

Review

A Review of the Direct Measurement of Total OH Reactivity: Ambient Air and Vehicular Emission

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Abstract: Total OH reactivity, an index utilized to evaluate the overall effect of atmospheric reactive species on hydroxyl radicals, has been assessed over the past half century, particularly in ambient air. The direct measurement of OH reactivity for vehicular sources has also been conducted, further enhancing our understanding of chemical compounds and processes in source emissions. However, the current summary on OH reactivity dominantly focuses on ambient, and the review of OH reactivity measurements and characteristics for vehicular sources was lacking. Herein, we comprehensively reviewed and compared the measurement techniques, values of total OH reactivity, reactive chemical species, and missing OH reactivity for ambient air and vehicular sources involving exhaust and evaporation. The OH reactivity values for ambient air are comparable to those for evaporative emission (around $0\text{--}10^2\text{ s}^{-1}$), whereas they are all lower by 2–3 orders of magnitude than exhaust emission. In areas dominated by anthropogenic emissions, inorganic reactivity dominates the OH reactivity, while in biogenic-dominated areas, organic reactivity is the main contributor. For vehicular sources, inorganic reactivity dominates the calculated OH reactivity for exhaust emissions, while volatile organic compound reactivity (especially alkene reactivity) can almost explain all the calculated OH reactivity for evaporative emissions. The missing reactivity for ambient air and vehicular emission might derive from unmeasured, even unknown, organic species. We finally discussed possible new directions for future studies of total OH reactivity.

Keywords: OH reactivity; reactive chemical species; missing source; ambient air; vehicular source



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1. Introduction

Severe atmospheric complex pollution, characterized by the coexistence of primary and secondary pollution, appeared in China, especially in urban cities. Despite the reduction in the concentrations of primary pollutants, secondary pollution such as ozone (O_3) and secondary organic aerosol is getting worse. The O_3 average trends for the focus megacity clusters are 3.1 ppb a^{-1} , 2.3 ppb a^{-1} , 0.56 ppb a^{-1} , and 1.6 ppb a^{-1} for North China Plain, Yangtze River Delta, Pearl River Delta, and Szechwan Basin, respectively [1]. The tropospheric ozone is generated by the photolysis of nitrogen dioxide (NO_2) in radical cycling. Within the radical cycling, the hydroxyl radicals (OH), the dominant daytime oxidant in the troposphere, initiate the degradation of trace gases and pollutants [2,3]. The OH radicals can react with primary pollutants (carbon monoxide (CO), nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), O_3 , volatile organic compounds (VOCs), etc.) and are converted into peroxy radicals involving hydroperoxyl radicals (HO_2) and organic peroxy radicals (RO_2). The HO_2 and RO_2 radicals are transformed into OH radicals via the reactions with NO. Among the interconversion of OH, HO_2 , and RO_2 radicals, the primary pollutants are converted into secondary pollutants.

In the classical radical mechanism, the sources of OH radicals include the primary sources (mainly photolysis of nitrous acid [HONO], photolysis O_3 , ozonolysis of alkenes)

and secondary sources (mainly $\text{HO}_2 + \text{NO}$ and $\text{HO}_2 + \text{O}_3$). In terms of the sinks of OH radicals, it is considered that OH radicals mainly react with CO, NO_x, O₃, and VOCs. However, only a small fraction of the VOCs number has been measured [4], which causes difficulty in the accurate calculation of OH sinks. The total OH reactivity (k_{OH}) with a unit of s^{-1} , which was first proposed in 2001 [5], can help with the evaluation of the total OH destruction rates. k_{OH} is a vital parameter to quantify atmospheric oxidation capacity. It represents the pseudo first-order rate coefficient of OH radicals and is equivalent to the reciprocal atmospheric OH lifetime. k_{OH} is the sum of the reactivity of all reactive species in the troposphere, as shown in Equation (1) [6,7]. Based on the direct and indirect methods developed in the past decade, k_{OH} values have been directly measured in the different environmental conditions involving the forest, suburban, and urban areas. The k_{OH} values, diurnal variation, chemical composition, and missing reactivity sources have been presented differently in different environmental conditions. The direct measurement of k_{OH} , which is a bottom-up molecular approach, can help to test the completeness of VOC measurements. Additionally, the k_{OH} values can be applied to calculate the missing OH sources, which is the difference between the total OH destruction rate (the product of the observed OH concentration and k_{OH}) and the known OH production rate. Therefore, the direct measurement of k_{OH} values is significant to the exploration of radical chemistry.

$$k_{\text{OH}} = k_{\text{OH}+\text{NO}_x}[\text{NO}_x] + k_{\text{OH}+\text{CO}}[\text{CO}] + k_{\text{OH}+\text{SO}_2}[\text{SO}_2] + k_{\text{OH}+\text{O}_3}[\text{O}_3] + k_{\text{OH}+\text{VOC}_i}[\text{VOC}_i] + \dots$$

$$= \sum k_{\text{OH}+\text{X}_i}[\text{X}_i] \quad (1)$$

where $[\text{X}_i]$ represents the concentration of a reactive component (CO, NO_x, VOCs, etc.) and $k_{\text{OH}+\text{X}_i}$ denotes the corresponding bimolecular reaction rate constant.

Besides the observation in the ambient air, k_{OH} values have been measured in vehicular sources since 2010 [8]. To effectively control the VOCs originating from vehicular emission, prior studies have explored the emission characteristics (mainly emission factors) of VOCs in-depth, involving alkanes, alkenes, aromatics, oxygenated VOCs, intermediate-volatility organic compounds (IVOCs), and semi-volatile organic compounds (SVOCs). As the emission standards upgrade, a significant tendency for pollutants to decrease has been observed, which might be attributed to the improved combustion efficiency and after-treatment technology [9–11]. For instance, dramatic progress in the reduction of tailpipe emissions for the U.S. on-road fleet over the past 60 years has been observed [12]. In addition, VOC emissions reduced obviously from “Limits and measurement methods for emissions from light-duty vehicles” (China I–VI), as well as the reactive species, vary significantly, along with the more rigorous emission standards [9]. The mass fraction of alkanes, alkenes, and aromatics reduced with the upgrading of emission standards, whereas the percentage of oxygenated VOCs (OVOCs) in VOCs increased [9,10]. As for the IVOCs, Qi et al. (2021) [10] reported that the emission factors decreased from 377 mg/kg-fuel for China II–III vehicles to 67 mg/kg fuel for China V vehicles [10]. The impacts of startup temperature, fuels, engines, and after-treatment technology on vehicular emissions have been reported [13–18]. The variations in VOC emission factors and reactive species illustrate that the comprehensive exploration of the reactive species for vehicular sources is needed and will have an essential impact on vehicle emission control policy. Nevertheless, the complexity of the number and species of VOCs and the limitations of VOC measurement instruments both lead to the unachievable measurement of many VOC species [6]. Still, the undetected or unidentified reactive species might add uncertainty to understanding the roles of VOCs in atmospheric chemistry and, thus, significantly impact the generation of secondary pollutants. To fully characterize the reactive VOC species of vehicular sources, Nakashima et al. (2010) evaluated the k_{OH} of the exhaust emissions for the first time [8]. Thereafter, more k_{OH} measurements for vehicular sources occurred over the past decade [19–21]. The direct measurement of k_{OH} for vehicular sources can help us to identify whether the measurement of reactive species originating from vehicles is

complete and, thus, it could further improve the accuracy of the evaluation for secondary pollutant formation from vehicular sources.

Two reviews have been published to comprehensively introduce the measurement and observations of OH reactivity [6,22]. Yang et al. (2016) [22] summarized the measurement methods, the results of observed OH reactivity, and the comparison of observed and calculated OH reactivities for ambient air. Yang et al. (2019) [6] also focused on reviewing the OH reactivity for ambient air, involving the measurement techniques, OH reactivity observations, and the implications in radical closure experiments. To the best of our knowledge, few studies reviewed the k_{OH} measurements for vehicular sources, especially the comparison between ambient air and emission sources. It is crucial to incorporate a comprehensive review to provide a holistic understanding of the progression in the field of vehicular VOC emissions and their control technologies. This review firstly integrates the insights from a total of 366 articles sourced from the Web of Science spanning from 1976 to 2023 (<https://webofscience.clarivate.cn/>, last accessed 11 November 2023). The search keywords were “OH reactivity”, “measurement”, and “atmosphere”. The publications per year in this field are gradually increasing to a peak in 2018. After that, there was a slight but not significant decrease in the publications per year. The high citations per year occurred in 2021 and 2022, demonstrating that the research of this field has become more popular in recent years.

This review will focus on the recent updates in k_{OH} measurement technology, the direct k_{OH} measurement results for ambient air and vehicular emissions, and the comparison of k_{OH} values between ambient air and vehicular emissions. We also provided our insight into the direct k_{OH} measurement and the more detailed VOC measurement to understand tropospheric photochemistry more comprehensively in the future. This review not only offered a valuable historical perspective on the changes in VOCs emissions over the past decades, but it also provided significant guidance for future research directions and the formulation of environmental policies.

2. Measurement Techniques of Total OH Reactivity

2.1. Total OH Reactivity Measurement System for Ambient Air

In the past several decades, two methods have been utilized for the direct measurement of k_{OH} in the ambient air: the direct method and the indirect method. The direct method is based on the decay of OH concentrations with a reaction time to obtain the k_{OH} values directly. The OH decay is obtained from the reaction of anthropogenically produced OH radicals with reactive species in ambient air. The direct method mainly contains three types: Total OH Loss-rate Measurement (TOHLM) [5], Laser flash Photolysis–Laser Induced Fluorescence (LP–LIF) [23], and Chemical Ionisation Mass Spectrometry (CIMS) [24]. The indirect method refers to the comparative reactivity method (CRM) [25]. The principle of CRM is that a known concentration of the reference substance (usually pyrrole), which is not present in the air, is passed into a reaction tube and reacts with an artificially generated high OH concentration. The concentration decay of the reference species is measured in zero air and ambient air, respectively. By comparing the concentration of the reference species in zero air and ambient air, the competition of the two reactions, one is the reaction of the reference species and the reactive species in ambient air and another is the reaction of the reference species and OH radicals were determined and then k_{OH} was indirectly measured.

The above methods have been introduced in detail by Yang et al. (2016) [22] and Yang et al. (2019) [6]. Herein, we present only the latest developments in k_{OH} measurement methods since 2019. In 2021, an improved comparative reactivity method (ICRM) was newly proposed [26]. As introduced by Yang et al. (2019) [6], the already developed methods are severely disturbed in high NO levels, especially TOHLM and CRM. The interference originates from the anthropogenic production of OH radicals, which is generated by H_2O photolysis, as shown in (R1). Along with the generation of OH radicals, H atoms are also produced, which will continue to react with O_2 to form HO_2 radicals. The generated HO_2 radicals subsequently react with NO to generate OH radicals again, so that

(R2) and (R3) would interfere with the k_{OH} measurement due to radical cycling in high NO concentrations.



Recently, scientists improved the k_{OH} measurement instruments based on the original methods, mainly the CRM instrument. To solve the OH regeneration in high NO concentrations, Wang et al. (2021) [26] designed a new-and-improved CRM reactor (ICRM). The advantages of the ICRM system include: (1) HO_2 concentrations were designed to be suppressed by adding NO into the system continuously; (2) The deviation derived from the reactions of VOCs and OH radicals in the reactor under different ambient NO concentrations has to be realized to be correlated; (3) In terms of the interference from pyrrole photolysis, the authors improved the structure of the glass reactor, which would reduce the amount of ultraviolet light generated by the mercury lamp reaching the main body of the glass reactor. Overall, the new ICRM system has already realized successful application in field campaigns, even under high-NO-environmental conditions [26].

2.2. Total OH Reactivity Measurement System for Vehicles

Despite the widely adopted approaches for k_{OH} measurement in ambient air, it is not reasonable to directly apply the k_{OH} measurement instrument for ambient air to vehicular sources. Prior studies measured the k_{OH} values for exhaust emission based on the chassis dynamometer [8,20,21,27]. As shown in Figure 1, the schematic diagram of the measurement system is presented, including the detection and sampling systems. In the detection system, CO, NO, NO_2 , and VOC species are measured along with the total OH reactivity generally, and the LP-LIF system is usually used for the k_{OH} measurement of vehicles in previous studies [8,20,21]. In terms of the principle for the LP-LIF approach, high OH concentrations are generated artificially in the flow tube. The OH radicals will decay with the reactions via reactive species in the sampling gas, and then the k_{OH} can be quantified by fitting the decay of OH concentrations. Additionally, the artificial OH radicals in the flow tube are produced by 266-nm laser photolysis of ozone and the successive reaction with water vapor, as shown in (R4) and (R5) [6,8]. The OH concentration is detected by the laser-induced fluorescence (LIF) based on the fluorescence assay by a gas-expansion technique. In principle, OH resonance fluorescence is released in the OH excitation by a 308-nm pulsed laser, and then OH radicals are detected directly [28,29].

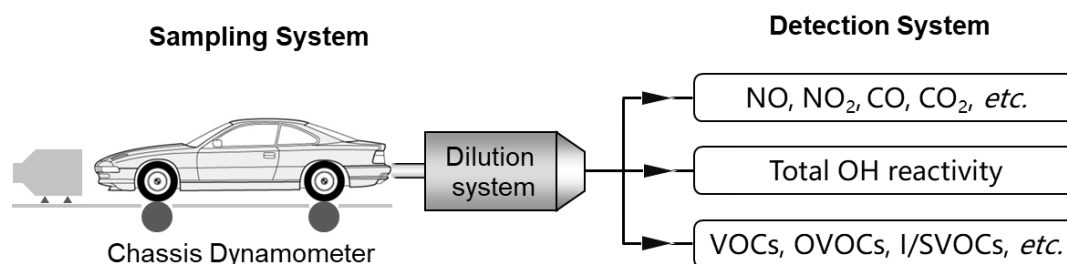
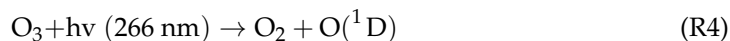


Figure 1. Schematic diagram of the measurement system for total OH reactivity.

For the sampling system, the exhaust gas from the vehicular sources, which has a high temperature, high relative humidity, and high pollutant concentrations, needs to be first diluted in the dilution system. Nevertheless, the NO concentration is still sufficiently high to generate the interference, leading to no OH radicals being produced in high NO conditions [20,21]. Thus, the diluted gas is mixed with excessive O₃ before being pumped into the flow tube to circumvent NO interference [20,21]. The appropriate O₃ concentration should be calculated to ensure the complete oxidation of NO with no oxidation of VOCs.

The inter-comparison of different instruments for the total OH reactivity in the ambient air has been conducted [30–32]. Still, few studies once reported the inter-comparison of measurement instruments for vehicular sources. In the future, for vehicular sources, it is necessary to compare the instruments of different methods to determine the most suitable methods.

3. Total OH Reactivity Observations

Over the past decades, k_{OH} values have been measured in ambient air and emission sources. The ambient environmental conditions include forest, suburban, urban, marine, and aircraft areas. The emission sources mainly involve vehicular emissions, including exhaust and evaporation sources. In this section, we present the k_{OH} values, temporal variation of k_{OH} , and the reactive species for k_{OH} in ambient air and vehicular sources.

3.1. The Measured OH Reactivity for Ambient Air

For ambient air, the k_{OH} values were measured mainly in three types of environmental conditions. Those are the areas dominated by anthropogenic emissions, the areas dominated by biogenic emissions, and remote areas with clean environmental conditions.

3.1.1. Areas Dominated by Anthropogenic Emissions

The areas dominated by anthropogenic emissions are generally located in or near urban areas and are susceptible to emissions from traffic and industrial sources, or they are located in suburban sites when influenced by continental air. The k_{OH} in areas dominated by anthropogenic emissions varies from a few to over a hundred. The mean or median k_{OH} values observed in Nashville (USA) [33], Helsinki (Finland) [34], New York City (USA) [35], Mexico City (Mexico) [36], Houston (USA) [37], and Mainz (Germany) [25] were below 20 s^{−1}, while the k_{OH} varied within 10–130 s^{−1} in the MEGAPOLI campaign in Paris (France) [38].

We summarized the diurnal profiles of k_{OH} observed in areas dominated by anthropogenic emissions in Figure 2 [34–37,39–41]. The distinctive characteristic of the diurnal variation for k_{OH} is that it shows a morning and evening peak, which might be associated with rush hours of traffic flows. Figure 3 shows the relative proportion of inorganic reactivity and organic reactivity in the calculated OH reactivity in different areas [7,31,35,39,42–52]. The distributions of proportions of inorganic reactivity and organic reactivity seem like a linear correlation with a slope of 1. It is because the calculated OH reactivity consists of two components, which are inorganic reactivity and organic reactivity. Thus, the sum of the proportion of inorganic reactivity and the proportion of organic reactivity is equal to 100%. NO_x is the dominant inorganic species. The distribution of active species in areas dominated by anthropogenic emissions is concentrated in intervals of high inorganic activity and low organic activity, which differs markedly from the other two regions in the distribution of active substances.

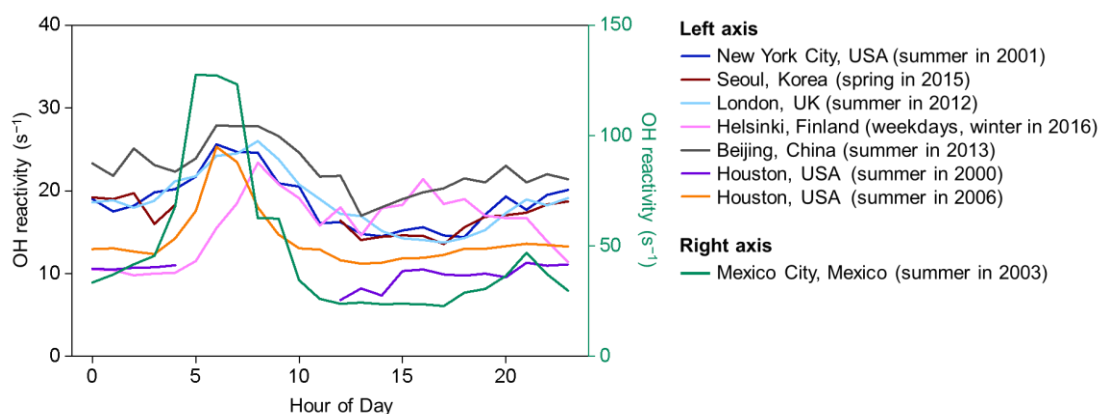


Figure 2. The diurnal profile of OH reactivity in areas dominated by anthropogenic emissions [34–37,39–41].

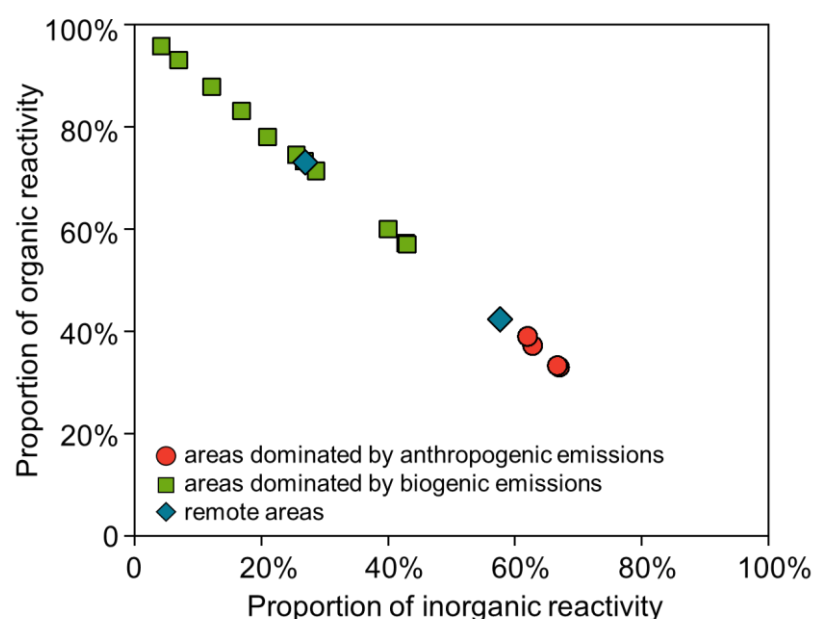


Figure 3. The relative proportion of inorganic reactivity and organic reactivity in the calculated OH reactivity in areas dominated by anthropogenic emissions, areas dominated by biogenic emissions, and remote areas [7,31,35,39,42–52].

3.1.2. Areas Dominated by Biogenic Emissions

Forest regions are mainly affected by biogenic emissions involving the known reactive species (e.g., isoprene and terpenes) and some other unmeasured or unknown BVOCs. Since the first k_{OH} measurement in a northern Michigan forest area in 2004 by Di Carlo et al. (2004) [44], scientists have conducted numerous campaigns to measure k_{OH} values in different environmental conditions, covering tropical, temperate, and boreal forests. Figure 4 shows the diurnal profiles of k_{OH} in previous field campaigns [31,45,47,48,50,51,53–57]. The k_{OH} values are spread over a wide range, and a previous study reported that k_{OH} values could reach over 70 s^{-1} around noontime during dry seasons in the Amazon rainforest [53]. Nevertheless, k_{OH} values in temperate and boreal forests are lower than those observed in tropical forests. The diurnal values of k_{OH} observations were below 15 s^{-1} , even at noontime, in temperate coniferous forests in Japan, boreal forests in Finland, and pine forests in America [45,47,48]. Additionally, significant seasonal variations of k_{OH} have been observed. Noelscher et al. (2016) [53] observed low k_{OH} values in the wet season and high values in the dry season. They also reported k_{OH} values as a function of season in Amazon rainforest air reactivity. It is indicated that the k_{OH} vertical gradients to the canopy in the wet season were significantly less than in the dry season [53]. Moreover, the k_{OH}

emission rate referring to the emitted k_{OH} -per-unit needle, dry-weight-per-unit enclosure, and volume per unit time has been reported to be related to season [58]. Noelscher et al. (2013) [58] observed higher k_{OH} emission rates in early summer and late summer than in spring and autumn. Nevertheless, seasonal variations in k_{OH} remain understudied and underreported, suggesting that continuous k_{OH} measurements and the analysis of seasonal variations in k_{OH} should be strengthened thereafter.

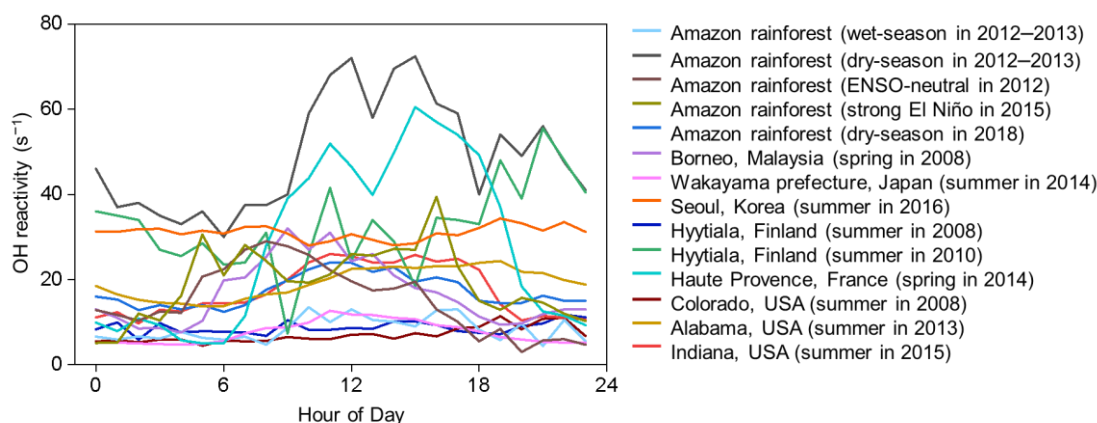


Figure 4. The diurnal profile of OH reactivity in areas dominated by biogenic emissions [31,45,47,48,50,51,53–57].

The k_{OH} values show similar diurnal behavior, with a maximum value displayed around noontime. It might be related to the composition of k_{OH} , with a high contribution of isoprene and terpene, which are greatly affected by light and temperature. In the PROPHET 2000 campaign conducted in a northern Michigan forest, isoprene could account for about half of the calculated k_{OH} [44]. The contribution of isoprene to the calculated k_{OH} could reach 83% inside the canopy in the CANOPEE campaign conducted in Haute Provence in France [31]. For boreal forests with low isoprene and high terpenes, monoterpenes might be the most important active species [31,45,56]. Compared to the urban areas, the percentages of organics in calculated k_{OH} for areas dominated by anthropogenic emissions are significantly higher (Figure 3), and BVOCs dominate the organic reactivity.

3.1.3. Remote Areas

Remote areas are characterized by environmental features that are less affected by emission sources. As shown in Figure 5, the diurnal profiles of k_{OH} values for most campaigns in remote areas differ from those of areas dominated by anthropogenic and biogenic emissions, with an insignificant diurnal trend [7,39,41–43,59], since remote areas are not exposed to either heavy biogenic, transportation, or industrial sources. However, similar diurnal trends to those in areas dominated by anthropogenic emissions were observed at the Backgarden site in Guangzhou (China), showing a minimum mean value of 20 s^{-1} at local noon and a maximum mean value of 50 s^{-1} at daybreak [7]. Lou et al. (2010) [7] reported that the temporal pattern is highly correlated with variations of anthropogenically emitted pollutants.

The relative proportions of inorganic and organic reactivity for areas characterized by different environmental conditions are different. The areas dominated by anthropogenic emissions have higher proportions of inorganic reactivity, whereas the areas dominated by biogenic emissions have higher proportions of organic reactivity. For the remote areas, the distribution of active species is not particularly well-characterized (Figure 3), which depends on the emission sources exposed.

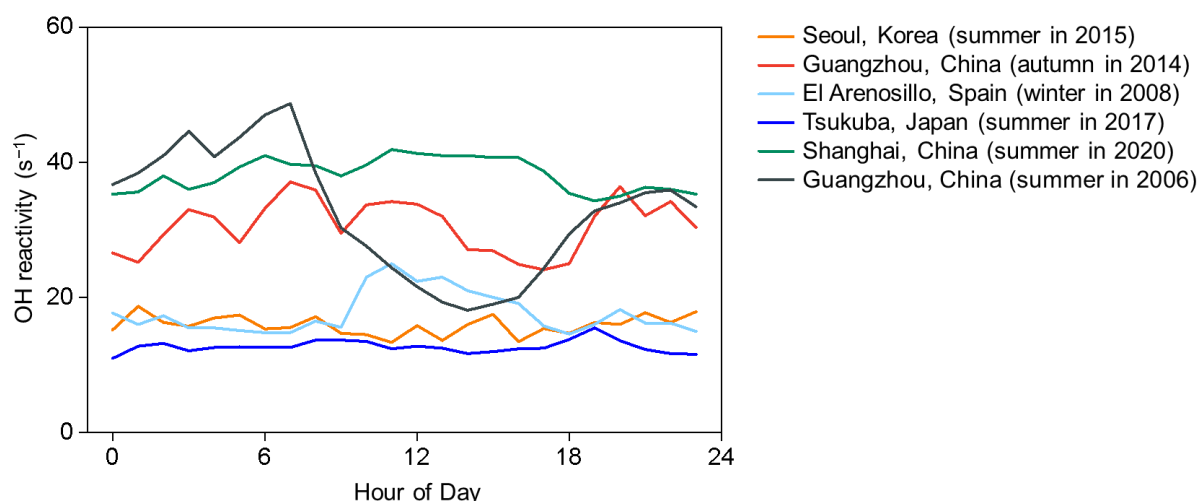


Figure 5. The diurnal profile of OH reactivity in remote areas [7,39,41–43,59].

3.2. The Measured Total OH Reactivity for Vehicular Sources

Besides the k_{OH} measurement for ambient air, scientists began to conduct k_{OH} measurements for vehicular sources since the first k_{OH} measurement on vehicles was reported by Nakashima et al. (2010) [8]. Only five direct k_{OH} measurements for vehicular emission have been conducted so far, including four measurements for exhaust emission and only one measurement for evaporative emission [8,19–21,27].

3.2.1. The Total OH Reactivity Values

Prior studies have indicated that the measured k_{OH} values varied within different orders of magnitude depending on many parameters (fuel types, emission standards, driving cycles, mileage, etc.) [8,19–21,27]. The reported k_{OH} values from exhaust emission were mainly based on the chassis dynamometer, and those from evaporative emission were from gasoline headspace. We summarize the measured k_{OH} values from vehicle sources in Figure 6. The k_{OH} values from exhaust emission varied from 500 s^{-1} to $17 \times 10^4 \text{ s}^{-1}$, and the k_{OH} from evaporative emission varied within $30\text{--}50 \text{ s}^{-1}$. It is indicated that there is a significant discrepancy in k_{OH} values between exhaust emission and evaporative emission.

For the exhaust emission of gasoline vehicles, the k_{OH} values depend on the different driving conditions, emission standards, and the temperature of the engine or catalyst. Nakashima et al. (2010) [8] measured the k_{OH} values of gasoline vehicles under various driving conditions with a chassis dynamometer [8]. The results showed that the k_{OH} values for the cold start were about 10 times higher than those for the hot start, indicating that the vehicular reactivity depends on whether the catalyst or engine is hot or cold [8]. Nevertheless, the k_{OH} values from light-duty gasoline vehicles in China, which were measured in the Economic Commission of Europe (ECE) driving cycle by Liu et al. (2023) [27], were comparable between cold and warm starts. The results are different from those reported by Nakashima et al. (2010) [8] mainly due to the different driving conditions between the two studies. Additionally, the upgrades of emission standards would influence the k_{OH} values, with a notable drop as emission standards were upgraded. The k_{OH} values for China VI-a vehicles were only about one-tenth of those for China I, and the k_{OH} values for China V/China VI-a vehicles and the k_{OH} values for the cold start of gasoline vehicles in Japan were comparable [8,27]. Besides the startup temperature and the emission standards, driving conditions might have an essential impact on k_{OH} values, and it is reported that the k_{OH} values were higher during the startup stage than those during the stable driving stage [27].

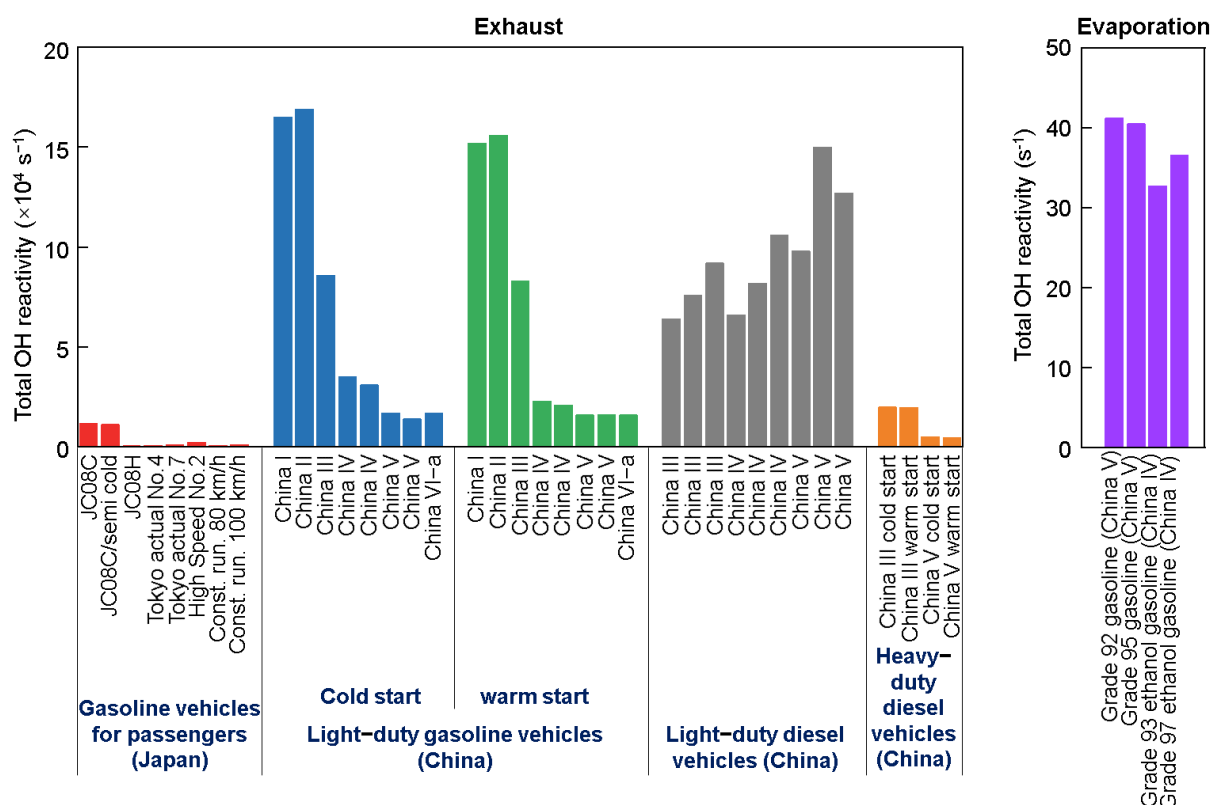


Figure 6. The measured total OH reactivity for vehicular sources in different studies [8,19–21,27]. Red columns denote the gasoline vehicles that had passed the latest Japanese emission control standard (2005). Blue and green columns denote the in-use light-duty gasoline vehicles covering all the issued emission standards in China with cold and warm starts, respectively. Grey columns denote the light-duty diesel trucks with different emission standards in China (China III–V) with a hot start. The orange columns denote the heavy-duty diesel vehicles with different emission standards in China (China III and China V).

For the exhaust emission of diesel vehicles, a notable increasing trend of k_{OH} from light-duty diesel truck exhaust in China was observed with the upgrade of emission standards, while an opposite trend of k_{OH} from heavy-duty diesel truck exhaust in China [20,21]. The k_{OH} values from heavy-duty diesel truck vehicles were comparable between cold start and warm start in Acceleration Simulation Mode (ASM), which are about 0.47×10^4 and $2.0 \times 10^4 \text{ s}^{-1}$ for China III and China V vehicles, respectively [20]. The k_{OH} from light-duty diesel truck vehicles at the warm start of the ECE driving cycle varied from 5×10^4 to $17 \times 10^4 \text{ s}^{-1}$, with an increasing trend with the emission standard upgrades [21]. Moreover, cumulative mileage has been reported to be an important influencing factor of k_{OH} values, with a strong positive relationship between mileage and k_{OH} [21]. The positive relationship can be attributed to the engine combustion efficiency because the lower efficiency due to the increasing mileage can promote the generation of incomplete combustion products [21]. Overall, the k_{OH} values of China III and China V heavy-duty diesel vehicles were also comparable to the values of China IV, China V, and China VI-a light-duty gasoline vehicles, while they were lower than the values of China III, China IV, and China V light-duty diesel vehicles [8,20,21,27]. Compared to the k_{OH} measured from exhaust emissions, the k_{OH} values from the gasoline headspace were much lower, with a range of $30\text{--}50 \text{ s}^{-1}$ [19]. The k_{OH} from gasoline evaporation was comparable to the values from the ambient air [6].

Overall, the direct k_{OH} measurements for vehicular sources have been conducted since 2010 and have covered light-duty gasoline vehicles, light-duty diesel trucks, heavy-duty diesel trucks, and gasoline evaporation. The k_{OH} values from exhaust emissions are 2–3 orders of magnitude higher than those from gasoline evaporation. With the upgrades

of emission standards, an increasing trend of k_{OH} values from light-duty diesel trucks has been found, while a decreasing trend of k_{OH} from light-duty gasoline vehicles and heavy-duty diesel trucks has been observed. It is indicated that further exploring the impacts of the engine and after-treatment upgrades on vehicular k_{OH} values is necessary.

3.2.2. The Relative Species

The reactive species consist of inorganics and VOCs (alkanes, alkenes, aromatics, OVOCs, etc.), and the percentage of reactive species in the calculated OH reactivity in different studies is presented in Figure 7 [8,19–21,27]. A significant discrepancy in the contribution percentage of reactive species between gasoline and diesel vehicles was found, although the inorganics play an essential role in both gasoline and diesel vehicles. In the contribution percentages of reactive species for gasoline vehicular exhaust emission, the contributions of CO and NO_x are comparable, while the contribution of CO can be negligible for diesel vehicular exhaust emission. CO accounts for 8–35% of the gasoline vehicles in Japan (except for the high-speed No.2 driving cycle) and 3–40% of the gasoline vehicles in China. For light-duty gasoline vehicles, the mean contribution of CO to the calculated OH reactivity for the cold start is about 20%, which is almost the same as that for the warm start. For the light-duty and high-duty diesel vehicles, the contributions of CO to the calculated OH reactivity are below 10%. The difference in CO percentages between gasoline vehicles and diesel vehicles might be related to the chemical composition of gasoline and diesel.

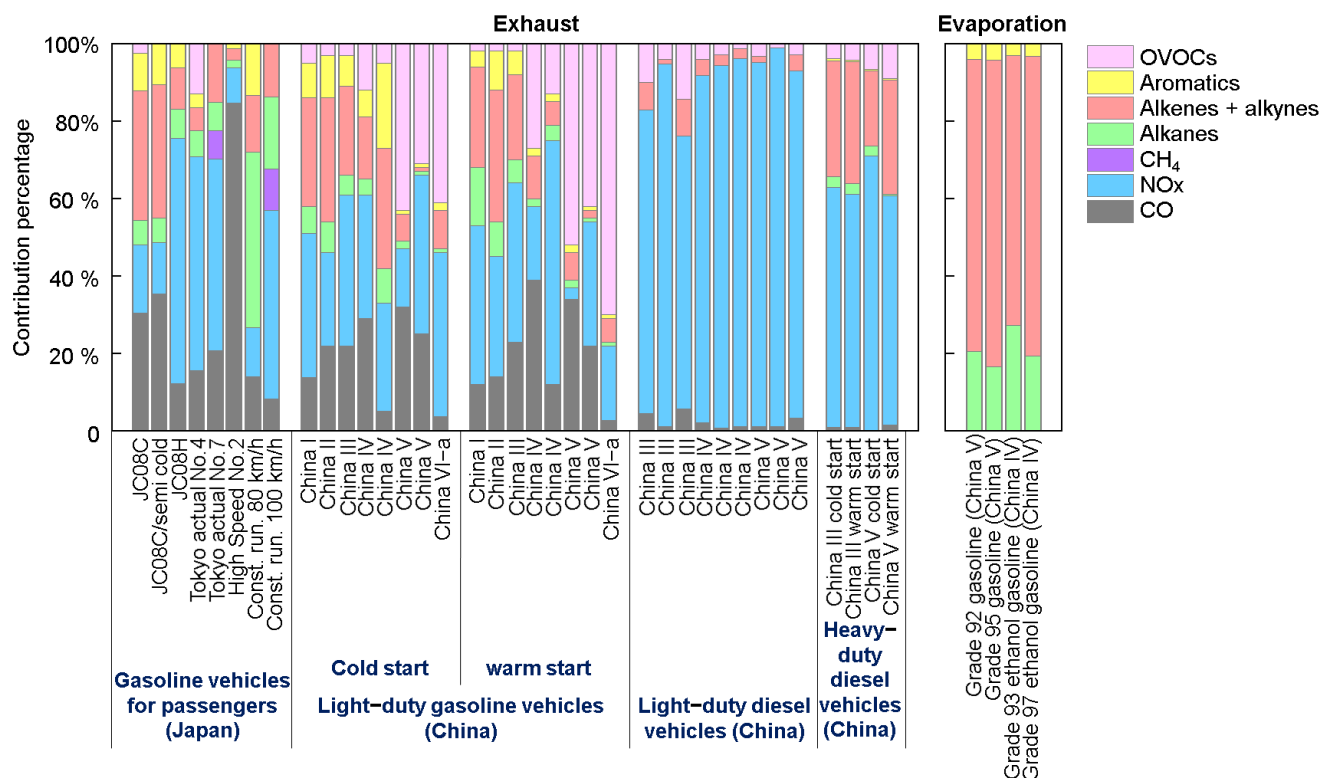


Figure 7. The contribution percentages of reactive species in the calculated OH reactivity for vehicular sources in different studies involving gasoline vehicles, light-duty gasoline vehicles, light-duty diesel vehicles, heavy-duty diesel vehicles, and gasoline evaporation [8,19–21,27].

Compared to the low percentage of CO for diesel vehicles, the vast majority of the calculated OH reactivity is attributed to NO_x, with a contribution of 70–98% and 60–70% to light-duty diesel vehicles and heavy-duty diesel vehicles, respectively. For gasoline vehicles, the contribution of NO_x to the calculated OH reactivity for Japanese vehicles varies between 10%–70% in different driving cycles, with an average of approximately 35%.

NO_x reactivity accounts for 30% in both cold and warm start for Chinese vehicles, and no significant variation as the emission standards upgrade is observed.

The contributions of VOCs (mainly alkanes, alkenes, alkynes, aromatics, and OVOCs) to the calculated OH reactivity for gasoline vehicles are significantly higher than those for diesel vehicles. VOC species account for about 20–75% of the different driving cycles for Japanese vehicles (except for the high-speed No.2 driving cycle), with a higher contribution in the cold start (JC08C and JC08C/semi-cold driving cycles) than those in the hot start (other driving cycles except for JC08C, JC08C/semi-cold, and const. run. 80 km h^{−1}). As for the Chinese vehicles, no notable variation in VOC contributions for the cold start and warm start was observed, with a range for VOC contributions of 35–70% and 25–80% in the cold and warm starts, and with average VOC contributions of approximately 50% in the cold and warm starts. For China I, China II, China III, and China IV vehicles, the most significant VOC species are alkenes and alkynes, followed by alkanes and aromatics. As the emission standards upgraded, a decreasing trend in the contributions of alkenes and aromatics for gasoline vehicles in China was observed, which can be attributed to the decrease in the alkenes and aromatics contents in gasoline fuels [27]. Nevertheless, OVOC species play a more critical role in the calculated OH reactivity for gasoline vehicles in China with the upgrades of emission standards, with a contribution of around 40% in the cold start and approximately 70% in the warm start for China VI-a vehicles. The higher contribution of OVOCs might be related to the adoption of gasoline direct-injection (GDI) engines for China V and China VI-a vehicles [27]. As for the gasoline evaporation, the most significant contributor to the calculated OH reactivity for the four kinds of gasoline headspace (Grades 92 and 95 gasoline samples following China V, and Grades 93 and 97 ethanol gasoline following China IV) is n-alkenes, followed by alkanes. No significant discrepancy between the different gasoline samples was found, and the mean contributions of n-alkenes, alkanes, and aromatics to the calculated OH reactivity are 76%, 20%, and 4%, respectively [19].

3.3. Comparison of Total OH Reactivity between Ambient Air and Vehicular Emissions

Compared to the k_{OH} measurement for vehicular sources since 2010, the direct measurements of k_{OH} values for ambient air have been conducted over the past decades, covering the different environmental conditions involving urban, rural, and forest areas. The observed k_{OH} values in rural environments at the Backgarden (China), Yufa (China), Weybourne (England), and Pennsylvania (USA) sites were 10–120 s^{−1}, 10–30 s^{−1}, 4.9 s^{−1}, and 6.1 s^{−1} [7,60–62]. The k_{OH} in urban environments at the Wangdu (China), Lille (France), and Tokyo (Japan) sites were 10–20 s^{−1}, 70 s^{−1}, and 33.4 s^{−1} [62–64]. The k_{OH} values in forest environments at Michigan (USA), Hyytiala (Finland), Brownsburg (Suriname), and New York (USA) sites were 3–33 s^{−1}, 3–76 s^{−1}, 53 s^{−1}, and 5.6 s^{−1} [25,56,65,66]. A significant discrepancy in the observed k_{OH} values between vehicular exhaust emission and ambient air has been found, whereas the k_{OH} values for gasoline evaporation and those for ambient air are comparable.

As for the chemical composition, inorganics reactivities, especially the NO_x reactivity, are the most significant contributions to the calculated OH reactivity for vehicular exhaust emission compared to ambient air. The proportion of VOC species is usually higher than that of inorganics for the ambient air, especially in biogenic-dominated areas, and alkenes dominate the calculated OH reactivity of gasoline evaporation.

4. Missing OH Reactivity

Most of the reactive gas concentrations were simultaneously measured along with the direct k_{OH} measurement, and, thus, the reactivity of each species can be calculated. The sum of the reactivity of the measured species is usually called the calculated OH reactivity. It is difficult to obtain the reactivities of all kinds of reactive gases due to the richness of the VOC species, leading to an underestimation of k_{OH} . The discrepancy between measured OH reactivity and calculated OH reactivity is referred to as the missing OH reactivity

(MOR), which represents the reactivities of the unknown or unmeasured reactive species and, thus, the completeness of understanding for the measurement for reactive species. Generally, the more reactive a species, the lower the MOR values. Additionally, the ratio of missing OH reactivity to total OH reactivity can be represented by the missing ratio, as shown in Equation (2).

$$\text{Missing ratio} = \text{MOR}/k_{\text{OH}} \quad (2)$$

The existence of missing reactivity for both vehicular sources and ambient air is universal. The missing ratios for the forest areas, which are almost within 30–70% [25,44,45,47,55,56], are generally higher than those in urban and rural environments. For the urban and rural sites, an OH reactivity closure can be achieved in some environments [32,34,35,37,38], whereas a significant missing reactivity can be found in some environments characterized by high OVOCs [23,33,36,38,64,67,68]. The missing k_{OH} may come from the primary VOC species and its secondary oxidant products. In the forest areas, missing k_{OH} might derive from the unmeasured BVOCs. For example, terpenes showing a positive correlation with temperature might be a significant source for missing k_{OH} in a northern Michigan forest [44]. Moreover, secondary oxidation products from the photo-oxidation of isoprene by OH radicals could contribute greatly to missing reactivity in the forest [47]. For the areas dominated by anthropogenic areas, missing k_{OH} may be from the unmeasured, even unknown, primary VOCs, mainly from chemical production, solvent usage, and vehicle emissions. On the other hand, prior studies reported that the observed k_{OH} could be reproduced by the model coupling the generation of OVOCs [7]. Moreover, highly oxidized products from continental air masses could contribute to the missing k_{OH} [38]. For vehicular exhaust emission, the missing ratios depend on the startup temperature, emission standards, and so on. In terms of the possible source of missing reactivity, previous studies reported that the missing reactivity in ambient samples was attributed to either unknown/unmeasured primary or secondary VOC species [6]. In addition, vehicular exhaust emissions might mainly come from the unspiciated species (I/SVOCs, oxygen- or sulfur-containing species, highly oxygenated VOCs, inorganic acids, etc.) [21,27]. Undetected or unidentified branched alkenes might be the missing species for gasoline evaporation. The universal existence of missing reactivity illustrates that more reactive species should be further measured in the future.

For vehicular emissions, we summarized the missing ratio of gasoline vehicular exhaust emission, diesel vehicular exhaust emission, and gasoline evaporation, as shown in Figure 8 [8,19–21,27]. The impact of some influencing factors (startup temperature, emission standards, driving conditions, etc.) on missing OH reactivity has been illustrated. For the gasoline vehicular exhaust emission, the influences of the startup temperature on the missing ratio are different between the Japanese and Chinese vehicles. For the gasoline vehicles in Japan, the missing ratios for cold starts and hot starts are comparable, and they are 17.5% and 17% for cold starts and hot starts, respectively. Nevertheless, there is a significant difference in the missing ratios for the gasoline vehicles in China between cold starts and warm starts. For China I, China II, China III, and China IV gasoline vehicles, a near-cessation of OH reactivity is found for the cold starts, whereas the missing ratios are about 40% for the warm starts. For the China V and China VI—a gasoline vehicles, the missing ratios for the cold and warm starts are comparable, and the average missing ratios are around 40%. The unimportant impact of startup temperatures on missing ratios for China V and China VI—a vehicles is mainly related to the application of an electrically heated catalyst (EHC), which can shorten the preheating periods of vehicles and reduce the difference between the two start conditions [27,69].

For diesel vehicular exhaust emission, the missing ratios increase with the upgrades of emission standards for both light-duty and heavy-duty diesel vehicles [20,21]. A near-closure of OH reactivity for the China III light-duty and heavy-duty diesel trucks has been reported, indicating that almost reactive species from the exhaust emission have been measured. However, as the emission standards upgrade, an approximately 40% missing ratio was found in China V light-duty and heavy-duty diesel trucks, indicating some

undetected or unidentified reactive species that must be explored. The startup temperature has no significant influence on missing ratios for the heavy-duty diesel trucks, with 43.5% and 39% for the cold starts and warm starts, respectively [20].

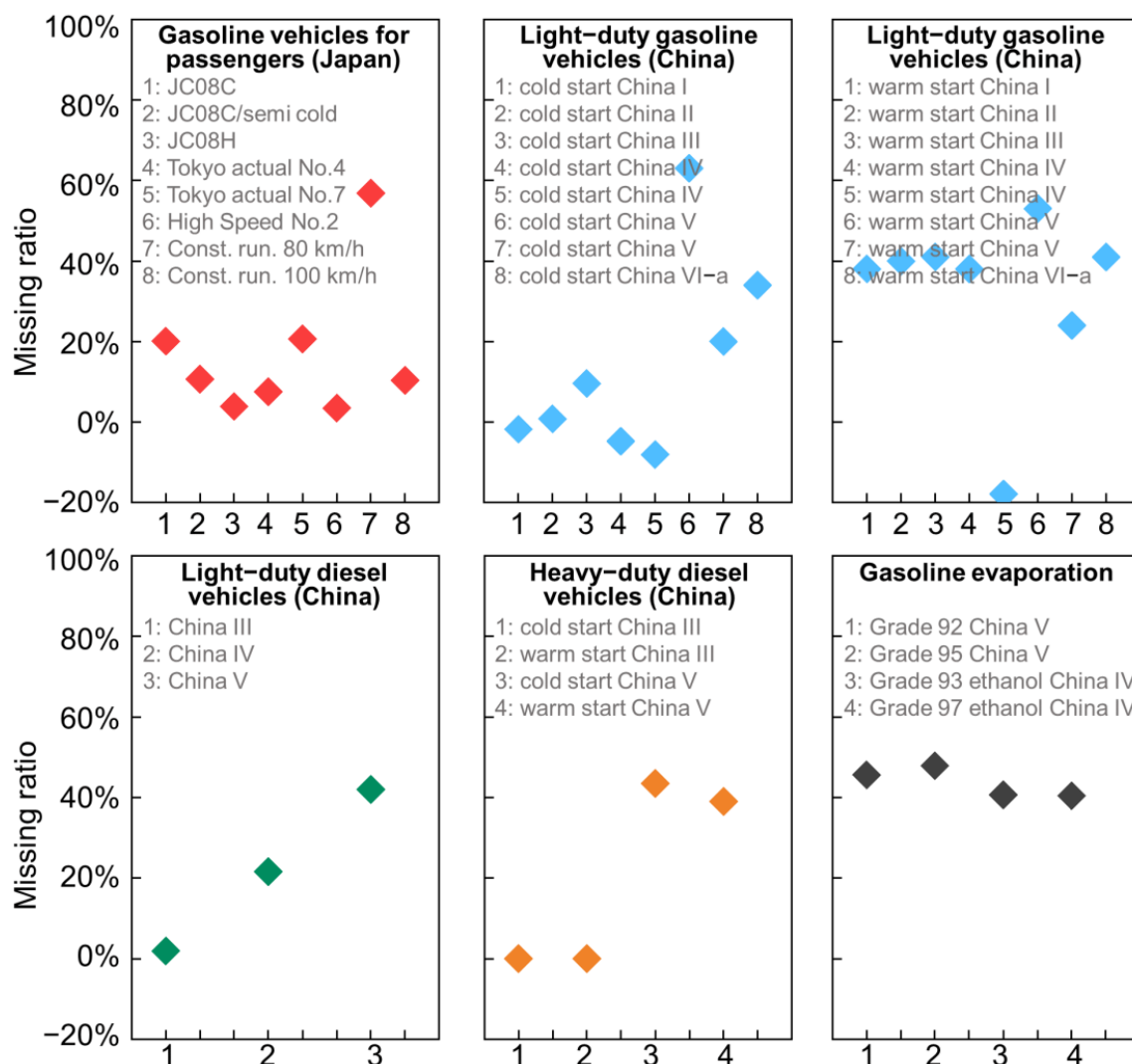


Figure 8. The missing ratio (the ratio of missing OH reactivity to total OH reactivity) for vehicular sources in different studies involving gasoline vehicles, light-duty gasoline vehicles, light-duty diesel vehicles, heavy-duty diesel vehicles, and gasoline evaporation [8,19–21,27].

The possible compositions of missing OH reactivity have been reported in previous studies. Liu et al. (2023) [27] proposed that OVOCs and missing reactivity might have a similar production process, indicating the missing OH reactivity might derive from the undetected or unidentified OVOC species. The generation of OVOC species mainly comes from the stable driving stage when the higher efficiency of the catalyst can promote the oxidation of VOCs, and, thus, the duration of the stable driving stage tightly influences the missing OH reactivity [27]. Possible missing species for exhaust emission are speculated to be the I/SVOCs [27], oxygen- or sulfur-containing species with a molecular weight of more than 400 [27], as well as highly oxygenated VOCs (carboxylic acids, etc.) [21] and inorganic acids (isocyanic acid, nitric acid, nitrous acid, etc.) [21]. The missing species for gasoline evaporation might come from undetected or unidentified branched alkenes [19].

5. Discussion

5.1. Significance of Total OH Reactivity

As an indicator for evaluating the completeness of chemical species measurements in the troposphere, the exploration of total OH reactivity is significant for radical chemistry, as well as global sustainable development.

From the implications for radical chemistry, k_{OH} is a significant parameter in conducting the OH experimental budget. The OH experimental budget is an effective tool to test our understanding of radical chemistry in the troposphere due to the extremely short photochemical lifetimes of OH radicals. The OH experiment budget refers to the comparison of the OH production rate (P_{OH}) and destruction rate (D_{OH}). For the OH destruction rate, k_{OH} is the crucial parameter because D_{OH} is the product of the observed OH concentrations and k_{OH} . Thus, D_{OH} denotes the total OH sinks. Under the photochemical steady-state hypothesis, the total OH production rate is equal to the total OH destruction rate. Therefore, the direct measurement of k_{OH} would help the investigation of missing OH sources, which is the difference in the OH destruction rate and production rate. Thanks to the direct measurements of k_{OH} , OH regeneration mechanisms have been proposed [70–75], but the deviation between the observed and modeled OH concentrations is still not fully explained. It further highlights the importance of searching for missing reactivity sources that may be closely related to OH regeneration in the troposphere. For vehicular emissions, the direct measurement of k_{OH} could determine chemical reactive species with a high-formation potential of secondary pollutants. Additionally, the k_{OH} observations could identify the completeness of chemical species measurements in vehicular emissions. Exploring the source of missing reactivity would help us identify more unmeasured or unknown active chemical species, which would further enlighten the development of radical-related mechanisms and, thus, facilitate radical closures in the troposphere.

From the implications for sustainable development, the review of total OH reactivity for ambient air and source emission could provide a comprehensive understanding for reactive chemical species in the troposphere. It will help to further assess the generation potential of secondary pollutants, as well as the health potential of reactive chemical species, which would contribute to the accurate identification of chemical species requiring special attention. Additionally, this study would further enrich the understanding of global environmental issues such as human health. Chronic or acute adverse health effects could be caused by an exposure to VOC species, especially severe emissions from vehicles [76]. Identifying the pollutants with adverse effects on human health will help to promote the development of emission reduction policies, which will facilitate the achievement of the Sustainable Development Goals (SDGs) adopted by the United Nations.

5.2. Existing Problems and Prospects

Previous studies have explored the k_{OH} for ambient air in detail, while further explorations on OH reactivity are needed, as shown below.

1. Exploring the possible interactions between OH radicals and particles, further improving the aerosol simulations.
2. Developing more measurement techniques about the total reactivity of other radicals (NO_3 , HO_2 , etc.).

For the k_{OH} of vehicular emissions, prior studies mainly focused on the effect of different emission standards and startup temperatures on the k_{OH} of exhaust emissions and evaporative emissions of gasoline. Considering the current process of k_{OH} for vehicular sources, several critical issues to help improve the exploration of the total OH reactivity in the field of mobile sources are outlined below.

3. Exploring the impact of fuels, engines, after-treatment systems, and driving speed on the total OH reactivity for exhaust emission under strict quality control.
4. Evaluating the total OH reactivity in different evaporation emission processes (diurnal, hot soak, permeation, refueling, etc.) besides the headspace.

5. Adding the observation of OVOCs, I/SVOCs, and other organic reactive gases and, thus, evaluating the concentrations of mobile sources to the atmospheric chemistry.
6. Strengthening the measurement of total OH reactivity for more mobile sources (non-road machinery, ship, aviation, etc.).

6. Conclusions

Total OH reactivity is an indicator for evaluating the amounts of reactive species in terms of the loss of OH radicals. The OH reactivity for ambient air has been widely characterized, while OH reactivity for vehicular sources, a significant source of abundant atmospheric pollutants, is poorly understood. Herein, we reviewed and compared the OH reactivity for ambient air and vehicular sources to illustrate the OH reactivity measurement instruments, reactivity values, chemical active species, and missing reactivity in depth. Firstly, for ambient air, the direct OH reactivity measurements were mainly conducted in areas dominated by anthropogenic emissions, areas dominated by biogenic emissions, and remote areas. The diurnal OH reactivity values for areas dominated by anthropogenic emissions exhibit morning and evening peaks, which are similar to NO_x emissions by traffic. The OH reactivity values for areas dominated by biogenic emissions present peaks around noontime, and those for remote areas show a weaker diurnal variation. The OH reactivity for anthropogenic-dominated areas is generally dominated by inorganic species, while organic species might be the major contributor to OH reactivity in biogenic-dominated areas. Secondly, for vehicular sources, a significant discrepancy in OH reactivity between exhaust emissions and evaporation emissions has been found. The OH reactivity values for exhaust emission are 2–3 orders of magnitude higher than those from gasoline evaporation. Inorganic and organic reactivities are comparable for gasoline exhaust emission, whereas the highest fraction of the calculated OH reactivity was NO_x reactivity for diesel exhaust emission. For the gasoline evaporation emission, the contribution of alkenes to the calculated OH reactivity is the largest. The missing reactivity has been determined in previous studies, and the missing reactivity for vehicular sources might derive from the unspciated species. Thirdly, compared to ambient air, the OH reactivity for exhaust emissions is much higher due to the high concentrations of reactive species, and the fraction of inorganics reactivity in the calculated OH reactivity for exhaust emission is much higher. Nevertheless, the OH reactivity for gasoline evaporation is comparable to that for ambient air, and all calculated OH reactivity for gasoline evaporation derives from VOC species.

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References

1. Li, K.; Jacob, D.J.; Liao, H.; Shen, L.; Zhang, Q.; Bates, K.H. Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China. *Proc. Natl. Acad. Sci. USA* **2019**, *116*, 422–427. [[CrossRef](#)] [[PubMed](#)]
2. Ehhalt, D.H. Photooxidation of trace gases in the troposphere. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5401–5408. [[CrossRef](#)]
3. Lu, K.; Guo, S.; Tan, Z.; Wang, H.; Shang, D.; Liu, Y.; Li, X.; Wu, Z.; Hu, M.; Zhang, Y. Exploring atmospheric free-radical chemistry in China: The self-cleansing capacity and the formation of secondary air pollution. *Natl. Sci. Rev.* **2019**, *6*, 579–594. [[CrossRef](#)] [[PubMed](#)]
4. Goldstein, A.H.; Galbally, I.E. Known and unexplored organic constituents in the earth's atmosphere. *Environ. Sci. Technol.* **2007**, *41*, 1514–1521. [[CrossRef](#)] [[PubMed](#)]
5. Kovacs, T.A.; Brune, W.H. Total OH loss rate measurement. *J. Atmos. Chem.* **2001**, *39*, 105–122. [[CrossRef](#)]

6. Yang, X.; Wang, H.; Tan, Z.; Lu, K.; Zhang, Y. Observations of OH Radical Reactivity in Field Studies. *Acta Chim. Sin.* **2019**, *77*, 613–624. [[CrossRef](#)]
7. Lou, S.; Holland, F.; Rohrer, F.; Lu, K.; Bohn, B.; Brauers, T.; Chang, C.C.; Fuchs, H.; Haeseler, R.; Kita, K.; et al. Atmospheric OH reactivities in the Pearl River Delta—China in summer 2006: Measurement and model results. *Atmos. Chem. Phys.* **2010**, *10*, 11243–11260. [[CrossRef](#)]
8. Nakashima, Y.; Kamei, N.; Kobayashi, S.; Kajii, Y. Total OH reactivity and VOC analyses for gasoline vehicular exhaust with a chassis dynamometer. *Atmos. Environ.* **2010**, *44*, 468–475. [[CrossRef](#)]
9. Duan, L.; Yuan, Z.; Sha, Q.e.; Wang, M.; Liu, X.; Liu, Y.; Hao, Y.; Zheng, J. Investigation on the trend of emission characteristics of volatile organic compounds from motor vehicle exhaust under different emission standards. *Acta Sci. Circumstantiae* **2021**, *41*, 1239–1249.
10. Qi, L.; Zhao, J.; Li, Q.; Su, S.; Lai, Y.; Deng, F.; Man, H.; Wang, X.; Shen, X.e.; Lin, Y.; et al. Primary organic gas emissions from gasoline vehicles in China: Factors, composition and trends. *Environ. Pollut.* **2021**, *290*, 117984. [[CrossRef](#)]
11. Cao, X.; Yao, Z.; Shen, X.; Ye, Y.; Jiang, X. On-road emission characteristics of VOCs from light-duty gasoline vehicles in Beijing, China. *Atmos. Environ.* **2016**, *124*, 146–155. [[CrossRef](#)]
12. Wallington, T.J.; Anderson, J.E.; Dolan, R.H.; Winkler, S.L. Vehicle Emissions and Urban Air Quality: 60 Years of Progress. *Atmosphere* **2022**, *13*, 650. [[CrossRef](#)]
13. Zhang, Z.; Man, H.; Zhao, J.; Jiang, Y.; Zeng, M.; Cai, Z.; Huang, C.; Huang, W.; Zhao, H.; Jing, S.; et al. Primary organic gas emissions in vehicle cold start events: Rates, compositions and temperature effects. *J. Hazard. Mater.* **2022**, *435*, 128979. [[CrossRef](#)] [[PubMed](#)]
14. Karavalakis, G.; Short, D.; Vu, D.; Villela, M.; Asa-Awuku, A.; Durbin, T.D. Evaluating the regulated emissions, air toxics, ultrafine particles, and black carbon from SI-PFI and SI-DI vehicles operating on different ethanol and iso-butanol blends. *Fuel* **2014**, *128*, 410–421. [[CrossRef](#)]
15. Suarez-Bertoa, R.; Zardini, A.A.; Platt, S.M.; Hellebust, S.; Pieber, S.M.; El Haddad, I.; Temime-Roussel, B.; Baltensperger, U.; Marchand, N.; Prevot, A.S.H.; et al. Primary emissions and secondary organic aerosol formation from the exhaust of a flex-fuel (ethanol) vehicle. *Atmos. Environ.* **2015**, *117*, 200–211. [[CrossRef](#)]
16. Saliba, G.; Saleh, R.; Zhao, Y.; Presto, A.A.; Larnbe, A.T.; Frodin, B.; Sardar, S.; Maldonado, H.; Maddox, C.; May, A.A.; et al. Comparison of Gasoline Direct-Injection (GDI) and Port Fuel Injection (PFI) Vehicle Emissions: Emission Certification Standards, Cold-Start, Secondary Organic Aerosol Formation Potential, and Potential Climate Impacts. *Environ. Sci. Technol.* **2017**, *51*, 6542–6552. [[CrossRef](#)] [[PubMed](#)]
17. Zhang, M.; Ge, Y.; Li, J.; Wang, X.; Tan, J.; Hao, L.; Xu, H.; Hao, C.; Wang, J.; Qian, L. Effects of ethanol and aromatic contents of fuel on the non-regulated exhaust emissions and their ozone forming potential of E10-fueled China-6 compliant vehicles. *Atmos. Environ.* **2021**, *264*, 118688. [[CrossRef](#)]
18. Yang, J.; Roth, P.; Durbin, T.D.; Johnson, K.C.; Cocker, D.R., III; Asa-Awuku, A.; Brezny, R.; Geller, M.; Karavalakis, G. Gasoline Particulate Filters as an Effective Tool to Reduce Particulate and Polycyclic Aromatic Hydrocarbon Emissions from Gasoline Direct Injection (GDI) Vehicles: A Case Study with Two GDI Vehicles. *Environ. Sci. Technol.* **2018**, *52*, 3275–3284. [[CrossRef](#)]
19. Wu, Y.; Yang, Y.-D.; Shao, M.; Lu, S.-H. Missing in total OH reactivity of VOCs from gasoline evaporation. *Chin. Chem. Lett.* **2015**, *26*, 1246–1248. [[CrossRef](#)]
20. Shen, X.; Liu, S.; Yuan, B.; Yuan, Z.; Yang, H.; Chen, J.; Lou, S. Measurement of OH Reactivity of Diesel Vehicles Exhaust Based on LIF Method. *J. Atmos. Environ. Opt.* **2020**, *15*, 269–284.
21. Sha, Q.E.; Liu, X.; Yuan, Z.; Zheng, J.; Lou, S.; Wang, H.; Li, X.; Yu, F. Upgrading Emission Standards Inadvertently Increased OH Reactivity from Light-Duty Diesel Truck Exhaust in China: Evidence from Direct LP-LIF Measurement. *Environ. Sci. Technol.* **2022**, *56*, 9968–9977. [[CrossRef](#)] [[PubMed](#)]
22. Yang, Y.; Shao, M.; Wang, X.; Noelscher, A.C.; Kessel, S.; Guenther, A.; Williams, J. Towards a quantitative understanding of total OH reactivity: A review. *Atmos. Environ.* **2016**, *134*, 147–161. [[CrossRef](#)]
23. Sadanaga, Y.; Yoshino, A.; Watanabe, K.; Yoshioka, A.; Wakazono, Y.; Kanaya, Y.; Kajii, Y. Development of a measurement system of OH reactivity in the atmosphere by using a laser-induced pump and probe technique. *Rev. Sci. Instrum.* **2004**, *75*, 2648–2655. [[CrossRef](#)]
24. Muller, J.B.A.; Elste, T.; Plass-Duelmer, C.; Stange, G.; Holla, R.; Claude, A.; Englert, J.; Gilge, S.; Kubistin, D. A novel semi-direct method to measure OH reactivity by chemical ionization mass spectrometry (CIMS). *Atmos. Meas. Tech.* **2018**, *11*, 4413–4433. [[CrossRef](#)]
25. Sinha, V.; Williams, J.; Crowley, J.N.; Lelieveld, J. The comparative reactivity method—A new tool to measure total OH reactivity in ambient air. *Atmos. Chem. Phys.* **2008**, *8*, 2213–2227. [[CrossRef](#)]
26. Wang, W.; Qi, J.; Zhou, J.; Yuan, B.; Peng, Y.; Wang, S.; Yang, S.; Williams, J.; Sinha, V.; Shao, M. The improved comparative reactivity method (ICRM): Measurements of OH reactivity under high-NO_x conditions in ambient air. *Atmos. Meas. Tech.* **2021**, *14*, 2285–2298. [[CrossRef](#)]
27. Liu, X.; Yuan, Z.; Sha, Q.E.; Lou, S.; Wang, H.; Li, X.; Zheng, J.; Yuan, B.; Shao, M. Direct identification of total and missing OH reactivities from light-duty gasoline vehicle exhaust in China based on LP-LIF measurement. *J. Environ. Sci.* **2023**, *133*, 107–117. [[CrossRef](#)] [[PubMed](#)]

28. Holland, F.; Hessling, M.; Hofzumahaus, A. In-Situ Measurement of Tropospheric OH Radicals by Laser-Induced Fluorescence—A Description of the Kfa Instrument. *J. Atmos. Sci.* **1995**, *52*, 3393–3401. [[CrossRef](#)]
29. Holland, F.; Hofzumahaus, A.; Schafer, R.; Kraus, A.; Patz, H.W. Measurements of OH and HO₂ radical concentrations and photolysis frequencies during BERLIOZ. *J. Geophys. Res.-Atmos.* **2003**, *108*, PHO 2-1–PHO 2-23. [[CrossRef](#)]
30. Fuchs, H.; Novelli, A.; Rolletter, M.; Hofzumahaus, A.; Pfannerstill, E.Y.; Kessel, S.; Edtbauer, A.; Williams, J.; Michoud, V.; Dusanter, S.; et al. Comparison of OH reactivity measurements in the atmospheric simulation chamber SAPHIR. *Atmos. Meas. Tech.* **2017**, *10*, 4023–4053. [[CrossRef](#)]
31. Zannoni, N.; Gros, V.; Lanza, M.; Sarda, R.; Bonsang, B.; Kalogridis, C.; Preunkert, S.; Legrand, M.; Jambert, C.; Boissard, C.; et al. OH reactivity and concentrations of biogenic volatile organic compounds in a Mediterranean forest of downy oak trees. *Atmos. Chem. Phys.* **2016**, *16*, 1619–1636. [[CrossRef](#)]
32. Hansen, R.F.; Blocquet, M.; Schoemaeker, C.; Leonardis, T.; Locoge, N.; Fittschen, C.; Hanoune, B.; Stevens, P.S.; Sinha, V.; Dusanter, S. Intercomparison of the comparative reactivity method (CRM) and pump-probe technique for measuring total OH reactivity in an urban environment. *Atmos. Meas. Tech.* **2015**, *8*, 4243–4264. [[CrossRef](#)]
33. Kovacs, T.A.; Brune, W.H.; Harder, H.; Martinez, M.; Simpas, J.B.; Frost, G.J.; Williams, E.; Jobson, T.; Stroud, C.; Young, V.; et al. Direct measurements of urban OH reactivity during Nashville SOS in summer 1999. *J. Environ. Monit.* **2003**, *5*, 68–74. [[CrossRef](#)] [[PubMed](#)]
34. Praplan, A.P.; Pfannerstill, E.Y.; Williams, J.; Hellen, H. OH reactivity of the urban air in Helsinki, Finland, during winter. *Atmos. Environ.* **2017**, *169*, 150–161. [[CrossRef](#)]
35. Ren, X.R.; Harder, H.; Martinez, M.; Leshner, R.L.; Oligier, A.; Shirley, T.; Adams, J.; Simpas, J.B.; Brune, W.H. HO_x concentrations and OH reactivity observations in New York City during PMTACS-NY2001. *Atmos. Environ.* **2003**, *37*, 3627–3637. [[CrossRef](#)]
36. Shirley, T.R.; Brune, W.H.; Ren, X.; Mao, J.; Leshner, R.; Cardenas, B.; Volkamer, R.; Molina, L.T.; Molina, M.J.; Lamb, B.; et al. Atmospheric oxidation in the Mexico City Metropolitan Area (MCMA) during April 2003. *Atmos. Chem. Phys.* **2006**, *6*, 2753–2765. [[CrossRef](#)]
37. Mao, J.; Ren, X.; Chen, S.; Brune, W.H.; Chen, Z.; Martinez, M.; Harder, H.; Lefer, B.; Rappenglueck, B.; Flynn, J.; et al. Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies. *Atmos. Environ.* **2010**, *44*, 4107–4115. [[CrossRef](#)]
38. Dolgorouky, C.; Gros, V.; Sarda-Estève, R.; Sinha, V.; Williams, J.; Marchand, N.; Sauvage, S.; Poulain, L.; Sciare, J.; Bonsang, B. Total OH reactivity measurements in Paris during the 2010 MEGAPOLI winter campaign. *Atmos. Chem. Phys.* **2012**, *12*, 9593–9612. [[CrossRef](#)]
39. Kim, S.; Sanchez, D.; Wang, M.; Seco, R.; Jeong, D.; Hughes, S.; Barletta, B.; Blake, D.R.; Jung, J.; Kim, D.; et al. OH reactivity in urban and suburban regions in Seoul, South Korea—An East Asian megacity in a rapid transition. *Faraday Discuss.* **2016**, *189*, 231–251. [[CrossRef](#)]
40. Whalley, L.K.; Stone, D.; Bandy, B.; Dunmore, R.; Hamilton, J.F.; Hopkins, J.; Lee, J.D.; Lewis, A.C.; Heard, D.E. Atmospheric OH reactivity in central London: Observations, model predictions and estimates of in situ ozone production. *Atmos. Chem. Phys.* **2016**, *16*, 2109–2122. [[CrossRef](#)]
41. Yang, Y.; Shao, M.; Kessel, S.; Li, Y.; Lu, K.; Lu, S.; Williams, J.; Zhang, Y.; Zeng, L.; Noelscher, A.C.; et al. How the OH reactivity affects the ozone production efficiency: Case studies in Beijing and Heshan, China. *Atmos. Chem. Phys.* **2017**, *17*, 7127–7142. [[CrossRef](#)]
42. Li, J.; Sakamoto, Y.; Kohno, N.; Fujii, T.; Matsuoka, K.; Takemura, M.; Zhou, J.; Nakagawa, M.; Murano, K.; Sadanaga, Y.; et al. Total hydroxyl radical reactivity measurements in a suburban area during AQUAS-Tsukuba campaign in summer 2017. *Sci. Total Environ.* **2020**, *740*, 139897. [[CrossRef](#)] [[PubMed](#)]
43. Yang, G.; Huo, J.; Wang, L.; Wang, Y.; Wu, S.; Yao, L.; Fu, Q.; Wang, L. Total OH Reactivity Measurements in a Suburban Site of Shanghai. *J. Geophys. Res.-Atmos.* **2022**, *127*, e2021JD035981. [[CrossRef](#)]
44. Di Carlo, P.; Brune, W.H.; Martinez, M.; Harder, H.; Leshner, R.; Ren, X.R.; Thornberry, T.; Carroll, M.A.; Young, V.; Shepson, P.B.; et al. Missing OH reactivity in a forest: Evidence for unknown reactive biogenic VOCs. *Science* **2004**, *304*, 722–725. [[CrossRef](#)] [[PubMed](#)]
45. Sinha, V.; Williams, J.; Lelieveld, J.; Ruuskanen, T.M.; Kajos, M.K.; Patokoski, J.; Hellen, H.; Hakola, H.; Mogensen, D.; Boy, M.; et al. OH Reactivity Measurements within a Boreal Forest: Evidence for Unknown Reactive Emissions. *Environ. Sci. Technol.* **2010**, *44*, 6614–6620. [[CrossRef](#)] [[PubMed](#)]
46. Hens, K.; Novelli, A.; Martinez, M.; Auld, J.; Axinte, R.; Bohn, B.; Fischer, H.; Keronen, P.; Kubistin, D.; Noelscher, A.C.; et al. Observation and modelling of HO_x radicals in a boreal forest. *Atmos. Chem. Phys.* **2014**, *14*, 8723–8747. [[CrossRef](#)]
47. Nakashima, Y.; Kato, S.; Greenberg, J.; Harley, P.; Karl, T.; Turnipseed, A.; Apel, E.; Guenther, A.; Smith, J.; Kajii, Y. Total OH reactivity measurements in ambient air in a southern Rocky mountain ponderosa pine forest during BEACHON-SRM08 summer campaign. *Atmos. Environ.* **2014**, *85*, 1–8. [[CrossRef](#)]
48. Ramasamy, S.; Ida, A.; Jones, C.; Kato, S.; Tsurumaru, H.; Kishimoto, I.; Kawasaki, S.; Sadanaga, Y.; Nakashima, Y.; Nakayama, T.; et al. Total OH reactivity measurement in a BVOC dominated temperate forest during a summer campaign, 2014. *Atmos. Environ.* **2016**, *131*, 41–54. [[CrossRef](#)]

49. Lew, M.M.; Rickly, P.S.; Bottorff, B.P.; Reidy, E.; Sklaveniti, S.; Leonardis, T.; Locoge, N.; Dusanter, S.; Kundu, S.; Wood, E.; et al. OH and HO₂ radical chemistry in a midlatitude forest: Measurements and model comparisons. *Atmos. Chem. Phys.* **2020**, *20*, 9209–9230. [\[CrossRef\]](#)
50. Pfannerstill, E.Y.; Reijrink, N.G.; Edtbauer, A.; Ringsdorf, A.; Zannoni, N.; Araujo, A.; Ditas, F.; Holanda, B.A.; Sa, M.O.; Tsokankunku, A.; et al. Total OH reactivity over the Amazon rainforest: Variability with temperature, wind, rain, altitude, time of day, season, and an overall budget closure. *Atmos. Chem. Phys.* **2021**, *21*, 6231–6256. [\[CrossRef\]](#)
51. Sanchez, D.; Seco, R.; Gu, D.; Guenther, A.; Mak, J.; Lee, Y.; Kim, D.; Ahn, J.; Blake, D.; Herndon, S.; et al. Contributions to OH reactivity from unexplored volatile organic compounds measured by PTR-ToF-MS—A case study in a suburban forest of the Seoul metropolitan area during the Korea-United States Air Quality Study (KORUS-AQ) 2016. *Atmos. Chem. Phys.* **2021**, *21*, 6331–6345. [\[CrossRef\]](#)
52. Ramasamy, S.; Nagai, Y.; Takeuchi, N.; Yamasaki, S.; Shoji, K.; Ida, A.; Jones, C.; Tsurumaru, H.; Suzuki, Y.; Yoshino, A.; et al. Comprehensive measurements of atmospheric OH reactivity and trace species within a suburban forest near Tokyo during AQUAS-TAMA campaign. *Atmos. Environ.* **2018**, *184*, 166–176. [\[CrossRef\]](#)
53. Noelscher, A.C.; Yanez-Serrano, A.M.; Wolff, S.; de Araujo, A.C.; Lavric, J.V.; Kesselmeier, J.; Williams, J. Unexpected seasonality in quantity and composition of Amazon rainforest air reactivity. *Nat. Commun.* **2016**, *7*, 10383. [\[CrossRef\]](#) [\[PubMed\]](#)
54. Pfannerstill, E.Y.; Noelscher, A.C.; Yanez-Serrano, A.M.; Bourtsoukidis, E.; Kessel, S.; Janssen, R.H.H.; Tsokankunku, A.; Wolff, S.; Soergel, M.; Sa, M.O.; et al. Total OH Reactivity Changes Over the Amazon Rainforest During an El Nino Event. *Front. For. Glob. Change* **2018**, *1*, 12. [\[CrossRef\]](#)
55. Edwards, P.M.; Evans, M.J.; Furneaux, K.L.; Hopkins, J.; Ingham, T.; Jones, C.; Lee, J.D.; Lewis, A.C.; Moller, S.J.; Stone, D.; et al. OH reactivity in a South East Asian tropical rainforest during the Oxidant and Particle Photochemical Processes (OP3) project. *Atmos. Chem. Phys.* **2013**, *13*, 9497–9514. [\[CrossRef\]](#)
56. Noelscher, A.C.; Williams, J.; Sinha, V.; Custer, T.; Song, W.; Johnson, A.M.; Axinte, R.; Bozem, H.; Fischer, H.; Pouvesle, N.; et al. Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010. *Atmos. Chem. Phys.* **2012**, *12*, 8257–8270. [\[CrossRef\]](#)
57. Kaiser, J.; Skog, K.M.; Baumann, K.; Bertman, S.B.; Brown, S.B.; Brune, W.H.; Crounse, J.D.; de Gouw, J.A.; Edgerton, E.S.; Feiner, P.A.; et al. Speciation of OH reactivity above the canopy of an isoprene-dominated forest. *Atmos. Chem. Phys.* **2016**, *16*, 9349–9359. [\[CrossRef\]](#)
58. Noelscher, A.C.; Bourtsoukidis, E.; Bonn, B.; Kesselmeier, J.; Lelieveld, J.; Williams, J. Seasonal measurements of total OH reactivity emission rates from Norway spruce in 2011. *Biogeosciences* **2013**, *10*, 4241–4257. [\[CrossRef\]](#)
59. Sinha, V.; Williams, J.; Diesch, J.M.; Drewnick, F.; Martinez, M.; Harder, H.; Regelin, E.; Kubistin, D.; Bozem, H.; Hosaynali-Beygi, Z.; et al. Constraints on instantaneous ozone production rates and regimes during DOMINO derived using in-situ OH reactivity measurements. *Atmos. Chem. Phys.* **2012**, *12*, 7269–7283. [\[CrossRef\]](#)
60. Lu, K.D.; Hofzumahaus, A.; Holland, F.; Bohn, B.; Brauers, T.; Fuchs, H.; Hu, M.; Haeseler, R.; Kita, K.; Kondo, Y.; et al. Missing OH source in a suburban environment near Beijing: Observed and modelled OH and HO₂ concentrations in summer 2006. *Atmos. Chem. Phys.* **2013**, *13*, 1057–1080. [\[CrossRef\]](#)
61. Ren, X.R.; Brune, W.H.; Cantrell, C.A.; Edwards, G.D.; Shirley, T.; Metcalf, A.R.; Leshner, R.L. Hydroxyl and peroxy radical chemistry in a rural area of Central Pennsylvania: Observations and model comparisons. *J. Atmos. Chem.* **2005**, *52*, 231–257. [\[CrossRef\]](#)
62. Ingham, T.; Goddard, A.; Whalley, L.K.; Furneaux, K.L.; Edwards, P.M.; Seal, C.P.; Self, D.E.; Johnson, G.P.; Read, K.A.; Lee, J.D.; et al. A flow-tube based laser-induced fluorescence instrument to measure OH reactivity in the troposphere. *Atmos. Meas. Tech.* **2009**, *2*, 465–477. [\[CrossRef\]](#)
63. Fuchs, H.; Tan, Z.; Lu, K.; Bohn, B.; Broch, S.; Brown, S.S.; Dong, H.; Gomm, S.; Haeseler, R.; He, L.; et al. OH reactivity at a rural site (Wangdu) in the North China Plain: Contributions from OH reactants and experimental OH budget. *Atmos. Chem. Phys.* **2017**, *17*, 645–661. [\[CrossRef\]](#)
64. Yoshino, A.; Nakashima, Y.; Miyazaki, K.; Kato, S.; Suthawaree, J.; Shimo, N.; Matsunaga, S.; Chatani, S.; Apel, E.; Greenberg, J.; et al. Air quality diagnosis from comprehensive observations of total OH reactivity and reactive trace species in urban central Tokyo. *Atmos. Environ.* **2012**, *49*, 51–59. [\[CrossRef\]](#)
65. Hansen, R.F.; Griffith, S.M.; Dusanter, S.; Rickly, P.S.; Stevens, P.S.; Bertman, S.B.; Carroll, M.A.; Erickson, M.H.; Flynn, J.H.; Grossberg, N.; et al. Measurements of total hydroxyl radical reactivity during CABINEX 2009-Part 1: Field measurements. *Atmos. Chem. Phys.* **2014**, *14*, 2923–2937. [\[CrossRef\]](#)
66. Ren, X.; Brune, W.H.; Olliger, A.; Metcalf, A.R.; Simpas, J.B.; Shirley, T.; Schwab, J.J.; Bai, C.; Roychowdhury, U.; Li, Y.; et al. OH, HO₂, and OH reactivity during the PMTACS-NY Whiteface Mountain 2002 campaign: Observations and model comparison. *J. Geophys. Res.-Atmos.* **2006**, *111*, D10S03. [\[CrossRef\]](#)
67. Chatani, S.; Shimo, N.; Matsunaga, S.; Kajii, Y.; Kato, S.; Nakashima, Y.; Miyazaki, K.; Ishii, K.; Ueno, H. Sensitivity analyses of OH missing sinks over Tokyo metropolitan area in the summer of 2007. *Atmos. Chem. Phys.* **2009**, *9*, 8975–8986. [\[CrossRef\]](#)
68. Kato, S.; Sato, T.; Kajii, Y. “A method to estimate the contribution of unidentified VOCs to OH reactivity”. *Atmos. Environ.* **2011**, *45*, 5531–5539. [\[CrossRef\]](#)
69. Ning, J.; Yan, F. Temperature Control of Electrically Heated Catalyst for Cold-start Emission Improvement. In Proceedings of the 8th IFAC Symposium on Advances in Automotive Control (AAC), Norrköping, Sweden, 20–23 June 2016; pp. 14–19.

70. Lelieveld, J.; Butler, T.M.; Crowley, J.N.; Dillon, T.J.; Fischer, H.; Ganzeveld, L.; Harder, H.; Lawrence, M.G.; Martinez, M.; Taraborrelli, D.; et al. Atmospheric oxidation capacity sustained by a tropical forest. *Nature* **2008**, *452*, 737–740. [[CrossRef](#)]
71. Peeters, J.; Nguyen, T.L.; Vereecken, L. HOx radical regeneration in the oxidation of isoprene. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5935–5939. [[CrossRef](#)]
72. Hofzumahaus, A.; Rohrer, F.; Lu, K.; Bohn, B.; Brauers, T.; Chang, C.-C.; Fuchs, H.; Holland, F.; Kita, K.; Kondo, Y.; et al. Amplified Trace Gas Removal in the Troposphere. *Science* **2009**, *324*, 1702–1704. [[CrossRef](#)] [[PubMed](#)]
73. He, G.; Ma, J.; Chu, B.; Hu, R.; Li, H.; Gao, M.; Liu, Y.; Wang, Y.; Ma, Q.; Xie, P.; et al. Generation and Release of OH Radicals from the Reaction of H₂O with O₂ over Soot. *Angew. Chem.-Int. Ed.* **2022**, *61*, e202201638. [[CrossRef](#)] [[PubMed](#)]
74. Baral, A.; Das, D.P.; Minakshi, M.; Ghosh, M.K.; Padhi, D.K. Probing Environmental Remediation of RhB Organic Dye Using α -MnO₂ under Visible- Light Irradiation: Structural, Photocatalytic and Mineralization Studies. *Chemistryselect* **2016**, *1*, 4277–4285. [[CrossRef](#)]
75. Ash, B.; Nalajala, V.S.; Popuri, A.K.; Subbaiah, T.; Minakshi, M. Perspectives on Nickel Hydroxide Electrodes Suitable for Rechargeable Batteries: Electrolytic vs. Chemical Synthesis Routes. *Nanomaterials* **2020**, *10*, 1878. [[CrossRef](#)] [[PubMed](#)]
76. Palmgren, F.; Berkowicz, R.; Ziv, A.; Hertel, O. Actual car fleet emissions estimated from urban air quality measurements and street pollution models. *Sci. Total Environ.* **1999**, *235*, 101–109. [[CrossRef](#)]

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