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Charles J. Weschler, PhD

Ozone, Hydroxyl Radicals and Indoor Environments; What Inspection and Remediation Pros Should Know

This week we welcomed Dr. Charles Weschler for a show about a topic of great interest to IEQ and restoration professionals. Restoration contractors are inundated with claims for equipment to help when fires, wildfires and other odor events affect indoor environments. What should practitioners know about ozone, hydroxyls, TI02 and other technologies when investigating or remediating indoor environments? We spoke to a renowned authority about these issues.

Charles J. Weschler -After completing his Ph.D. in Chemistry at University of Chicago (1974), Dr. Weschler did postdoctoral studies with Fred Basolo at Northwestern University. In 1975 he joined Bell Laboratories (Physical Chemistry Division) and was made a Distinguished Member of Technical Staff in 1986. He worked at Bell Labs and its successor institutions for twenty-five years. In 2001 he accepted positions at the Environmental & Occupational Health Science Institute, Rutgers University, and the International Centre for Indoor Environment and Energy, Technical University of Denmark, and in 2010 joined the Building Science department at Tsinghua University as an ongoing Visiting Professor. He continues in those positions. His research interests include chemicals in indoor environments, their sources, their chemistry, and their interactions with building occupants. From 1999-2005 Weschler served on the US EPA's Science Advisory Board. He has also served on four committees for the National Academy of Sciences, Engineering, and Medicine. From 2012 to the present, he has been an advisor to the Sloan Foundation's program on Chemistry in Indoor Environments. He was elected to the International Academy of Indoor Air Sciences in 1999 and received the Pettenkofer Award, its highest honor, in 2014. Weschler has also received the 2017 Haagen-Smit Prize from Atmospheric Environment; been made "Distinguished Visiting Professor" at Tsinghua University (2018); awarded "Doctor Technices Honoris Causa" from the Technical University of Denmark (2018); and was elected a Fellow of the American Association for the Advancement of Science (2020). His h-index is 69 (Web of Science) and 79 (Google Scholar). http://eohsi.rutgers.edu/eohsi-directory/name/charles-weschler/

Nuggets mined form today's episode:

- Ozone, because it can be easily measured, has been studied by scientists since the 1860's.
- Study of OH is much more recent because they are much more difficult to measure. Measuring OH requires sophisticated and very costly equipment.

What piqued your interest in ozone? While working at Bell Labs in the 1980s, Charlie suspected that damage to telephone switch gear in Bell's Atlanta, GA office might be ozone related. Using an ozone meter, Charlie investigated and was able to confirm his theory.

Background info on ozone and hydroxyls:

- The majority of O3 found indoors is from outdoor sources. Normal indoor levels of ozone are 5-20 PPB. Normal indoor levels of O3 are considered livable.
- The OH found indoors is from indoor sources, ozone reacting with alkenes and gases. Indoor OH levels are generally so small that they are measured in molecules per cubic centimeter $4 \text{ X } 10^{-6}$ (range from 100,000-1,000,000). Normal OH levels indoors are considered livable.
- Conversion for PPB and molecules per cubic centimeter $2.46 \text{ X } 10^{10}$
- O3 reacts with carbon-carbon double bonds
- Carbon-carbon double bonds found in approximately 10% of organic substances indoors.
- O3 + alkenes generate OH
- OH is much more reactive than O3, wanting to become water it reacts with almost all organics. OH increases the oxygen to carbon ratio in the organics it reacts with, making substances more water soluble. OH typically pulls off a hydrogen, leaving an alkyl radical that then reacts with O2 to produce alkyl peroxy radicals.

- OH reacts with organics much, much faster than O3 reacts with organics (example of isoprene). OH doesn't get far before it reacts, OH rarely gets to surfaces.
- Geosmin is the pleasant smell of soil and that earthy scent that comes with and after rain.
- At typical indoor concentrations, O3 reacts with isoprene too slowly to compete with typical air change rates. (The molecules are swept out of indoor air before they can react with one another.) OH reacts with isoprene fast enough to compete with air change rates.
- Cyclic organic compounds formed by the addition of ozone to an alkene's double bond are also called primary ozonides.
- Isoprene is a metabolic byproduct. Isoprene is always found in occupied spaces indoors. Indoors when we exercise or eat, isoprene levels go up. Isoprene is ½ a terpene. [Isoprene, or 2-methyl-1,3-butadiene, is a common VOC _with the formula $CH_2=C(CH_3)-CH=CH_2$. In its pure form it is a colorless volatile liquid. Isoprene is an unsaturated hydrocarbon. It is produced by many plants and animals (including humans).]
- Methacrolein, or methacrylaldehyde, is an unsaturated aldehyde. It is a clear, colorless, flammable liquid. Methacrolein is one of two major products resulting from the reaction of isoprene with OH in the atmosphere, the other product being methyl vinyl ketone. Wikipedia.
  [Methacrolein was used to study the effect of parts per billion levels of oxidation products on human eye blink frequency.
- The half-life of OH is very short, 10-50 milliseconds. Alkyl peroxides and hydroperoxides are formed in its initial reactions. Hydroperoxides may have adverse health effects.
- O3 is removed indoors primarily by surface chemistry.
- OH is removed indoors almost exclusively by gas-phase chemistry.
- Very few OH molecules ever make it to a surface.
- Total OH reactivity (s-1) -- define -- recent estimates & measurements indoors
- Total OH reactivity of 50 s-1 equivalent to an OH half-life of 0.014 s

Outdoors the combination of OH and rain has been described as Mother Nature's vacuum cleaner. Indoors we have OH, but we don't have rain.

Is the ozone the same when produced by corona discharge or UV lights? The ozone is the same, the difference is that when ozone is produced with corona discharge, nitrogen oxides are produced. Ozone without byproducts can be produced with UVC ozone producing bulb and bottled oxygen. Nitrogen oxides and nitrogen dioxide are also combustion products.

Ion Generators? Ion generators impart a charge on particles, which increase the rate at which they deposit on indoor surfaces. A Chinese study on ion generators in which PM <2.5 and biomarkers were studied found that ion generators decreased PM <2.5 and that biomarkers indicative of oxidative stress increased (Liu et al. Negative ions offset cardiorespiratory benefits of PM2.5 reduction from residential use of negative ion air purifiers, Indoor Air, 2021). These biomarker results are not well understood. Oxidative stress is a health concern.

The health impact of inhaling ozone depends on the concentration and time. Simply inhaling ozone before exercise will decrease lung function. Current ozone exposure limits are based primarily upon epidemiology studies conducted using ozone measurements from outdoor monitoring sites. O3 exposure is shown to increase both short-term and long-term hospitalizations, morbidity and mortality.

I have personally seen a fog, or cloud develop in a room where the hydroxyl machine is running. I've heard this described as "ultrafine particles". Of what are these particles comprised and do they pose health risks either while airborne or after settlement? I have not personally seen these fogs. Ultrafine Particles (UFPs) are 100 nanometers or $1/10^{th}$ of a micron aerodynamic diameter. They have been made in the lab by combining limonene and ozone. The photocatalysis of peroxide (H202 Vapor) might also create them. Depending on their chemical composition, UFPs can be harmful when breathed deeply into the lungs; some even are small enough to enter the bloodstream. Whether or not a fog occurs likely depends on how OH is being generated. I would only be making an educated guess.

What are the health effects of exposure to hydroxyls? I am not aware of any good data on health effects of OH exposure at elevated concentrations (i.e., higher than what occurs naturally outdoors). Adding hydroxyls to indoor air results in creation of quite reactive molecules such as: RO2 (organic peroxy radicals), alkyl peroxides, and hydroperoxides which have the potential to contribute to oxidative stress when inhaled. Reactions among ROO radicals increase the oxygen to carbon ratio for organics that are present. Some will stay gases that can be removed with ventilation. As the Oxygen to Carbon ratio increases the vapor pressure decreases and this causes sorption of some of the oxidation products onto surfaces which may become reservoirs. Many oxidation products are benign some are offensive. Different peroxides pose different potential health risks. Dr. Weschler advises. It's a messy issue; pay attention to the oxidation mechanism.

Would you stay in your home with a hydroxyl machine operating? Due to the precautionary principle he would not. Presumably OH would increase in the home while the device is operating and we don't know the magnitude of this increase.. [The precautionary principle is a broad epistemological, philosophical and legal approach to innovations with potential for causing harm when extensive scientific knowledge on the matter is lacking. It emphasizes caution, pausing and review before leaping into new innovations that may prove disastrous. Wikipedia]

Efficacy of hydroxyl radicals on fungi, bacteria and virus? I'm not an expert on the impact of OH on microbes. My best guess is that OH as a gas would be unable to collide with a microbe in sufficient quantity to be lethal. OH initiated chemistry such as creation of stable hydroperoxides could be lethal to microbes.

Would you agree with Dr. Delphine Farmer who stated that use of Ozone or Hydroxyls indoors changes indoor chemistry and if so what about potential health effects of these changes? O3 is a gas that also reacts with surfaces and gas-phase species. OH as a gas will create other oxidizing products, some of which react with surfaces. The deliberate use of ozone or OH indoors increases the oxidation chemistry that occurs indoors resulting in changes to the indoor chemistry. In regard to health hazards, it depends upon toxicity and concentration -- a universal answer.

Can you comment on chlorine dioxide? Chlorine dioxide has been used for multiple remediation strategies including addressing terrorist use of anthrax. Dr. Rich Corsi studied the effect of CLO2 on building materials. Chlorine dioxide reactions with indoor materials during building disinfection: surface uptake
Heidi Hubbard[1], Dustin Poppendieck, Richard L Corsi

Can hydroxyl output of a hydroxyl machine be measured or quantified in real time? Only with very expensive equipment (e.g., a FAGE instrument). Refer to study: N Carslaw , L Fletcher , D Heard, T Ingham , H Walker, Significant OH production under surface cleaning and air cleaning conditions: Impact on indoor air quality

Hydroxyl measurement studies? In one study using a FAGE instrument (N Carslaw , L Fletcher , D Heard, T Ingham , H Walker, Significant OH production under surface cleaning and air cleaning conditions: Impact on indoor air quality) ozone and limonene were used to create hydroxyl radicals in a chamber. There was a 10-100 X increase.

Do hydroxyls remain within the generating device or do they leave the generating device? When hydroxyls are formed with UVC light and titanium dioxide, the hydroxyls are created on the titanium dioxide by surface chemistry and remain in the device.

Byproducts of oxidation can create methyl cyanide, bromomethane and formaldehyde; can hydroxyls create these same hazardous gases? Similar oxidation initiated chemistries can create similar products.

Final Comment from Dr. Weschler:
Ozone and OH indoors is a fascinating subject. The more we understand the better we can answer questions regarding the use of these products for remediation.

Z-Man signing off

Trivia:
Name the combination of terms by which hydroxyl radicals were originally called?

Answer:
Open Air Factor
Discovered by the UK's Ministry of Defense in the early 1960s, hydroxyl radicals (originally called the 'Open Air Factor', often just called 'hydroxyls') are highly reactive molecules of oxygen (O) and hydrogen (H); their chemical formula is OH.