Untangling links between nitrogen oxides and airborne sulfates helps tackle hazy air pollution

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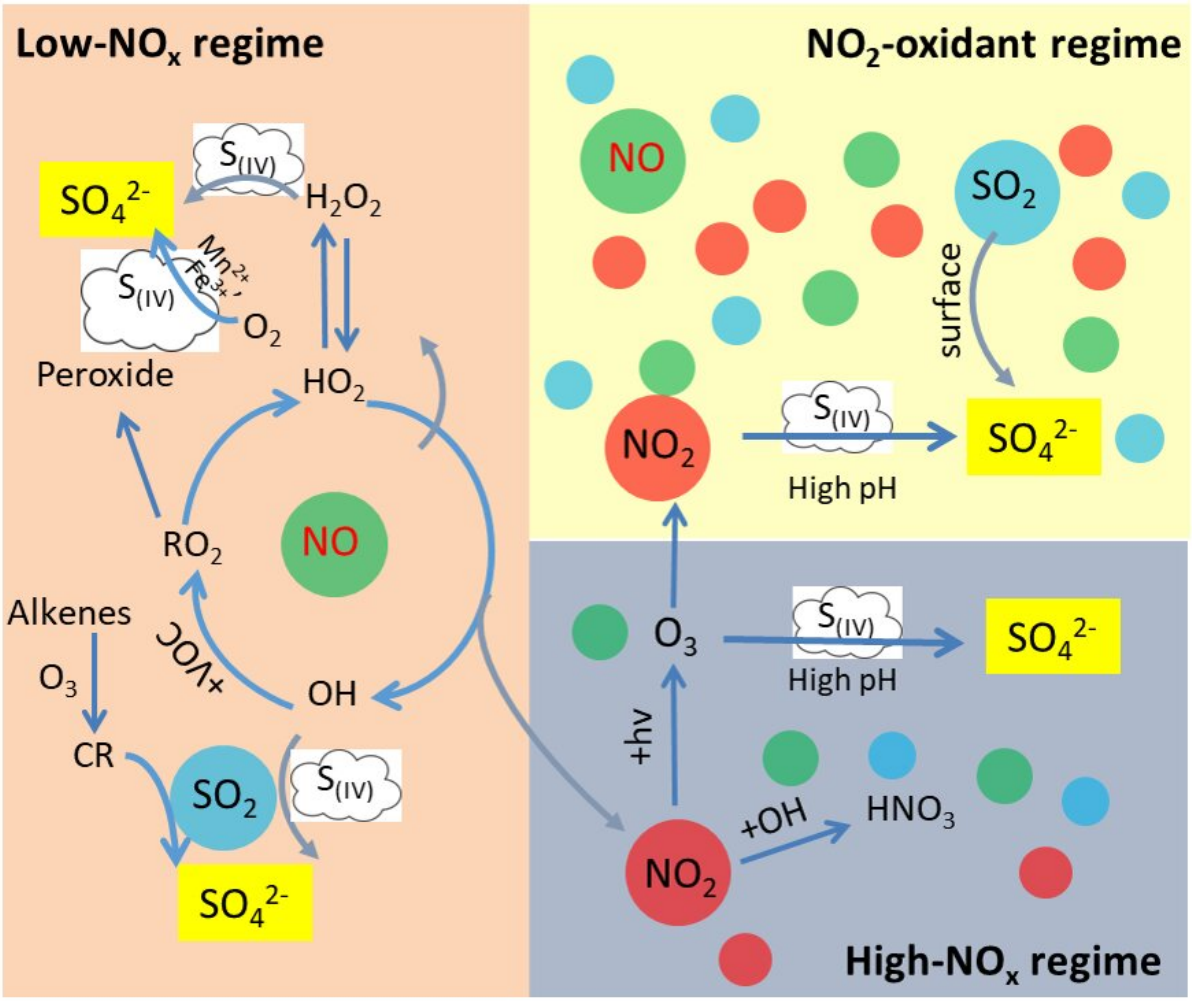
Hebei is one of the Mainland provinces most affected by hazy weather. The photo was taken on December 1, 2019. Credit: Liu Guorui

Dense, hazy fog episodes characterized by relatively high humidity, low visibility and extremely high PM2.5 have been a headache to many megacities, including those in mainland China. Among pollutants that are less than 2.5 microns in diameter (PM2.5), airborne sulfate is one of the most common components of hazy air pollution formed atmospherically via the oxidation of sulphur dioxide (SO_2).

While the reactant-product link between sulphur dioxide and airborne sulfate formation is common knowledge, the complex oxidants and mechanisms that enable this transformation are not. In particular, the role of nitrogen oxides in sulfate production is unclear. Managing sulfate pollution has dogged researchers and governments alike, It is not produced directly from pollution sources, unlike nitrogen oxides, which are clearly emitted from vehicle exhaust and the combustion of fossil fuels including coal, diesel and natural gas. This is the first study systematically examining the multiple roles of nitrogen oxides in affecting oxidants that enable this set of chemical reactions.

In collaboration with the California Institute of Technology, a research team led by Prof. YU Jianzhen, Professor at HKUST's Department of Chemistry and Division of Environment and Sustainability, identified three formation mechanism regimes corresponding to the three distinct roles that nitrogen oxides play in sulfate production depending on the chemical surroundings. Under low NO_x conditions, NO_x catalyzes the cycling of hydroxyl radicals, an effective oxidant of SO_2, and thus promotes formation of sulfate. Under extremely high NO_x levels common in haze-fog conditions, NO_x types act as dominant oxidants of SO_2 and thus also promote formation of sulfate. But in an environment with a medium-high level of NO_x, nitrogen dioxide (a member of the NO_x family) would actually serve as a sink for hydroxyl radicals, which suppresses the oxidation of sulphur dioxide and thus inhibits sulfate formation.



The three newly-discovered formation mechanism regimes of how NOx affects the production of airborne sulfate. Credit: HKUST

These findings indicate that in order to reduce sulfate levels in highly polluted haze-fog conditions, co-control of SO_2 and NO_x emissions is necessary. However, since NO_x would inhibit sulfate formation when its emissions are intermediately high, suppressing NO_x in such an environment would thus bring up sulfate levels in the air.

"Since sulfate is formed atmospherically and cannot be controlled directly, we must target its precursor components (such as sulphur dioxide and nitrogen oxides). Effective reduction of sulfate content in the air relies on knowledge of the quantitative relationship it has with its precursors. This work lays the conceptual framework to delineate the relationship between sulfate and one set of its controllable precursors, nitrogen oxides (NO_x)—the low and extremely high concentration of NO_x could both fuel up the production of sulfate. The policymakers should pay attention to when they try to control the emission of NO_x," explained Prof. Yu.

As sulfate is one of the major components that leads to haze formation and acid rain, this study laid the groundwork for formulating more effective measures of targeting this major pollutant involved in such events—which do not just block the views or make aquatic environments more acidic, but also compromise human health. With greater understanding and better control, this will lead to improved air quality and better protection of public health and ecological systems as a whole.

The team's findings were recently published in the scientific journal *Nature Geoscience*.

More information: Jian Xue et al, Efficient control of atmospheric sulfate production based on three formation regimes, *Nature Geoscience* (2019). DOI: 10.1038/s41561-019-0485-5

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