

New Directions: Ozone-initiated reaction products indoors may be more harmful than ozone itself[☆]

Epidemiological studies have found associations between ozone concentrations measured at outdoor monitoring stations and certain adverse health outcomes. As a recent example, Gent et al. (2003, *Journal of the American Medical Association* 290, 1859–1867) have observed an association between ozone levels and respiratory symptoms as well as the use of maintenance medication by 271 asthmatic children living in Connecticut and the Springfield area of Massachusetts. In another example, Gilliland et al. (2001, *Epidemiology* 12, 43–54) detected an association between short-term increases in ozone levels and increased absences among 4th grade students from 12 southern California communities during the period from January to June 1996. Although children may spend a significant amount of time outdoors, especially during periods when ozone levels are elevated, they spend a much larger fraction of their time indoors. I hypothesize that exposure to the products of ozone-initiated indoor chemistry is more directly responsible for the health effects observed in the cited epidemiological studies than is exposure to outdoor ozone itself.

During periods of elevated outdoor ozone concentrations even moderate air exchange across a building's envelope results in sufficient indoor ozone to drive oxidative chemistry (Weschler, 2000, *Indoor Air* 10, 269–288). Typically 5–10% of airborne organic compounds contain unsaturated carbon–carbon bonds (Brown et al., 1994, *Indoor Air* 4, 123–134) and many of these compounds react with ozone at rates fast enough to compete with air exchange rates. The percentage of unsaturated species is significantly increased by the use of cleaners and air fresheners containing terpenoids (Nazaroff and Weschler, 2004, *Atmospheric Environment* 38, 2841–2865). For each molecule of ozone consumed, roughly a molecule of the hydroxyl radical is produced (Atkinson and Arey, 2003,

Atmospheric Environment 37 (suppl. 2), 197–219). The hydroxyl radical reacts with saturated as well as unsaturated airborne organics at meaningful rates. Additionally, analogous to outdoor chemistry that occurs at night, ozone is anticipated to react with nitrogen dioxide in room air producing the nitrate radical (Weschler et al., 1992, *Environmental Science and Technology* 26, 179–184). At realistic indoor concentrations, the nitrate radical reacts with certain unsaturated organic compounds and polycyclic aromatic hydrocarbons (PAHs) at rates even faster than ozone and the hydroxyl radical (Nazaroff and Weschler, 2004). In addition to gas-phase reactions, ozone and ozone derived oxidants can also react with organic compounds on indoor surfaces. These processes do not have the same time constraints as gas phase processes, and, even when surface-bound organics are oxidized at slower rates than air-exchange, such reactions can significantly influence indoor air concentrations of oxidation products. For example, ozone initiated surface chemistry has been shown to produce formaldehyde and higher molecular weight aldehydes that subsequently are released from surfaces into the gas phase (Reiss et al., 1995, *Environmental Science and Technology* 29, 1906–1912; Morrison and Nazaroff, 2002, *Environmental Science and Technology* 36, 2185–2192).

At reduced air exchange rates, indoor ozone levels tend to be low in comparison to outdoor ozone levels. However, this does not mean that outdoor ozone had no effect on the indoor environment. The ozone concentration measured indoors during such occasions is the residual ozone concentration—the ozone that remains after most has been consumed by reactions with indoor surfaces and airborne species. (If ozone were non-reactive, its steady-state concentration would equal its outdoor concentration and low air exchange rates would simply lengthen the time required to reach steady state.) Ozone scavenging may generate products that add to the pollutant mix inhaled by building occupants.

The products of ozone-initiated chemistry include short lived, highly reactive compounds as well as secondary organic aerosols that can serve as carriers

[☆] Something to say? Comments on this article, or suggestions for other topics, are welcome. Please contact: new.directions@uea.ac.uk, or go to www.uea.ac.uk/~e044/apex/newdir2.html for further details.

for some of the more volatile reaction products. The effects of exposure to such products may be of greater concern to human health than exposure to ozone itself. Terpene and glycol ether autooxidation products have been shown to be potent contact allergens (Karlberg et al., 1992, *Contact Dermatitis* 26, 332–340; Bodin et al., 2000, *Contact Dermatitis* 43, 82–89; Skold et al., 2002, *Contact Dermatitis* 46, 267–272). In some of these systems, hydroperoxides have been identified as the active agents. The same hydroperoxides can be formed, and at much faster rates, when O_3 , OH and NO_3 are the oxidants rather than O_2 . At present we do not know the consequences of children inhaling these contact allergens. Other health effects are also germane. Leikauf (2002, *Environmental Health Perspectives* 110, 505–526) has developed a list of 28 compounds anticipated to induce or exacerbate asthma; several of these are known products of ozone initiated chemistry (e.g., formaldehyde, acetaldehyde, acrolein). Kleno and Wolkoff (2004, *International Archives of Occupational and Environmental Health* 77, 235–243) have recently demonstrated that 20 min exposures to the products of ozone reacting with limonene, at realistic indoor concentrations, increases the rate of blinking in human subjects. NO_3 / N_2O_5 react with PAHs to produce known mutagens and carcinogens such as nitroarenes (Pitts et al., 1985, *Environmental Science and Technology* 19, 1115–1121; Gupta et al., 1996, *Atmospheric Environment* 30, 3157–3166). Ozone/alkene derived hydroxyl radicals oxidize malathion, expected to be present on indoor surfaces after outdoor spraying, to the significantly more toxic malaoxon (Brown et al., 1993, *Environmental Science and Technology* 27, 388–397).

Outdoor ozone concentrations (in the absence of indoor sources of ozone) correlate with the concentrations of the products of ozone-initiated indoor chemistry. Indoor concentrations of organic compounds that are oxidized and the air exchange rate also influence the concentrations of the products of indoor chemistry. The hypothesis presented in the first paragraph can be tested by comparing models that account for these additional

factors (and outdoor ozone) to models based only on outdoor ozone. It may also be possible to explore the validity of this hypothesis through intervention studies (e.g., removing ozone from the ventilation air of a school and observing the subsequent impact on the use of medication or emergency room visits by asthmatic children).

Reducing ozone levels in urban areas has proven to be a difficult and costly problem. It is easier to remove ozone from indoor air than from outdoor air. Filters are available to accomplish this with only small energy penalties. At present, the health consequences of exposure to the products of ozone initiated indoor chemistry are poorly characterized; adverse effects are inferred from several loosely connected studies. However, further examination of the hypothesis expressed in this article is warranted since it affects overall mitigation strategies. For example, if even partially true, it would be beneficial to remove ozone from the supply air of mechanically ventilated buildings, especially schools, hospitals and daycare centers located in regions that continue to experience elevated outdoor ozone concentrations.

Acknowledgements

I thank Hal Levin, Building Ecology Research Group, William W. Nazaroff, University of California Berkeley, Jan Sundell, Technical University of Denmark, and Louise B. Weschler for helpful discussions and useful suggestions.

Charles J. Weschler^{a,b,1}

^aUMDNJ-RW Johnson Medical School & Rutgers University, Piscataway, NJ, USA

^bInternational Centre for Indoor Environment and Energy, Technical University of Denmark,

DK2800 Lyngby, Denmark

E-mail address: weschlch@umdnj.edu.

¹Charles Weschler has been captivated by indoor chemistry for more than 25 years, first as a researcher at Bell Laboratories and its derivatives, more recently as a Professor at the International Center for Indoor Environment and Energy and an Adjunct Professor at UMDNJ/RW Johnson Medical School.