MODELING CHEMICAL REACTIONS IN THE INDOOR ENVIRONMENT BY CFD

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Summary

The concentrations of ozone and a terpene that react in the gas-phase to produce a hypothetical product were investigated by computational fluid dynamics (CFD) for two different air exchange rates. Ozone entered the room with the ventilation air. The terpenes were introduced as a localized source with an emission pattern similar to an air freshener; this was in contrast to an otherwise identical earlier study in which the terpene was introduced as a floor source with an emission pattern similar to a floor care product (Sørensen and Weschler, 2002). The results show that there are large concentration variations within the room.

Introduction

Chemical reactions can significantly alter the concentrations of indoor pollutants, producing products that might otherwise not be present. For example, the oxidation of d-limonene may create skin allergens (Karlberg et al. 1992) and the reaction of ozone with carpet emissions produces a series of aldehydes including formaldehyde and nonanal (Weschler et al. 1992).

Under well-mixed conditions a one-compartment mass-balance model with appropriate source and sink terms may be constructed (Weschler and Shields, 2000). However, when the well-mixed assumption does not hold, significant deviations in pollutant concentration may exist inside the ventilated space. This was shown in an earlier study where we used CFD to predict the flow field and concentrations of ozone, a terpene and a hypothetical product of the ozone/terpene reaction in a large two-dimensional room (Sørensen and Weschler, 2002). The present study is similar to its predecessor in all respects except one. Whereas in the former study the terpene source was distributed uniformly across the floor as might occur when using a floor-care product, in the present study the terpene source is localized on the inlet wall as might occur with a wall mounted air freshener. Otherwise the set-up for the two studies was identical. The reactions studied were those occurring between ozone and two different terpenes – d-limonene, which reacts with ozone at a moderate rate, and α-terpinene, which reacts with ozone at a relatively fast rate. The impact of imperfect mixing on the pollutant concentrations was investigated under steady-state conditions, including ozone removal at surfaces. Ozone was present because of outdoor-to-indoor transport. Two different ventilation scenarios were considered; $0.5h^{-1}$ and $2.0h^{-1}$.

Comparisons have been made among these four scenarios as well as with the results obtained using a standard mass-balance model, assuming perfect mixing conditions (Weschler and Shields, 2000). For the scenarios examined the CFD-calculations showed large spatial differences in pollutant concentrations within the room and these results have implications for assessing the exposure of humans and their artifacts to airborne pollutants.

Governing equations

The Reynolds-averaged Navier-Stokes equations in a two-dimensional, steady, and isothermal form were used (STAR-CD, 1999), closed with a low Reynolds number k-ε turbulence model (Lien et al. 1996). Standard values were used for the turbulence model, and the turbulent Schmidt number was 0.9. A second order scheme was used for the convection terms. The bimolecular chemical reaction studied here, is a process in which A reacts with B to create a product P: $A + B \rightarrow P$. The reaction is governed by the second order rate constant, k_b. Besides entering the reaction, deposition onto surfaces is a major sink of ozone in the indoor environment (Weschler, 2000). For a full description of the methods, see Sørensen and Weschler (2002).

Case set-up

We used the set-up from Restivo (1979) (see Figure 1). However, the original data is made for a relatively high air exchange rate, which was considered inappropriate for the present

study. To maintain the Reynolds number as in the experiments, while lowering the air exchange rate to 0.5h^{-1}, we considered an upscaled room with a downscaled supply velocity. The scale factor was 4.52, resulting in a relatively large room (Figure 1). Furthermore, we considered an air exchange rate of 2.0h^{-1}. For a detailed description of the room geometry and boundary conditions, see Sørensen and Weschler (2002). Species A originated outdoors and entered the room with a concentration of 80 ppb (comparable to outdoor ozone levels in an urban area during a summer afternoon). Species B originated indoors as a localized source (0.3x0.6 m), positioned 5 cm from the inlet wall at a height of 2.7 m with a constant source strength of 5 ppb·h^{-1}, a realistic value for a commercial air freshener.
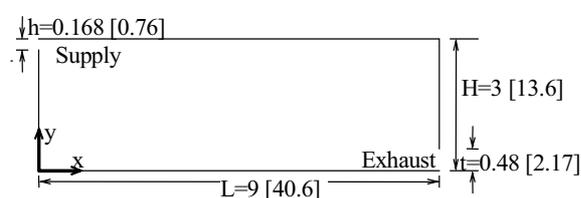

Figure 1. Sketch of the two-dimensional test room (Restivo, 1979); all lengths are in meters. Values in brackets are those used in the present study.

For the chemical species considered here, the binary diffusion coefficients in air were defined as: 18.2·10^{-6} m^2·s^{-1} for species A (corresponding to ozone, from Cano-Ruiz et al. 1993), 6.2·10^{-6} m^2·s^{-1} for species B (corresponding to d-limonene or α-terpinene, from Yaws, 1995) and 6.0·10^{-6} m^2·s^{-1} for product P (assumed value). The second order rate constants used for the chemical reactions were either: k_b=0.0184 ppb^{-1}·h^{-1} (comparable to the ozone/d-limonene reaction) or k_b=0.756 ppb^{-1}·h^{-1} (comparable to the ozone/α-terpinene reaction) (Atkinson et al. 1990). Surface deposition of species B and P was assumed to be negligible. Species A was assumed to deposit on all surfaces inside the room, with a Boltzmann velocity of $<v>$=360 m·s^{-1} (comparable to ozone); the mass accommodation coefficient was assumed to be $γ$=20·10^{-6}, which has been measured for latex paint (Reiss et al. 1994).

See Sørensen and Weschler (2002) for details about the validation of the flow field and for the grid-dependency study.

Results and discussion
Figure 2 shows a plot of the velocity vectors for the case of E$_x$=0.5h^{-1}. The inlet jet prevails along most of the ceiling, deflecting at around x=0.9L, forming a large re-circulating zone in the middle of the room with reversed, low-velocity flow along most of the floor. Above the outlet, a large downward velocity is present at the right wall. Below the inlet, a small upward velocity is present. At the lower left and upper right corners, regions with re-circulating secondary flows appear. For the case of E$_x$=2.0h^{-1}, the inlet velocities are four times larger, resulting in larger velocities and thinner boundary layers inside the room. However, the main flow features are identical to the ones described above.
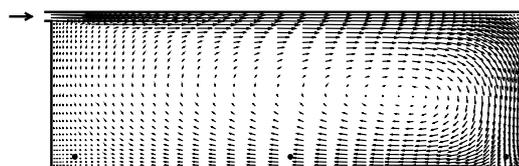

Figure 2. Velocity distribution. Note the two re-circulating zones in the lower left and upper right corner. Only a subset of the available velocity vectors is shown.

Turning to the CFD predictions of the species concentrations, Figure 3 contains the concentration distributions (in parts per billion) for the d-limonene case at an air exchange rate of E$_x$=0.5h^{-1}. The figure contains the distribution of ozone (A), d-limonene (B), and product (P). Ozone enters the room through the inlet at a concentration of 80 ppb, but due to surface deposition and chemical reaction, the concentration of ozone in the bulk of the room varies from roughly 15 ppb near the left wall to around 55 ppb at the right wall. The surface deposition results in large gradients in ozone concentration close to the surfaces. The concentration of d-limonene is very large near the localized source, decreasing away from the source due to reaction as well as dilution. It may be noted that a high concentration of d-limonene exists below the source, close to the left wall, even though the velocity at the source is directed upwards (Figure 2). This is due to transport by diffusion, which is significant in this low-velocity region. For similar reasons, the product concentration is large (above 25 ppb) all along the left wall, decreasing in the bulk of the room because of dilution.

Next, we increase the air exchange rate to E$_x$=2.0h^{-1} (Figure 4). As expected, the dilution results in a d-limonene concentration that is lower than in the E$_x$=0.5h^{-1} case. However, because of the increased air exchange rate, less time is available for the reaction with ozone, re-

sulting in less d-limonene consumption for the $E_x=2.0h^{-1}$ case compared with the $E_x=0.5h^{-1}$ case. The net result is a concentration in the $E_x=2.0h^{-1}$ case which is around two times smaller than in the $E_x=0.5h^{-1}$ case. The product concentration is five to six times smaller in the $E_x=2.0h^{-1}$ case than in the $E_x=0.5h^{-1}$ case due to both dilution and less time for the reaction to occur.
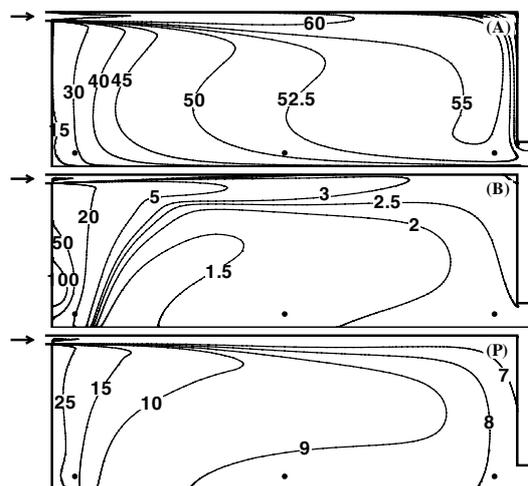

Figure 3. Distribution of ozone (A), d-limonene (B), and product (P), $E_x=0.5h^{-1}$.

The increased velocities, compared to the $E_x=0.5h^{-1}$ case, result in diffusion exerting less of an influence; the high-concentration region of d-limonene is convected upwards by the flow field. The increased transport of d-limonene away from the source is also seen to result in a significantly lower product concentration at the left side of the room, even when the fourfold increase in dilution is taken into account. An additional factor contributing to the low product concentrations is the fact that there is less time available for the reaction with ozone to occur.

For the α-terpinene case at $E_x=0.5h^{-1}$ (Figure 5), the concentration of α-terpinene is near zero, except very close to the source, because of the fast reaction rate. This is also seen in the ozone distribution, which decreases rapidly approaching the left wall. Because of the insignificant α-terpinene concentration in the bulk of the room, most of the product is created close to the source. Thus, the creation of product is almost equivalent to a localized source, and the distribution of product depends primarily on dilution with clean air, rather than on the reaction itself.

Finally, Figure 6 shows the results for the high air exchange case. The increased amount of

available ozone inside the room results in a reaction which is even faster, and therefore more localized, than for the $E_x=0.5h^{-1}$ case.
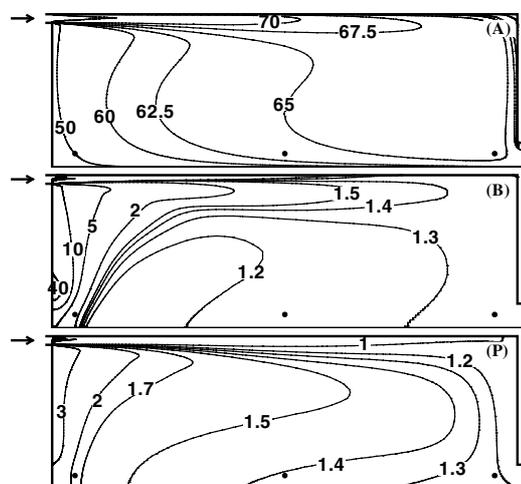

Figure 4. Distribution of ozone (A), d-limonene (B), and product (P), $E_x=2.0h^{-1}$.

The concentration of reactants and product were extracted in three points (marked with circles in Figures 3-6) inside the room to further investigate the spatial variations (Table 1). Furthermore, the table contains the results calculated by a one-compartment model assuming perfect mixing (Weschler and Shields, 2000). The deposition velocity used in the perfect mixing model was calibrated from CFD calculations without chemical reactions (Sørensen and Weschler, 2002). Table 1 emphasise the discussions to Figures 3-6 – imperfect mixing may result in large concentration variations.

Case		Left	Centre	Right	Mixing
Limonene, 0.5h⁻¹	A	27.3	50.7	54.2	51.6
	B	21.5	1.82	2.35	3.5
	P	17.6	8.79	7.86	6.5
Limonene, 2.0h⁻¹	A	50.0	63.7	65.5	65.2
	B	2.58	1.25	1.33	1.6
	P	1.87	1.39	1.22	0.9
Terpinene, 0.5h⁻¹	A	13.9	49.8	52.6	49.3
	B	5.26	<0.01	<0.01	0.1
	P	33.8	10.6	10.2	9.9
Terpinene, 2.0h⁻¹	A	48.3	62.9	64.6	64.0
	B	0.14	<0.01	<0.01	0.1
	P	4.30	2.64	2.55	2.4

Table 1. Concentrations (ppb) of reactants and product at 3 locations within the room. "Left" is 2 m off the left wall, "Centre" between the walls, and "Right" is 2 m from the right wall; all three points are 1.2 m off the floor.
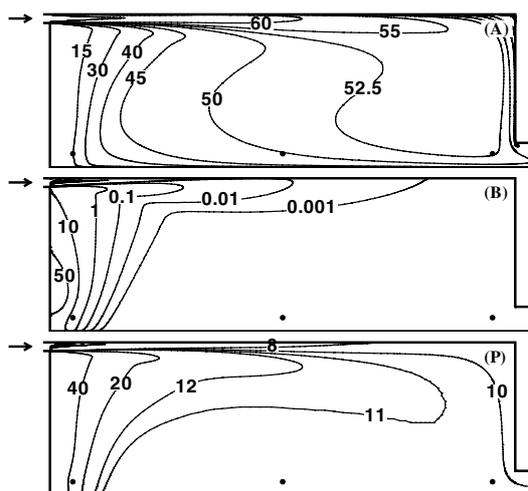
Figure 5. Distribution of ozone (A), α-terpinene (B), and product (P), E_x=0.5h^{-1}.
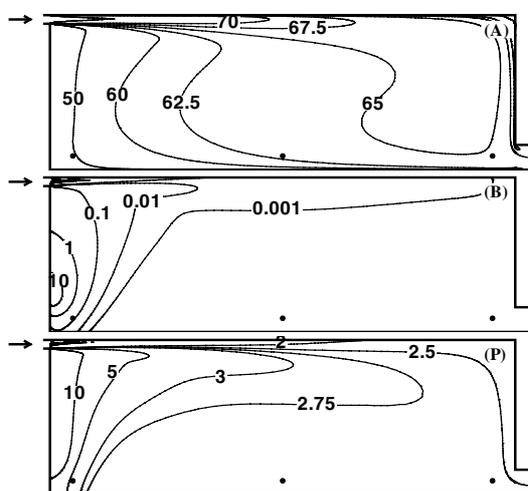

Figure 6. Distribution of ozone (A), α-terpinene (B), and product (P), E_x=2.0h^{-1}.

Conclusions

The present study used CFD to examine reactions between ozone and two common terpenes in a relatively large room under four hypothetical scenarios. For the conditions investigated, there were large concentration differences inside the room because of imperfect mixing amplified by the fact that the time available for reactions varied with the location in the room. The present set-up favors these differences; the modelled room is quite large, the supply velocity is low, and buoyancy effects are ignored. However, even though enhanced mixing is expected for properly scaled conditions, the study indicates that incomplete mixing may, in some situations, result in reactant and product concentrations significantly different from those predicted by a model that assumes fully mixed conditions. This outcome has very real implications for anyone attempting to assess the exposures of an entity (human being, sensitive electronic equipment, valuable painting, ancient sculpture, etc.) to airborne pollutants. The assumption of fully mixed conditions should always be carefully scrutinized.

References
Atkinson, R., Hasegawa, D. and Aschmann, S. M. (1990) "Rate constants for the gas-phase reactions of O-3 with a series of monoterpenes and related-compounds at 296-K +/- 2K", *Int. J. Chem. Kinet.* 22(8), 871-887

Cano-Ruiz, J. A., Kong, D., Balas, R. B. and Nazaroff, W. W. (1993) "Removal of Reactive Gases at Indoor Surfaces: Combining Mass Transport and Surface Kinetics", *Atmospheric Environment*, 27A(13), 2039-2050

Karlberg, A. T., Magnusson, K. and Nilsson, U. (1992) "Air oxidation of d-limonene (the citrus solvent) creates potent allergens", *Contact Dermatitis*, 26(5), 332-340

Lien, F. S., Chen, W. L. and Leschziner, M. A. (1996) "Low-Reynolds-Number Eddy-viscosity Modeling based on non-linear stress-strain/vorticity relations", Proceedings of the 3rd symposium on engineering turbulence modelling and measurements, Crete, Greece

Reiss, R., Ryan, P. B. and Koutrakis, P. (1994) "Modeling Ozone Deposition Onto Indoor Residential Surfaces", *Environmental Science & Technology*, 28(3), 504-513

Restivo, A. (1979) "Turbulent flow in ventilated rooms", Thesis, University of London, UK

STAR-CD (1999), "Methodology, STAR-CD Version 3.10 A", Computational Dynamics Limited

Sørensen, D. N. and Weschler, C. J. (2002) "Modeling Gas Phase Reactions in Indoor Environments Using Computational Fluid Dynamics", *Atmospheric Environment* 36(1), 9-18

Weschler, C. J., Hodgson, A. T. and Wooley, J. D. (1992) "Indoor chemistry - ozone, volatile organic-compounds, and carpets", *Environmental. Science & Technology*, 26(12), 2371-2377

Weschler, C. J. (2000) "Ozone in Indoor Environments: Concentration and Chemistry", *Indoor Air*, 10(4), 269-288

Weschler, C. J. and Shields, H. C. (2000) "The influence of ventilation on reactions among indoor pollutants: Modeling and experimental observations", *Indoor Air*, 10(2), 92-100

Yaws, C. L. (1995) "Handbook of Transport Property Data", Gulf Publishing Company