A brief review of indoor ozone chemistry as it relates to the California Air Resources Board proposed regulation of ozone generating air cleaners

Author: Glenn Morrison, PhD

Affiliation: University of Missouri-Rolla, USA

Address: 221 Butler-Carlton Hall, University of Missouri, Rolla, MO 65409.

Tel: (573) 341-7192

Fax: (573) 341-4729

Email: gcm@umr.edu

1. Introduction

The California Air Resources Board has proposed to regulate ozone emitting air cleaners. The effect of this regulation is to reduce consumer exposure to ozone, a Criteria pollutant recognized to be associated with morbidity and mortality (Bell et al., 2005). The regulation has the further benefit of reducing exposure to the byproducts of ozone reactions with surfaces and some gas-phase compounds. I support the California Air Resource Board's efforts to reduce Californian's exposure to ozone and its byproducts, and provide the following outline of known indoor ozone chemistry. That ozone chemistry generates numerous chemicals with known and suspect adverse health outcomes, suggest that efforts to reduce indoor ozone levels are to be applauded and supported.

2. Ozone and related chemistry

Ozone is ozone. Whether it seeps into buildings from smog, or if it is generated by an electronic device. Ozone can and will react directly with some indoor materials at substantial rates. These reactions generate a suite of oxidized products. Early on, Weschler and Shields suggested ozone reactions with terpenes could lead to a substantial increase in aldehydes, radicals and even aerosols. Ozone reactions can generate irritants, carcinogens and aerosols. Formaldehyde, a carcinogen and irritant, is formed with a "yield" of ~0.9 (Atkinson and Arey, 2003) when it reacts with the compound, β-pinene, a "pine" smelling scent compound emitted by consumer products and natural materials.

This means that nearly every ozone molecule that reacts creates a formaldehyde molecule. Destaillats et al. (2005) and Singer et al. (2006) show that, when relatively high levels of ozone react with these kinds of scents emitted from cleaners, formaldehyde rises to levels (10-35 ppb) much greater than the California reference exposure level of 2 ppb. The reaction products include other carbonyl compounds and carboxylic acids which have low odor and irritancy thresholds (Cometto-Muñiz et al., 1998). Pinonaldehyde, a stable di-aldehyde that is formed at high yield in ozone-α-pinene reaction, is a suspected irritant. Organic acids are about 10-times more irritating than their analogous aldehydes; a number of acids (formic acid), di-acids (pinic acid) and acid/aldehyde compounds (norpinonic acid) are also formed.

Several animal and human studies have evaluated the subjective and objective health effects of these ozone-terpene reaction mixtures. In animal studies of reactions of ozone with isoprene (Wolkoff et al., 2000), α-pinene (Wolkoff et al., 1999) and d-limonene (Clausen et al., 2001), identified products that acted as airway irritants. Neither the individual reactants nor the aged products were as irritating as the mixture during reaction. Further, the more aged reaction mixtures were less irritating than younger mixtures (Wilkins et al., 2003), suggesting that unidentified products, such as short-lived radicals, were responsible for the irritation. Simlarly, Tamás et al. (2006) found that the sensory load, for 20 human subjects exposed to an ozone-limonene reaction mixture, was much greater than for either compound alone. The reaction mixture also caused eye-blink frequency to increase in human subjects (Kleno and Wolkoff, 2004). Rohr et al. (2002) observed limited respiratory flow and possible long-term sensitization in mice exposed to reaction products.

Low-vapor pressure oxidation products can self-nucleate to form small aerosols, or condense on and increase the mass of existing aerosols. Collectively, these are known as secondary organic aerosols (SOAs). Weschler and Shields (1999) observed increases in submicron SOA concentrations in an office with elevated ozone and either limonene, α-terpinene or a terpene mixture from a cleaner. For experiments using outdoor ozone (instead of injected ozone), particle concentrations followed the rise and fall of indoor ozone concentrations. Similarly, Long, et al. (2000) showed that a pine-scented cleaner

increased submicron particle concentrations in the presence of infiltrated ozone. In a laboratory chamber, the limonene-ozone reaction resulted in a 7 to 100 fold increase in the number concentration of particles with diameters less than 0.5 μm (Rohr et al., 2003; Wainman et al., 2000). Sarwar et al.(2004) showed, in laboratory chamber experiments, that SOAs increase substantially when realistic levels of ozone combine with terpenes from cleaners, air fresheners and perfumes. Shown in Figure 1 is an experiment (Sarwar et al., 2004) in which a solid air freshener is introduced into a chamber with an air exchange rate of 0.62 h^{-1}, and with ozone initially at ~110 ppb. A sharp increase in aerosols occurs due to the reaction of the terpene mixture and ozone, and is sustained for several hours. Note that the reported particle mass concentration rises above outdoor standards. Similarly, Singer et al. (2006) observed an increase of as much as 100 μg m^{-3} in aerosol mass concentration due to the use of terpenoid containing cleaners in the presence of ozone. Hubbard et al. (2005) recently demonstrated that ozone generating particle filters, advertised as "air cleaners" designed to reduce indoor particle concentrations, actually increase particle mass substantially in the presence of terpene fragrances.

Aerosol generation by the ozone-terpene reaction can significantly increase indoor levels of small aerosols. A large body of epidemiological literature indicates that increases in ambient aerosol concentrations are associated with increased mortality. In particular, an increase of 25 μg m^{-3} in particle mass concentration for PM2.5 (total particle mass for particles with an aerodynamic diameter < 2.5 μm) is correlated with a 1-3.5% increase over baseline mortality and a 1-12% increase in hospitalization for respiratory and cardiovascular disease (USEPA, 2004). For typical indoor ozone concentrations, in the presence of a pine cleaner, Weschler and Shields (1998) observed a 15-20 μg m^{-3} increase in particles <1.0 mm in diameter. Similarly, Wainman et al. (Wainman et al., 2000) found that a 20 μg m^{-3} increase due to these reaction is probable under typical indoor conditions. Where ozone is introduced by an ozone generating air filter in field homes, Hubbard et al. (2005) observed a 10-20 μg m^{-3} increase in particles <1.0 mm in diameter due to the ozone reaction with a variety of terpene sources. A recent screening study indicates that perfume wearers will be subjected to a "personal reactive cloud" of

reaction products, such as fine aerosols (Karamalegos et al., 2005). Increasing ventilation rates tends to decrease SOA concentrations by dilution, but also tends to shift the respirable particle size distribution to smaller sizes (Weschler and Shields, 2003) because the particles have less time to grow or coagulate. Although these reactions result in increased respirable aerosol mass, little is known about human health effects associated with these particular condensed reaction products. Tamás et al. (2006) observed a correlation between the number concentration of SOAs, from the limonene-ozone reaction in an office, and sensory load reported by 20 human subjects.

Ozone will also react with indoor surfaces, and carbonyls (aldehydes and ketone) are the prominent products observed. In ozone reactions with carpet, Morrison and Nazaroff (2002) found the aldehyde yield to range from 0.1 to 0.74 for summed aldehydes. Interestingly, lower-volatility products may also contribute to aerosol growth by partitioning from the indoor surface to existing aerosols (Aoki et al., 2005; Bekö et al., 2005). In the first study of its kind, Weschler et al. (1992) discovered that ozone reacted with carpet surfaces generating formaldehyde, acetaldehyde and C4-C10 aldehydes. Ozone converted some of the condensed phase material on the carpet to volatile species, demonstrating for the first time that surface chemistry can increase the gas-phase VOC concentration. Morrison and Nazaroff (2002) observed similar reaction products, but also observed unsaturated aldehydes generated on new carpet. Based on product yield studies, 2-nonenal was predicted to significantly exceed odor thresholds under typical conditions and that odorous conditions could persist for years. Field measurements of secondary emissions from carpet (Wang and Morrison, 2006) showed that one- to two-year old carpet is more reactive and aldehyde yields are higher than for carpet that had been installed for over 10 years. Thus, secondary emissions can persist for at least two years. Knudsen et al. (2003) performed sensory evaluations on carpet and other materials that had been exposed to ozone. They found that carpet in particular exhibited significantly higher odor intensity as a result of secondary emissions.

Reiss et al. (1995) showed that ozone reactions with latex paint generates formaldehyde, acetone and acetaldehyde. Older painted surfaces were not as reactive. They estimated that ozone reactions on newly applied paint would constitute 10 – 15% of the total emission rate of formaldehyde measured in field homes (Reiss et al., 1995). By isolating

wall sections in field homes and exposing the sections to ozone, Wang and Morrison (2006) confirmed a small generation rate of aldehydes from latex painted walls.

Over time, indoor surface reactants will eventually become depleted. Therefore, ozone reactivity and secondary emissions of byproducts should decrease as the cumulative ozone exposure increases. However, consumer activities repeatedly coat surfaces with cooking oils, soaps, tobacco products and even human skin oils, all of which have been shown to react with ozone to form volatile products.

The surfaces in HVAC systems may be regenerated by continuous deposition of reactive aerosols. Morrison et al. (1998) observed that used duct liners from commercial HVAC systems consumed more significantly ozone than new duct liners . In related work, several studies have recently shown that soiled HVAC filters are more ozone reactive than clean filters (Hyttinen et al., 2006; Hyttinen et al., 2003; Zhao et al., 2006). Hyttinen et al. (2003) observed formaldehyde as the only reaction product from a subset of these filters. Bekö et al. (2006) inferred that reaction byproducts were formed on used filters that were treated with ozone because they perceived as “less acceptable” than filters treated with plain air or nitrogen. They suggest that this chemistry may account for previous observations that sick building syndrome symptoms and poor occupant performance correlate with the presence of loaded HVAC filters (Clausen et al., 2002; Wargocki et al., 2003; Wyon et al., 2000). Fine aerosols have also been observed as indicators that semi-volatile reaction products form and partition from the soiled filter surface to aerosols (Bekö et al., 2005).

Wang et al. (2005) showed that countertops that become coated with cooking oils or soaps will generate volatile aldehydes in the presence of ozone, in chemistry akin to Scheme 2. They verified in field studies (Wang and Morrison, 2006) that kitchen counters are a major emitter of secondary aldehydes (on a unit area basis).

Wisthaller et al. (2005) studied ozone-surface reactions in a simulated aircraft environment that included used carpet, seats and other inner airplane surfaces. They also evaluated the presence of t-shirts worn by volunteers for a day. A key finding was that ozone consumption increases due to reactions with human skin oils, specifically

squalene, on t-shirts and other airplane surfaces. Using a very sensitive proton-transfer mass spectrometry system, they observed volatile oxidation products of the ozone-squalene reaction including acetone and 6-methyl-5-heptenone. Recent work has gone further to look at individual materials within an aircraft (Coleman et al., 2007) and complete cabin settings with live subjects (Weschler et al., 2007). They identified aldehydes, similar to those observed from earlier carpet studies, which may be generated from reactions with airline carpet and upholstery. Subjects in these studies reported a higher prevalence of symptoms (including headache, dizziness, mental tension, claustrophobia) when ozone levels were in the range of 60-70 ppb (Strom-Tejsen et al., 2007). Note that these ozone levels are roughly in the range that arise when ozone generators are used indoors.

Ozone-nicotine surface chemistry has recently been identified by Destaillats et al.(2006). Nicotine and other products of tobacco smoking adsorb strongly to indoor surfaces. In the presence of ozone, surface nicotine can form a variety of products including formaldehyde.

Taken as a whole, it is probable that some fraction of ozone uptake and secondary emission in commercial and residential buildings is due to reactions with soaps, cooking oils, human skin oils, terpenes and other products of human inhabitation. As our understanding of indoor chemistry expands, we may discover chemical mechanisms that we can engineer to clean the air. However, commercial efforts to chemically improve indoor air with ozone have been misguided at best, dangerous at their worst. The fact that ozone can react rapidly to remove a small number of organic compounds have led manufacturers of ozone generating “air cleaners” to claim that their products effectively destroy organic pollutants (Boeniger, 1995). The reaction rates with most indoor odors are far too small to effect any significant change in exposure. For those compounds that are “destroyed”, such as the “terpenes” already discussed, the products of these reactions appear to be worse than the original compound.

3. References

Aoki, T., Tanabe, S., Funaki, R., Tanaka, H., Nakagawa, T., Kihara, I., Shibue, T. 2005. Generation of sub-micron particles and secondary emissions from building materials by ozone reaction. the 10th International Conference on Indoor Air Quality and Climate, INDOOR AIR '05, Beijing, China.

Atkinson, R., Arey, J. 2003. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: A review. Atmospheric Environment 37(Supp. 2): S197-S219.

Bekö, G., Halás, O., Clausen, G., Weschler, C. J. 2006. Initial studies of oxidation processes on filter surfaces and their impact on perceived air quality. Indoor Air 16: 56-64.

Bekö, G., Tamás, G., Halás, O., Clausen, G., Weschler, C. J. 2005. Ultra-fine particles as indicators of the generation of oxidized products on the surface of used air filters. the 10th International Conference on Indoor Air Quality and Climater, INDOOR AIR '05, Beijing, China.

Bell, M. L., Dominici, F., J.M., S. 2005. A meta-analysis of time-series studies of ozone and mortality with comparison to the national morbidity, mortality, and air pollution study. Epidemiology 16(4): 436-445.

Boeniger, M. F. 1995. Use of ozone generating devices to improve indoor air quality. American Industrial Hygiene Association 56: 590-598.

Clausen, G., Alm, O., Fanger, P. O. 2002. Sensory strength of used ventilation filters. the 9th International Conference on Indoor Air Quality and Climate. INDOOR AIR '02, Monterey, CA.

Clausen, P. A., Wilkins, C. K., Wolkoff, P., Nielsen, G. D. 2001. Chemical and biological evaluation of a reaction mixture of r-(+)-limonene/ozone - formation of strong airway irritants. Environment International 26(7-8): 511-522.

Coleman, B. K., Destaillats, H., Hodgson, A. T., Nazaroff, W. W. 2007. Ozone consumption and volatile byproduct formation from surface reactions with aircraft cabin materials and clothing fabrics. Environmental Science & Technology in press.

Cometto-Muñiz, J. E., Cain, W. S., Abraham, M. H. 1998. Nasal pungency and odor of homologous aldehydes and carboxylic acids. Experimental Brain Research 118: 180-188.

Destaillats, H., Singer, B. C., Coleman, B. K., Lunden, M. M., Hodgson, A. T., Weschler, C. J., Nazaroff, W. W. 2005. Secondary pollutants from cleaning products and air fresheners in the presence of ozone. 10th International Conference on Indoor Air Quality and Climate (Indoor Air 2005), Beijing, China, Tsinghua University Press.

223 Destaillats, H., Singer, B. C., Lee, S. K., Gundel, L. A. 2006. The effect of ozone on
224 nicotine desorption from model surfaces: Evidence for heterogeneous chemistry.
225 Environmental Science & Technology: in press.
226
227 Hubbard, H. F., Coleman, B. K., Sarwar, G., Corsi, R. L. 2005. Effects of an ozone-
228 generating air purifier on indoor secondary particles in three residential dwellings. Indoor
229 Air 15(6): 432.
230
231 Hyttinen, M., Pasanen, P., Kalliokoski, P. 2006. Removal of ozone on clean, dusty, and
232 sooty supply air filters. Atmospheric Environment 40: 315-325.
233
234 Hyttinen, M., Pasanen, P., Salo, J., Björkroth, M., Vartiainen, M., Kalliokoski, P. 2003.
235 Reactions of ozone on ventilation filters. Indoor and Built Environment 12: 151-158.
236
237 Karamalegos, A., Simon, H., Zhao, P., Morrison, G. C., Siegel, J. A., Corsi, R. L. 2005.
238 Personal reactive clouds: Introducing the concept of near head chemistry. the 10th
239 International Conference on Indoor Air Quality and Climate, INDOOR AIR '05, Beijing,
240 China, Tsinghua University Press.
241
242 Kleno, J., Wolkoff, P. 2004. Changes in eye blink frequency as a measure of trigeminal
243 stimulation by exposure to limonene oxidation products, isoprene oxidation products and
244 nitrate radicals. International Archives of Occupational and Environmental Health 77(4):
245 235-243.
246
247 Knudsen, H. N., Nielsen, P. A., Clausen, P. A., Wilkins, C. K., Wolkoff, P. 2003.
248 Sensory evaluation of emissions from selected building products exposed to ozone.
249 Indoor Air 13(3): 223-231.
250
251 Long, C. M., Suh, H. H., Koutrakis, P. 2000. Characterization of indoor particle sources
252 using continuous mass and size monitors. Journal of the Air and Waste Management
253 Association 50(7): 1236-1250.
254
255 Morrison, G. C., Nazaroff, W. W. 2002. Ozone interactions with carpet: Secondary
256 emissions of aldehydes. Environmental Science & Technology 36(10): 2185-2192.
257
258 Morrison, G. C., Nazaroff, W. W., Cano-Ruiz, J. A., Hodgson, A. T., Modera, M. P.
259 1998. Indoor air quality impacts of ventilation ducts: Ozone removal and emissions of
260 volatile organic compounds. Journal of the Air and Waste Management Association
261 48(10): 941-952.
262
263 Reiss, R., Ryan, P., Koutrakis, P., Tibbetts, S. 1995. Ozone reactive chemistry on interior
264 latex paint. Environmental Science & Technology 29(8): 1906-1912.
265
266 Reiss, R., Ryan, P. B., Tibbetts, S., Koutrakis, P. 1995. Measurement of organic acids,
267 aldehydes, and ketones in residential environments and their relation to ozone. Journal of
268 Air & Waste Management Association 45: 811-822.

Rohr, A. C., Weschler, C. J., Koutrakis, P., Spengler, J. D. 2003. Generation and quantification of ultrafine particles through terpene/ozone reaction in a chamber setting. Aerosol Science and Technology 37(1): 65-78.

Rohr, A. C., Wilkins, C. K., Clausen, P. A., Hammer, M., Nielsen, G. D., Wolkoff, P., Spengler, J. D. 2002. Upper airway and pulmonary effects of oxidation products of (+)-alpha-pinene, d-limonene, and isoprene in balb/c mice. Inhalation Toxicology 14(7): 663-684.

Sarwar, G., Olson, D. A., Corsi, R. L., Weschler, C. J. 2004. Indoor fine particles: The role of terpene emissions from consumer products. Journal of the Air & Waste Management Association 54(3): 367-377.

Singer, B. C., Coleman, B. K., Destaillats, H., Hodgson, A. T., Lunden, M. M., Weschler, C. J., Nazaroff, W. W. 2006. Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone. Atmospheric Environment 40(35): 6696-6710.

Strom-Tejsen, P., Weschler, C. J., Wargocki, P., Myskow, D., Zarzycka, J. 2007. The influence of ozone on self-evaluation of symptoms in a simulated air-craft cabin. Journal of Exposure Science and Environmental Epidemiology in press.

Tamás, G., Weschler, C. J., Toftum, J., Fanger, P. O. 2006. Influence of ozone-limonene reactions on perceived air quality. Indoor Air 16: 168-179.

USEPA 2004. Integrative synthesis. In air quality criteria for particulate matter, US Environmental Protection Agency. II**:** 9.1-9.121.

Wainman, T., Zhang, J., Weschler, C. J., Lioy, P. J. 2000. Ozone and limonene in indoor air: A source of submicron particle exposure. Environmental Health Perspectives 108: 1139-1145.

Wang, H., Morrison, G. C. 2006. Ozone initiated secondary emission rates of aldehydes from indoor surfaces in four homes. Environmental Science & Technology(40): 5263-5268.

Wang, H., Springs, M., Morrison, G. C. 2005. Ozone initiated secondary emissions of aldehydes from indoor surfaces. Air and Waste Management Association 2005 Meeting, Minneapolis, MN.

Wargocki, P., Wyon, D. P., Fanger, P. O. 2003. Call-centre operator performance with new and used filters at two different outdoor air supply rates. Healthy Buildings 2003, Singapore.

Weschler, C. J., Hodgson, A. T., Wooley, J. D. 1992. Indoor chemistry: Ozone volatile organic compounds, and carpets. Environmental Science & Technology 26: 2371-2377.

Weschler, C. J., Shields, H. C. 1998. Indoor ozone/terpene reactions as a source of indoor particles. 1-15.

Weschler, C. J., Shields, H. C. 1999. Indoor ozone/terpene reactions as a source of indoor particles. Atmospheric Environment 33: 2301-2312.

Weschler, C. J., Shields, H. C. 2003. Experiments probing the influence of air exchange rates on secondary organic aerosols derived from indoor air chemistry. Atmospheric Environment 37: 5621-5631.

Weschler, C. J., Wisthaler, A., Cowlin, S., Tamás, G., Strøm-Tejsen, P., Hodgson, A. T., Destaillats, H., Herrington, J., Zhang, J., Nazaroff, W. W. 2007. Ozone initiated chemistry in an occupied simulated aircraft cabin. Environmental Science & Technology 41(In press).

Wilkins, C. K., Wolkoff, P., Clausen, P. A., Hammer, M., Nielsen, G. D. 2003. Upper airway irritation of terpene/ozone oxidation products (tops). Dependence on reaction time, relative humidity and initial ozone concentration. Toxicology Letters 143(2): 109-114.

Wolkoff, P., Clausen, P. A., Wilkins, C. K., Hougaard, K. S., Nielsen, G. D. 1999. Formation of strong airway irritants in a model mixture of (+)-alpha-pinene/ozone. Atmospheric Environment 33: 693-698.

Wolkoff, P., Clausen, P. A., Wilkins, C. K., Nielsen, G. 2000. Formation of strong airway irritants in terpene/ozone mixtures. Indoor Air 10: 82-91.

Wyon, D. P., Tham, K. W., Croxford, B., Young, A., Oreszczyn, T. 2000. The effects on health and self-estimated productivity of two experimental interventions which reduced airborne dust levels in office premises. Healthy Buildings 2000, Espoo, Finland.

Zhao, P., Siegel, J. A., Corsi, R. L. 2006. Ozone removal by hvac filters. Atmospheric Environment: in review.