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

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Abstract

Peroxy radicals were measured by a PeRCA (Peroxy Radical Chemical Amplifier) instrument in the boundary layer during the DOMINO (Diel 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 ($RO_2^* = HO_2 + \Sigma RO_2$) 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 RO_2 production initiated by reactions of NO_3 with organic trace gases was estimated to be significant but not sufficient to account for the concentrations of RO_2^* observed in air masses carrying high pollutant loading. The nocturnal production of peroxy radicals seems therefore to be dominated by ozonolysis of volatile organic compounds.

RO_2^* diurnal variations were consistent with other HO_2 measurements available at the site. HO_2/RO_2^* ratios generally varied between 0.3 and 0.4 in all wind directions. Occasional $HO_2/RO_2^* \geq 1$ seemed to be associated with periods of high RO_2^* variability and with RO_2 interferences in the HO_2 measurement in air masses with high RO_2 load.

1 Introduction

Hydroperoxy- (HO_2) and alkyl peroxy (RO_2; R = organic chain) radicals are short lived species involved in most of the photoxidation 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 O_3, and termination mechanisms i.e., radical to radical reactions forming peroxides. RO_2 and HO_x ($HO_x = HO_2 + OH$) 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 O_3 production for a particular environment. Recent investigations indicate 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 O_3 and NO_3. As identified by Platt et al. (1990) nighttime RO_2 production in coastal areas and under certain other specific conditions, 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., 2001, 2003; Andrés Hernández et al., 2001). Under such conditions, relatively low nighttime mixing ratios of peroxy radicals have been measured, reaching occasionally 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). Furthermore, diel measurements of peroxy radicals in complex environments are scarce and 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 complex photochemical environment influenced by emissions of urban and industrial origin. The role of day and night-time peroxy radicals was investigated by complementing the peroxy radical 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 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 $RO_2^* = HO_2 + \Sigma RO_2$ (R stands for an organic chain) 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, etc. (Kartal et al., 2010; Andrés-Hernández et al., 2010). NO_2 is measured by detecting the chemiluminiscence of its reaction with luminol (3-aminophthalhydrazide: $C_8H_7N_3O_2$).

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 with the standard PerCA methodology, the *background signal* does not need to be interpolated during the measurement of the *amplification signal*, what 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 were monitored during DOMINO by performing two NO_2 calibrations per day and detector. Glass reactors were used during DOMINO as in previous ground based measurements (Burkert et al., 2001, 2003; Andrés Hernández et al., 2001). Similar to Reichert et al., (2003) the CL was characterised in the laboratory for dry and wet conditions, and continuous relative humidity measurements at the site were used for the calculation of RO_2^* mixing ratios. The DUALER detection limit and accuracy are closely related to the Relative Humidity (RH) dependency of the CL (Reichert et al., 2003). For the set up deployed within DOMINO the total 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 5 min Savitzky Golay averages.

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).

Other data

A suite of chemical species was measured during DOMINO by different research institutes and has mostly been described in publications within the ACP DOMINO special issue (http://www.atmos-chem-phys.org/special_issue246.html; Sörgel et al., 2011; Crowley et al., 2011; Sinha et al., 2012). Table 1 briefly summarises the main features of the instruments providing data for the present study.

Regarding meteorological information, 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). Generally, northerly wind directions coming from NW and NE predominate (see Fig. 1 with a map of the location). Prior to mixing with low wintertime biogenic emissions from the pine and eucalyptus forest in the national park at the measurement site (Song et al., 2012) the air masses are likely exposed to fresh urban and industrial emissions of Huelva (the industrial area is located a 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.

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

3 Results and discussion

3.1 General peroxy radical features during DOMINO

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 most characteristic peroxy radical features encountered during DOMINO are summarised in Fig. 2 which displays RO_2^* mixing ratios measured on the 23 November 2008. Continental air masses from the NE impacted the site on this day, characterised by high temperatures and clear sky. RO_2^* reached the maximum midday value of the campaign (45 ± 10 pptv). Apart from photochemical RO_2^* production during daylight, most diel periods showed significant production in the evening hours with RO_2^* generally reaching a maximum around midnight and further decreasing as dawn approached.

Figure 3 summarises the distribution of RO_2^* according to the local wind direction at the site. Only mixing ratios measured at wind speed $> 1.5\,\mathrm{m\,s^{-1}}$ 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) are separated from the rest. Three periods of similar meteorological conditions can be distinguished during the campaign: until the 28 November clear sky conditions predominate and the highest diurnal mixing ratios are associated with the continental sector. In the night prevail stable conditions and the site is often impacted with air masses coming from the urban sector transporting emissions of the industrial area of Huelva. Due to instrumental calibrations RO_2^* data are not available on the 25 November.

Frequent cloudy conditions were observed between 28 and 30 November with much lower diurnal temperature gradients (2–3 °C) than in previous days. The air masses have urban/industrial character with sometimes a marine component. Except on the 2 December, colder and cloudy conditions characterise the period 1 to 8 December.

HO_2 radicals measured by Fluorescence Assay with Gas Expansion (FAGE) with the HORUS instrument (Table 1) present a similar distribution (Fig. 4). Due to instrumental calibrations, nighttime HO_2 data was not always available.

3.2 Diurnal photochemical radical production

RO_2^* measured during clear sky conditions, i.e., most favouring photochemical radical production, are summarised in Fig. 5. Throughout the campaign RO_2^* reached a maximum at about 12:00–13:00 (UTC). Note that the solar zenith is at 11:30 UTC. The RO_2^* maximum was considerably higher on the 23 and 24 November (45 ± 10 and 35 ± 10 pptv respectively) which reached the highest temperatures of the campaign (T_{max} 22 °C and 18 °C respectively). From the 24 November the maximum temperature decreased considerably (12–16 °C) and the RO_2^* maximum reached values between 10 and 20 pptv.

This apparent positive relation with the temperature has been interpreted in previous work as an indirect temperature effect in the formation of radicals, driven by variations in the emission of radical precursors of biogenic origin with the temperature. In that context, the measured variations of potential biogenic precursors like isoprene and monoterpenes were closely analysed. On the 23 November isoprene did increase steadily to 120 pptv in the afternoon (16:00 UTC), a value about a factor 10 higher than the average during the measurement period. Song et al. (2012) interpret the delay in the isoprene maximum 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. In any case, on the 24 November isoprene did not exceed the average value of the campaign, but the level of monoterpenes, comprising α-pinene, limonene, 1, 8-cineole and camphor was 40 pptv, about twice the level measured under clear sky conditions (Song et al., 2012).

Other unmeasured radical precursors might have been present on the sampled air masses. 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 due to the presence of OH reactants in the air mass) in air masses from the continental sector, indicating high organic load which generally resulted in NO_x limited O_3 production at the site. According to the backward trajectories on the 23 November the air mass had passed over Madrid within the previous 11 h. HO_2 and RO_2^* are the highest measured during the campaign while the HO_2/RO_2^* ratio remains around 0.3 (Fig. 5). The variation with the wind sector of O_3 and NO mixing ratios and OH reactivity on these days is shown in Fig. 6.

Concerning peroxy radical diurnal patterns, HO_2 obtained from the HORUS instrument agree reasonably well with the RO_2^* profiles throughout the measurement campaign (Fig. 5). Penkett et al. (1997) reported about poor correlations between RO_2^* and $J(O^1D)$ and broadening of the RO_2^* diurnal cycle with respect to the $J(O^1D)$ shape in the presence of significant sources of HO_x from the photolysis of compounds other than O_3, like HCHO and HONO. Daylight levels of HCHO and $(CH_3)_2CO$ during DOMINO generally remained around 500 and 200 pptv respectively. RO_2^* tracked $J(O^1D)$ closely and the correlations both with $J(O^1D)$ and $\sqrt{(JO^1D)}$ were good ($r^2 > 0.6$) in November on the 23 ($r^2 = 0.9$), on the 26 and on the 27 as well as on the 2 December. These correlations were poor for the rest of the measurement campaign although the levels of carbonyls only increased significantly on the 27 and 28 November (up to 1.4 ppbv HCHO and 800 pptv $(CH_3)_2CO$). However, as the corresponding measured air masses were mainly coming from the urban/port sector (Fig. 3) they might have been affected by combustion emissions of ships in route to the harbour of Huelva. This is partly reflected in SO_2 spikes measured and in the general distribution of SO_2 versus wind direction during DOMINO, as shown in Fig. 7. Both the RO_2^* and the HO_2 profiles on the afternoon of the 28 November (Fig. 9) are clearly broader than that of $J(O^1D)$, as observed previously in the marine boundary layer (Burkert et al., 2003; Fleming et al., 2006). O_3 increased to 40 ppbv and remained practically constant till the 30 November at 03:00 UTC, reflecting the predominance of transport rather than local production as result of the lower insolation and higher cloudiness of those days.

Finally, measured diurnal RO_2^* were compared with estimations based on the deviation of the photostationary state (PSS) between NO, NO_2 and O_3 (Leighton, 1961):

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad k_{NO+O_3} \tag{R1}$$

$$NO_2 \xrightarrow{h\nu} NO + O \qquad J(NO_2) \tag{R2}$$

$$O_2 + O \xrightarrow{M} O_3 \tag{R3}$$

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:

$$[RO_2^*] = \frac{J(NO_2)}{k_{NO} + RO_2{}^*} \frac{[NO_2]}{[NO]} - \frac{k_{NO+O_3}}{k_{NO+RO_2{}^*}}[O_3] \tag{1}$$

where:

$$NO + RO_2^* + O_2 \longrightarrow NO_2 + HO_2 + RCOR' \tag{R4}$$

Calculated $RO_{2\,PSS}^*$ and measured RO_2^* mixing ratios are compared in Fig. 8 for $k_{NO+RO_2^*} = 8.0 \times 10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$. The agreement improves 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 the measured by at least a factor 2. This has already been reported for several studies in different environments (Carpenter et al., 1998; Burkert et al., 2001b, and references herein; Mannschreck et al., 2004; Griffin et al., 2007). Apart from uncertainties associated with the subtraction of two terms of similar magnitude in Eq. (1) which enhances the effect of instrumental errors, the disagreement can be related 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 as summarised by Sadanaga et al. (2003).

3.3 Nocturnal peroxy radicals

Significant RO_2^* were observed in nocturnal periods during DOMINO, as shown in Fig. 3. In fact, nocturnal RO_2^* mixing ratios vary considerably (mean 47 ± 53 pptv) and on many diel cycles the RO_2^* levels were higher in the night than in daylight periods. This possibly reflects low photochemical activity in this time of the year and abundant anthropogenic sources of radical precursors favouring nocturnal chemistry.

According to the measurements, the chemical content 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. There is information about biogenic alkenes during DOMINO available: namely isoprene and terpenes, which are reactive toward NO_3. There is information about aromatics (benzene, toluene) which can react with OH but at much lower rates with O_3 or NO_3 (Carter, 1990). NO and VOC profiles were plume-like rather than having a structured reproducible diel pattern over the campaign. Most of the nocturnal plumes until the 3 December can be attributed to industrial emissions from Huelva trapped in a stable nocturnal boundary layer (Diesch et al., 2012). Occasionally nocturnal plumes of the measured VOC and carbonyls did have the same temporal evolution as RO_2^* indicating a very effective local production of radicals or a source of radical precursors simultaneously emitted.

The nocturnal periods on the 27 and 30 November and 1 December at dawn illustrate the chemical heterogeneity of the air masses measured during DOMINO (Fig. 9). On the 27 November in the morning high NO_3, low RO_2^*, NO_2, isoprene and α-pinene mixing ratios were measured at the site, after the air masses passed over Seville. In the evening, a much more polluted air mass arrived at the site from the urban sector. Toluene, NO_2 and SO_2 reach 500 pptv, 12 ppbv and 15 ppbv, respectively, RO_2^* 25 pptv, and the highest PAN and HCHO mixing ratios of the campaign were measured (1800 and 1500 pptv respectively). Though the local wind direction and speed did not change significantly, the concentrations of aromatics decreased at about midnight, indicating the discontinuous nature of the industrial plume, while terpenes and NO_3 increased at dawn on the 28 November. RO_2^* and NO_3 remained anticorrelated most of the time. On the 28 November at around 07:00 UTC a peak in RO_2^* up to 25 pptv was accompanied by SO_2 and NO_2 plumes in a transition period with winds of low speed turning to the Atlantic Sector. These marine conditions persisted from that moment up to the 30 December in the evening, with frequent NO_2 and SO_2 plumes, likely originating from ship emissions and associated with peak RO_2^*. On the 30 December in the evening local winds from urban/Huelva sector were established. Generally the load in aromatics and carbonyls increases in air masses passing over the petrochemical industry situated NW of the site 25 km upwind. As can be seen in Fig. 9 this wind sector is associated to the highest RO_2^* nocturnal levels.

Despite the complexity and variability of the air masses measured, the nocturnal production of peroxy radicals can basically be expected from:

a. the gas phase reaction of O_3 with alkenes, which is an important source of nocturnal OH, which will react with e.g. CO or hydrocarbons to generate RO_2^*. This 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 like in winter due to the low radiation (Heard et al., 2004).

b. NO_3 chemistry through reaction with aldehydes and alkenes forming HO_2 and nitratoalkylperoxy radicals respectively or directly with DMS (Platt et al., 1990; Sommariva et al., 2007, 2009).

In both cases the chemistry is quite complex (Platt et al., 1981, 1990; Wayne et al., 1991; Sadanaga et al., 2003). 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). If NO concentrations are sufficiently low, as in the night, the radical-radical reactions can gain in importance and constitute the main sink of peroxy radicals by production of peroxides, alcohols and carbonyls. The peroxy radical formation from the reaction of NO_3 with alkenes is also highly uncertain (Finlayson-Pitts and Pitts, 2000; Holloway and Wayne, 2010, and references herein), and the relative contribution of these different mechanisms depends on the chemical environment, as simulated by Bey et al. (2001a,b) by using a two layer box model for 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 and O_3, and high levels of biogenic compounds, while at lower NO_x, ozonolysis reactions dominate the radical initiation. The interconversion among HO_x species (i.e., HO_2 and OH) at night is driven by $RO_2 + NO$ or $RO_2 + RO_2$ reactions. In rural and semirural cases the VOC + NO_3 reactions initiate at the most 25 % of the net OH production. 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 ocassionally to nighttime RO_2 exceeding the daytime levels.

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; Kanaja et al., 2002, 2007; Platt et al., 2002; Martinez et al., 2003). 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. Within a seasonal study in an urban area in England, Heard et al. (2004) reported high OH and HO_2 radical levels in winter resulting from carbonyl photolysis and from the reaction of O_3 with alkenes. 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. This is in agreement with the results of Martinez et al. (2003) but in contrast with Geyer et al. (2003) who attributed the 77 % and 56 % of the RO_2 and HO_2 nighttime production to the reaction of NO_3 with terpenes. Both studies based on measurements from semi-urban atmospheres in summer.

Nocturnal RO_2^* production from NO_3 chemistry

In view of the results presented in the preceding section, the potential origin of the nocturnal RO_2^* measured during DOMINO was further 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_2O_5. NO_3 up to 20 pptv was calculated from the measurements of N_2O_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_2O_5 during DOMINO have been discussed in detail by Crowley et al. (2011).

During DOMINO dawn and evening periods no unambiguous clear correlations between RO_2^* and NO_3 were observed. Potential RO_2 vs. NO_3 correlations can partially be masked by the effect of other sources of RO_2 radicals as the ozonolysis of alkenes like butadiene. This will be important at the high VOC levels in the emissions of the petrochemical industry nearby. Furthermore, the measurement of RO_2^* comprises a variable amount of HO_2, i.e., a source of OH radicals which, in contrast to NO_3 and O_3, are reactive towards all VOC. In the presence of alquenes like dimethylbutene in concentrations significantly higher than NO, the respective reactions with NO_3 can effectively compete and still enable the OH production by the reaction of HO_2 with NO.

Previous observations in the boundary layer indicated both positive and negative correlations between NO_3 and RO_2 (Mihelcic, 1993; Geyer et al., 2003 and references herein). RO_2 and NO_3 can correlate negatively in the case that NO is very low, the VOC are the dominant sink of NO_3 which produces RO_2, and the NO_3 production rate is independent from the VOC level. This has been reported in rural forested areas (Mihelcic, 1993). Positive correlations in other environments have been attributed to the common effect of NO which is a sink for both radicals (Geyer et al., 2003).

The rate of production of RO_2 from NO_3 and organics during DOMINO can be estimated by considering the following simple reaction scheme:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad k_{NO_2+O_3} \tag{R5}$$

$$NO_3 + VOC \rightarrow RO_2 \qquad k_{NO_3+VOC} \tag{R6}$$

$$NO_3 \rightarrow \text{loss of } NO_3 \qquad k_{loss} \tag{R7}$$

in a steady state analysis

$$\frac{\partial[NO_3]}{\partial t} = k_{NO_2+O_3}[NO_2][O_3] - k_{NO_3+VOC}[NO_3][VOC] - k_{loss}[NO_3] = 0 \tag{2}$$

$$[NO_3] = \frac{k_{NO_2+O_3}[NO_2][O_3]}{k_{NO_3+VOC}[VOC] + k_{loss}} \tag{3}$$

According to Crowley et al. (2010), k_{NO_3+VOC} $[VOC] + k_{loss}$ is the total loss frequency, $f(NO_3)$, calculated on the basis of the observed concentration and production term; and k_{NO_3+VOC} [VOC] is calculated by assuming that all losses of NO_3 apart from those constrained by aerosol uptake of N_2O_5 or direct reaction of NO_3 with NO or dry deposition of NO_3 or N_2O_5 are due to reaction with organics.

Therefore, the RO_2 production rate in ppt s^{-1} can roughly be calculated as:

$$\frac{\partial[RO_2]}{\partial t} = k_{NO_3+VOC}[NO_3][VOC] \tag{4}$$

and,

$$\frac{\partial[RO_2]}{\partial t} = \frac{k_{NO_3+VOC}[VOC]}{k_{NO_3+VOC}[VOC] + k_{loss}} \times k_{NO_2+O_3}[NO_2][O_3] = \alpha\, k_{NO_2+O_3}[NO_2][O_3] \tag{5}$$

where α is the fraction of NO_3 that is lost to organics.

Steady state mixing ratios of RO_2 produced from NO_3, i.e., $[RO_2]_{ss}$, can be calculated by assuming that in the absence of NO at night, RO_2 are uniquely lost by peroxy radical self reactions with a rate coefficient $k_{RO_2+RO_2}$:

$$[RO_2]_{SS} = \sqrt{\frac{\alpha\, k_{NO_2+O_3}[NO_2][O_3]}{2\, k_{RO_2+RO_2}}} \tag{6}$$

Atkinson et al. (2006), reported $k_{RO_2+RO_2}$ for reactions between HO_2 and various RO_2 varying between 1.2×10^{-11} and $7.8\times10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$. During DOMINO, $[RO_2]_{ss}$ can be brought into good agreement with most of the nocturnal RO_2^* measurements if $k_{RO_2+RO_2}$ is set to a value of $4\times10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$, as exemplary shown in Fig. 10 for the night between 1 and 2 December. On average, $[RO_2]_{ss}$ can account for 62 ± 20 % (min 8 %; max 99 %) of the RO_2^* on those nocturnal periods with available NO_3 data. Only for 20 % of those measured data, $[RO_2]_{ss} < 0.4\ RO_2^*$. The nighttime HO_2 mixing ratios measured did not exceed 8 pptv and normally varied between 2 and 6 pptv.

Basically, $[RO_2]_{ss}$ cannot account for the organic peroxy radical fraction in the RO_2^* mixing ratios measured on the 2 December (18:00 to 02:00 UTC), on the 30 November (18:00 to 06:00 UTC on the 1 December) and on the 24 November (00:00–04:00 UTC). All these periods (Figs. 10–11) were associated with emissions arriving from the Huelva sector. Highest mixing ratios of anthropogenic VOC and secondary oxidation products like acetone and formaldehyde were also characteristic of these events. Other VOC leading to peroxy radicals by ozonolysis can presumably be present as well. In particular on the 30 November around midnight benzene, toluene and acetone are close to 3 ppbv (Fig. 10). In that context, measurements of anthropogenic alkenes would have greatly complemented the interpretation of results; however, they are not available due to a serious instrument failure shortly before the campaign.

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 (Jensen et al., 1992). In particular during the event on the 24 November (Fig. 11), 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 (Fig. 10) 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 do not seem to disturb the agreement between $[RO_2]_{ss}$ and RO_2^* measured. The latter seem to be the case when the SO_2 are accompanied by NO_2 plumes with winds of marine origin, indicating another source of emissions.

In summary, emissions from the industrial area of Huelva in late autumn and winter often impact 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 concentration levels comparable to those of summer photochemical conditions. Using the simplified chemical approach above it can be concluded that the nocturnal formation of peroxy radicals from NO_3 and VOC is significant but not always sufficient to reproduce the RO_2^* measurements in industrial pollution events.

3.4 Diel HO_2/RO_2^* ratio and OH reactivity

The HO_2/RO_2 ratio for daylight and nighttime periods was calculated from the RO_2^* DUALER and HO_2 HORUS measurements during DOMINO, and the distribution versus wind direction was further investigated (Figs. 12 and 13). As pointed out in Sect. 3.1., data for wind speed $< 1.5\,\mathrm{m\,s^{-1}}$ have not been considered in the analysis in order to rule out any effect of stagnant conditions.

The HO_2/RO_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_2 in HO_2 in anthropogenic regimes. However, there is neither a significant correlation between HO_2/RO_2 or RO_2^*

and NO, which was close to the detection limit most of the nights, or NO_x. It can be concluded that the radical chemistry was mainly VOC controlled.

Interestingly, the ratio HO_2/RO_2^* reaches occasionally values >1 for wind directions around 260° and 330°, as on the 2 December night and 3 December daytime periods. These wind sectors indicate the arrival of air masses affected by the emissions of the industrial and port areas of Huelva. As RO_2^* comprises HO_2 this must be related with the use of data from two different instruments which can be subject to different experimental interferences.

In that context, Fuchs et al. (2011) recently reported interferences in the HO_2 measurement by laser induced fluorescence (LIF) instruments, like HORUS, of some RO_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_2 mixing ratios measured by LIF can actually be the sum of HO_2 and a significant fraction of RO_2 mixing ratios. The effect of this interference depends on the measurement conditions (retention time and NO concentration) and is presently being quantified for the HORUS instrument. Concerning DOMINO, as this interference only affects the HO_2 data, it could explain the $HO_2/RO_2^* > 1$ in some of the air masses. From the interfering substances investigated by Fuchs et al. (2011) only benzene and isoprene were measured during DOMINO. Therefore the measured HO_2 is considered as an upper limit. This issue requires further investigation.

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 change length used for the calculation of the RO_2^* might change significantly with the set up as result of peroxy radical losses, especially HO_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 $HO_2 + RO_2$ mixtures indicated that for 50 % HO_2 in the air mass, RO_2^* is 15 % underestimated by the DUALER reactor used for DOMINO (Andrés-Hernández et al., 2012).

Furthermore, RO_2^* versus HO_2 has been investigated for different OH reactivities measured during DOMINO for different wind sectors as defined by Sinha et al. (2012). Generally, the proportion of HO_2 in the total sum of peroxy radicals (RO_2^*) slightly increases as the OH reactivity increases (Fig. 14a). Highest OH reactivities during DOMINO (≈ 50–60 s^{-1}) are related to air masses within the continental sector, and generally associated with highest RO_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^{-1} and 2–10 s^{-1} respectively) with lower HO_2 proportion in RO_2^*.

The chemical heterogeneity of the air masses within the urban/Huelva sector which comprises a large number of industrial emission sources is reflected in the broad range of RO_2^*, HO_2, mixing ratios and OH reactivities in Fig. 14b. In particular the OH reactivity values support the idea suggested by the calculated $[RO_2]_{ss}$ from NO_3 (Sect. 3.3.1) of high nocturnal RO_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 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.

Calculated RO_2^* production rates from NO_3 steady state concentrations showed that reactions of NO_3 with VOCs were a significant source of nighttime organic peroxy radicals ($[RO_2]_{ss}$). On average, calculated $[RO_2]_{ss}$ can account for 62 ± 20 % of the RO_2^* measured on those nocturnal periods with available NO_3 data. However, during peak events at the highest measured VOC of anthropogenic industrial origin the estimated NO_3 production rates cannot account for the measured concentration levels, indicating

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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 O_3 and VOC reactions as RO_2 source could not be directly evaluated.

The HO_2/RO_2^* ratio derived from RO_2^* PeRCA and HO_2 LIF measurements usually remained around 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. The proportion of organic peroxy radicals in RO_2^* was investigated by calculating the corresponding HO_2/RO_2 ratios. Generally, the HO_2 proportion in the total varied between 25 % and 45 %. Highest HO_2/RO_2 ratios were though measured in air masses of continental origin with the highest values of RO_2^* and OH reactivity, indicating the presence of some RO_2 in the air mass interfering in the HO_2 determination.

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 ($\approx 10\,s^{-1}$). This, in turn, confirms the importance of the nocturnal production of peroxy radicals from the ozonolysis of non measured VOCs during DOMINO.

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Table 1. Main features of the DOMINO instruments used in this study.

Instrument/ Institute	Principle	Species	time resolution (s)	Detection limit	Uncertainty	Reference
DUALER/ IUP-UB	Chemical amplification	$RO_2^* = HO_2 + \Sigma RO_2$	60	1–3 pptv (RH ≤ 50 %) 5–10 pptv (RH > 70 %)	30 % for RH ≤ 50 %; 60 % for RH > 70 %	this paper
HORUS/ MPI-Mainz	LIF (FAGE)	OH, HO_2	60	0.037 pptv 0.29 pptv	18 % 18 %	Martinez et al. (2010)
/MPI- Mainz	OA-CRD	NO_3, N_2O_5	5	5–7 pptv*	35 %*	Crowley et al. (2011)
CLD-790 SR Ecophysics/ MPI-Mainz	Chemilum./ Phot. con.	NO, NO_2	1	6 pptv 8 pptv	5 % 8 %	Hosaynali Beygi et al. (2011)
Airpointer/ U. Mainz	UV photometry UV fluorescence	O_3, SO_2	6	< 1 ppbv	1 ppbv	Diesch et al. (2012)
Aero Laser AL 4021/ MPI-Mainz	Hantzsch reaction	HCHO	160	22 pptv	29 %	Kelly and Fortune, (1994)
/MPI-Mainz	TD-GC-MS	VOC	3600	ca. 1 pptv	15 %	Song et al. (2011)
/MPI-Mainz	CRM-PTR-MS	OH reactivity	60	$3.5\,s^{-1}$	20 %	Sinha et al. (2008)

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_3 was calculated from measured N_2O_5 and NO_2 (see Crowley et al., 2011 for details).

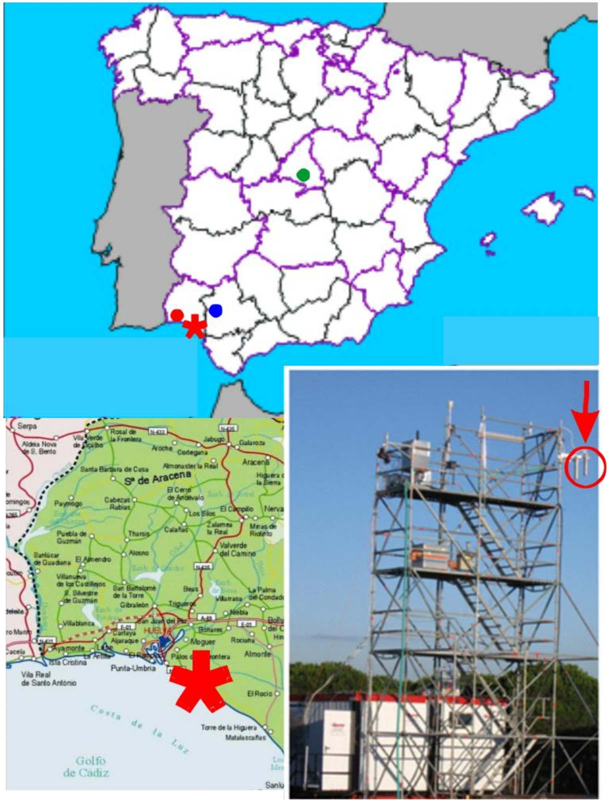

Fig. 1. Map of the site. El Arenosillo is highlighted by a red star. Main urban locations in the prevailing wind directions are also marked by dots: Huelva (red), Sevilla (blue) and Madrid (green). On the right side of the picture an arrow indicates the position of the DUALER inlet on the top of the 10 m scaffold for DOMINO measurements.

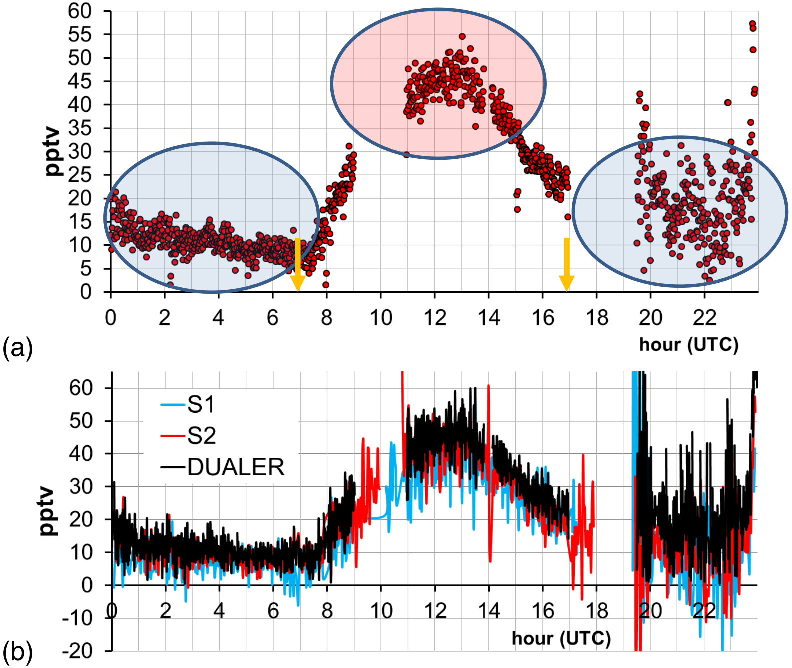

Fig. 2. (a) DUALER peroxy radical mixing ratios RO_2^* measured on the 23 November 2008, exemplifying diel patterns observed during DOMINO: non photochemical production (blue) at dawn and in the evening and photochemical production (red) in daylight periods. Savitzky-Golay 5 min averages are plotted for clarity. The time is given in hours (UTC) and the yellow arrows mark sunrise and sunset (UTC), **(b)** RO_2^* 1 min values obtained from individual measurement channels (S1 and S2) and by combining both signals (DUALER).

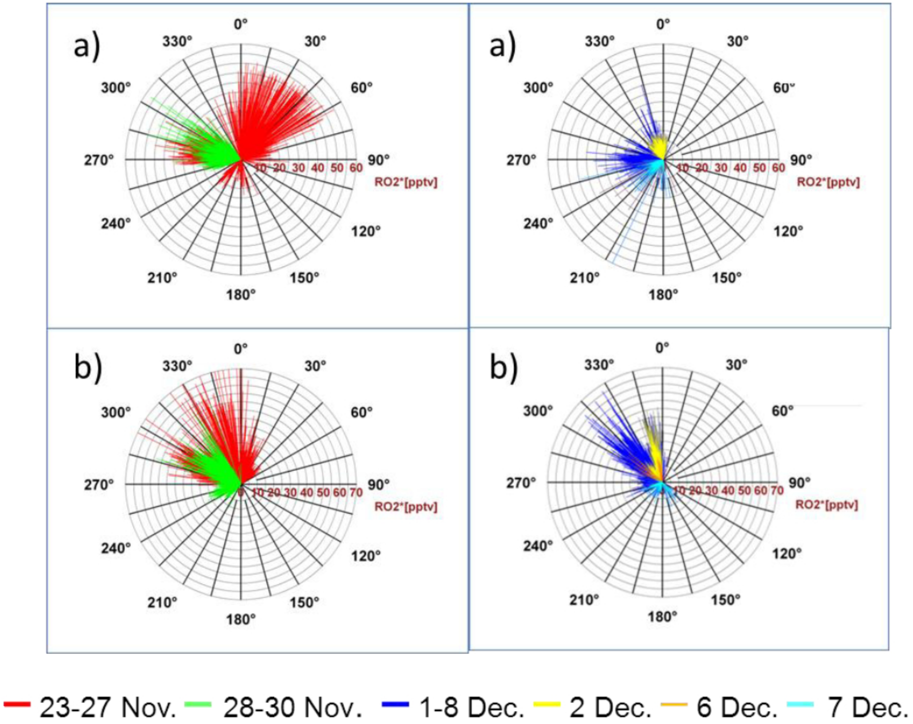

Fig. 3. Distribution of RO$_2^*$ mixing ratios measured by DUALER according to local wind direction. Data are classified according to periods of **(a)** photochemical (06:00–17:00 UTC) and **(b)** non photochemical (00:00–06:00 and 17:00 to 24:00 UTC) radical production.

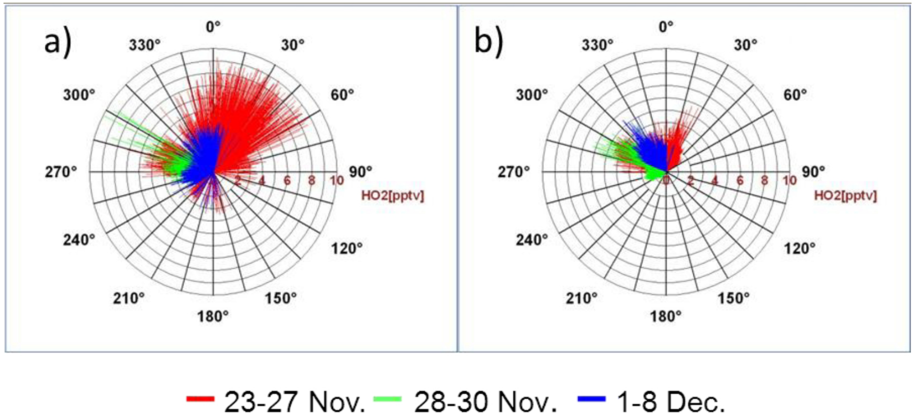

Fig. 4. Distribution of HO_2 mixing ratios measured by HORUS according to local wind direction. Data are classified according to periods of **(a)** photochemical (06:00–17:00 UTC) and **(b)** non photochemical (00:00–06:00 and 17:00 to 24:00 UTC) radical production.

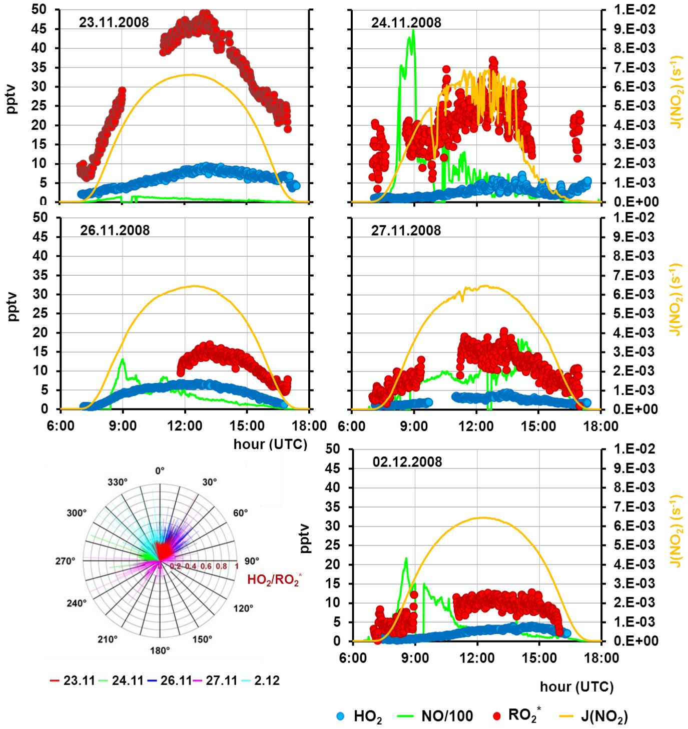

Fig. 5. Daylight RO_2^* and HO_2 measured by DUALER and HORUS respectively under clear sky conditions during DOMINO. Periods without DUALER data corresponds with calibration of one of the NO_2 detectors, in which the DUALER method of analysis cannot be applied (see text). The photolysis frequency $J(NO_2)$ 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).

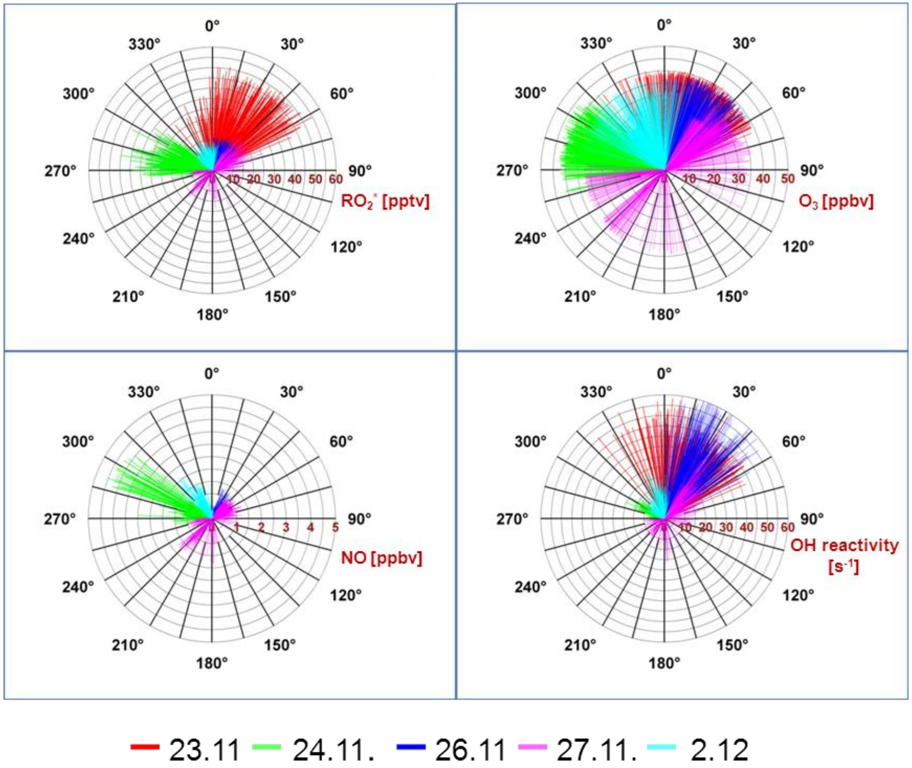

Fig. 6. Measured RO$_2^*$, O$_3$, NO mixing ratios and OH reactivity versus wind direction under clear sky conditions. Only periods of photochemical activity (06:00–17:00 UTC) are considered.

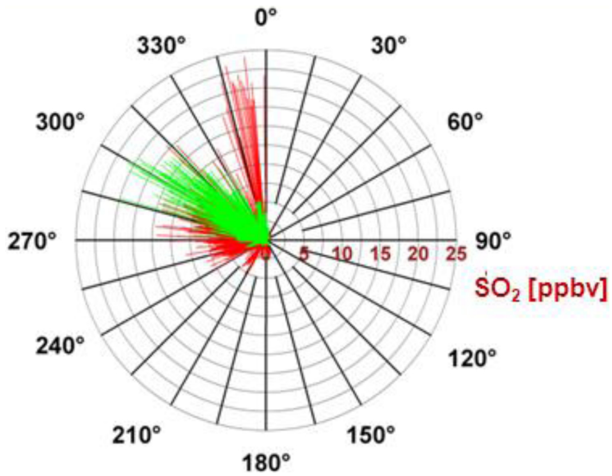

Fig. 7. SO_2 distribution versus wind direction. Periods of photochemical (06:00–17:00 UTC) and non photochemical (00:00–06:00 and 17:00 to 24:00 UTC hours) activity are depicted in red and green respectively. Only data corresponding to wind speeds $> 1.5\,\mathrm{m\,s^{-1}}$ are considered in the analysis.

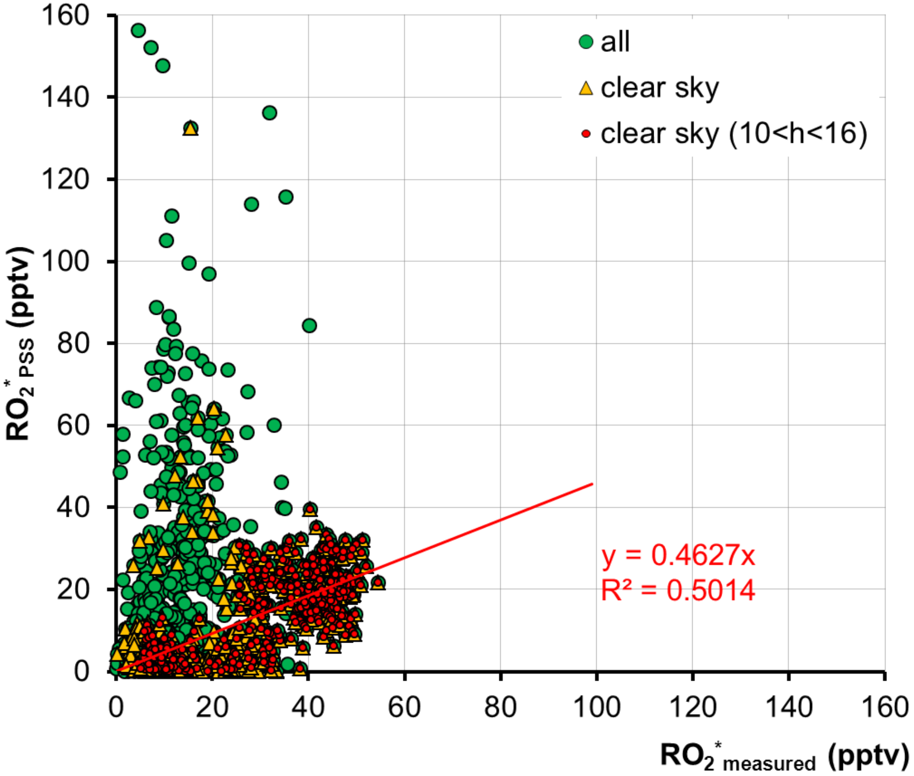

Fig. 8. RO_2^* mixing ratios calculated from the Photostationary State (PSS) versus RO_2^* measured by the DUALER. The correlation improves for periods of maximum insolation between 10:00 and 16:00 UTC (red dots).

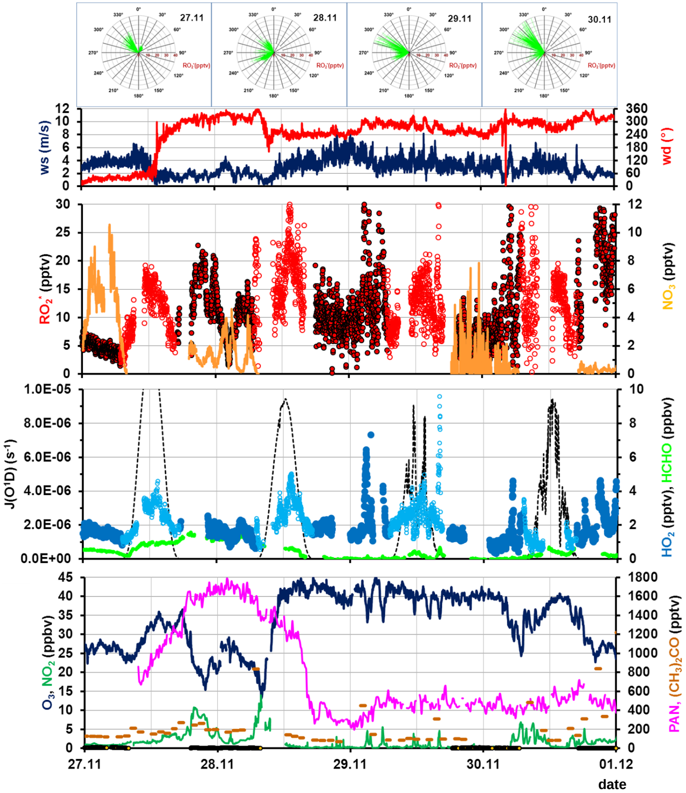

Fig. 9. Trace gases measured during the 27–30 November. ws: wind speed; wd: wind direction. Nocturnal HO_2 and RO_2^* mixing ratios are highlighted. The top panel shows wind roses of the measured nocturnal RO_2^* for the period. Generally NW directions are associated to higher RO_2^* levels.

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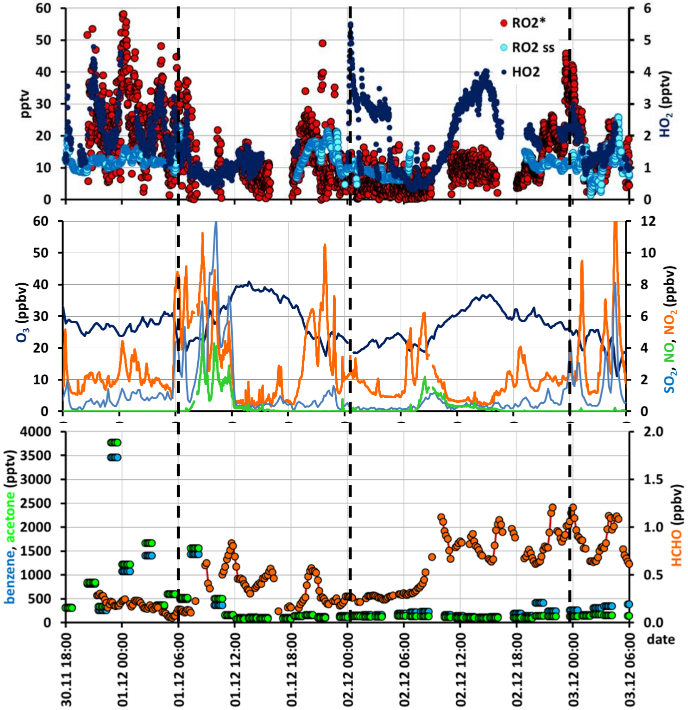

Fig. 10. Comparison between $[RO_2^*]ss$ calculated from NO_3 production and RO_2^* measured by DUALER during events of high VOC: 30 November–1 December and 2–3 December. Mixing ratios of other measured trace gases are also included for clarification.

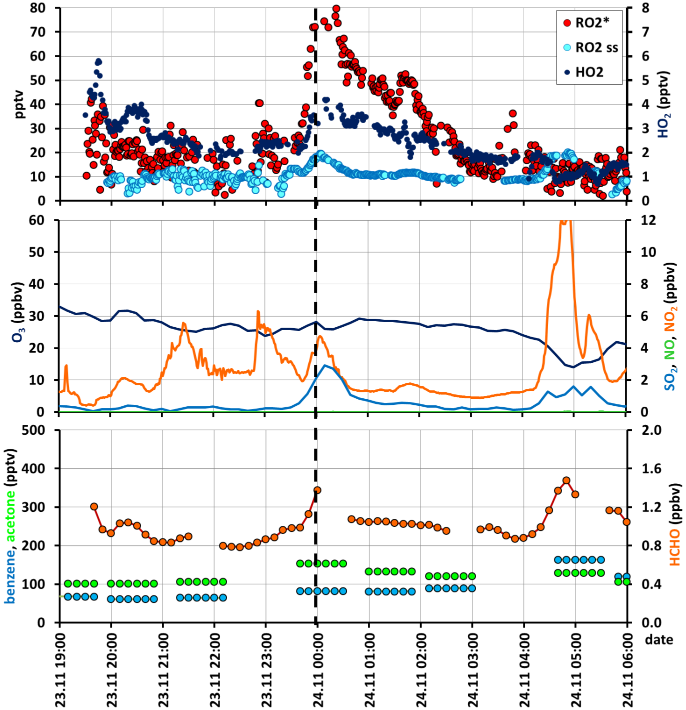

Fig. 11. Comparison between $[RO_2^*]$ss calculated from NO_3 production and RO_2^* measured by DUALER during events of high VOC: 23–24 November. Mixing ratios of other measured trace gases are also included for clarification.

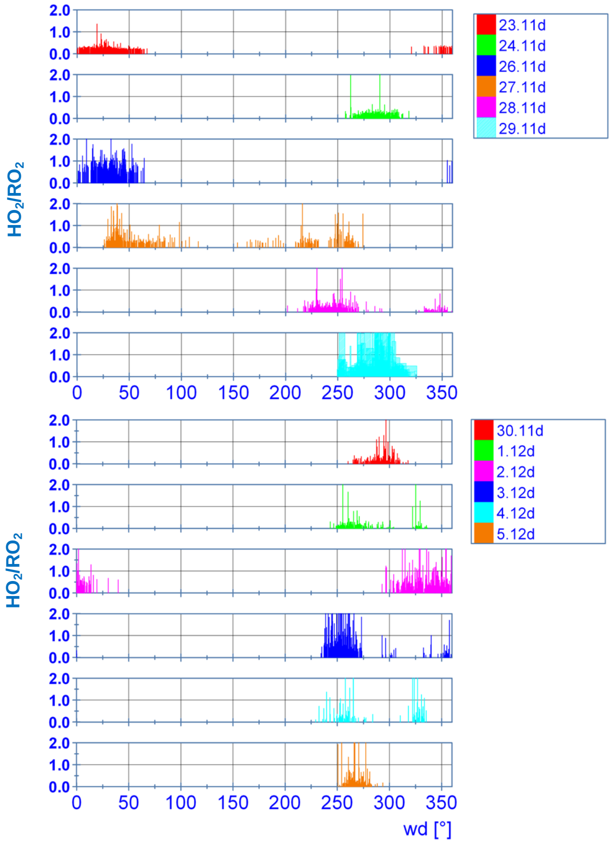

Fig. 12. HO$_2$/RO$_2$ ratios derived from the HO$_2$ and RO$_2^*$ measured in the daylight periods by HORUS and DUALER respectively.

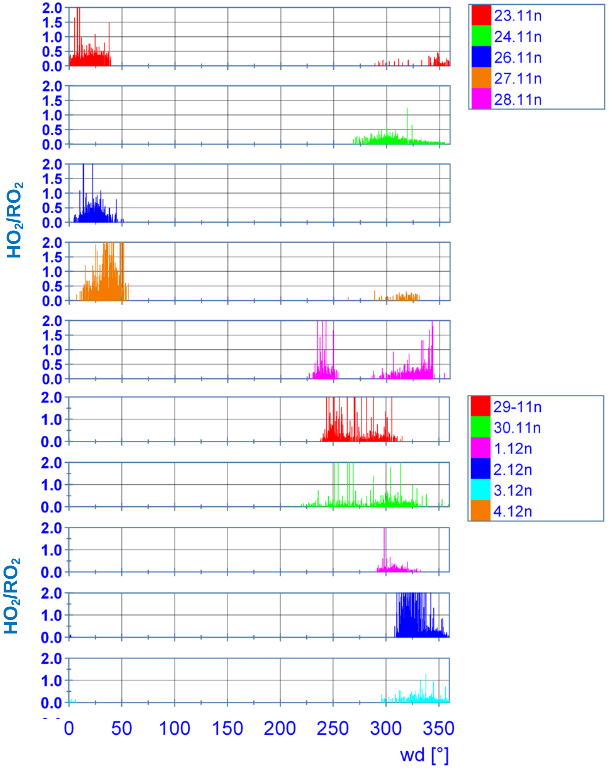

Fig. 13. HO_2/RO_2 ratios derived from the HO_2 and RO_2^* measured in the nighttime periods by HORUS and DUALER respectively.

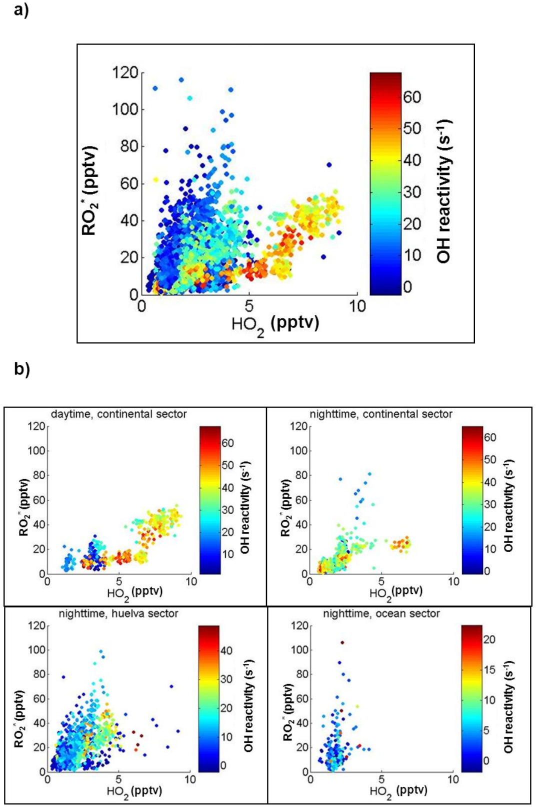

Fig. 14. RO_2^* versus HO_2 for different OH reactivities measured during DOMINO **(a)** all measurements; **(b)** different selected wind sectors.