

INSIGHTS



PERSPECTIVES

ATMOSPHERIC CHEMISTRY

An indoor chemical cocktail

The chemistry that determines human exposure to indoor pollutants is incompletely understood

By Sasho Gligorovski¹ and Jonathan P. D. Abbatt²

In the past 50 years, many of the contaminants and chemical transformations that occur in outdoor waters, soils, and air have been elucidated. However, the chemistry of the indoor environment in which we live most of the time—up to 90% in some societies—is not nearly as well studied. Recent work has highlighted the wealth of chemical transformations that occur indoors. This chemistry is associated with 3 of the top 10 risk factors for negative health outcomes globally: household air pollution from solid fuels, tobacco smoking,

and ambient particulate matter pollution (1). Assessments of human exposure to indoor pollutants must take these reactive processes into consideration.

A few studies illustrate the nature of multiphase chemistry in the indoor environment. As Sleiman *et al.* have shown (2), a highly carcinogenic class of compounds—the tobacco-specific nitrosamines—forms via the reaction of gas-phase nitrous acid (HONO) with cigarette nicotine that is adsorbed onto indoor surfaces similar to those in a typical smoker's room. HONO is also produced indoors directly by other combustion sources such as gas stoves and by the gas-surface reactions of gaseous nitrogen oxides on walls, ceilings,

and carpets (3). Likewise, carcinogenic polycyclic aromatic hydrocarbons (PAHs) and their often more toxic oxidation products are mobile, existing both on the walls of most dwellings and in the air (4); PAHs arise from combustion sources such as smoking and inefficient cookstoves. This is a particularly important issue in developing countries, where the adverse health effects from cooking with solid fuels is a leading cause of disease (5). As another example, use of chlorine bleach to wash indoor surfaces promotes oxidizing conditions not just on the surfaces being washed but throughout the indoor space (6). Reactive chlorinated gases (such as HOCl and Cl₂) evaporate from the washed surface, can oxidize other surfaces in a room, and may be broken apart by ultraviolet (UV) light to form reactive radicals.

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Reactive chemicals in an indoor environment arise from cooking, cleaning, humans, sunlight, and outdoor pollution.

It is not only human activities such as cooking, smoking, and cleaning that affect the indoor environment. The mere presence of humans affects the oxidative ability of the air. Wisthaler and Weschler (6) have shown that human occupancy can dramatically affect ozone levels, such that concentrations of this oxidant dropped by half within 30 minutes when two people entered a test chamber similar in size to a typical indoor room. At the same time, the concentrations of various carbonyl compounds increased. The reactions are so fast that many chemically reactive oils on human skin may be transformed into more oxidized molecules on time scales of tens of minutes (7). Recent measurements in heavily occupied spaces such as classrooms illustrate the wealth of human emissions of not only naturally formed molecules (such as small organic acids) but also personal care products (such as siloxanes) (8, 9). A key uncertainty is the degree to which indoor environments are oxidizing. Outdoor light levels drive the production of radicals, such as hydroxyl (OH), which act as atmospheric cleansing agents. Without high levels of UV light indoors, what levels of OH will be present? Gómez Alvarez *et al.* have reported the detection of indoor OH radicals, formed from the sunlight-driven decomposition of nitrous acid (10); they observed OH concentrations similar to those that form outdoors.

These findings have placed emphasis on indoor radical chemistry. It remains unclear, however, whether light is necessarily involved, or whether dark sources of OH from the oxidation of gas-phase alkenes by ozone dominate instead. In particular, terpene oils, which are components of cleaning, fragrances, and cooking materials, are widely present indoors. Ozonolysis of such alkenes leads to the formation of highly reactive molecules, the Criegee intermediates. The latter sometimes decompose to form OH radicals but in other circumstances may react with a wide range of other indoor constituents. In 2017, Berndt *et al.* reported the direct mass spectrometric measurement of gas-phase Criegee intermediates (11); this work opened up the potential for measuring such species in indoor environments. Criegee intermediates may also form when indoor surfaces that are coated with chemically unsaturated skin cells and cooking oils are exposed to ozone. Although largely unstudied, such chemistry may form highly reactive and potentially harmful products, including peroxides and ozonides, on indoor surfaces (12).

The atmospheric chemistry field has undergone a dramatic transformation in its understanding of how volatile organic compounds (VOCs) are oxidized (13). Highly oxidized organic compounds arise via auto-oxidation mechanisms initiated by either ozone or radical attack. Reaction with a single oxidant molecule can form multiple oxygenated functional groups on an organic reactant within seconds, changing it from a volatile gas to a molecule that will condense to form secondary organic aerosol (SOA) particles (14). Given that levels of VOCs, such as terpenes, can be much higher indoors than outdoors, this pathway may be an important indoor aerosol formation mechanism. Because of very high levels of outdoor pollution, VOC concentrations in industrially developing areas such as China may be much higher than in European and North American homes.

The building science research community has long identified the importance of ventilation for the state of indoor environments. Open windows expose us to outdoor air, whereas well-sealed houses are subject to emissions from furnishings, building materials, chemical reactions, and people and their activities. Climate change (15) and outdoor air pollution are leading to efforts to better seal off indoor spaces, slowing down exchange of outdoor air. The purpose may be to improve air conditioning, build more energy-efficient homes, or prevent the inward migration of outdoor air pollution. As exposure to indoor environments increases, we need to know more about the chemical transformations in our living and working spaces, and the associated impacts on human health. ■

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NEUROSCIENCE

Toward an optically controlled brain

Noninvasive deep brain stimulation can be achieved by optical triggers

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Neurons can be modified with light-gated ion channels, which cause them to become excited upon illumination (1, 2). This discovery has given rise to the field of optogenetics, with impressive examples such as triggering the beat of a heart with light (3). There is, however, one technical limitation: Light-gated ion channels are typically stimulated with blue-green light, which is heavily scattered by tissue. Thus, deep brain stimulation, focused on small regions, is a major challenge. On page 679 of this issue, Chen *et al.* (4) use transgenic mice implanted with upconverting nanoparticles (NPs) to locally activate light-gated ion channels and modulate neuronal activity, even deep inside the brain. This method might eventually lead the way for clinical applications to optically control neuronal dysfunctions, such as Parkinson's disease or even paralysis.

The brain is a gigantic assembly of interconnected neurons. A neuron "fires" a nerve impulse when a sufficient amount of Na⁺ ions enter the cell through membrane-bound ion channels. Neuronal Na⁺ channels are unusual in that they open even more as Na⁺ ions pass through, rendering the inside of the cell increasingly positively charged (meaning that these channels are voltage-gated). Thus, a wave of positive charge spreads along the nerve fiber as a nerve impulse. Likewise, communication between

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