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The Changing Face of Urban Air Pollution

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The atmospheric chemistry that leads to photochemical smog and climate-active aerosols requires the presence of volatile organic compounds (VOCs) (1, 2). The VOCs in urban air typically derive from the prevailing energy and transport technologies as well as the use of petrochemical-derived products. On page 760 of this issue, McDonald et al. (3) report that a notable change in emissions may be under-way in U.S. cities, with effects on secondary pollutants such as organic aerosols. Shifting from an urban atmosphere dominated by transport-related VOCs to one dominated by VOCs from coatings, adhesives, and consumer products would alter predictions of urban air quality and challenge the existing policy framework for emissions control.

The composition of VOCs in urban air has historically been influenced by the presence or absence of a natural gas network or refining industries; the relative balance in the urban transport fleet between gasoline, diesel, public, and private (4, 5); and, more recently, the extent of vehicle electrification. Natural emissions from plants and trees can also be important in the warmer months of the year. Transport, industrial, and natural emissions can be predicted with some precision, but estimating highly diffuse VOC sources from consumer products is very challenging and often depends on predictions of air exchange between indoor and outdoor environments.

Many countries already regulate the emission of VOCs from sectors such as fuel storage and distribution, transportation, and industrial solvent use. International conventions such as the Gothenburg Protocol set limits on the transboundary export of VOCs between some countries. Multidecadal reductions in carcinogenic benzene and 1,3-butadiene have been particularly notable in North America and Europe, along with a more general decline in those regions in the total amount of short-chain hydrocarbons in ambient air. The modern three-way catalytic converter has been particularly effective at eliminating tailpipe VOC emissions from gasoline vehicles. An outlier to this long-term global decline has been a recent rise in atmospheric ethane across the Northern Hemisphere, thought to result from the expansion of unconventional hydrocarbon industries in the United States (6).

Although it is tempting to treat VOCs as a single pollutant, they have enormously diverse chemistries; each compound follows a unique pathway from initial emission through atmospheric degradation to an end product. They are short-lived in the atmosphere and are susceptible to oxidative attack by hydroxyl radicals (during daytime) and nitrate radicals (during the night); some also react with ozone. Lifetimes range from several months to only a few minutes, with oxidation occurring through multiple steps that ultimately

produce CO and water. The complexities of VOC degradation can be staggering: Atmospheric oxidation of isoprene (C₅H₈) is estimated to involve 1928 different steps and 602 unique intermediate organic species before CO and water are finally formed (7). Most of this chemistry is hidden from experimental view, and there is a reliance on theoretical predictions provided by the detailed chemical models used for air pollution forecasting (8). Only in 2012 was one of the most fundamental species in VOC oxidation chemistry, the Criegee intermediate, experimentally detected for the first time (9).

As VOCs oxidize, they can form other stable organic compounds that are functionalized with oxygen- and nitrogen-containing groups. Functionalized intermediates of VOC oxidation often have a lower vapor pressure than the starting compound and therefore tend to condense to aerosols, rather than staying in the gas phase. They can participate in heterogeneous processes that form or modify aerosol properties. Understanding these degradation processes is therefore vital for both air quality and climate applications. Models that represent some of this chemistry predict formation of thousands of different potentially condensable compounds in a complex web of reactions from a small number of initial VOC emissions (see the figure). Changing the blend of those starting VOC compounds in cities could generate a different suite of condensable products, in turn affecting how much ozone and secondary aerosols are formed.

The development of analytical techniques has played a very important role in advancing knowledge of VOCs in air. Mass spectrometry, in particular, can now provide exceptional detail on the amounts and exact chemical structures of VOCs released into air. Goldstein and Galbally (10) estimated that VOCs in the air may comprise more than 10,000 different structures. This diversity is daunting, but not necessarily beyond the capabilities of the very latest high-resolution instruments.

The shift in U.S. VOC sources that McDonald et al. report highlights the need for continued surveillance of VOCs as pollutants. Changing patterns of VOC emissions may potentially be seen most clearly by analyzing indoor air—a type of atmosphere that has received considerably less research attention than outside air (11). Volatile chemicals in cleaning products, such as limonene, can dominate the air in modern homes, displacing solvents such as xylenes that have been reduced in paints, glues, and coatings (12). Yet, few operational air pollution models include VOCs that are specific to sources such as personal care products, and none take into account synthetic forms of VOCs such as cyclic volatile siloxanes (13). These models must be adapted to capture the changing pattern of emissions. As knowledge of VOC chemistry improves, it will become possible to develop more targeted approaches to reducing impacts. Prioritizing those VOCs with the greatest aerosol formation potential—for example, through reformulation of consumer products—would be one option. Industry sectors that have until now been left outside of VOC emissions controls may, in a cleaner electrified future, receive more direct attention from regulators.

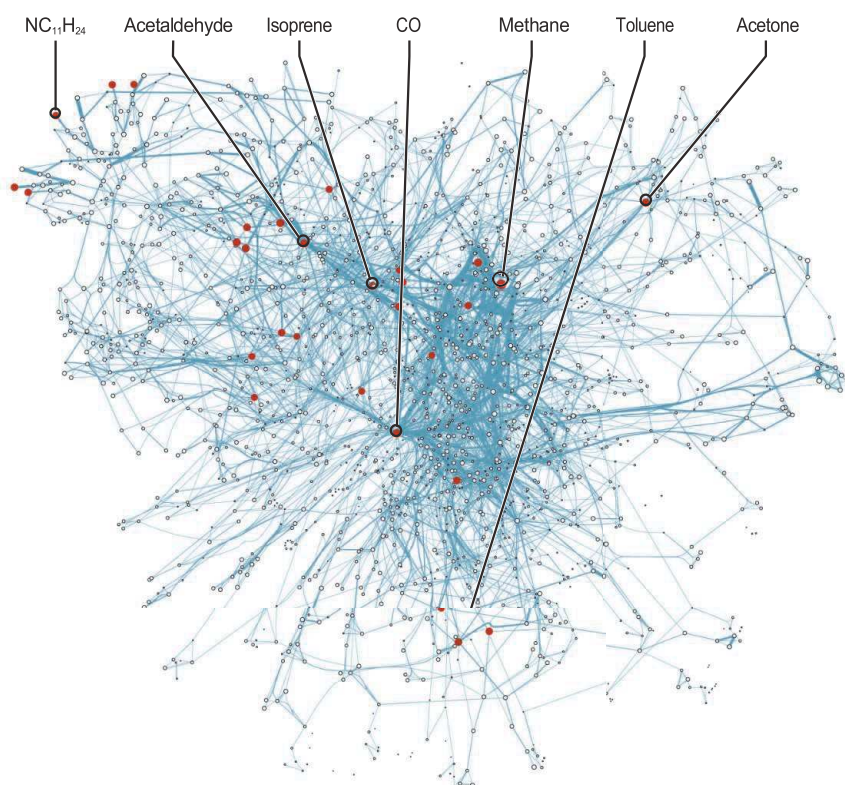


Figure. A small number of initial emitted VOCs (red dots) react in the atmosphere to form a vast number of secondary compounds (white dots). In this graph representation, blue lines denote the reactions between compounds. See (8) for details.

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