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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 transit⁶. Less travel (passenger vehicles, public transit, aircraft) reduces emissions of nitrogen oxides (NO_x = NO + NO₂), a major combustion byproduct. Pervasive declines in atmospheric NO₂, a pollutant associated with adverse respiratory effects, through the Spring of 2020 exemplify the effect of these lowered emissions. NO₂ 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

42 particularly stark in regions dominated by diesel vehicles (which are higher NO_x emitters than their
43 gasoline counterparts⁷). While the ease with which satellite images of NO₂ are generated has led
44 many to focus on NO_x emissions changes, attributing this decline to COVID-19 is complicated by
45 a number of factors. For example, meteorology and emissions are seasonally variant, generally
46 leading to a decline in NO₂ from winter to spring in the Northern Hemisphere⁸. Furthermore, air
47 quality regulations (e.g. the Clean Air Act in the United States) in North America, Europe, and,
48 more recently China, and resulting reductions of emissions from point and mobile sources, are
49 responsible for long-term declines in NO_x^{e.g.,9,10}. As a result, in many regions of the world, NO₂
50 itself is no longer a pollutant of leading concern (e.g., in 2019 the entirety of the United States was
51 in compliance with the air quality standards for NO₂¹¹). Thus, any COVID-19-driven decline must
52 be disentangled from this pre-existing trajectory, as well as from meteorologically-driven
53 variability^{e.g.,12,13}.

54 While the decline in NO₂ undoubtedly mitigates the health burden associated with this pollutant,
55 it is merely one air pollutant of many; human activities emit a wide range of gases and particles
56 into the atmosphere. Though emissions from passenger vehicles and aviation have undeniably
57 dropped during the pandemic, emissions from many other sectors (e.g. freight trucking, power
58 generation, agriculture) are largely unaffected by COVID-19, as of course are emissions from
59 natural sources (e.g. plants, wildfires, dust, volcanoes). Thus the emissions of pollutants other than
60 NO_x – such as sulfur dioxide (SO₂), ammonia (NH₃), and various volatile organic compounds
61 (VOCs) – are likely to exhibit changes that are quite different from what has been observed for
62 NO₂, and these differences are likely to vary from location to location. We might even anticipate
63 an increase in certain emissions, for example of volatile chemical products¹⁴ from increased
64 household and workplace cleaning. Moreover, these direct emissions are considered “primary
65 pollutants”, whereas the preponderance of pollutants that are deleterious to human health are
66 “secondary” – that is, resulting from chemical processing in the atmosphere. These include ozone
67 (O₃), and the majority of PM_{2.5} (particulate matter less than 2.5 μm in diameter), the leading air
68 pollutants of concern for human health, exposure to which has been estimated to be responsible
69 for over 8 million premature deaths per year¹⁵. Therefore, to fully assess the global air quality
70 consequences of COVID-19, we must investigate the impact of changes in primary pollutant
71 emissions on these secondary chemical reactions.

72

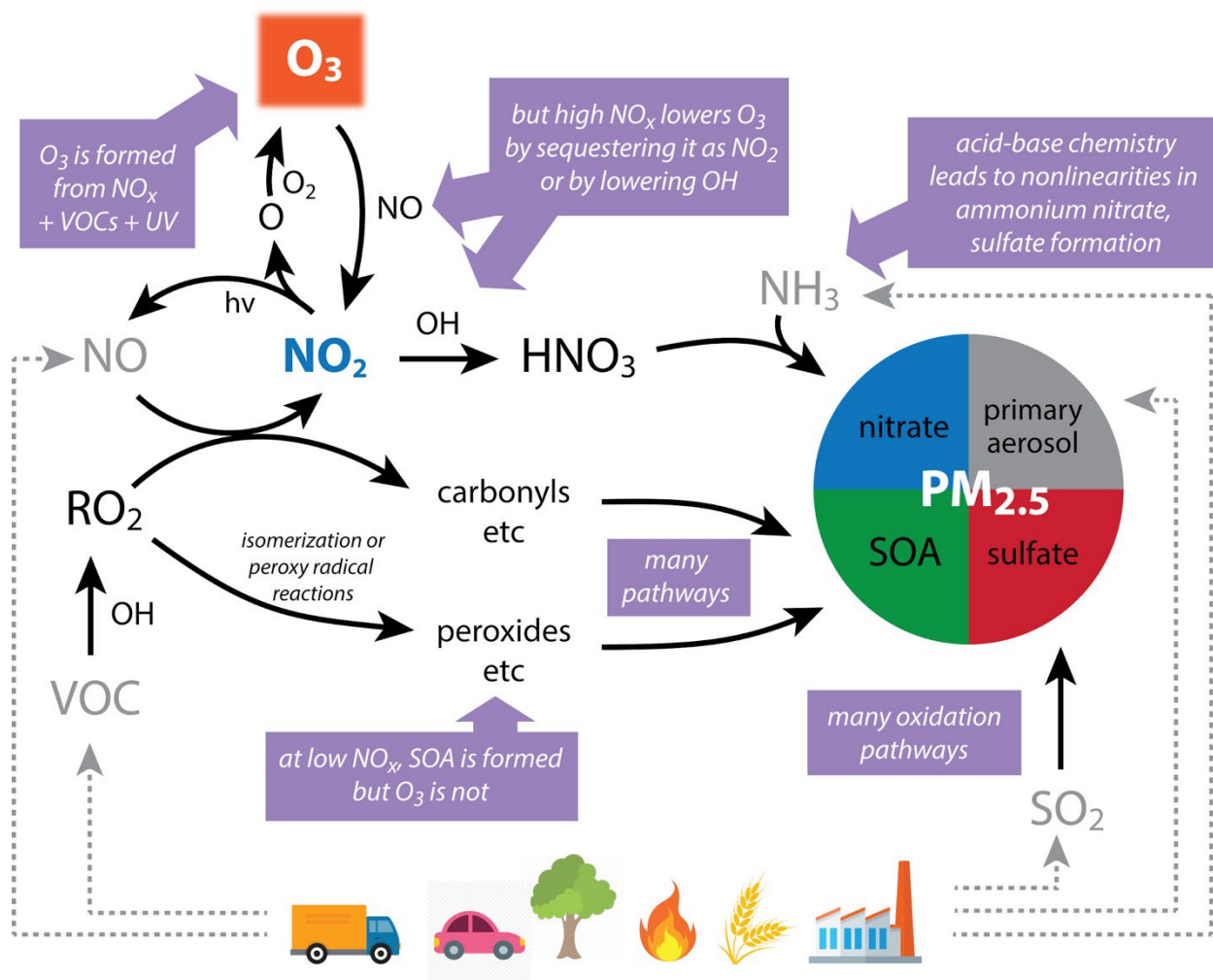
73 *Atmospheric chemical reactions and secondary pollutants*

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

81 Shown in Figure 1 is an overview of our understanding of this chemistry. Atmospheric
82 photooxidation is initiated by a handful of strong oxidants (most importantly the hydroxyl radical,
83 OH) that can react with a wide range of species emitted into the atmosphere. This includes
84 inorganic species (e.g., NO_x, SO₂, CO) as well as organic ones, emitted into the atmosphere from

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

92



93 **Figure 1.** Simplified overview of the atmospheric chemistry of ozone and $\text{PM}_{2.5}$ formation, highlighting
 94 key nonlinearities and uncertainties. Primary emissions are denoted by dashed grey arrows; secondary
 95 chemical reactions are denoted by black arrows.

96

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

101 with more NO_x. In fact, the opposite occurs: the additional NO_x serves as a sink for OH radicals,
102 slowing down VOC oxidation and suppressing ozone production. Moreover, NO_x can sequester
103 O₃ in temporary reservoirs such as NO₂ and N₂O₅. This chemistry has important implications for
104 the relationship between emissions and air quality, since under these conditions, lower NO_x
105 emissions can actually lead to *higher* ozone levels. This causes the well-documented “weekend
106 effect”, with ozone going up on weekends due to lower NO_x levels from reduced traffic. Thus, the
107 observation that ozone in polluted cities is not dropping as fast as other pollutants – or is even
108 increasing – during the pandemic is unsurprising, as it is a direct consequence of chemistry known
109 since at least the late 1980s^{18,19}. But the actual magnitude (and even sign) of the change in ozone
110 at a given location is not obvious, as it depends critically on a number of local factors other than
111 NO_x level, such as the amount and reactivity of the VOCs, oxidant levels, as well as meteorology;
112 understanding how these conditions regulate the response of ozone to emission changes is central
113 to interpreting COVID-19’s impact on air quality.

114 The chemistry of particulate matter formation is even more complex and challenging to
115 disentangle. Some fraction of PM_{2.5} is primary, emitted directly from combustion and other
116 sources; when such particles dominate, changes to primary PM may dominate the air quality
117 response to COVID-19. However, in much of the world, PM_{2.5} is largely secondary in nature,
118 produced when gas-phase species react to form products of low enough volatility to condense into
119 the particle phase. Key classes of secondary PM include sulfates (formed from SO₂ oxidation),
120 nitrates (formed from NO₂ oxidation), and secondary organic aerosol (SOA, formed from VOC
121 oxidation). PM levels are thus a strong function of the emissions of these precursors, which again
122 are each affected differently by COVID-19 policies. The chemical transformations involved in
123 each of these types of secondary PM add additional complexity, and are currently the subject of
124 intense study. SO₂ oxidation to H₂SO₄ can occur via a number of pathways, which are still being
125 elucidated²⁰. The oxidation of NO₂ to form HNO₃ is well understood, but nitrate partitioning to
126 the particle phase is driven by acid-base chemistry (typically involving NH₃), and so depends on
127 factors such as temperature, relative humidity, and particle pH^{21,22}. SOA is more complex still,
128 being formed from scores of precursor VOCs, each of which react via numerous pathways to form
129 a complex mixture of hundreds or thousands of reaction products²³. SOA formation is thus strongly
130 dependent on the ambient VOC mixture as well as on reaction conditions, both of which are likely
131 to have been affected during the pandemic. For example, reductions in NO_x may lead to increased
132 production of SOA, potentially offsetting changes resulting from decreased VOC emissions²⁴;
133 however, changes in oxidant levels also need to be taken into account²⁵. Changes in chemical
134 regime may also impact the volatility of the VOC oxidation products, potentially altering the
135 prevalence of new particle formation²⁶. Finally, all of these components of PM – secondary nitrate,
136 sulfate, and organics – can interact and undergo further reactions in the condensed phase, altering
137 the volatility and atmospheric lifetime of the PM in ways that depend on the detailed composition.
138 Because of the chemical complexity of the system, these dependencies are nonlinear and uncertain,
139 and are a major focus of modern atmospheric chemistry.

140

141 *Opportunities for improved atmospheric chemical understanding*

142 Decreases in emissions of air pollutants (e.g., NO_x, SO₂, VOCs) are critical for achieving improved
143 air quality worldwide. However, because of the above interdependencies and nonlinearities in
144 chemistry – many of which remain poorly understood – the response of secondary pollutants
145 (namely O₃ and PM_{2.5}) to COVID-19-induced emissions changes is complex and uncertain. While
146 reports of concentration changes for a small handful of pollutants may be a first step in improving
147 our understanding of these linkages, they in themselves provide little insight into this chemistry
148 and its consequent effects on air quality.

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

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

169 - *Key emissions*. What is the influence of specific chemical compounds or classes on local O₃ and
170 PM formation? What do the effects of differential changes to key precursor species (VOCs/NO_x
171 in the case of O₃, SO₂/NO_x/NH₃/VOCs in the case of PM) tell us about the underlying chemistry?

172 - *Chemical regime*. How do emissions changes influence oxidant levels, peroxy radicals (RO₂ and
173 HO₂), and local chemical regimes (e.g., NO_x-limited vs. NO_x-saturated conditions)? What effect
174 do these have on secondary pollutants?

175 - *PM chemistry and impacts*. How have number concentrations, mass concentrations, and chemical
176 composition of PM changed? Do such changes have an impact on the toxicity or cloud-forming
177 potential of the PM?

178 - *Global atmosphere*. Are changes to atmospheric composition limited to urban/polluted regions,
179 or do they extend to more remote/pristine ones as well?

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

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

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

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