

PERSONAL REACTIVE CLOUDS: INTRODUCING THE CONCEPT OF NEAR HEAD CHEMISTRY

A Karamalegos¹, H Simon¹, P Zhao¹, G Morrison², J Siegel¹, and RL Corsi^{1,*}

1 Department of Civil, Architectural and Environmental Engineering, University of Texas, Austin, Nation of Texas USA

2 Department of Civil, Architectural and Environmental Engineering, U. of Missouri-Rolla

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 many personal care products. A screening assessment was completed based on reaction rates between ozone and four reactive organic compounds that are commonly employed in personal care products. Reaction times (for homogeneous reactions in the breathing zone) were assumed to be on the order of 1 s. Screening results suggest the potential for observable decreases in ozone concentration and the subsequent presence of reaction products in the human breathing zone due to near head chemistry.

INDEX TERMS

Ozone, Terpenes, Chemistry, Breathing zone, Reaction products

INTRODUCTION

Lotions, perfumes and other scented personal care products are applied to the head region and often contain elevated levels of terpenes and terpenoids that can participate in ozone-initiated reactions. The resulting near head chemistry may lead to elevated levels of ozonides, carbonyls, and mono- and bi-radical species in the breathing zone of those who wear such products. Sarwar *et al.* (2004) used an initial ozone concentration of 15 ppb in the presence of a perfume in a large chamber with an air exchange rate of 0.83/hr. The perfume contained limonene, α -pinene, B-pinene, and 3-carene. When reacted with products emitted from the perfume the ozone concentration in the chamber dropped significantly, and the concentration of particulate matter with diameters less than 0.7 μm increased by 2 $\mu\text{g}/\text{m}^3$. The potential importance of near head chemistry is highlighted by the increasing prevalence of personal care products in today’s society. The annual sales figure for the worldwide cosmetic industry is around \$122 billion. 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 (\$72) billion. (European Cosmetic Toiletry and Perfumery Association 2002).

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 reaction. Similar results were reported for ozone/ α -pinene reactions (Wolkoff *et al.* 1999). However, Wilkins *et al.* (2003) later reported that the irritation was lower as relative humidity was increased, indicating that some chemical intermediates associated with ozone/terpene reactions may react with water vapor to yield less irritating products. This finding is potentially relevant in the humid breathing zone of humans.

The mechanism for ozone reactions with the C=C bond in alkenes was established by Criegee (1975). Ozone breaks the C=C bond to form a primary ozonide which then decomposes into Criegee biradicals and carbonyls. Subsequent reaction mechanisms lead to products that include a range of free radicals, carbonyls, and carboxylic acids, depending on the nature of the reactive organic compound. Given sufficient time, heavy organic reaction products can 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

* Corresponding author email: corsi@mail.utexas.edu

(Rohr *et al.* 2003, Sarwar *et al.* 2004, Weschler *et al.* 1999).

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 commonly 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 with initial ozone concentration and constant elevated concentration of 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 Equation 1. Integration of Equation 1 to solve for the ozone concentration as a function of time yields Equation 2.

$$\frac{dC_{O_3}}{dt} = -k_{rxn} C_f C_{O_3} \quad (1)$$

$$\frac{C_{O_3}}{C_{O_3,0}} = e^{-k_{rxn} C_f t_b} \quad (2)$$

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, 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-1s-1). The time derivative represents the rate of molar depletion of ozone (ppb/s), which in turn equals the rate of production of primary ozonides (ppb/s), i.e., the initial reaction product. We have assumed in this screening analysis that the terpenes or other reactive species exist at high concentration (C_f) relative to ozone in the breathing zone and, for purposes of determining ozone depletion, can be assumed constant over time t_b .

To complete this screening analysis, four parameters are required: k_{rxn} , t_b , C_f , and $C_{O_3,0}$.

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. The reaction rate constants with ozone have only been experimentally determined for ten of the 98 compounds, primarily ozone/terpene reactions since they have significance in outdoor atmospheric chemistry. The odor threshold could only be found for four of the ten remaining compounds. As such, for this analysis we focused on the four compounds listed in Table 1, along with their corresponding reaction rate constants and odor thresholds.

Table 1. Reaction rate constants and odor thresholds for four common fragrance compounds

Compound	k_{rxn} (1/ppb-s) 296 °K	Odor threshold (ppb)	References
allyl alcohol	3.5×10^{-7} *	1400	k_{rxn} : Grosjean <i>et al.</i> 1993 Odor: New Jersey Dept. of Health 1998
d-limonene	4.9×10^{-6}	449	k_{rxn} : Shu <i>et al.</i> 1994 Odor: Grimsrud <i>et al.</i> 1975
α -pinene	2.1×10^{-6}	700	k_{rxn} : Atkinson <i>et al.</i> 1990 Odor: Grimsrud <i>et al.</i> 1975
linalool	1.1×10^{-5}	1000	k_{rxn} : Atkinson <i>et al.</i> 1995 Odor: Cometto-Muniz <i>et al.</i> 1998

To place some perspective on the relative extent of reaction in the breathing zone we considered reactions that would occur in a thin turbulent boundary layer in the breathing zone and those that would occur in a well-mixed room within which the emission source, an individual wearing scented personal care product, exists. For such conditions the reaction rate constants in the breathing zone and bulk room air would be identical and, as such, the ratio of change in reactant concentration in the boundary layer to that of bulk room air is given by Equation 3 (the complete derivation is omitted here due to space constraints):

$$R = \frac{\Delta C_{f,b}}{\Delta C_{f,r}} = \frac{t_b k_{rxn} C_{f,b} C_{O_3,b}}{t_r k_{rxn} C_{f,r} C_{O_3,r}} \approx \frac{t_b C_{f,b}}{t_r C_{f,r}} = \frac{t_b}{t_r} \left\{ 1 + \frac{aQ_v}{v_t A_f} \right\} \quad (3)$$

The subscripts b and r refer to breathing zone (in boundary layer) and bulk room air, respectively, and f refers to the unsaturated organic fragrance compound. The left-hand-side of Equation 3 represents the change in mean reactant concentration due to reaction with ozone in a turbulent boundary layer adjacent to the skin where a product is applied normalized by the change in reactant concentration in a well-mixed room. This ratio should be approximately equal to the additional fraction of reaction products inhaled by a person wearing a scented personal care product relative to what others in the room inhale. The parameter Q_v is the air flow rate through the room (m^3/s), v_t is a transport limited deposition velocity (mass transfer coefficient) across the turbulent boundary layer (m/s), and A_f is the area of face covered by the reactive species (m^2).

Parameters used in Equations 2 and 3 are listed in Table 2.

Table 2. Parameters used in screening analysis

Parameter	Magnitude and units	Notes
k_{rxn}	see Table 1	
C_f	1 to 10 x odor threshold	see odor thresholds in Table 1
t_b	0.3 – 1 s	
t_r	900 s	
α	0.1	turbulent boundary layer
Q_v	$0.055 m^3/s$	$50 m^3$ room, $1.1 \times 10^{-3}/s$ air exchange rate
v_t	$5 \times 10^{-4} m/s$	
A_f	$0.02 m^2$	

For simplicity, only the effects of individual compounds were considered, i.e., as opposed to the net effects of multiple fragrance compounds that are more typical of personal care products.

RESULTS

Application of Equation 2 for the conditions described above and parameters listed in Tables 1 and 2 leads to the results shown in Figure 1. Predicted ozone reductions over 1s ranged from 0.05% (allyl alcohol at odor threshold) to 10% (linalool at $10\times$ odor threshold).

Application of Equation 3 with the parameter values described above leads to a predicted value of $R = 0.62$, i.e., the individual wearing the scented personal care product would be exposed to 62% more reaction product than others in the same room.

DISCUSSION

Application of Equation 2 suggests a wide range of ozone reduction percentages depending on specific organic reactants. For linalool, the percent reduction in ozone concentration at $10\times$ the odor threshold was estimated to be 10%. Thus, the results presented herein, while approximate, do suggest a potential for observable ozone-initiated near-head chemistry in the breathing zone of individuals who use scented personal care products.

The results described herein suggest that linalool may play a major role as a pre-cursor to near head chemistry and associated by-products. Linalool is a common terpenoid alcohol with a floral scent, and is common in many personal care products. Cooper *et al.* (1992) observed linalool in 21 of 31 products tested, including soaps, colognes, and perfumes, and found that linalool comprised, 51 to 75 % of the fragrance in the products in which it was detected. The citrus and pine scents associated with d-limonene and α -pinene, respectively, are also widely employed in fragrances used for personal care products. For example, Rastogi *et al.* (1998) observed limonene in 48 of 71 deodorants.

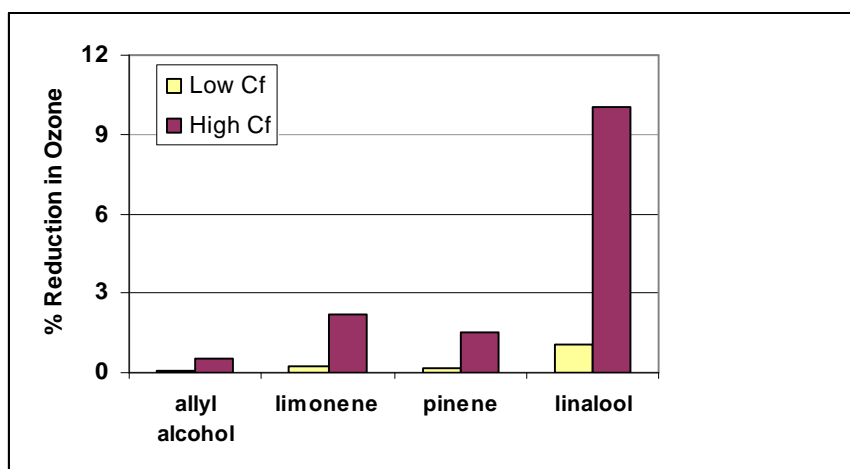


Figure 1. Reductions in breathing zone ozone concentration

The products associated ozone reactions with terpenes, terpenoids and other unsaturated compounds observed in many fragranced personal care products are numerous and not entirely identified. Examples include primary and secondary ozonides, Criegee bi-radicals, various other radical species (hydroxyl, alkoxy, hydroperoxy radicals), hydrogen peroxide, hydroperoxides, formaldehydes and heavier aldehydes, acetone and heavier ketones, formic acid and heavier carboxylic acids, multi-functional oxidation products with carbonyl, carboxylate and/or hydroxyl groups, and secondary organic aerosols (Nazaroff and Weschler 2004, and references presented therein). A major oxidation product associated with linalool is 5-methyl-5-vinyl-tetrahydrofuran-2-ol (MVT), with a molar yield of MVT for the ozone/linalool 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).

The authors acknowledge the screening nature of this study and potential for uncertainties. Several parameters have a significant impact on results. For example, if the time in breathing zone (t_b) is reduced to 0.3 s, the percent ozone reduction for linalool at 10 \times odor threshold is reduced to 3%. If the time in breathing zone is reduced to 0.3 s and the room air exchange rate is decreased by a factor of four, $R = 0.01$. This analysis is also based on an assumption that all reactions in the breathing zone occur in a thin boundary layer adjacent to the face region, likely an underestimation of the extent of breathing-zone reactions. In addition, for this analysis we considered only individual reactive species. In reality, most scented personal care products contain multiple reactive species that would react, to different degrees, with ozone simultaneously. 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. Future studies will focus on the measurement of actual reactive organic species, ozone and by-product concentrations in the breathing zone and bulk air (away from breathing zone) before and after the application of various types of personal care products.

CONCLUSIONS AND IMPLICATIONS

In this paper we present the novel concept of near head chemistry associated with the use of personal care products which contain unsaturated organic compounds that will react rapidly with ozone in the human breathing zone. Taken together, this screening analysis and recent research by others suggest that, at a minimum, there is potential for respiratory and eye irritation in individuals who are exposed to elevated levels of ozone in the presence of unsaturated organic compounds that are common in many personal care products applied to the head region. However, the factors that affect by-product formation and associated health outcomes require more research before the significance of near head chemistry is confirmed.

Additional research is warranted to characterize associated reaction products and health consequences associated with near head chemistry and associated personal reactive clouds.

ACKNOWLEDGEMENTS

The authors thank Dan Isola of the Research Institute for Fragrance Materials for helpful comments and information regarding fragrance components in personal care products. Heather Simon is funded by a fellowship from the National Science Foundation. The corresponding author wishes to thank Roxanne A. Shepherd for her inspirational attitude.

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