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Ozone removal by occupants in a classroom

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HIGHLIGHTS

- Ozone deposition velocities were measured in a real classroom.
- Velocities agree well with lab experiments.
- Ozone indoors may predominantly be removed by humans.
- Avoiding product exposure means reducing ozone concentration.

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ABSTRACT

Ozone concentrations were measured in a classroom with and without occupants, with the purpose to quantify effects on indoor O_3 concentrations. The teacher and 24 11-year old pupils each removed O_3 at a rate, first order in O_3, corresponding to a rate constant of $(2.5 \pm 0.6) \times 10^{-5}\ s^{-1}$ in the present locality and to a deposition velocity of 0.45 cm s^{-1}. The O_3-removal caused by the occupants was approximately 2.6 times larger than that of the available surfaces belonging to the classroom and its furniture. Observation of 6-methyl-5-hepten-2-one and 4-oxopentanal at maximum concentrations of 0.2 ppb and 0.7 ppb, respectively, suggested squalene from human skin oil as a reactive, ozone-consuming substance. There are indications of a source of 4-oxopentanal in the classroom, even some time after the pupils left for the day. The work presented is important for a proper description of indoor exposure, both to ozone itself and some of its reaction products when trying to quantify relations between exposure and health effects.

1. Introduction

Early investigators of air pollution were often interested in outdoor O_3 levels in connection with its negative influence on human health, vegetation and property (Bernstein, 2004; Cape, 2008; Massey, 1999) while indoor O_3 levels were largely overlooked. Still, measurements made in the 1970s indicated that indoor O_3 could cause significant human exposure (Thompson, 1971; Shair and Heitner, 1974). Since then, several accounts in the literature show that O_3 is transported indoors from the outside and that out- and indoor concentration follow each other to some extent (Weschler, 2000 and references therein). Measurements in buildings without O_3 sources, e.g. private dwellings and hospitals showed O_3 indoor-to-outdoor (I/O) concentration ratios from 0.05 to 0.85 but most often falling in the range from 0.2 to 0.7 (Weschler, 2000). The actual value of the I/O ratio depends on factors such as the building air exchange rate (AER), the type of ventilation system (natural or mechanical), ventilation filter material, air-tightness of the building and the nature of indoor surfaces (Weschler, 2000).

Indoor O_3 is partly removed by reaction with, and decomposition on various surfaces (e.g. Schripp et al., 2012; Weschler, 2011) and enhanced surface reactivity with O_3 has been observed for terpenes, e.g. limonene and 3-carene (Springs et al., 2011), α-terpineol (Shu and Morrison, 2011) and squalene (Wells et al., 2008). The rate at which O_3 is removed by surfaces is most often proportional to the concentration of O_3 and to a first order rate coefficient k, expressed by Equation (1).

$$k = \sum V_{di} S_i / V \qquad (1)$$

S_i is the area of surface i with a characteristic deposition velocity v_{di}, and V is the total volume of the locality under consideration. Mass transfer may be the limiting process for very active surfaces. Outside the laboratory, it is often only possible to observe k, i.e. the

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sum of the effect of all surfaces present. A summary of removal rate coefficients was presented by Weschler (2000); the values range from 1.4 h^{-1} to 7.6 h^{-1} (0.0004 s^{-1} to 0.002 s^{-1}) for real and laboratory conditions. Both measurements in the laboratory and modeling studies showed consistency in the v_d-values, ranging from 0.0007 cm s^{-1} to 0.8 cm s^{-1}, for materials found in typical rooms/houses, including so called "green" building materials (Lee et al., 1999; Morrison, 1999; Klenø et al., 2001; Grøntoft and Raychaudhuri, 2004; Nicolas et al., 2007; Hoang et al., 2009; Lamble et al., 2011; Schripp et al., 2012).

Indoor reactions between O_3 and organic compounds in the gas phase have recently obtained recognition (e.g. Weschler and Shields, 1997; Nazaroff et al., 2003; Weschler, 2004a, 2011). Certain unsaturated organic compounds may react with O_3 at rates comparable to or faster than the AER of a building. Thus, they are potentially important for indoor air quality (IAQ) since products of indoor air chemistry involving O_3 are sometimes suggested to be more harmful than O_3 itself (Weschler, 2004b; Weschler et al., 2006; Carslaw et al., 2009; Wolkoff et al., 2013). Ozone-initiated air chemistry may also be an indoor source of free radicals that, in turn, may produce oxygenated, often multifunctional stable compounds such as carbonyls, carboxylic acids, alcohols, and other species (Fischer et al. 2013). Indoor O_3 exposure has been estimated to give 45–75% of total exposure (Weschler, 2006). Chen et al. (2012) have done an assessment of the short-term effect on mortality of an O_3 increase and found that the observed mortality difference between various cities can partly be attributed to changes in the concentration of O_3 indoors resulting from differences in ventilation rates.

Indoor O_3 may be reduced by filtration (active carbon filters) of supply air or in a passive way by intentional introduction of materials, highly reactive with O_3 while giving few products with potential to affect the IAQ (Kunkel et al., 2010). However, one of the most efficient sinks of indoor O_3 is humans. Evidence has been presented for indoor O_3 removal by humans or by human surrogates (Weschler et al., 2007; Rim et al., 2009; Wisthaler et al., 2005; Tamás et al., 2006), by worn clothing fabric (Coleman et al., 2008) and even by human hair (Pandrangi and Morrison, 2008).

Human skin is covered by a layer of lipids consisting of, among other compounds, unesterified fatty acids and squalene (Nicolaides, 1974). Squalene represents approximately 10% and the fatty acids about 25% of human skin lipids. The level of squalene was found to increase from adolescence to maturity and then decrease significantly at old age (Passi et al., 2002). These low-volatility compounds contain unsaturated C=C bonds that make them highly reactive with O_3. Fruekilde et al. (1998) have established acetone, 4-oxopentanal (4-OPA), 6-methyl-5-hepten-2-one (6-MHO) and geranyl acetone as the main reaction products from the squalene/O_3 reaction. The rate coefficient for O_3 reaction with 6-MHO was determined by Grosjean et al. (1996) to 3.9×10^{-16} cm^3 $molecule^{-1}$ s^{-1} at 289 K. Fruekilde et al. (1998) determined an upper limit of the rate coefficient of 4-OPA with ozone to 5×10^{-20} cm^3 $molecule^{-1}$ s^{-1}.

A recent study by Wisthaler and Weschler (2010) using Proton Transfer Reaction–Mass Spectrometry to quantify the volatile reaction products gave information about the O_3 reaction with human skin lipids and squalene in particular. The presence of two adult individuals in a reactor furnished as an office caused a reduction in the O_3 concentration from 32 to 17 ppb during a 4-h stay and a considerable increase of the 6-MHO and 4-OPA concentrations. Studies of O_3 reacting with surface-bound squalene resulted in a reaction probability of $(45 \pm 14) \times 10^{-5}$ (Wells et al., 2008) indicating a substantial increase in reactive collisions, compared to the gas phase. Also the previously determined reaction products were confirmed in this study and found both in the gas phase and on surfaces.

Wolkoff et al. (2013) exposed mice to, among other compounds, 4-OPA and 6-MHO and derived human reference values for both sensory irritation and airflow limitation. The sensory irritation reference value given for 6-MHO is 0.3 ppm and the airflow reference value is 0.5 ppm. For 4-OPA only an airflow reference value of 0.03 ppm is given.

This article concerns measurements of indoor O_3 in a Swedish classroom during normal workday conditions and relates indoor O_3 losses to occupancy.

2. Material and methods

2.1. Location and measurements

Indoor O_3 and volatile organic compounds (VOC) were measured in an operating classroom of a primary school located in a semi-rural area of southwestern Sweden.

There were normally 24 pupils, 11 years of age and one teacher in the classroom, but during some lessons only half of the class was present. The activities followed a weekly schedule from 8.15 with short breaks between lessons, a lunch break at 12.10 and normally, one lesson after lunch. The work finished at 13:40, except one day that ended at 14:20. The classroom with a volume of 182 m^3 is accessed by either of 2 doors and has 4 large windows facing east in the long side wall of the rectangular room. The doors were normally closed and windows were always closed during the measurements. The flooring is made of vinyl, walls are painted with acrylic latex paint and the furniture is steel framed with chipboard and laminated surfaces. The floor was mopped at around 7 each morning.

Supply air devices in the form of two perforated ducts are located below the ceiling and run parallel to the long walls of the room, one at 1/4 and the other at 1/2 of the short wall length away from the window wall. The extract air devices are located in the opposite long wall, just beneath the ceiling and in the far corner of the room. The ventilation in the classroom was turned on at 7.15 at the latest and off at 16.00 at the earliest during the investigation.

The measurement of O_3 was made in the main extract air duct, some distance downstream of the point where the ducts from the extract devices join to form the main duct. A traverse across the duct, perpendicular to the flow direction and using the O_3 monitor as detector, showed no systematic concentration differences over the cross section where the subsequent measurements were made. This implies that the O_3 measurements are representative for a well-mixed classroom. The VOC and CO_2 measurements were done in the classroom, 1.8 m above floor level below one of the extract air devices.

Ozone was monitored continuously by UV absorption (Environment SA, O_3 42 M) and data were recorded as 1-min averages. The instrument has a detection limit of 1 ppb and an accuracy of 4% of the displayed value. The ozone instrument was calibrated against a standard reference photometer at the Bureau International des Poids et Mesures, Paris, France. Volatile organic compounds were collected in duplicates on Tenax TA adsorbent tubes by active sampling using a pump flow of 100 mL min^{-1} during 30 or 60 min. Carbon dioxide was monitored continuously by a Q-Trak IAQ Monitor model 8551 and recorded as 1 min averages.

The Tenax tubes were stored at −18° C and analyzed within 24 h. The tubes were thermally desorbed (Perkin Elmer TurboMatrix 650, 7 min, 275 °C) and analyzed by gas chromatography. The gas chromatograph (GC) was an Agilent 6980N equipped with one Agilent 5975C mass selective detector in electron impact mode for compound identification and one flame ionization detector for simultaneous quantification. The GC was equipped with a BPX-5 (SGE) capillary column (5% phenyl polysilphenylene-siloxane