Effect of aging on decorative and renovation products containing biocides: Assessment of its impact on indoor air quality

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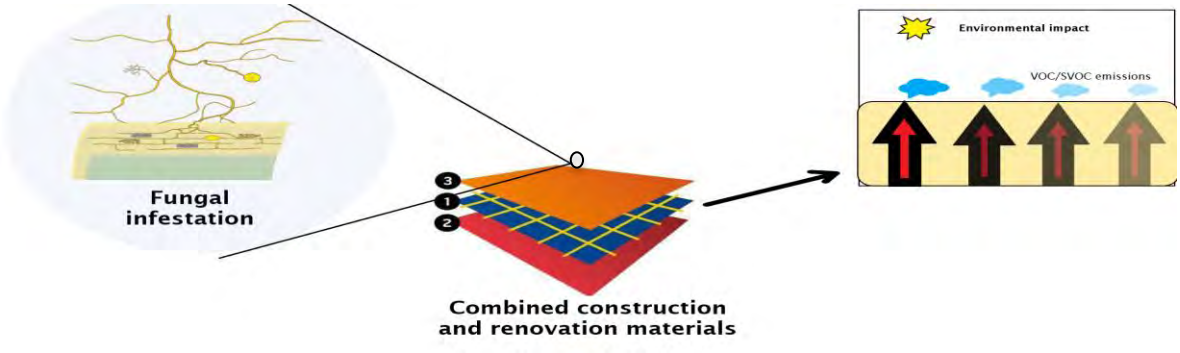
GRAPHICAL ABSTRACT



ABSTRACT

To evaluate the impact of the aging (the use of detergent and exposure to light, high relative humidity, and temperature) on the efficiency of biocides present in the renovation plaster after being added to polyester cellulose (combined material) and on VOC and SVOC emissions, an inoculation of innate and aged materials with fungal spores was carried out in this study using a dry aerosolization system. VOCs and SVOCs emitted from these different materials before and after inoculation were characterized using gas (TD-GC-MS/FID) and liquid (HPLC) chromatography.

On the microbial level, the results of the inoculation process showed a proliferation of inoculated mold on the surface of the innate polyester-cellulose whereas no visible growth was detected on the aged polyester-cellulose and the combined material.
Regarding VOC/SVOC emissions, the aging or inoculation process led to a decrease in the emission rates of most compounds and the appearance of some "new" ones. However, the combined effect of aging and inoculation on VOC/SVOC emissions showed a more variable behavior.

Keywords: Fungi, VOC and SVOC emissions, aging process, building and finishing materials, antifungal treatments

INTRODUCTION

In developed countries, people spend 90% of their time in confined spaces (housing, workplaces, and even public places) which might have a crucial effect on their health. Poor indoor air quality (IAQ) can be responsible for a number of disorders, starting from respiratory diseases to lung cancer (Awada et al. 2020).

The deterioration of IAQ could be due to the presence of various indoor pollutants, including fungal spores and Volatile Organic Compounds (VOCs). Twenty percent of the European and American buildings have been found to be affected by the presence of visible mold (ANSES 2016). Moreover, VOCs concentration was found to be 2 to 100 times higher indoors than outdoors (Jia, Batterman, et Godwin 2008).

The results from various building surveys suggest that building materials, whether structural or furnishing, as well as human activities such as cleaning, are the main sources of these pollutants (ADEME 2017).

Indeed, the exposure of building and furnishing materials to certain environmental conditions (temperature, relative humidity, light, ozone...) can lead to a physico-chemical aging process and promote microbial growth (Laycock et al. 2017). The aging process may also affect IAQ throughout the emission of certain VOCs and semi-volatile organic compounds (SVOCs) (Singh et Sharma 2008; Zervos 2010).

However, aging processes can differ according to the atmosphere where the material is present and the texture and chemical composition of the material itself. For instance, the main degradation pathway of paper

or cellulose under acidic conditions during accelerated dry or wet thermal aging is the hydrolysis of the

glycosidic bonds of the cellulose macromolecule which will lead to paper embrittlement due to the loss of fiber strength. Nevertheless, under neutral and alkaline conditions, the mechanism is complex and oxidation seems to be a major factor (Zervos 2010).

In addition, fungal growth is also strongly dependent on climatic conditions, in particular the availability of high relative humidity (more than 75%) and moderate temperature (20-29 °C) (Deacon 2005). These conditions may enhance the germination of airborne spores and the formation of hyphae on the contaminated surface causing accelerated aging of the material (Deacon 2005; Johansson et al. 2012).

The interaction between the material and mold may result in the release of metabolites and wastes (microbial VOCs, CO_2...) that can have adverse effects on both IAQ and occupants health (Korpi, Järnberg, et Pasanen 2009; ANSES 2016).

Therefore, in order to reduce chemical (VOC/SVOC) and biological pollutants, it is necessary to limit emissions from the sources. For this reason, the French Ministry of Ecology has issued in 2012 an obligatory labelling of building materials based on their VOCs emission (FFB 2018); moreover, the addition of biocides to certain building materials has been adopted to prevent microbial growth. Nevertheless, there are only a few papers reporting the lifespan of these antifungal treatments (Silva et al. 2020).

The aim of this study is divided into two main objectives: 1) developing a methodology to assess the impact of the aging process on the effectiveness of biocides and 2) characterizing the evolution of VOCs and SVOCs emissions with time (before and after aging).

MATERIAL AND METHODOLOGY

1. Building and decorative materials

In order to represent real-life conditions, a combination of building and decorative materials was made prior to sampling. Polyester cellulose and renovation plaster were selected in this study due to their low VOCs emissions and content of antifungal products, respectively:

- **Polyester-cellulose** is a smooth renovation wall covering containing at least two polymers (polyester and cellulose) and is classified as very weakly emissive (A^+) of VOCs according to the French label (FFB 2018).
- **Renovation plaster** with an unknown composition is generally used for the renovation and decoration of walls and ceilings. It contains 50 ppm of the biocide 1,2-benzothizol-3(2H)-one. This biocide was proved to have an antibacterial (tested on *Escherichia coli ATTC 8739* and *Pseudomonas aeruginosa ATTC 9027* according to UNI EN ISO 846/1999 - Method C) and antifungal (tested on *Aspergillus niger, Penicillium purpurogenum, Cladsporium cladosporoides, and Alternaria alternata* according to EN 15457/2008) actions. It is also classified as A^+ for VOC emissions.

2. Sample preparation

Twenty-one polyester-cellulose samples were cut into circles of 63.61 cm^2, out of which fourteen were covered by a layer of renovation plaster (1.23 ±0.61g) (named combined materials) and seven remained intact (termed “uncovered” samples).

The fourteen combined materials were divided into:

- Four (2 innate and 2 aged) samples to evaluate the impact of aging process on the variation of VOC and SVOC emission rates.
- Ten samples to consecutively evaluate the aptitude of materials to promote fungal growth before and after aging and to assess the impact of fungal growth and incubation process on the variation of VOC and SVOC emissions rate. For this purpose, the ten samples (called "inoculated and incubated materials") were inoculated with fungal spores before being divided into six (3 innate and 3 aged) samples for the quantification of fungal growth as CFU cm^{-2} and four others (2 innate and 2 aged) for the assessment of VOC and SVOC emissions.

The seven “uncovered samples” were used to estimate the contribution of renovation coatings in VOC/SVOC emissions and resistance to fungal growth. For this purpose, the seven samples were partitioned into one innate sample, for the evaluation of VOC and SVOC emission rates, and six others (3 innate and 3 aged inoculated and incubated samples) for the measurement of fungal concentration as CFU cm^{-2}.

3. Materials aging

The aging process used is a physico-chemical process that takes place over a period of 30 days. It consists of:

- Adding a commercially bought cleaning product, with the aim to accelerate the aging process and imitate real-life conditions and daily habits. This product is made up of >30% water, 5%-15% vegetable alcohol, <5% surface agent (anionic, nonionic, amphoteric), citric acid, and perfume (Limonene and citral). It was applied twice a day for one month with a sprayed volume of 750µL upon each use.
- Exposure of the material to a visible light spectrum (400-450nm to 600-650nm) for 24h for 30 days. The distance between the light and the samples was equal to 48cm.

The aging process was conducted at a T = 35±9 °C and a relative humidity (RH) = 25±17% in a sealed chamber.

4. Fungal Inoculation

In order to select the environmental fungi that may be susceptible to grow on the polyester-cellulose, preliminary tests were carried out including an impaction inoculation test (using Air-sampler system MAS-100NT for 1000L/ 10min sampling) and culturing on diverse synthetics solids mediums.

These tests showed that only the *Aspegillus niger* species has the ability to grow on polyester-cellulose (uncovered material) during all stages of research regardless of the inoculation and incubation conditions.

Based on this result, this strain was grown on Rose Bengal Chloramphenicol Dichloran Agar (DRBC, Biokan Diagnostics) at 25±2°C until spore generation (3 days), and then it was inoculated on sixteen samples (innate, aged, covered, and uncovered) using a dry aerosolization system. The latter process provides an air flow over the *Aspegillus niger* culture. The fungal spores are thus transported by this air flow to a sealed chamber containing the samples. The inoculation will be achieved after sedimentation of the airborne spores within about 45min.

The inoculated samples are then incubated for 30 days under high relative humidity (93±6%) and moderate temperature (23±2°C).

The inoculation and incubation of the materials could be conceived as a second aging process including the impact of fungal growth and high relative humidity on the target material.

5. Quantification of airborne spores

The quantification is performed by recovering the fallen spores from the small empty petri dishes using an isotonic solution ($MgSO4\ 10^{-2}$ M and 0.25% Tween 20), performing a series of dilutions at $1/10^{th}$, from which 0.1mL is taken from each dilution and spread on the DRBC medium, and finally determining the fungal concentration as CFU cm^{-2}.

6. Fungal growth assessment

The evaluation of fungal growth on the inoculated surface of each test sample is carried out by visual inspection followed by a quantitative evaluation which consists of counting the number of developed fungi using the same protocol as the quantification of sedimented spores.

The visual inspection (qualitative assessment) is performed according to the following rating scales: **(0)** as no apparent growth with the naked eye or under the microscope **and (1)** visual fungal growth on the surface of the specimens.

7. Impact of the cleaning product on fungal growth

In order to have an idea on the effect of the cleaning product on the fungal growth, a diffusion test on a disc was carried out.

During this test, a DRBC agar plate dish was covered with an *A. niger* culture, then dried paper disks impregnated with a cleaning agent were placed on it, and the dish was then left to incubate at 25°C for three days. During the incubation period, the *A. niger* strain can easily grow on the DRBC medium. However, if the detergent has a negative impact on fungal growth (kills or stops *A. niger* growth), an inhibition zone will appear around the disc.

8. VOC/SVOC emissions

8.1. VOC analysis

The Field and Laboratory Emission Cell (FLEC) was used in this study to characterize VOC/SVOC emissions.

The cell was directly placed on the studied samples. A flow of 50% humid, VOC-free air of 500±20 mL/min was supplied to the FLEC. Samples were actively collected on 2,4-Dinitrophenylhydrazine (DNPH) cartridges for trapping carbonyls and Tenax TA tubes for collecting the other VOCs and SVOCs. Two cartridges or tubes were connected in series to prevent breakthrough. The sampled volume was equal to 36 L (3 hours sampling with an air flow rate of 200 mL/min).

The DNPH cartridges were then eluted by 3 mL of acetonitrile and analyzed using an HPLC/UV (High Performance Liquid Chromatography coupled to Ultra Violet Detector, Dionex Ultimate 3000, Thermo Scientific U.S.A.) equipped with an Acclaim RSLC Carbonyl column (2.2 µm, 2.1 x 150 mm, Thermo Scientific, U.S.A.).

The Tenax TA tubes were analyzed using TD-GC-MS/FID system (Thermal Desorption Gas Chromatography, Clarus 680 - Mass Spectrometry and Flame Ionization Detection, Clarus SQ 8T, Perkin Elmer, U.S.A.) with a CP-Sil 5CB column (60 m x 0.25 mm x 1 µm, Agilent U.S.A.).

The used HPLC and TD-GC-MS/FID methods in this study are those used by (Tobon Monroy 2020). The limit of detection (LOD) of the GC method for toluene was equal to 0.004 µg m^{-3} while that of the HPLC method ranged from 0.2 to 0.6 µg m^{-3}, depending on the oxygenated VOC, for an air sampled volume equal to 25 L.

8.2. VOC calibration

Calibrations were run before each analysis depending on the targeted compounds:

- **Label VOCs in GC** (toluene, tetrachloroethane, ethylbenzene, (ortho-, para-, meta-) xylene, styrene, 2-butoxyethanol, 1,2,4-trimethylbenzene and 1,4-dichlorobenzene) were calibrated individually.

- **For Carbonyls analysis by HPLC,** calibration was performed using a standard solution of 20 compounds: formaldehyde, acetaldehyde, propanone, acrolein, propanal, methyl vinyl ketone (MVK), crotonaldehyde,

methyl ethyl ketone (MEK), methylpropenal, butanal, benzaldehyde, isopentanal, pentanal, glyoxal, tolualdehyde (ortho-, meta-, and para-), methylglyoxal, hexanal and 2,5-dimethylbenzene.

- All the other VOCs were quantified as toluene equivalents.

8.3. Cell Blanks

A blank measurement of the FLEC took place before each experiment to verify the absence of contamination. As this contamination is considered to be a point contamination, the VOC concentrations calculated from the blank were deducted from the analyzed samples.

8.4. Calculation of emission rate

The emission rates (ER, µg m^{-2} h^{-1}) of the emitted VOCs and SVOCs at the outlet of the FLEC were calculated:

$$\mathbf{ER} = \frac{\text{Mass concentration } (\mu g\ m^{-3}) \text{ X air flow rate } (m^3\ h^{-1})}{\text{Sample surface area } (m^2)}$$

RESULTS AND DISCUSSION

1. Assessment of material's resistance to fungal development

Visual inspection of fungal growth revealed that aged polyester-cellulose (aged uncovered sample) and all combined samples (innate or aged) are classified as category 0, due to absence of any fungal growth (fig. 1).

Fig 1. Pictures of samples classified -0-

Whereas the innate uncovered sample showed the presence of macroscopic stains (fig. 2), which highlighted the effectiveness of the inoculation test and the biodegradability of polyester-cellulose in the absence of coating (such as renovation plaster).

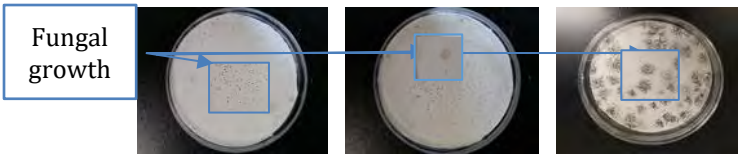


Fig 2. Fungal growth pictures of samples classified-1-

The obtained results by the visual inspection were confirmed by the quantitative assessment (fig. 3).

Figure 3 shows the Log change of *A. niger* that occurs on the surface of the materials. The concentration of the inoculated spores was equal to 10^3 CFU cm^{-2}. After 4 weeks of incubation, this concentration increased to 10^4 CFU cm^{-2} on the surface of the uncovered samples, which is 10 times higher than the initial concentration. On the other hand, the aged uncovered samples had not shown any signs of fungal development. The same is true for the combined samples (innate or aged).

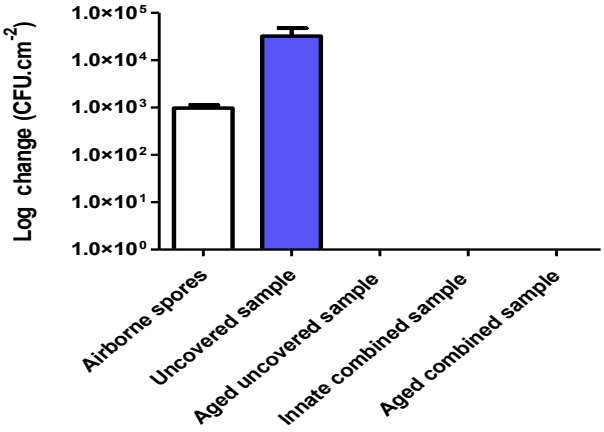


Fig 3. Log change of *Aspergillus niger* inoculated on the uncovered and on the combined samples after 4 weeks of incubation.

These results highlight the fact that the renovation coating ensures the material's resistance to fungal development, and that the aging process provides further protection against fungal growth.

The resistance to fungal growth provided by the coating material could be due to its biocide content or the non-biodegradability of its chemical composition.

Vacher et al. (2010) reported in their study that adding a thin layer of wallpaper (80 g m^{-2}) to the surface of the biocide-free gypsum board resulted in a rapid fungal infestation of the substrate, indicating that the use of thin wallpapers can be considered as a nutrient source for fungal growth. On the other hand, thick wallpapers (240 g m^{-2}) did not allow fungal growth; the same phenomenon applies to plasterboard treated with biocides (2.5% of 1,2-benzisothiazol-3(2H)-one + 2.5% of 2-methyl-4-isotiazol-3-one) combined with thick or thin wallpaper. These results indicate that the nature of the wallpaper has an effect on fungal growth and that the biocide treatment confers the resistance of the material to mold development. It was also indicated in this study that *A. niger* and *Penicillium sp*. were the main species to invade the wallpaper which confirms the obtained results.

Therefore, and according to figure 3, the biocide content of the renovation plaster might have a negative impact on fungal growth, but this cannot be confirmed without defining the lifetime of these incorporated biocides and identifying the chemical composition of the used coating. Moreover, the aging process increased the resistance of the material to mold growth.

2. Impact of the cleaning product on fungal growth

The action of the cleaning agent on the fungal growth was studied using a diffusion test on detergent disks (fig 4).

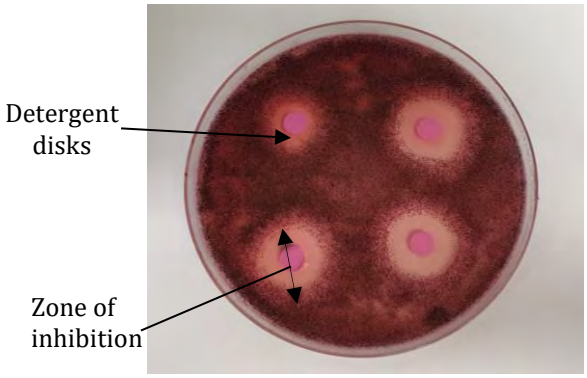


Fig 4. The impact of the used detergent on *A. niger* growth

Figure 4 shows the presence of an inhibition zone around each deposited disc. These results explain the previous findings (Figure 3), that the fungal non-proliferation on the aged uncovered samples was due to the application of the cleaning product.

Terpene molecules (such as limonene and α- and β-pinene), frequently used in cleaning products (Carslaw 2013; Wolkoff 2013), may be responsible for this biocidal effect. Many studies reported that terpenes have a biocidal action against bacteria, yeasts, and molds. Due to their lipophilic character, they can act on the cell structures and membranes causing an inhibition of membrane enzymes and the increase in membrane fluidity; moreover, they can act on ion transport and microbial respiration (Andrews, Parks, et Spence 1980; Helander et al. 1998 ; Alma et al. 2004). For example, α-pinene has been shown to have a biocidal effect against *Aspergillus spp, Penicillium notatum,* and other fungi (Magwa et al. 2006). On the other hand, β-pinene has shown a higher antifungal effect than α-pinene against *Fusarium culmorum*, *F. solani,* and *F. poaes* (Krauze-Baranowska et al. 2002).

The study conducted by Cai et al. (2019) on the antifungal activity and mechanism of citral, limonene, and eugenol against *Z. rouxii* showed that all three compounds have antifungal activity and that the most potent compound is citral followed by eugenol and limonene. Besides, the antifungal mechanism of these three ingredients in essential oils was very similar, but there are still some nuances concerning their time of action and effect. In addition to this, the study by Chee, Mm, et Lee (2009) has also demonstrated the antifungal effect of limonene, particularly against *Trichophyton rubrum*, using two methods: microdilution of the broth and contact with vapor.

3. Evolution of biocide emissions contained in renovation plaster

In order to assess the contribution of biocides to the fungal resistance induced by the renovation plaster, a measurement of biocide release from the samples in different states (innate, innate inoculated and incubated, aged, and aged inoculated and incubated) was performed by TD-GC-MS/FID (Fig. 5).

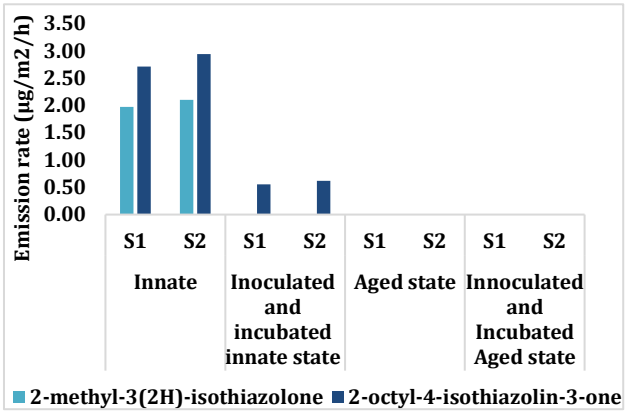


Fig 5. Evolution of biocide emission rate.

Two samples were characterized for each type of material with, S1 and S2 being two replicates from the same sample.

Two biocides: 2-methyl-3(2H)-isothiazolone (MIT) and 2-octyl-4-isothiazolin-3-one (OIT) have been quantified. However, the biocide 1,2-benzisothiazol-3(2H)-one (BIT), initially present as an ingredient in the product label, could not be detected using our method.

According to Figure 5, the innate emission rates of MIT were 1.97 and 2.10 µg m^{-2} h^{-1} for the first and second samples, respectively after which the emission rate of this compound decreased to values below the detection limit for all samples taken after inoculation, aging, and after aging and inoculation combined processes.

The same is true for the compound OIT, which showed an emission rate of 2.71 and 2.94 µg m^{-2} h^{-1} for the first and second innate samples, respectively after which the emissions dropped to 0.55 and 0.62µg$m^{-2}h^{-1}$ for the first and second inoculated and incubated samples, respectively and could not be detected in the other samples.

These results demonstrate the depletion of biocides in the ambient air emissions after the aging process and after the inoculation and incubation processes. Indeed, during the incubation process, the material was conditioned at RH=93±6% and T=23±2°C. Under these conditions, the material absorbed water from the air, causing the leaching of biocides from the surface of the material and thus the decrease in their emission rates. These results appear to be consistent with numerous studies that have demonstrated that OIT, MIT, BIT, and other biocides are leached from the material when they come in contact with water (Burkhardt et al. 2012;

Bollmann et al. 2017). During the aging process, the cleaning product might have the same impact as water and promote the leaching of these substances. In fact, once the cleaning product (containing more than 30% water) comes in contact with the material, solubilization of the biocide molecules is achieved followed by diffusion of these compounds and water-soluble substances through the pores of the material towards the surface causing their leaching from the material. This leaching phenomenon is accelerated and becomes particularly important when a wet/dry cycle is introduced into the aging process, especially when the material remains wet during leaching (Styszko, Bollmann, et Bester 2015). The relatively high temperature (35°C) used during aging can lead to an increase in VOC emission rates from the studies materials and the degradation of the material itself (Wangler et al. 2012; Bollmann et al. 2017). Similar leaching profiles have been observed during the spraying of herbicides and insecticides on concrete and polymer resin surfaces (Luo et al. 2013; Wangler et al. 2012). It has also been shown that an amount of biocides (<20% relative to the initial content) is leached out over time and that this leaching phenomenon is predominant only in the middle of the first year and decreases significantly thereafter (Styszko, Bollmann, et Bester 2015).

4. Emission of VOC from the combined material

4.1. Organic compounds emitted from the combined innate material

The combined innate material released around 66 organic compounds, of which 5 compounds are SVOCs and 61 are VOCs. Table 1 shows some VOC emission rate (µg m^{-2} h^{-1}) from innate and uncovered materials.
As shown in table 1, two oxygenated volatile organic compounds (OVOCs), propylene glycol and the co-eluting benzoic and octanoic acids, were highly emitted compared to other compounds, with emission rates up to 194 and 25.7 µg m^{-2} h^{-1} respectively.
A comparison between the compounds emitted from the combined innate material and the uncovered material was carried out in order to assign the origin of each detected compound.
Thus, 71 compounds were released in total from the two materials, of which 25 compounds are in common, 42 compounds are released only from the coating, and 4 compounds are emitted only from the uncovered material.
According to table 1, the uncovered material is less emissive than the innate material which shows that the common compounds mainly originate from the renovation plaster.
Indeed, 45% of VOC emissions come from the use of solvents in coating materials (ADEME 2018). This is the case of propylene glycol and the co-elution of benzoic and octanoic acid which are mainly used as solvents in various building materials, such as in paints and coatings (INERIS 2015).

4.2. Impact of aging on VOC/OVOC emissions from the combined material

In order to estimate the impact of aging on VOC/OVOC emissions, a comparison between two samples of the combined innate material and two others of the combined aged material was performed.
A total of 83 compounds were released by the two materials, of which 27 compounds are in common, 40 compounds were only released by the innate material, and 16 compounds are emitted only from the aged material. Table 2 shows a comparison of the emission rates of some VOCs/OVOCs emitted from innate and aged materials.
According to Table 2, three types of behaviors were observed:
- Decrease in VOC emissions with aging. It is the case of the major common compounds, more specifically propylene glycol which showed a significant decrease in the emission rate between innate and aged materials (from 194 and 102 µg m^{-2} h^{-1} for the 1st and 2nd innate materials, respectively to 3.5 and 3.0 µg m^{-2} h^{-1} for the 1st and 2nd aged materials, respectively).
- Constant VOC emissions between the innate and aged states, but from which it is difficult to draw a reliable conclusion on their exact behavior. This is the case for the co-elution of benzoic and octanoic acids which shows a higher difference in emission rates between two innate samples S1 (25.74 µg m^{-2} h^{-1}) and S2 (9.70 µg m^{-2} h^{-1}) compared to their emission rates from the two aged samples S1 (32.49 µg m^{-2} h^{-1}) and S2 (25.81 µg m^{-2} h^{-1}). This variation in emission rates between two samples of the same state may be due to the time difference in sample analysis.
- VOCs that appeared as a result of aging, including a hydrocarbon C_7H_{10} and an alcohol $C_{10}H_{16}O$, which could be due to the use of the cleaning product. Indeed, during the aging process, limonene ($C_{10}H_{16}O$) and other chemical compounds present in the cleaning product may be released from the aged material and may also react with the reactive gases (O_3, OH) and form a number of secondary products that might have adverse health effects (L. Walser et al. 2008; Carslaw 2013).

In addition to the effect of the cleaning product, the three other parameters that are involved in the aging process (temperature, visible light spectrum, and relative humidity) have also a direct and significant impact on VOC emissions. High temperatures, 35°C in this study, have an effect on VOCs vapor pressure and their diffusion within the material resulting in higher emission rates (Fang, Clausen, et Fanger 1999). However, the decrease in VOC emissions to low levels after a long conditioning period (4 weeks in our study)

could be due to the fact that their emission becomes controlled by diffusion instead of evaporation which leads to the exhaustion of VOCs in the material. These findings appear to be consistent with numerous studies investigating the effect of temperature and relative humidity on VOC emissions from building materials (Sollinger, Levsen, et Wünsch 1994; Wolkoff 1995; Haghighat et De Bellis 1998; Wolkoff 1998; Fang, Clausen, et Fanger 1999). For instance, the study carried out by (Wolkoff 1995; 1998) on the evolution of VOC emissions from five construction materials (carpet, PVC flooring, sealant, water-based wall paint, and floor varnish) over time revealed that the emission of most of the analyzed VOCs increased by more than 20% when the temperature increased from 23 to 60°C. The effect of temperature was significant on the initial emission of VOCs; however, after three weeks of ventilation, this latter became independent of temperature change, more precisely in the range of 23 to 35°C. Similarly, Haghighat and De Bellis (1998) found that VOC emissions from paints and varnishes increased with increasing temperature from 15 to 35°C to decrease after few hours of incubation to values close to exhaustion. However, the individual compounds did not necessarily follow the same trend as that established by the Total Volatile Organic Compounds (TVOCs).

Regarding relative humidity (25±17%) used during the aging process, it was found to have a negligible effect on VOC emissions as stated by Sollinger, Levsen, et Wünsch (1994) in their study on the coupled impact of temperature (23-71°C) and humidity (0-45%) on VOC emissions from textile floor coverings.

The light (400-450nm to 600-650nm) used during the aging process could have an impact on the photoinitiators. Photoinitiators are usually introduced into the coating system to prevent the undercuring of the coating film. However, when these compounds are exposed to light, a fragmentation process is initiated resulting in the emission of a number of VOCs, such as benzaldehyde and alkyl-substituted benzaldehyde, that can contribute to indoor air pollution (Uhde et Salthammer 2007).

4.3. Impact of inoculation and incubation processes on VOC/OVOC emissions

4.3.1. Impact on the innate material

The impact of inoculation and incubation on VOC/OVOC emissions was assessed by comparing the emissions of the two innate samples with those of the inoculated and incubated innate matter. 76 compounds were emitted in total, of which 40 compounds are in common, 27 compounds were released only by the innate material, and 9 compounds were emitted by the inoculated and incubated material.

Table 3 shows a comparison of the emission rates of some VOCs/OVOCs detected in innate and inoculated and incubated materials.

Based on Table 3, the ER of the major common compounds decreased upon inoculation and incubation process. For example, propylene glycol showed a significant decrease in ER from 194 and 102µg m^{-2} h^{-1} from the 1st and 2nd innate materials, respectively to 29.6 and 10 µg m^{-2} h^{-1} from the 1st and 2nd inoculated and incubated material.

These results show that high relative humidity (93±6%) used in the incubation process has a significant impact on VOC and OVOC emissions. It is likely that the increase in air humidity can lead to the extraction of the more hydrophilic OVOCs (such as acetic acid, isopentanal, 2-ethyl hexanoic acid, propylene glycol...) from the material surface and thus results in an increase in their emission rates (Fang, Clausen, et Fanger 1999; Tobon Monroy 2020). However, this increase occurs rapidly after one or two weeks of conditioning to become stabilized by the third week (Wolkoff 1998).

The incubation temperature (23±2°C) appears to have a small influence on VOC emissions (Fang, Clausen, et Fanger 1999).

The new compounds released, including 1-octanol, butyl acetate, and benzene, could be derived from the fungal growth (Korpi, Järnberg, et Pasanen 2009; Stotzky, Schenck, et Papavizas 2008). However, according to the previous results, no fungal growth was recorded. Therefore, the probable source of these compounds is only material emissions.

4.3.2. Impact on the aged material

The comparison between the emissions of the aged material and those of the inoculated and incubated aged material showed that out of 64 compounds emitted, 30 compounds were emitted in common, 13 compounds were emitted by only the aged material, and 21 compounds by the inoculated and incubated material. From these 21 compounds, 13 compounds were newly detected under the impact of the inoculation and incubation processes while the other (8 compounds) were already present in the innate state (Table 4).

In fact, as shown in Table 4, the compounds as a whole did not follow the same trend i.e each individual compound behaved differently from the other:

- VOCs whose emission rate, decreased such as monochloro-acetic acid isopropyl ester (from 0.44 and 0.33 µg m^{-2} h^{-1} for the 1st and 2nd aged materials, respectively to values below the limit of detection for both inoculated and incubated materials).
- VOCs with a relatively stable emission rate such as benzaldehyde, 2,3-dehydro-1,8-cineole and 1-methyl-4-(1-methylethenyl) benzene.
- VOCs whose emission rate increased after a decrease under the effect of aging, such as propylene glycol and

acetic acid (from 1.41 and 1.11 µg m^{-2} h^{-1} for the 1st and 2nd aged materials, respectively to 1.70 and 2.57 µg $m^{-2}h^{-1}$ for the 1st and 2nd inoculated and incubated materials, respectively).

- VOCs that appear as a result of inoculation and incubation processes like n,n-dibutyl formamide, 1-octanol, benzene, and 1,2-etanediol.

The fluctuating behavior of some compounds, such as acetic acid and propylene glycol, could be caused by the use of the cleaning product during aging. In the humid/dry aging cycle, the temperature allowed the evaporation of some of the cleaning product from the humid sample while preventing the emission of polar VOCs during this period due to hydrogen bonding (Haghighat et De Bellis 1998). Once the material is in the moist conditions, the water molecules compete with the hydrophilic VOCs present on the adsorption sites of the material, and would cause the adsorption equilibrium to shift to the gas phase(Tobon Monroy 2020).

Finally, the following study aimed to mimic real conditions by exposing a renovation coating and polyester-cellulose to a combination of parameters (temperature, relative humidity, light, and cleaning product). Thus, the combination of these aging parameters (Table 4) induces a variable and complex behavior of the emissions. However, it must be noted that VOCs can present much more complex behaviors in real conditions due to the interactions that may occur within emissions or between them and the reactive gases (NO_3, O_3, OH) (Uhde et Salthammer 2007).

This study presents only one example of a combination of building and consumer materials; however, other combinations of building materials should be characterized in order to have a global vision on the impact of aging on VOC emission and therefore on IAQ.

CONCLUSION

The impact of the aging process on the effectiveness of biocides and on VOC and SVOC emissions has been highlighted and discussed in this paper. This study showed that:

- Renovation plaster protects polyester-cellulose against fungal growth due to its non-biodegradable composition. However, biocides contained in this plaster might not have a significant impact on fungal growth. It has been proven that the aging process and high relative humidity promote the loss of these antifungal ingredients with time.
- The cleaning product, used during the aging process, showed an antifungal activity since it contained terpenic substances.
- Renovation plaster and polyester-cellulose wallpapers are low in VOC emissions, rated A+. However, propylene glycol and co-elution of octanoic and benzoic acids are the predominant VOCs.
- Moderately high temperatures (35±9°C) and high relative humidity (93±6%) have a significant effect on VOC emissions. It was noted that after 4 weeks of conditioning, the emissions of the major VOCs decreased while others VOCs newly appeared due to the use of cleaning products.
- Conditioning of aged materials at high relative humidity led to a fluctuating behavior of some detected compounds and the appearance of some other compounds. This effect cannot be described in a general emission trend.

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Table 1. VOC/OVOC emissions rates (µg m^{-2} h^{-1}) from combined innate and uncovered materials

COMPOUNDS	INNATE MATERIAL		UNCOVERED MATERIAL
	S1	S2	S1
BUTANAL	0.75	1.41	0.18
BENZALDEHYDE	1.39	2.20	0.56
PENTANAL	0.61	0.68	0.89
ACETIC ACID	NQ[1]	2.99	0.68
PROPYLENE GLYCOL	194	102	<LOD
CHLORINATED COMPOUND	5.21	5.94	<LOD
METHOXY PHENYL ACETIC ACID	3.53	2.33	<LOD
HEXAMETHYL CYCLOTRISILOXANE	1.58	1.68	0.42
ISOCAPROLACTONE	<LOD[2]	<LOD	3.17
HEPTANOIC ACID	1.56	1.49	<LOD
NITROSO-3-PYRROLINE	<LOD	<LOD	1.45
2-ETHYL HEXANOIC ACID	1.40	1.26	<LOD
BENZOIC ACID + OCTANOIC ACID	25.7	9.70	<LOD
OXALIC ACID + DIMETHYL BENZAMIDE	6.38	4.78	<LOD
6-METHYL OCTADECANE	1.38	2.00	<LOD
METHYL PARABEN	1.90	3.17	<LOD

[1]NQ = Not quantified; [2]LOD = Limit of detection

Table 2. VOC/OVOC emissions rates (µg m^{-2} h^{-1}) from combined innate and aged materials

COMPOUNDS	INNATE MATERIAL		AGED MATERIAL	
	S1	S2	S1	S2
PROPYLENE GLYCOL	194	102	3.53	3.00
METHYL PARABEN	1.90	3.17	<LOD	<LOD
CHLORINATED COMPOUND	5.21	5.94	<LOD	<LOD
ACETIC ACID	NQ	2.99	1.41	1.11
METHOXY PHENYL ACETIC ACID	3.53	2.33	<LOD	<LOD
HEPTANOIC ACID	1.56	1.49	<LOD	<LOD
DIFLUOROMETHYL SILANE	0.51	0.23	0.62	0.64
PENTANAL	0.61	0.68	0.37	0.82
PHENOL + HEXANOIC ACID	3.27	1.52	1.05	1.22
BENZOIC ACID + OCTANOIC ACID	25.7	9.70	32.5	25.8
METHYLGLYOXAL	0.89	<LOD	0.59	0.80
DIMETHYL SILANEDIOL	<LOD	<LOD	0.54	0.33
MONOCHLOROACETIC ACID ISOPROPYL ESTER	<LOD	<LOD	0.44	0.33
2,3-DEHYDRO-1,8-CINEOLE	<LOD	<LOD	1.04	0.95
1-METHYL-4-(1-METHYLETHENYL) BENEZENE	<LOD	<LOD	2.00	1.82
ALCOHOL $C_{10}H_{16}O$	<LOD	<LOD	4.57	3.80
HYDROCARBON C_7H_{10}	<LOD	<LOD	1.60	1.24
N-DECANOIC ACID	<LOD	<LOD	7.91	4.29

Table 3. VOC/OVOC emissions rates (μg m^{-2} h^{-1}) from combined innate and inoculated and incubated materials

COMPOUNDS	INNATE MATERIAL		INCUBATED AND INOCULATED MATERIAL	
	S1	S2	S1	S2
BUTANAL	0.75	1.41	0.72	0.91
BENZALDEHYDE	1.39	2.20	0.19	0.86
ISOPENTANAL	1.66	2.47	<LOD	<LOD
ACETIC ACID	NQ	2.99	NQ	2.54
BENZENE	<LOD	<LOD	0.25	0.23
PROPYLENE GLYCOL	194	102	29.6	10
CHLORINATED COMPOUND	5.21	5.94	0.67	0.82
BUTYL ACETATE	<LOD	<LOD	0.32	0.26
METHOXY PHENYL ACETIC ACID	3.53	2.33	0.71	0.86
HEXAMETHYL CYCLOTRISILOXANE	1.58	1.68	0.49	0.52
HEPTANOIC ACID	1.56	1.49	0.58	0.36
2-ETHYL HEXANOIC ACID	1.40	1.26	<LOD	<LOD
BENZOIC ACID + OCTANOIC ACID	25.7	9.70	8.77	4.44
OXALIC ACID + DIMETHYL BENZAMIDE	6.38	4.78	1.66	1.19
6-METHYL OCTADECANE	1.38	2.00	<LOD	<LOD
METHYL PARABEN	1.90	3.17	<LOD	<LOD
1-DODECANOL	<LOD	<LOD	0.94	0.71

Table 4. VOC/OVOC emissions rates (μg m^{-2} h^{-1}) from combined aged and inoculated and incubated aged materials.

COMPOUNDS	AGED MATERIAL		INCUBATED AND INOCULATED AGED MATERIAL	
	S1	S2	S1	S2
BUTANAL	<LOD	0.59	0.66	0.87
BENZALDEHYDE	0.06	0.60	0.68	0.05
PENTANAL	0.37	0.82	0.70	0.17
ACETIC ACID	1.41	1.11	1.70	2.57
BENZENE	<LOD	<LOD	0.21	0.32
1.2-ETANEDIOL	<LOD	<LOD	0.93	1.20
PROPYLENE GLYCOL	3.53	3.00	31.7	29.1
HYDROCARBON C_7H_{10}	1.60	1.24	1.48	0.82
DIMETHYL SILANEDIOL	0.54	0.33	<LOD	<LOD
MONOCHLOROACETIC ACID ISOPROPYL ESTER	0.44	0.33	<LOD	<LOD
HEXAMETHYL CYCLOTRISILOXANE	0.32	0.50	0.39	<LOD
2,3-DEHYDRO-1,8-CINEOLE	1.04	0.95	0.93	0.60
HEPTANOIC ACID	<LOD	<LOD	0.37	0.34
1-OCTANOL	<LOD	<LOD	1.37	1.24
1-METHYL-4-(1-METHYLETHENYL) BENEZENE	2.00	1.82	1.96	1.26
BENZOIC ACID + OCTANOIC ACID	32.5	25.8	27.2	18.3
ALCOHOL $C_{10}H_{16}O$	4.57	3.80	3.50	2.72
N,N-DIBUTYL FORMAMIDE	<LOD	<LOD	3.19	2.79
N-DECANOIC ACID	7.91	4.29	3.83	2.74
1-DODECANOL	<LOD	<LOD	6.79	5.01