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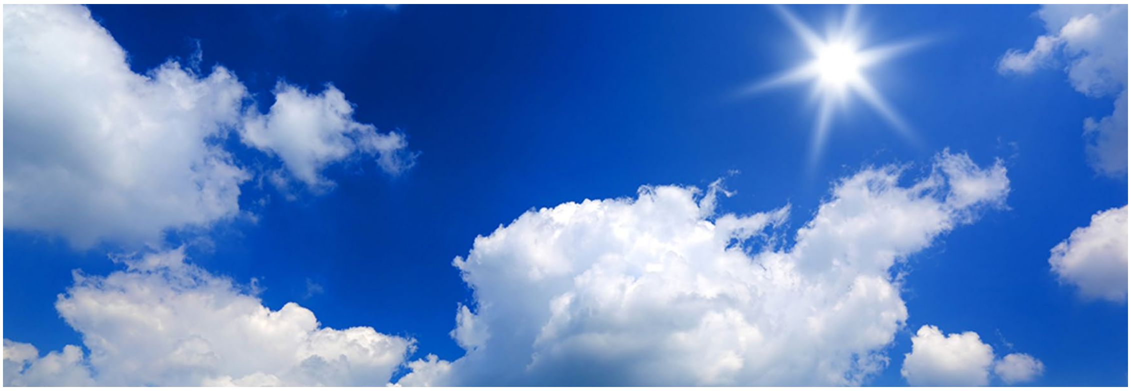

Credit: Getty images/macroworld

ATMOSPHERIC CHEMISTRY

# Up in the clouds

“This finding changes our view of how important cloud droplets are for processing chemicals in the atmosphere”

Fine particles suspended in air or liquid droplets, known as aerosol particles, have a profound effect on our climate: they scatter and absorb solar radiation, modify the properties of clouds and contribute to air pollution. Clouds play a key part in the formation and transformation of organic aerosol particles, yet uncertainty surrounds the mechanisms of these reactions, involving OH radicals (·OH), and the amount of particles generated. Writing in *Science Advances*, Suzanne Paulson and colleagues now reveal a substantial source of ·OH within cloud droplets that could be central to the processing of organic aerosols.

“Cloud droplets have many roles in our climate system, one of which is that they act as tiny chemical reactors that transform gases into materials that add to aerosol particles and remain after the cloud evaporates,” says Paulson. These transformations are thought to be mediated by ·OH, but the concentration and origin of this species in cloud droplets is one of the principal uncertainties in the process. Uptake from the gas phase is generally considered to be the main source of ·OH in cloud droplets. Additionally, ·OH can form within droplets in reactions of hydroperoxides catalysed by transition metals, the classic example of which is the Fe-catalysed Fenton reaction:

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)} + \cdot OH + {}^{-}OH$$

Probing ·OH in cloud droplets is challenging. “Cloud droplets form when water condenses on aerosol particles; however, current analytical methods aren’t sensitive enough to measure ·OH or related species in individual cloud droplets,” explains Paulson. To overcome this problem, the team simulate the formation of cloud droplets in the laboratory by adding water to ambient aerosol samples in ratios typical of cloud droplets. As the composition of aerosol particles (mixtures of inorganic salts, organics, metals and soot) is dependent on the local environment, samples were collected from various locations at different times of the day and year. Freshly prepared water–particle mixtures are subsequently illuminated with near-UV light. The $[\cdot OH_{(aq)}]$ can be determined using terephthalate as a probe for ·OH, with which it reacts to form a fluorescent product.

Upon the initial addition of water to the particles and illumination, there is a surprisingly sharp increase in $[\cdot OH_{(aq)}]$. Under dark conditions, however, ·OH does not form. The rate of ·OH formation upon illumination exceeds those of established sources. Moreover, despite sample variation in $[\cdot OH_{(aq)}]$, the average $[\cdot OH_{(aq)}]$ is either equal to or larger than that of other ·OH sources, suggesting that this light-driven burst could be a dominant source of ·OH in cloud droplets. “This finding changes our view of how important cloud droplets are for processing chemicals in the atmosphere,” states Paulson.

The team show that the burst of ·OH produced in ambient samples can be reproduced by illuminating mixtures of peracetic acid and Fe(II) with near-UV light. In this case, ·OH also forms under dark conditions, albeit in lower yields than when illuminated. A new Fenton-like reaction is proposed as a likely mechanism for the formation of ·OH under dark conditions, the products of which can yield additional ·OH under illumination:

$$\mathrm{Fe(II)} + \mathrm{MeC(O)OOH} \rightarrow \mathrm{Fe(III)} + \mathrm{OH} + \mathrm{MeC(O)O^{-}}$$

$$\mathrm{Fe(III)} + \mathrm{MeC(O)O^{-}} + h\nu \rightarrow \mathrm{Fe(II)} + \mathrm{Me(O)O} \rightarrow \rightarrow \cdot OH$$

Thus, the reaction of an organic peroxide, a species commonly found in organic aerosols, with Fe(II) could be the source of the ·OH burst in the ambient samples. The identification of this new major source of ·OH is a step towards elucidating the chemical processes in cloud droplets. Paulson and her team aim to continue to explore this new phenomenon and investigate its chemistry to assess the implications for the climate and air pollution.

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**ORIGINAL ARTICLE** Paulson, S. E. et al. A light-driven burst of hydroxyl radicals dominates oxidation chemistry in newly activated cloud droplets. *Sci. Adv.* **5**, eaav7689 (2019)