

## LANDMARK: ATMOSPHERIC CHEMISTRY

# A radical shift in air pollution

Fifty years ago, Levy identified hydroxyl radicals as the driver of chemistry in the troposphere

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The lower atmosphere, or troposphere, contains ~90% of the mass of the atmosphere, including the air that we breathe at the surface of Earth. Fifty years ago, during a time when scientists were focused on understanding the chemistry of the ozone layer and urban smog, the troposphere was thought to be largely chemically inert and simply a receptacle for emissions and for gases transported from the stratosphere above. In 1971 in *Science* (1), Levy discovered that hydroxyl (OH), a highly reactive radical, could be formed efficiently in the lower atmosphere. This revelation shifted the paradigm of atmospheric chemistry and shapes how we view both air quality and climate forcing today (see the figure).

Prior to 1971, only a few regions of the atmosphere were thought to be chemically active, driven by ultraviolet (UV) radiation from the Sun. In 1930, Chapman (2) proposed that ozone (O<sub>3</sub>) was generated in the stratosphere from the UV photolysis of O<sub>2</sub>. This process forms O atoms that add to O<sub>2</sub> to make O<sub>3</sub>. Subsequent work by other researchers found that the photolytic reactions of trace stratospheric species form a host of free radicals (such as OH, HO<sub>2</sub>, NO, and NO<sub>2</sub>) that take part in a complex network of radical-radical and radical-molecule reactions. The net result of this photochemistry is the stratospheric ozone layer, which shields living creatures at the surface from the damaging effects of UV radiation.

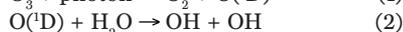
However, the absorption of UV radiation by the ozone layer implies diminished photochemistry in the underlying troposphere. As a result, it was believed that most of the troposphere was essentially inert, involving only slow atmospheric reactions initiated by ozone (descending from the stratosphere) or the occasional O atom. Anthropogenic air pollutants could therefore accumulate in the troposphere; for example, there were concerns that carbon monoxide (CO) emitted from vehicles

might reach toxic levels and become a widespread public health threat.

The main exception to this view of the inert troposphere was the polluted urban atmosphere. The late 1940s saw the emergence of “Los Angeles smog,” a noxious mix of gases and particles leading to eye irritation, damage to plants, and reduced visibility. Studies (3, 4) quickly revealed that this pollution included ozone (which at ground level is a major respiratory irritant and phytotoxin) and other oxidants, and moreover was photochemical in nature, formed by the irradiation of hydrocarbons and nitrogen oxides (both emitted in high quantities from vehicles). Researchers focused on understanding this photochemistry, to predict and ultimately mitigate smog formation (5).

By the late 1960s, there were indications that the troposphere was more photochemically active than was generally assumed. The atmospheric lifetime of CO was found to be surprisingly short (6, 7), indicating a large unknown reactive sink. Although it was understood that urban O<sub>3</sub> was formed from the near-UV photolysis of NO<sub>2</sub>, its fast formation, which required the rapid oxidation of hydrocarbons and conversion of NO to NO<sub>2</sub>, could not be explained by existing mechanisms (8). These gaps provided hints that the atmospheric oxidation of trace species (CO, hydrocarbons, and other pollutants) was much faster than was appreciated, and it was suggested that highly reactive OH radicals might be responsible (7, 8). However, there was no known viable tropospheric source of OH.

Levy solved this conundrum, by showing that the hydroxyl radical (OH) could be efficiently formed throughout the troposphere (what he referred to as the “normal atmosphere”) by the UV photolysis of ozone. The process involves two steps. In the first, photolysis forms O(<sup>1</sup>D) (electronically excited O atoms) caused by absorption of a photon. In the second, O(<sup>1</sup>D) reacts with water vapor:



These same reactions were known to produce OH in the stratosphere, but they had been assumed not to occur in the troposphere because of the lack of high-energy UV photons (wavelengths of <320 nm) required

for reaction 1. However, Levy pointed out that the very small fraction of low-wavelength UV that did make it through the ozone layer, combined with the high water-vapor concentrations in the lower atmosphere, was sufficient to lead to substantial OH generation throughout the troposphere.

The impact of the troposphere being a highly reactive environment was immediate and profound. The ubiquity of the OH radical explained the short chemical lifetimes of CO (and other pollutants), as well as the rapid formation of urban ozone pollution. It also led to many new discoveries that are now central to our understanding of the lower atmosphere. For example, within just a few years, it was shown that the oxidation of methane by OH had an enormous impact on the global atmosphere, not only serving as the main source of CO (9) but also leading to the formation of ozone throughout the entire troposphere (10, 11), and not just the stratosphere or polluted urban areas, as previously thought. This realization also placed a new focus on trace compounds that do not react with OH (such as CO<sub>2</sub>, CFCs, and N<sub>2</sub>O). Because these species could accumulate in the atmosphere, they have outsized impacts on stratospheric ozone depletion, climate, or both.

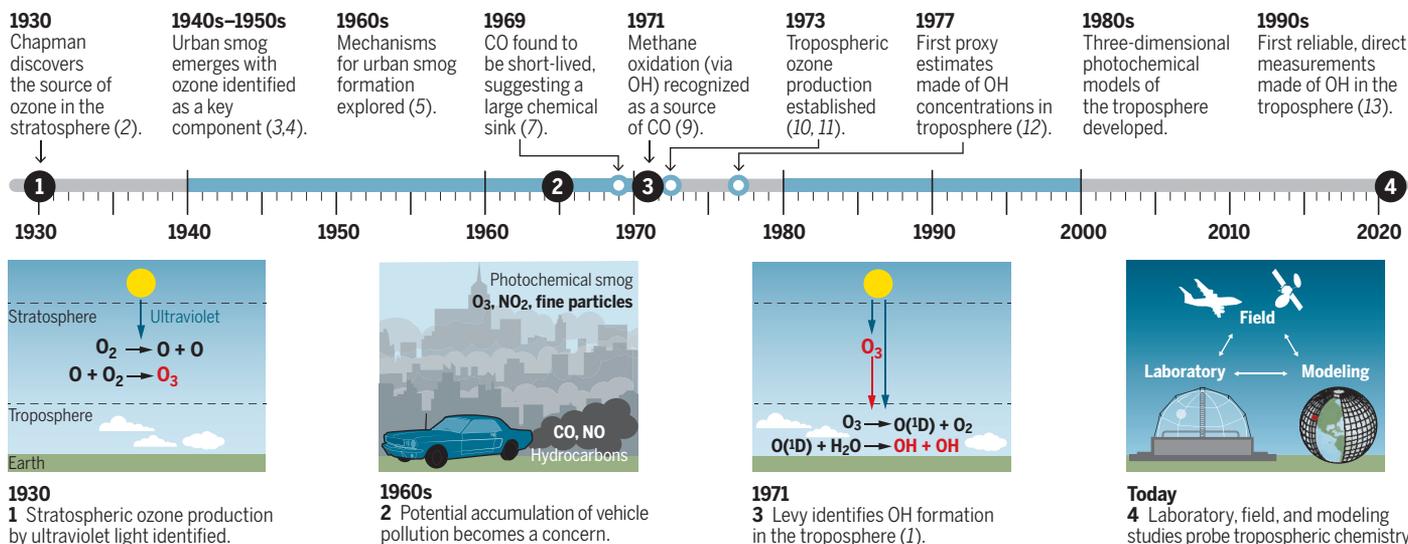
It would be many more years before atmospheric OH levels were measured. The high reactivity of OH ensures that its atmospheric concentration is exceedingly small—below parts per trillion by volume—and posed a daunting measurement challenge. Measurements of long-lived halocarbons (whose main sinks were oxidation by OH) provided the first estimates of OH concentrations (12). Direct, spectroscopic detection of OH with laser-induced fluorescence proved to be highly challenging, and it would be decades before OH could be detected reliably in the troposphere (13). Currently, OH measurements remain challenging and relatively sparse, but it is generally accepted that global OH has a concentration on the order of  $1.2 \times 10^6$  molecules cm<sup>-3</sup> (14), in reasonable agreement with the early estimates by Levy.

The production of OH in the troposphere underpins our modern understanding of the chemistry of the troposphere, and particularly the relationships between emissions, air quality, and anthropogenic

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## A century of atmospheric chemistry

The timeline shows key discoveries in tropospheric chemistry and its effects on our understanding of pollution. In 1971, Levy showed that hydroxyl radical (OH) could be formed efficiently throughout the troposphere, when it had been thought that such radicals could only be generated in the stratosphere. The ubiquity of tropospheric OH gives rise to complex networks of chemical reactions that control the levels of air pollutants and climate forcers. The ongoing study of this chemistry, from 3D models, laboratory investigations, and fieldwork, continues to inform our understanding of tropospheric pollutants and efforts to mitigate their effects.



climate change. To illustrate this point, consider a hypothetical world without tropospheric OH. Leading air pollutants of concern, which are typically regulated for their deleterious effects on human health, would shift toward primary (that is, directly emitted) species. For example, as feared in the 1960s, the present-day tropospheric burden of CO would soar, putting a large fraction of the global population at risk for CO poisoning. Similarly, concentrations of sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) would rise along with attendant exposures to SO<sub>2</sub> and NO<sub>2</sub> that increase the risk of respiratory disease.

At the same time, concentrations of secondary pollutants would fall. In a troposphere without OH, there would be little to no tropospheric production of O<sub>3</sub> and thus no urban O<sub>3</sub> air quality concerns, largely alleviating the health burden of O<sub>3</sub>. Fine particulate matter (PM<sub>2.5</sub>, particles less than 2.5 μm in diameter), which leads to the premature deaths of millions of people every year, would also decrease sharply because of lower formation rates of secondary sulfate, nitrate, and organic aerosols. Air quality regulation, both policy and the deployment of control technology, would be far simpler, because pollutants of concern could be moderated directly (and linearly) through emissions cuts.

Similarly, Earth's climate and our understanding of anthropogenic climate forcing would also be greatly altered in a world without tropospheric OH. Atmospheric concentrations of methane, a leading green-

house gas, would surge. However, given that a substantial fraction of methane sources are natural, methane would have accumulated in (and warmed) the preindustrial atmosphere, such that anthropogenic additions of methane would contribute more modestly to climate forcing. Coupled with the lack of anthropogenic O<sub>3</sub> production in the troposphere and the greatly diminished anthropogenic source of PM<sub>2.5</sub>, there would be much less climate forcing from what are currently referred to as short-lived climate forcers (SLCFs).

It is also probable that a troposphere without OH would produce any number of new environmental concerns. Longer-lived tropospheric gases could be transported upward to the stratosphere, likely exacerbating the destruction of the ozone layer. Concentrations of harmful pollutants known to be removed by OH could increase rapidly and require new air pollution policies. The production of OH in the troposphere, identified 50 years ago by Levy, precludes this counterfactual of a simple but markedly different troposphere.

In 1971, the work of Levy showed that, counter to prevailing assumptions at the time, the lower atmosphere is not inert, but rather is a complex chemical reactor. This revelation is what necessitated and created the field of tropospheric chemistry. The work of the last 50 years has revealed generations of oxidative chemistry in the troposphere, highlighted the prominence of secondary pollutants, identified intricate interactions between natural and

anthropogenic emissions, and elucidated the nuanced response of air pollutants and SLCFs to regulatory policies and a changing climate. It would be convenient but unrealistic (and even counterproductive) to assume that air-pollution policy can be developed with a knowledge of emissions alone. The challenge initiated by Levy is to understand how these emissions evolve in the reactive troposphere. ■

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