Personal reactive clouds: Introducing the concept of near-head chemistry

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Abstract

The "personal cloud" effect and its impact on human exposure to airborne pollutants are well documented. A great deal is also known regarding indoor air chemistry, particularly as related to ozone reactions with mono-terpenes. In this paper we hypothesize the presence of personal *reactive* clouds that result from ozone reactions with terpenes and terpenoids emitted from personal care products. A proof of concept assessment was completed based on reaction rates between ozone and five reactive organic compounds that are found in personal care products. Screening experiments were also completed 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. Additional research is needed to characterize reaction products and health consequences associated with near-head chemistry and associated personal reactive clouds.
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1. Introduction

Lotions, perfumes and other scented personal care products are applied to the head region and often release terpenes and terpenoids that can participate in gas-phase reactions with ozone. Since the fragrance concentration near the wearer is most certainly higher than that near other occupants, the wearer may experience higher levels and a different composition of reaction byproducts. But can this near-head chemistry lead to elevated and potentially harmful levels of ozonides, carbonyls and mono- and bi-radical species in the breathing zone of those who wear such products?

The products of ozone reactions with terpenes, terpenoids and other unsaturated compounds released from fragranced personal care products are likely to include primary and secondary ozonides, Criegee bi-radicals, various other radical species (hydroxyl, alkoxy, hydroperoxy radicals), hydrogen peroxide, hydroperoxides, formaldehyde and heavier aldehydes, acetone and heavier ketones, formic acid and heavier carboxylic acids, multi-functional oxidation products with carbonyl, carboxylate and/

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or hydroxyl groups and secondary organic aerosols (Nazaroff and Weschler 2004, and references presented therein). Heavy organic reaction products can self-nucleate or condense onto existing particles in air, and several researchers have shown that ozone/terpene reactions lead to elevated particulate mass concentrations in smog chambers and in actual indoor environments (Rohr et al., 2003; Sarwar et al., 2004; Weschler and Shields, 1999). Sarwar et al. (2004) observed a $2\,\mu g\,m^{-3}$ increase in the mass concentration of particles with diameters less than $0.7\,\mu m$ when a small amount of perfume was exposed to just 15 ppb of ozone in an $11\,m^3$ ventilated chamber.

There is some evidence that the products of ozone reactions with terpenes and terpenoids may have adverse impacts on the eyes and respiratory system. For example, Kleno and Wolkoff (2004) observed increased eye blink frequency when human subjects were exposed to ozone and limonene, relative to only ozone or limonene, and concluded that products of limonene/ozone reactions may cause eye irritation. Clausen et al. (2001) reported significant sensory irritation (33% reduction of mean respiratory rate) in mice exposed to the products of limonene/ozone reactions. Similar results were reported for α-pinene/ozone reactions (Wolkoff et al., 2000).

The potential importance of near-head chemistry is highlighted by the prevalence of personal care products. For example, in 2002, the annual sales in the cosmetic market solely for the member states of European Union rose by 3.4% to a total of €54.2 (US $72) billion (European Cosmetic Toiletry and Perfumery Association, 2002).

Since reactive terpenes and ozone are present in the breathing zone of a person wearing fragrances, homogeneous oxidation will occur. The question is one of extent of reaction, and whether measurable changes in the composition of air occur in the short period of time that air passes through the breathing zone. In this paper we demonstrate that ozone can be consumed by these reactions in the brief residence time of the breathing zone, and that measurable increases in reaction products are observed.

2. Screening calculations

A screening model was developed to explore the extent of ozone-initiated reactions in the breathing zone for several unsaturated compounds that are used in personal care products. The percent ozone depletion due to homogeneous bi-molecular reactions was used as a metric for extent of reaction. A Lagrangian framework was employed to follow a well-mixed parcel of air, i.e., fixed mass of air, with an initial ozone concentration and constant elevated concentration of a fragrance compound for a short time period in the breathing zone. The corresponding expression for the time rate of change of ozone in the air parcel is given by Eq. (1). Integration of Eq. (1) to solve for the ozone concentration as a function of time yields Eq. (2)

$$\frac{dC_{O_3}}{dt} = -k_{rxn}C_f C_{O_3}, \tag{1}$$

$$\frac{C_{O_3}}{C_{O_3,0}} = e^{-k_{rxn}C_f t_b}. \tag{2}$$

Here, C_{O_3} is the ozone concentration in the breathing zone (ppb), $C_{O_3,0}$ is the ozone concentration in the Lagrangian air parcel as it enters the breathing zone (ppb), t_b is time in the breathing zone (s), C_f represents the concentration of the reactive fragrance compound in the breathing zone (ppb) and k_{rxn} is a bi-molecular rate constant $(ppb^{-1}s^{-1})$. The time derivative represents the rate of molar depletion of ozone $(ppb\,s^{-1})$, which in turn equals the rate of production of primary ozonides $(ppb\,s^{-1})$, i.e., the initial reaction product. Since fragranced products are meant to be detected by the consumer, it seems logical that their concentrations in the breathing zone, C_f, will be at least as great as their odor thresholds for some period of time. We have assumed in this screening analysis that the terpenes or other reactive species exist at a high concentration (C_f) relative to ozone in the breathing zone, and can be assumed constant over time t_b. This is a reasonable assumption in indoor environments, since ozone concentrations should be much lower than the odor thresholds of many fragrance compounds. For example, indoor ozone concentrations range from a few ppb to approximately 50 ppb in most residential settings (Weschler, 2000). These mixing ratios are far below the odor thresholds of all but one fragrance compound (α-terpineol), and far below the odor threshold of the most dominant fragrance compound (linalool alcohol), described below.

Numerous fragrance chemicals were screened to evaluate those that are likely to produce the highest exposure to reaction products. We identified 98 fragrance compounds which contain non-aromatic

C $=$ C bonds likely to react with ozone. Published reaction rate constants with ozone have only been experimentally determined for 12 of the 98 compounds, primarily terpene/ozone reactions since they have significance in outdoor atmospheric chemistry. The odor threshold could only be found for five of the 10 remaining compounds. In this analysis we have selected five chemicals that are commonly used in fragrance and personal care products to explore the potential extent of near-head chemistry: citronellol, d-limonene, linalool alcohol (linalool), α-pinene and α-terpineol. Reaction rate constants were obtained from the published literature (Atkinson et al., 1990, 1995(α-pinene and linalool); Ham et al., 2006 (citronellol); Shu and Atkinson, 1994 (d-limonene); Wells, 2005 (α-terpineol)).

The concentration of each chemical was varied from 0 to 5000 ppb. This range encompasses all of the known odor thresholds for the chemicals listed above. For simplicity, only the effects of individual compounds were considered, i.e., we neglect the net effects of multiple fragrance compounds that are more typical of personal care products. We assumed that a parcel of air remains in the near-head region for 1 s ($t_b = 1$ s), based on typical head dimensions and measured air speeds in the breathing zone of approximately $10-20$ cm s^{-1} (Sørensen and Voigt, 2003). It is possible that recirculating zones located above the shoulders, e.g., as predicted by Sørensen and Voigt (2003) for natural convection flows, can lead to longer reaction times and subsequent accumulation of reaction byproducts. However, we have simplified the screening analysis by neglecting such features.

Application of Eq. (2) results in percent ozone reductions as presented in Fig. 1. Relatively low ozone concentration reductions were predicted for all of the compounds, particularly if the analysis is focused on concentrations just near the odor thresholds. However, although fragrances account for a modest percentage change in ozone individually, combined they may contribute to a substantial reaction extent in the breathing zone. It is important to recognize that compounds such as d-limonene and other terpenes are often added to perfumes as top notes that evaporate relatively quickly, e.g., within 5–10 min of application, and as such their contributions to near-head chemistry change rapidly and are limited in duration. However, the study of a model perfume suggested that peak linalool evaporation rates from skin occur
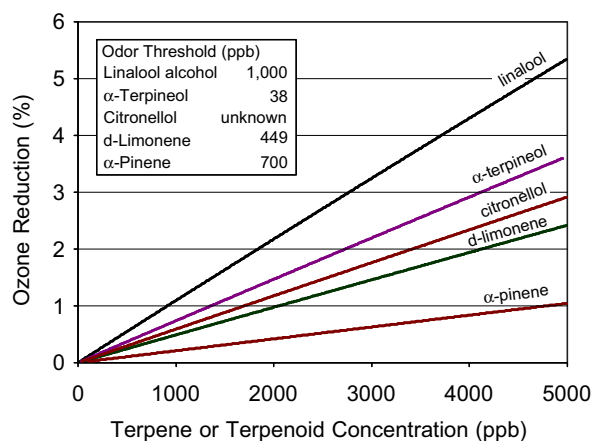

Fig. 1. Predicted reductions in ozone concentrations in the breathing zone as a function of reactive organic compound concentration. Odor thresholds were obtained from several sources: linalool (Cometto-Muniz et al., 1998), d-limonene and α-pinene (Grimsrud et al., 1975), α-terpineol (Mølhave et al., 2000).

15–75 min after product application, and were still detected 7.25 h following application (Letizia et al., 2003, and references described therein). As such, the most reactive compound considered as an example in this paper may continue to contribute to near-head chemistry long after its application.

The results described herein suggest that linalool may play a relatively major role as a precursor to near-head chemistry and associated byproducts. The percent reduction in ozone concentration at 5 ppm (5× the odor threshold) for linalool was estimated to be greater than 5%. Linalool is a terpenoid alcohol with a floral scent, and is common in a wide range of household fragrance products, including decorative cosmetics, fine fragrances, shampoos, toilet soaps and other toiletries, household cleaners and detergents (Letizia et al., 2003). Cooper et al. (1992) observed linalool in 21 of 31 products tested, including soaps, colognes and perfumes. The worldwide use of linalool in fragrances has been reported at greater than 1000 metric tons per year (Bickers et al., 2003). A major oxidation product associated with linalool is 5-methyl-5-vinyl-tertahydrofuran-2-ol (MVT), with a molar yield of MVT for the linalool/ozone reaction of 0.85 (Calogirou et al., 1999). Additional products include formaldehyde, acetaldehyde, acetone, hydroxyl-dialdehydes, hydroxyl-carboxylic acids and 4-oxopentanal (from reactions between MVT and hydroxyl radicals) (Calogirou et al., 1999).

3. Preliminary experiments

Five experiments were completed to verify the potential for near-head chemistry. The experimental system consisted of a 28-L electropolished stainless steel chamber designed for easy placement over the head of a human subject. The system was open at the bottom, allowing for an air exchange rate of $1-2\,min^{-1}$ in the absence of a human subject. Ozone was generated in a mixing chamber using a Prozone™ (model PZ 6 Air) ozone generator and injected at 70 ppb in air through a perforated Teflon™ tube that extended across one wall of the chamber, thus distributing the air flow around one side of the head at approximate nose level. Ozone was measured using a single-cell UV-absorbance ozone detector (2B Technologies, model 202) connected to a sample port and distributed Teflon™ collection tube on the opposite side of the chamber from ozone injection. A sample port was also used to draw air samples for continuous analysis of ultra-fine particles using a condensation nuclei counter (TSI P-TRAK™). Temperature, relative humidity and carbon dioxide concentrations were also measured in the breathing zone using a Q-TRAK™ (TSI model 8551).

Three different perfumes and two hairsprays were tested. For each, a sequence involving four steps was employed: Step 1 = background measurements in the absence of a human subject, Step 2 = measurements with a human subject in the absence of personal care products, Step 3 = repeat of Step 1, Step 4 = measurements with a human subject, approximately 20–30 min (measured by digital timer) after the subject had applied a personal care product. The product was applied outside of the laboratory, in a room located 70 m from the laboratory and in a part of the building with a separate HVAC system. Each product was applied by spray and involved two to three instantaneous pumps of the applicator, typical of such products. The 20–30 min time period from product application to chamber test was likely sufficient to evaporate a large fraction of many top notes. Had this time been shortened the degree of near-head chemistry would presumably have been greater than reported here. Each step required approximately 30 min for completion. Increases in mean particle measurements (Step 2 minus Step 1; Step 4 minus Step 3) were compared to examine relative increases in ultra fine particle formation due to gas-phase chemistry involving ozone and components of the personal care products.

The results of these preliminary experiments confirm the potential for near-head chemistry. Statistically significant ($\alpha = 0.05$) increases in ultra fine particle number concentrations, corrected for background measurements as described above, were observed for two of the three perfumes and both hairsprays. The concentration increases ranged from 1000 to over $3000\,cm^{-3}$. The percent increases in particle number concentration following the use of a personal care product, i.e., relative to the particle concentration in the empty chamber just prior to product usage, were 12% (not statistically significant), 23% and 210% for the three perfumes and 7% and 28% for the two hairsprays. Because particle formation generally occurs after the formation of short-lived intermediates, e.g., hydroxyl radicals, ozonides, carbonyls and carboxylic acids, it is likely that these species are also present. Decreases in ozone concentrations were not observed, possibly because perfume compounds were found to absorb UV light at the same wavelengths as ozone, and/or because the small change in ozone concentrations may have been within the accuracy ($\pm 1.5\,ppb$) of ozone monitors employed in this study.

4. Summary

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, and that corresponding reaction products may be exposure relevant. However, the authors acknowledge the screening nature of this study, potential for uncertainties and need for more detailed research. Future research should consider the complex mixtures that characterize most personal care products. Ozone will also react heterogeneously with residual fragrance compounds on the skin, hair and clothing, each of which could lead to additional reaction products in the breathing zone. Additional research is needed to characterize reaction products and health consequences associated with near-head chemistry and associated personal reactive clouds.

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