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Impact of photocatalytic paints on indoor VOCs in a full-scale study: focus on regulated and reactive compounds

Adrien Gandolfo[1*], Hui Chen[2], Alexander Kukui[2], Amandine Durand[1], Brice Temime-Roussel[1], Jörg Kleffmann[3], Henri Wortham[1], Sasho Gligorovski[1,4]

[1]Aix Marseille Université, CNRS, LCE, UMR 7376 Marseille, France
[2]Université d'Orléans, CNRS-INSU, LPC2E, Orléans, France
[3]Physical and Theoretical Chemistry, University of Wuppertal, Germany
[4]Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

[*]*Corresponding email: ad.gandolfo@gmail.com*

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1 Introduction

Volatile organic compounds (VOCs) are ubiquitous indoor, emitted from various indoor sources. In novel airtight and mechanically controlled ventilation equipped buildings, the VOC concentration is expected to rise, enhancing, therefore, public health risks. Investigators suggest that photocatalytic paints could reduce VOC levels indoor, but some studies showed that photocatalytic degradation of the paint organic binder could be an additional VOC source. While several studies report photocatalytic material limits in laboratory conditions1, none have been conducted in a full- scale study. Here we present the first real-scale study of photocatalytic paint impacts on indoor air quality through measurement of regulated indoor VOCs like formaldehyde, acetaldehyde, and benzene and also with insight into VOCs formed under typically highly oxidative conditions as peroxide and multi-oxygenated bearing compounds.

2 Materials/Methods

Indoor time-resolved measurements of VOCs held in an unfurnished building office in Martigues, situated in the southeast of France during October 2016. A PTR-ToF-MS (Ionicon Analytik GmbH, Innsbruck, Austria) was used to record VOC levels at low concentrations (as low as a few pptv) under high mass resolution. The identification of the compounds is based on fragmentation patterns and literature revue. Specific rate constants were used for quantification, and relative humidity corrections were applied. Two kinds of paint were studied: one standard white paint which serves as a reference and one white photocatalytic paint (3.5 % w/w, PC500 nanoTiO2). Both paint formulations, based on an organic binder, are identical except nanoTiO2 content. To avoid solvent emission during the campaign, plasterboards were covered by paints 6 weeks before starting measurements and stored in controlled environmental conditions (RH: ~50%, Temperature: ~20°C, in the complete absence of light). During experiments, indoor temperature shows a quasi-semblable day-by-day profile with a minimum (~20 °C) in the morning just before room isolation and reaches a maximum of around 30 °C in the afternoon. Relative Humidity was constant around the typical indoor level (45%). No mechanical ventilation has been used during the campaign, thus the air exchange rate occurred only through building leaks at a rate between 0.3 and 0.5 h-1.

3 Results and Discussion

Observed trends in VOC concentrations clearly state an accumulation mode from the moment the room is isolated from outdoor. VOC levels increased reaching a plateau 3-5 hours later depending on the air exchange rate and paint emission rates intensity. Figure 1 depicts the experiment conducted in the presence of photocatalytic paint.

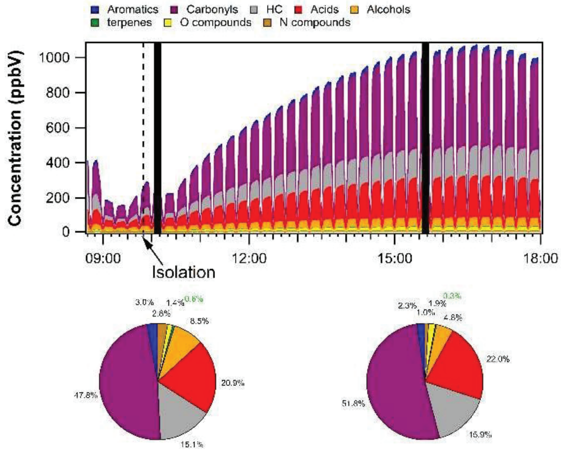

Figure 1: VOCs measurements conducted in an unfurnished office room in presence of photocatalytic paints and UV- Transparent windows. Dash line shows the room isolation time. Pie charts represent 5 minutes measurements represented by the black rectangular. Measurement are alternatively conducted indoor (10 mins) and outdoor (5 mins), designing the crenel aspect of the figure)

59 ions have been attributed to one of the 7 groups from m/z 21.022 to 373.075. Total ppb levels raised from about 200 at the isolation time to 1000 ppb in the afternoon. The 1 ppm mixing ratio is the maximum observed during all the campaigns. For example, in quite similar environmental and experimental conditions but in presence of reference paint, the background VOC total mixing ratio is 190 ppb and the VOC level reaches up a maximum of around 400 ppb being 60 % lesser than in presence of photocatalytic paints.

On figure 1, isolation held a few minutes before 10h00. At this point, carbonyl compounds represent almost 48% of total concentration mainly dominated by formaldehyde and acetaldehyde. The acid group is the second major contributor to VOC levels followed by hydrocarbon (HC) group and alcohol group with respectively 21, 15, and 8.5 %. At 15h30, the contribution of carbonyls, HC, and acids increased 4, 1, and 1 % respectively while alcohol drop by 4 %. HC group gather compounds with CxHy chemical formula. Under our instrumental conditions, it is important to note that aldehyde above C3 tends to lose and their H2O pattern and respond as HCs in the PTR-MS instrument. Thus, here, we can argue that the increase of HC levels and contribution is supported by the increase of C4 and above aldehyde compounds.

While their levels are low, it is noticeable to observe a contribution increase from 1.4 to 1.9 % of the oxygenated group. It regroups all the compounds bearing 2 or more oxygenated atoms in their formula which has not been identified as acid compounds. Among those, unique observation of ions CH4O2H+ (m/z 49.028), C2H6O2H+ (m/z 63.044), CH4O3H+ (m/z 65.024)

C3H8O2H+ (m/z 77.059), which have been ascribed here as peroxide compounds, respectively namely methyl hydroperoxide, dimethyl peroxide, hydroxymethyl hydroperoxide, and isopropyl hydroperoxide occurred. Peroxide2 compounds are formed through a radical termination reaction route (RO2 (HO2) + RO2 ROOR(ROOH). RO2, HO2 being

peroxy, and hydroperoxy radicals. In addition, ion, C3H4O2H+ at m/z 77.023, which have been associated with PeroxyAcyl Nitrate (PAN)3 reach

1.2 ppb during the experiments showed in Figure

1. The formation of that compound is the mark of an important indoor oxidative capacity. Radical

compounds measurements during this experiment support it showing OH and RO concentration higher by 50 and 200 % in presence of photocatalytic paint in comparison of reference paint (ref).

4 Conclusions

The emerged outcomes of this comprehensive study suggest the need to use more adequate binders in photocatalytic paints to avoid additional VOC emissions. The presence of TiO2 as a photocatalyst in paints leads to a more toxic and reactive indoor environment not allowing yet to state the benefits of photocatalytic air remediation technology.

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