

Atmospheric science: the self-cleansing ability of prehistoric air

Article

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Atmospheric science

Prehistoric air's self-cleansing ability

Isotopic data from an ice core have been used to estimate atmospheric oxidant levels during past climate transitions — pointing to relatively unexplored climate feedbacks as drivers of atmospheric composition. See Letter p.XXX

Michaela I. Hegglin

The atmosphere has a self-cleansing ability¹ that stops certain air pollutants and greenhouse gases from accumulating, thus preventing catastrophic consequences for air quality and climate, respectively². The rate of self-cleansing — known as the oxidation capacity — determines the lifetime of such pollutants and gases, and depends on the abundance of oxidants in the troposphere, the lowest layer of the atmosphere. It would be useful to know how tropospheric oxidant levels varied during past periods of climate change, to inform models used to predict future climate, but such information has been conspicuously absent. On page XXX, Geng *et al.*³ present a promising proxy data set for such oxidants during the most recent glacial–interglacial cycle, based on an isotopic quantity known as the oxygen-17 excess of nitrate, $\Delta^{17}\text{O}(\text{NO}_3^-)$.

The primary oxidant in the atmosphere is the hydroxyl radical (OH), which is generated by photochemical processes involving water vapour, ozone and

ultraviolet radiation (Fig. 1). Because OH has a short lifetime of just a few seconds (ref. 2), its atmospheric concentration is highly variable and difficult to measure. Researchers have therefore developed techniques that allow atmospheric OH levels to be quantified indirectly by measuring concentrations of trace gases⁴ whose lifetimes are much longer and depend on OH abundances.

Inferring the abundance of tropospheric oxidants is even more challenging when trying to look into the past. Long-lived trace gases can be analysed readily from air trapped in ice cores, but short-lived species cannot, because they are too reactive to be preserved. This has led to a lack of information on past oxidant levels.

To address this problem, Geng *et al.* collected $\Delta^{17}\text{O}(\text{NO}_3^-)$ data from a Greenland ice core that preserves a record of the most recent glacial–interglacial cycle (the past 100,000 years). $\Delta^{17}\text{O}(\text{NO}_3^-)$ had previously been suggested⁵ to be a valuable proxy for the tropospheric oxidation capacity — more specifically, for the ratio of the concentration of ozone (O_3) to that of HO_x (the group of atmospheric compounds that includes OH and other oxidants called peroxy radicals). If the long-term evolution of O_3/HO_x is known, feedbacks between atmospheric chemistry and climate can be investigated.

The O_3/HO_x ratio was previously believed to be directly proportional to temperature, because emissions of ozone precursors from biological sources are expected to increase as climate warms^{6,7}. Geng and colleagues' proxy data set

surprisingly reveals an inverse relationship between O_3/HO_x and temperature, both at glacial-to-interglacial timescales and during a Dansgaard-Oeschger event (an episode characterized by rapid warming over a few decades, followed by gradual cooling over hundreds to thousands of years). Puzzlingly, however, the authors observed that O_3/HO_x was, in fact, directly proportional to temperature during another Dansgaard-Oeschger event characterized by a moderately warmer cooling period.

To interpret their results, the authors used a modelling framework that simulates the effects of climate and of the biosphere on tropospheric chemistry. On this basis, they infer that the primary factors responsible for the changes in oxidant levels were the chemistry of halogen-containing compounds in the atmosphere and transport of ozone from the stratosphere to the troposphere. Those inferences are certainly plausible, but have to be regarded as speculative given the limitations of their modelling framework.

Climate models that simulate interactions between atmospheric chemistry and climate, and which include a well-resolved stratosphere, have indeed shown that stratosphere-to-troposphere transport of ozone increases under a warming climate^{7,8}. But the impact of the simulated transport changes on tropospheric ozone depends strongly on the region involved, and can lead locally to either increases or decreases of ozone levels⁸. These models have not yet been used to study stratosphere-to-troposphere transport in past colder climates. They also generally

do not incorporate the complex halogen chemistry invoked by Geng *et al.*; when this chemistry is added to the basic tropospheric chemistry typically used in models, tropospheric ozone levels can reduce significantly in simulations of modern conditions⁹. All things considered, Geng and colleagues' proposal is probably the best current hypothesis to explain the observed changes of oxidant levels.

The new results highlight once again how little we understand about the complexity of chemistry–climate feedbacks, and more generally of how strongly Earth-system processes are interconnected. Tropospheric composition is driven in different ways by the ocean, cryosphere (the part of the Earth system that is frozen water), lithosphere (Earth's rocky, outermost shell), and the land and marine biospheres, but also by the stratosphere. It will be crucial to develop a better understanding of the feedback mechanisms to more accurately predict how anthropogenic emissions might affect climate and air quality in the future. In particular, a deeper understanding of how atmospheric composition — especially the lifetime of greenhouse gases — is affected by climate change will be important when interpreting information from climate models to make policy decisions about how to limit global warming below certain temperature targets.

A new generation of Earth-system models that encompass all of the processes and feedbacks that determine climate — including those associated with the stratosphere — will be needed to answer questions of how atmospheric composition and climate interact. Simulations should not simply be 'tuned' to

provide the best reproduction of present climate, but should be built on an understanding of the processes involved, to allow the credible simulation of both past and present climates. Most crucially, these models should be compared continuously with observations and proxy palaeoclimate data, to test their validity and to inform further development. This in turn will require strong collaborations between modellers and data-collecting scientists, and will need palaeoclimate researchers to join their expertise with that of experts studying present and future climate.

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¹⁰ Schmidt, J. A., et al. Modeling the observed tropospheric BrO background: Importance of multiphase chemistry and implications for ozone, OH, and mercury, *J. Geophys. Res. Atmos.* **121**, 11,819–11,835, doi:10.1002/2015JD024229, 2016.

Figure 1 | Factors influencing the self-cleansing ability of the troposphere. The atmosphere has a ‘self-cleansing’ ability that depends on the abundance of oxidants in the troposphere, the lowest layer of the atmosphere — particularly the abundance of the hydroxyl radical (OH). The primary production of OH depends on the availability of ozone (O₃, part of which is generated in the stratosphere and transported to the troposphere), water vapour and ultraviolet light. Secondary

processes recycle OH in reactions driven by emissions of nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs) from anthropogenic and biological sources. Halogen radicals produced in sea spray tend to decrease OH levels. The relative contributions of the different processes to the overall OH budget are expected to change as climate changes. Geng *et al.*³ report isotopic measurements that act as a proxy for tropospheric oxidant levels during the most recent glacial–interglacial transition, and argue that the main influencing factors were the chemistry of halogen radicals and stratosphere-to-troposphere transport of ozone.