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The complex chemical effects of COVID-19 shutdowns on air quality

Stay-at-home policies in response to COVID-19 have led to well-publicized reductions in some air pollutants. The extent to which such decreases translate to improved air quality is dictated by not only emissions and meteorology, but also chemical transformations in the atmosphere.

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Compelling satellite images of reductions in air pollutants, first in Asia, then in Europe and North America, as governments enforced quarantine and social-distancing policies, have sparked widespread suggestions that the COVID-19 pandemic has led to cleaner air. This has propelled efforts to measure and analyze changes to air quality (defined here as the abundance of gases and particles harmful to human health), and a rush to publish scientific studies characterizing the links between the pandemic and air pollution[e.g., 1-4]. (For a continually-updated list of papers, see ref. 5) Much of this discussion, both in media reports and in the scientific literature, has neglected the central role of chemical reactions and transformations in dictating the abundance of harmful pollutants in the atmosphere, or has suggested that the role of this chemistry is unexpected. However, atmospheric chemical reactions are essential links between emissions and atmospheric composition. Because these linkages can be highly nonlinear, atmospheric chemistry complicates how pandemic-induced emission changes have and will continue to impact air quality; overlooking this chemistry undermines public understanding of air pollution, and risks erroneous decision-making.

Air pollution: more than just NO_x emissions

The COVID-19 pandemic has undoubtedly altered emissions, as, for example, people spend more time in their homes and less time in transit[6]. Less travel (passenger vehicles, public transit, aircraft) reduces emissions of nitrogen oxides (NO_x = NO + NO_2), a major combustion byproduct. Pervasive declines in atmospheric NO_2, a pollutant associated with adverse respiratory effects, through the Spring of 2020 exemplify the effect of these lowered emissions. NO_2 is easily observed from space and is concentrated in urban regions (due to vehicle emissions and a short chemical lifetime), thus, satellite images have provided clear evidence of declines in populated regions in recent months that have spurred commentary on improving air quality[1,2]. Reductions have been

particularly stark in regions dominated by diesel vehicles (which are higher NO_x emitters than their gasoline counterparts[7]). While the ease with which satellite images of NO_2 are generated has led many to focus on NO_x emissions changes, attributing this decline to COVID-19 is complicated by a number of factors. For example, meteorology and emissions are seasonally variant, generally leading to a decline in NO_2 from winter to spring in the Northern Hemisphere[8]. Furthermore, air quality regulations (e.g. the Clean Air Act in the United States) in North America, Europe, and, more recently China, and resulting reductions of emissions from point and mobile sources, are responsible for long-term declines in NO_x[e.g.,9,10]. As a result, in many regions of the world, NO_2 itself is no longer a pollutant of leading concern (e.g., in 2019 the entirety of the United States was in compliance with the air quality standards for NO_2[11]). Thus, any COVID-19-driven decline must be disentangled from this pre-existing trajectory, as well as from meteorologically-driven variability[e.g.,12,13].

While the decline in NO_2 undoubtedly mitigates the health burden associated with this pollutant, it is merely one air pollutant of many; human activities emit a wide range of gases and particles into the atmosphere. Though emissions from passenger vehicles and aviation have undeniably dropped during the pandemic, emissions from many other sectors (e.g. freight trucking, power generation, agriculture) are largely unaffected by COVID-19, as of course are emissions from natural sources (e.g. plants, wildfires, dust, volcanoes). Thus the emissions of pollutants other than NO_x – such as sulfur dioxide (SO_2), ammonia (NH_3), and various volatile organic compounds (VOCs) – are likely to exhibit changes that are quite different from what has been observed for NO_2, and these differences are likely to vary from location to location. We might even anticipate an increase in certain emissions, for example of volatile chemical products[14] from increased household and workplace cleaning. Moreover, these direct emissions are considered "primary pollutants", whereas the preponderance of pollutants that are deleterious to human health are "secondary" – that is, resulting from chemical processing in the atmosphere. These include ozone (O_3), and the majority of $PM_{2.5}$ (particulate matter less than 2.5 μm in diameter), the leading air pollutants of concern for human health, exposure to which has been estimated to be responsible for over 8 million premature deaths per year[15]. Therefore, to fully assess the global air quality consequences of COVID-19, we must investigate the impact of changes in primary pollutant emissions on these secondary chemical reactions.

Atmospheric chemical reactions and secondary pollutants

The role of atmospheric chemical reactions in the formation of air pollutants was first identified by Haagen-Smit[16,17]. In a series of laboratory experiments aimed at reproducing "Los Angeles smog", it was shown that the noxious components of smog included ozone and aerosol particles, formed when a mix of VOCs and NO_x (both emitted from vehicles, as well as from other sources) are exposed to sunlight. In the decades since, atmospheric chemists have worked to unravel the underlying chemistry of ozone and aerosol formation, both in polluted urban regions where they are harmful to human health, and in the global atmosphere where they impact climate.

Shown in Figure 1 is an overview of our understanding of this chemistry. Atmospheric photooxidation is initiated by a handful of strong oxidants (most importantly the hydroxyl radical, OH) that can react with a wide range of species emitted into the atmosphere. This includes inorganic species (e.g., NO_x, SO_2, CO) as well as organic ones, emitted into the atmosphere from

both anthropogenic sources and natural ones. The products and byproducts of these oxidation reactions depend not only on the compound being oxidized but also on the concentrations of other species that may affect this oxidation chemistry. Most important is NO_x, which controls the fate of peroxy radical intermediates (HO_2 and RO_2, formed as intermediates in the oxidation of VOCs and other species). Under relatively "clean" (low-NO) conditions, peroxy radicals will react with other peroxy radicals, or (in the case of RO_2) isomerize. But under polluted urban conditions, they will react with NO; this forms NO_2, which rapidly photolyzes in daytime to produce ozone.

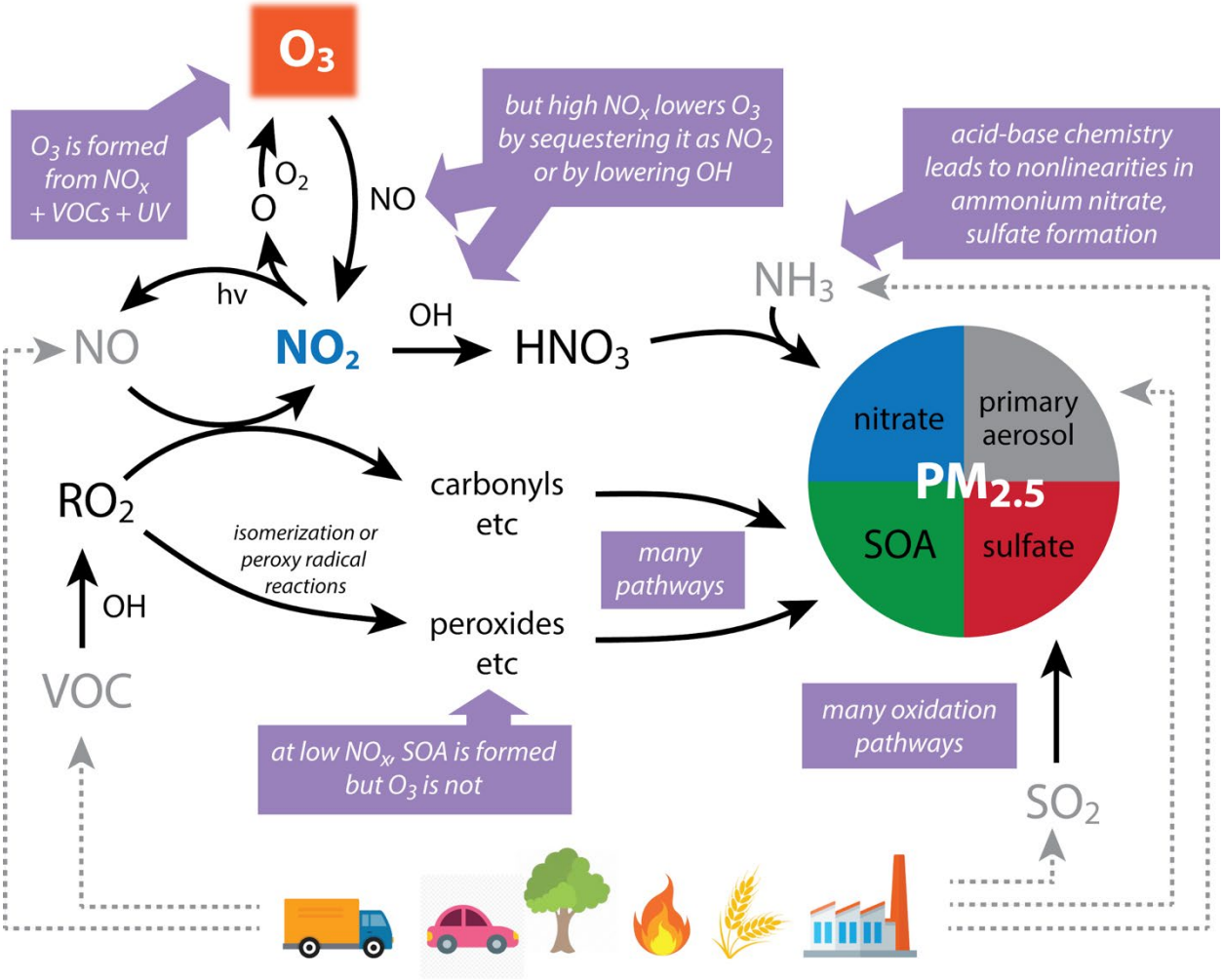

Figure 1. Simplified overview of the atmospheric chemistry of ozone and $PM_{2.5}$ formation, highlighting key nonlinearities and uncertainties. Primary emissions are denoted by dashed grey arrows; secondary chemical reactions are denoted by black arrows.

The dependence of ozone production on VOC and NO_x concentrations is complex and nonlinear. Under conditions in which VOC levels are high but NO_x levels are low, the chemistry is "NO_x limited", where more NO_x means more ozone. But at higher NO_x, the case in many polluted cities worldwide, the system can become "NO_x saturated", with no further increase in ozone production

with more NO_x. In fact, the opposite occurs: the additional NO_x serves as a sink for OH radicals, slowing down VOC oxidation and suppressing ozone production. Moreover, NO_x can sequester O_3 in temporary reservoirs such as NO_2 and N_2O_5. This chemistry has important implications for the relationship between emissions and air quality, since under these conditions, lower NO_x emissions can actually lead to *higher* ozone levels. This causes the well-documented "weekend effect", with ozone going up on weekends due to lower NO_x levels from reduced traffic. Thus, the observation that ozone in polluted cities is not dropping as fast as other pollutants – or is even increasing – during the pandemic is unsurprising, as it is a direct consequence of chemistry known since at least the late 1980s[18,19]. But the actual magnitude (and even sign) of the change in ozone at a given location is not obvious, as it depends critically on a number of local factors other than NO_x level, such as the amount and reactivity of the VOCs, oxidant levels, as well as meteorology; understanding how these conditions regulate the response of ozone to emission changes is central to interpreting COVID-19's impact on air quality.

The chemistry of particulate matter formation is even more complex and challenging to disentangle. Some fraction of $PM_{2.5}$ is primary, emitted directly from combustion and other sources; when such particles dominate, changes to primary PM may dominate the air quality response to COVID-19. However, in much of the world, $PM_{2.5}$ is largely secondary in nature, produced when gas-phase species react to form products of low enough volatility to condense into the particle phase. Key classes of secondary PM include sulfates (formed from SO_2 oxidation), nitrates (formed from NO_2 oxidation), and secondary organic aerosol (SOA, formed from VOC oxidation). PM levels are thus a strong function of the emissions of these precursors, which again are each affected differently by COVID-19 policies. The chemical transformations involved in each of these types of secondary PM add additional complexity, and are currently the subject of intense study. SO_2 oxidation to H_2SO_4 can occur via a number of pathways, which are still being elucidated[20]. The oxidation of NO_2 to form HNO_3 is well understood, but nitrate partitioning to the particle phase is driven by acid-base chemistry (typically involving NH_3), and so depends on factors such as temperature, relative humidity, and particle pH[21,22]. SOA is more complex still, being formed from scores of precursor VOCs, each of which react via numerous pathways to form a complex mixture of hundreds or thousands of reaction products[23]. SOA formation is thus strongly dependent on the ambient VOC mixture as well as on reaction conditions, both of which are likely to have been affected during the pandemic. For example, reductions in NO_x may lead to increased production of SOA, potentially offsetting changes resulting from decreased VOC emissions[24]; however, changes in oxidant levels also need to be taken into account[25]. Changes in chemical regime may also impact the volatility of the VOC oxidation products, potentially altering the prevalence of new particle formation[26]. Finally, all of these components of PM – secondary nitrate, sulfate, and organics – can interact and undergo further reactions in the condensed phase, altering the volatility and atmospheric lifetime of the PM in ways that depend on the detailed composition. Because of the chemical complexity of the system, these dependencies are nonlinear and uncertain, and are a major focus of modern atmospheric chemistry.

Opportunities for improved atmospheric chemical understanding

Decreases in emissions of air pollutants (e.g., NO_x, SO_2, VOCs) are critical for achieving improved air quality worldwide. However, because of the above interdependencies and nonlinearities in chemistry – many of which remain poorly understood – the response of secondary pollutants (namely O_3 and $PM_{2.5}$) to COVID-19-induced emissions changes is complex and uncertain. While reports of concentration changes for a small handful of pollutants may be a first step in improving our understanding of these linkages, they in themselves provide little insight into this chemistry and its consequent effects on air quality.

At the same time, analyses of the changes in atmospheric composition over the last few months, and in the months to come with easing (and possible re-tightening) of COVID-19-based restrictions, will provide new insight into the detailed chemistry linking emissions and secondary air pollution[4,27,28], and moreover into what policy interventions might be most efficient for improving future air quality. Such analyses are not trivial, since it can be extremely challenging to derive process-level understanding and establish causation from concentration measurements. In the past, such challenges have been addressed by examining responses of secondary pollutants to changes in conditions and emissions; examples include the weekday-weekend effect, temperature-driven variability, and the decades-long decline in emissions due to various control policies. The COVID-induced changes in anthropogenic emissions add a powerful new lens for such analyses, since the magnitude and rate of the present changes are arguably the largest ever seen in modern atmospheric chemistry.

Given the complexity of the atmospheric chemical system, new insight into the reactions governing secondary pollutant formation will require data not just from routine air quality measurements and satellite measurements, but also from advanced research-grade instrumentation, to provide measurements of individual organic species and PM composition, as well as from state-of-the-art chemical-transport models, to evaluate the consistency of these measurements with our understanding. Such studies, tracking COVID-19-related changes to emitted compounds, secondary species, and pollutant levels, will provide new information on several fundamental components of the atmospheric chemical system:

- *Key emissions*. What is the influence of specific chemical compounds or classes on local O_3 and PM formation? What do the effects of differential changes to key precursor species (VOCs/NOx in the case of O_3, $SO_2/NO_x/NH_3$/VOCs in the case of PM) tell us about the underlying chemistry?
- *Chemical regime*. How do emissions changes influence oxidant levels, peroxy radicals (RO_2 and HO_2), and local chemical regimes (e.g., NO_x-limited vs. NO_x-saturated conditions)? What effect do these have on secondary pollutants?
- *PM chemistry and impacts*. How have number concentrations, mass concentrations, and chemical composition of PM changed? Do such changes have an impact on the toxicity or cloud-forming potential of the PM?
- *Global atmosphere*. Are changes to atmospheric composition limited to urban/polluted regions, or do they extend to more remote/pristine ones as well?

Such studies, especially when carried out in multiple regions across the globe, can serve to directly inform the development of future air quality policies. In particular, the rapid and large changes to pollutant emissions owing to COVID-19-related changes provide a glimpse into a future of

intentionally lowered emissions. An improved understanding of how specific emissions sectors (passenger vehicles, air traffic, industry, etc.) influence the formation of secondary pollutants will provide insight into which potential interventions (e.g., electrification of the vehicle fleet, decarbonization of the electricity grid) will be most effective at mitigating air pollution and climate change in the future.

The COVID-19 perturbation to air quality is on-going and dynamic, as regions undergo tightening and loosening of restrictions on human mobility. In the fullness of time, careful analysis of the resulting perturbations to emissions and atmospheric composition may yield vital new insights into how chemistry controls air quality, on both the local and global scales.

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