VOC in indoor environment

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Volatile organic compounds (VOCs)

- The European Union defines a VOC as "any organic compound having an initial boiling point less than or equal to 250 °C.”
- Volatile organic compounds (VOCs) have been measured from the indoor air already since the 80’s. (e.g. aldehydes, alcohols, aliphatic and aromatic hydrocarbons, carboxylic acids, glycols, esters, ethers, siloxanes, and terpenes) *(Shah and Singh, 1988; De Bortoli et al., 1989; Mølhave., 1991; Knöppel and Wolkoff, 1992; Brown et al., 1994; Wolkoff 1998).*
- The method based on gas chromatography with thermodesorption injection is well established and routinely used in-house inspections and material emission testing.

VOCs can be categorizes into classes by their volatilization (boiling point) (WHO 1989)

Category description	Acronym	Boiling-point range, °C	Typical sampling method
Very volatile (gaseous) organic compounds	VVOC	<0 to 50-100	Batch sampling, adsorption on charcoal / reactive adsorbent
Volatile organic compounds TVOC	**VOC**	**50-100 to 240-260**	**Adsorption on Tenax, carbon molecular black, or charcoal**
Semivolatile organic compounds	SVOC	240-260 to 380-400	Adsorption on polyurethane foam or XAD-2
Organic compounds associated with particulate matter or particulate organic matter	POM	>380	Collection on filters

Total Concentration of Volatile Organic Compounds (TVOC)

- Total Concentration of Volatile Organic Compounds (sum of VOCs in size range between hexane to hexadecane (C_6-C_{16}). Can be detected analytically with TD-GC-MS of GC-FID when using a non-polar column. (ISO-16000-6)
- Measured by toluene standard, which underestimates concentrations of polar compounds.
- Ease to measure. Gives data about overall behavior of VOCs in indoor environment. Used when testing material emissions.
- No cause-effect relationship exists between TVOC concentrations and health effects (*Wolkoff 1995, Andersson et al. 1997, ECA, 1997, Wolkoff and Nielsen 2001*). → use of TVOC not relevant from a health point of view

Sources of VOCs in *Indoors*

- VOCs have numerous sources. They can be originated i.e. from:
  - Outdoor air: Biological *(e.g. plants)* and anthropogenic sources *(e.g. energy production, traffic, industrial processes)*
  - **Materials and equipment (building and renovation materials, furnishings,** heating ventilation and air-conditioning (HVAC) systems).
  - **Man and his activities** (*body odors*, *household activities*: *cooking and cleaning, smoking..*)

VOC concentrations in different environments

- Total **outdoor air** concentration of VOCs is usually very low below 50 µg/m^3.
- Average **indoor air** contains typically tens (even hundreds) of VOCs. Total concentration range is usually 10-400 µg/m^3. Concentration of single compound is typically below 5 µg/m^3.
- In **occupational environments** where solvents are used, VOC concentration can be 50-500 **mg**/m^3 or even higher.
  → Health risks are estimated by irritating effects of chemicals (VOCs), which has been in occupational use.

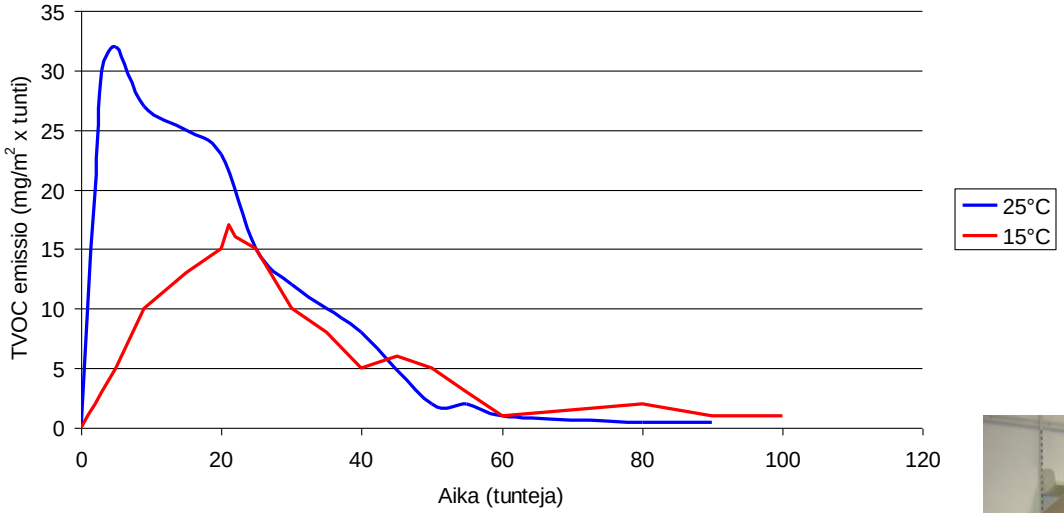
Factors affecting VOC emissions *indoors*

- Age of the material/product
- Ventilation (air exchange rate)
- Temperature and relative humidity
- Air flow at surface
- Material thickness, density, surface characteristics
- Material influence on sink effect (adsorption/desorption)
- *High surface to volume ratios (S/V)* →***surface reactions are potentially very important.*** ***(Weschler et al. 2001)***
- ***E.g. Parquet compared to carpet***

Primary VOC emissions

- **Primary and secondary emissions** are important for both material testing and estimation of human exposure.
- **Primary emissions** evaporate from the surface of the material and / or diffusion within the product.
- Decreasing from high initial levels to low and near-constant levels.
- **Time scale is usually under one year.**

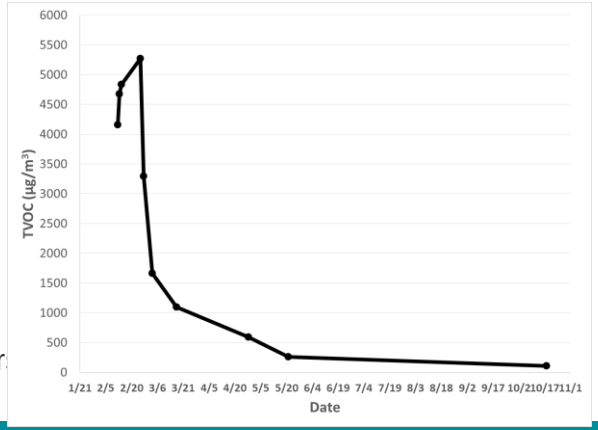
Primary emissions of VOCs decrease relatively fast



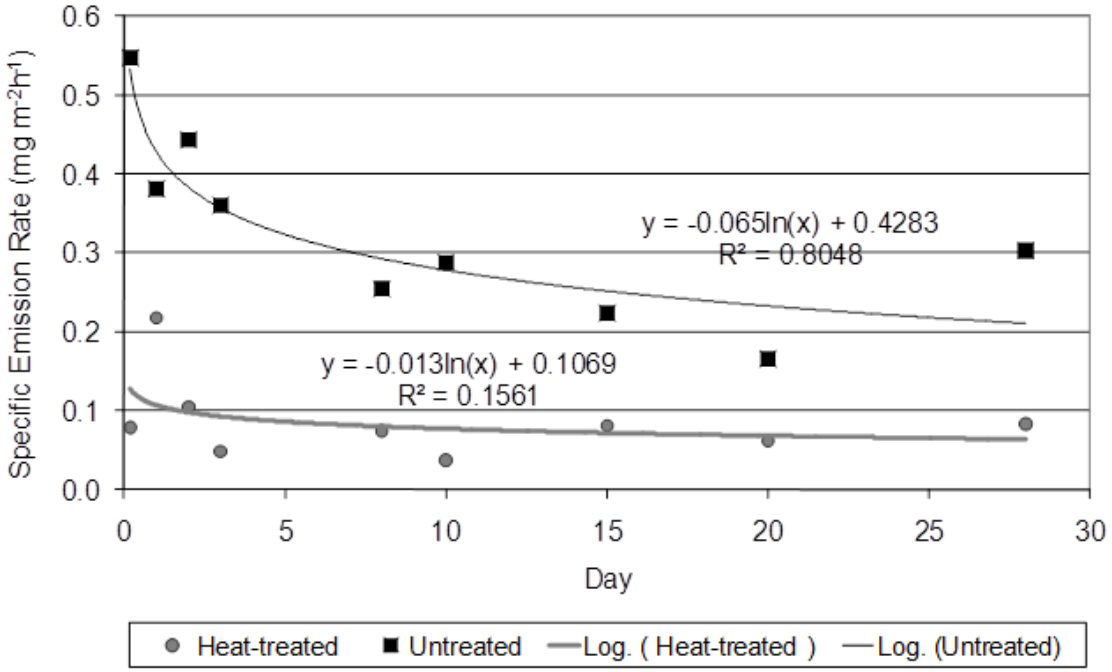
VOC emissions from painted surface in function of time (15 and 25°C) (water-based acrylic paint 10,2g/sample, loading factor 0,8m^2/m^3, air exchange 1.2 h^{-1}. *Haghihat and Bellis, Building and Environment, Vol 33, 1998)*

VOCs during and after the construction of the house (µg/m³). Ventilation was turned on 20th Feb, family moved to the house 22nd Feb.

Date	12.2.14	13.2.14	14.2.14	25.2.14	3.3.14	17.3.14	28.4.14	21.5.14	18.10.14
Total (including some VVOC)	4350	4890	5070	5630	3140	1130	630	290	120
TVOC (C6-C16)	4150	4680	4830	5270	3290	1090	590	260	105
1-Propanol, 2-methyl-	614	393	373	237	107	11	5	2	2
1-Butanol	244	279	229	202	219	13	6	5	2
2-Butanone, oxime	255	134	157	49	15	nd	nd	nd	nd
2-Propanone, oxime	82	48	61	11	2	nd	nd	nd	nd
Hexanal	119	229	192	195	80	24	13	7	5
2-Heptenal, (E)-	7	15	11	9	nd	2	nd	nd	nd
Toluene	53	106	115	34	14	4	2	1	nd
Xylenes	274	196	139	80	32	10	3	2	nd
Acetic acid, butyl ester	94	133	75	56	21	4	13	1	nd
Butanoic acid, butyl ester	72	81	101	166	139	32	27	18	nd
Methane, diethoxy-	193	138	120	124	91	14	10	7	nd
Cyclopentasiloxane, decamethyl-	23	37	46	75	47	70	24	38	1
Alpha-Pinene	626	958	229	1180	630	245	184	65	48
Delta-carene	319	640	726	609	290	107	77	22	19
Limonene	59	81	106	258	74	134	17	5	6



VOC Emissions Between Air-dried and Heat-treated Norway Spruce (*Picea abies*) *Hyttinen et al. 2010 Atmos Environ.*



Main VOCs from air-dried wood sample: Alpha-pinene, Limonene and other terpenes and hexanal

Main VOCs (heat-treated): Acetic acid and furfural

Secondary emissions of VOCs

- **Secondary emissions** formed as a result of ***chemical reaction***.
- It can occur when reactive compounds are introduced into the building materials (e.g. ozone) or condition of the material changes:

E.g. PVC flooring material is glued to concrete slab that is not sufficiently dried. High moisture and pH of the concrete promotes hydrolysis of phthalates and plasticizers of the PVC material.

Secondary emission products are often more irritating/odorous than primary secondary products *(including alcohols, aldehydes, alkoxyalcohols, carboxylic acids, etc.)*

Time scale of secondary emission is usually much more than one year.

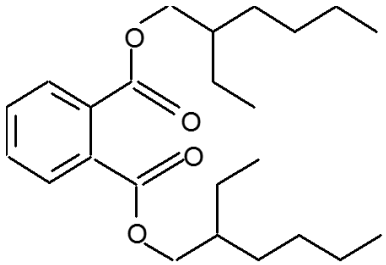
Factors affecting secondary emissions

- Oxidation reactions (e.g., O_2, **O_3**, OH, NO_3); can occur in gas phase and surfaces
- Acid/base chemistry; gas phase and surfaces
- Decomposition reactions (high temperatures and UV radiation); gas phase and surfaces
- **Hydrolysis reactions** promoted by high humidity and basic (high pH) surfaces; primarily on surfaces

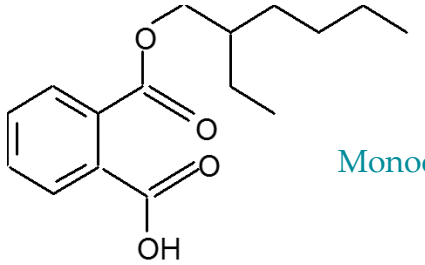
Weschler 2004

Secondary emissions (phthalates in PVC flooring)

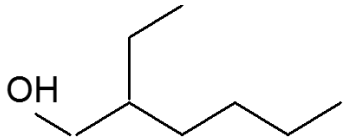
DEHP



H_2O +pH



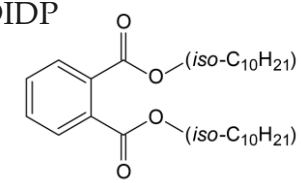
Monoethyl hexyl phthalate



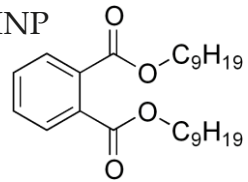
2-ethylhexanol
(odorous VOC)

Primary used as a plasticizer for PVC.

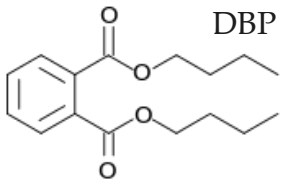
DIDP



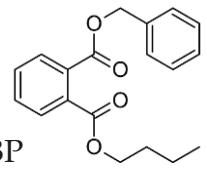
DINP

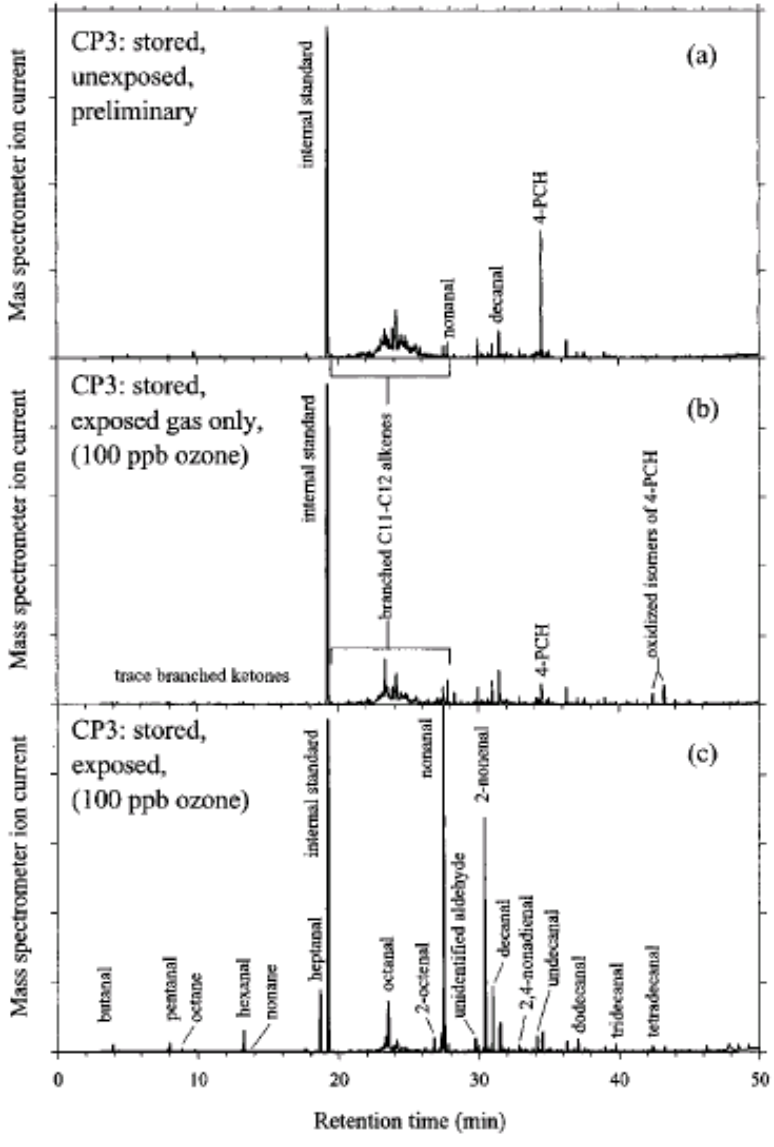


DBP



BBP





Glenn Morrison and William Nazaroff, 2002. Ozone Interactions with Carpet: Secondary Emissions of Aldehydes

a) **Primary emissions** (residential, nylon fiber, cut pile carpet): VOCs: branched alkanes, 4-phenylcyclohexene (4-PCH)

b) **Emissions of ozone and VOCs in air only**

c) **Secondary emissions. Interactions of carpet and ozone**: Most of the secondary aldehyde-emissions occurred.

Chemical reactions on surfaces are important!

VOCs indoors

Trends in Europe

- Development of low VOC emitting building materials continues.

→ VOC concentrations indoors relatively low.

→ Typical concentrations of VOCs cannot explain the reported complaints in the non-industrial working environment (Wolkoff et al., 2005)

TVOC in offices in Finland [µg/m^3]

Nowadays, concentrations of individual VOCs and TVOC are low in office buildings in Finland.
Part of the reason: Labeled low emitting building materials and high ventilation rates.

TVOC:

- 80 µg/m^3 (Offices (wintertime), Finland, 2001-2006) Salonen H. 2009
- 91 µg/m^3 (Offices (summertime), Finland, 2001-2006) Salonen H. 2009
- (176 buildings) TVOC (open offices 75µg/m^3, rooms 88µg/m^3)

Home cleaning and VOCs

Fragrance compounds are used to provide scent to everyday detergents and household cleaning products.

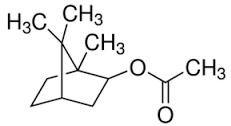
Scented chemicals are often terpenes (VOC): e.g. (S)-limonene (citrus odor), alpha-pinene (pine-wood) → reactive → *terpenes react with oxidizing compounds (e.g. Ozone) forming secondary organic pollutants*

Odor Lemon, grapefruit, floral

Classic pine scent
pine oil 8.7%

CASE: Home cleaning: Periodic cleaning in household (mopping). Using typical scented general cleaner (smell of forest pine).Concentrations of organic compounds

Compound	Before	During the cleaning	After the cleaning 30min
Total	132	782	129
Isobornyl acetate	-	162	12
Alpha-pinene	31	156	22
Isopropyl alcohol	20	146	10
Campher	-	30	3
Delta-carene	23	28	12
2-ethyl-1-hexanol	-	22	6
Decanal	6	14	8
Nonanal	3	14	7
Limonene	4	6	3
Terpineol	-	7	-



VOCs and Odor
Personal expectations

- **Subjects were able to adapt odors more easily if they were under impression that odor was good for them or smelled pleasant.**

- Subjects that were told that the odor was bad for them or perceived it as harmful reported higher odor intensities, irritation and significantly more health effects. (Dalton et. al. 1997)

References

- Andersson, Bakke, jørseth, Bornehag CG et al., 1997. TVOC and Health in Non-industrial Indoor Environments. Indoor air. 78-91.
- Brown S.K., Sim M., Abramson M.J., Gray C.N. 1994. Concentrations of Volatile Organic Compounds in Indoor Air – A Review, Indoor air, 4, 123-134.
- Dalton P., Wysocki C., Brody M., Lawley H. 1997. The influence of cognitive bias on the perceived odor, irritation and health symptoms from chemical exposure. Int. Arch. Occup environ health. 407-417.
- De Bortoli M., Knöppel H., Pecchio E., Vissers H., 1989. Performance of a thermally desorpable diffusion sampler for personal and indoor air monitoring, Environ. Int., 15, 427-434.
- Hyttinen M., Masalin-Weijo M., Kalliokoski P., Pasanen P., 2010, Comparison of VOC emissions between air-dried and heat-treated Norway spruce (Picea abies), Scots pine (Pinus sylvesteris) and European aspen (Populus tremula) wood, Atmos. Environ., 44, 5028-5033.
- ISO 16000-6, 2004, Indoor air - Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS/FID, 2004, 1-25.
- Knöppel H., Wolkoff P. (eds.), Chemical, Microbiological , Health and Comfort Aspects of Indoor Air Quality – State of the Art in SBS, 1992 ECSC, Brussels and Luxembourgh, 37-48.
- Mølhave L., 1991, Volatile organic compounds, Indoor air quality and health, Indoor air, 1, 357-376.
- Morrison G. Nazaroff W., 2002. Ozone Interactions with Carpet: Secondary Emissions of Aldehydes
- Salonen H., Pasanen A-L., Lappalainen S. et al. 2009. Volatile organic compounds and formaldehyde as explaining factor on reported complaints and symptoms in the office environment. J Occup Environ Hyg. 6:239-247.
- Shah J., Singh H., 1988, Distribution of volatile organic chemicals in outdoor and indoor air: a national VOCs data base, Environ. Sci. Technol., 22, 1381–1388.
- Weschler C. 2004. Chemical reactions among indoor pollutants: what we've learned in the new millennium. Indoor Air, 184-194
- Wolkoff 1995. Volatile Organic Compounds Sources, Measurements, Emissions, and the Impact on Indoor Air Quality. Indoor air. 5-73.
- Wolkoff P., 1998, Impact of air velocity, temperature, humidity, and air on long-term VOC emissions from building products, Atmos. Environ., 32, 2659–2668.
- Wolkoff and Nielsen 2001. Organic compounds in indoor air—their relevance for perceived indoor air quality. Atmos environ. 4407-4417.
- Wolkoff, C.K. Wilkins, P.A. Clausen, G.D. Nielsen 2005. Organic compounds in office environments—sensory irritation, odor, measurements and the role of reactive chemistry. Indoor Air. 1-13