

Fragrances and aerosol during office cleaning.

Zarogianni Aikaterini Maria, Loupa Glykeria*, Rapsomanikis Spyridon

*Laboratory of Atmospheric Pollution and of Control Engineering of Atmospheric Pollutants,
Faculty of Engineering, Department of Environmental Engineering, Democritus University of
Thrace, V. Sofias 12, 67100 Xanthi, Greece.*

* Corresponding author. Tel: +30-25410 79314; Fax: +30-25410 79379

E-mail address: gloupa@env.duth.gr

METHODS

The office (Fig. S1) under study is located within the campus of the Democritus University of Thrace (DUTH), in the suburbs of the city of Xanthi, Greece. The office is naturally ventilated and the floor has plastic tiles and no carpeting.

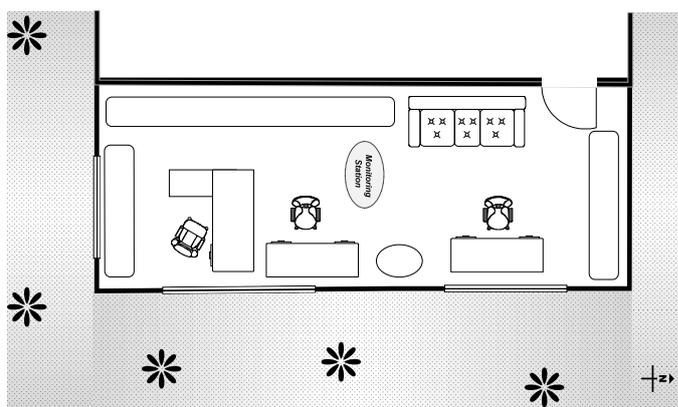


Fig. S1. Floor plan of the office (6m x 3m x 3m) and the monitoring station.

Air Sampling of VOCs.

An air sampler, Desaga G301 (Sarstedt AG & Co., Germany) equipped with stainless steel prepacked thermal desorption sample tubes filled with Carbotrap 349 (PerkinElmer, Massachusetts, USA) was employed for air sampling during and after the cleaning of the office. Sampling flow was set at 1 l/min and the duration of each sampling was 15 min. Before each sampling the sorbent tubes were conditioned by thermal desorption on the ATD-GC/MS (vide

infra; Tube temperature: 230 °C, Valve temperature: 200°C, Purge time: 1 min, Conditioning time: 30min) under a 105 mL min⁻¹ flow of zero air).

PM sampling.

Indoor and outdoor atmospheric particle number concentration and size distribution measurements were performed in the office, with a particle size analyzer, (Promo 2000 particle, Palas GmbH, Germany). This scattered-light aerosol spectrometer system was set to count and classify the particles into 28 size channels (bins), at the frequency of 0.1 Hz, particles with aerodynamic diameter from 0.20 µm to 10 µm. Indoor (at breathing height) and outdoor measurements were carried out sequentially. I/O ratio in each size range was calculated by dividing one hour indoor values with the preceding one hour outdoor values.

Microclimatic parameters monitoring.

Microclimatic parameters were monitored with the “Microtherm” indoor air quality instrument (Casella CEL Ltd., UK), which includes sensors for air temperature, relative humidity, air velocity, light intensity and a black globe (40 mm) thermometer.

CO₂ sampling.

Indoor CO₂ concentrations were measured with a real-time infrared CO₂ analyzer (Gas Card II, infrared gas monitor, Edinburgh Sensors, UK). The air exchange rate of each office was

calculated from a simple mass balance model (Eq.S1), using CO₂ as a tracer gas. Outdoor CO₂ concentrations were measured for 24 hours, a day with normal outdoor activity (i.e. the cars of the stuff arriving and leaving the campus).

$$C_{in} = C_{ss} + (C_{in(0)} - C_{ss})e^{-\lambda t} \quad (S1)$$

C_{in} are the indoor and outdoor CO₂ concentrations (ppmv), $C_{in(0)}$ is the initial indoor CO₂ concentration (at time $t=0$); the term C_{ss} is the steady-state CO₂ concentration, λ (h^{-1}) is the air exchange rate. The CO₂ deposition rate constant was assumed to be zero. A nonlinear regression technique (Statistica 9) was used to calculate air exchange rate (λ) during times that the CO₂ concentrations decayed and C_{ss} converged to the outdoor CO₂ concentration.

Materials

Analytical standards of d-limonene, α -pinene, eucalyptol, 3,7-dimethyl-3-octanol (tetrahydrolinalool hereafter), ethylene glycol butyl ether (or 2-butoxyethanol, 2-BE hereafter), α -terpineol, 1,3,5-trimethylbenzene (1,3,5-TMB hereafter) at a concentration of 5000 μ g/mL in methanol and diphenyl ether at a concentration of 2000 μ g/mL in methanol, were obtained from Sigma-Aldrich (Taufkirchen, Germany). Anhydrous diethyl ether ($\geq 99.7\%$) containing 1 ppm

butylated hydroxytoluene (BHT) as inhibitor (Sigma-Aldrich, Taufkirchen, Germany) was also used as a solvent in the preparation of standards of varying concentrations.

The selection of eight calibration standards, which were selected as the target fragrance ingredients for quantification, was based on previous qualitative study of detergents (Zarogianni et al., 2017). Details of calibration standards are presented in Table S1.

Table S1. Summary of VOC-fragrance quantified in this study.

Compounds	CAS	MW	Retention Time (min)	MS ion	Density (g m ⁻³)	Limit of detection (ppbv)
Ethylene glycol butyl ether (2-Butoxyethanol) ^a	111-76-2	118.18	12:31	57, 45, 41	0.902	0.075
α -Pinene	80-56-8	136.24	13:09	93, 91, 92	0.858	0.097
1,3,5-Trimethylbenzene (Mesitylene) ^a	108-67-8	120.20	14:28	105, 120, 77	1.499	0.014
d-Limonene	5889-27-5	136.24	16:35	68, 67, 63	0.842	0.422
Eucalyptol (1,8-cineole) ^a	470-82-6	154.26	16:39	43, 81, 108	0.927	0.008
3,7-Dimethyl-3-octanol (Tetrahydrolinalool) ^a	78-69-3	158.29	19:18	73, 69, 55	0.828	0.011
α -Terpineol	10482-56-1	154.00	22:16	59, 93, 121	0.934	0.008
Diphenyl ether	101-84-8	170.21	26:08	170, 51, 77	1.075	0.021

^a In parenthesis synonyms of fragrance ingredients

Calibration standard solutions were prepared and analysed within 48 hours and stored at 4°C.

To obtain calibration curves with TD tubes an aliquot of 20 μ l of each calibration standard mix was injected into a sorbent tube which was analysed with the ATD-GC/MS. The TDs selected during the experiment were also analysed using the same conditions as for the standards.

Triplicates were used to ensure the precision of the sampling.

Analytical methods

ATD-GC/MS analysis

The analysis of all stainless steel sorption tubes was performed using an Automated Thermal Desorber, Turbo Matrix ATD 50, (PerkinElmer, Massachusetts, USA), connected to HP5890II Gas Chromatograph (GC) interfaced with a VG Trio 1000 Mass Spectrometer. Helium 99.999% (Linde Hellas, Greece) was used as the carrier gas at a constant column flow of 1.0 mL min^{-1} . A DB 5MS fused silica capillary column (30 m, i.d. 0.25 mm, film thickness 0.25 μm , J&W Scientific, Agilent Technologies, Delaware, U.S.A.) was coupled to the ion source.

A two-stage desorption took place in ATD with Tube temperature: 210°C ; Valve temperature: 200°C ; Transfer line temperature: 210°C ; Trap High and Low temperature: 220°C and -20°C with a rate $40^\circ\text{C min}^{-1}$. The purge time was set at 1 min and the desorption time at 5 min under a 1 mL min^{-1} column flow, 10 mL min^{-1} desorb flow and outlet flow at 9 ml/min. The inlet split was set at 35.8ml/min. Pressure was set at 12.5psi.

A 31 min program was set in the GC. The GC oven temperature program started at 35°C (isothermal hold for 3min) to 100°C at 5°C min^{-1} (held for 2min); to 180°C at $13^\circ\text{C min}^{-1}$ (held for 1min); and a final ramp to 200°C (held 5min) at $25^\circ\text{C min}^{-1}$. The electron impact ionisation mode conditions were: ion energy 70 eV; ion source temperature 200°C ; mass scan range 15–650 amu. Compounds were identified by comparing their mass spectra with the NIST mass spectral library.

RESULTS

SOA formation

During summertime, the outdoor ozone concentration (measured with a DOAS instrument, in the yard) was 67 ppbv (O=outdoor) on average (Karali et al., 2017). The indoor (I=indoor) O₃ concentrations were calculated with a simplified equation, assuming steady-state conditions during the time of experiments (Weschler and Shields, 2000):

$$\frac{I}{O} = \frac{\lambda}{\lambda + k_d \frac{A}{V}} \quad (S2)$$

where λ is the air exchange rate (h⁻¹), $k_d = u_d \times A/V$ the ozone deposition rate (h⁻¹), where u_d is the average deposition velocity (m h⁻¹), A is the total interior surface area (m²) and V is the volume of the building (m³). In the office $A/V=1.67$ m⁻¹ and the u_d was assumed as 0.54 m h⁻¹, due to the three large windows. Hence, indoor O₃ concentrations ranged between 13 -38 ppbv (average 25 ppbv). In the following Table S2, the last column presents the reaction rate constants between some reactants and O₃. For d-limonene the reaction rate was faster than air exchange rate, hence SOA can be formed (Waring et al., 2011). The same can be said for α -pinene, but not for eucalyptol.

Table S2. Reaction rates of common terpenes with indoor O₃.

Reactant	k (ppbv ⁻¹ s ⁻¹) (Nazaroff and Weschler, 2004)	k (h ⁻¹) for 25 ppbv O ₃
d- limonene	5.20E-06	0.48
α-pinene	2.10E-06	0.19
eucalyptol	3.75E-09	0.00

REFERENCES

- Karali, D., Rapsomanikis, S. and Christoforidis, A. (2017). Decomposition kinetics of non-volatile alkanes on urban aerosol. *Atmosphere* 8: 89.
- Nazaroff, W. and Weschler, C. (2004). Cleaning products and air fresheners: Exposure to primary and secondary air pollutants. *Atmos. Environ.* 38: 25.
- Waring, M.S., Wells, J.R. and Siegel, J.A. (2011). Secondary organic aerosol formation from ozone reactions with single terpenoids and terpenoid mixtures. *Atmos. Environ.* 45: 4235-4242.
- Weschler, C.J. and Shields, H.C. (2000). The influence of ventilation on reactions among indoor pollutants: Modeling and experimental observations. *Indoor Air* 10: 92-100.
- Zarogianni, A.-M., Loupa, G. and Rapsomanikis, S. (2017). A comparison of fragrance ingredients in green and nongreen detergents. *Environmental Forensics* 18: 110-121.