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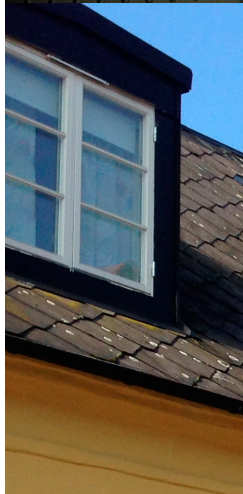
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Determination and control of some pollutants in indoor environments

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Determination and control of some pollutants in indoor environments

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DOCTORAL DISSERTATION

By due permission of the Faculty of Medicine Lund University, Sweden.

To be defended in the Rune Grubb Lecture Hall, Sölvegatan 23, Lund
on Friday the 28th of November 2014 at 9:00 am.

Faculty opponent

Professor Rafał Górny, PhD

Central Institute for Labour Protection,
National Research Institute Warszawa, Poland

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<p>Abstract</p> <p>Unsatisfactory indoor air quality (IAQ) may result from polluting emissions that are spread from building materials such as volatile organic compounds (VOCs) and/or microbial components or from various kinds of human activity such as smoking. Different methods are available to limit the exposure to unwanted pollutants and improve human wellbeing and health.</p> <p>One goal of this thesis was to determine two microbial markers (3-hydroxy fatty acids of bacterial lipopolysaccharide and ergosterol of fungal biomass) in waterpipe smoke. A second goal was to study the influence of relative humidity (RH) on room air concentrations of VOCs. A third goal was to study the performance of a new device called the surface emissions trap (cTrap) in controlling indoor pollutants.</p> <p>Smoking waterpipe was found to generate a bioaerosol rich in microbial components, polycyclic aromatic hydrocarbons (PAHs), and small size particles. Rapidly increasing RH was found to influence air concentrations of VOCs emitted from building materials as studied both in a climate chamber and in a room with dampness-related floor emissions. The cTrap cloth was found to be efficient in reducing emissions of VOCs, stopping mycotoxins, and improving the perceived IAQ in a damp school building. The device was proved to be efficient in reducing and trapping moisture-driven floor emissions. Preliminary results also showed that the cloth may be used in reducing smoking generated VOCs and particles which may migrate between rooms within a building.</p>		
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Paweł Markowicz

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*“There cannot be a greater mistake than that of looking
superciliously upon the practical applications of science.*

The life and soul of science is its practical application...”

Lord Kelvin

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List of papers

This thesis is based on the following papers which are referred to by their Roman numerals:

- I. Markowicz P., Löndahl J., Wierzbicka A., Suleiman R., Shihadeh A., Larsson L. (2014). **A study on particles and some microbial markers in waterpipe tobacco smoke.** Science of the Total Environment. 499C:107-113.
- II. Markowicz P., Larsson L. (2014). **Influence of relative humidity on VOC concentrations in indoor air.** Environmental Science and Pollution Research. *In press*.
- III. Markowicz P., Larsson L. (2012). **The surface emissions trap: a new approach in indoor air purification.** Journal of Microbiological Methods. 91:290–4.
- IV. Markowicz P., Larsson L. (2014). **Improving the indoor air quality by using a surface emissions trap.** Atmospheric Environment. <http://dx.doi.org/10.1016/j.atmosenv.2014.04.056>.

Abstract

Unsatisfactory indoor air quality (IAQ) may result from polluting emissions that are spread from building materials such as volatile organic compounds (VOCs) and/or microbial components or from various kinds of human activity such as smoking. Different methods are available to limit the exposure to unwanted pollutants and improve human wellbeing and health.

One goal of this thesis was to determine two microbial markers (3-hydroxy fatty acids of bacterial lipopolysaccharide and ergosterol of fungal biomass) in waterpipe smoke. A second goal was to study the influence of relative humidity (RH) on room air concentrations of VOCs. A third goal was to study the performance of a new device called the surface emissions trap (cTrap) in controlling indoor pollutants.

Smoking waterpipe was found to generate a bioaerosol rich in microbial components, polycyclic aromatic hydrocarbons (PAHs), and small size particles. Rapidly increasing RH was found to influence air concentrations of VOCs emitted from building materials as studied both in a climate chamber and in a room with dampness-related floor emissions. The cTrap cloth was found to be efficient in reducing emissions of VOCs, stopping mycotoxins, and improving the perceived IAQ in a damp school building. The device was proved to be efficient in reducing and trapping moisture-driven floor emissions. Preliminary results also showed that the cloth may be used in reducing smoking generated VOCs and particles which may migrate between rooms within a building.

Abbreviations

ADHD	Attention-Deficit/Hyperactivity Disorder
APM	Aerosol particle mass analyzer
BP	Boiling point
cTrap	The surface emissions trap
DNPH	2,4-Dinitrophenylhydrazine
EI	Electron ionization
ESI	Electrospray ionization
GC-MS	Gas chromatography mass spectrometry
HPLC	High performance liquid chromatography
IAQ	Indoor air quality
IQ	Intelligence quotient
LPS	Lipopolysaccharide
MEA	Malt extract agar
MS smoke	Mainstream smoke
MS/MS	Tandem mass spectrometry
MW	Molecular weight
MVOCs	Microbial volatile organic compounds
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PE	Polyethylene
PM	Particulate matter
POM	Particulate organic matter
PVC	Polyvinyl chloride

Q	Quadrupole
RH	Relative humidity
SH smoke	Second hand smoke
SIM	Selected ion monitoring
SMPS	Scanning mobility particle sizer
SRM	Selected reaction monitoring
SS smoke	Sidestream smoke
SVOCs	Semivolatile organic compounds
TEOM	Tapered element oscillating microbalance
TPM	Total particulate matter
TVOCs	Total volatile organic compounds
TXIB	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate
UFPs	Ultrafine particles
VOCs	Volatile organic compounds
VVOCs	Very volatile organic compounds
WHO	World Health Organisation
Z	The water vapor resistance
2-EH	2-Ethyl-1-hexanol
3-OH FAs	3-Hydroxy fatty acids

Introduction

Healthy and unhealthy indoor air

An indoor environment free from hazardous pollutants is important for human wellbeing and health. It has been estimated that approximately 11 000 liters of air pass through the human respiratory tract every day (1). Air-borne pollutants lead to decreased indoor air quality (IAQ) and by being inhaled they may be absorbed and migrate to different organs of the human body. Research has shown that even short-term exposure to unsatisfactory indoor air adversely influences human productivity, which improves again when the source of pollutants is removed (2). Mendell et al. (3) suggested that only in the US improving IAQ may result in health benefits for more than 16% of indoor workers, with expected economic benefits of 5 to 75 billion dollars every year. Clearly, large economic losses result from factors such as workers absenteeism and medical care. Moreover, long-term exposure to polluted air may amplify symptoms of allergies and asthma (4). It has also been suggested that long-term exposure may lead to development of chronic illnesses like cardiovascular disease (5) or lung cancer (6). It is well known that exposure to air pollutants even at relatively small concentrations may trigger a variety of health effects including e.g. headache, allergy, or mucus membrane irritation (7).

Indoor air pollutants

Indoor air pollutants may exist as gases such as radon, very volatile organic compounds (VVOCs), volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), and microbial volatile organic compounds (MVOCs). Particulate pollutants of different size may exist as an aerosol with e.g. SVOCs. Particle-bound pollutants are for example microbial components including endotoxins and mold fragments containing for example mycotoxins.

Volatile organic compounds

VOCs represent a group of compounds found in the gas phase at ambient temperature due to their high vapor pressure, generally increasing with decreasing boiling point (BP). Such molecules become air-borne by evaporation from liquid phase or sublimation from solid phase. By definition of the World Health Organization (WHO) (8), VOCs are compounds with a BP between 50 and 260°C. Compounds with lower BP are classified as VVOCs and those with higher BP as SVOCs. Compounds with BP higher than 380°C are known as POM (particulate organic matter). Since the 1980s, VOCs have been of interest to many researchers in efforts aiming to link such pollutants to IAQ. VOCs can be emitted from indoor materials including furniture, building materials, or household products. They can also occur due to reactions between water and building materials (9), for example, sometimes followed by secondary reactions with other molecules such as ozone (10). The effects of VOC on human health are still unclear (11, 12) since some results are in disagreement, for example, the possible relationship between VOCs and asthma among children (13, 14).

The most well-known VVOC known to affect IAQ is formaldehyde which can be found in wood-based materials and is used in various industrial processes. Acute exposure to formaldehyde leads to human mucus membrane irritation (eyes, nose, skin) and respiratory tract symptoms (sneezing and coughing) (15). Some studies showed that it has neurotoxic (16) and carcinogenic (17) properties during chronic exposure.

Among the SVOCs are the polychlorinated biphenyls (PCBs), compounds used in capacitors and transformers all over the world during the 1950s-1970s, as well as in certain building materials such as sealants. PCBs are persistent in the environment and highly toxic; therefore they were banned in the late 1970s (18). Research shows that exposure to PCBs may cause diseases such as stomach and lung cancer (19). PCBs are also known to be hormone disruptors of teratogenic effect. The human fetus is especially at risk since PCBs are capable of migrating from the mother's tissues into the developing child. Latest research speculates that exposure to PCBs may increase the prevalence of Attention-Deficit/Hyperactivity Disorder (ADHD) and may lower intelligence quotient (IQ) among children (20). PCBs may persist in the indoor environment for many years, being spread from the primary source (e.g. sealants of window frames) to adjacent materials (window frames, adjacent walls) and into the indoor air, thus contaminating other building materials, and also furniture, clothes or food (21).

Other examples of SVOCs are the polycyclic aromatic hydrocarbons (PAHs), mainly resulting from incomplete combustion of materials rich in carbon e.g. coal or tobacco. Some PAHs of low molecular weight (MW) (typically 2-3 rings) are small enough to remain in gas phase, while larger PAHs tend to form and/or attach to particles. Such

particles may remain for a long time in atmospheric environments and undergo different processes, including photodegradation or transformation to other harmful pollutants (22). PAHs are harmful for all living organisms due to their mutagenic, carcinogenic and teratogenic properties (22, 23).

Microbial pollutants

Water intrusion and/or moisture in a building promote the growth of mold and bacteria, which leads to undesired emissions of cell fragments, spores, MVOCs, and other harmful substances. More than 200 VOCs are known to be produced by microorganisms (24). The human nose is very sensitive to some MVOCs which, even at low concentrations not detectable by any analytical instrument, may compromise IAQ. An example of such a VOC, described as a musty, earthy odorant is geosmin produced, for example by *Streptomyces spp.* (25). Microbial production of odorous and irritating VOCs may depend upon environmental factors such as temperature or availability of nutritious media (26). Interestingly, indoor molds were recently found to generate very small particles (less than 0.3 μm (27)) which have been shown to contain mycotoxins (28). The production of these secondary metabolites depends upon many factors e.g. water content, pH, source of major elements or competition with other microorganisms etc. (29). Some mycotoxins e.g. sterigmatocystin of *Aspergillus versicolor* may represent up to 1% of the total fungal biomass (28), making them very prominent and potentially harmful indoor pollutants.

Particulate matter

Unsatisfactory IAQ can also result from emissions of particulate matter (PM). PM may be a mixture of particles and liquid droplets containing organic or inorganic compounds small enough to form an aerosol (30). Products holding mineral fibers such as asbestos (31), human activity such as smoking or cooking (32), as well as outdoor sources such as car exhaust (33) are important sources of indoor PM. Components of complex mixtures of indoor-generated aerosols (34) may travel deep into the airways, where they may remain for a long time causing adverse health effects and/or being transported into the bloodstream (35).

Smoking generated pollutants

Human activity can generate many air pollutants. For example, we constantly shed skin flakes containing microorganisms such as bacteria and fungi. We may also spread pollutants deliberately. Cigarette smoke contains approximately 4000 compounds including many hazardous VOCs, gases and particles, among of 50 are known to be

carcinogenic (36). It is important to distinguish between different types of smoke. Second hand (SH) smoke is a mixture of the mainstream (MS) smoke which is exhaled by a smoker, and sidestream (SS) smoke comes from the tip of the burning cigarette. Fresh SS smoke (which is approximately 85% of total SH smoke) has been found to be four times more toxic than MS smoke (37). Smoking cigarettes also creates a bioaerosol rich in microbial components which has been revealed by the detection of 3-hydroxy fatty acids (3-OH FAs) of lipopolysaccharide (LPS) and ergosterol of fungal biomass (38). LPS, a family of highly potent glycolipids, is found in the outer membrane of Gram-negative bacteria and may be analyzed by its 3-OH FAs markers. Typically, one molecule of LPS carries four molecules of 3-OH FAs of different chain length (C8-C18) (39). Biologically active LPS is called endotoxin. Exposure to endotoxins is known to trigger airway inflammation and is associated with the development of non-allergic asthma or worsening of its symptoms if already developed (40). Ergosterol is one of the components of the cellular membranes of filamentous fungi and is commonly used in estimation of fungal biomass (41). The amount of ergosterol may vary depending upon species, growth phase (42), exposure to UV radiation (43) etc.; typically 1 gram of dry fungal biomass contains approximately 5 mg of ergosterol (44). By measuring ergosterol, the content of fungi in different samples such as dust, mold-affected building materials or tobacco and smoke can be estimated (39, 45). Ergosterol is increasingly being used as a marker of mold contamination of indoor environments (42, 46).

Dilution and removal of indoor air pollutants

As a consequence of the increased time spent by humans indoors and the growing number of aging individuals in the society as well as individuals with immunodeficiency due to modern intensive care therapy, many different methods for improving IAQ have become available. Increasing ventilation rates may be the easiest way of restoring IAQ. Unfortunately, as mentioned in Table 1, the efficiency may be limited due factors such as outdoor air contamination from industry and car exhausts, and due to unfavorable weather conditions. Alternative air cleaning techniques have been developed and are used to dilute and/or remove unwanted pollutants. Research has shown that air purifiers have varying efficiency and may even produce harmful by-products (see Table 1).

SH smoke present indoors tends to contaminate all exposed surfaces e.g. furniture, building materials, and personal belongings, migrating between different rooms and dwellings within a building. Tobacco smoke pollutants can be removed by increasing ventilation rates and by using different air cleaners. In a study of Bohac et al. (47) an approach of reducing tobacco smoke migrating from a smoker's flat to a nonsmoker's flat was tested by increasing the ventilation rate and by using air sealants. Results

showed a 29% reduction in the generated pollutants that migrated into the neighbouring flats. Unfortunately, pollutants may migrate rapidly between flats in a building through ventilation systems. Filters used to remove and/or reduce such pollutants may quickly become saturated and deposited molecules may return back into the location from which they were originally removed (36, 48).

Table 1. Different methods for diluting and/or removing indoor pollutants.

Method		Targeted pollutants	Some advantages	Some limitations	Ref.
Increased ventilation		Air pollutants	Efficient in removing many pollutants	High costs, efficiency depends on weather conditions and outdoor air	(49, 50)
Filtration	Air filters	Particles	Reduction of indoor pollutants	Insufficient in removal of settled particles	(51, 52)
	Gas-phase filters	Gases		Short lifetime	(53, 54)
Portable air cleaners	PCO cleaners	VOCs, inorganic gases, air-borne microbes	Decomposition products supposed to be CO ₂ and H ₂ O; products not accumulated on a filter surface	Incomplete decomposition leading to production of harmful by-products; different factors e.g. RH and/or intensity of UV light influence the performance; should be avoided while humans are present indoors	(55, 56)
	Ozone generators	Gaseous pollutants, air-borne microbes	Reduce some odorants	May generate high levels of ozone	(53)
	Ion generators	Particles	Particle precipitation	Tend to produce ozone as a byproduct	(53, 57)
	UVGI cleaners	Air-borne microbes	Inactivation of some microbial pollutants	Spores tend to be resistant to UV radiation, may generate ozone	(53, 58)

Moisture in buildings - occurrence and consequences

Relative humidity (RH), defined as the ratio of the amount of water vapor in the air to the maximum amount of water vapor needed to saturate the air at a defined temperature (59), is an important factor for human well-being and health. RH between 40 and 60% is recommended for human comfort (60). RH depends on many factors including the outdoor climate, building ventilation rates, human activities, and surface buffering properties of surrounding materials. At equilibrium, the RH of the ambient

air is the same as on the surface of building materials (61). Building materials are able to sorb water molecules, and such water content in building materials is called water activity (62). Both parameters are closely related, however water activity is expressed as a fraction instead of a percentage. Due to factors such as the climate change, human mistakes, or improper maintenance of buildings, the content of water in building construction may increase leading to dampness. Such processes, if not properly addressed, may create different adverse outcomes like mold growth or degradation of the materials with a subsequent production of emissions. The susceptibility of building materials to microbial and/or chemical degradation depends upon the type of material and different parameters including temperature, RH or time of exposure (63, 64).

Polyvinyl chloride (PCV) and linoleum flooring are popular worldwide. When attached on a moist concrete slab compounds in the adhesives used may undergo hydrolysis leading to the production of a range of VOCs like alcohols (9, 65), typically 2-ethyl-1-hexanol (2-EH) and n-butanol. Briefly, as suggested by Sjöberg and Ramnäs (66), a high pH of concrete slabs, between 11 and 13, seems to be crucial for the degradation of adhesives containing poly(butyl acrylate-co-2-ethyl-hexyl acrylate) by breaking ester bonds between the butyl group and 2-ethyl-hexyl group (64). Research has shown that the amounts of air-borne VOCs increase with increased amount of sub-flooring moisture (67) thus compromising the IAQ (68, 69). These problems are commonly reported from Scandinavia (70) and Japan (71, 72). Interestingly, such VOC emissions slightly decrease with time and tend to follow periodic variations in air concentrations between winter and summer seasons as affected by room temperature (71).

Remediation of damp buildings

Damp buildings with or without viable mold growth and/or emitting unpleasant odors need to be subjected to different remediation measures. The most efficient way is to replace contaminated materials by new ones; alternatively, to use different methods for cleaning affected surfaces and allowing them to dry out. It is crucial to address such problems immediately to avoid spreading of pollutants indoors. For example, water-affected materials may be colonized by mold within 48 hours of exposure to moisture (73). Sometimes remediation measures are very difficult to process. For example, 2-EH and n-butanol, formed from alkaline degradation of adhesives and/or PVC flooring, may migrate several centimeters down into the concrete (66). Approximately 15% of concrete consists of pores which may store and release VOCs for a long period of time (74). In such cases, removing perhaps a 10-cm layer concrete may be perilous; installing ventilated floors and/or using different sealants may represent an acceptable solution.

Aims of the study

The aims of this thesis were:

1. To measure markers of bacterial lipopolysaccharide and fungal biomass in waterpipe tobacco and smoke in addition to smoking generated PAHs and particles (**paper I**).
2. To study the influence of RH on indoor air concentrations of VOCs emitted from building materials (**paper II**).
3. To develop a new device (the surface emissions trap) for reducing and/or stopping surface emissions (**paper III and IV**, information in the thesis).
4. To test the efficiency of the surface emissions trap for reducing emissions of VOCs at different conditions (RH, temperature, after accelerated aging), for stopping mycotoxins (**paper III and IV**), and for reducing smoking generated pollutants (preliminary study).
5. To test the performance of the surface emissions trap to improve IAQ in a school building and to affect human perception of the resulting VOCs reduction (**paper IV**).

Methods

This chapter contains an overview of used methods and techniques. Detailed information can be found in papers I-IV.

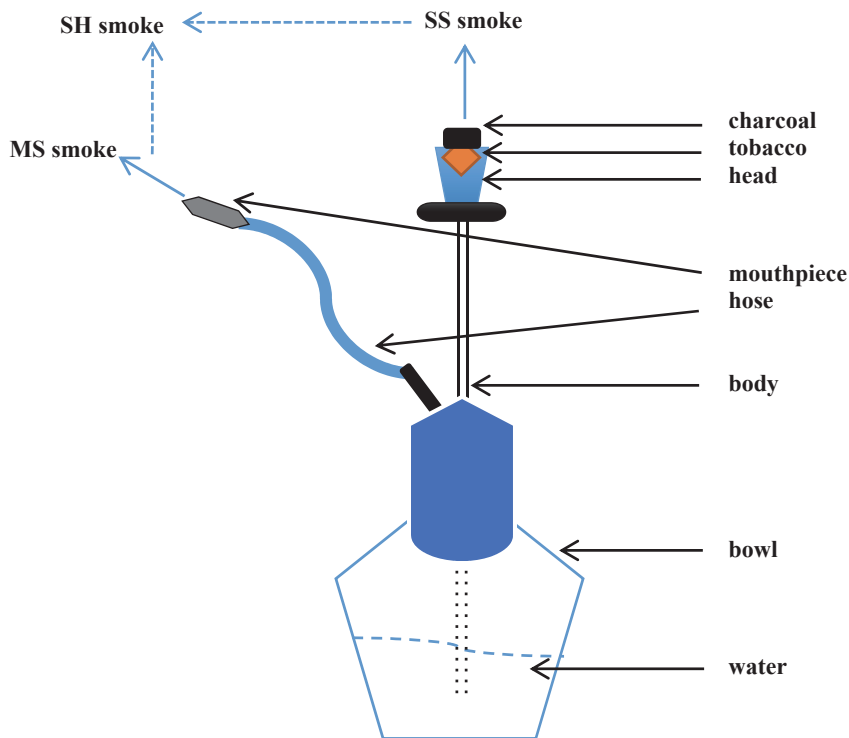
Waterpipe tobacco smoke (paper I)

Two microbial markers (3-OH FAs of LPS and ergosterol of fungal biomass) were studied in waterpipe tobacco as well as in MS, SS, and SH smoke.

Samples of 8 commercially available brands of waterpipe tobacco purchased at local retail outlets in Beirut were homogenized prior analysis. MS and SS waterpipe smoke were generated by using a smoking machine (75, 76). MS smoke was drawn through four parallel glass fiber filters, which were changed periodically as needed (typically 3-5 filters per smoking session). SS smoke was collected in an enclosure surrounding the waterpipe head and then drawn through a glass fiber filter. To determine total particulate matter (TPM), filters were pre- and post- weighed. Filters from 10 replicate smoking sessions were analyzed.

SH cigarette and waterpipe smoke were generated in an 21.6 m³ aerosol chamber. In three repetitions the smoker was asked to smoke the waterpipe (see Figure 1) filled with 10 g of tobacco. For comparison, three additional experiments were performed under the same chamber conditions but with smoking 5 cigarettes. Polycarbonate filters were used to collect air samples for analysis of 3-OH FAs, ergosterol, and PAHs. Particle number size distributions (10-650 nm range) were measured by a scanning mobility particle sizer (SMPS). Mass concentration was analyzed by a tapered element oscillating microbalance mass concentration (TEOM) with a cyclone for measuring the particle fraction below 1 μm (PM₁). The effective density of the particles was measured by an aerosol particle mass analyzer (APM) set to operate in the range of 70-420 nm. All filters were analyzed as described in Table 3.

Figure 1. A narghile waterpipe. The waterpipe consists of a head, body, water bowl, and hose. A moistened, flavored tobacco mixture is placed in the head and covered with a piece of perforated aluminum foil. Burning charcoal is placed on top of the aluminum foil to provide the heat needed to generate the smoke. When a user takes a puff, air and hot charcoal fumes are drawn through the tobacco mixture, and eventually through the water bubbler, hose and mouthpiece. Similar quantities of charcoal and tobacco mixture are consumed in a typical 1 hour café use session.



Emissions of volatile organic compounds (paper II)

A range of VOCs were selected as emission models representing different classes of organic molecules with a broad variety in their physicochemical properties and indoor origin. The VOC mixtures were prepared by diluting pure compounds (see Table 2 for details) (concentrations are given elsewhere) in distilled water with a few microliters of detergent.

Three samples of gypsum drywall, wood, and concrete were exposed for 24 h to the VOCs. A 1-ml aliquot of an aqueous VOC solution was added to one set of samples on the surface of each material, which was then stored in a closed 400-ml Petri dish. A second set of samples was transferred into a 1-L beaker containing a 50-ml beaker with a 1-ml aliquot of VOC solution, thereafter, the larger beaker was closed. These experiments were performed to expose the materials to volatile pollutants in the aqueous and gaseous phase, respectively. After 24 h of exposure, the contaminated building material samples were stored at room temperature in a ventilated hood for 30 days. Thereafter, one sample at the time was placed in a climate chamber following air sampling at 30 °C (see Table 3). Afterwards, the sample was taken back into the hood. The first air sampling was performed at RH of 40% and after 24 h a second measurement was performed at RH 85%. The procedure was repeated for each sample two weeks after the first sampling. In a similar way, air samplings of five pieces of impregnated wood (180 g) emitting an unpleasant odor were performed in the climate chamber at low (40%) and high (85%) RH.

In a separate study, two rooms, one with a disturbing odor due to dampness and a previously known problem with floor emissions due to degradation of adhesives (room A, 5.7 m, with a PVC flooring) and a second room with no signs of dampness (room B, 25 m, with a wooden floor), were studied. In both cases, air samplings were taken first at ambient RH (21-22% RH in room A, 34-35% RH in room B). Thereafter, by using a humidifier, RH was rapidly increased and reached 75% in room A and 68% in room B. During the increase of RH two additional air samplings were made and the humidifier was switched off. The last sampling was taken 16 hours later, at ambient RH. The room temperatures were 22-24 °C during the experiments.

Table 2. Some properties of the studied VOCs.

Compound	Molecular formula*	MW [Da]*	BP [°C] at 760 mmHg*	Vapor pressure at 25°C [mm Hg]*	Examples of indoor origin	Ref.
Formaldehyde ^a	CH ₂ O	30.0	-19.5 ±9.0	3463.8	Wooden materials, VOCs/ozone reactions	(10, 77)
Ethanol ^b	C ₂ H ₆ O	46.1	72.6 ±3.0	82.8 ±0.2	MVOC, cosmetics, household products	(78)
Acetone ^b	C ₃ H ₆ O	58.1	46.5 ±3.0	348.4 ±0.1	MVOC, cosmetics, household products	(78)
1-Propanol ^b	C ₃ H ₈ O	60.1	95.8 ±3.0	26.3 ±0.3	Solvents, paints, disinfection agents	(79)
2-Methyl-1-propanol ^{b,f}	C ₄ H ₁₀ O	74.1	105.0 ±0.8	16.4 ±0.4	MVOC	(80)
n-Butanol ^{c,d,e,g}	C ₄ H ₁₀ O	74.1	117.7 ±3.0	8.5 ±0.4	Floor covering materials e.g. PVC and adhesives	(66, 67, 81)
Benzene ^b	C ₆ H ₆	78.1	78.8 ±7.0	100.9 ±0.1	Paint, adhesives, linoleum flooring	(12)
2-Methylfuran ^{b,f}	C ₅ H ₆ O	82.1	64.5 ±9.0	176.1 ±0.1	MVOC, smoke	(82, 83)
Ethyl acetate ^b	C ₄ H ₈ O ₂	88.1	73.9 ±3.0	117.7 ±0.1	MVOC, cosmetics	(80, 84)
3-Methyl-2-butanol ^{c,d,e}	C ₅ H ₁₂ O	88.1	113.6 ±8.0	10.6 ±0.4	MVOC	(85)
3-Methyl-1-butanol ^{c,e}	C ₅ H ₁₂ O	88.1	131.2	4.2 ±0.5	MVOC	(82, 83)
2-Methyl-1-butanol ^f	C ₅ H ₁₂ O	88.1	128.7	4.8 ±0.5	MVOC	(82)
1-Methoxy-2-propanol ^b	C ₄ H ₁₀ O	90.1	118.5 ±8.0	8.2 ±0.4	Building materials, consumer products	(86, 87)
Toluene ^{d,e}	C ₇ H ₈	92.1	110.6 ±3.0	27.7 ±0.1	Building materials e.g. wall panels, adhesives	(88, 89)
Phenol ^{d,g}	C ₆ H ₆ O	94.1	181.8	0.6 ±0.3	Building materials e.g. vinyl flooring, smoke	(49, 88, 89)
Dimethyl disulfide ^{c,d,e}	C ₂ H ₆ S ₂	94.2	109.7	28.7 ±0.2	MVOC, furniture, smoke	(82, 83)

Compound	Molecular formula*	MW [Da]*	BP [°C] mmHg*	Vapor pressure at 25°C [mm Hg]*	Examples of indoor origin	Ref.
n-Hexanal ^{c,e,g}	C ₆ H ₁₂ O	100.2	127.9 ±3.0	10.9 ±0.2	Building materials e.g. floor coverings, plywood	(88, 89)
Styrene ^{c,d,e,f}	C ₈ H ₈	104.1	145.2 ±7.0	6.2±0.1	MVOC, furniture	(82, 83, 90)
Benzaldehyde ^{c,e}	C ₇ H ₆ O	106.1	178.8	1.0 ±0.3	UV-cured coatings, household products	(90, 91)
Anisole ^{c,d,e}	C ₇ H ₈ O	108.1	153.6	4.2 ±0.2	MVOC	(92)
2-Heptanone ^{c,e}	C ₇ H ₁₄ O	114.2	151.2 ±3.0	4.7 ±0.3	MVOC	(80, 83)
1-Octen-3-ol ^{c,d,e,f}	C ₈ H ₁₆ O	128.2	168.4	0.5 ±0.6	MVOC, fungal secondary metabolite	(82, 83)
2-Ethyl-1-hexanol ^{c,d,e,g}	C ₈ H ₁₈ O	130.2	184.6	0.2 ±0.7	Floor covering materials e.g. PVC and adhesives	(66, 67, 81)
Limonene ^e	C ₁₀ H ₁₆	136.2	175.4 ±20.0	1.5 ±0.2	Wooden building materials, household products	(93, 94)
α -Pinene ^{c,d,e}	C ₁₀ H ₁₆	136.2	157.9 ±7.0	3.5 ±0.1	Wooden building materials, household products	(93, 94)
2-Chloroanisole ^g	C ₇ H ₇ ClO	142.6	198.5	0.5 ±0.3	Microbial degradation of wood preservatives	(90, 95)
2-Methylisoborneol ^d	C ₁₁ H ₂₀ O	168.3	208.7 ±8.0	0.0 ±0.9	Microbial degradation of wet building materials	(26, 96)
Geosmin ^d	C ₁₂ H ₂₂ O	182.3	270.0	0.0 ±1.2	Microbial degradation of wet building materials	(26, 96)
Trichloroanisole ^g	C ₇ H ₅ Cl ₃ O	211.5	246.0	0.0 ±0.4	Microbial degradation of wood preservatives	(90, 95)
TXIB ^g	C ₁₆ H ₃₀ O ₄	286.4	280.0	0.0 ±0.5	Floor covering materials e.g. PVC and adhesives	(74, 97)

* - (98)

a - VVOC*b* - VOCs used in mixture 1*c* - VOCs used in mixture 2*d* - VOC mixture used in the experiment of human perception of VOCs reduction due to the use of the cTrap*e* - VOC mixture used for studying the influence of RH on air concentrations of VOCs*f* - MVOCs produced by *A. versicolor**g* - emissions from damp building material

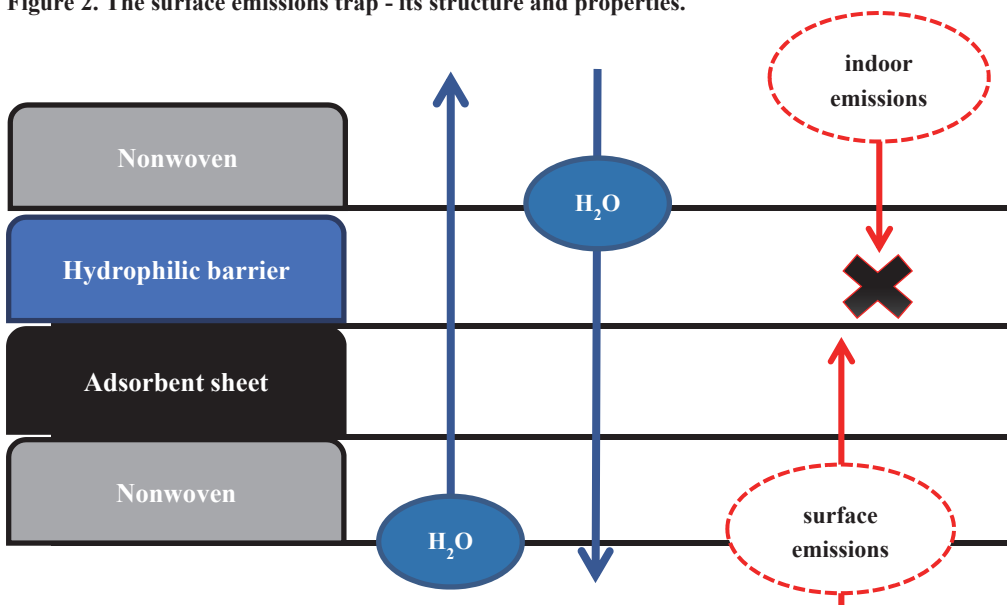
A new device for improving IAQ - the surface emissions trap (paper III and IV)

A new device for reducing and/or stopping pollutants was developed. Ideally, the device should stop all gaseous and particulate emissions from surfaces. It should also bind VOCs. Water vapor should pass through the device with minimal resistance in order to avoid build-up of moisture, with a risk of mold growth. In the present study, the performances of several commercially available absorbents, adsorbents, and barriers were analyzed (unpublished results). A combination of an adsorbent layer and a hydrophilic polymer sheet (as a barrier) was further tested as a cTrap prototype for its ability in

- 1) reducing unwanted emissions of VOC at different environmental conditions (RH, temperature and after accelerated aging) (**paper III and IV**),
- 2) trapping VOCs (capacity tests) (**paper III**),
- 3) reducing MVOC emissions (**paper III**),
- 4) stopping mycotoxins (**paper III**),
- 5) improving IAQ in a school building (**paper IV**),
- 6) affecting the human perception of VOCs reduction (**paper IV**),
- 7) reducing VOCs from a damp PVC flooring (**paper IV**),
- 8) reducing particle and VOC emissions generated from tobacco smoking (unpublished results).

The device, called the surface emissions trap (cTrap), is an adsorbent sheet with a hydrophilic barrier surrounded by two protective sheets of nonwoven fabric (see Figure 2). Through its structure, the device allows easy passage of water vapor in both directions but VOCs are trapped and collected in the adsorption layer. Moreover, the hydrophilic barrier enhances the efficiency of the device in reducing VOCs and in stopping particles (e.g. particle-bound mycotoxins). The barrier does not adsorb indoor emissions (present above the hydrophilic barrier), which could lead to decreased capacity of the cTrap.

Figure 2. The surface emissions trap - its structure and properties.



Reducing air pollutants by using the surface emissions trap

Laboratory experiments

The performance of the cTrap was studied in a series of laboratory experiments. Aqueous solutions of VOCs including one mixture of 8 VOCs (mixture 1), another mixture of 12 VOCs (mixture 2), and an aqueous solution of formalin (source of formaldehyde) or 2-chloroanisole (see Table 2) were used to study the efficiency of the device in reducing VOC emissions (paper III and IV). As shown in Figure 3, before collecting air samples, a solution was transferred into a glass Petri dish located inside a 2.6-L plastic box with a narrow slit in the lid (14.5 x 1 cm). The lid was then either covered by a piece of the cTrap or left uncovered. The boxes were placed in a wooden closet for sampling at ambient conditions and in a climate chamber for sampling at different RH and temperatures.

Figure 3. Two procedures used to test the efficiency of the cTrap in reducing VOCs.



Transferring a mixture of VOCs to a container



Closing a slit by a layer of the cTrap



Placing into a wooden closet



Placing into a climate chamber



Air sampling



Air sampling

The efficiency of the device for reducing VOCs at different temperatures (30 and 40 °C) and RH (35, 60, and 85%) was studied (paper IV). Non-covered plastic boxes containing a selected VOC mixture were studied for comparison (23 °C, 55% RH). The device was also subjected to accelerated aging simulating up to 10 years. In this study, pieces of the cTrap were stored at 75 °C and 60% RH following a 10-degree rule of doubling the rate of chemical reactions by increasing temperature by 10 °C (99). Samples with 1, 5, and 10 simulated years of age were studied for their ability to reduce VOC emissions at ambient conditions (see details in Table 3).

The ability of the cTrap cloth to trap molecules was studied further (paper III). After the device had been used for 24 h to trap VOC emissions from mixture 2, a 1cm² piece was extracted with dichloromethane, diluted, and analyzed (see Table 3). A parallel piece of the device, prepared in the same way but exposed only to water, was analyzed for comparison. Also the adsorption capacity was determined (paper III). Briefly, two aqueous solutions containing 2-EH and 1-octen-3-ol, respectively, were prepared in several 250-ml beakers which were then covered by pieces of the cTrap. Every second day the solution was replaced with a new one until, as judged by gas chromatography-mass spectrometry (GC-MS) analysis, the device was saturated by the studied VOC.

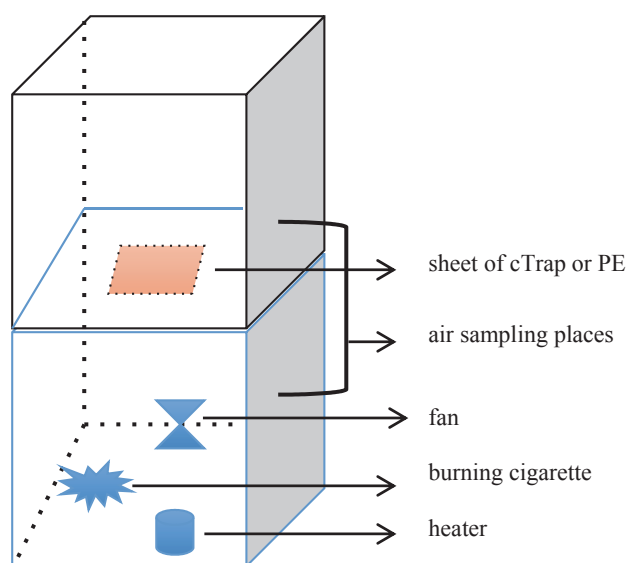
A separate experiment was undertaken to study if the reduction of VOCs due to the function of the cTrap was consistent with human perception (paper IV). Two plastic boxes with a mixture of 11 VOCs (see Table 2) were used. Briefly, 15 male volunteers (randomly assigned to one of the two exposure groups) were asked to sniff the air above the plastic box covered by the device (1st group) or by two nonfunctional nonwoven layers taken from the device (2nd group) placed in a ventilating hood. Thereafter, all volunteers were asked to fill in a simple questionnaire on their perception of the perceived odor intensity.

Microorganisms may contaminate the indoor environment by producing and spreading many different pollutants including MVOCs and mycotoxins. In one experiment (paper III), cultures of *Aspergillus versicolor* growing on malt extract agar (MEA) Petri dishes were studied. One of the plates was covered by the cTrap while the second plate was left uncovered; both were stored for 72 h following air samplings. In a separate experiment (paper III), a bioaerosol of freeze-dried molds (*Stachybotrys chartarum*, *Penicillium expansum* and *A. versicolor*) was created by using a magnetic stirrer into two plastic containers with a plastic sieve. The cTrap was used to cover one sieve while the second one was left uncovered. Samples were collected by washing surfaces of the cTrap and the uncovered sieve by cotton swabs pre-wetted in methanol after 16, 22, and 40 hours of stirring, and analyzed for three mycotoxins, viz. stachybotrylactam, roquefortic C, and sterigmatocystin.

Finally, the extent to which the cTrap cloth could reduce pollutants of cigarette smoke was studied. Briefly, in a chamber of 1.89 m³, equally divided in an upper and lower part, a 20x20 cm piece either of the cTrap or of a plastic sheet of polyethylene (PE)

was applied to cover an opening of a separating wall. Cigarette smoke equally distributed by a fan was generated in the lower part of the chamber. A small heater was used for obtaining overpressure (1-2 Pa) in the lower part. Air samplings were collected on Tenax TA in the lower and upper part of the chamber (see Figure 4). Ultrafine particles (UFPs) of cigarette smoke were monitored by using an UFP counter Nano Tracer PNT 1000 set to scan total number of particles in the range of 10-300 nm, concentration 0-10⁶. The experiment (n=2) was carried out for one hour from the moment where the UFP counter was overloaded by smoke particles (>10⁶ UFPs/cm³) (unpublished results, see also Table 3).

Figure 4. Schematic view of the used chamber.



Field studies

The performance of the cTrap in improving the IAQ in a classroom (30 m²) of a school built in the 1970s (paper IV) was studied. There had been considerable complaints on the air quality resulting in high absenteeism, headache, fatigue etc. among the pupils and the school staff. Increased ventilation and use of air purifiers in the room had not shown any significant improvement. Previous investigations had strongly suggested that the IAQ problems were due to emissions from the floor. The cTrap cloth was applied directly on the existing PVC flooring using a double sided

adhesive tape and above the device a laminated flooring was installed (see Picture 1). Following the installation for 13 months, 5 air samplings and 5 pieces of the cTrap (from under the laminate flooring) were taken at different time periods and analyzed for the amounts of adsorbed 2-EH. A simple form was handed out to the 24 school teachers before and after the installation with questions on the perceived air quality. Materials from surfaces of the cTrap cloth, PVC flooring, and laminated flooring were collected 13 months after the installation by an adhesive tape and used for mold microscopy.

Separate studies were performed (paper IV) in an office room with a PVC flooring and an unpleasant smell. Two desiccator lids were placed on the PVC flooring. In one case a piece of the cTrap cloth had previously been attached on top of the flooring (see Picture 1). The remaining part of the floor, excluded from the experiment, was covered by aluminum foil. Air was sampled under the lids 3 months after the installation was made (see Table 3).



Picture 1. Installation of the cTrap above the source of emissions in a school building (left) and an office room (right, courtesy Jörgen Grantén, Lund, Sweden).

Sampling air pollutants

Different filters are currently used to collect air-borne particles indoors that may contain e.g. bacteria and mold. Volatile organic vapors may be collected by sampling tubes that contain one or several sorbents. Such pollutants are physically adsorbed on porous material where the strength of the forces depends on the adsorbent surface and pores properties. The selection of sampling procedures depends on many factors and include e.g. the type of pollution, concentrations, and environmental conditions. In the present thesis, several different sampling methods were used:

Active sampling - samples were collected by pumping air (at different flow rates, see Table 3) through a sampling device. Glass fiber/polycarbonate filters were used for collecting microorganisms and/or microbial fragments as well as PAHs. Tenax TA, Anasorb 747 sorbent tubes, and DNPH (2,4-dinitrophenylhydrazine) columns were used for sampling VOCs (see Table 3).

Passive sampling - Tenax TA and the cTrap cloth were exposed to the emissions for a week (Tenax TA) or up to several months (the cTrap). The mechanisms behind passive (diffusive) air sampling can be explained by two processes: Fick's law and the concentration gradient across a barrier (e.g. an air gap between the sample holder and the adsorbent bed). In the case of Tenax TA an active air sampling performed at a flow rate of 0.5-1.0 ml/min may correspond to uptake rates of 2ng/ppm/min when using passive air sampling (100).

All sampling methods (see Table 3), especially those used for collecting VOCs have their own advantages and disadvantages. The methods used in the individual experiments were selected with respect to their ability to sample a wide range of different molecules while accepting limitations with respect to accuracy (recovery, artifacts formation etc.) for some molecules.

DNPH impregnated C18 columns are especially designed for sampling very volatile aldehydes (e.g. formaldehyde) and reactive ketones. Briefly, DNPH reacts with carbonyl group of the target molecules creating stable hydrazones (101).

Tenax TA contains a porous polymer of 2,6-diphenyl-p-phenylene oxide that efficiently adsorbs organic molecules in the range of C4-C26. Tenax TA is very hydrophobic and due to its low specific surface area (30-35 m²/g) it is not recommended for sampling VVOCs and larger quantities of VOCs. Low background of impurities makes Tenax TA suitable for sampling VOCs at very low concentrations (ppt-ppb range) (100, 102).

Anasorb 747 (200 mg sorbent) is an adsorbent made from synthetic carbon, relatively hydrophobic and with a high surface area (about 1000 m²/g), making it suitable for sampling a very wide range of both polar and non-polar compounds, even at high concentrations (ppb-ppm range) (103).

According to existing knowledge the impact of RH on the sampling performances of Tenax TA and Anasorb 747 is negligible, even at relatively high RH (103, 104). Such tubes can therefore be used for studying VOCs emissions at different RH (paper II, IV). As shown in Table 3, different chambers and sampling methodologies and study conditions were used for the different pollutants.

Table 3. Sampling procedures used in the studies.

Place of sampling	Device used for sampling	Technique of sampling	Ventilation rate [air change/h]	Sample preparation	Paper
<i>VOCs in mixture 1</i>					
A wooden chamber and a climate chamber	Tenax TA	Active: 100 [ml/min]	0.06	Thermal desorption*	III, IV
<i>VOCs in mixture 2</i>					
A wooden chamber and a climate chamber	Anasorb 747	Active: 250 [ml/min]	0.14	Extraction with dichloromethane	III, IV
A covered 2.6-L plastic box	The cTrap	Passive: 24 h	n.a.	Extraction with dichloromethane	III
<i>Exposure to 2-EH or 1-octen-3-ol (capacity test)</i>					
A covered 250-ml beaker	The cTrap	Passive: several weeks	n.a.	Extraction with dichloromethane	III
<i>A damp PVC flooring</i>					
A school room (30 m ²)	Tenax TA	Passive: 1 week	2-2.5	Thermal desorption*	IV
	The cTrap	Passive: up to several months	n.a.	Extracted with dichloromethane	
Surfaces of the cTrap and surrounding floor	Adhesive tape	13 months after installation	n.a.	Mold microscopy*	IV
A 1-L glass lid	Tenax TA	Active: 3 months after installation	n.a.	Thermal desorption*	IV
<i>2-chloroanisole</i>					
A wooden chamber	Anasorb 747	Active: 250 [ml/min]	0.14	Extraction with dichloromethane	IV
<i>Formaldehyde (VOCs)</i>					
A wooden chamber	DNP columns	Active: 200 [ml/min]	0.11	According to (101)*	IV
<i>Human perception of VOCs reduction due to the cTrap</i>					
A ventilated hood	Human nose	A 3 s sniff	500 l/s	n.a.	IV

Place of sampling	Device used for sampling	Technique of sampling	Ventilation rate [air change/h]	Sample preparation	Paper
MVOCs					
A 5.8-L glass container	Tenax TA	Passive: 72 h	n.a.	Thermal desorption*	III
Mycotoxins					
A 600-ml plastic container	Cotton swabs	Collection from the surface	n.a.	Extraction with methanol	III
Smoke generated particles, PAHs, and microbial markers					
Machine generated	Polycarbonate or glass filters	Active: 1.6 [l/min]	n.a.	According to (105) for PAHs*, and (38) for microbial pollutants, SMPS, TEOM, APM for particles	I
An aerosol chamber		Active: 10 [l/min] (on average)	0.5		
Smoke generated particles and VOCs					
An 1.89 m ³ chamber	Tenax TA; UFP counter	Active: 100 [ml/min]; real time monitoring	0.25 (lower), 0.39 (upper) part	Thermal desorption*; real time monitoring	Inf. in the thesis
RH induced VOCs (laboratory contaminated building materials ^a , sill wood samples ^b , rooms ^c)					
A climate chamber ^{a,b}	Tenax TA	Active: 100 ml/min	0.14	Thermal desorption*	II
A room with a wood floor (5.7 m) ^c	Tenax TA	Active: 100 ml/min	n.a.	Thermal desorption*	II
A room with a PVC flooring (25 m) ^c			0.38		

n.a. - not applicable

* - analyzed by IVL (Stockholm/Gothenburg, Sweden)

Analysis of air pollutants using chromatography and mass spectrometry

VOCs and MVOCs were analyzed by GC-MC after thermal desorption (Tenax TA) or after extraction with dichloromethane (Anasorb 747, the cTrap). Formaldehyde was analyzed by high performance liquid chromatography (HPLC). Microbial markers were analyzed by GC-MS/MS and mycotoxins by HPLC-MS/MS (see Table 4).

GC-MS analysis - is an analytical chromatographic technique for separating different molecules in gas phase. Compounds are transported by heated carrier gas (the mobile phase), typically helium, from the injector to the chromatographic column containing a stationary phase, where they are separated mainly according to polarity and BP. Compounds leave the stationary phase at different times, pass through the transfer line and are thereafter introduced to the ionization chamber. The most common type of ionization in GC-MS is electron ionization (EI) where eluted molecules are destroyed into fragment ions by free electrons emitted by a charged filament. The information of ionized mass fragments is translated by a multiplier into an electrical signal, monitored and presented as a chromatography peak. Samples may be analyzed in SIM (selected ion monitoring), SCAN, or MS/MS mode. In GC-MS/SCAN the instrument is set to analyze all masses within a pre-selected range instead of specific masses of interest molecules as in GC-MS/SIM. Typically SIM mode gives 10-100 times better sensitivity than SCAN mode.

As mentioned in Table 3, all samples were analyzed by GC-MS after they had been extracted or thermally desorbed from sampling tubes. Sensitivity in thermal desorption is very high since the content of the entire tube is analyzed without dilution. An advantage of solvent extraction is a possibility to repeat analyses. Disadvantages are low sensitivity as a consequence of dilution, variable recovery from sorbent tubes, high background or presence of a solvent peak that may mask other compounds.

HPLC-MS/MS - is an analytical technique used for separating and detecting less volatile or polar molecules. A sample is delivered in a liquid (mobile) phase where different molecules are separated on a column (the stationary phase). Eluent from the HPLC is sprayed through a charged thin capillary, and the occurring nebulizing and evaporation processes involved in ESI (electrospray ionization) chamber, leads to the formation of ions that are introduced to a quadrupole mass analyzer. Tandem mass spectrometry utilizes three quadrupoles. The first quadrupole (Q1) is set to scan for a daughter ion of molecule of interest; thereafter the found molecule passes the second quadrupole called the collision cell (Q2). Molecules collide with a collision gas (usually argon) and are fragmented into fragment ions. The last quadrupole (Q3) is scanning for selected fragment masses in the so-called selected reaction monitoring (SRM) mode.

Table 4. A summary of the chromatography techniques used. Note: Data for formaldehyde, VOCs of mixture 1, and PAHs are given elsewhere.

Compound	Analyzed ions	Analytical column	Analytical method	Studied in paper
VOCs				
1-Butanol	56, 41	VF5ms, 60m x 0.25 mm ID, 1 µm film thickness	GC-MS	II-IV
3-Methyl-2-butanol	45, 55			II-IV
3-Methyl-1-butanol	70, 55			II-IV
Toluene	91, 92			II
Dimethyl disulfide	94, 79			II-IV
Hexanal	56, 57			II-IV
Styrene	104, 103			II-IV
Benzaldehyde	106, 77			II-IV
Anisole	108, 78			II-IV
2-Heptanone	58, 57			II-IV
1-Octen-3-ol	57, 72			II-IV
2-Ethyl-1-hexanol	57, 55			II-IV
Limonene	68, 93			II
α-Pinene	93, 92			II-IV
2-Chloranisole	141, 99			IV
Mycotoxins				
Sterigmatocystein	325.0>> 281, 310	RP-18 Polaris 5µm C-18A, 150 x 2.0 (ID) mm	HPLC-MS/MS	III
Stachybotrylactam	386.0>> 178, 150			III
Roquefortin C	390.0>> 193.2, 322.3			III
Microbial markers				
Ergosterol	363>> 157, 239	CP-Sil 8 CB, 30 m x 0.25 mm ID, 0.25 µm film thickness	GC-MS/MS	I
3-OH FAs	175>> 131			I

Discussion of the results

This chapter contains a brief discussion of the results. Detailed information can be found in papers I-IV.

Waterpipe tobacco smoke

It was previously reported that smoking of cigarettes creates a bioaerosol containing detectable amounts of microbial compounds e.g. 3-OH FAs of bacterial LPS and ergosterol of fungal biomass. However, no information concerning such pollutants in waterpipe tobacco and smoke was available. The present study was prompted by this gap in knowledge and by the fact that waterpipe smoking is increasing in popularity in many parts of the world (106).

Waterpipe tobacco was found to contain similar amounts of 3-OH FAs and ergosterol as previously found in international brands of cigarette tobacco by Larsson et al. (38). These results may seem surprising since only 1/3 of "waterpipe tobacco" is tobacco leaves, the rest is a mixture of additives such as glycerol, flavors etc. Waterpipe MS and SS smoke contained detectable amounts of 3-OH FAs and ergosterol, while only 3-OH FAs were identified in waterpipe SH smoke. Waterpipe MS smoke generated during one smoking session contained on average 1800 pmol of LPS and 84.4 ng of ergosterol which is approximately 100 times more than in waterpipe SS smoke. Similar amounts of 3-OH FAs and 4-12 times higher amounts of ergosterol were previously reported while smoking one cigarette (45). Waterpipe MS contained approximately 2% of the total content of ergosterol in the tobacco, and 9% of 3-OH FAs. These results may be explained by the fact that 3-OH FAs may be more resistant to heat than ergosterol. A strong correlation was found between waterpipe MS smoke total particulate matter (TPM) and MS LPS ($R^2=0.6593$). Waterpipe SS as well as (previously shown) cigarette SS smoke (45) contain only traces of ergosterol and 3-OH FAs probably because of thermal degradation.

In general, SH smoke generated from waterpipe smoking contained less of the microbial studied compounds than SH smoke from cigarette smoking. Thus, waterpipe SH smoke contained 2.8 pmol/m³ of LPS while the amount of ergosterol was under the detection limit. In comparison, smoking five cigarettes gave 22.2. pmol/m³ of LPS

and 87.5 ng/m^3 of ergosterol. The total particle number for the two types of smoke were similar, but cigarette SH smoke contained larger particles than waterpipe SH smoke. As a consequence, higher mass concentration was found in cigarette SH smoke. However, it was estimated that similar amounts of SH smoke particles may be deposited in the respiratory tract (cigarette smoke 15%, waterpipe smoke 18%), indeed smoking tobacco products generates a large fraction of small particles ($<200 \text{ nm}$). Taking into the consideration that similar amounts of waterpipe and cigarette tobacco were used in the SH smoke experiments, SH waterpipe smoke contained half as much of PAHs as cigarette smoke. On the other hand, the more carcinogenic 5- and 6-rings PAHs were found in higher concentration in the waterpipe smoke.

Emissions of VOCs from building materials

It has long been known that emissions of VOCs from building materials may increase with increased RH. However, there have been few studies on how RH affects VOCs concentrations inside a building.

The present study concerned two rooms, one with previously known water damage and another room with no apparent damage. It was found that a rapid increase of RH from 40 to 85% in the room with a damp PVC flooring gave a 3-fold increase of air concentrations of 2-EH and a 2-fold increase of 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate (TXIB). These results may be explained by the fact that the increased RH increased the diffusion rates of volatile pollutants from the source of emissions into the air, as a consequence of the so-called sink effect (107). Volatile pollutants, especially at low ventilation rates, may even migrate through building materials within dwellings (108). However, the air in a room without any noticeable dampness showed unchanged concentrations of VOCs upon the increase of RH, probably because of low amounts of VOCs attached to walls and the floor.

Air samples collected from the impregnated wooden sill samples at RH 85% were found to contain larger amounts of VOCs than those sampled at RH 40%. For example, the concentration of n-butanol rose from $2 \text{ } \mu\text{g/m}^3$ (40% RH) to $43 \text{ } \mu\text{g/m}^3$ (85% RH) and of trichloroanisole from 1 to $10 \text{ } \mu\text{g/m}^3$. In addition, air concentrations of four unknown compounds were under the detection limit at RH 40% while at RH 85% the concentrations reached $8\text{-}16 \text{ } \mu\text{g/m}^3$. Similar patterns were seen for all of the three types of laboratory contaminated building materials, both for VOCs of lower and higher polarity. Among the three different types of building materials, wood samples were found to emit the largest amount of VOCs.

Pores and/or capillaries in the building materials play an important role in the sink effect. Even at low RH, e.g. 45%, water may condense in the pores of some materials and release previously trapped VOCs by competition for active sites (108). The three

most prevalent VOCs from the laboratory contaminated samples were 3-methyl-2-butanol, 1-octen-3-ol and 2-EH, often described as markers of microorganisms, mold, and damp floor respectively (24, 109). Such compounds may be present more often than other VOCs due to their sorption/desorption characteristics. As suggested by Meininghaus et al. (108), RH and temperature strongly influence the sink process. A few studies show have focused at the influence of seasonal variations of RH on VOC emission pattern (72, 110). Such influence may be explained by ongoing hydrolysis of building materials (72), ventilation (111), reactions with ozone (10), or a combination of many factors. Here was shown that a rapidly increased RH (2 h, to an RH of 85%) may influence the VOC concentrations in indoor air and lead investigators to misleading conclusions with regards to the IAQ of the studied location. For example, in indoor air concentrations of a single compound, as recommended by some researchers (112, 113), should not exceed 10% of 300 μm^3 of total volatile organic compounds (TVOCs). Taking the present study results into consideration, it may be recommended to monitor and record RH during sampling.

Use of the surface emissions trap in reducing and/or stopping pollutants

For optimal functioning the cTrap adsorption cloth should stop and bind all harmful or irritating emissions while at the same time allowing ready passage of water vapor. A series of experiments was performed for investigating the extent it could fulfill this goal.

A summary of the most important experiments is shown in Table 5. In short, air above the covered boxes with different VOC mixtures had reductions of 95.2% (mixture 1) and 99.7% (mixture 2) of the studied pollutants. In similar experiments the cTrap cloth reduced 98.5% of the air concentrations of formaldehyde and 99% of 2-chloroanisole. Different RH (35, 60 and 85%), temperatures (30, 40°C), and age (accelerated aging simulating up to 10 years) did not affect the performance of the cTrap. After a short exposure (24 h) to the VOCs mixture the cTrap was found to contain all studied VOCs (9.3-145.5 $\mu\text{g/g}$ of the device). The reduction of VOCs due to the cTrap was consistent ($p=0.03108$) with human perception of the odorants.

The cloth was also found to be efficient for reducing MVOC emissions produced by *Aspergillus versicolor*. Above a plate with mold growth uncovered by cTrap, five MVOCs including styrene, 1-octen-3-ol, 2-methyl-1-butanol, 2-methylfuran, and 2-methyl-1-propanol were identified, in concentrations of 2.6-82 $\mu\text{g/m}^3$. Covering a plate containing (according to the naked eye) a similar amount of mold hyphae by the cTrap resulted in 88% reduction of 1-octen-3-ol, 98% of styrene and 100% of the remaining emission compounds. No traces of the studied mycotoxins

(stachybotrylactam, roquefortin C, and sterigmatocystin) were found to be able to pass through the cTrap cloth.

An important characteristic, and limitation, of the cTrap when applied in water-damaged buildings, for example, is that the source of emissions must be known. Indeed, covering different surfaces indoors with the cTrap and thereafter measuring VOCs in the air and/or VOCs adsorbed on the cTrap cloth may be used as a tool to determine the source of emissions, which can be very helpful as a guidance in the remediation process. The perceived IAQ of the school building was improved according to the school staff already a few days after application of the cTrap. Increasing amounts of 2-EH (from 0 to 280.3 μg after 13 months of use) found in samples extracted from the device demonstrated that the floor was emitting pollutants. Notably, 280.3 μg of 2-EH corresponds to approximately 1% of the cloths adsorption capacity for 2-EH ($27.1 \pm 6\%$ and $14 \pm 16\%$ mg/g for 1-octen-3-ol). The air concentrations of 2-EH ($6\text{--}7 \mu\text{g}/\text{m}^3$) found in samples collected before the remediation were similar to those found by Andersson et al. in school classrooms where pupils and the school staff complained about IAQ (114). Much higher concentrations have been found under carpets (2-EH $> 1\,100 \mu\text{g}/\text{m}^3$, n-butanol $> 5\,000 \mu\text{g}/\text{m}^3$, TVOCs $> 30\,000 \mu\text{g}/\text{m}^3$) and ammonia (10-200 ppm) indicating a massive decomposition of casein (114). Poor IAQ may be due to a synergistic effect of different VOCs which even at relatively small concentrations may cause adverse health outcomes (114). After the remediation 2-EH was still present in the air of the classroom but at lower concentrations ($2 \mu\text{g}/\text{m}^3$) probably due to desorption of the compound from uncovered surfaces (ceiling and walls). Thus, the unsatisfactory IAQ in the studied classroom might be due to presence of VOCs in concentrations too low to be detectable by the analytical methods used. Samples collected by an adhesive tape of material taken from surfaces of the device and a surrounding floor and analyzed by microscopy did not contain any mold hyphae.

The performance of the cTrap in reducing certain floor emissions was convincingly demonstrated in the experiments with the desiccator lids. Thus, air samples taken above the floor covered by the cTrap contained, after three months, 89% less of n-butanol, 99% of 2-EH and TXIB, and 97% of TVOCs in comparison with air samples taken above non-covered floor that contained $1\,620 \mu\text{g}/\text{m}^3$ of n-butanol, $1\,201 \mu\text{g}/\text{m}^3$ of 2-EH, $608 \mu\text{g}/\text{m}^3$ TXIB and $11\,108 \mu\text{g}/\text{m}^3$ of TVOCs.

Table 5. The efficiency of the cTrap for preventing pollutants - summary of results.

Type of pollutants	Effect of application	Comments	Limitations of the study
VVOC - formaldehyde	98.5% reduction	Laboratory study, exposure to high levels	Not studied in indoor air
VOCs of mixture 1	95.2% reduction	Laboratory study	Some level of uncertainty (air sampling, methodology etc.)
VOCs of mixture 1 at different temperatures, RH, and with cTrap after accelerated aging	97.8% (different RH and temp.) and 96.1% (accelerated aging) reduction	Laboratory study	See above
VOCs of mixture 2	99.7% of reduction	Laboratory study	See above
VOCs of mixture 2 at different temperatures, RH and with cTrap after accelerated aging	98.0% (different RH and temp.) and 99.9% of (accelerated aging) reduction	Laboratory study	See above
MVOCs	88-100% reduction	Laboratory study	See above
Mycotoxins	100% prevention from spread of a bioaerosol containing mycotoxins	Laboratory study of an air tight material	Only three mycotoxins studied
Emissions from a damp flooring	Improved perceived IAQ	Some emissions still present in air samplings besides a positive effect of the installation on IAQ	Indoor environment (especially school) is a complex environment and may be influenced by many factors
VOCs subjected to human perception study	Significant improvement of perceived IAQ	Study on 15 volunteers sniffing a mixture of 15 different VOCs	Study made only on one group of people (healthy young males)
Emissions from a damp PVC flooring	89-99% reduction of high air concentrations of VOCs	The performance of the device three months after being installed on a damp PVC flooring	Lack of negative control, inlet air used for sampling was not purified.
Tobacco smoke*	99 % reduction of UFP and 97.8% of TVOCs	Preliminary laboratory study	Not studied in indoor air

*- unpublished results

Tobacco smoke - unpublished results

It is known that even small amounts of smoke pollutants may be harmful for human health and wellbeing (36, 115). The cTrap may represent a new solution for stopping such unwanted emissions especially due to its low resistance for water vapor ($Z=200$ s/m). Installation of cTrap on a floor, wall, or ceiling will not affect the water vapor balance in the building.

The preliminary results suggest that the cTrap cloth may be used for reducing smoke generated VOCs and particles that may penetrate dwellings. Tobacco smoke was found to contain a number of VOCs (Table 6). The most prominent VOCs found in lower part of the chamber were toluene, benzene and limonene. TVOCs in the air of lower chamber were $4\,735\ \mu\text{g}/\text{m}^3$ (while testing cTrap) and $6\,490\ \mu\text{g}/\text{m}^3$ (while testing PE sheet). It was found that by using the cTrap to separate between two parts of the chamber simulating two apartments, VOCs were reduced by 97.8% (see Table 5) and UFP by 99%. A similar effect was seen while testing the PE plastic sheet. In a study of Afshari et al. (116), it was shown that approximately 9% of the UFP of SH smoke may migrate through cracks in the building construction from a lower flat of a smoker into a higher flat of a passive smoker. The practical applicability of using the cTrap to reduce unwanted spread of tobacco smoke VOC and particles between apartments needs to be studied further.

Table 6. Air concentrations ($\mu\text{g}/\text{m}^3$) of VOCs found in upper and lower part of the chamber separated by the cTrap and PE sheet respectively.

Compound	cTrap (n=2)		PE sheet (n=2)	
	Lower chamber	Upper chamber	Lower chamber	Upper chamber
Benzene	238	1	208	1
n-Decane	9	2	7	nd
Toluene	381	2	331	2
n-Hexanal	71	17	nd	34
n-Butanol	68	24	58	41
Limonene	183	1	126	2
2-EH	17	3	20	5
m-Xylene	144	nd	125	1
3-Carene	5	nd	4	nd
Mesitylene	6	nd	5	nd
Benzyl alcohol	6	nd	5	nd
TVOCs	4 735	105	6 490	176

nd - not detected

Conclusions

- Waterpipe smoking creates a bioaerosol containing bacterial and fungal components.
- RH may affect indoor air VOC concentrations in buildings with dampness.
- A new device, the surface emissions trap (cTrap), was found to reduce moisture-driven indoor air pollutants by up to 100%.
- The cTrap cloth can be used for improving the perceived IAQ by reducing unwanted emissions from building materials.
- Indoor air contaminated by low concentrations of VOCs may compromise IAQ.

Populärsammanfattning (Summary in Swedish)

Det är känt att kvalitén på inomhusluften har en avgörande betydelse för folkhälsan bla avseende astma, eksem samt luftvägsinfektioner. Detta är ett för samhället mycket kostsamt problem.

I avhandlingen har studerats vissa luftföroreningar inomhus som kan bli följden av att en byggnad drabbats av fuktskada. När fukt påverkar byggnadsmaterial frigörs och bildas en rad organiska ämnen, såsom olika reaktions- och nedbrytningsprodukter, mögelämnen mm, som sprids i luften inomhus. I avhandlingen visas att resultaten från luftmätningar inomhus avseende vissa sådana ämnen starkt påverkas av den relativa fuktigheten vilket är ett fynd av stor betydelse då sådana mätningar ofta används för bedömning av luftkvalitén och får styra efterföljande åtgärder. En ny metod och ett nytt material, den så-kallade cTrap-duken, utvecklades och tillämpades för att reducera luftkoncentrationerna av ämnen som sprids från ytor inomhus (golv, väggar och tak), framför allt vid fuktskada, och som därför kan komma att spela en stor roll i strävan efter en förbättrad folkhälsa. cTrap-duken visade sig kunna reducera luftkoncentrationerna av sådana föroreningar med upp till 100%.

cTrap-duken visade sig också vara effektiv för att stoppa partiklar och organiska ämnen i tobaksrök. I avhandlingen har särskilt studerats rök från vattenpipa eftersom denna typ av tobaksrökning blir alltmer populär. Studierna visade att vattnet i vattenpipan kunde minska koncentrationerna i röken av vissa mikrobiella ämnen men att avsevärda koncentrationer av sådana ämnen samt av vissa polyaromatiska kolväten ändå kvarstår i röken.

De resultat som vunnits av detta avhandlingsarbete kan komma att förbättra möjligheterna att snabbt och enkelt återställa en god luftkvalité inomhus efter att en byggnad drabbats av fuktskada.

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