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THE BIG INDOOR AIR EMISSIONS THREAT – SECONDARY EMISSIONS

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Summary

Substantial progress has been made understanding volatile organic chemical (VOC) emissions from indoor sources including building materials, furnishing, and some cleaning and maintenance products. During the past two decades, emissions from building materials and other sources have declined significantly in many developed countries. Researchers have begun to understand the potentially larger health threat posed by secondary emission, the chemicals formed by the interactions between oxidants in indoor air and chemicals on surfaces, and by hydrolysis. Many of the by-products of these interactions are more irritating, odorous, or toxic and may pose a far greater health hazard than the chemicals from which they are formed. Building materials, cleaning products, and many consumer products contain chemicals that react with oxidants to form formaldehyde and other, higher molecular weight aldehydes, acidic aerosols, and fine or ultrafine particles. Researchers have identified some of the most important indoor sources that combine with ozone (O_3) at common indoor concentrations to form these secondary products. The fundamental processes and critical building material and cleaning products have been identified along with recommendations for minimizing occupant exposure to hazardous chemicals resulting from indoor air chemistry and secondary emissions. Exposure to harmful secondary emissions can be reduced to improve indoor air quality

Key words: Indoor air quality, secondary emissions, volatile organic chemicals, ozone.

Background

Contaminants found in indoor air come from either indoor or outdoor sources. Among the most important of the indoor sources are building materials and furnishings, especially when they are new. Surfaces exposed to the interior are important, especially if they are periodically cleaned, re-finished, or renewed with wet-applied products that emit many of their constituents while drying or curing. The quantity of such materials can be very large over the lifetime of a building, and for some regularly-applied cleaning and maintenance products, large over even short periods of time. For example, the total mass of floor wax applied to a resilient floor product following manufacturer's instructions for regularly renewal can equal the mass of the flooring itself in a period of one or two years (Levin, 1999). Other indoor air pollutants enter a building from the outdoors and are carried in by ventilation air from mechanical or natural ventilation or through infiltration. Finally, occupant activities such as food preparation, cleaning, and personal hygiene, or from equipment and appliances can be sources of indoor air pollutants. Among the most well-known and important of these pollutants are volatile organic chemicals ((VOCs), chemicals that are found in air at normal indoor conditions of temperature and pressure.

Volatile organic chemicals in indoor air

Substantial progress has been made understanding VOC emissions from primary sources indoors including building materials, furnishing, and even some cleaning and maintenance products. As early as the late 1970s, researchers in Denmark were measuring emissions of formaldehyde from building materials and furnishings (Mølhave, 1981). By the mid-1980s, emissions testing of formaldehyde from composite wood products (particle board, plywood, fiberboard) used in federally-subsidized or insured housing and mobile homes in the U.S. was required. Apart from the formaldehyde emissions, early reports of emissions testing from building materials were primarily from research projects and were not generally reflected in guidelines and standards for building materials and finishes. In the mid-80s and onward, emissions testing began being applied to buildings in design (Levin, 1985; 1986; 1989; Tucker, 1990; Levin and Hodgson, 1996). And in the 1990s, emissions testing of many building products began to become increasingly common, at least in "green" building design processes (Tichenor, 1996; 2007). A comprehensive review of emissions testing became available in 2007 (Tichenor).

During the past two decades, concentrations of VOCs emitted from building materials and other sources have declined significantly in many developed countries. The decline is partly attributable to emissions testing and increased awareness of the importance of emission in determining indoor air quality. According

to one review, a large fraction may also be attributable to regulation of emissions into ambient air where many VOCs are precursors of photochemical smog (Hodgson and Levin, 2003a; Levin and Hodgson, 2006).

Figures 1 and 2 (from Hodgson and Levin, 2003a) present results of VOC measurements from several studies. Figure 1 compares survey results from offices and residences reported between 1990 and 2001. Figure 2 compares Figure 1 residential results to surveys done prior to 1990. From the results it is clear that with several exceptions, the concentrations of most of these VOCs generally found indoors had decreased significantly from the levels found prior to 1990.
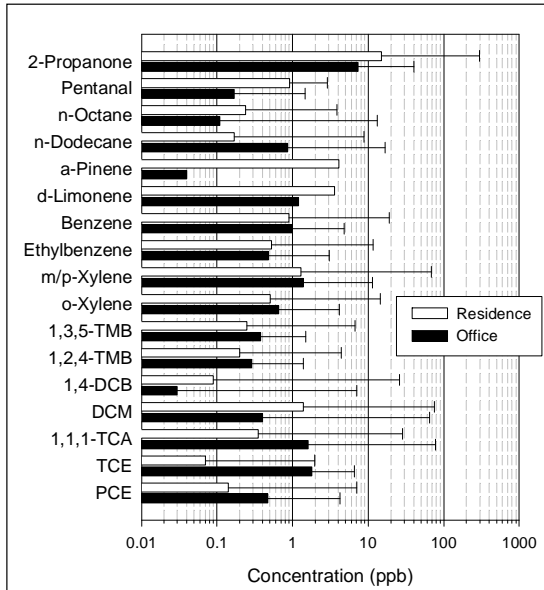

Figure1: Residential vs Office buildings: Comparison of central tendency and maximum concentrations (whiskers) of selected VOCs (1990-2001 studies). TMB = trimethylbenzene, DCB = dichlorobenzene, DCM = dichloromethane, TCA = trichloroethane, TCE = trichloroethene, PCE = tetrachloroethene.
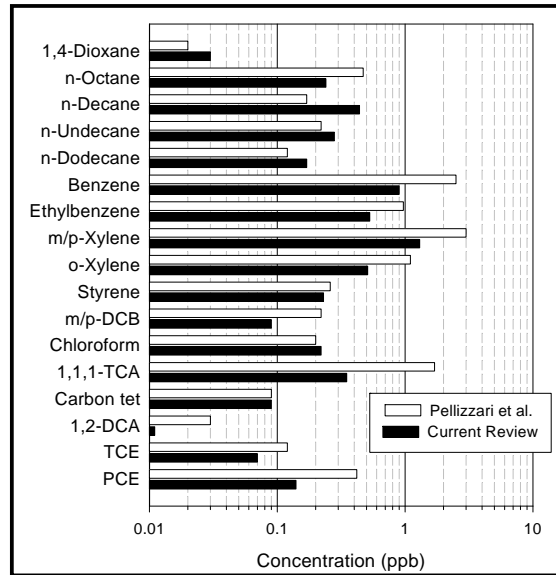
Figure 2: Residential buildings: Comparison of geometric mean (GM) concentrations of 17 VOCs (U.S. EPA TEAM studies prior to 1990 as reported by Pellizzari et al.1986 vs 1990-2001 studies). DCA = dichloroethane.

Formaldehyde

Not shown in these two figures is formaldehyde, probably the most well-characterized of indoor air pollutants in terms of health effects which include nose, eye, and skin irritation, upper respiratory tract irritation, and cancer. In the late 1970s and into the 1980s in the United States (U.S.), formaldehyde concentrations in indoor air often were found exceeding one part per million (ppm). The U.S. Occupational Safety and Health Administration's guideline value for protection of workers exposed to formaldehyde was 3 ppm, and this concentration was occasionally approached in indoor air where large quantities of plywood, particleboard, and hardwood veneer plywood were used, especially in mobile homes and manufactured housing where these materials dominated interiors. More commonly, in new homes and offices, concentrations often reach several hundred parts per billion (ppb).

Today, the OSHA regulations require that employers whose workers are exposed to more than 300 ppb inform the workers of their exposures, and formaldehyde measurements in new buildings in the U.S. are more commonly in the 10 to 30 ppb range, a decrease of roughly a factor of 10 generally and as much as a factor of 100 in extreme cases. It was not unusual to find concentrations exceeding 100 ppb throughout the 1980s and even into the 1990s. Formaldehyde has once again become a pollutant of major concern indoors because a lot of composite wood products entering the U.S. and Europe from Asia have very high formaldehyde emissions. So designers and builders need to continue verifying that the products they are specifying and using are low emitting products. The State of California has recently passed regulations that would limit the emissions of composite wood products to the 100 ppb range.

Emissions testing and product labeling

Other volatile organic chemicals also continue to be a concern, and emissions testing and certification programs are becoming common means of screening products for green or sustainable buildings. However, these screening programs are often driven by the product manufacturers rather than public health agencies

or population concerns, so there continues to be much to do to limit occupant exposure to emissions from building materials and furnishings (Tichenor, 2007).

Early concern about secondary emissions

While there is still substantial and appropriate concern regarding VOC emissions from new building materials as well as from cleaning and maintenance products and occupant activities, recent interest among many of the pioneers of emissions testing and indoor air research has shifted to "secondary emissions." In the last 15 years researchers have begun to recognize the potential importance including the large health threat posed by secondary emissions, the chemicals formed by the interactions between oxidants in indoor air and chemicals on surfaces. Many of the by-products of these interactions are more irritating, odorous, or toxic than the chemicals from which they are formed.

Nazaroff, Cass, and other early indoor air chemistry researchers

One of the earliest to document the importance of these chemical reactions in indoor air reactions was William W Nazaroff of UC Berkeley. Nazaroff studied chemical reactions indoors both in air and on surfaces in southern California museums. His 1986 paper written together with Glen Cass of Cal Tech, "Mathematical Modeling of Chemically Reactive Pollutants in Indoor Air," described some of the basic processes that form the background of indoor air chemistry research since that time. Their work was funded to investigate the impact of polluted air on art works, and what better place to study this than in Los Angeles of the early 1980s? Their article's abstract reads, in part: "A general mathematical model is presented for predicting the concentrations of chemically reactive compounds in indoor air. The model accounts for the effects of ventilation, filtration, heterogeneous removal, direct emission, and photolytic and thermal chemical reactions." Near the end of the paper, it states: "The model is formulated to be a general tool for studying chemically reactive air pollution systems." In other words, their work could be used to estimate the effects of increasing or decreasing outdoor air ventilation rates as well as the use of filtration but also to predict the impact of airborne chemical reactions on building and other indoor material surfaces and on airborne concentrations of various pollutants.

Several researchers prior to Nazaroff and Cass had looked at indoor air chemistry; a very early publication was by MG Wilson in 1968 (Wilson, 1968).) An early paper on by-product formation from surface reactions was by James Pitts (1985). But nobody really pursued the topic of secondary emissions vigorously, and it did not gain much attention from the indoor air research community until the early 1990s.

Charles J. Weschler, Ozone, and Indoor Air Chemistry

Among the most important of those who took up the challenge and opportunity highlighted by the Nazaroff and Cass paper and the earlier work by Wilson, Pitt, and others is Charles J. Weschler. Much of the present awareness of indoor air chemistry is due to Weschler's work. First he called attention to the significant ozone concentrations indoors at a time when it was widely believed that concentrations indoors were inconsequential due to ozone's reactivity (Weschler et al, 1989). He reported that indoor concentrations of ozone were inversely related to the outdoor air ventilation rate and directly related to the outdoor ozone concentration. A typical office ventilation rate of just under 1 air change per hour (h^{-1}) results in an indoor-outdoor (I-O) ozone ratio of approximately 0.2. A school or assembly space with an air change rate of ~3 h^{-1} will have an I-O O_3 ratio of ~0.5. and a laboratory or other space with approximately 6 air changes per hour has an I-O O_3 ratio of about 0.7. To this day there are still many building, health, and chemical scientists who hold to the myth that ozone is not present in significant concentrations or important in indoor air.

Weschler raised awareness of ozone reactions indoors and the resulting secondary emissions in his 1992 paper reporting experiments with ozone and carpets (Weschler et al, 1992). He showed that the emissions from carpet of styrene and of 4-phenylcyclohexene (4-PCH), a by-product of the styrene butadiene rubber (SBR) latex manufacturing process, would rapidly react with ozone indoors to form formaldehyde, acetaldehyde, and other, higher molecular weight aldehydes. SBR latex backings were the most common on commercial carpet in that era and represented about 85% of the commercial carpet market. Weschler reported that the concentrations of VOCs that were markedly reduced "…in the presence of O_3 are those that contain unsaturated carbon-carbon bonds (4-phenylcyclohexene, styrene, and 4-ethenylcyclohexene)."

Not long after Weschler presented his findings described in the 1992 *Environmental Science and Technology* article, the present author received a call from an architect whose client, a law firm, had just moved into a newly renovated office space. All the secretaries were complaining of eye and skin irritation among other symptoms by the end of the first week in the office. Each secretary had their own laser printer at their work station, and laser printers emit ozone. The firm had called an industrial hygienist to measure the 4-PCH in the air, but the hygienist found very low concentrations. The apparent reason was that the ozone from the printers was reacting with the 4-PCH so that there was no 4-PCH left in the air to measure. As a result of the reaction, formaldehyde and other aldehydes were formed, and these are known irritants. Thus, the lessons of the researchers began to inform the design of buildings, and laser printers were recommended to be isolated in rooms equipped with exhaust directly to the outdoors. This kind of finding led Weschler to the title of a talk on his ozone and carpet research titled "Indoor VOCs: Is What You Measure on

Tuesday Night the Same as What You Measure on Wednesday Afternoon?" The title conveyed dramatically the problems indoor air chemistry causes for investigators of indoor air complaints and illustrates the importance of understanding indoor air chemistry processes.

Weschler has since published many papers on the subject of indoor air chemistry and especially reactions of materials commonly found indoors with ozone, and he has collaborated with others in experiments in Europe and America, in the lab, in buildings, and in simulated aircraft cabins. These experiments have shown that the ozone concentrations are lower indoors than outdoors because the ozone was reacting with indoor surfaces. He (and many others as well) reported that the products of these reactions included formaldehyde, higher molecular weight aldehydes, acidic aerosols, and ultrafine particles. The outcome, as Weschler has often said, is that the ozone is removed but the reaction products are more hazardous than the chemicals from which they are formed. Two of his most important and useful overview papers are "Ozone in Indoor Environments: Concentration and Chemistry" (Weschler, 2000) and "Ozone's Impact on Public Health: Contributions from Indoor Exposures to Ozone and Products of Ozone-Initiated Chemistry" (Weschler, 2006).

Fundamentals of ozone chemistry in air and on surfaces

Ozone is very reactive and easily reacts with unsaturated compounds that are commonly found in typical buildings. These compounds include citrus based solvents, the so-called "green" solvents (containing d-Limonene and other citrus oils) that have gained popularity as replacements for the toxic traditional solvents formerly found in many products. They also include chemicals found in many softwoods, the terpenes like alpha-pinene. Pine oil cleaner is an example of such products. Ozone also reacts with the oils found in linseed oil resulting in the very strong and persistent odor of linoleum floor covering. These oils, composed primarily of esters of linolenic, linoleic, and oleic acids, have also been found by other researchers to form the aldehydes and odorous compounds emitted from linoleum and other products using linseed oil in their formulation (Morrison and Nazaroff, 2002). What these chemicals have in common is unsaturated double carbon bonds that react very quickly with ozone.

Researchers have begun to understand the processes involved in the generation of secondary emissions and have identified some of the most important indoor sources that combine with ozone at common indoor concentrations to form these secondary products. In 2007 at UC Berkeley, some of the leading researchers gathered to discuss "interfacial chemistry in indoor environments" at a workshop sponsored by the National Science Foundation and the California Air Resources Board and organized by Glenn Morrison of the University of Missouri, Rolla. The following section summarizes some of the presentations and discussions at that workshop based largely on Morrison's report of the workshop to the sponsoring agencies (Morrison, 2007) and his article in the journal *Environmental Science and Technology* (Morrison, 2008).

The fundamentals of indoor air chemistry are illustrated in Figure 3 provided by Glenn Morrison from his presentation at Healthy Buildings 2006 in Lisbon, Portugal.
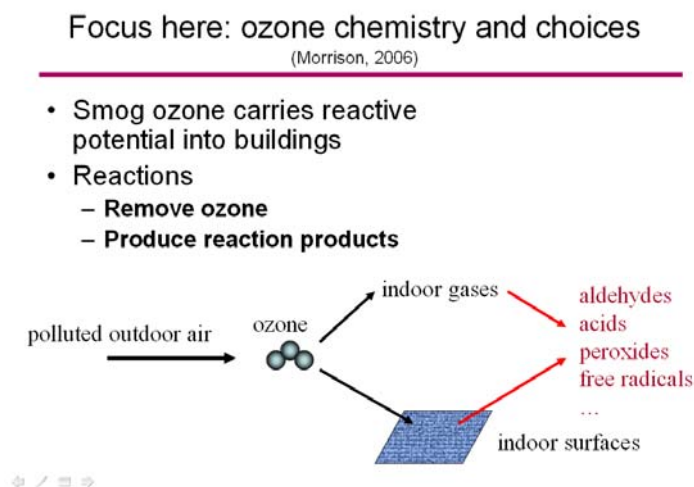

Figure 3. Fundamentals of Indoor Air Ozone Chemistry (source: Morrison, 2006)

Ozone Reactions with Surfaces

Many of the most widely-used building materials, cleaning products, and consumer products are made from chemicals that react with ozone and other oxidants to form formaldehyde and other, higher molecular weight aldehydes, acidic aerosols, and fine or ultrafine particles (Weschler 2000; Nazaroff and Weschler, 2004;

Nazaroff et al, 2006). Thus, as indoor air researchers probed deeper into the sources of the chemicals found in indoor air as well as the disappearance of some that enter the air but are not found in the expected concentrations, they discovered the importance of chemical reactions for explaining the presence of (and determining the fate of) some of the more important chemicals.

One of the active and most productive research areas has been the study of ozone reactions with various indoor surfaces and compounds found on these surfaces. The basic schematic relationships are shown in Figure 3 below from a 2006 presentation by Glenn Morrison. Ozone readily reacts with an ample supply of unsaturated compounds that generally exist in typical buildings at concentrations many times greater than observed outdoors. Products of this chemistry include carcinogens (formaldehyde, acrolein), irritants (carbonyls, dicarbonyls, acids), free radicals, and other oxidation products of concern (e.g. pesticide oxidation products). The volatile products have been coined "secondary emissions", and the resulting concentrations of chemical reaction products are large enough to have health and comfort consequences at typical indoor ozone levels.

Perhaps the most important overall finding is that reactions between ozone and indoor surfaces strongly influence human exposure to ozone, the chemicals and surfaces with which ozone reacts, and to the chemical by-products. As illustrated by Weschler and Shields (1989) and later by Lee et al (1999), the reactions of O_3 on indoor surfaces reduce occupant exposure by factors ranging from 2 to 10. The surface area available for such reactions is extremely large, far larger than the planar surface area because the reactions take place at the molecular level and the surface area available is large compared to the building volume. The reaction products can be attached to surfaces by sorption thus extending the average length of time the products are indoors and increases the probability that conversions will occur, and unique compositions and morphologies at indoor surfaces can promote some reactions or promote selectivity in reaction pathways.

Chemicals in Products Applied to Surfaces

One of the major concerns emerging from the interfacial chemistry research is that many of the O_3 reactions occur with chemicals commonly found and unintentionally applied to indoor surfaces. Ozone reacts with the common pesticide cypermethrin (Segal-Rosenheimer and Dubowski, 2007). It also reacts with the terpenes used as the active ingredient in cleaning or other scented products (Singer et al, 2007). Researchers have now found that cleaning products and air fresheners increase the ozone deposition on surfaces (Singer et al, 2007). Compounds that had sorbed to the surfaces made up as much as half of the ozone reactions.

Two examples, orange oil cleaner and pine oil cleaner, are presented in Figure 4. The concentration of ozone introduced in these experiments, 40 ppb, is not uncommon in indoor environments. In residences without air conditioning or mechanical ventilation, open windows can easily result in such concentrations on a summer day in most cities in North America. What is most impressive here is how long the concentration of formaldehyde formed by the reaction lingers in the air after application on an apparently "dry" cleaned surface.
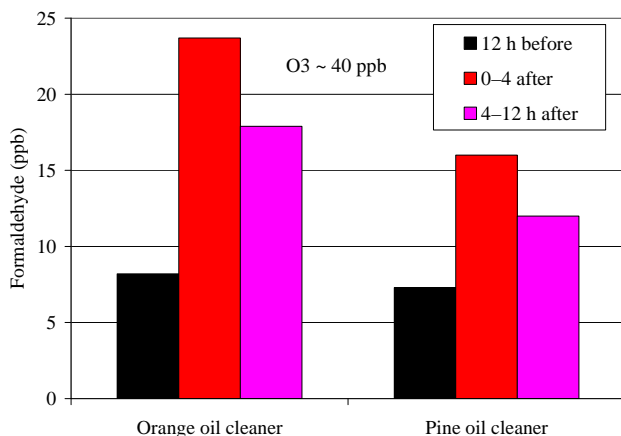

Figure 4. Cleaning products exposed to O_3 and formaldehyde formation (Singer et al, 2007)

Reactions of ozone with people

An extremely interesting and potentially very important finding is that the interfacial chemistry is taking place at the "human surface". This became apparent in simulated aircraft cabin experiments, densely occupied with human subjects (Weschler et al, 2007; Wisthaler et al, 2006) and in studies of the "personal cloud," (Corsi et al, 2008). Ozone delivered by the fresh air system in aircraft cabins forms compounds somewhat unique to its reaction with human skin oils or sebum. The researchers also concluded that in aircraft cabins, people are major O_3 sinks – larger than carpet, seats and dirty HEPA filters combined, and that O_3 and its

oxidation products adversely affected 12 of 29 self-reported symptoms based on questionnaires from occupants. Evaluation of individual aircraft surfaces, in small-chamber experiments, confirmed these findings (Coleman et al, 2007). Coleman also found ozone chemistry formation far higher with soiled human clothing than with laundered clothing, suggesting that the skin oils, perhaps among other accumulated chemicals on soiled clothing, were reacting with the ozone to form formaldehyde, acetaldehydes, and other typical ozone reaction products (see Figure 5).
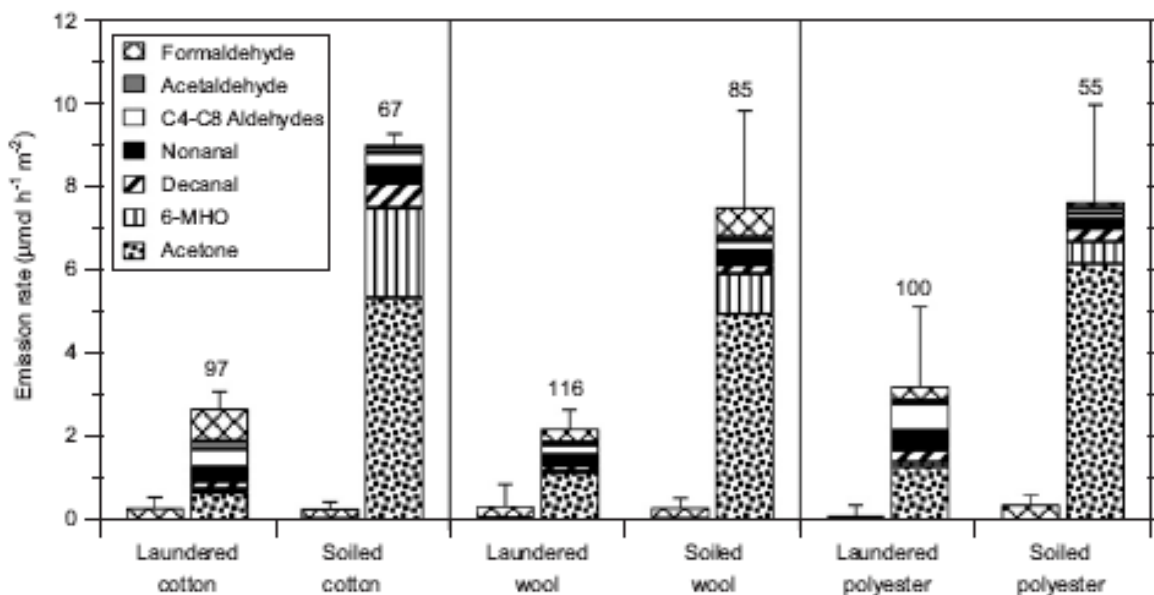

Figure 5. Clean and soiled clothing exposed to O₃ and chemical by-product formation (Coleman et al, 2008). For each material presented, the left bar represents the average emissions without ozone during a 180-min conditioning period (no ozone), and the right bar represents the average emissions during the initial 90-min ozone exposure period. The number above the right bar is the 90-min average residual ozone concentration in ppb; the supply air concentration was always 160 ppb. Error bar indicates plus one standard deviation from analysis of replicate integrated samples

Corsi et al (2008) investigated the presence of personal reactive clouds that result from ozone reactions with terpenes and terpenoids emitted from personal care products. "Screening experiments were performed with three perfumes and two hairsprays to determine the extent of secondary organic aerosol formation in the breathing zone of a subject who had applied these products. The results of screening calculations and preliminary experiments confirm that chemistry occurs in the "near-head region" of individuals who apply scented personal care products to their hair or facial skin."

Even human hair reacts with ozone. Studies showed a very high probability of ozone reacting with hair follicles (Pandrangi and Morrison, 2007). When humans are in densely occupied environments such as classrooms, theatres, or airplanes, their aggregated reactivity will reduce their exposure to ozone but increase their exposure to the products of ozone-sebum reactions.

Reactions of other outdoor air pollutants with indoor surfaces

Reactions of other components of smog such as nitrous oxides (NOx) (Sakamaki et al, 1983) have also been studied on indoor surface; Pitts et al. (1989) showed that this chemistry also occurs on indoor surfaces and can generate nitrous acid (HONO) levels that exceed outdoor levels when NOx is released from indoor sources such as improperly vented gas burners.

Hydrolysis

Some important chemical reactions and physical processes indoors do not involve pollutants that are part of photochemical smog. The importance of hydrolysis (the decomposition of a chemical compound by reaction with water, such as the dissociation of a dissolved salt or the catalytic conversion of starch to glucose) is now recognized as an important source of indoor air pollutants as well as the potential deterioration of building materials. These processes in indoor environments are known to cause toxic and odorous chemical emissions.

One of the more important of these breakdown processes is the hydrolysis of plasticizer (e.g., di-ethylhexylphthalate -DEHP) generates mono-ethylhexylphthalate (EHP) (Lundgren et al, 1999) which may be associated with asthma (Norback et al, 2000). Plasticizers are often used in vinyl flooring and in

adhesives to improve their functional properties. When vinyl flooring is applied to insufficiently cured concrete (high moisture content), hydrolysis will occur. Concrete flooring and gypsum board which are both highly basic can help catalyze this hydrolysis. (Corsi et al, 2007). Hydrolysis reactions depend on local pH and moisture conditions, but these parameters are rarely quantified accurately or sufficiently, and their influence on hydrolysis is poorly understood.

Indoor Chemistry and Occupant Health

"Secondary emissions", the reaction products of ozone chemistry, include carcinogens (formaldehyde and acrolein), many irritants (including carbonyls, dicarbonyls, and acidic aerosols), free radicals, as well as other products of the oxidation process (e.g. pesticide oxidation products). It is apparent that the concentrations of these chemicals produced by such reactions have potentially important occupant health and comfort implications at ozone concentrations typically found indoors (Weschler, 2004).

Exposure to these secondary emissions may pose a far greater health hazard than the chemicals from which they are formed (Weschler, 2004; 2006). Weschler has also suggested that since a significant fraction of people's exposure to ozone does occur indoors due to the far larger fraction of a typical person's day spent indoors and since when ozone is removed from indoor air through indoor air chemistry, many of the reaction products are toxic, that some significant fraction of the morbidity and mortality reported by epidemiologists during periods of high outdoor ozone may be attributed at least in part to pollutant exposures that occur indoors (Weschler, 2006).

Some provocative recent findings

Ozone is nearly always present in sufficient concentrations in outdoor air to present concern for the health of building occupants. A recent analysis of the U.S. EPA's BASE study data showed that outdoor ozone concentrations were associated with increased SBS symptoms (Apte et al, 2008). Additional analysis of the same data showed that a combination of higher outdoor ozone and synthetic fiber filters resulted in very large increases in the risk of SBS symptoms (Buchanan et al, 2008).

Summary of health implications

As is the case for most indoor pollutants, little is known about the health outcomes of exposure to most of the reaction products of indoor chemistry. Weschler's analysis (2006) suggests that the reported epidemiological correlations between outdoor levels of ozone and morbidity or mortality are due, in large part, to indoor exposures to ozone and the byproducts of its reaction with other species indoors. His estimate is that indoor exposure to ozone transported indoors from outdoors is conservatively 2/3 to 3 times that of outdoor exposure to ozone. Meanwhile, indoor exposure to ozone oxidation products is often many times greater than outdoor ozone exposure. It can be anticipated that indoor levels of reaction products may correlate with outdoor levels of ozone, but this hypothesis still needs to be fully evaluated in field settings. Many human and animal experiments have shown adverse reactions to homogeneous ozone chemistry (see references in Tamás, G. et al, 2006). It appears, therefore, that real toxins, irritants, sensitizers and so forth are generated, and seemingly generated at levels of concern.

Controlling Indoor Chemistry

"Controlling indoor chemistry means controlling sources, reactants and conditions that promote that chemistry…. Indoor air and outdoor air are part of the same continuum. Yet scientific, legislative, and philosophical separation of these domains has adversely affected our ability to target efficient solutions for reducing exposure to smog and its consequences. We now see that smog chemistry does not stop at the door, but churns away in the indoor spaces where we spend most of our time. Thus indoor air and its chemistry need the same attention given to ambient air for the past 50 years" (Morrison, 2008).

What can be done?

There is a general agreement in the indoor air research and professional communities that source control is the alternative of choice. Then, after eliminating indoor pollution sources, authorities recommend dilution and removal by ventilation for indoor source pollutants. But ozone and its reaction products indoors present a dilemma in terms of the ventilation strategy. Where outdoor air contains any significant quantity of ozone, it may be important to limit the amount of outdoor air intentionally introduced into a building.

One of the ways to address the problems presented by indoor ozone reactions is to select materials that are less likely to react with ozone or to form harmful reaction products. It would clearly be wise to avoid introducing products that contain many of the chemicals that are especially reactive such as citrus-based solvents and cleaning products and terpenes (e.g., pine oil cleaners) that have been shown to react strongly with ozone to form undesirable products. Glenn Morrison has illustrated the processes and provided some preliminary data on ozone and formaldehyde formation with common indoor materials as shown in Figures 6. Extension of his work with more materials and application of the results can reduce occupant exposure to formaldehyde and other important indoor air pollutants from the ozone that is almost always present in sufficient concentrations to cause the reactions.

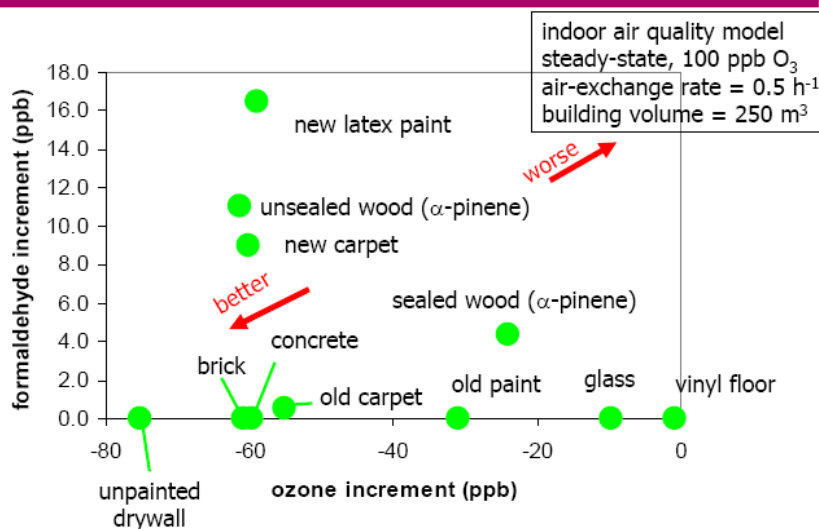## Building materials comparison: formaldehyde vs ozone increments (Morrison, 2006)

Figure 6. Building materials comparison: Formaldehyde vs Ozone increments (source: Morrison, 2006)

An alternative to attempting to address the ozone indoors by careful selection of materials is to remove the ozone by air cleaning when mechanical ventilation systems are used. Controlling indoor chemistry means controlling sources, reactants and conditions that promote that chemistry. Ozone is a clear target and its removal from buildings is anticipated to lower indoor concentrations of aldehydes, ketones, organic acids, free radicals and secondary organic aerosols. Activated carbon (AC) filtration is available for commercial buildings and is effective at removing ozone, and some VOCs, from supply air. Standard 62.1 from the American Society of Heating Refrigeration and Air Conditioning Engineers (ASHRAE) requires AC filtration for high ozone areas, but the standard is rarely implemented and is not enforceable unless adopted or incorporated by reference by the jurisdiction having code authority. ASHRAE is currently revising Standard 62.1 to make intentional ozone removal (e.g., activated carbon filters) more widespread in commercial buildings. No standards exist for AC filtration in residential buildings and its use is negligible (Siegel, 2007). A proprietary catalytic agent available from BASF is used in aircraft cabin air systems to remove ozone when aircraft fly at high altitudes or latitudes where stratospheric ozone concentrations can result in ozone entry into aircraft cabins. Without removal, ozone concentrations can reach 200 ppb in aircraft cabins, and that is after the removal that occurs by interfacial chemistry.

Charles Weschler has written: "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 [The associations between ozone concentrations measured outdoors and both morbidity and mortality may be partially due to indoor exposures to ozone and ozone-initiated oxidation products].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." (Weschler, 2006).

Acknowledgments

References

Apte, M.G., I. S. H. Buchanan, M. J. Mendell, 2008. Outdoor ozone and building-related symptoms in the BASE study. Indoor Air 2008; 18: 156–170

Buchanan, I. S. H., M. J. Mendell, A. G. Mirer, M. G. Apte, 2008. Air filter materials, outdoor ozone and building-related symptoms in the BASE study. Indoor Air, 18: 144–155.

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. *Atmospheric Environment*, DOI: 10.1016/j.atmosenv.2007.10.001.

Corsi, R. L. 2007. In *Emissions of texanol ester alcohol from latex paints: possible role of hydrolysis*, Workshop on Interfacial Chemistry in Indoor Environments, Berkeley, CA, Berkeley, CA.

Corsi, R.L. J. Siegel, A. Karamalegos, H. Simon, and G.C. Morrison, 2008. Personal reactive clouds: Introducing the concept of near-head chemistry. *Atmospheric Environment* 41 3161–3165

Destaillats, H.; Singer, B. C.; Lee, S. K.; Gundel, L. A., 2006. The effect of ozone on nicotine desorption from model surfaces: evidence for heterogeneous chemistry. *Environmental Science & Technology*.

Hodgson, A.T. and H. Levin, 2003a. Volatile Organic Compounds in Indoor Air: A Review of Concentrations Measured in North America Since 1990. LBNL Report 51715. Berkeley. http://eetd.lbl.gov/ied/pdf/LBNL-51715.pdf.

Hodgson, A.T. and H. Levin, 2003b. Classification of Measured Indoor Volatile Organic Compounds Based on Noncancer Health and Comfort Considerations. LBNL 53308. Berkeley. http://eetd.lbl.gov/ied/pdf/LBNL-53308.pdf.

Levin, H, 1985. A preliminary report on materials evaluation for a new office building, In Abstracts: Characterization of contaminant emissions from indoor sources A meeting held May 13-15, Chapel Hill, North Carolina. Sponsored by the United States Environmental Protection Agency.

Levin, H, 1987. "The Evaluation of Building Materials and Furnishings for a New Office Building." Practical Control of Indoor Air Problems, Proceedings of IAQ '87, May 18-20, 1987 (Atlanta: American Society of Heating, Refrigerating, and Air Conditioning Engineers, 1987), pp. 88-103.

Levin, H. 1989. "Building Materials and Indoor Air Quality," in, Hodgson, M. and Cone, J., eds., *Problem Buildings, Building Associated Illness and Sick Building Syndrome, State of the Art Reviews in Occupational Medicine*, Fall 1989.

Levin, H, 1999. Integrating Indoor Air Quality Considerations into Materials Life Cycle Assessment, Plenary Lecture, *Proceedings of Indoor Air '99.* Edinburgh, Scotland.

Levin, H., and Hodgson, A. T., 1996. "Screening and Selecting Building Materials and Products Based on Their Emissions of VOCs," in Tichenor, B. ed., *Methods for Characterizing Indoor Sources and Sinks* (STP 1287) Philadelphia: American Society for Testing and Materials.

Lundgren, B.; Jonsson, B.; Ek-Olausson, B., 1999. Materials emission of chemicals - PVC flooring materials. *Indoor Air-International Journal of Indoor Air Quality and Climate*, 9, (3), 202-208.

Morrison G, 2006. Presentation at "Healthy Buildings 2006," Lisbon, Portugal. June, 2006.

Morrison, G, 2007. Workshop on Interfacial Chemistry in Indoor Environments, July 17-18, 2007 University of California, Berkeley, CA. Report and Research Priorities. http://web.mst.edu/~gcm/References/WICIE%20final%20Report.pdf.

Morrison, G. C. 2007. *Workshop on interfacial chemistry in indoor environments*; National Science Foundation: Berkeley, CA.

Morrison, G, 2008. Interfacial Chemistry in Indoor Environments. In press, *Environmental Science and Technology*.

Morrison, GC and W.W Nazaroff, 2002. Ozone interactions with carpet: Secondary emissions of aldehydes, ES&T, 36, 2185.

Nazaroff, WW, and GR Cass, 1986. Mathematical Modeling of Chemically Reactive Pollutants in Indoor Air, *Environ. Sci. Technol*: 20: 924-934.

Nazaroff, WW and Weschler, CJ, 2004. Cleaning products and air fresheners: exposure to primary and secondary air pollutants. *Atmospheric Environment*, 38 2841–2865.

Nazaroff, W. W., Coleman, B. K., Destaillats, H., Hodgson, A., Liu, T.D. L., Lunden, M. M., Singer, B. C. and Weschler C. J. (2006) Indoor Air Chemistry: Cleaning Agents, Ozone and Toxic Air Contaminants. ARB Contract No. 01-336, California Air Resources Board and the California Environmental Protection Agency: California Air Resources Board, Sacramento, CA.

Norback, D.; Wieslander, G.; Nordstrom, K.; Walinder, R., 2000. Asthma symptoms in relation to measured building dampness in upper concrete floor construction, and 2-ethyl-1-hexanol in indoor air. *International Journal of Tuberculosis and Lung Disease*, 4, (11), 1016-1025.

Pandrangi, L.; Morrison, G. C. 2007. In *Ozone interactions with human hair: ozone uptake rates and product formation*, Air and Waste Management Association Annual Conference, Pittsburgh, PA,.

Pellizzari ED, Hartwell TD, Perritt RL, et al. 1986. Comparison of indoor and outdoor residential levels of volatile organic chemicals in five U.S. geographical areas. *Environ. Int.* 12: 619-623.

Pitts J.N., et al., 1985. Identification and measurement of nitrous acid in an indoor environment, *Atmospheric Environment* 19, 763

Pitts, J.; Biermann, H.; Tuazon, E.; Green, M.; Long, W.; Winer, A., 1989. Time-resolved identification and measurement of indoor air pollutants by spectroscopic techniques: gaseous nitrous acid, methanol, formaldehyde and formic acid. *JAPCA: Journal of the Air and Waste Management Association*, 39, (10), 1344-1347.

Segal-Rosenheimer, M.; Dubowski, Y., 2007. Heterogeneous ozonolysis of cypermethrin using real-time monitoring FTIR techniques. *Journal of Physical Chemistry C*, 10.1021/jp072937t.

Siegel, J.A. 2007. HVAC filtration and indoor surface chemistry, Workshop on Interfacial Chemistry in Indoor Environments, Berkeley, CA, 2007;.

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.

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.

Tichenor, B. ed., 1996. *Characterizing Sources of Indoor Air Pollution and Related Sink Effects.* STP 1287. West Conshohocken, PA: ASTM. www.astm.org.

Tichenor, B.,2007. "Criteria for Evaluating Programs that Assess Materials/Products to Determine Impacts on Indoor Air Quality" http://www.epa.gov/iaq/pdfs/tichenor_report.pdf.

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.

Weschler, C. J., 2004. New directions: Ozone-initiated reaction products indoors may be more harmful than ozone itself. *Atmospheric Environment*, 38, 5715-5716.

Weschler, C. J., Hodgson, A.T., and Wooley, J.D., 1992 "Indoor Chemistry: Ozone, Volatile Organic Compounds, and Carpets," *Environmental Science Technology*, 26, 2371–2377.

Weschler, C. J., Shields, H. C., and Naik, D. V. (1989) "Indoor ozone exposures," *J. Air Pollut. Control Assoc.*, 39, 1562-1568.

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, 6177-6184.

Weschler, C.J., 2000. "Ozone in Indoor Environments: Concentration and Chemistry." *Indoor Air* 10: 269-288.

Weschler, C.J. and Shields, H. 2004. New Directions: Ozone-initiated reaction products indoors may be more harmful than ozone itself. *Atmospheric Environment.* 38 5715–5716

Weschler, C.J., 2006. Ozone's Impact on Public Health: Contributions from Indoor Exposures to Ozone and Products of Ozone-Initiated Chemistry. *Enivronmental Health Perspectives.* 114, Number 10, 1489-1496. www.ehponline.org.

Wilson, M.J.G., 1968. Indoor air pollution, *Proceedings of the Royal Society*, Series A, 307, 215,

Wisthaler, A.; Tamas, G.; Wyon, D. P.; Strom-Tejsen, P.; Space, D.; Beauchamp, J.; Hansel, A.; Mark, T. D.; Weschler, C. J., 2005. Products of ozone-initiated chemistry in a simulated aircraft environment. *Environmental Science & Technology*, 39, (13), 4823-4832.