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# Unintended Consequences of Air Cleaning Chemistry

Douglas B. Collins
*Bucknell University*, dbc007@bucknell.edu

Delphine K. Farmer
*Colorado State University*

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Perspective

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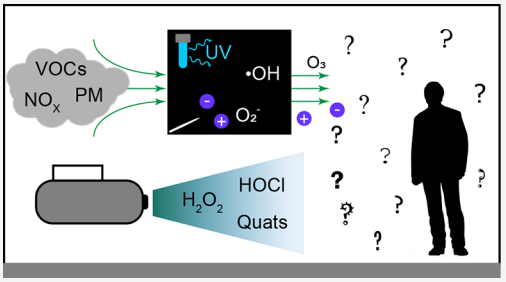
**ABSTRACT:** Amplified interest in maintaining clean indoor air associated with the airborne transmission risks of SARS-CoV-2 have led to an expansion in the market for commercially available air cleaning systems. While the optimal way to mitigate indoor air pollutants or contaminants is to control (remove) the source, air cleaners are a tool for use when absolute source control is not possible. Interventions for indoor air quality management include physical removal of pollutants through ventilation or collection on filters and sorbent materials, along with chemically reactive processes that transform pollutants or seek to deactivate biological entities. This perspective intends to highlight the perhaps unintended consequences of various air cleaning approaches via indoor air chemistry. Introduction of new chemical agents or reactive processes can initiate complex chemistry that results in the release of reactive intermediates and/or byproducts into the indoor environment. Since air cleaning systems are often continuously running to maximize their effectiveness and most people spend a vast majority of their time indoors, human exposure to both primary and secondary products from air cleaners may represent significant exposure risk. This *Perspective* highlights the need for further study of chemically reactive air cleaning and disinfection methods before broader adoption.




**KEYWORDS:** *air cleaning, indoor air, secondary chemistry, hypochlorous acid, plasma air cleaning, bipolar ionization, photocatalytic oxidation, bioaerosol*



## INTRODUCTION

The COVID-19 pandemic has amplified interest in indoor environmental quality. Since the SARS-CoV-2 virus can be transmitted through airborne pathways,[1,2] gathering places like schools, factories, and other buildings need to be made safe for occupants. The urgent need to mitigate airborne disease transmission has led to growth in commercial air cleaning technologies, many of which rely on oxidation chemistry, ion−molecule reactions, or airborne release of disinfectants. Expanded use of existing air cleaning methods and the implementation of emerging technologies raise important questions of both efficacy and safety. The air cleaning industry is largely unregulated, with few standards to provide performance and safety benchmarks. However, existing studies of the technology behind many air cleaners[3,4] along with modern understanding of atmospheric chemistry can provide insight into unintended chemical consequences of air cleaner use. As an example, outdoor air quality is influenced by direct ("primary") emissions of pollutants along with the "secondary" products of chemical reactions between pollutants after their release into the environment. While studies on the byproducts of some air cleaning technologies exist,[5−8] less attention has been paid to the broader chemical side effects of air cleaners on indoor chemistry.[3] The field of indoor air quality management is ripe for development of new materials and technologies, but a firm understanding of their fundamental chemistry and broader impact on air quality is needed.

Indoor air quality is influenced by the contents and activities within a building, along with the properties of the building itself and its environmental setting.[9,10] Good air quality is typically characterized by the lack of pollutants like airborne particles and harmful trace gases. The concentration of any component of indoor air is set by a balance between the rates of production ("sources") and removal ("sinks"). Primary sources of trace gases and particulate matter (PM) include cooking, cleaning, building materials, and commercial products. Secondary chemistry can transform primary pollutants, especially when oxidant levels are elevated. Whereas much of outdoor atmospheric chemistry is driven by photo-oxidation processes, indoor environments may be subject to lower light (except near windows in direct sunlight)[11,12] and a high surface area-to-volume ratio.[9,10,13] Thus, the development of organic and aqueous films on indoor surfaces strongly influence indoor air as they mediate multiphase chemical reactions and equilibrium partitioning of semivolatile components.[13−16] Indoor gas-phase chemistry occurs with ozone ($O_3$), hydroxyl (OH) radicals, and other oxidants. $O_3$ is mainly introduced

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into the indoor environment from outdoor air or commercial products,[17−19] while OH radicals can be chemically produced indoors.[18,20,21] Secondary oxidation chemistry removes some compounds (e.g., alkenes), but produces others (e.g., aldehydes, peroxides), and can lead to an increased mass concentration of particulate matter and increased number concentration of ultrafine aerosol.[17,19,22−24] The array of trace gas sources coupled to the relative time scales for secondary reaction versus exchange with outdoor air mean that indoor air typically has higher concentrations of semivolatile and volatile organic compounds (SVOCs and VOCs) but lower average concentrations of oxidants compared to outdoors.[9,10,18] PM concentrations are variable. With weak indoor sources, the depositional sink to surfaces leads to relatively low particle levels, but strong sources like cooking can dramatically increase PM for short periods of time.[25] While human breath is a source of biological PM of particular relevance for transmission of some diseases,[1,26] human lungs are also efficient sinks of particles.[27] Overall, humans take in many more particles than they exhale.

The optimal way to maintain good air quality is to limit pollutant sources in the first place. This axiom is true for pollutants of nearly all kinds and applies to both indoor and outdoor environments. However, once contaminants are introduced to a building, ventilation and filtration of air are well-established, effective strategies for mitigation.[3,28−30] Using chemistry (including ion generation) to clean indoor air leads to the introduction of new chemically reactive material to the building and initiates an unintended cascade of reactions.[3,17,19,23,31−33] Hypochlorous acid (HOCl), a potent oxidant that can be used as a nonspecific biocide, represents a key example in which the chemical side-effects of cleaning agent use are strong, but are often underestimated. Keeping indoor environments healthy requires a multipronged approach, but must avoid the use of air cleaning techniques that create unintended chemical consequences.

## AIR CLEANING AND DISINFECTION

Several approaches to air cleaning that have gained recent traction include: (1) removing or degrading gaseous pollutants like VOCs and $NO_x$ (= NO + $NO_2$), (2) removing airborne particulate matter (regardless of composition), and (3) targeting biological PM for removal or disinfection. Some approaches assert an ability to solve multiple issues at the same time. Overall, there are considerable chemical side effects to many air cleaning approaches (Figure 1). One of the challenges with evaluating air cleaning technologies is the combination of variability in design of devices with similar operating principles and a general lack of studies that have investigated most types of devices in real-world deployments. The combined variability across devices and studies results in a poor understanding of potential effects on indoor air quality.

**Removing and Degrading Gases.** Ventilation, defined as the deliberate introduction of outdoor air to the indoor environment with coincident exhaust of indoor air, is one method used to reduce concentrations of VOCs and reactive trace gases that have indoor sources and low outdoor concentrations. However, ventilation must be maintained constantly for best effectiveness, as pollutant sources may remain active and reservoirs of semivolatile components develop on indoor surfaces over time, which enable elevated indoor concentrations to be re-established once enhanced ventilation ceases.[14,15] Targeted extraction of air near localized

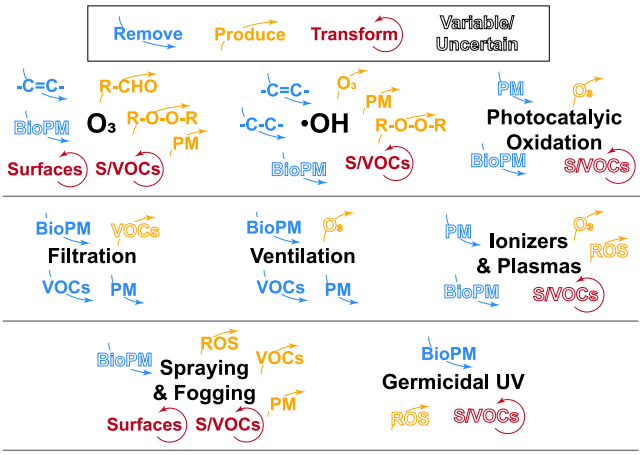


**Figure 1.** Qualitative summary of chemical effects of select air cleaning and disinfection technologies. BioPM refers to biological PM, S/VOC refers to semivolatile and volatile organic compounds, —C═C— refers to alkenes, —C—C— refers to alkanes, R-CHO refers to aldehydes, and R—O—O—R refers to peroxides. All other abbreviations are defined in the text. Icons with outlined lettering denote effects that are not well studied, highly variable across studies, variable with device operational settings, or remain scientifically uncertain. The summary is not quantitative, and thus does not describe a scale of magnitude for each process.

sources of pollutants (e.g., cooking, combustion) is one notable ventilation approach used in many residential and commercial buildings.[34]

Trapping trace gases on solid sorbent materials can be an effective way to reduce their concentrations.[4,28,35,36] Sorbents that collect VOCs and other trace gases through adsorption, absorption, or chemisorption,[35] will eventually saturate or may become fouled,[37] requiring replacement at regular intervals. Continued advancements in sorbent technology should be aimed at increasing capture capacity, reducing fouling, and optimizing regeneration of the sorbent material, while bearing both organic (VOC) and inorganic (e.g., $NO_x$, HONO, $O_3$) trace gases in mind.

Ventilation can introduce outdoor pollutants. For example, $O_3$ concentrations may be typically low indoors (ca. 5 ppb) because of removal by rapid gas-phase and multiphase oxidation reactions,[9,13,38] but $O_3$ formed outdoors can be introduced to indoor air through ventilation. Introducing $O_3$ scrubbing systems or sorptive materials to the building[36] could mitigate the hazard potential while retaining benefits of reducing the concentrations of gases that have indoor sources (and, thus, higher mixing ratios in indoor air) with ventilation. Indeed, introducing $O_3$ to indoor air may reduce the mixing ratios of certain reactive VOCs, but many gaseous and particulate oxidation products with known hazards to human health would be formed in the process.[17,39]

Some emerging air treatments involve the deliberate removal of gases from indoor air via chemical transformation to more oxidized compounds.[4,40,41] In concept, chemical transformation of air pollutants is often intended to yield $CO_2$ ("mineralization") and $H_2O$.[42] In practice, production and release of reactive species by ionizers, hydroxyl radical generators, photocatalytic oxidation devices, plasma devices, or $O_3$ generators result in the formation of oxidized VOCs, generation of PM via secondary chemistry, and/or collateral damage to indoor materials.[4,17,32,39,40,43] At present, the California Air Resources Board (CARB) enforces a regulation


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that limits the production of $O_3$ in air cleaning systems to less than 50 ppb. However, studies indicate acceptable concentrations for human exposure less than 10 ppb,[44] and the American Society for Heating, Refrigeration, and Air Conditioning Engineers (ASHRAE) Standard 62.1 2019 "prohibits the use of ozone generators" and require that "air cleaners meet UL 2998" which sets a 5 ppb limit for $O_3$.[45] While $O_3$ production by air cleaners has been a major focus of regulators and the air cleaning industry, the use and/or release of other oxidants (e.g., OH radicals) into the indoor environment introduce their own concerns.[3,8,21] Production of oxygenated VOCs and ultrafine particles resulting from VOC oxidation[8,18,21,32] increase the risk for negative health effects.[46,47] For example, photocatalytic oxidation devices, in which ultraviolet or visible light is shone on catalytic surfaces to form oxidants that then react with VOCs, are well established to produce an array of unintended byproducts depending on the composition of air flowing through the device and its design, including aldehydes, phosgene, and chlorinated VOCs.[7,48−50] Overall, substantial concerns remain regarding exposure to oxidants generated, and byproducts formed, by air cleaning devices that are intended to remove trace gases through chemical transformation. Caution is warranted before more concrete, peer-reviewed studies of their safety are completed.

**Removing Particles Regardless of Composition.** High efficiency particulate air (HEPA) filters are useful tools to reduce indoor PM.[28] Filtration has relatively minor effects on chemical processes in indoor air: as PM is removed it can no longer act as a condensation sink for semivolatile compounds,[51] and buildup of material on filter media can slowly re-emit semivolatiles, and/or react with oxidants to produce byproducts.[39,52,53] Ventilation and localized air extraction are also highly effective measures for PM mitigation[54] with relatively few chemical consequences, as discussed above. Ionization devices seek to remove particles by reacting them with ions, thereby charging the particles to enhance coagulation and/or deposition rates.[4,41] The efficacy of ionizers for PM removal in realistic environments is poorly understood; a recent assessment of one commercial bipolar ionizer indicated minimal PM removal.[31] Air cleaning devices that rely on ion-mediated processes, of which there are multiple variations, pose important potential chemical consequences.[41] Gas-phase ions react with VOCs and other trace gases to form an array of oxidized products,[3,4] mimicking the complex chemistry that is well-understood in atmospheric chemistry to induce new particle formation.[55,56] Ionization systems using nonthermal plasmas can produce $NO_x$ and $O_3$, so postplasma treatment of air in the device outflow may be necessary.[57] Overall, further study of ion-mediated air cleaners is needed.

**Targeting Biological Particles.** A variety of chemical treatments that were designed for surface application are now being sprayed or fogged into indoor spaces, intended for *both* surface and air disinfection.[23,58] Chemical disinfectants implemented in fogging or spraying include strong oxidizers (e.g., hypochlorous acid,[59] peracetic acid,[60] hydrogen peroxide[61]), quaternary ammonium compounds,[58] and triethylene glycol vapor.[62] While it may seem obvious to focus mainly on the chemistry involving active ingredients, most disinfectant solutions are mixtures containing many "inactive" ingredients, each with a unique chemical fate and exposure risk after release into the environment.[23,63] While some disinfecting agents have been used on surfaces or in specialized environments, few have been rigorously assessed for toxicity due to repeated or extended *inhalation* exposure.[58] If fogged or sprayed chemical disinfectants are continuously dispersed or applied with the intention of reducing disease transmission risk while indoor spaces are occupied, substantial secondary chemistry can occur[23,61,64] and/or exposures outside the limits of current health risk assessments may be experienced.[58,65] Ultraviolet germicidal radiation (UVGI) systems[66] are widely used in healthcare settings, and are regarded as safe when individuals avoid direct UV exposure, but secondary chemistry could occur upon photolysis of UV-active VOCs under certain conditions. UV photolysis of acetone is thought to be a source of peroxy radicals[67] and the exposure of various VOCs to intense 254 nm light can produce a mixture of oxidized byproducts and newly formed particulate matter.[43] A wide variety of VOCs have appreciable photolysis quantum yields[68] at common UVGI wavelengths (UV−C; 100−290 nm), but careful selection of the UV wavelength and light intensity used in these devices may be able to mitigate unintended chemistry.

## DISTURBING THE BALANCE

The concentrations of many gaseous components in indoor air are dictated by equilibrium with a condensed phase reservoir on indoor surfaces.[14,15,69] Any introduction of new air constituents or removal of existing constituents will cause compound-specific equilibria to respond.[70] Even the removal of particles onto filters or via electrostatic precipitation can induce subsequent multiphase chemistry.[4,39,52] In some cases where relatively high, steady-state concentrations of pollutants exist indoors, it may be in the best interest of air quality to perturb these equilibria with ventilation to reduce indoor human exposure, as in the case of nitrous acid (HONO).[14] The application of acidic or basic surface cleaning agents releases chemical species from surfaces to indoor air according to the pH-dependent equilibrium coefficient of each compound.[14,71] Similar chemistry would be expected when fogging acidic (HOCl) or alkaline (quaternary ammonium) disinfectants indoors. Air "cleansing" chemicals and any SVOCs present in their formulations that are introduced to indoor air will deposit or partition to surfaces.[23] Depending on partition coefficients, SVOCs could have removal time scales from days to decades with typical air change rates.[15,69,70] Even compounds that are considered to be quite volatile outdoors (e.g., monoterpenes) can partition to indoor surfaces.[14] Thus, avoiding the introduction of unnecessary chemical components to indoor environments is the safest practice.

## THE UNDERAPPRECIATED CHEMISTRY OF HOCL

HOCl fogging is an important case study of technology deployed in commercial and medical settings[59,72−74] without full consideration of the indoor chemical side effects. A substantial body of research exists on the reactivity and biochemistry of HOCl in the immune system, on the details of its reactivity with organic compounds, and on its proclivity to induce inflammation.[75−77] HOCl has a reacto-diffusive length of a few micrometers in biological systems,[76] and its biochemical activity is thus highly localized. Introduction of HOCl to biological environments that are not tailored to its in situ production and reactivity (e.g., within the membranes of neutrophils) can lead to inflammation.[75,77] The rapid and broad reactivity of HOCl with organic matter can limit its performance against pathogens in water and hard surface


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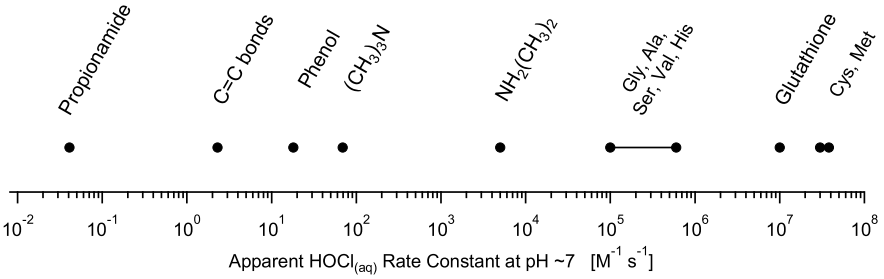


**Figure 2.** A comparison of the apparent rate constant of $HOCl_{(aq)}$ with a variety of chemicals that represent examples for a variety of functional groups. While gas-phase and multiphase reaction rate constants may differ, one can derive a sense for relative reactivity with different functional groups or chemical classes. Amino acids with reactive side chains are labeled with their three-letter abbreviations (Gly: glycine, Ala: alanine, Ser: serine, Val: valine, His: histidine, Cys: cysteine, Met: methionine).

disinfection, highlighting the formation of disinfection byproducts as a major concern.[78]

A variety of cleaning solutions contain HOCl, including but not limited to those made from sodium hypochlorite (chlorine bleach), sodium dichloroisocyanurate (NaDCC), or those produced via electrolysis of an aqueous sodium chloride solution. The formation of byproducts has been shown from the use of various HOCl-containing systems.[64,78,79] While several indoor air studies have investigated this chemistry using chlorine bleach,[33,64,80,81] since HOCl is the most reactive ingredient in sodium hypochlorite solutions and is responsible for most of the disinfecting action,[82] similar chemistry is likely to occur across various types of hypochlorite and HOCl-containing cleaning agents. Reaction rates of HOCl with various chemical functionalities have been investigated in the aqueous phase[83,84] and are depicted in Figure 2. While the rate constants of gas-phase or multiphase HOCl reactions may differ from aqueous reactions, it is important to highlight both the broad-spectrum reactivity and the wide range of reaction rates.[83,85] Use of hypochlorite bleach leads to the formation of volatile HOCl, $Cl_2$, chloramines, chloraldimines, and chlorocarbons, through homogeneous and multiphase reactions.[33,64,79,81] The direct impact of HOCl on respiratory health is not well-known, but HOCl forms in the respiratory tract upon $Cl_2$ inhalation,[86] so links may be drawn between these two "active chlorine" species. Studies involving cleaning professionals indicate that repeated exposure to hypochlorite bleach solutions can lead to degraded respiratory health,[58] suggesting that HOCl and/or its volatile byproducts lead to negative health effects.

Less recognized and perhaps more broadly impactful, however, is the impact of volatile HOCl on indoor chemistry. Liberation of HOCl to the gas phase can lead to the formation of OH and Cl radicals[33] that accelerate oxidative gas- and multiphase chemistry. The chemistry of HOCl within hypochlorite bleach vapors can lead to an increase in the indoor concentrations of key reactive species (e.g., $NO_2$, $O_3$,HONO, OH),[33,64,71,87] generate oxygenated and chlorinated VOCs,[33,64,79] chemically modify organic surface films,[64] and lead to the formation of secondary PM under fluorescent or solar illumination.[80] Releasing potent oxidizers indoors will amplify the oxidizing capacity of air and increase the quantities of oxidation products present. While some of the associated reaction products are known to be health hazards (e.g., $O_3$, $NO_2$, $CCl_3$, secondary PM), insufficient compound-specific toxicology or exposure data is available for many chemicals. Still, there is broad evidence for the negative health effects of poor indoor air quality based on the presence of similar chemical mixtures in air.[17,47,88] Hence, the use of oxidizing cleaning agents, especially those that are volatile (e.g., HOCl, $H_2O_2$), have important and wide-reaching chemical implications for indoor air quality, some of which have only recently been directly studied.

## AN OPPORTUNITY FOR HEALTHIER BUILDINGS

Taking steps to implement interventions for improved indoor air quality in this time of heightened awareness due to the COVID-19 pandemic will have a lasting impact. Improving scientific understanding of the chemistry of indoor environments represents a significant opportunity to guide the public to safe and effective indoor air quality solutions. Environmental scientists have, for many years, worked through case studies where the use of chemicals outpaced a full understanding of their safety, resulting in serious negative ecological and/or health outcomes (e.g., DDT, chlorofluorocarbons, perfluoroalkyl substances). Using the precautionary principle is prudent: unnecessary use of chemical products and reactive processes should be avoided until the broader environmental and health impacts of such interventions are understood. In the case of air cleaning technologies, decades of fundamental indoor and outdoor atmospheric chemistry knowledge provides a strong footing. The field lacks sufficient scientific information to arrive at a comprehensive, fully quantitative assessment of byproduct formation from many air cleaning technologies. This *Perspective* highlights some of the unknown aspects of air cleaning technologies and the potential for unintended chemical consequences. There is an urgent need to apply existing knowledge and perform specific chemistry studies associated with air cleaning technologies in realistic scenarios. Until then, the prolific use of chemical disinfectants and reactive processes for air cleaning warrants extreme caution.

## AUTHOR INFORMATION

### Corresponding Author

**Douglas B. Collins** − *Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837, United States;* orcid.org/0000-0002-6248-9644; Email: dbc007@bucknell.edu

### Author

**Delphine K. Farmer** − *Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, United States;* orcid.org/0000-0002-6470-9970

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.1c02582

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

### Biographies

Douglas B. Collins is an Assistant Professor of Chemistry at Bucknell University. His research involves the atmospheric chemistry of indoor and outdoor environments, especially pertaining to processes at chemically complex gas−solid and gas−liquid interfaces. He is also interested in new applications of mass spectrometry to environmental issues, connections between ecology and atmospheric chemistry, surface analysis, and ion mobility-mass spectrometry. Prof. Collins earned a B.A. in chemistry from Colgate University and a Ph.D. in atmospheric chemistry from the University of California, San Diego working with Prof. Kimberly A. Prather. He has held positions as Managing Director of the Center for Aerosol Impacts on Chemistry of the Environment and as a postdoctoral fellow with Prof. Jonathan P. D. Abbatt at the University of Toronto.

Delphine K. Farmer is an Associate Professor of Atmospheric Chemistry at Colorado State University. Dr. Farmer's research focuses on outdoor atmospheric and indoor chemistry with an emphasis on understanding the sources and sinks of reactive trace gases and particles and their effects on climate, ecosystems, and human health. Dr. Farmer earned an MS in Environmental Science, Policy and Management and a PhD in Chemistry from the University of California, Berkeley. Dr. Farmer received NOAA Climate and Global Change Postdoctoral Fellowship in 2007 and an Arnold and Mabel Beckman Young Investigator Award in 2013.

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