003, suggesting an underestimation of surface heating at this site in the model.' in the revised version of the manuscript (see lines 248-250, pages 9-10).

- General comment on figures. I find some of the figures quite difficult to read. Could (for instance) figures 3 and 4 be done in colour to make the gradient maps clearer (at least for the web version of the manuscript).

  → Fixed. We understand that there will be a cost attached to colour figures.

- Minor editorial comments:
  Line 51 'was 'should be 'were'

  → Fixed (see line 51, page 2)

- Line 65 'of' not required and 'reaction' should be 'reactions'

  → Fixed (see line 65, page 3).

- Line 78 'observation' should be 'observed'

  → This sentence has been deleted in the revised version of the manuscript.

- Figure 8 caption it would help if the acronyms were shown in the caption as well as the text.

  → Fixed.

Author's checklist for submission of revised manuscripts

Please ensure that all revised manuscripts comply with the following:

Short abstract/summary	☒
4-6 keywords of your own choice	☒
Complete reference list	☒
All tables cited in the text are supplied	☒
All **original** figures are supplied (not photocopies)	☒
All figure legends are supplied	☒
Tables, figures and figure legends are supplied separately, not embedded in text	☒
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If paper is accepted the corresponding author wishes for the following figures to be published in colour and is aware and accepts the charges (Euro 295 for the first figure and Euro 295 for subsequent figures).

Figs to be printed in colour: Fig 3., Fig 4. ☒

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Highlights

- First application of WRF-CMAQ to investigate 2003 Ozone episode over SE England
- Entrainment of ozone from the residual layer increases the surface ozone concentration
- Surface convergence of westerly and easterly winds enhances ozone levels
- Ozone evolution can be influenced critically by scale dependent meteorological processes

Mechanisms responsible for the build-up of ozone over South East England during the August 2003 heatwave

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ABSTRACT

The Community Multiscale Air Quality (CMAQ) model is used in order to quantify reasons for the build-up of ozone over South East England during the August 2003 heatwave. Unlike previous studies, the effects of individual meteorological and chemical processes on the temporal evolution of the episode are assessed quantitatively in the present work. The performance of the modelling system was briefly evaluated. The modelling system was able to capture the evolution of the episode, with increasing ozone levels during the period 1-4 August 2003, and maximum values afterwards. Analysis of the results of the CMAQ model indicates that three mechanisms were mainly responsible for the episode: (i) horizontal transport from mainland Europe in the presence of a long-lived high-pressure system, (ii) convergence of westerly and easterly near-surface winds, and (iii) downward entrainment of ozone-rich air from residual layers in the free troposphere. The downward entrainment of ozone from residual layers in the morning is found to be key to enhancing ozone levels during the day. The relevance of this mechanism is

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supported by the good agreement of the model vertical ozone distribution with that derived from Light detection and ranging (Lidar) measurements. The process analysis of the rate of change of ozone concentration shows that both horizontal transport and vertical transport were equally important in explaining the variability of ozone. The contribution of chemical processes to the increase of ozone concentration as simulated by the modelling system is relatively small close to the surface. However, its contribution to the decrease of ozone concentration there becomes as important as that of meteorological processes. By investigating the role of separate meteorological and chemical mechanisms, this study hopes to add to the current understanding of the evolution of air pollution episode.

Keywords: Process rate analysis; Ozone; Heatwave; CMAQ

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1. Introduction

The summer 2003 heatwave was one of the hottest periods ever recorded in Europe with record-breaking temperatures across Europe. The heatwave was associated with unusual weather conditions and unprecedented air pollution events in Europe and worldwide. During the period June – August 2003, observed temperatures were about 20 – 30 % above the seasonal average over most parts of the Europe. The average near-surface temperature during the heatwave period was about 3 ^{o}C higher than that of the equivalent periods in 1961 – 1990 (Schär et al., 2004). The period broke temperature records dating back to the year 1500. Heatwave periods are becoming more frequent in the present climate. A study, reconstructing monthly and seasonal temperature fields in Europe, indicated that the European climate is becoming warmer, especially from early 21st century (Luterbacher et al., 2004). This trend in warming of the European climate is attributed to the increase in frequency of summer heatwaves.

The unusual hot and dry summer triggered several prolonged air pollution episodes over Europe. Several studies indicated exceptionally intense, long-lasting, and spatially extensive episodes of high ozone concentration over the regions with the highest temperatures, especially during the first two weeks of August 2003 (e.g. Grynszpan, 2003). During this period, the limit value of 120 µg m^{-3} (about 60 ppb) for ozone concentration was repeatedly breached in the UK, especially in South East (SE) England.

Severe socio-economic effects, in relation to the summer 2003 heatwave, were observed in most parts of western Europe. The most affected sector was public health, and especially the elderly population, who were not only exposed to high temperatures, but also long exposures to high concentration of pollutants, notably ozone and

particulate matter. The associated total death toll across Europe was estimated to be about 35,000 (Vandentorren et al., 2004). The European countries strongly affected were France, Germany, Spain, Italy, the UK, the Netherlands, Portugal, and Belgium, with France reporting the highest number of deaths (De Bono et al., 2003). In the UK, especially in SE England, between 21 and 38 % of the excess mortality during the summer 2003 heatwave was estimated to be attributable to exposure to high concentrations of ozone and particulate matter (Johnson et al., 2005). Stedman (2004) investigated the air pollution related deaths in the UK during August 2003 and found a 45 μg m^{-3} increase in population-weighted mean ozone concentration, as compared with the same period in 2002.

The heatwave during the first two weeks of August 2003 resulted primarily from a high-pressure ridge located over western Europe holding back the rain bearing low-pressure systems that usually enter the continent from the Atlantic Ocean. An analysis of ozone simulations (Vautard et al., 2005) suggested that, for most of the period, the associated anticyclonic wind re-circulated the warm air throughout Europe and over the Mediterranean region, leading to a build-up of pollutants together with a rise in temperature.

Most tropospheric ozone is formed and destroyed through reactions involving nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in the presence of sunlight (Sillman, 1999; Jenkin and Clemitshaw, 2000). A reduction of 30 %, in peak ozone concentration at the European Monitoring and Evaluation Programme (EMEP) stations in the UK, was identified over the period 1986 – 1999 (NEGTAP, 2001). This downward trend in episodic peak ozone levels is attributed to the effective reduction in emissions of ozone precursors, notably NO_x and some VOCs, during that period (Derwent et al., 2003). This correlates well with a reduction, in annual emissions of NO_x and VOCs in western and central Europe, in the range 23 – 32 % during the period 1991 – 2002 reported by Vestreng et al. (2004). However, in spite of the overall reduction in precursors of tropospheric ozone, air pollution events are still often observed during heat wave periods.

A number of factors, which contributed to the prolonged heatwave in Europe and associated degradation of air quality, have been discussed in the literature (Solberg et al., 2008, and references therein). Less attention has been paid to the ozone smog episode in SE England. Lee et al. (2006) suggested that the initial morning increase of ozone concentration was caused primarily by entrainment of air from higher levels, further enhanced by increased emissions of isoprene in the afternoon. The high levels of peroxy radicals observed during the episode indicated a high level of local photochemical activity. A sensitivity study using the EMEP unified model for the UK (EMEP4UK) indicated that meteorology, boundary conditions, and chemistry all played significant roles in

contributing to the magnitude of the UK surface ozone concentration during the heatwave period (Vieno et al., 2010).

The accumulation of tropospheric ozone over the UK is often attributed to transport of pollutants from adjacent European countries. Jenkin et al. (2002) analyzed back trajectories to identify the origin and day-of-week dependence of photochemically active ozone episodes in the UK and found that the highest ozone concentrations generally occur under summertime anticyclonic conditions, when air masses from mainland Europe overlapped the UK. Derwent et al. (2004) conducted a model study using a global three-dimensional Lagrangian chemistry-transport model and showed that intercontinental transport can have a significant impact on ozone levels at ground surface sites in Europe. Li et al. (2002) found that transport in the boundary layer and subsidence from the free troposphere enhanced ground surface ozone concentrations over mainland Europe by 2 – 4 ppb during summertime and 5 – 10 ppb during transatlantic transport events from North America.

The meteorological and chemical mechanisms contributing to the high ozone episode over SE England during the August 2003 heatwave have not been quantified so far. The primary focus of the present study is to quantify the contributions of the key meteorological and chemical mechanisms to the build-up of ozone over SE England. Results from this study are expected to provide a greater appreciation of the processes responsible for the build-up of ozone associated with summer heatwaves, which is needed for reliable air quality predictions and to make effective control strategies for episodic conditions.

The Community Multi-scale Air Quality (CMAQ) model coupled with the Advanced Research core of the Weather Research and Forecasting (WRF) model is used to characterize the build-up of ozone, during the first two weeks of August 2003. Section 2 gives a brief description of the setup of the modelling system and the observation data used for this study. The synoptic situation associated with the high ozone episode and reasons for the build-up of ozone are explored in Section 3. The respective role of horizontal transport and vertical transport are discussed to identify whether that episode was mainly driven by local and/or regional effects. By performing an Integrated Process Rate (IPR) analysis, the contributions of the individual meteorological and chemical processes that combine to produce the predicted hourly ozone concentration are quantified. Concluding remarks are given in Section 4.

2. Modelling system and observation data

The modelling system used in this study consists of the CMAQ chemistry-transport model (Byun and Schere, 2006) version 4.6 coupled with the WRF meteorological model (Skamarock et al., 2008) version 3. Meteorological fields, simulated by WRF, were supplied to CMAQ every hour by using the Meteorology-Chemistry Interface Processor (MCIP). Hourly emissions were prepared using the Sparse Matrix Operator Kernel Emissions (SMOKE) pre-processor (Houyoux et al., 2000) version 2.4. The UK National Atmospheric Emission Inventory (NAEI), which provides annual averaged emission from point sources and area sources at a horizontal resolution of 1 km, were used for the grid cells inside the UK. The annual anthropogenic emission data from the European Pollution Emission Register (EPER), for point sources, and from the European Monitoring and Evaluation Programme (EMEP), for area sources, at a horizontal resolution of 50 km were used for the grid cells outside the UK. The chemical interactions for gas chemistry were treated with the Carbon Bond mechanism CB05 in the CMAQ simulation. The simulation was performed for the year 2003 (Chemel et al., 2010), which contained several pollution episodes.

2.1. Model setup and configuration

The WRF model was setup with three nested grids using one-way nesting. The domains (see Fig. 1) used horizontal resolutions of 45 km (D1), 15 km (D2), and 5 km (D3). The outer domain D1 covers the whole of Europe while the innermost domain D3 covers the whole of the UK and the Republic of Ireland. Note that the domains used for the CMAQ simulation matches those of the WRF simulation with 5 grid cells less in each horizontal direction. The model was run on 28 vertical levels up to 50 hPa and the grid was stretched along the vertical axis to accommodate a high resolution (about 40 m) close to the ground. The averaged vertical grid spacing was 500 m. We used the United States Geological Survey (USGS) geographical data (e.g. digital elevation, soil type, land cover) provided with the WRF pre-processing system. The 6-hourly analyses from the European Centre for Medium-range Weather Forecasts (ECMWF), at a horizontal resolution of 0.5^{o}, were used for the initial and lateral boundary conditions for D1. In order to shorten the spin-up time and to constrain the model towards the analyses, a grid nudging technique (Stauffer and Seaman, 1990) was employed over D1, every 6 hours. The physics options selected included: the YSU non-local boundary layer parameterization scheme (Hong et al., 2006), the Monin Obukhov

surface-layer scheme, the Noah soil-vegetation model (Ek et al., 2003), the CAM3 radiation package (Collins et al., 2006), the microphysical scheme by Thompson et al. (2004, 2006), and the ensemble cumulus scheme by Grell and Dévényi (2002) for D1 and D2 only. The monthly mean concentration of gaseous species, derived from the UK Met Office Lagragian chemistry-transport model STOCHEM for the year 2000 were used as the chemical initial and boundary conditions for the CMAQ simulation. Further details of the setup of the modelling system are given in Chemel et al. (2010). The model results from D3 are analyzed in this study.

2.2. Integrated process rate analysis of modelled ozone concentration

An Integrated Process Rate (IPR) analysis (Jeffries and Tonnesen, 1994; Godowitch et al., 2008; Xu et al., 2008; Yu et al., 2008) is used to study the effect of different processes on the prediction of ozone concentrations. The IPR analysis allows the effects of key meteorological and chemical processes on model predictions to be assessed separately. The contributing terms in the conservation equation for ozone were processed every hour for each grid cell in the 'SE England domain' (region delimited by 2.0^{o} W to 1.5^{o} E and 51.5^{o} N to 53.0^{o} N, see Fig. 1). These terms represent the contributions of vertical advection (VADV) and diffusion (VDIF), horizontal advection (HADV) and diffusion (HDIF), dry deposition (DDEP), cloud processes (CLD), and chemical processes (CHEM). Results of the IPR analysis are discussed in Section 3.3 in order to determine quantitatively the relative importance of the different meteorological and chemical processes that drive the spatial and temporal distribution of ozone.

2.3. Observation data

The predicted ground-level ozone concentrations are compared with the surface ozone measurements from the UK Automatic Urban and Rural Network (AURN) in Section 3.1. The surface ozone measurements from 18 monitoring sites of suburban, urban and rural background types, over SE England were considered for this study. The first field campaign of the Tropospheric ORganic CHemistry experiment (TORCH), was carried out during the period 27 July – 30 August 2003 at Writtle College (51° 44′ 12″ N; 0° 25′ 28″ E in Fig. 1). This campaign study collected valuable air quality and meteorological measurements during the high ozone episode. The site description and the details of pollutants measured during the campaign study are described in Lee et al. (2006). The planetary

boundary-layer height, derived from wind profiler data, and ozone profiles, obtained from Light detection and ranging (Lidar) data, at Writtle, are compared with model results for the heatwave period in Section 3.2. The Lidar system used was the Facility for Ground-based Atmospheric Measurement (FGAM) Ozone and Aerosol Profiler (Ricketts, 2009).

3. Results and discussion

3.1. Overall meteorological features and performance of the modelling system

The UK Met Office observations reported that August 2003 was a very hot, sunny, and exceptionally dry period across the UK. At Brogdale (51.297 ^{o}N, 0.881 ^{o}E) near Faversham (Kent), a record-breaking temperature of 38.5 ^{o}C was measured on 10 August 2003. Synoptic conditions during the first two weeks of August 2003 were particularly favourable to the establishment of the heat wave episode. A low-pressure system formed to the north west of the UK, over the Atlantic Ocean, on 1 August 2003 and decayed rapidly. Subsequently, a high-pressure system formed over the UK over the next 10 days leading to the severe heatwave and several pollution episodes. The steady-state anticyclonic system yielded clear skies, prolonged sunshine, high temperature, subsidence of air, and the build-up of ozone throughout the UK during the period 4 – 10 August 2003.

In order to evaluate the performance characteristics of the modelling system in simulating ground-level ozone, the time series of observed maximum daily running 8-hour mean ozone averaged over 18 ozone monitoring sites (see Section 2.3) for the period 1 – 12 August 2003 are compared with model results in Fig. 2. A sharp increase in ozone concentration (in the order of 30 ppb) occurred during the period 1 – 4 August 2003. The model successfully captured this build-up of ozone, with a maximum value of 65 ppb on 5 August 2003. The threshold of 60 ppb for ozone was exceeded as from 5 August 2003. The model effectively predicted ozone concentration above the 60 ppb threshold, for the period 6 – 12 August 2003. The peak ozone mixing ratio was simulated one day after that observed and was underestimated. This underestimation of high-ozone peaks during the August 2003 heatwave is consistent with the findings of Vautard et al. (2005). The source of this underestimation has not yet been identified. However, the possible reasons for this underestimation are extreme dryness of the soil, resulting in a decrease in dry deposition during that period, an underestimation of emissions of VOCs (including isoprene) as suggested by

Utembe et al. (2005), and inadequate model resolution to properly represent the spatial distribution of ozone precursors.

3.2. Horizontal features

Meteorological fields, namely sea level pressure (SLP), 2-m temperature, wind, and boundary-layer height have been analyzed to understand the synoptic conditions that were responsible for the heatwave episode triggering the pollution episode. Black et al. (2004) studied factors contributing to the summer 2003 European heatwave and concluded that a blocking regime persisted over the whole of Europe in August 2003, enhancing radiative forcing because of the absence of cloud, and increasing surface temperatures.

Fig. 3 shows the SLP and 2-m temperature fields extracted from the WRF simulation for the period 1 – 12 August 2003 at 15 UTC. The spatial variability of the SLP and 2-m temperature, on all days of the episode, is well reproduced when compared with that reported by Burt (2004). The predicted 2-m temperature pattern corresponds well to observations during this period for the whole of the UK. The model successfully reproduces high temperatures, in excess of 35 ^{o}C over SE England, in particular on 6, 9, and 10 August 2003 as was reported by Black et al. (2004). The high-pressure (1017 – 1025 hPa) system over the UK during the episode, discussed by Black et al. (2004), is well reproduced by the model (see Fig. 3c – 3l).

In order to understand the contribution of the meteorological process to the build-up of ground-level ozone during the heatwave episode, the spatial distribution of ground surface ozone and 10-m wind field are displayed, in Fig. 4, for the period 1 – 12 August at 15 UTC. During 1 – 3 August 2003 (see Fig. 4a – 4c), a westerly flow brought cool and moisture-rich air from the Atlantic Ocean over the UK resulting in light rainfall. During the next five days (see Fig. 4d – 4h) the air mass in the UK experienced anticyclonic circulation due to the presence of a blocking high (see Fig. 4g). As a result of the blocking high over the UK, an easterly flow from mainland Europe, with wind speeds greater than 15 m s^{-1}, pushed the westerly flow from the Atlantic Ocean towards the North. A convergence zone developed along the western side of the UK on 9 August 2003 (see Fig. 4i), which turned into a cold front on 10 August 2003 (see Fig. 4j). Due to the presence of the cold front, SE England (the region ahead of the cold front) experienced high temperatures (see Fig. 3j). The anticyclonic activity decayed on 12 August 2003 and a westerly flow from the Atlantic Ocean pushed the polluted air mass eastwards.

Fig. 4a and 4b show that there is no transport of ozone-rich air from the Atlantic Ocean, for the period 1 – 2 August 2003 with the westerly flow setting the background concentration (about 40 ppb). The build-up of ozone during the next 10 days is predominantly associated with horizontal transport of ozone from mainland Europe in the presence of the blocking high over Europe. Easterly winds from mainland Europe transported ozone towards the UK on 4 and 5 August 2003 (see Fig. 4d and 4e). The transported ozone was blocked in SE England on 6 August 2003 (see Fig. 4f) due to the convergence of westerly and easterly flows. The next four days were characterized by high levels of ozone, with concentrations in excess of 90 ppb, over the south-western part of England on 9 August 2003 (see Fig. 4i). Ozone concentration decreased as the anticyclonic system decayed over the next two days (see Fig. 4k and 4l). It is worth noting that the high temperature regions coincide with the high ozone concentration regions during this episode (see Fig. 3 and 4).

The next section discusses the vertical distribution of ozone, where the maximum ground-level ozone was observed, so as to identify the role of vertical transport in the build-up of ozone over SE England.

3.3. Vertical features

The variability of the boundary-layer height, along with the vertical distribution of ozone across SE England at 0^{o} longitude is displayed in Fig. 5 for the period 1 – 12 August 2003 at 15 UTC. It is noteworthy that the ozone within the boundary layer is well mixed, over land, in the afternoons. The boundary layer is very shallow (in the range 0 – 200 m) over the English Channel and the North Sea while being well developed over land with a maximum height of approximately 1 – 2 km. Fig. 5f and 5g show ozone concentration in excess of 80 ppb within the boundary layer on 6 and 7 August 2003. Interestingly, on 10 and 11 August 2003, the model simulated the maximum ozone concentration above the boundary layer (see Fig. 5j and 5k).

Consistent with observations (Lee et al., 2006), our work reveals that the maximum ground-level ozone occurred on 6 August 2003 and that maximum temperatures occurred on 10 August 2003. Fig. 6 depicts the vertical distribution of ozone and the boundary-layer height from 08 UTC to 18 UTC on 6 and 10 August 2003, respectively. The simulated boundary-layer height is also compared with that observed at Writtle, on 6 and 10 August 2003. The boundary-layer height reaches a maximum at 14 UTC (see Fig. 6d and 6j) and then decreases in the evening (see Fig. 6f and 6l). The simulated boundary-layer height is comparable to that of observations at Writtle, although it is

lower in the afternoon and decays more rapidly on 6 August 2003, suggesting an underestimation of surface heating at this site in the model. Ozone mixing ratios are as large as 80 ppb in the range 500 – 2000 m in the afternoon (see Fig. 6d and 6j). The strong convective activity within the boundary layer causes ozone mixing during daytime.

The boundary-layer height reaches the level where ozone concentration was trapped during the morning (i.e. a residual layer) and entrains ozone downwards, further increasing ground-level ozone in the later hours. This mechanism is similar to that discussed by Zhang and Rao (1999) and Rappenglück et al. (2008) in that ozone and its precursors trapped aloft in the nocturnal residual layer influence ground-level ozone concentrations on the following day as the surface-based inversion starts to break up.

Fig. 7 shows the vertical cross-section of ozone concentration derived from the Lidar data and predicted from the modelling system for the levels in the range 400 – 2000 m, at Writtle, on 9 and 10 August 2003. The Lidar indicated ozone concentration greater than 100 ppb, in the range 800 – 1500 m, from late evening on 9 August 2003. While the model underestimated ozone levels, it successfully reproduced the observed vertical distribution of ozone concentration and its evolution in time on 10 August 2003. The Lidar measurement on 10 August 2003 suggested that ozone trapped at the level of 1400 m during morning hours was entrained downwards, further increasing ground-level ozone in the later hours. The model reproduced well the increased ground-level ozone concentration due to ozone entrainment from the residual layer.

The analysis of model results and observations have revealed some of the mechanisms that contributed to the enhancement of ground-level ozone concentration during the first two weeks of August 2003, in particular, horizontal transport of ozone from mainland Europe in the presence of prolonged anticyclonic conditions, convergence of easterly and westerly flows, with stagnant conditions over the south east of the UK, and vertical transport of ozone over SE England.

3.4. Process rate analysis

An IPR analysis was performed to quantify the relative contributions of the processes driving ozone concentration in the CMAQ model (see Section 2.2) at different vertical levels for the ‘SE England domain’ (see Fig. 1). The contributions of cloud processes (CLD), and chemical processes (CHEM) were combined into one chemistry-related contribution and referred to as CHEM thereafter. Fig. 8 summarizes results of the IPR analysis on

6 and 10 August 2003. The time series of the rate of change in ozone concentration due to each contribution (VADV, VDIF, HADV, DDEP, and CHEM) at different model heights (namely, 46 m, 372 m, 837 m, and 1303 m) are shown in Fig. 8. Dry deposition (DDEP) is relevant only for the near-surface layer (46 m). The contribution of horizontal diffusion (HDIF) is found negligible and thus is not discussed thereafter. The contribution of the chemistry-related processes (CHEM) is found to be small, compared with the meteorological processes especially near the ground surface.

Fig. 8a and 8e show that the removal of ozone due to DDEP is compensated by VDIF in the near-surface layer (46 m). On 6 August 2003, HADV contributes to increasing ozone concentration there, while VADV decreases ground-level ozone. The contributions of HADV and VADV to the change in ground-level ozone concentration are more variable and tend to compensate each other on 10 August 2003. CHEM contributes to the increase of ozone concentration at all levels, except close to the ground surface where ozone is dry deposited and depleted. This consumption of ozone during the daytime due to the titration by nitrogen monoxide (NO) was reported in Wang et al. (2010).

On 6 August 2003, it is found that in the morning hours the horizontally advected ozone is removed by VADV in the upper levels. This finding may be explained by the convergence of westerly and easterly flows on that day (see Section 3.2). During daytime, CHEM and HADV contribute to the increase of ozone concentration up to the height 837 m but above that height (see Fig. 8d), CHEM and VADV are the main contributors to the increase of ozone concentration. Indeed, during daytime the horizontally trapped (advected) ozone in the residual layer further increases ozone levels in the presence of sunlight. At the height of 1303 m, HADV removes ozone locally produced during the daytime. Some ozone is also transported downward (positive values of VADV) from upper levels. The vertically transported ozone from the upper level is advected horizontally within the SE England domain (positive value of HADV) at heights below 1303 m. The increase of ozone concentration is also contributed by the convergence of westerly and easterly winds as depicted in Fig. 4f on 6 August 2003.

The situation is more complicated in explaining the contribution of different processes on 10 August 2003 (see Fig. 6g-l and Fig. 8f-8h). Similarly to the near-surface layer, the contributions of HADV and VADV to the change in ozone concentration are noticeably variable and tend to compensate each other. Above the boundary layer, ozone levels are increased due to HADV, and decreased due to VADV. Also, they decrease as height increases from 372 m to 1303 m.

Tables 1 and 2 report time-averaged (7 UTC-19 UTC) values of the contributions of HADV, VADV, VDIF, DDEP, and CHEM to the ozone concentration at 46, 372, 837, and 1303 m on 6 and 10 August 2003, when the ozone concentration increased (i.e. $\Delta O_3/\Delta t > 0$) and when it decreased (i.e. $\Delta O_3/\Delta t < 0$), respectively. As shown in Fig. 8, when the ozone concentration increased, VDIF (24 ppb/hr on average for 6 and 10 August 2003, respectively) played the major role in increasing ozone levels, and DDEP (-22 ppb/hr on average) in decreasing ozone levels in the near-surface layer (46 m). As mentioned above, when the ozone concentration decreased, both VDIF (16 ppb/hr) and DDEP (-13 ppb/hr) played significant roles in increasing and decreasing ozone levels respectively, near the ground surface. As height increases, CHEM played a significant role along with HADV (except for 10 August 2003, when ozone increased) in contributing to the increase of ozone level for both $\Delta O_3/\Delta t > 0$ (1 ppb/hr on average) and $\Delta O_3/\Delta t < 0$ (1 ppb/hr on average). VADV and VDIF were the main contributors to the decrease of ozone concentrations at upper levels.

4. Concluding remarks

The mechanisms responsible for the high ozone episode over SE England during the August 2003 heatwave have been investigated using the CMAQ chemistry-transport model coupled with the WRF meteorological model. This period is of particular interest since such extreme weather conditions provide conspicuous events for air quality analysis. The horizontal and vertical day-to-day variability of ozone during the episode have been discussed. The enhancement of ozone due to the distribution of various ozone enrichment processes has been investigated by employing an IPR analysis in the CMAQ model. The horizontal analysis showed a maximum ozone concentration region over SE England on 6 August 2003. Our study has revealed that transported ozone from mainland Europe was trapped due to the convergence of westerly and easterly flows over the UK on 6 August 2003, and thus increased ozone levels in the following days. The vertical distribution of ozone over SE England on 6 and 10 August 2003 suggested that the strong convective activity, during the daytime, entrained ozone from the residual layer downwards during the afternoon hours, increasing ground surface ozone levels. The vertical cross-section of ozone concentration from the model simulation compared well with that derived from Lidar measurements. The IPR analysis for ozone has indicated that the main contributors to the increase of ozone concentration were horizontal transport and vertical transport in the morning hours. The enhancement of ozone concentration on 6 August 2003

due to horizontal advection and vertical diffusion processes is supported by the convergence of westerly and easterly winds over the SE England domain on that day. The modelling study has shown that chemical processes have contributed much less to the ozone build up during the episode. Nonetheless, we cannot rule out a more important contribution of chemical processes. Indeed, about 10 – 15 ppb of ozone were not accounted for by the modelling simulation, when comparing the simulated maximum daily running 8-hour mean ozone concentration, averaged over 18 sites in the 'SE England domain', with observations. In general, our study adds to the current understanding of the role of meteorological and chemical processes in the variability of ozone concentration during episodic conditions. Also, this research demonstrates the value of process analysis to understand the causes of the evolution of air pollution episodes and how their description can be generalised.

Acknowledgments

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Tables

Table 1. Time-averaged values of the contributions of HADV, VADV, VDIF, DDEP, and CHEM to the ozone concentration (ppb/hr) at 46, 372, 837, and 1303 m when ozone concentration increased, i.e. $\Delta O_3/\Delta t > 0$.

Height	6 August 2003					10 August 2003				
(m)	HADV	VADV	VDIF	DDEP	CHEM	HADV	VADV	VDIF	DDEP	CHEM
46	2.52	-3.28	24.25	-20.40	-1.04	-1.41	1.47	24.61	-21.66	-1.53
372	1.40	-1.35	-0.85	0.00	1.13	-2.29	2.60	-0.33	0.00	1.32
837	0.98	-0.88	-1.16	0.00	1.53	1.73	-1.77	-0.65	0.00	0.89
1303	0.67	-0.95	-0.65	0.00	1.47	-0.47	0.52	-0.84	0.00	1.01

Table 2. Time averaged values of the contributions of HADV, VADV, VDIF, DDEP, and CHEM to the ozone concentration (ppb/hr) at 46, 372, 837, and 1303 m when ozone concentration decreased, i.e. $\Delta O_3/\Delta t < 0$.

Height	6 August 2003					10 August 2003				
(m)	HADV	VADV	VDIF	DDEP	CHEM	HADV	VADV	VDIF	DDEP	CHEM
46	2.49	-2.85	15.83	-12.80	-4.33	2.35	-1.85	15.86	-13.52	-4.75
372	1.48	-1.37	-1.64	0.00	0.28	5.28	-5.03	-1.44	0.00	0.27
837	0.48	-0.16	-1.23	0.00	1.31	5.86	-5.89	-1.02	0.00	0.51
1303	-0.38	-0.10	-1.33	0.00	1.32	3.65	-4.00	-0.26	0.00	0.38

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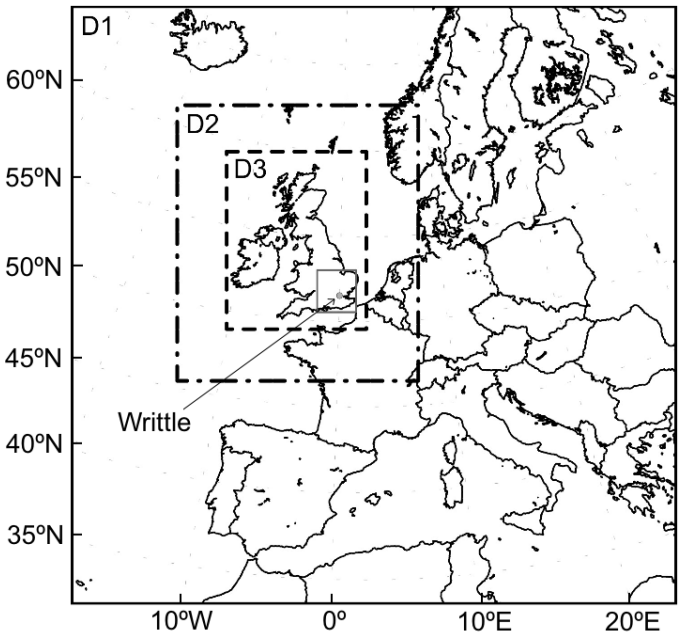
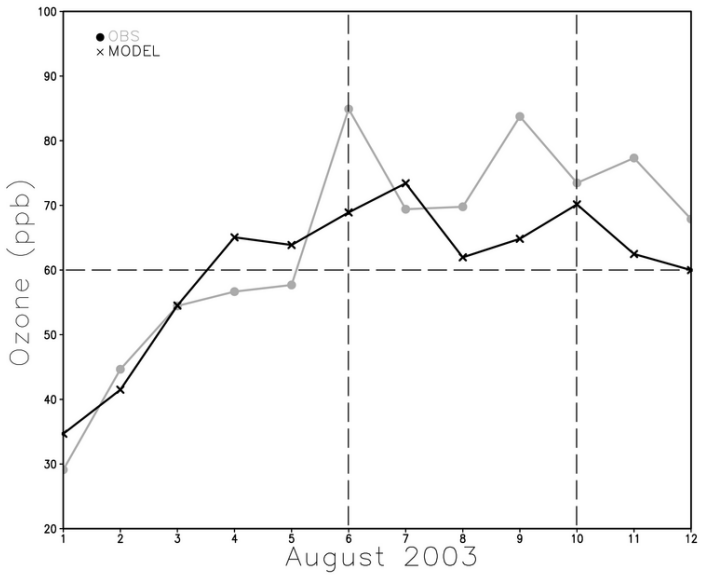
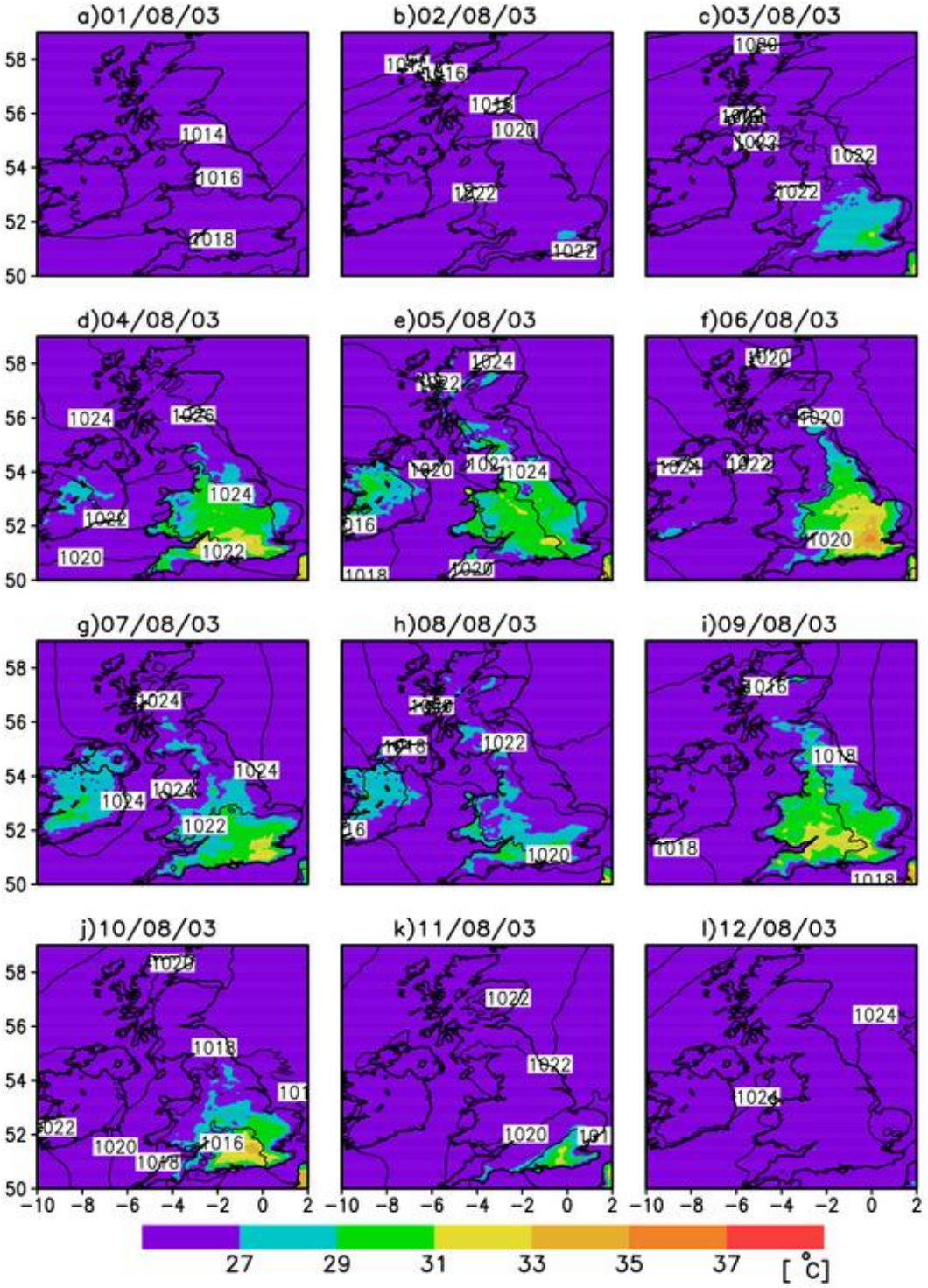


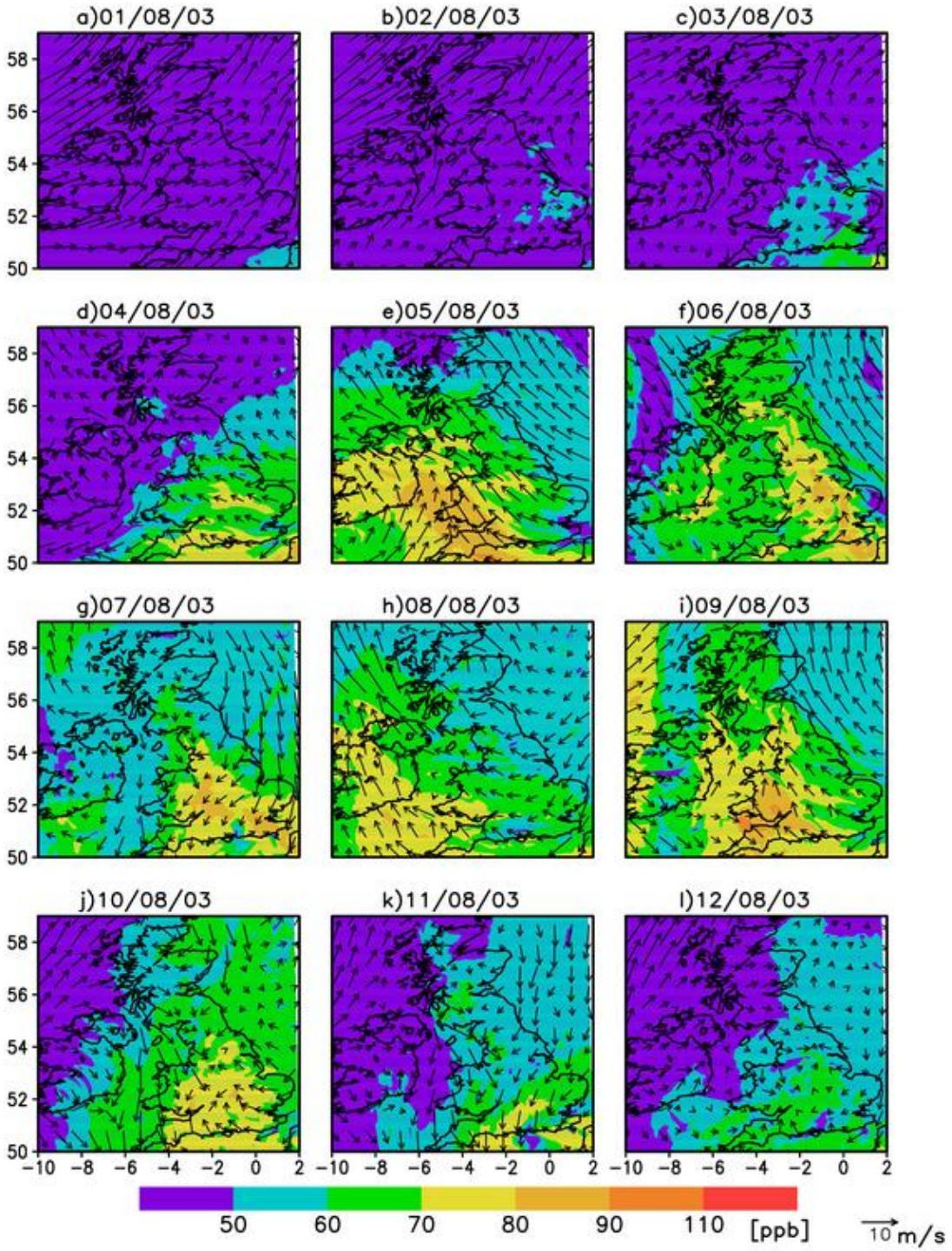
Fig. 1. CMAQ model domains (D1: 45 km, D2: 15 km, and D3: 5km horizontal resolutions). The rectangular box inside D3 delineates the 'South East England domain'.



490 Fig. 2. Time series of observed and predicted maximum daily running 8-hour mean ozone concentration (ppb)
491 averaged over 18 ozone monitoring sites in SE England for the period 1 – 12 August. The horizontal dashed line
492 indicates the limit value of 120 µg m^{-3} (about 60 ppb).



493 Fig. 3. Sea-level pressure (hPa) and 2 m temperature (^{o}C) for the period 1 – 12 August 2003 at 15 UTC



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495 Fig. 4. Ground-level ozone concentration and 10-m wind speed (m s^{-1}) for the period 1 – 12 August 2003 at 15 UTC.

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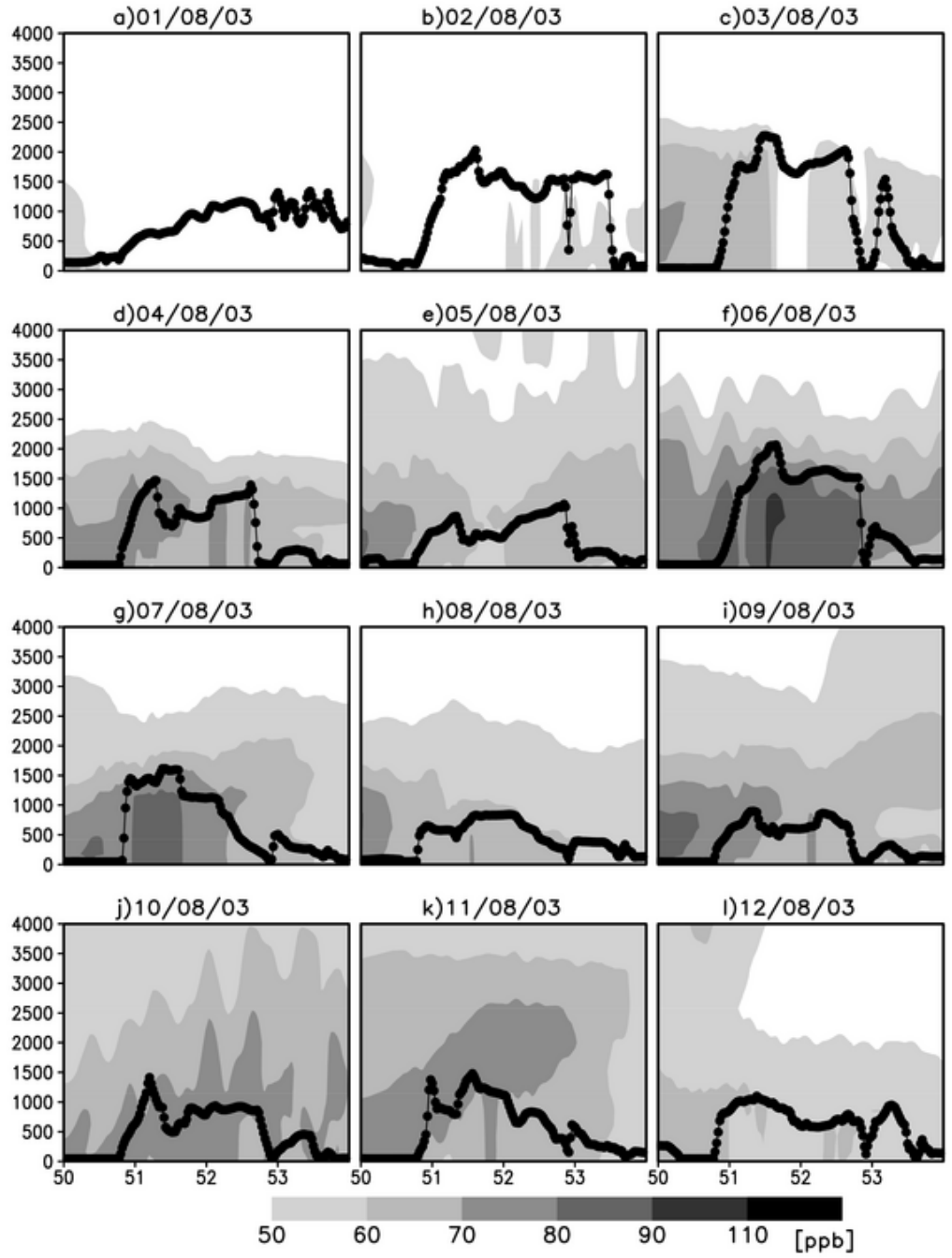

497 Fig. 5. Vertical cross section of ozone concentration (ppb) and boundary-layer height (m) along latitude (x-axis)
498 across SE England at 0^{o} longitude for the period 1 – 12 August 2003 at 15 UTC.

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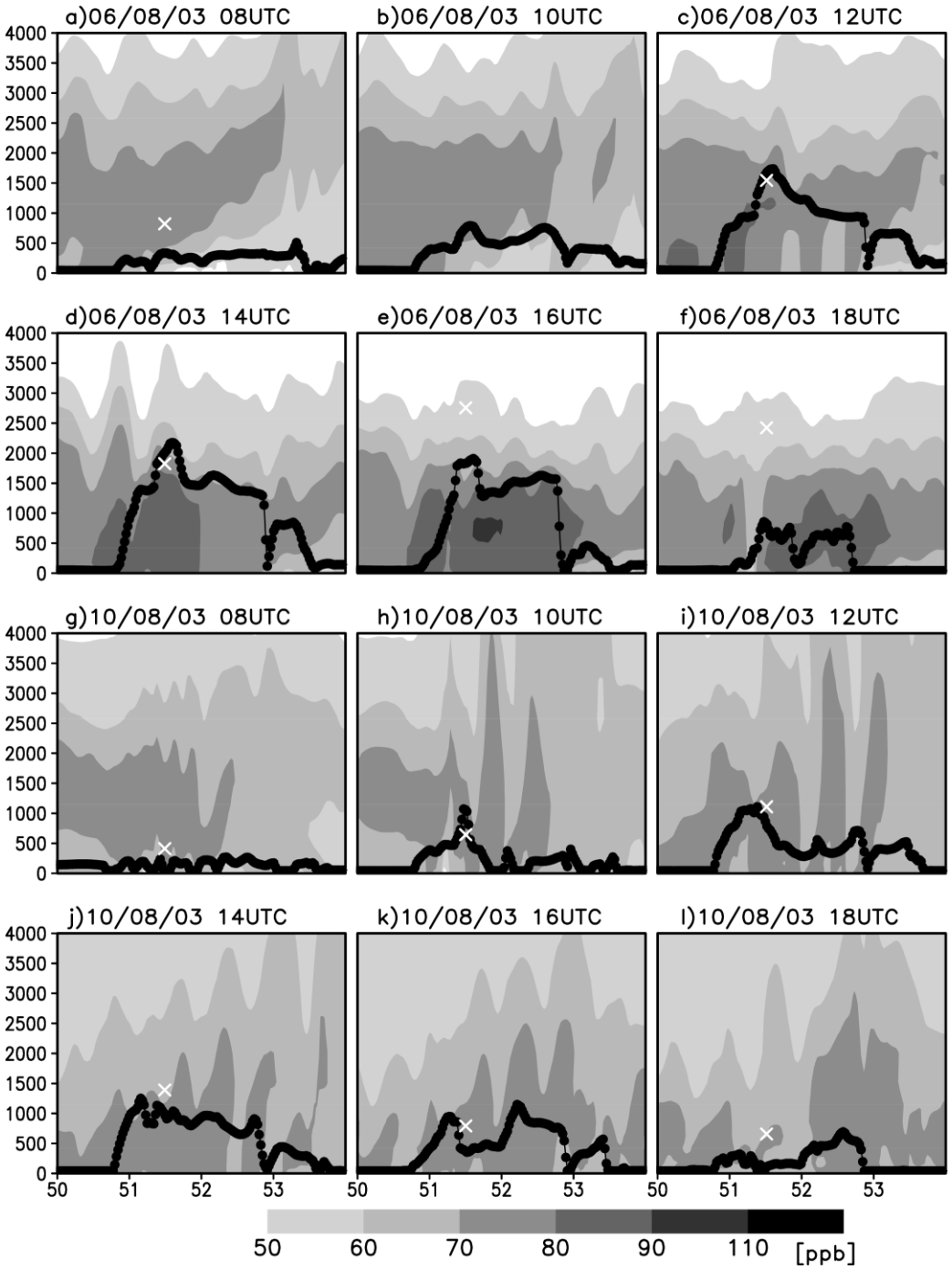
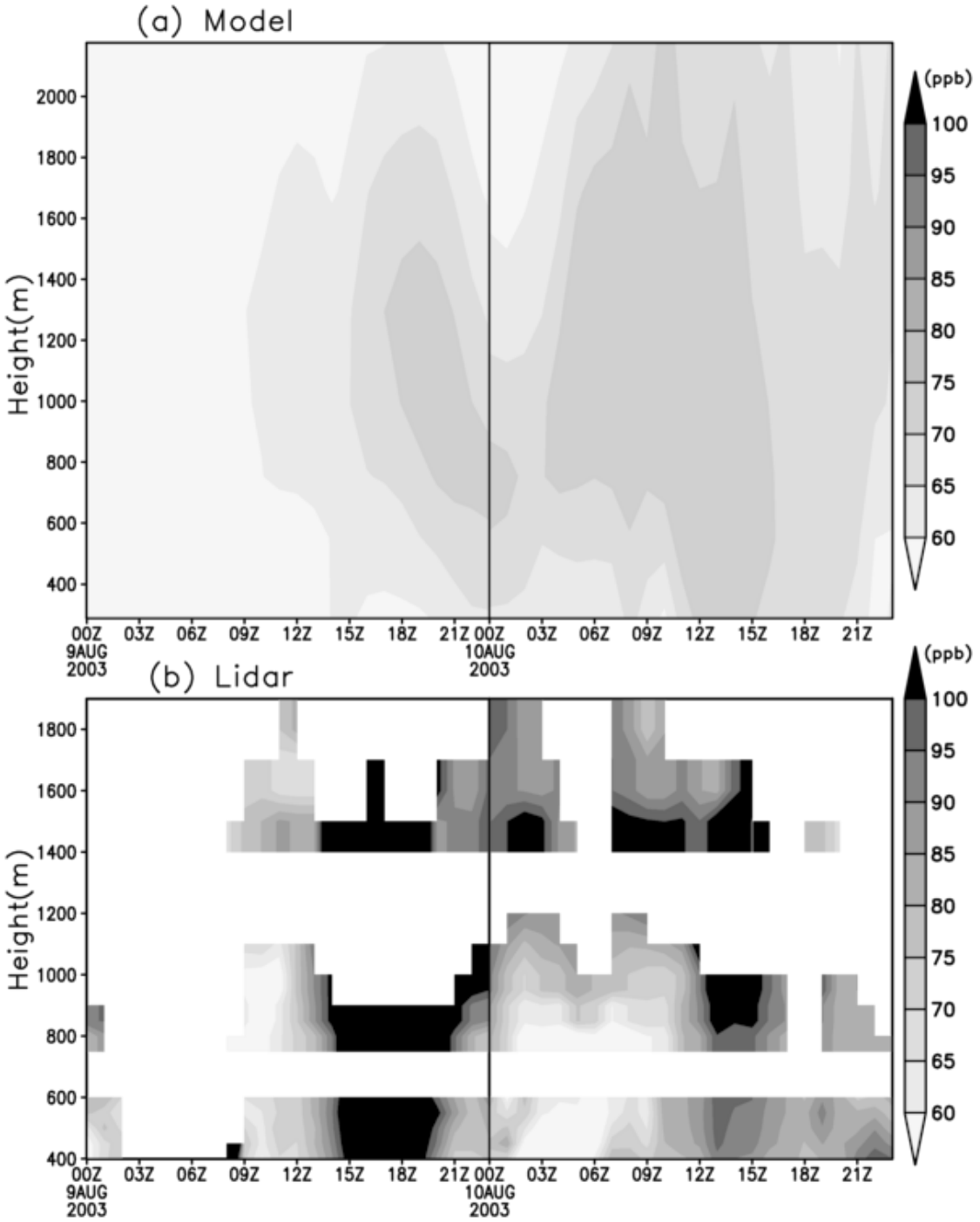


Fig. 6. Vertical cross section of ozone concentration (ppb) and boundary-layer height (m) along latitude (x-axis) across SE England for 6 and 10 August 2003 at 08, 10, 12, 14, 16, and 18 UTC. The white 'x' symbol represents the boundary-layer height observed at Writtle (51° 44′ 12″ N; 0° 25′ 28″ E in Fig. 1).



504 Fig. 7. Vertical cross-section of predicted and observed ozone concentration (ppb) at Writtle (51° 44′ 12″ N; 0° 25′

505 28″ E in Fig. 1) for the period 9 – 10 August 2003.

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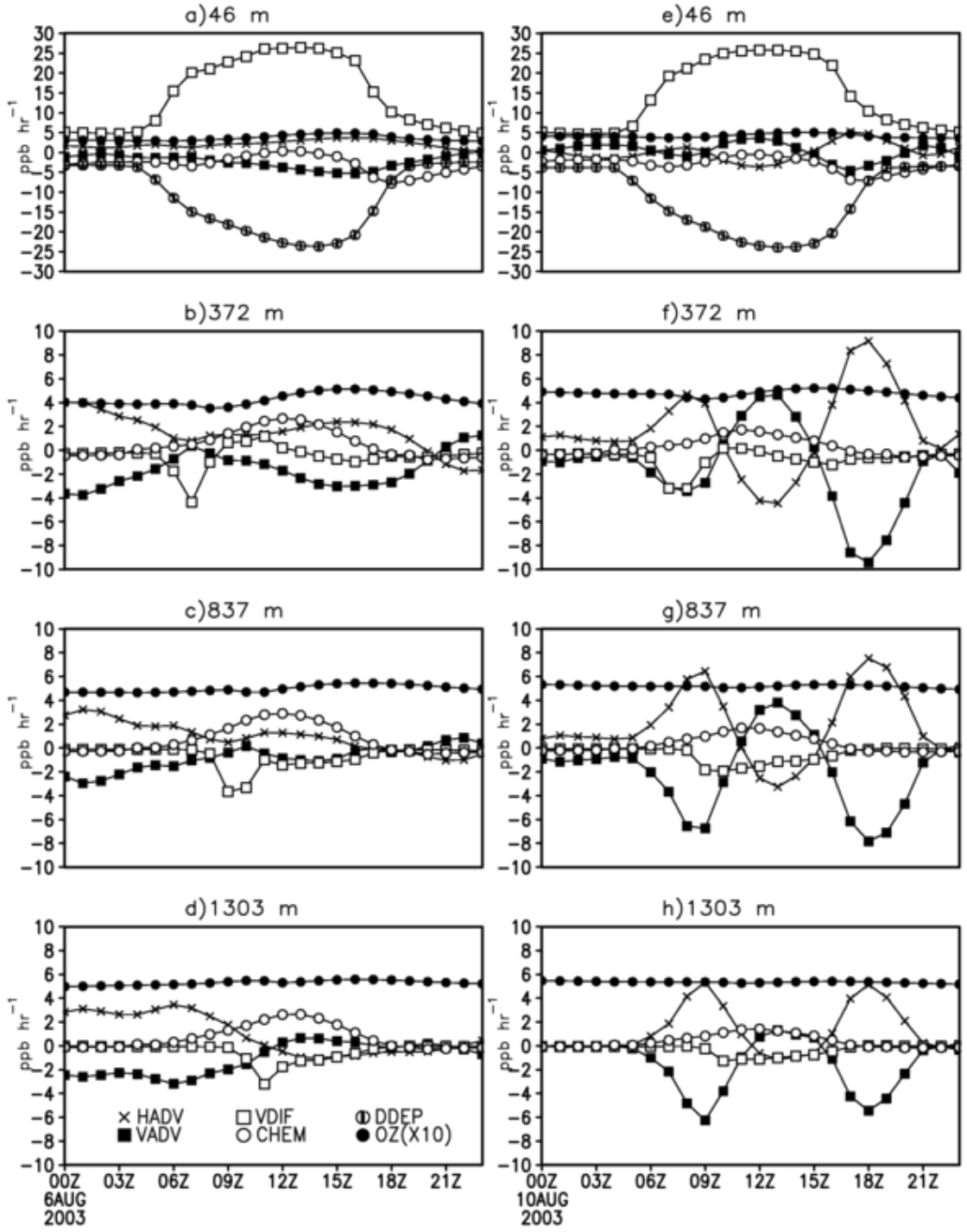

507 Fig. 8. Time series of the rate of change in ozone concentration due to horizontal advection (HADV), vertical
508 advection (VADV), vertical diffusion (VDIF), dry deposition (DDEP), and chemistry-related (CHEM) processes,
509 and ozone levels for 6 and 10 August 2003 at different model heights.