Diel peroxy radicals in a semi-industrial coastal area: nighttime formation of free radicals

M. D. Andrés-Hernández¹, D. Kartal¹, J. N. Crowley², V. Sinha²,³, E. Regelin², M. Martínez-Harder², V. Nenakhov¹, J. Williams², H. Harder², H. Bozem²,³, W. Song², J. Thieser², M. J. Tang², Z. Hosaynali Beigi³, and J. P. Burrows¹

¹Institute of Environmental Physics, University of Bremen, Bremen, Germany
²Max Planck Institute for Chemistry, Mainz, Germany
³Indian Institute of Science Education and Research Mohali, Department of Chemical Sciences, Sector 81, S.A.S. Nagar, Manauli PO, Punjab 140306, India

*now at: Institute for Atmospheric Physics, University of Mainz, Mainz, Germany

Correspondence to: M. D. Andrés-Hernández (lola@iup.physik.uni-bremen.de)

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Abstract. Peroxy radicals were measured by a PeRCA (Peroxy Radical Chemical Amplifier) instrument in the boundary layer during the DOMINO (Diels Oxidant Mechanisms In relation to Nitrogen Oxides) campaign at a coastal, forested site influenced by urban-industrial emissions in southern Spain in late autumn. Total peroxy radicals (RO₂⁺ = HO₂ + ΣRO₂) generally showed a daylight maximum between 10 and 50 pptv at 13:00 UTC, with an average of 18 pptv over the 15 days of measurements. Emissions from the industrial area of Huelva often impacted the measurement site at night during the campaign. The processing of significant levels of anthropogenic organics leads to an intense nocturnal radical chemistry accompanied by formation of organic peroxy radicals at comparable levels to those of summer photochemical conditions with peak events up to 60–80 pptv. The RO₂ production initiated by reactions of NO₃ with organic trace gases was estimated to be significant, but not sufficient to account for the concentrations of RO₂⁺ observed in air masses carrying high pollutant loading. The nocturnal production of peroxy radicals in those periods seems therefore to be dominated by ozonolysis of volatile organic compounds, in particular alkenes of industrial petrochemical origin.

RO₂⁺ diurnal variations were consistent with HO₂ measurements available at the site. HO₂/RO₂⁺ ratios generally varied between 0.3 and 0.6, though on some occasions this ratio was likely to have been affected by instrumental artifacts (overestimated HO₂) associated with high RO₂ loads.

1 Introduction

Hydroperoxy (HO₂) and alkyl peroxy (RO₂⁺; R = organic chain) radicals are short-lived species involved in most of the photo-oxidation mechanisms taking place in the troposphere. General features of the radical chemistry in the troposphere are determined by the presence of NO and volatile organic compounds (VOC), (Monks, 2005 and references therein) and comprise radical propagation mechanisms leading to formation of secondary oxidants like O₃, and termination mechanisms i.e., radical recombination forming peroxides. RO₂ and HO₂ (HO₂ = HO₂ + OH) are intermediates of many reactions and due to the balance between propagation and termination mechanisms it remains difficult to predict the actual radical levels and their effect on O₃ production for a particular environment. Recent investigations indicate the impact of halogen chemistry and the existence of still unknown radical recycling mechanisms which might be crucial in explaining discrepancies between modelled and measured radical concentrations in some environments (Lelieveld et al., 2008; Dillon and Crowley, 2008; Hofzumahaus et al., 2009; Kubistin et al., 2010; Whalley et al., 2010, 2011).

Peroxy radicals can also be non-photochemically generated by reactions of organic species with O₃ and NO₂. As identified by Platt et al. (1990) nighttime RO₂ production in coastal areas and under certain other specific conditions, like in forests or air masses affected by urban emissions or biomass burning, can be as significant.
as photochemical production. For example, dimethyl sulfide (DMS) can react with NO$_3$ (formed by the reaction of NO$_2$ with O$_3$) and produce significant levels of peroxy radicals (Sommariva et al., 2007). Nighttime chemistry in clean coastal and marine areas has generally been investigated with emphasis on the characterisation of O$_3$ destruction events (Carslaw et al., 2002; Burkert et al., 2001a, 2003; Andrés Hernández et al., 2001). Under such conditions, relatively low nighttime mixing ratios of peroxy radicals have been measured, occasionally acquiring mixing ratios up to 25 pptv (Salisbury et al., 2001; Fleming et al., 2006a).

Peroxy radical chemistry has generally received little attention in late autumn and winter periods when levels of solar radiation are low and photochemistry is less effective. However, some seasonality studies show that in winter significant oxidant levels are sustained while the net effect with respect to production of ozone is unclear (Harrison et al., 2006; Fleming et al., 2006b; Heard et al., 2004; Kanaya et al., 2008). Furthermore, diel measurements of peroxy radicals in complex environments are scarce yet important for a better understanding of the combined effect of natural and anthropogenic emissions on local and regional air quality.

The present paper reports on the radical chemistry observed during the DOMINO (Diel Oxidant Mechanisms In relation to Nitrogen Oxides) measurement campaign in late autumn and early winter 2008 in a photochemically complex environment. The role of day and night-time peroxy radicals was investigated by measuring peroxy radicals along with a suite of simultaneously measured chemical and meteorological parameters.

2 Experimental

The DOMINO measurement campaign took place at the Spanish atmospheric research station “El Arenosillo” (37°05′58″ N, 6°44′17″ W) in November–December 2008. Due to its location in the nature reserve Doñana near the Atlantic Coast and close to the industrial and harbour area of the city of Huelva, the measurement site is periodically influenced by emissions of marine, biogenic, urban and industrial origin. In particular, the industrial area includes one of the most important European oil refineries and the largest pulp/paper mill of Spain. The measurement site has been described in detail in Crowley et al. (2011), Sinha et al. (2012), and Song et al. (2011).

The Institute of Environmental Physics of the University of Bremen (IUP-UB) participated in DOMINO with the measurement of the total sum of peroxy radicals, defined as RO$_2^+$ = HO$_2$ + ΣRO$_2$ from 23 November to 11 December 2008. RO$_2^+$ was measured using a DUALER (DUAl channel Peroxy radical chemical amplifier) adapted for ground based measurements. This instrument is based on the PeRCA (Peroxy Radical Chemical Amplification) technique using two identical lines working in alternate modes, i.e., the amplification mode resulting from the chemical conversion of RO$_2^+$ into NO$_2$ in a chain reaction above the NO$_2$ background levels, and the background mode comprising NO$_2$ and all NO$_2$ sources other than radicals in the air sampled and up to the detector such as reaction of NO with O$_3$ or the decomposition of PAN in the inlet, etc. (Kartal et al., 2010; Andrés-Hernández et al., 2010). NO$_2$ is measured by detecting the chemiluminescence of its reaction with luminol (3-aminophthalhydrazide: C$_8$H$_7$N$_3$O$_2$).

The DUALER methodology as first suggested by Cantrell et al. (1996) enables the calculation of RO$_2^+$ mixing ratios from the difference between the simultaneous NO$_2$ amplification signal of one of the detectors and the NO$_2$ background signal of the other, provided the length of the amplification chain (i.e., chain length: CL) at the reactors is known and both detectors are well characterised. In contrast to the standard PeRCA methodology, the background signal does not need to be interpolated during the measurement of the amplification signal, which effectively increases the temporal resolution. Careful characterisation of both measurement lines (i.e., NO$_2$ and RO$_2^+$ calibrations of detectors and reactors, respectively) is therefore required in order to prevent biases in the measurement. Variations in the NO$_2$ detector sensitivities are monitored by performing NO$_2$ calibrations. Each detector was calibrated twice per day during DOMINO. Glass reactors were used during DOMINO as in previous ground based measurements (Burkert et al., 2001b, 2003; Andrés Hernández et al., 2001). The DUALER detection limit and accuracy are closely related to the relative humidity (RH) dependency of the CL. Similar to Reichert et al. (2003) the CL was characterised in the laboratory for various RH. Continuous RH measurements at the site were used for the calculation of time dependent CL values and RO$_2^+$ mixing ratios.

For the set up deployed within DOMINO the total 1σ uncertainty of 1 min RO$_2^+$ averages is 30 % and the detection limit 1–3 pptv for RH up to 50 %. Those values increase to 60 % and 5–10 pptv, respectively, for RH between 70 % and 90 %. Except when otherwise specified, the DUALER RO$_2^+$ data presented in this work are 10 min Savitzky Golay averaged. Due to instrumental calibrations RO$_2^+$ data are not available on the 25 November.

As with most other DOMINO instruments, the DUALER double inlet for the RO$_2^+$ measurements was located on the top of a 10 m scaffold approximately 4 m above the canopy and was connected to the instrumental rack placed in a container on the ground (Fig. 1).

2.1 Other data

A suite of chemical species was measured during DOMINO by different research institutes and has mostly been described in publications within a DOMINO special issue in this journal (http://www.atmos-chem-phys.org/specialissue246.html; Sörgel et al., 2011; Crowley et al., 2011; Sinha et al., 2012;
Diesch et al., 2012). Table 1 briefly summarises the main features of the instruments providing data for the present study.

HO$_2$ radicals were measured by Fluorescence Assay with Gas Expansion (FAGE) with the HORUS instrument during DOMINO. A detailed description of the HORUS instrument can be found in Martinez et al. (2010). HORUS is based on the ATHOS instrument, for which a detailed study of possible interferences was performed by Ren et al. (2004). Recently Fuchs et al. (2011) reported on an RO$_2$ interference for HO$_2$ measurements by laser induced fluorescence (LIF) which is dependent upon detection cell design, residence time within the cell and NO level injected to titrate HO$_2$ to OH. This interference can be significant in conditions with very high VOC and low NO$_x$. HO$_2$ data presented here should be considered as an upper limit for HO$_2$, which is henceforth defined as HO$_2$ = HO$_2$ + $\varepsilon$RO$_2$; $\varepsilon$ was not quantified for HORUS during this campaign. Although $\varepsilon$ depends highly on the kind of RO$_2$ present, values of $\varepsilon < 0.2$ have been observed in two other ground-based measurement campaigns using the HORUS setup.

Local winds measured on the site at approximately inlet height (Diesch et al., 2012), were complemented by backward trajectories calculated using HYSPLIT for the classification of the air masses measured during DOMINO (Draxler and Rolph, 2011).

3 Results and discussion

The measurements reveal that the composition of the air masses arriving at the DOMINO site is the result of a complex mixture of weak biogenic (Song et al., 2012) and strong anthropogenic sources nearby. This is reflected in the high variability in the concentration level of most of the trace gases studied. NO$_x$ and VOC profiles were plume-like rather than having a structured reproducible diel pattern over the campaign. Time series of some selected trace gases are plotted in Figs. 2 and 3.

Generally, northerly wind directions coming from the NW and NE predominate (see a map of the location in Fig. 1). Prior to mixing with low wintertime biogenic emissions from the pine and eucalyptus forest in the national park (Song et al., 2012), the air masses were often exposed to fresh urban and industrial emissions of Huelva (the industrial area is located at 25 km NW) or Seville (at 70 km NE). Southwesterly winds associated with air masses of clean marine origin with occasional ship traffic occurred less frequently.
Table 1. Main features of the DOMINO instruments used in this study. IUP-UB: Institute for Environmental Physics of the University of Bremen; MPI: Max Planck Institute; U. Mainz: University of Mainz; LIF (FAGE): Laser Induced Fluorescence (Fluorescence Assay with Gas Expansion); OA-CRD: Off Axis Cavity Ring Down; Chemilum./Phot. con.: Chemiluminiscence/Photolytical conversion; TD-GC-MS: Thermal Desorption Gas Chromatography – Mass Spectrometry; CRM-PTR-MS: Comparative Reactivity Method Proton Transfer Mass Spectrometry. (*) NO\textsubscript{3} was calculated from measured N\textsubscript{2}O\textsubscript{5} and NO\textsubscript{2} (see Crowley et al., 2011 for details).

<table>
<thead>
<tr>
<th>Instrument/Institute</th>
<th>Principle Species</th>
<th>Time Resolution (s)</th>
<th>Detection limit</th>
<th>Uncertainty</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUALER/ IUP-UB</td>
<td>Chemical amplification ( \text{RO}_2^* = \text{HO}_2 + \Sigma \text{RO}_2 )</td>
<td>60</td>
<td>1–3 pptv (( \text{RH} \leq 50% ))</td>
<td>30% for ( \text{RH} \leq 50% )</td>
<td>this paper</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5–10 pptv (( \text{RH} &gt; 70% ))</td>
<td>60% for ( \text{RH} &gt; 70% )</td>
<td></td>
</tr>
<tr>
<td>HORUS/ MPI-Mainz</td>
<td>LIF (FAGE) ( \text{OH, HO}_2 )</td>
<td>60</td>
<td>0.037 pptv</td>
<td>18%</td>
<td>Martinez et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>OA-CRD ( \text{NO}_3, \text{N}_2\text{O}_5 )</td>
<td>5</td>
<td>0.29 pptv</td>
<td>18%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5–7 pptv*</td>
<td>35%*</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Crowley et al. (2011)</td>
</tr>
<tr>
<td>CLD-790 SR Ecophys/MPI-Mainz</td>
<td>Chemilum./Phot. con. ( \text{NO, NO}_2 )</td>
<td>1</td>
<td>6 pptv</td>
<td>5%</td>
<td>Hosaynali Beygi et al. (2011)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8 pptv</td>
<td>8%</td>
<td></td>
</tr>
<tr>
<td>Airpointer/ U. Mainz</td>
<td>UV photometry UV fluorescence ( \text{O}_3, \text{SO}_2 )</td>
<td>6</td>
<td>&lt;1 ppbv</td>
<td>1 ppbv</td>
<td>Diesch et al. (2012)</td>
</tr>
<tr>
<td>Aero Laser AL 4021/ MPI-Mainz</td>
<td>Hantzsch reaction ( \text{HCHO} )</td>
<td>160</td>
<td>22 pptv</td>
<td>29%</td>
<td>Kelly and Fortune (1994)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Song et al. (2011)</td>
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<td></td>
<td>Sinha et al. (2008)</td>
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</tbody>
</table>

**Fig. 2.** Time series of selected trace gases measured during DOMINO.

Sinha et al. (2012) and Diesch et al. (2012) investigated the consistency in the air mass classification based on back trajectories and wind direction measured at the site during DOMINO and identified three major wind sectors: continental, comprising aged air masses coming from the interior of the Peninsula; 340–110°; urban-industrial, corresponding to city, port and industrial area of Huelva: 270–340°; and marine: 150–270°. Diesch et al. (2012) defined further subsectors: 65–82° for air passing across Seville city, and 265–300° for urban air masses having marine influence.

### 3.1 General peroxy radical features during DOMINO

Figure 4 depicts the RO\textsubscript{2}\textsuperscript{*} time series measured during the campaign. Most diel periods showed a RO\textsubscript{2}\textsuperscript{*} maximum at about 12:00–13:00 UTC reflecting photochemical RO\textsubscript{2}\textsuperscript{*} production during daylight (note that the solar zenith is at 11:30 UTC; sunrise and sunset at 07:00 and 17:00 UTC, respectively) and significant production in the evening hours with RO\textsubscript{2}\textsuperscript{*} generally reaching a maximum around midnight. HO\textsubscript{2} radicals measured by the HORUS instrument are also included for comparison. RO\textsubscript{2}\textsuperscript{*} and HO\textsubscript{2} diurnal variations did mostly agree throughout the campaign. However, due to instrumental calibrations, nighttime HO\textsubscript{2} data was not always available.

Variations in the short-lived species such as peroxy radicals, which are not transported significantly, are expected to be indicators of the in-situ composition of the air mass. The influence of meteorology and air mass type on radical concentrations was investigated by analysing the distribution of RO\textsubscript{2} with respect to the local wind direction at the site (Fig. 5). For this, measurements on three periods of similar meteorology defined by Diesch et al. (2012) were examined together: until the 3 December sunny days, clear skies and stable nocturnal boundary layer prevailed except on the
28 November to 30 December when short rain periods occurred in the night. The rest of the campaign was cloudy with nearly constant temperature (15–16 °C) and relative humidity (>70%) near the ground. Only mixing ratios measured at wind speed > 1.5 m s\(^{-1}\) are considered in order to rule out potential local interferences due to stagnant conditions at the site. Radicals measured during daylight periods (06:00–17:00 UTC, uppermost windroses) are separated from the rest.

As expected, highest \(\text{RO}_2^*\) mixing ratios are associated with clear sky stable conditions prevailing until the 28 November. For the rest of the campaign \(\text{RO}_2^*\) levels are lower (around 10–15 pptv daylight maximum).

No definite air mass dependence of the \(\text{RO}_2^*\) mixing ratios is expected in such a complex environment. VOC originating from different sources may provide different mixtures of precursors leading to the in-situ production of the \(\text{RO}_2^*\) measured. However, general patterns related to known chemistry (e.g., anti-correlation of NO with \(\text{RO}_2^*\) due to their common reaction, high \(\text{RO}_2^*\) at high organic loads accompanied by high OH reactivities, etc.) are expected to be identifiable. In that context, two features can be highlighted during DOMINO:

1. The highest daylight mixing ratios and tightest correlations between \(\text{RO}_2^*\) and \(\text{HO}_2^*\) (Fig. 6) were associated with air masses within the continental sector, which in turn were linked to clear sky conditions, favouring photochemical radical production, and,

2. enhanced nocturnal \(\text{RO}_2^*\) were observed mainly when the site was impacted with air masses coming from the urban-industrial sector transporting emissions from Huelva.

Concerning (1) the highest daytime \(\text{RO}_2^*\) maximum was found on the 23 and 24 November (47 ± 10 and 35 ± 10 pptv, respectively) when the highest temperatures of the campaign were reached (\(T_{\text{max}}\) 22 °C and 18 °C, respectively) as shown in Fig. 4. This positive relation with the temperature has been interpreted in previous work as an indirect effect driven by increases in the emission of radical precursors of biogenic origin with the temperature. In this context, pine trees tend not to generate monoterpenes instantaneously in response to light or temperature, but rather continuously through respiration with the monoterpenes being stored in resin ducts within the needle, the rate of release increasing with the temperature.

This is only partly reflected in the measurements. The monoterpenes \(\alpha\)-pinene, limonene, 1,8-cineole and camphor generally did not show any clear diel cycle. However, on the 24 November the mean mixing ratio of the sum of monoterpenes was 37 ± 25 pptv, in contrast to 23 ± 13 pptv measured on the 23 November. This is about twice the level measured on all other clear days (Song et al., 2012). On the 23 November isoprene increased steadily and reached a 120 pptv maximum in the afternoon at 16:00 UTC, a value of about a factor 10 higher than the average during the whole measurement period. Song et al. (2012) interpret the delay in the isoprene maximum with respect to the temperature maximum as an indication of isoprene not being emitted from the local forest, but transported from other more distant forests and orange groves in the NE direction.

Concerning (2) the importance of local forest emissions in the nighttime measurements was further investigated. Despite differences in the measurement time resolution, \(\text{RO}_2^*\) and isoprene diel variations agreed reasonably, and nocturnal maxima were often accompanied by \(\alpha\)-pinene peak concentrations as on the 24 November at midnight. These nighttime maxima suggest the release of monoterpenes into a shallow nocturnal boundary layer. However, the \(\text{RO}_2^*\) production estimated from the ozonolysis of isoprene and \(\alpha\)-pinene can account for maximum 10% and 30%, respectively, of the \(\text{RO}_2^*\) measured. The nocturnal \(\text{RO}_2^*\) production is discussed more in detail in Sect. 3.3.

3.2 Diurnal photochemical radical production

\(\text{RO}_2^*\) and \(\text{HO}_2^*\) measured during clear sky conditions, are summarised in Fig. 7. Except for the 24 November, air masses arriving on clear sky days at the site belong to the continental sector. Sinha et al. (2012) reported the highest average OH reactivity (defined as the total loss rate of OH radicals) in air masses from the continental sector, indicating high organic load which generally resulted in \(\text{NO}_x\) limited \(\text{O}_3\) production at the site. This is confirmed by the variation
with the wind sector of $O_3$ and NO mixing ratios and OH reactivity on these days depicted in Fig. 8. Highest OH reactivity correlates with lowest NO and highest RO$_2^*$ mixing ratios. As indicated in the previous section, the highest RO$_2^*$ and HO$_2$ diurnal mixing ratios were measured on the 23 November while NO remained below 200 pptv. At significant NO concentrations RO$_2^*$ and NO are expected to be anticorrelated as a result of their reaction forming NO$_2$. However, no clear correlation between RO$_2^*$ and NO was observed during the campaign (see Fig. S1 in the Supplement). The variation of the HO$_2$/RO$_2$ ratio with NO is discussed more in detail in Sect. 3.4.

The measured RO$_2^*$ were compared with estimations based on the deviation of the photostationary state (PSS) between NO, NO$_2$ and O$_3$ (Leighton, 1961):

\[
\text{NO} + O_3 \rightarrow NO_2 + O_2 \quad k_{\text{NO}+O_3} \quad (R1)
\]
\[
\text{NO}_2 \quad h\nu \rightarrow \text{NO} + O \quad J(\text{NO}_2) \quad (R2)
\]
\[
O_2 + O \quad M \rightarrow O_3 \quad (R3)
\]

Provided that RO$_2^*$ radicals are the only oxidation agent causing the PSS deviations, the $[RO_2^*]$ expected for midday periods with sufficient solar radiation can be calculated as:

\[
[RO_2^*]_{\text{PSS}} = \frac{J(\text{NO}_2)}{k_{\text{NO}+RO_2^*}} \frac{[\text{NO}_2]}{[\text{NO}]} - \frac{k_{\text{NO}+\text{O}_3}}{k_{\text{NO}+RO_2^*}} [O_3] \quad (1)
\]

where:

\[
\text{NO} + RO_2^* + O_2 \rightarrow NO_2 + HO_2 + R\text{COR}\quad (R4)
\]

Calculated RO$_2^*$ PSS and measured RO$_2^*$ mixing ratios are compared in Fig. 9 assuming $k_{\text{NO}+\text{RO}_2} = 8.0 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The agreement is best on days under clear sky conditions, especially for the period of maximum solar radiation (between 10:00 and 16:00 UTC). However, except for the latter case, the PSS derived RO$_2^*$ levels are higher than those measured by at least a factor of 2. This has already been reported for several studies in different environments (Carpenter et al., 1998; Burkert et al., 2001b, and references therein; Mannschreck et al., 2004; Griffin et al., 2007). Significant uncertainties can be associated with the subtraction of two terms of similar magnitude in Eq. (1) which enhances
Fig. 5. Distribution of RO$_2^*$ measured by DUALER according to local wind direction for the time periods of similar meteorology defined in Sect. 3.1: 23 to 27 November, 28 to 30 November and 1 to 7 December 2008. Data for (a) photochemical (06:00–17:00 UTC) and (b) non-photochemical (00:00–06:00 and 17:00 to 24:00 UTC) radical production are plotted separately. HO$_2^*$ measured by HORUS are also depicted for comparison (lowermost windroses). Wind sectors are indicated as additional information.

Fig. 6. RO$_2^*$ to HO$_2^*$ correlations for main wind sectors defined in the text. Data for (a) photochemical (06:00–17:00 UTC) and (b) non-photochemical (00:00–06:00 and 17:00 to 24:00 UTC) radical production are plotted separately. Regression parameters are indicated as additional information.
Fig. 7. Daylight RO$_2$ and HO$_2$ measured by DUALER and HORUS, respectively, under clear sky conditions during DOMINO. Periods without DUALER data corresponds with calibration of one of the NO$_2$ detectors, in which the DUALER method of analysis cannot be applied (see text). The photolysis frequency $J$(NO$_2$) and NO data are also included as additional information. RO$_2$ Savitzky-Golay 5 min averages are depicted without error bars to simplify the picture. The distribution of corresponding HO$_2$/RO$_2$ ratios according to the local wind direction is additionally plotted (bottom left).

the effect of instrumental errors. However, the agreement did not improve significantly when only considering those values for a NO$_2$/NO ratio < 10 as shown in Fig. 9.

As summarised by Sadanaga et al. (2003) further disagreement can be attributed to local sources and sinks of NO$_x$, to spatially inhomogeneous irradiance (Mannschreck et al., 2004), to the validity of $k_{NO+RO_2}$ for the sum of peroxy radicals, and to the meteorological conditions. In that context, the inlets for the DUALER and the NO/NO$_x$ and $J$(NO$_2$) instruments were very close together at the same height, on top of the measurement platform, so that the disagreement cannot be attributed to differences in the air mass sampled. The PSS assumption between species is only valid when O$_3$ and solar radiation levels assure that the NO-NO$_2$ conversion occurs with a time constant of a few minutes. The difference observed under clear and non clear sky conditions is interpreted to be related to the uncertainty derived from $J$(NO$_2$) short-term variations in the calculation of the PSS radicals. If only sunny days at the maximum irradiation time are considered, the PSS calculated values remain generally lower than the RO$_2$ measured. This might be an indication that the NO$_2$ photolysis within the air mass measured does not exactly correspond with the $J$(NO$_2$) values measured on the top of the structure. As indicated by Mannschreck et al. (2004), the NO$_2$ photolysis in air masses transported within a forest canopy can be substantially reduced due to reduced light penetration. The mixture of air parcels from within the forest and above might affect the PSS.
3.3 Nocturnal peroxy radicals

Significant RO$_2^*$ were observed in the night during DOMINO, as shown in Fig. 4. Nocturnal RO$_2^*$ mixing ratios varied considerably (mean 47 ± 53 pptv) and on many diel cycles the RO$_2^*$ levels were higher in the night than in daylight periods. This unusual situation may reflect a combination of low photochemical activity at this time of the year and abundant anthropogenic sources of radical precursors favouring nocturnal chemistry.

The nocturnal production of peroxy radicals can result from:

a. the gas phase reaction of O$_3$ with alkenes. The reaction of O$_3$ with alkenes is believed to occur via formation of Criegee intermediates the decomposition of which leads to OH, HO$_2$ and alkyl radicals in different yields depending on the structure of the alkene (Lightfoot et al., 1992). The OH thus generated will react with e.g., CO or hydrocarbons (Carter, 1990) to produce RO$_2^*$. The ozonolysis of alkenes can also be of significance during daytime if the concentration of anthropogenic large alkenes is high (Paulson and Orlando, 1996), and if the OH formation from O$_3$ photolysis is reduced due to low radiation levels in winter (Heard et al., 2004). If NO concentrations are sufficiently low, as in the night, the reactions between peroxy radicals can
gain in importance and constitute the main sink, leading to production of peroxides, alcohols and carbonyls.

b. NO$_3$ reactions (Platt et al., 1981, 1990; Wayne et al., 1991; Sadanaga et al., 2003; Brown and Stutz, 2012) with

- HCHO and longer chain aldehydes forming HO$_2$ and RO$_2$, respectively,
- alkenes, forming nitroxyalkyperoxy radicals. These can further react with NO$_2$, NO$_3$ and other RO$_2^*$. This can lead to both positive and negative correlations between NO$_3$ and RO$_2$. Negative correlations have been observed in rural forested areas at very low NO levels, where NO$_3$ reacts mainly with VOC while the NO$_3$ production rate is independent of the VOC level (Mihelcic, 1993). Positive correlations in other environments have been attributed to the presence of NO which is a sink for both radicals (Geyer et al., 2003).
- DMS especially in coastal areas (Winer, 1984; Platt et al., 1990) leading to CH$_3$SCH$_2$O$_2$ which can further react with NO$_3$ to form CH$_3$S and HCHO. Recently, Sommariva et al. (2007, 2009) simulated daytime and nighttime sources and sinks of radicals in the marine boundary layer and reported on the dominance of the DMS + NO$_3$ chemistry leading occasionally to nighttime RO$_2$ exceeding the daytime levels.

The mechanism for peroxy radical formation is highly uncertain (Finlayson-Pitts and Pitts, 2000; Holloway and Wayne, 2010, and references therein), and the relative contribution of the different routes to RO$_2$ depends on the chemical environment. Bey et al. (2001a, b) used a two-layer box model to examine a broad range of NO$_x$, biogenic and anthropogenic VOC mixtures. According to their simulations, NO$_3$ radicals can play a significant role in the primary formation of peroxy radicals in environments with significant NO$_x$, O$_3$, and high levels of biogenic compounds, while at lower NO$_x$, ozonolysis reactions dominate the radical initiation. Any significant interconversion among HO$_x$ species (i.e., HO$_2$ and OH) at night is found to be driven by RO$_2$ + NO or RO$_2$ + RO$_2$ reactions. In the rural and semirural cases investigated the VOC + NO$_3$ reactions initiate at the most 25% of the net OH production.

Only a few observations of nighttime peroxy radicals can be found in the literature and most of them have been measured in summer (Mihelcic et al., 1993; Kanaya et al., 2002; Platt et al., 2002; Martinez et al., 2003) or fall (Kanaya et al., 2007). Furthermore, RO$_2$ in winter has been mostly measured in remote areas (Carslaw et al., 1997; Penkett et al., 1999; Fleming et al., 2006a, b) and some of those RO$_2$ data are not corrected for the relative humidity interference reported by Mihele et al. (1998, 1999) and therefore not comparable with the present measurements. Kanaya et al. (2007) measured up to 5 pptv nocturnal HO$_2$ in a pollution free coastal site in Japan. Modelling studies indicated a predominant radical production via reactions with monoterpenes emitted in the forest nearby. Within a seasonal study in an urban area (NO$_x$ typically 10–30 ppbv) in Birmingham (England), Heard et al. (2004) reported high OH and HO$_2$ radical levels in winter both during day and night. The corresponding modelling analysis of the radical budget (Emmerson et al., 2005) indicates that HO$_2$ and RO$_2$ formation at night involved primarily the reaction of O$_3$ with alkenes, whilst the termination of RO$_2$ was dominated by formation of peroxyacetyl nitrates. In contrast, HO$_2$ mixing ratios measured in New York by Ren et al. (2006) were lower by a factor of ~15, with nocturnal values generally <0.3 pptv. NOx/VOC ratios were higher in New York than in Birmingham with NO mostly 25–40 ppbv in the night. In addition the radical production was slowed down by the low temperatures in New York down to ~25°C. Modelling studies underestimated both diurnal and nocturnal HO$_2$. HO$_2$ budget analysis showed that HO$_2$ production was dominated by the reaction of O$_3$ with alkenes in the night.

In contrast Geyer et al. (2003) attributed 77% and 53% of the RO$_2$ and HO$_2$ nighttime production to the reaction of NO$_3$ with terpenes, and 12% and 47% to ozonolysis, respectively. This study is based on measurements from a semi-urban atmosphere in summer with high nighttime levels of NO$_2$ and O$_3$ (5–15 ppbv and 60–10 ppbv, respectively).

### 3.3.1 Nocturnal RO$_2^*$ production from NO$_3$ chemistry

In view of the results presented in the preceding section, the origin of the nocturnal RO$_2^*$ measured during DOMINO was investigated. NO$_2$ and O$_3$ were present in the air mass arriving at night at the DOMINO site, favouring the formation of NO$_3$/N$_2$O$_5$. NO$_3$ up to 20 pptv was calculated from the measurements of N$_2$O$_5$ and NO$_2$ (Crowley et al., 2011). These data are broadly consistent with DOAS measurements close to the site. Sinks and sources of NO$_3$ and N$_2$O$_5$ during DOMINO have been discussed in detail by Crowley et al. (2011).

During DOMINO dawn and evening periods no clear correlations between RO$_2^*$ and NO$_3$ were observed. This is expected to be the case if NO$_3$ lifetimes are short due to an abundance of reactive VOCs. In addition (as indeed observed in this campaign, Crowley et al., 2010), RO$_2$ vs. NO$_3$ correlation can also be masked if other sources of RO$_2$ radicals such as the ozonolysis of alkenes are present. This may be important at the anticipated high VOC levels in the emissions of the petrochemical industry nearby. Furthermore, the measurement of RO$_2^*$ comprises a variable amount of HO$_2$.

In the presence of alkenes like dimethylbutene in concentrations significantly higher than NO, the respective reactions with NO$_3$ can effectively compete and still enable OH production by the reaction of HO$_2$ with NO$_3$. NO was measured and generally lower than the detection limit of a few pptv.
The NO measurements are described in more detail in Crowley et al. (2010).

The rate of production of RO2 from NO3 and organics during DOMINO can be estimated by considering the following simple reaction scheme:

\[ \text{NO}_2 + O_3 \rightarrow \text{NO}_3 + O_2 \quad k_{\text{NO}_2 + O_3} \] (R5)

\[ \text{NO}_3 + \text{VOC} \rightarrow \text{RO}_2 \quad k_{\text{NO}_3 + \text{VOC}} \] (R6)

\[ \text{NO}_3 \rightarrow \text{loss of NO}_3 \quad k_{\text{loss}} \] (R7)

\( k_{\text{loss}} \) is a first order term \( (s^{-1}) \) which includes all the losses of NO3 except the direct, gas phase reaction with organics (Reaction R6), and includes reaction with NO, indirect loss by aerosol uptake and dry deposition of N2O5 and the dry deposition of NO3. In a steady state analysis:

\[ \frac{\partial [\text{NO}_3]}{\partial t} = k_{\text{NO}_2 + O_3}[\text{NO}_2][O_3] - k_{\text{NO}_3 + \text{VOC}}[\text{NO}_3][\text{VOC}] - k_{\text{loss}}[\text{NO}_3] = 0 \] (2)

\[ [\text{NO}_3] = \frac{k_{\text{NO}_2 + O_3}[\text{NO}_2][O_3]}{k_{\text{NO}_3 + \text{VOC}}[\text{VOC}] + k_{\text{loss}}} \] (3)

According to Crowley et al. (2010), \( k_{\text{NO}_2 + \text{VOC}}[\text{VOC}] + k_{\text{loss}} \) is the total loss frequency, \( f(\text{NO}_3) \), calculated from the observed NO3 concentration and its production term \( (k_{\text{NO}_2 + \text{O}_3} [\text{NO}_2][O_3]) \); and \( k_{\text{NO}_3 + \text{VOC}}[\text{VOC}] \) is calculated by assuming that all losses of NO3 apart from those constrained by aerosol uptake of N2O5 or direct reaction with NO or dry deposition of NO3 or N2O5 are due to reaction with organics.

Therefore, the RO2 production rate in pptvs\(^{-1}\) can roughly be calculated as:

\[ \frac{\partial [\text{RO}_2]}{\partial t} = k_{\text{NO}_3 + \text{VOC}}[\text{NO}_3][\text{VOC}] \] (4)

and substituting Eq. (3) into Eq. (4):

\[ \frac{k_{\text{NO}_3 + \text{VOC}}[\text{VOC}]}{k_{\text{NO}_3 + \text{VOC}}[\text{VOC}] + k_{\text{loss}}} \times \frac{k_{\text{NO}_2 + O_3}[\text{NO}_2][O_3]}{\alpha k_{\text{NO}_2 + O_3}[\text{NO}_2][O_3]} = \frac{\alpha k_{\text{NO}_2 + O_3}[\text{NO}_2][O_3]}{2k_{\text{RO}_2 + \text{RO}_2}} \] (5)

where \( \alpha \) is the fraction of NO3 that is lost to organics. \( \alpha \) can vary between \( \sim 0 \) (i.e., when NO is responsible for NO3 loss) and 1 (when the NO3 loss rates were dominated by reactions with organic trace gases). \( \alpha \) was calculated for each time step and used to calculate the production rate of RO2 assuming that loss of 1 NO3 (with organics) leads to 1 RO2. On average (but depending on which scenario was used for the N2O5 heterogeneous loss, see Crowley et al., 2010) \( \alpha \) was between 0.7 and 0.9.

Nocturnal steady state mixing ratios of RO2 produced from NO3, i.e., [RO2]\(_{\text{iss}}\), can be calculated by assuming that, in the absence of NO at night, RO2 are uniquely lost by peroxy radical self reactions with a rate coefficient \( k_{\text{RO}_2 + \text{RO}_2} \):

\[ [\text{RO}_2]_{\text{iss}} = \frac{\alpha k_{\text{NO}_2 + O_3}[\text{NO}_2][O_3]}{2k_{\text{RO}_2 + \text{RO}_2}} \] (6)

Based on Sander et al. (2011), Orlando and Tyndall (2012) and Calvert et al. (2011), two \( k_{\text{RO}_2 + \text{RO}_2} \) reaction rates were assumed for the DOMINO data: (a) \( 1.1 \times 10^{-11} \) and (b) \( 7.1 \times 10^{-12} \) cm\(^3\) molec\(^{-1}\) s\(^{-1}\), representing a radical mixture dominated by HO2+RO2 or by RO2+RO2.

On average, and depending on the value assumed for \( k_{\text{RO}_2 + \text{RO}_2} \), [RO2]\(_{\text{iss}}\) can account for between 47 ± 16% and 54 ± 17% of the RO2 on those nocturnal periods with available NO3 data. In Fig. 10, the [RO2]\(_{\text{iss}}\) obtained for the case (b) are shown. The CL of the nocturnal peroxy radicals containing a nitrate group is not known for the unknown mixture of hydrocarbons reacting with NO3 during DOMINO. It is expected that these RO2 have a shorter CL than CH3O2 used for the CL calibrations. Therefore, if these peroxy radicals predominate in the air mass sampled, the RO2 calculated are underestimated and the contribution of the [RO2]\(_{\text{iss}}\) above to the observed signal will be smaller. The nighttime HO2 mixing ratios measured did not exceed 8 pptv and normally varied between 2 and 6 pptv. Basically, [RO2]\(_{\text{iss}}\) cannot account for the organic peroxy radical fraction in the RO2 mixing ratios measured in periods associated with emissions arriving from the urban-industrial sector. This is the case on the 24 November, on the 30 November (18:00 to 06:00 UTC on the 1 December) and on the 2 December (18:00 to 02:00 UTC). The highest mixing ratios of anthropogenic VOC and secondary oxidation products like acetone and formaldehyde were also observed during these high nocturnal RO2 events. Other VOC leading to peroxy radicals by ozonolysis can presumably be present as well.
In particular, on the 30 November around midnight benzene and acetone are close to 3.5 ppbv (see Fig. 3). Measurements of anthropogenic alkenes would have greatly aided the interpretation of results, but were not available due to instrument failure. The potential contribution of ozonolysis of alkenes to the observed nocturnal RO$_2^*$ is discussed in more detail in Sect. 3.3.2.

Crowley et al. (2011) speculate on the potential importance of the NO$_3$ induced oxidation of reduced sulphur compounds emitted by the paper mill in the Huelva industrial area during DOMINO, producing HCHO, SO$_2$ and RO$_2$, as reported by Jensen et al. (1992). In particular, during the event on the 24 November, RO$_2^*$ reached the highest nocturnal value (90 pptv) and HCHO 1.5 ppbv at the time a plume of SO$_2$ (3 ppbv) arrived at the site. Similarly, on the 2 December 6 ppbv SO$_2$, 1 ppbv HCHO, 1 ppbv PAN and 45 pptv RO$_2^*$ were concurrently measured. However, SO$_2$ remained ≤1 ppbv during the event on the 30 November in the evening while on the 3 December at dawn SO$_2$ plumes up to 8 ppbv did not seem to disturb the agreement between [RO$_2^*$]$_{ss}$ and RO$_2^*$ measured (see Fig. 2). The latter seems to be the case when the SO$_2$ are accompanied by NO$_2$ plumes with winds of marine origin, indicating another source of emissions. It is not obvious how the DUALER responds to peroxy radicals generated from reaction of NO$_3$ with sulphur precursors.

### 3.3.2 Nocturnal RO$_2^*$ production from ozonolysis

As mentioned above, neither the mixture nor the diurnal behaviour of anthropogenic alkenes during the DOMINO campaign are known. In the case of ozonolysis a simple calculation, like for NO$_3$ in Sect. 3.3.1, is not possible as the chemical lifetime of O$_3$ with respect to reaction with olefins can not be straightforwardly defined and the reaction rates of olefins with O$_3$ are very variable. However, the potential importance of ozonolysis reactions was investigated by assuming an alkene mixture from the Houston petrochemical plume as published by Leuchner et al. (2010). Benzene measurements in Houston and DOMINO were used as reference and dimethylbutene (DMB), methylpentene (MP) and butadiene (BD) mixing ratios were normalised to the benzene measured ratios, on the basis of their relative proportion to benzene in the Houston plume, i.e., 18 %, 5 % and 100 %, respectively. This implies that benzene and those olefins are assumed to have during DOMINO a common source and/or identical diurnal behaviour. According to these calculations, average mixing ratios were assumed to be 35 ± 25 pptv for DMB, 10 ± 7 pptv for MP, and 192 ± 140 pptv for BD, with 623 pptv, 173 pptv and 3460 pptv maximum mixing ratios, respectively. Expected RO$_2$ steady state mixing ratios were calculated for each alkene (Alk$_i$) by using the O$_3$ measured during DOMINO, according to:

$$[\text{RO}_2^*]_{ss} = \sqrt{\frac{k_{\text{Alk}_i+\text{O}_3}[\text{O}_3][\text{Alk}_i]}{2k_{\text{RO}_2+\text{RO}_2}}} \quad (7)$$

With $k_{\text{DMB}+\text{O}_3} = 1.13 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $k_{\text{MP}+\text{O}_3} = 5.6 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $k_{\text{BD}+\text{O}_3} = 6.3 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, and the same RO$_2$ + RO$_2$ reaction rates used for the estimation of steady state mixing ratios of RO$_2$ produced from NO$_3$ (i.e., (a) $1.1 \times 10^{-11}$ and (b) $7.1 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$). These calculated RO$_{2ss}$ produced from ozonolysis are compared in Figs. 10 and 11 with the RO$_2^*$ measured. Except on the 23 November the RO$_{2ss}$ calculated for the measured isoprene and 2-pinene represents in average around 4 % and 8 %, respectively of the total RO$_{2ss}$ calculated for the alkene mixture assumed.

The sum of the RO$_{2ss}$ calculated can be considered as an upper limit. The results show that the RO$_{2ss}$ calculated from a plume of these alkene characteristics arriving at the site would account for the average of 59 % ± 19 % or 68 % ± 20 % of the RO$_2^*$ observed most of the nights for $k_{\text{RO}_2+\text{RO}_2} = 1.1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ or $7.1 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Dimethylbutene appeared to be the most important alkene for RO$_2^*$ generation.

In addition, most events associated with emissions arriving from the urban-industrial sector (e.g., on the night of 24 November, 30 November, and 2 December) could be explained this way. On the 24 December at dawn, however, both alkenes and NO$_3$ can each only account for about 25 % of the RO$_2^*$ measured.

In summary, emissions from the industrial area of Huelva often impacted the measurement site at night during the campaign. The processing of significant levels of anthropogenic organics leads to an intense nocturnal radical
chemistry accompanied by the formation of organic peroxy radicals at concentration levels comparable to those of summer photochemical conditions. Using the simplified chemical approach presented in Sect. 3.3.1, it can be concluded that the nocturnal formation of peroxy radicals from NO\textsubscript{3} and VOC is significant but not always sufficient to reproduce the RO\textsubscript{2}\textsuperscript{*} measurements in industrial pollution events. The RO\textsubscript{2}\textsuperscript{*} levels observed in those periods might be explained by the ozonolysis of a mixture of alkenes of industrial petrochemical origin simultaneously emitted with the benzene measured at the site.

### 3.4 Diel HO\textsubscript{2}/RO\textsubscript{2}\textsuperscript{*} ratio and OH reactivity

The HO\textsubscript{2}/RO\textsubscript{2} ratio for daylight and nighttime periods was calculated from the RO\textsubscript{2}\textsuperscript{*} DUALER and HO\textsubscript{2}\textsuperscript{*} HORUS measurements during DOMINO, and the distribution versus wind direction was further investigated. As pointed out in Sect. 3.1., data for wind speed < 1.5 m s\textsuperscript{-1} have not been considered in the analysis in Fig. 5 in order to rule out any effect of stagnant conditions.

The calculated HO\textsubscript{2}/RO\textsubscript{2} ratio generally varied between 0.3 and 0.8, with higher values for the continental and urban sectors on the 26 and 29 November, and on the 2 and 3 December. This could indicate a more effective conversion of RO\textsubscript{2} in HO\textsubscript{2} in anthropogenic regimes. However, as mentioned above, there is neither a significant correlation between RO\textsubscript{2} and NO, which was close to the detection limit most of the nights, nor NO\textsubscript{3}. Figure 12 depicts measured HO\textsubscript{2}\textsuperscript{*} vs. RO\textsubscript{2}\textsuperscript{*} for different NO missing ratios measured during DOMINO. During the day HO\textsubscript{2}/RO\textsubscript{2} generally varies around 0.15 for NO<1 ppb and presents no correlation at higher NO mixing ratios. In the night, NO remains mostly below 0.1 ppb and the HO\textsubscript{2}/RO\textsubscript{2} is significantly lower (Fig. 13). It can be concluded that the radical chemistry especially in the night was mainly determined by the abundance, nature and chemistry of the VOC acting as peroxy radical precursors in the air mass.

The ratio HO\textsubscript{2}/RO\textsubscript{2} occasionally reached values >1 for wind directions around 260° and 330° where the air mass was affected by the emissions of the industrial and port areas of Huelva, as on the 2 December night and 3 December daytime periods. As RO\textsubscript{2} comprises HO\textsubscript{2} this must be an artifact related with the use of data from two different instruments which can be subject to different experimental interferences. As mentioned in Sect. 2.1., Fuchs et al. (2011) recently reported interferences in the HO\textsubscript{2} measurement by LIF instruments with chemical conversion of HO\textsubscript{2} to OH by adding NO, like HORUS, of some RO\textsubscript{2} produced by alkenes and aromatics. As a consequence, and especially in polluted environments and areas with large emissions of alkenes or aromatics, the nominal HO\textsubscript{2} mixing ratios measured by LIF can actually be the sum of HO\textsubscript{2} and a significant fraction of RO\textsubscript{2} mixing ratios. As stated in Sect. 2.1., the effect of this interference depends on the measurement conditions and is unknown for the HORUS instrument. Concerning DOMINO, as this interference only affects the HO\textsubscript{2} data, it could explain the [HO\textsubscript{2}]/[RO\textsubscript{2}] = 1 in some of the air masses as to be [HO\textsubscript{2}]/[RO\textsubscript{2}]. From the interfering substances investigated by Fuchs et al. (2011) only benzene and isoprene were measured during DOMINO.

Concerning DUALER, the response of the PeRCA technique to a wide range of radicals has been proved to be very similar (Ashbourn et al., 1998). The effective chain length used for the calculation of the RO\textsubscript{2} might change significantly with the set up as the result of peroxy radical losses, especially HO\textsubscript{2}, before the amplification zone, which depend on the material and shape of the reactor. This can lead to an underestimation of the total sum of radicals. Laboratory experiments using different HO\textsubscript{2} + RO\textsubscript{2} mixtures indicated that for 50% HO\textsubscript{2} in the air mass, RO\textsubscript{2} is 15% underestimated by the DUALER reactor used for DOMINO. There is no information available about the composition of the sampled peroxy radical mixture. Therefore, no correction was applied to the RO\textsubscript{2} data. If the load of organic peroxy radicals with low wall loss rates is very high compared to HO\textsubscript{2}, RO\textsubscript{2} can be significantly underestimated. This, together with the artificially increased [HO\textsubscript{2}] due to the LIF interference can occasionally lead to [HO\textsubscript{2}]/[RO\textsubscript{2}] ratios higher than 1 in very polluted air masses. Overall the analysis of the HO\textsubscript{2}/RO\textsubscript{2} ratio should therefore rather be considered as qualitative.

Furthermore, the HO\textsubscript{2}/RO\textsubscript{2} relative abundance was investigated in relation to the OH reactivities measured during DOMINO by Sinha et al. (2012). Generally, the fraction of HO\textsubscript{2} in RO\textsubscript{2} slightly increases as the OH reactivity increases (Fig. 13) and the HO\textsubscript{2}/RO\textsubscript{2} ratio remains between 0.05 and 0.15. The highest OH reactivities (≈50–60 s\textsuperscript{-1}) are related to air masses within the continental sector (Fig. 14), and generally associated with highest RO\textsubscript{2} levels, except for some radical plume events. Air masses affected by emissions of the Huelva industry and of ship traffic, as in the nighttime urban and ocean sector, respectively, present lower but still significant OH reactivity (≈10–30 s\textsuperscript{-1} and 2–10 s\textsuperscript{-1}, respectively).

The chemical heterogeneity of the air masses within the urban-industrial sector which comprises a large number of industrial emission sources is reflected in the broad range of RO\textsubscript{2}, HO\textsubscript{2}, mixing ratios and OH reactivities (Fig. 14). In particular, the OH reactivity values support the idea suggested by the [RO\textsubscript{2}]* calculated from NO\textsubscript{3} and estimated from a potential mixture of alkenes (Sect. 3.3) of high nocturnal RO\textsubscript{2} production through ozonolysis of unmeasured reactive organic compounds arriving to the site.

### 4 Summary and conclusions

Free radical chemistry was investigated under mild weather conditions in late autumn at a coastal site influenced by emissions of weak biogenic and strong urban-industrial origin. Maximum diurnal peroxy radical mixing ratios ranged from
Fig. 12. HO$_2^*$ versus RO$_2^*$ for different NO mixing ratios (NO in ppbv) measured during DOMINO. Data for (a) photochemical (06:00–17:00 UTC) and (b) non-photochemical (00:00–06:00 and 17:00 to 24:00 UTC) radical production are plotted separately.

Fig. 13. HO$_2^*$ versus RO$_2^*$ for different OH reactivities (OHr in s$^{-1}$) measured during DOMINO. Data for (a) photochemical (06:00–17:00 UTC) and (b) non-photochemical (00:00–06:00 and 17:00 to 24:00 UTC) radical production are plotted separately.

10 to 50 pptv. Very significant nocturnal RO$_2^*$ were observed, with peak mixing ratios (up to 80 pptv) mostly associated with the arrival of VOC emission plumes of industrial origin to the site. Reactions of NO$_3$ with VOCs were a significant source of nighttime organic peroxy radicals. On average, calculated $[RO_2]_{\text{loss}}$ can account for between 47 ± 16% and
54 ± 17 % of the RO₂* measured on those nocturnal periods with available NO₃ data. During peak events at the highest measured VOC of anthropogenic industrial origin the estimated radical production from NO₃ reactions cannot account for the measured concentration levels, indicating the importance of other radical formation mechanisms such as ozonolysis of alkenes.

As measurements of neither anthropogenic alkenes nor nocturnal OH during the campaign are available, the significance of O₃ and VOC reactions as RO₂ source was indirectly
evaluated by assuming a mixture of alkenes on the basis of literature data for emissions of industrial petrochemical origin and of benzene measurements at the site. The results indicate that the RO$_2^*$ levels observed in most nocturnal events associated with emissions arriving from the urban-industrial sector were consistent with generation via ozonolysis of alkenes.

The HO$_2$/RO$_2^*$ ratio derived from RO$_2^*$ PeRCA and HO$_2$ LIF measurements usually remained between 0.3–0.4 in all wind directions, was slightly higher during nighttime, and close to 0.6 in air masses originating from the continental sector. However, this analysis and the corresponding calculated HO$_2$/RO$_2^*$ ratios must be rather considered as qualitative since the combined effect of [RO$_2^*$] underestimations and [HO$_2$] overestimations by DUALER and HORUS, respectively, can be of significance in very polluted air masses.

According to the general variation of HO$_2$/RO$_2^*$ with OH reactivity, air masses with higher content in organic peroxy radicals, mainly affected by industrial or ship emissions, are associated with significant OH reactivities ($\approx 10^4$ molecules cm$^{-3}$ s$^{-1}$). This, in turn, substantiates the importance of the nocturnal production of peroxy radicals from the ozonolysis of non-measured VOCs during DOMINO.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/13/5731/2013/acp-13-5731-2013-supplement.pdf.

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