Total OH Reactivity

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Contents

Abstract Total OH reactivity is defined as the total loss rate of reaction of the hydroxyl radical OH with atmospheric chemical compounds. It represents the inverse of the OH radical lifetime. Since OH is the main atmospheric oxidant during daytime, measuring the total OH reactivity represents an estimate of the total loading of reactive molecules in the atmosphere. This chapter presents the measurement principle of total OH reactivity and then results from measurements in the Mediterranean basin, which are placed in the general context of worldwide measurements. The major applications of such measurements are highlighted: first, the total OH reactivity is compared to the sum of OH reactivities of individual VOCs,

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which allows one deriving a missing non-measured part. Then instantaneous photochemical ozone formation rates, and the chemical regime of such ozone formation, are presented.

1 Total OH Reactivity Concept and Applications

Total OH reactivity (R) is defined as the total loss rate of reaction of the hydroxyl radical OH with atmospheric chemical compounds and represents the inverse of the OH radical lifetime. Since OH is the main atmospheric oxidant during daytime, measuring the total OH reactivity represents an estimate of the total loading of reactive molecules in the atmosphere. Concurrently, a large number of reactive atmospheric compounds can be measured with the available current technologies in order to determine their concentration, therefore their reactivity to OH. The latter is done by considering the sum of the products between the concentration X_{i} of each measured molecule i and the rate constant of reaction k of i with OH (Eq. 1). This parameter is often named calculated OH reactivity.

$$R = \sum_{i} k_{\mathrm{Xi\,+\,OH}} X_i \tag{1}$$

Total OH reactivity and calculated OH reactivity represent, respectively, an experimental and theoretical approach of the same parameter, used to examine the number and abundance of reactive hydrocarbons in the atmosphere. Measuring the OH reactivity is relevant for many aspects as listed below.

1.1 OH Radical Sources

Measures of the total OH sink (OH reactivity) are helpful to constrain the total OH source when the concentration of the hydroxyl radical is known. Whalley et al. (2011) compared OH production rates, OH sink, and OH measurements carried out in the tropical rainforest of Borneo and found out that OH in the tropics is produced at a rate ten times greater than the identified OH sources. Their predictions of OH concentration further highlighted that this parameter is underestimated by measurements, with important implications for understanding VOC degradation and methane lifetime in the tropics.

1.2 Unmeasured Atmospheric Constituents

Measurements of OH reactivity can be performed together with measurements of ambient air constituents. In an environment where every single air component has been quantified and its reaction rate constant with the hydroxyl radical is known, the measured OH reactivity and the calculated OH reactivity will be the same. If the calculated OH reactivity is smaller than the measured OH reactivity, then a fraction of the composition of the air remains unidentified. This fraction is usually regarded as "missing OH reactivity". Missing OH reactivity was found to different extents in many environments and was generally highest where biogenic VOCs dominated (Di Carlo et al., 2004; Nölscher et al., 2016; Zannoni et al., 2017). Comparisons of missing OH reactivity results should be done with caution, as the unidentified fraction depends on the number and type of chemical compounds monitored and used to determine the calculated OH reactivity. Nevertheless, this approach is useful for analyzing time series and improving our current understanding of environmental and atmospheric processes. It can also be used as a quality control measure of the deployed techniques.

1.3 Ozone Production Potential

Rates of instantaneous ozone production potential and regimes can be derived from measurements of OH reactivity when combined with measurements of NO_x, OH, and peroxy radicals. Sinha et al. (2012) developed this type of approach to analyze the impact of point sources on regional ozone levels during the DOMINO campaign on the southwestern coast of Spain. They found out that the ozone production potential was higher when the coastal site was more influenced by continental air masses. They also identified the NO_x point sources that were limiting such an effect. Nevertheless, a limitation of the method is that the ozone production potential so determined assumes that ozone production is not limited by availability of NO_x. An alternative method to determine net ozone production from quasi-Lagrangian isopycnic balloon measurements is presented in the following chapter (Gheusi, 2022).

1.4 Particle Formation

OH reactivity offers a direct link between VOC emission and new particle formation, which will be addressed in the three following chapters by Sellegri & Rose (2022), Sartelet (2022), and Michoud (2022). Mogensen et al. (2011) analyzed the particle formation events that occurred during 1 month of field campaign in the Finnish boreal forest with the measured OH reactivity. They found out that the missing OH reactivity increased during the particle formation event. Correlations between measured and missing reactivity with the condensation sink confirmed that the missing reactivity could not be explained by OH loss on particle surface, but rather by OH oxidation with VOCs forming higher oxidized semi-volatile compounds.

2 Measuring the OH Reactivity

In 1993, William H. Brune conceived for the first time the concept of total OH reactivity as the direct measurement of OH loss rate (Kovacs & Brune, 2001). A few years later, the first measurements of total OH reactivity were performed independently by two research groups, (i) in the laboratory using a differential absorption lidar technique (Calpini et al., 1999) and (ii) in ambient air based on laser-induced fluorescence for detecting OH (Kovacs & Brune, 2001). Currently, the total OH reactivity can be measured using two main approaches: the direct measurement of the decay of artificially produced OH and indirectly measuring the concentration of a reference molecule whose reactivity to OH is established. Direct measurement of OH reactivity is achieved with three main types of instruments. The first type consists in detecting the OH decay in a flow tube where ambient air is drawn, whereas OH is continuously produced from photolysis of H_2O and monitored through laser-induced fluorescence (Mao et al., 2009). The second type deploys a flow tube combined with chemical ionization mass spectrometry (CIMS) in order to detect H_2SO_4 from the chemical conversion of OH (Muller et al., 2018). The third type, laser photolysis-laser-induced fluorescence (LP-LIF), detects OH through LIF, whereas OH is artificially produced by ozone photolysis using short laser pulses at a low repetition rate (Sadanaga et al., 2004; Fuchs et al., 2017a). The indirect method, known as comparative reactivity method (CRM), generally uses proton transfer reaction mass spectrometry (PTR-MS) to monitor the concentration of a reference molecule reactive to OH mixed in a glass reactor with artificially produced OH and ambient air (Sinha et al., 2008). Alternatively, a gas chromatography-photoionization detector (GC-PID) can be used instead of a PTR-MS (Nölscher et al., 2012). Intercomparisons of the same method (Zannoni et al., 2015) or different methods (Hansen et al., 2015) and of all methods (Fuchs et al., 2017b) have been carried out in recent years aiming at assessing the performances of the discussed techniques. Direct methods demonstrated to be more precise, have a better time resolution and lower limit of detection. Nevertheless, indirect methods have the advantage that they do not require a large sampling flow and therefore can be assembled from instruments already in use in many laboratories studying VOCs.

3 OH Reactivity Measurements in the Mediterranean Basin

Total OH reactivity was measured in a few studies conducted in the Mediterranean basin, including at background sites located in the western basin (Corsica; Zannoni et al., 2017) and eastern basin (Cyprus; Keßel, 2016), over open waters (Pfannerstill

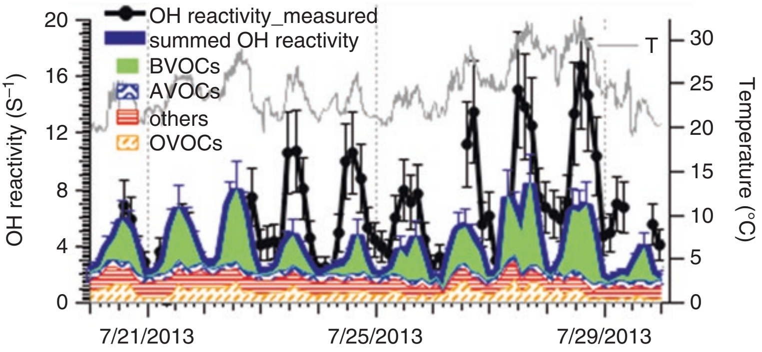

Fig. 1 Total measured and calculated (summed) OH reactivity and ambient temperature (in grey) during summer 2013 at the remote site of Ersa (42.969°N, 9.380°E) in Cape Corsica (France). The origins of the air masses for the reported time were classified as from the North (21–23/07), West (23–26/07), and South (26–30/07). Summed OH reactivity represents the sum of reactivities of biogenic volatile organic compounds (BVOCs), anthropogenic volatile organic compounds (AVOCs), oxygenated organic compounds (OVOCs), and others (sum of CO, methane, and NO_x contributions). More information can be found in Zannoni et al. (2017) and Michoud et al. (2017)

et al., 2019), in a forest (Zannoni et al., 2016), over an agricultural region in the Po Valley (Kaiser et al., 2016), and at a near coastal SW Spanish site in vicinity of the basin (Sinha et al., 2012). The main objectives of these studies were either to determine and investigate OH missing reactivity or to investigate the ozone formation potential. In parallel to other efforts, the ChArMEx program added to existing literature new measurement points in the region, especially over the western part of the basin (Zannoni et al., 2016, 2017).

Zannoni et al. (2017) investigated the OH reactivity based on CRM measurements performed at the station of Ersa (42.969°N, 9.380°E) on the north of Cape Corsica ("Cap Corse" in French) in July 2013, on a crest at the northeastern tip of Corsica island, within the ChArMEx program (see Dulac et al., 2023 and the book appendix). This site can be considered as a background site, with low local anthropogenic influence, and is under the influence of various air masses with different origins (marine influenced or anthropogenically influenced as those from southern France or northern Italy). Nevertheless, in the absence of major pollution events, and with relatively clean local air, the air masses' origin had little effect on the measured reactivity. In contrast, local biogenic emissions from the scrub type of vegetation surrounding the measurement site (specifically, macchia and low aromatic plants) had the largest impact on OH reactivity. OH reactivity in Corsica was on average 17 ± 6 s^{-1} and had a campaign maximum of 22 s^{-1}. Despite this, a significant missing OH reactivity was found (up to 50%) and attributed to oxidation products of BVOCs (Fig. 1).

Significantly lower levels (mean campaign value of 1.8 s^{-1}; Keßel, 2016) were found in spring-summer 2014 in Cyprus island, in the eastern Mediterranean basin. The main explanation for the observed differences is given by the local ecosystems and impact of direct biogenic VOC emissions to the OH reactivity. Indeed, the measurement site in Corsica was influenced by dense macchia, while the site in Cyprus was very dry and with very little vegetation, showing only low biogenic VOC concentrations (sum of isoprene and terpenes maximum typically about 500 pptv; see Derstroff et al., 2017).

In September 2017, Pfannerstill et al. (2019) performed shipborne OH reactivity measurements with CRM during the AQABA campaign, departing from southern France, crossing the Mediterranean eastward to reach the Suez Canal, and then exploring the surroundings of the Arabian Peninsula. Aged and therefore rather clean air masses were encountered during the crossing of the Mediterranean, and the corresponding mean OH reactivity was low ($7.2 \pm 2.9\ s^{-1}$) with the OVOC group accounting for the largest calculated OH reactivity. Higher OH reactivity levels were measured only during short periods corresponding to polluted air from the mainland. The levels were significantly higher in the Arabian Gulf, Gulf of Suez, and Suez Canal, where atmospheric composition was influenced by various anthropogenic sources (urban, industrial, and from oil and gas production and processing). These measurements were used to derive ozone production regimes in terms of the OH reactivities of VOCs and NO_x. In the Mediterranean, it was then found that 97% of the time, a regime with a VOC-to-NO_x ratio suitable for ozone formation was encountered (i.e., it was intermediate between NO_x and VOC limitation).

Also in the framework of the ChArMEx and CANOPEE programs, Zannoni et al. (2016) measured the OH reactivity (CRM method) in June 2014 in a forest of downy oaks (*Quercus pubescens*), a typical Mediterranean species known as a high isoprene emitter (Keenan et al., 2009). Measurements at the geophysical station of Observatoire de Haute Provence (OHP) (43°55′54″N, 5°42′44″E) were performed at two heights, inside and above the canopy (respectively, 2 and 10 m as the canopy height was about 5 m). High OH reactivity was found (daytime mean of 29 s^{-1} and campaign maximum of 69 s^{-1} at 2 m), and as expected, isoprene was its main contributor during daytime (83% and 72% inside and above the canopy, respectively). The comparison between measured total OH reactivity and calculated OH reactivity from the measured VOCs showed that no significant missing reactivity was present during daytime (neither inside nor above the canopy). This suggests that intra-canopy oxidation was low, in agreement with the measurements of low levels of isoprene oxidation products and with previous studies with isoprene and oxidation products' flux measurements (Kalogridis et al., 2014). In contrast, a missing reactivity up to 50% was found during night-time, possibly due to unmeasured oxidation products, very likely oxygenated compounds. During night, local isoprene emissions are lower, and transport from more distant sources is thus relatively more important.

Another study performed directly in a forested area is the one by Bsaibes et al. (2020) which is based on measurements (CRM method) obtained during the LANDEX campaign in summer 2017 over a pine forest in SW France. Maritime pine (*Pinus pinaster*) is mostly found in Portugal forests but also at sites from the French and Italian Mediterranean coasts and is known to be a terpene emitter. This study is also based on measurements inside and above the canopy (respectively, at 6 and 12 m with a mean canopy height of 10 m). Measured OH reactivity was very high with values up to 99 s^{-1} inside the canopy and 70 s^{-1} above the canopy (respective means of 19.2 s^{-1} and 16.5 s^{-1}), with maximum values of OH reactivity mostly recorded during the nights. For this site, the main contributor to calculated OH reactivity was by far the monoterpene class (about 68–65% during daytime and 92–89% during night-time inside and above the canopy, respectively) followed by isoprene (25–27% during daytime). Missing OH reactivity showed a day-night variability. The authors suggest that it was mainly related to temperature-enhanced primary emissions and secondary oxidation products during the day and could be linked to transported and accumulated long-lived species in the stable nocturnal boundary layer during the night.

Kaiser et al. (2015) have determined a vertical gradient in OH reactivity during the PEGASOS campaign, which took place on-board a Zeppelin over the Po Valley (Italy) in July 2012. They have measured an OH reactivity of 5 s^{-1} at the ground level (with NO_x contributing to 40%) and only 2 s^{-1} at 800 m over an agricultural area (with OVOCs and CO contributing to 60%). These values are close to typical values for background air, i.e., an environment not influenced locally by anthropogenic or biogenic sources.

Finally, Sinha et al. (2012) measured OH reactivity during the DOMINO campaign in southwestern Spain in fall 2008. They classified their results according to the air mass origins, and the levels of OH reactivity were varying from background levels ($6.3 \pm 6.6\ s^{-1}$) when sampling marine air masses up to $31.4 \pm 4.5\ s^{-1}$ under the influence of northeastern continental air masses. They proposed an approach to use the measured OH reactivity (combined with NO_x and peroxy radical measurements) to constrain both diel instantaneous ozone production potential rates and regimes. They found a peak value of about 20 ppbV $O_3\ h^{-1}$ for the studied site (and have estimated that this value would be double if the site was not NO_x-limited). These values are much larger than those derived from quasi-Lagrangian ozone measurements under boundary-layer pressurized balloons drifting over the western Mediterranean Sea (1–2 ppbV $O_3\ h^{-1}$; Gheusi et al., 2016; Gheusi, 2022). Nevertheless, we note that these latter values are net production (versus gross production); therefore, the comparison must be considered with caution.

4 Conclusions and Recommendations

Only a few studies of OH reactivity have been conducted in the Mediterranean basin so far (Fig. 2; see Yang et al. (2016) for the corresponding references). Among those, we can distinguish measurements in the western and eastern basin, over open water, in forests, and at anthropogenically influenced sites. Studies in the western and eastern basins have shown that the western basin has a larger OH reactivity, which was mainly attributed to biogenic VOC, specifically terpenes, and possibly their oxidation products. Biogenic VOCs are very reactive compounds; therefore, their influence on OH reactivity is mainly local, although they can have a wider

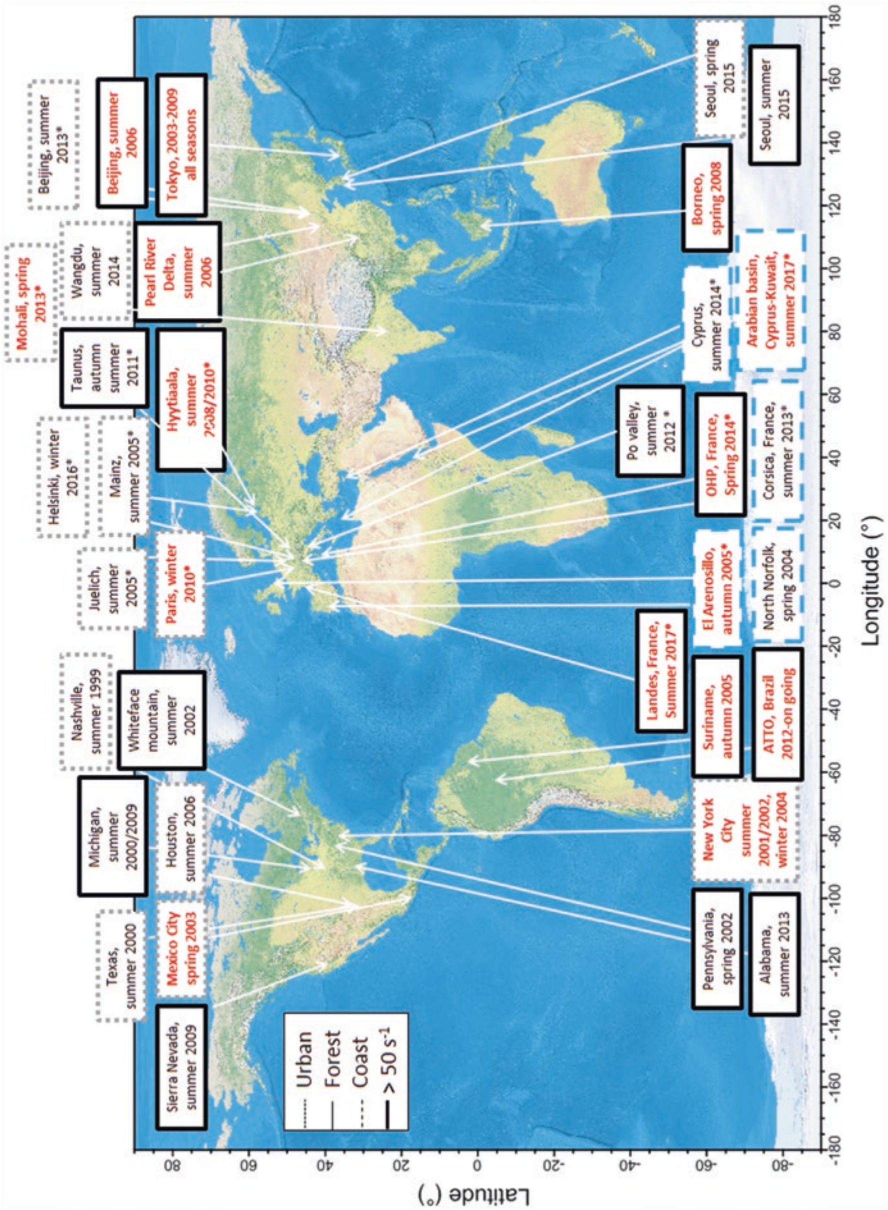

Fig. 2 Existing OH reactivity studies around the world. Studies conducted in the Mediterranean region are indicated with a *. High OH reactivity (and high concentration of very reactive VOCs) was reported in sites indicated in red. (Adapted from Zannoni, 2015)

impact through the transport of their oxidation products. Campaign periods with higher ambient temperature and sunlight triggered larger plant emissions and photochemistry, which explained the reported missing reactivity. The sites located in both the western and eastern basin were background sites, with weak pollution events; therefore, the different vegetation due to different latitudes was the driving factor for reactivity. The values measured at these sites are comparable to the reactivity measured over open water. Over open water, no local event occurred, and processed air masses, mainly containing OVOCs and CO, had a similar reactivity to the one measured in the western basin without the contribution of the local BVOCs. Sites under anthropogenic influence can also show high reactivity, when measurements are directly performed close to emission sources (see the case of megacities and urban agglomerates; Fig. 2).

As reported in Fig. 2, most measurements performed at coastal sites have been performed in the Mediterranean region. Therefore, the comparison with other non-Mediterranean coastal sites is limited. Nevertheless, as seen in other areas of the world, the environments usually associated with high OH reactivity (and often higher missing OH reactivity) are forested areas. This shows the importance to better characterize BVOC and their oxidation products. The development of a plant chamber facility (Hohaus et al., 2016) and similar facilities enabling controlled experiments will be of great help to investigate these chemical reactions and therefore to identify and quantify the oxidation products issued from BVOC compounds and their corresponding OH reactivity. In addition, for a complete understanding of OH reactivity in the Mediterranean basin, more measurements in different environments and seasons are needed. As an example, the Mediterranean region being often under the influence of biomass burning, OH reactivity measurements could also be useful to better characterize the corresponding pollution plumes, as done in another region of the world by Kumar et al. (2018). We note that OH reactivity is mostly useful when combined with other measurements. Therefore, we recommend to associate OH reactivity measurements to each field campaign deploying a large set of gaseous compound measurements, especially reactive VOCs. The objective is to determine whether there are any not measured compounds which lead to a significant missing OH reactivity and possibly investigate which ones when this is the case. If combined with measurements of NO_x, O_3, and OH radicals, the OH reactivity is also a useful parameter to help better constrain the OH budget and estimate the O_3 production potential. Finally, the explicit calculation of the total OH reactivity derived by atmospheric chemistry models (Whalley et al., 2016) with detailed chemical schemes would be very valuable to perform a direct comparison with measurements, but it is still challenging due to the large number of compounds (especially issued from multi-oxidation) involved.

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