Ozone pollution over the Arabian Gulf – role of meteorological conditions

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Abstract

The Middle East and particularly the Arabian Gulf region are characterised by highly favourable conditions for $\text{O}_3$ formation in summer. We investigated the role of meteorological conditions in $\text{O}_3$ formation using the WRF-chem model. The dispersion of air pollutants strongly depends on local wind patterns, in particular the persistent low-level north-westerly flow known as the summer Shamal, and recurrent land-sea breeze circulation systems.

A general finding from our simulations is that extreme pollution events, with $\text{O}_3$ mixing ratios exceeding $150 \text{ nmol mol}^{-1}$, can occur regularly over the Arabian Gulf, however, their location and magnitude can vary widely. $\text{O}_3$ mixing ratios are highest when the outflow of the regions with major anthropogenic emissions along the coast is advected over the Gulf, where pollution plumes are captured in the shallow and stable marine boundary layer allowing little ventilation. The sea-breeze circulation often causes onshore advection of the pollution in the afternoon, affecting the densely populated coastal regions along the western shoreline of the Gulf.

When the pollution is transported deeper over land, $\text{O}_3$ mixing ratios are generally lower due to rapid dilution of precursor gases in the very deep convective boundary layer over the desert.

1 Introduction

Enhanced levels of ozone ($\text{O}_3$) pollution can be a major problem by degrading air quality in (sub)urban and industrial areas, especially in summer when its photochemical formation by the oxidation of volatile organic compounds (VOC) and catalysed by nitrogen oxides ($\text{NO}_x$), is most efficient. From satellite observations it is known that $\text{NO}_x$ ($\text{NO}+\text{NO}_2$) concentrations in the Arabian Gulf area are exceptionally high (Stavrakou et al., 2008; van der A et al., 2008; Lelieveld et al., 2009). Mean concentrations of tropospheric $\text{NO}_2$ columns exceed $10 \times 10^{15} \text{ molec cm}^{-2}$ along the northern and western
coast of the Arabian Gulf (Beirle et al., 2011). Analysis of data retrieved from the TES satellite instrument reveal that O₃ concentrations are elevated in the lower and mid troposphere over the entire Middle East (Liu et al., 2009). Model calculations indicate that the Arabian Gulf region is strongly affected by photochemical smog due to high background levels of ozone by long-distance transport, highly favourable weather conditions for ozone formation and strong local pollution emissions (Lelieveld et al., 2009).

In general, climatic conditions over the Arabian Peninsula in summer are dry and hot with temperatures regularly exceeding 35 °C (Elagib and Abdu, 2010). Along the coast of the Gulf, humidity is often high in the afternoon hours due to the land-sea-breeze circulation (Hubert et al., 1983).

A frequent and persistent weather phenomenon over the Arabian Gulf in winter as well as summer are Shamal winds (Mernbel, 1983; Barth, 2001; Rao et al., 2003; Shi et al., 2004). The Shamal is a low level, thermally driven northerly to northwesterly flow, regularly reaching a speed of up to 30 m s⁻¹. During the night, the Shamal often weakens near the surface but strengthens at elevated levels (300–700 m) (Rao et al., 2003; Giannakopoulou and Toumi, 2011). Shamals are the predominant cause for dust outbreaks over Iraq and northern Saudi Arabia which impact visibility, air quality and the radiation budget throughout the Arabian Gulf region.

During winter, Shamals are known to be initiated after the southeastward passage of cold fronts (Perrone, 1979; Walters and Sjoberg, 1988). In summer, the semi-permanent high pressure system over the Eastern Mediterranean, which extends into northern Saudi Arabia, and a semi-permanent low pressure system over Iran lead to a north-westerly flow over the Arabian Peninsula and the Gulf (Rao et al., 2003). Rao et al. (2003) further hypothesised that conditions under which the monsoon low over India and Pakistan extends to the lee of the Zagros mountains and the south-eastern part of the Arabian Peninsula, are favourable for the outbreak of Shamals as the east-west pressure gradient is increased. The Zagros mountains to the east of the Gulf, which can exceed 2000 m altitude, strongly contribute to the channelling of the near surface air flow. Additionally they modulate the diurnal evolution of the Shamal
through orographic flows (Giannakopoulou and Toumi, 2011). Furthermore, the land-sea-breeze can modulate the Shamal by changes in the geostrophic wind component.

Particularly in summer a sea breeze regularly develops over the Arabian Gulf, however over the northern coast landward penetration of marine air masses is rare, whereas they can be advected more than 200 km inland along the south/south-western coast (Zhu and Atkinson, 2004; Eager et al., 2008). The vertical extent of the sea breeze is difficult to determine and in summer may reach an altitude of about 1.5 km (Zhu and Atkinson, 2004; Eager et al., 2008) with a return current above the onshore flow. At night the land-sea breeze over the Gulf is associated with uplift and convergence whereas during daytime it is associated with subsidence and divergence (Zhu and Atkinson, 2004). The sea breeze is initiated rather late during the day (13:00–14:00 LT) compared to other coastal areas (Eager et al., 2008). During strong Shamal conditions the sea breeze can be fully inhibited (Zhu and Atkinson, 2004).

The boundary layer over the Gulf is often very shallow and stable (Brooks and Rogers, 2000; Atkinson and Zhu, 2005; Brooks et al., 1999) as hot and dry air masses from the surrounding deserts are advected over the cooler sea resulting in a strong temperature inversion and a very shallow stable layer. Since this near-surface layer can form within an existing, deeper boundary layer it represents an “internal” boundary layer (Garratt, 1990; Angevine, 2008). If the Shamal is not too strong, thus allowing the sea breeze to develop, the onshore advection of relatively cool air from the Gulf toward the desert may also be associated with an internal boundary layer, possibly trapping air pollution near the surface in the coastal region. Highly stable marine boundary layers similarly occur e.g. over the Gulf of Maine affecting the transport and concentrations of trace gases as observed during the International Consortium for Atmospheric Research in Transport and Transformation (ICARTT)/New England Air Quality Study (Angevine et al., 2006; Fehsenfeld et al., 2006).

The objective of this study is to assess the influence of meteorological conditions (wind regime, high temperatures in summer, humidity conditions) on O$_3$ formation over the Arabian Gulf region. Further, we analyse the rate of photochemical O$_3$ formation
in view of uncertainties in the emission inventories of anthropogenic O$_3$ precursor sources.

2 Case study description

For our case studies, we have selected a period of five days in mid July (14–18) in the years 2009, 2010 and 2011. In general the potential for a buildup of high concentrations of O$_3$ is highest in summer (Lelieveld et al., 2009). During approximately half of the total of 15 days of simulation the wind direction in the boundary layer is northerly to north-westerly which is the predominant flow in July based on climatological data. However, the initial meteorological conditions on 14 July in all three years are rather distinct (Figs. 1 and 2) thus providing the opportunity to investigate O$_3$ formation under different ambient conditions, particularly focusing on (i) days and regions with and without the development of land-sea breeze systems and (ii) periods with and without Shamal winds.

2.1 Synoptic conditions

2.1.1 July 2009

Following the work of Rao et al. (2003) we have selected one simulation period favourable for a persistent Shamal over the Gulf. An upper level trough was located over Turkey accompanied by a ridge to the west across the Eastern Mediterranean and a ridge to the east over western Iran. The cyclone remained very stable over Turkey during the entire simulation period and propagated only slowly eastward. The surface pressure distribution shows a significant north-south gradient over the Arabian Gulf area as the Mediterranean high was strong with a ridge extending over central Saudi Arabia (Fig. 1). Such pressure conditions typically enhance the north-westerly flow near the surface (Rao et al., 2003). Compared to 2010 and 2011, wind speeds
over the Gulf were higher (maximum up to 20 m s\(^{-1}\)). Furthermore, the temperature on the simulation days in 2009 was lower (regionally more than \(\approx 5^\circ\text{C}\)) than in the years 2010 and 2011 (Fig. 2). The temperature differences between air masses over land and water were smaller leading to a higher boundary layer over water (compared to the years 2010 and 2011). Furthermore, meteorological conditions lead to a less efficient or inhibited sea breeze. A typical phenomenon over the Gulf is the development of a shallow inversion only a few hundred metres above the sea surface (\(\approx 950\text{ hPa}\)) capping a stable and moist marine boundary layer. At approximately 500 hPa a very dry subtropical subsidence inversion associated with the downward motion of the Hadley circulation is typical for most days in summer (Fig. 2) (Ackermann and Cox, 1982; Reid et al., 2008).

### 2.1.2 July 2010

On 14 July 2010 the 500 hPa flow over the eastern Mediterranean, Iraq and Iran was almost meridional. On 15 July a weak upper level trough formed over southern Turkey which slightly intensified in the following days while it slowly propagated north-eastward. The surface pressure chart is significantly different compared to the simulation period in 2009. A weakening of the Iranian low, with a simultaneous negative pressure tendency over central Saudi Arabia and the northern Gulf was unfavourable for the development of a Shamal (Fig. 1).

### 2.1.3 July 2011

On 14 July a cyclone was located over the Black Sea and propagated slowly south-eastward during the following days. Generally the surface pressure distribution was similar as during the Shamal period in 2009 with a distinctive surface low over the southern Gulf and a south-eastward penetrating Mediterranean high. However, a positive pressure tendency over central Iran, Qatar and the UAE weakened or inhibited the Shamal.
3 Model setup

The fully coupled chemistry version of the Weather Research and Forecasting model (WRF-chem) (Grell et al., 2005) version 3.3.1 was used for this study. The treatment of aerosols and aerosol-cloud interactions in WRF-chem is described in detail by Fast et al. (2006) and Chapman et al. (2009) and only a brief overview of the features most relevant in this study is given below.

Gas phase chemistry is calculated using the CBMZ mechanism (Zaveri and Peters, 1999). Direct and indirect aerosol effects are calculated in the model as described by Chapman et al. (2009). The representation of aerosol activation is based on the parametrisation by Abdul-Razzak et al. (1998) and its implementation into WRF-chem follows the description by Chapman et al. (2009) and references therein. Cloud microphysical processes are calculated using the scheme by Lin et al. (1983) with modifications in order to treat cloud drop numbers prognostically. For nests with horizontal resolutions requiring the usage of a convection parametrisation we use the scheme by Grell and Devenyi (2002). For calculating aerosol thermodynamics and microphysics the Module for Simulating Aerosol Interactions and Chemistry (MOSAIC) is used (Zaveri et al., 2008). Boundary layer physics is parametrised using the Yonsei University (YSU) PBL scheme (Hong et al., 2006).

Initial and boundary conditions for gas phase species for our simulations are derived from MATCH-MPIC (Model of Atmospheric Transport and Chemistry, von Kuhlmann et al., 2003) which is ran operationally as a global chemical weather forecasting model at the Max Planck Institute for Chemistry. Initial and boundary conditions for aerosol constituents are taken from simulations performed with the global chemistry-climate model EMAC (Pringle et al., 2010). For anthropogenic emissions we use the high resolution (0.1 x 0.1°) EDGAR-CIRCE emission inventory (Doering et al., 2009a) which has been prepared in the framework of the CIRCE Project (No. 036961) by the EDGAR group (Emission Database for Global Atmospheric Research) of the EC-Joint Research Center Ispra (Italy), Climate Change Unit and has been evaluated by Doering et al. (2009b).
The setup of our simulations comprises three nests with horizontal resolutions of 48 km, 16 km and 4 km and with a vertical resolution of 53 layers with narrowly spaced model levels in the lower troposphere. If not mentioned otherwise we refer in our analysis to the 16 km grid.

4 Results

4.1 O₃ distribution and variability

For our analysis we focus on the time of day when O₃ mixing ratios reach a maximum, i.e. at 12:00 UTC = 15:00 Local Time (Fig. 3). A general finding from our simulations encompassing a total time period of 15 days is that O₃ hot spots develop regularly over the Arabian Gulf, however the location and the intensity of the O₃ pollution can vary widely.

The boundary layer over the Gulf is shallow under all conditions, being relatively deepest for the simulation period in 2009 (∼200–400 m compared to ∼50–100 m in 2010 and 2011 around 12:00 UTC). It thus appears that the formation of O₃ hot spots over the Gulf is facilitated by the inhibition of vertical transport in regions with strong pollution emissions, so that both precursor gases and the resulting O₃ accumulate near the surface. Especially in the year 2009 the boundary layer is relatively low over the north-western part of the Gulf, which is in the region with highest VOC emissions.

On the first day (14 July, Fig. 3, first row) of the simulation period, high O₃ values are simulated during all three years over the northern Gulf region with a distinctive hot spot along the coast south of Kuwait. In 2010 and 2011 O₃ mixing ratios also exceed 80 nmol mol⁻¹ further inland in the late afternoon/early evening hours (especially in the area of Dammam/Al Jubayl) when the sea breeze transports polluted air over the coastal regions. Particularly on 14, 15 and 16 July 2010 the sea breeze is strong and O₃ mixing ratios are elevated (>60 nmol mol⁻¹) up to 50–100 km west of the coast line. On 15 July 2010, the weak background flow facilitates the earlier and stronger initiation of the sea breeze (about 08:00 UTC) compared to 14 July 2010, leading to the transport
of marine air masses over the coast during almost the entire day. At 12:00 UTC (15 July 2010) O$_3$ mixing ratios over the Gulf are very low, however, almost everywhere along the western coast they exceed 60 nmol mol$^{-1}$ (over land) with local maxima of more than 80 nmol mol$^{-1}$ (around 28° N). Especially in the area of Al Jubayl O$_3$ mixing ratios are higher on 15 July than on 14 July because (i) the sea breeze developed earlier, (ii) the boundary layer along the coast (up to ≈40 km inland) is lower on 15 July than on 14 July, thus trapping the locally formed pollution near the surface. In contrast to 2010 and 2011, on 14 July 2009 the pollution plume remains located over the sea during the whole day because the strong Shamal winds prevent the development of a sea breeze.

On the second day of the simulation (15 July 2009, Fig. 3, second row) high levels of O$_3$ build up again over the western Gulf where the persistent north-westerlies transport the pollution emitted in Kuwait over the Gulf which contributes to the photochemical transformation of local emissions further South, leading to the formation of O$_3$ mixing ratios of more than 100 nmol mol$^{-1}$. As a consequence of the rare event of a sea breeze developing over the northern part of the Gulf, on 15 July 2010 the highest local mixing ratios of O$_3$ (≈120–150 nmol mol$^{-1}$) are simulated along the coast of Kuwait. In the year 2011, O$_3$ mixing ratios are also elevated over the northern Gulf (≈80 nmol mol$^{-1}$) but in contrast to most other days extreme values of 100 nmol mol$^{-1}$ are not exceeded. The general explanation for the distinct horizontal distribution of surface O$_3$ on 15 July 2009, 2010 and 2011 is the changing wind direction. In 2009 the wind direction is persistently north-west, whereas it is southerly or south-easterly in 2010 during the night and in the morning. In 2011 the nighttime wind direction is also north-westerly, from Kuwait over the coastal area into northern Saudi Arabia. During the time of photochemical activity the outflow direction from Kuwait is southward over land. Mixing ratios of O$_3$ near the surface in that location are not as high as over the sea mainly due to the deep boundary layer (≈4.5 km in the outflow region south of Kuwait) leading to the efficient mixing and dilution of the O$_3$ plume. The same argument holds for the lack of O$_3$ hot spots over the Gulf on 16 and 17 July in 2009 and 2010.
The horizontal distribution of O$_3$, especially in the outflow region of Kuwait appears to be generally very similar on 16 July, (Fig. 3 third row) in 2009 and 2011 though mixing ratios are significantly higher in the latter year ($\approx 90$ nmol mol$^{-1}$ versus $\approx 60$ nmol mol$^{-1}$ in 2009) while the boundary layer height is very similar in both years. However, in 2011 a stable residual layer develops in the night between 15 and 16 July leading to elevated O$_3$ mixing ratios exceeding 60 nmol mol$^{-1}$ at 2000 m altitude throughout the night over north-eastern Saudi Arabia, facilitating long-distance transport from the north. When the boundary layer develops in the morning of 16 July the elevated O$_3$ mixing ratios from the lower free troposphere significantly contribute to the high near surface values (Fig. 4, right column).

As indicated above, the outflow of Kuwait can contribute strongly to the O$_3$ formation over the Arabian Gulf. On 15 July in 2011 pollution from Kuwait is transported mainly over Saudi Arabia or northward over Iraq. Despite the lacking transport of O$_3$ precursor gases from Kuwait (or more generally polluted coastal areas) over the sea, O$_3$ mixing ratios over the northern Gulf exceed 80 nmol mol$^{-1}$ at 12:00 UTC. In contrast, on 16 July in 2009 O$_3$ mixing ratios over the Gulf are relatively low ($\approx 40$ nmol mol$^{-1}$) even though the wind regime is similar as on 15 July in 2011. From Fig. 5a we can identify the regions with high VOC emissions over the northern Gulf region. The O$_3$ formation rate between 10:00 and 12:00 UTC on 16 July 2009 in the circled region in Fig. 5a, b is approximately 0.5–5 pmol (mol$^{-1}$ s) whereas it reaches values twice as high on 15 July 2011 (Fig. 5c), even though the emission strength of VOC’s in the area does not differ between the two years. Nevertheless, in 2011 surface VOC mixing ratios are almost a factor of two higher in this region (200–400 nmol mol$^{-1}$) compared to 2009 (50–100 nmol mol$^{-1}$). The difference is again a consequence of the substantially lower boundary layer over the Gulf in the nights between 14 and 15 July 2011 and 15 and 16 July 2009 ($\approx 100$ m in 2011 compared to 500 m in 2009). In addition to less efficient vertical mixing on 15 July 2011, the wind speed is lower than on 16 July 2009, and the reduced venting allows the buildup of high levels of O$_3$ precursor gases.
In our simulations we often see a second O$_3$ maximum building up off the coast of the United Arab Emirates (UAE). Especially in the area of Dubai (the location with highest NO$_x$ and VOC emissions in the UAE) a land breeze regularly develops during the night, transporting O$_3$ precursor gases and photochemcially produced O$_3$ from the previous days over the Gulf.

Interestingly, a third emission hot spot is located in the area of Dammam/Al Jubayl/Bahrain (Fig. 5a) though we rarely find very high O$_3$ mixing ratios (larger than 100 nmol mol$^{-1}$) directly related to precursor emissions from this region. Only under conditions that allow development of the nocturnal land-sea breeze, emissions from this region impact O$_3$ formation over the Gulf. However, these conditions (temperature gradients) are not as often fulfilled as along the UAE coast, at least in our simulation periods (e.g. 14 July 2010, 18 July 2011). Nevertheless, O$_3$ mixing ratios are regularly enhanced in this area with values of about 70 nmol mol$^{-1}$.

### 4.2 Chemical O$_3$ formation regimes

In several highly polluted regions around the globe model and field data analysis provide indications that O$_3$ formation is VOC limited (e.g. Song et al., 2010; Yang et al., 2011) whereas NO$_x$ limited O$_3$ production is reported for cities like Tokyo (Kanaya et al., 2008) and Chicago (Lin et al., 2010) for example. In the Arabian Gulf region NO$_x$ emissions are very high, mainly in and near the populated areas (Kuwait City, Dammam, Riyadh, Dubai) due to industry, the energy sector as well as land traffic and relatively intense ship emissions. High VOC levels are common in the atmosphere over the entire area due to emissions from oil drilling platforms in the Gulf, refineries located mainly near the coast as well as drilling fields and related industries further inland.

O$_3$ mixing ratios in locations for which NO$_x$ hot spots are simulated are never extraordinary high, partly due to O$_3$ titration by local NO emissions, whereas they can exceed 100 nmol mol$^{-1}$ in the outflow of the regions mentioned above. During night O$_3$ is almost completely depleted in these locations due to the titration by NO. Our simulations
indicate that O₃ formation is VOC limited only very close to the NOₓ sources while a few kilometres downwind O₃ formation rapidly enters into a NOₓ limited regime. To show the regional differences of O₃ formation regimes and compare the results with other studies, we apply the ratio of the production of hydrogen peroxide and nitric acid $P(\text{H}_2\text{O}_2)/P(\text{HNO}_3)$ as an indicator for VOC or NOₓ limited O₃ formation regimes (Sillman, 1995; Tonnesen and Dennis, 2000). Song et al. (2010) find that this ratio is always below 0.14 (= VOC limited) in Mexico City and mostly exceeds 0.24 (= NOₓ limited) downwind of the city with small areas where O₃ formation is in the transition regime. Figure 6 shows as an example $P(\text{H}_2\text{O}_2)/P(\text{HNO}_3)$ for 12:00 UTC on 14 July 2011. At this point in time O₃ mixing ratios exceed 100 nmol mol⁻¹ along the shoreline of the northern Gulf and over the centre of the Gulf. The wind direction in the morning hours of 14 July is westerly in northern Kuwait blowing polluted air masses eastward over the Gulf. The horizontal wind in Kuwait City has a stronger southerly component leading to a second outflow plume south of Kuwait which remains over land. O₃ formation in the southern plume is still VOC limited or in the transition regime up to ≈100 km downwind of the source region whereas it quickly turns into a NOₓ limited regime over the Gulf (≈30 km east of the coast). Several factors contribute to the differences in the chemical regimes of these two plumes: (i) the southern plume is blown over a region with little or no VOC emissions whereas the VOC load over the sea is much higher (due to local emissions there and to less efficient venting to higher altitudes) (ii) the southern plume is blown along the coast where the boundary layer is not as high as further inland which, on other days, leads to a more efficient (vertical) dilution of the plume (e.g. 15 July 2011, 16, 17 July 2009) and (iii) the wind speed along the coast is higher than over the northern Gulf leading to a faster removal by the southern plume by transport.

Similar as in Kuwait, O₃ formation is also VOC limited downwind of Dammam, Bahrain, Dubai and Riyadh.

Our results indicate that in general O₃ formation is mainly NOₓ limited during episodes of very high O₃ mixing ratios (>90 nmol mol⁻¹) with very few exceptions (Fig. 7). During the first hours of photochemical activity until ≈09:00 UTC O₃ formation
is VOC limited in more locations near the main emission sources, however only until the formation of NO$_2$ and HO$_2$ by VOC oxidation products start dominating O$_3$ formation over almost the entire Gulf region.

**4.3 O$_3$ response to changing emissions**

Since the simulated O$_3$ mixing ratios strongly depend on the emission source strength and as all state-of-the-art inventories for anthropogenic emissions are associated with substantial regional uncertainties, we performed a series of sensitivity simulations with varied emissions for NO$_x$ and VOC for the year 2011. Additionally, these sensitivity simulations help us quantifying the impact of the pollution outflow of certain coastal cities on O$_3$ formation over the Gulf. Since we found that especially the outflow of Kuwait can significantly impact O$_3$ formation over the Gulf region, a series of sensitivity simulations focus on emission reduction scenarios for Kuwait and the impact on O$_3$ formation downwind of the Kuwait outflow (Table 1). We have conducted a second set of sensitivity studies with reduced emissions for the entire region around the Arabian Gulf.

Reducing both, VOC and NO$_x$ emissions from Kuwait by 50% results in a decrease of O$_3$ mixing ratios in the outflow region by up to 10–15% on 15 July 2011 and by 15–20% on 16 July 2011 (Fig. 8). Decreasing VOC emissions only (VOC$_K$), leads to an even stronger decrease of O$_3$ mixing ratios downwind of Kuwait by more than 30% (15 July) and to a decrease of up to 65 nmol mol$^{-1}$ (more than 50%) for 16 July 2011 at times and locations of maximum O$_3$ (over the northern Arabian Gulf). Reducing only NO$_x$ emissions leads to a significant increase in O$_3$ mixing ratios in Kuwait and downwind of the city. Over the northern Gulf, O$_3$ mixing ratios are decreased due to lower NO$_x$ background levels due to reduced emissions from Kuwait.

Less efficient titration of O$_3$ by NO under conditions with lower NO$_x$ emissions contributes to the increase in O$_3$ mixing ratios in scenarios ALL$_K$ and NOX$_K$.

We discussed above that the relatively low O$_3$ mixing ratios on 15 July 2011 can be explained by the changing wind directions compared to 16 July, transporting polluted
air masses from the Kuwait area south over land. Indeed we hardly see any differences in O\textsubscript{3} mixing ratios from the emission reduction scenarios compared to our base simulation over the northern Gulf on 15 July (\(\Delta \text{O}_3 \approx 2 \text{nmol mol}^{-1}\)). However, mixing ratios in the outflow of Kuwait decrease significantly on 16 July 2011 in scenarios NOX\textsubscript{K}, VOC\textsubscript{K} and ALL\textsubscript{K}.

When decreasing anthropogenic emissions in the entire region around the Arabian Gulf, scenario NOX\textsubscript{A} leads to the strongest reduction in O\textsubscript{3} concentrations. Nevertheless, O\textsubscript{3} mixing ratios would still exceed strongly European and American air quality standards, though for a shorter time period.

5 Discussion

Our analysis of the O\textsubscript{3} build-up over the Arabian Gulf region indicates that meteorological conditions to a large degree control the strength of pollution events. The formation of thermal internal boundary layers over the Gulf and in coastal regions can strongly reduce vertical mixing and dilution of the emissions caused by traffic and industry, effectively trapping the air pollution near the surface. Near-surface boundary layer heights over the Gulf often do not exceed a few hundred meters. Further, the strength of the Shamal wind plays an important role, not only directly through the south-easterly transport of pollution plumes, but also indirectly by its regulatory role of sea breeze circulations. In turn, the strength of the Shamal is modulated by the pressure gradient between the eastern Mediterranean ridge and the Persian trough, the latter being an extension of the South Asian monsoon over the Arabian Sea. When the Shamal is strong the sea breezes can be suppressed, whereas in the reverse case, at wind speeds of a few meters per second or less, they typically develop in the afternoon. The sea breeze circulations transport relatively cool and moist surface air over land, and the temperature inversion between these marine air masses and the hot desert air aloft prevents vertical mixing from the internal boundary layer. Again this traps pollution near the surface, though not as efficient as in the very shallow boundary layer.
over the Gulf. Deeper inland, sometimes up to 100 kilometres from the coast, the dry convection over the desert erodes the inversion, leading to efficient vertical mixing up to 5 kilometres altitude. It was hypothesised by Lelieveld et al. (2009) and indicated in the studies by Li et al. (2001) and Liu et al. (2009) that the region is strongly influenced by long-range transport of air pollution, with the possible consequence that it is difficult to reduce $O_3$ mixing ratios over the Gulf by applying more strict local emission controls. Measurements of aerosol concentrations and back-trajectory calculations, conducted during the United Arab Emirates Unified Aerosol Experiment, also indicate that long-range transport of aerosols from eastern Europe and Africa contribute to the local particulate mass (Reid et al., 2008). Even though our present study does not focus on the contribution by long-range transport, we find that it is largely limited to the boundary layer. During one occasion (15–16 July 2011) it appears that long-range transport of $O_3$ enriched air contributed to enhanced $O_3$ mixing ratios in a night-time residual boundary layer ($\sim 2$ km altitude). After a deep convective boundary layer developed over the desert, the pollution was mixed to the surface. We also analysed the contribution of large-scale subsidence of $O_3$ rich mid-tropospheric air into the boundary layer, and do not find substantial effects on boundary layer $O_3$ mixing ratios. The largest contribution of large-scale subsidence (1–4 nmol mol$^{-1}$) is found over coastal areas in the late afternoon and early evening hours where subsidence is strong and the boundary layer can still reach altitudes of 1–3 km. Although these subsiding $O_3$-rich air masses pre-condition the photochemical regime, the development of extreme pollution events in summer, with near-surface $O_3$ levels exceeding 100 nmol mol$^{-1}$, are largely attributed to local emissions.

The study by Lelieveld et al. (2009), using a global chemistry-climate model (EMAC), suggests that $O_3$ mixing ratios generally exceed European air quality standards ($\sim 55$ nmol mol$^{-1}$ during 8 h) in summer over large areas. The present study, which provides greater detail by the simulation of small-scale meteorological conditions, shows that even though average $O_3$ mixing ratios are typically high along the western Gulf coast, episodes of very high ozone alternate with periods of moderate $O_3$ levels.
(<55 nmol mol\(^{-1}\)). The course grid resolution of EMAC (\(\sim 100 \text{ km}\)) is insufficient to resolve the sea breeze circulation systems, although the Shamal and the boundary layer height over the Gulf are reasonably well represented. For locations deeper inland, for example in Riyadh, being a city with very high NO\(_x\) emissions (Beirle et al., 2011), our present simulations show enhanced O\(_3\) mixing ratios (>55 nmol mol\(^{-1}\)) mostly in events during which pollution plumes are advected from Kuwait or the Bahrain/Dammam/Al Jubayl area, as the local emissions in Riyadh rather titrate O\(_3\), leading to high NO\(_2\) mixing ratios. Due to the high boundary layer over the desert (up to 5 km) the locally emitted pollutants are efficiently mixed and diluted throughout the lower atmosphere.

With a horizontal model resolution of 16 km, as used for most of our current analysis, we may nevertheless underestimate local O\(_3\) mixing ratios due to resolution limitations (Tie et al., 2010). Indeed, in the 4 km resolution domain O\(_3\) mixing ratios over the Gulf can even exceed 200 nmol mol\(^{-1}\) on 14 July 2010, and on 14 and 16 July 2011. However, the spatial patterns of O\(_3\) are very similar compared to the 16 km horizontal resolution version of the model, indicating that Shamal winds and sea breezes are represented realistically.

For a more accurate quantification of O\(_3\) mixing ratios in the region the major issue is probably the limited knowledge of NO\(_x\) and VOC emissions in and around the Arabian Gulf region, whilst the present study relies on a global emission dataset (Doering et al., 2009a,b). There is also a need to improve the knowledge of the speciation of VOCs emitted in the region since the O\(_3\) production potential among various VOCs can differ substantially (Butler et al., 2011). Finally, we recommend that measurements are performed and made available to test and improve model results.

6 Conclusions

We investigated the role of meteorological conditions in the build-up of O\(_3\) over the Arabian Gulf, including severe O\(_3\) pollution events. Episodes with O\(_3\) mixing ratios
exceeding 150 nmol mol\(^{-1}\) appear to occur regularly, however, the location and the magnitude of such events can vary widely. Important factors include the northwesterly Shamal winds and sea breeze circulation systems. Mixing ratios of O\(_3\) are highest in the outflow from regions with major anthropogenic emissions along the coast, typically when the air is advected over the sea where the pollution plume is captured in the very shallow and stable marine boundary layer allowing little ventilation. The emissions of O\(_3\) precursor gases from oil drilling platforms, trans-shipment activities and exhausts from ship traffic enhance the O\(_3\) production potential over the sea. However, without the transport of NO\(_x\) and VOC rich air masses from the coastal region, polluted by road transport, energy production and petrochemical industries, these offshore emissions would only moderately enhance the formation of O\(_3\) (~60 nmol mol\(^{-1}\)), and not lead to mixing ratios in excess of 100 nmol mol\(^{-1}\). Though we simulate maximum O\(_3\) mixing ratios over the Arabian Gulf, the onshore advection in sea breeze circulations affects the coastal region along the western shores, being most densely populated. In cases of advection of pollution plumes over land rather than over the sea, O\(_3\) mixing ratios are generally lower due to the more efficient mixing and dilution of O\(_3\) and precursor gases in the very deep convective boundary layers over the desert. Our analysis of O\(_3\) production regimes reveals that O\(_3\) formation is only VOC limited in urban regions with high NO\(_x\) emissions such as Kuwait, Bahrain, Dubai and Riyadh. Downwind of these cities and in most of the Arabian Gulf region the O\(_3\) formation is NO\(_x\) limited.

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Table 1. Overview of simulated scenarios with reduced anthropogenic emissions.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Description</th>
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<tbody>
<tr>
<td>ALL_K</td>
<td>NO\textsubscript{X}, VOC reduced by 50 % for Kuwait region</td>
</tr>
<tr>
<td>NOX\textsubscript{K}</td>
<td>NO\textsubscript{X} reduced by 50 % for Kuwait region</td>
</tr>
<tr>
<td>VOC\textsubscript{K}</td>
<td>VOC reduced by 50 % for Kuwait region</td>
</tr>
<tr>
<td>ALL_A</td>
<td>NO\textsubscript{X}, VOC increased by 50 % for the Gulf region</td>
</tr>
<tr>
<td>NOX\textsubscript{A}</td>
<td>NO\textsubscript{X} increased by 50 % for the Gulf region</td>
</tr>
<tr>
<td>VOC\textsubscript{A}</td>
<td>VOC increased by 50 % for the Gulf region</td>
</tr>
</tbody>
</table>
Fig. 1. Sea-level pressure (hPa) at the surface (upper row) and geopotential (gpm) at 500 hPa (lower row) at 12:00 UTC, 14 July 2009, 2010 and 2011 (48-km domain).
Fig. 2. Skew-log-T diagrams for Dammam at 00:00, 14 July and 12:00 UTC, 16 July. Dotted: WRF-chem, solid line: sonde measurements (University of Wyoming, http://weather.uwyo.edu/upperair/sounding.html).
Fig. 3. Surface O$_3$ mixing ratios at 12:00 UTC on 14–18 July 2009 (left column), 2010 (middle column) and 2011 (right column).
Fig. 4. Cross section along 28° N showing O$_3$ mixing ratios at 06:00, 08:00 and 10:00 UTC, 16 July. The black lines indicate the boundary layer height.
Fig. 5. Total VOC emissions (nmol mol$^{-1}$) in the lowest model layer (a). Net O$_3$ production (nmol/(mol$^{-1}$ h)) in the lowest model level at 12:00 UTC on 16 July 2009 (b) and 15 July 2011 (c).
Fig. 6. $P(\text{H}_2\text{O}_2)/P(\text{HNO}_3)$ at 12:00 UTC on 14 July 2011 at the surface.
**Fig. 7.** Surface $O_3$ mixing ratios for all grid points within the coastal area of the northern Gulf (see marked area in Fig. 3, 18 July 2009), 12:00 UTC, 14–16 July 2009 (left column), 2010 (middle column) and 2011 (right column). Lines in the plots indicate the 4:1, 8:1 and 15:1 ratios between VOC’s and NO$_x$. The colour bar shows $O_3$ mixing ratios (nmol mol$^{-1}$).
Fig. 8. Relative difference in surface O$_3$ mixing ratios (%) between scenarios with different emissions for Kuwait at 12:00 UTC, 15 July 2011 (upper row) and 12:00 UTC 16 July 2011 (lower row). The emission scenarios are listed in Table 1.