

The Lack of Knowledge about the Atmospheric Chemistry of Emitted Odorous Compounds and the Potential Resulting Impact on Smell

Radoslaw Barczak^{a,*}, Jean-Michel Guillot^b

^aUniversity of Warsaw, Faculty of Chemistry, Warsaw, Poland

^bIMT Mines Ales, GARANCe, Ales, France

r.barczak2@uw.edu.pl

Determining the general impact of odour emissions requires several levels of knowledge, such as characterizing the emissions, understanding the dispersion of odorants from the source to the receptor environment, and assessing the chemical effect and/or sensorial feeling at the considered location. From the kinetic emission fluxes characterization perspective, two main source types are considered: canalised or area. The emission type, which defines the source term in dispersion models, is a key point for estimating the impact of the odorous pollution. At the receptor level, tracers of odorous pollution can be identified using physicochemical analysis or highly sensitive artificial sensors. Still at the receptor level, the odour presence can be indicated by qualified panellists according to EN-16841 standard or citizen science with participation of the public. If all the process from emission to reception seems covered by techniques and expertise, it still exists a strong lack of knowledge considering the atmospheric chemistry of emitted odorous compounds. For selected species, the atmospheric chemistry is well described for reactions of compounds in the stratospheric layer; however, the impact of odorants in the lower tropospheric layer is neglected, assuming that the quickness of dilution and dispersion does not allow enough time for significant reactions and then for emitted mixture evolution. The goal of this paper is to highlight that the atmospheric evolution of odorous compounds has been little studied.

1. Introduction

This work, linked to a Polonium project (cooperation Poland-France), tried to show the knowledge gaps related to odour dispersion. Starting from the limited studies of radical reactions with odorants, considering the major chemical families that propose odorous compounds, integrating kinetic aspects (dispersion vs reactivity) and introducing uncertainty for both chemical reactions and measurement, this global process cannot be considered as a well-known phenomenon. Usually, in the odorous plume, a complex mixture of compounds (odorants and no-odorants) with their own reactivity is present. This reactivity is individual for each compound and varies from day to night. This article is dedicated to illustrate subdomains of this subject that are considered as partially known, such as hydroxy radical reactions, and others, such as night chemistry, where the lack of scientific knowledge is important. With only a reaction of some major odorous compounds during diffusion and transportation, even if the global chemical composition seems less affected, the odour can be modified, and then the impact on smell. This consideration is not applicable for very short distances, like a few meters from the source to the sniffing point. Some experiments carried out with a reactor at Warsaw University propose a way for testing reactivity and then data collection of odorant evolution, the article opens a new domain of research. In contrast to most atmospheric chemistry studies, odour-related investigations require consideration of much shorter temporal scales, ranging from seconds to hours, and finer spatial resolutions, typically within less than a few kilometres of the emission source. Despite their importance at these scales, high-resolution vertical profiles of atmospheric oxidants and their precursors have not been comprehensively characterized (Meng et al., 2020). To emphasize the relevance of such microscale temporal and spatial domains, the concept of *odour hours* can be applied. This approach defines exposure criteria based on ground-level odour concentrations at the 98th percentile, representing the maximum odour concentration that may be exceeded

during only 2% of the hours in a year (Capelli et al., 2013). Consequently, the use of inaccurate or oversimplified chemical kinetic parameters at these scales can introduce significant bias into odour dispersion and impact predictions. In the next paragraphs, the knowledge about the atmospheric chemistry of odorous compounds is synthesised to give a quick overview of the subject.

2. Atmospheric odorants

Atmospheric odorants can be carbon-based compounds, typically Volatile Organic Compounds (VOCs) including oxygenated compounds: organic acids and aldehydes (e.g., formaldehyde, acetaldehyde), and biogenic VOCs (e.g., isoprene, limonene). Atmospheric odorants are also sulphur compounds (hydrogen sulphide, methanethiol...) and nitrogen compounds (ammonia, amines). Unlike conventional air pollutants, odours are complex and dynamic mixtures whose perceived character may vary substantially with receptor distance from the emission source due to changes in chemical composition during transport (Wright et al., 2024). Sources of odorants are varied with numerous industrial emissions, wastewater treatment plants, landfills, biogenic emissions and agriculture (e.g., manure, livestock).

3. Atmospheric oxidants

All descriptions in this paper are focused on ambient air and not indoor air, even if specific reactions with odorants can occur, and a high surface-to-volume ratio indoors fundamentally alters radical lifetimes and partitioning. Degradation of atmospheric odorants cited in the previous paragraph predominantly occurs through oxidation. The most important oxidants, among others, are listed in Table 1. The atmospheric lifetime depends on the reactivity with listed oxidants and their concentrations in the air, which is affected, for example, by the UV radiation, the sunlight intensity, the planetary boundary layer height, the temperature, and the humidity. The variety of the chemical structure and bonds of odorous molecules makes their stability in a different range. With highly reactive compounds, the half-life ($T_{1/2}$) is carried out in a few minutes to a few hours, while less reactive compounds need days to decline their amount by half. For odour impact that is a local impact and not a regional or national transport of air pollutants, only a shorter lifetime must be considered.

Table 1: Key atmospheric oxidants and main characteristics for reaction

Oxidants	Formula	Reaction characteristic
Hydroxyl radical	•OH	Daytime oxidation
Ozone	O ₃	Reactivity with alkenes and sulphur compounds
Nitrate radical	•NO ₃	Nocturnal oxidation
Chlorine radicals	•Cl	Coastal and urban air chemistry

It must be noted that these four oxidants are key reactants for atmospheric chemistry and mainly considered for outdoor environments.

The synthesized information about the most abundant and most studied oxidant in the atmosphere, namely hydroxyl radical (•OH) is presented as follows. With an oxidation potential of approximately 2.8 V, •OH is the primary atmospheric oxidant and plays a central role in determining the chemical composition of the troposphere. Near the Earth's surface, •OH is formed predominantly through sunlight-driven photochemical processes involving ozone (O₃), nitrogen oxides (NO_x), and water vapour (Elshorbany et al., 2009; Xing et al., 2024). Owing to its extremely short atmospheric lifetime, typically ranging from 0.01 to 1 s, •OH exhibits pronounced spatial and temporal variability, posing significant challenges for direct observations and for resolving local- and regional-scale concentration gradients (Stone et al., 2012; Wolfe et al., 2019). On a global scale, •OH concentrations are strongly influenced by the ratio of CO to NO_x emissions, with a statistically significant linear relationship reported between this ratio and atmospheric •OH levels (Dalsøren and Isaksen, 2006). At local scales, however, •OH concentrations are governed primarily by site-specific chemical conditions, and new formation pathways continue to be identified (He et al., 2022; Lelieveld et al., 2002). Furthermore, the sources and sinks of •OH, and consequently the mechanisms controlling its local production, remain uncertain in many environments and are not yet fully understood (Yang et al., 2024). While there is broad consensus regarding the global •OH budget and cycling, substantial uncertainties persist concerning short-term variability and concentration fluctuations. Developing a reliable representation of •OH dynamics remains challenging because direct measurements are technically demanding and spatially sparse (Heald and Kroll, 2021).

Following Ferracci et al. (2018) it can be stated that, in some regions, as much as 80% of the observed •OH reactivity cannot be explained by currently measured atmospheric constituents, indicating the presence of unidentified reactive VOCs and/or secondary oxidation products. This so-called *missing •OH reactivity* has been

reported across a range of environments and remains a major challenge for accurately representing atmospheric oxidation processes in chemical transport models (Ferracci et al., 2018; Li et al., 2025). Odorous volatile organic compounds (OVOCs) may contribute to this unexplained reactivity. To date, $\bullet\text{OH}$ reactivity measurements have largely focused on compounds such as aromatic hydrocarbons (e.g., toluene, p-xylene, m-xylene, and 1,3,5-trimethylbenzene), alkenes (e.g., propene), and biogenic terpenes (e.g., isoprene and α -pinene) (Li et al., 2025; Sakamoto et al., 2022).

However, it is plausible that odorous compounds possessing substantially lower odour threshold values and therefore occurring at concentrations that are often overlooked in conventional atmospheric monitoring, may also contribute to the observed missing $\bullet\text{OH}$ reactivity. Describing the mechanisms of formation of oxidants is not part of this study; however, it has to be pointed out that it is complex and not well understood, similar to $\bullet\text{OH}$ chemistry.

4. Reaction and transformation pathways

The atmospheric lifetime of volatiles, so their degradation, is a fundamental parameter for assessing their persistence in the atmosphere and their potential for transport over varying spatial scales. Their removal is governed predominantly by reactions with the major atmospheric oxidants mentioned above (McGillen et al., 2020). Atmospheric lifetimes are typically estimated using a pseudo-first-order kinetic approach, which assumes that oxidant concentrations remain approximately constant over the timescale of the reaction (Bouguerra et al., 2025). Owing to the diversity of chemical structures and bonding patterns among odorous compounds, their atmospheric stability varies considerably.

Major reactions with examples and main impacts are listed in Table 2.

Table 2: Examples among the major atmospheric reaction processes

Reaction	Example	Impact
Oxidation	$\text{H}_2\text{S} \rightarrow \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$	Acid rain and aerosol formation
Oxidation	Terpenes + $\text{O}_3 \rightarrow$ small oxygenated compounds	Secondary organic aerosols (potentially odorants)
Photochemistry with sunlight	$\text{VOCs} + \text{NO}_x \rightarrow \text{O}_3$	Photochemical smog (contribution of oxygenated by-products)
Nitrogen chemistry with acids	$2 \text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow [\text{NH}_4]_2\text{SO}_4$ $\text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3$	Particulate pollution (sulphates and nitrates)
Chemical evolution	Odorous compounds	Potential odour modification

For the first line of Table 2, the oxidation is a radical process, and the global reaction is reported. This global reaction is detailed step by step with the precision about odour type for stable compounds:

- H_2S (hydrogen sulphide / strong rotten egg smell)
- $\text{H}_2\text{S} + \bullet\text{OH} \rightarrow \bullet\text{HS} + \text{H}_2\text{O}$ (R1)
- $\bullet\text{HS} + \text{O}_2 \rightarrow \bullet\text{HSO}_2$ (R2)
- $\text{HSO}_2^\bullet + \text{O}_2 \rightarrow \bullet\text{HO}_2 + \text{SO}_2$ (sulphur dioxide / pungent and irritating smell) (R3)
- $\text{SO}_2 + \bullet\text{OH} \rightarrow \bullet\text{HOSO}_2$ (R4)
- $\bullet\text{HOSO}_2 + \text{O}_2 \rightarrow \bullet\text{HO}_2 + \text{SO}_3$ (R5)
- $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ (sulphuric acid / sharp and penetrating smell) (R6)
- $\text{H}_2\text{SO}_4 \rightarrow$ sulphate particulates (odourless) (R7)

For the third line of Table 2, detailed reactions for VOCs (RH general formula) are:

- $\text{VOC} + \bullet\text{OH} \rightarrow \bullet\text{RO}_2$ (R8)
- $\bullet\text{RO}_2 + \text{NO} \rightarrow \text{NO}_2 + \bullet\text{RO}$ (R9)
- $\text{NO}_2 + \text{sunlight (hv)} \rightarrow \text{NO} + \bullet\text{O}$ (R10)
- $\bullet\text{O} + \text{O}_2 \rightarrow \text{O}_3$ (R11)

For the last line of Table 2, an odorous compound can be modified to another odorous compound (different odour intensity and different odour quality) or to an odourless compound. On the contrary, an odourless compound can react to produce an odorous compound.

Independently to odour aspects, a key characteristic of odorous compounds, odorants, can also generate other environmental and health impacts as presented in column 3 of Table 2. This impact can be linked to acid

deposition, the formation of tropospheric ozone, and the generation of fine particulates connected to potential respiratory irritations.

5. Potential particularities due to chemical structure

Odorous compounds can be from different chemical families, as presented in paragraph 2. Reactivity can be affected by the structure of the molecule. For example, as illustrated by hydroxyl radical rate constants (Table 3), a C=C double bond in alkenes generally makes a molecule much less persistent in the atmosphere than a C–C single bond of alkanes and usually less persistent than a C≡C triple bond of alkynes, because double bonds react very efficiently with atmospheric oxidants.

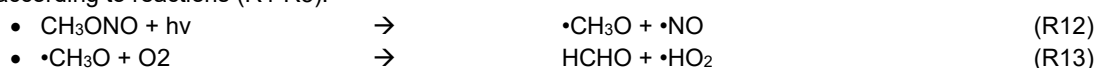
Table 3: Typical •OH rate constants at 298 K

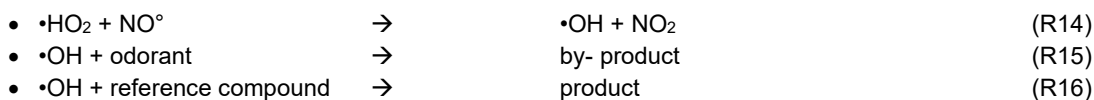
Bond type	Typical k_{OH} (cm ³ molecule ⁻¹ s ⁻¹)
C–C (saturated)	10^{-13} – 10^{-11}
C≡C (alkyne)	10^{-12} – 10^{-11}
C=C (alkene)	10^{-11} – 10^{-10}

Odorous compounds containing carbon–carbon double bonds (C=C), such as terpenes and allylic sulphur compounds, generally react with hydroxyl radicals one to three orders of magnitude faster than saturated odorants. Compounds containing carbon–carbon triple bonds (C≡C) exhibit intermediate reactivity, whereas saturated compounds containing only single carbon–carbon bonds (C–C) are typically the most persistent toward •OH oxidation. One caveat: for odorants, functional groups often exert a stronger influence on •OH reactivity than the carbon bond type itself. For example, Dimethyl disulfide contains only C–C single bonds but reacts with •OH ($\sim 2.5 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹) faster than many terpenes because of the highly reactive sulphur atoms. Typically, enantiomers and diastereoisomers are not recognized identically by human receptors and can lead to different odour types (or even a diastereomer can be odourless compared to another). Winska et al. (2014) gave examples of the configuration of the double bond of the isomers (E) and (Z) that usually have very different sensory profiles. Generally, it is considered that (Z)-isomers present a more pleasant smell and seem more “natural” than (E). Arrangement of the ring substituents is also a way to obtain different stereoisomers, and when multiple chirality centers are present in a molecule, each diastereoisomer can lead to various smell. Koppenhoefer et al. (1994) reported the different smell due to chirality for isomers like limonene (R-limonene is fresh, pleasant, orange-like and S-limonene is faint mint note, turpentine note) or for diastereoisomers of whiskey lactone (3R,4S isomer presents strong coconut note, reminiscent of celery; 3S,4R isomer presents piquant celery note, faint coconut note, green walnut note; 3R,4R isomer presents sweet woody, bright fresh coconut note and 3S,4S isomer presents faint coconut note, faint musty, earthy, reminiscent of hay). An oxidation of limonene leads to the carvone, a compound that still conserves a chirality with the R-carvone isomer that has a sweet, minty smell of green mint leaves, while the S-carvone isomer has a spicy aroma with notes of rye, and gives caraway seeds their characteristic odour. This odour type difference is also completed by a different aroma threshold: 43 ppb for R-carvone and 600 ppb for S-carvone (Morcia et al., 2016). Looking at the evolution of compounds, enantiomers present the same reactivity and the same kinetic of reaction, but as explained with limonene, starting from different structures implies different by-products is stereochemistry is not affected (and then potentially different smells). For diastereomers, different spatial arrangements lead to different reaction rates and potentially different by-products from a structural point of view.

6. Experiments and modelling of the kinetics of odorants

To study the lifespan of molecules in the atmosphere, different experimental and computational simulation approaches are conducted. Because the real atmosphere is an extremely complex reactor, it is very tough to conduct the experiments in it. Instead, the observations are done in simulation chambers and reactors. One of the examples is a controlled laboratory-scale photochemical reactor situated at the University of Warsaw, Laboratory for Radiochemistry and Atmospheric Chemistry. The •OH, is produced in situ through the photolysis of previously synthesized methyl nitrate. The process is initiated under UV irradiation at $\lambda > 355$ nm using a short-arc lamp equipped with a dichroic bandpass filter to control the wavelength. During the photolysis of methyl nitrite with known concentrations in ppm in the air, the following reaction sequence corresponds to reactions (R12-R14). In the presence of added odorant compounds, the •OH radicals react with these organic compounds according to reactions (R4-R5).





The verification of hydroxyl radical production was carried out by analysing the reduction in the concentration of odorous compounds, which leads to the formation of by-products as indicated in reaction (R15). A first test of the reactor using methane ($T_{1/2} = 6$ years) as an organic reagent to verify the success of the methyl nitrite synthesis protocol confirmed that •OH radicals were successfully produced. The degradation of methane concentrations over time made it possible to validate the reactivity after demonstrating the reactor's tightness (vacuum set to 32 Torr). The reaction mixture is sampled and injected into the gas chromatography (GC) combined with flame ionization detection (FID) at specific time intervals to monitor the odorant degradation rate under continuous generation of •OH.

In such experimental work, the rate constant of chemical species can be measured. Due to the technical difficulties and high cost of measurement devices in most of the simulation chambers and reactors worldwide, only a limited number of reactions can be measured at once. For example, the kinetics of one oxidant with one or multiple compounds. Such experiments are obviously simplified and do not consider interactions between multiple reactants, including reaction byproducts. To solve these difficulties, the theoretical modelling is applied. Different models are used, among which SOSAA (a model to simulate the concentrations of organic vapours, sulfuric acid and aerosols) is a good example. SOSAA is a 1-D chemistry transport model used to study the atmospheric composition inside the planetary boundary layer, including the characteristics of oxidant reactivities, oxidation of trace gases, and vertical exchange and biogenic VOCs (Chen et al., 2021). Recent modelling studies emphasize the importance of including multiple oxidants to capture the complex atmospheric fate of volatiles, particularly in polluted environments where Cl and NO_3 radicals can rival OH as dominant oxidants.

7. Conclusions

Globally, the odorants chemistry which happens during its dispersion is not a well-known phenomena. Filling this knowledge gap with experimental work on degradation rates of odorants and also theoretical computation modelling should improve our understanding of odour impact assessment. This lack of knowledge results mainly from two combined points. On the one hand, odorant compounds have rarely been studied in terms of atmospheric reactivity compared to pollutants like aromatics. On the other hand, since the odour impact concerns short distances compared to phenomena such as acid rain, the notion of kinetic evolution over relatively short times has not been the subject of many studies. This shows the interest in filling the knowledge gap regarding the modelling based on both reactivity and dispersion of emitted odorant compounds (including reaction by-products) to better understand the changes in odour perception that will result from the evolution of the emitted gas mixture. Experimentally, it is therefore necessary to be able to produce atmospheric oxidants and to have a reactor allowing the odorous compounds to react in order to determine the species obtained and the kinetics of evolution. It is on the construction of such databases that simulation models can be developed by adapting existing models for the odorant application and its fate.

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