



Under glass weathering of hemp fibers reinforced polypropylene biocomposites: Impact of Volatile Organic Compounds emissions on indoor air quality

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specifying limit concentration levels for 6 substances which are benzene, toluene, formaldehyde, xylene, ethylbenzene and styrene with limit levels ranging from $30 \mu\text{g m}^{-3}$ for benzene to $1600 \mu\text{g m}^{-3}$ for ethylbenzene [7,8]. After that, a study made by Korea Automobile Testing & Research Institute showed a significant concentration decrease in 5 years [9]. Car interior VOCs emissions are also coming under more scrutiny in China. Indeed, the standard GB/T 27630 implemented on 2012 is inspired from the recommendatory standard guideline for air quality assessment of passenger car issued on 2011 [10]. This applies the evaluation on binnacle air quality by proposing limit values for the previously mentioned 6 substances plus acetaldehyde and acrolein. Associations such as Japan Automobile Manufacturers Association (JAMA) and European Automobile Manufacturers Association (ACEA) recently made headway to improve VIAQ [11,12]. For instance, JAMA has drawn up the guideline “vehicle cabin VOC testing methods for passenger cars” for conducting the necessary VOC measurements. Nevertheless, the limit concentration levels are different between each country standard. Indeed, formaldehyde concentration limit ranges from $100 \mu\text{g m}^{-3}$ in Chinese and Japanese standards to $250 \mu\text{g m}^{-3}$ in Korean guideline. They only concern whole vehicle assessment whereas threshold values at the material scale are mostly imposed by automotive industries. In order to propose new vehicles complying with the VIAQ limit values, worldwide standards describing test methods for the determination of VOCs emissions from car trim components are already implemented. In Europe, ISO 12219 standards describe different protocols and scales for the determination of either VOCs concentrations in car indoor air or VOCs emission rate for materials [13–15].

Lots of studies dealt with pollutants emission in vehicles and the influence of different parameters on their concentrations. Most of the time, total VOCs (TVOCs) concentration is also measured, besides individual VOC levels, to evaluate indoor air quality [8,16–20]. In automotive and building industry, all VOCs whose retention times are between those of hexane and hexadecane under specific gas chromatographic conditions represent TVOCs [21]. It was shown that static conditions (parked, unventilated) favored higher TVOCs concentration in car cabins than specified driving conditions and ventilation. TVOCs level was decreased from $1980 \mu\text{g m}^{-3}$ in moderate-heat (almost 40°C) and static conditions to $100 \mu\text{g m}^{-3}$ under 90-min driving conditions in a 1997 Ford vehicle [20]. Vehicle age also plays a role. Indeed, Chien compared measured levels in new cars for specified products with levels found in literature [18]. It was observed that they could be three orders of magnitude higher than those of older cars, but they decrease over time [22]. VOCs emission is strongly temperature dependent [22] but other parameters like relative humidity and interior trim compositions have also an influence. Indeed, leather pieces emit higher quantities than fabric pieces with a big influence on toluene VIAQ concentration which can increase by 39% [17,18]. The contribution of materials to the VIAQ is therefore very important. That is highlighted by a study only focused on VOCs emissions from materials [19]. Long-chain aliphatic hydrocarbons and aromatic compounds, like toluene and xylenes, were mostly identified and counted for 52% and 42% of TVOCs concentration respectively. Other chemical families like halocarbons, carbonyls and esters were also detected. This kind of study is not very widespread and to our knowledge, no work is published regarding emissions of VOCs emitted by car interior finished parts made of biocomposites.

Vegetal fibers used in biocomposites are known to be sensitive face to climatic conditions such as ultraviolet (UV) rays, high temperatures and humidity. Physico-chemical properties of natural fillers composites are thereby affected by water absorption and oxidation reactions leading to mechanical performance loss, chemical composition and visual aspect changes [23–30]. Some works described qualitative and semi-quantitative analysis of VOCs evolved from biocomposites. A study has been done on emissions of VOCs sampled by HeadSpace - Solid Phase MicroExtraction (HS-SPME) after a thermal ageing of cellulose and hemp fibers reinforced polypropylene (PP) composites [31].

Different VOCs chemical families were identified such as aliphatic hydrocarbons, carboxylic acids and alcohols but also compounds specific to natural fibers like 2-furanmethanol. K.W. Kim et al. worked on the reduction of TVOCs emission from pineapple and destarched cassava flour reinforced polylactic acid (PLA) and polybutylene succinate (PBS) biocomposites by the bake-out process [16]. The study investigated the influence of temperature and baking time on TVOCs emission factor. They noted a factor increase with temperature and a decrease with baking time. Otherwise, neat PLA and PBS presented lower emission factor than loaded ones. In the same line, H.S. Kim et al. worked on the reduction of odor and VOC emissions of vegetal flour filled reinforced PLA and PBS composites by incorporating porous inorganic fillers [32]. Volatile products emissions caused by high temperature manufacturing like tridecane from the matrix and furfural from bamboo flour were decreased. Olfactometric analyses carried out on natural fillers composites allowed to understand the high responsibility of oxygenated compounds issued from both the polymer and natural fillers to unpleasant odor [5]. However, no study deals with the VOCs emissions of biocomposites under real conditions of use since the impact of natural fiber composites ageing on VOCs emission is poorly documented. Indeed, standard measurement methods (e.g. emission chamber methods) are complex to implement and time consuming for the monitoring of the temporal evolution of VOCs emissions [33,34]. As an alternative, HS-SPME is the most widely used technique for sampling VOCs emitted by polymeric materials [5,31,35–37]. Its advantages are simplicity and time saving according to short extraction times. But this method involves material destruction by cutting it in small pieces for introduction in the headspace vial. Hence, this sampling procedure is not relevant to provide quantitative data related to surface emission. The sampling methodology used for this work and previously developed in our laboratory, is based on a home-made emission cell coupled with SPME [38,39]. This simple and non-destructive passive sampling method allows determining the VOCs concentration at the material/air interface which is related to the emission rate by the first Fick's law of diffusion under steady state conditions [39].

This study aims to assess the impact of VOCs emitted by hemp fibers reinforced PP on air quality and the influence of material ageing on these emissions regarding hemp fibers rate and sampling temperature. A car interior environment was simulated by exposing laboratory-made materials under windshield glass for one year. Emitted VOCs were identified over the weathering and their concentrations at the material/air interface were determined. Results are discussed notably in terms of ageing impact, fiber contribution and health impact. For this latter, the European regulation classes of critical products according to their impact on human health and their concentrations were gathered as well as limit values already imposed, or at least advised, by VIAQ guidelines and national standards.

2. Materials and methods

2.1. Materials

Polypropylene grade H733-07 with a melt flow rate of 7.5 g/10 min (230°C , 2.16 kg) was purchased from Braskem (Sao Paulo, Brazil) and used as polymer matrix. Hemp fibers with size included in the 2–6 mm range were provided by AgroChanvre (Barenton, France). Their retting lasted 38 days and their cellulose, hemicelluloses, lignin and lipophilic extractives rates of 82, 8, 5 and 3 wt% respectively were determined by successive chemical extractions based on TAPPI T264, ASTM D1104 standards. Two hemp fibers loading, 10 wt% (PP10) and 30 wt% (PP30), were tested (Table 1). Maleic anhydride grafted polypropylene (MA-g-PP) with a 1 wt% grafting rate, under the trademark Orevac CA100 and supplied by Arkema (France), was added at 3.1 wt% of PP as coupling agent.

Table 1
Designation of materials.

	Composition (wt%)		
	PP	Hemp fibers	MA-g-PP
PP	100	–	–
PP10	87.3	10	2.7
PP30	67.9	30	2.1

2.2. Process conditions

Prior to extrusion, hemp fibers and MA-g-PP have been dried for 15 h at 60 °C to remove residual water. Granules of PP and MA-g-PP were mixed with hemp fibers in a BC21 Clextral co-rotating twin-screw extruder (L/D = 36 with D = 25 mm) (Clextral, France) with the following temperature profile 190-190-190-180-175-175-175 °C from feed to die and a screw speed of 220 rpm. Then, pellets were dried in an air-circulating oven for 3 days at 60 °C. Finally, extruded pellets were injection molded into specimens in a Krauss Maffei KM50-T180CX (Krauss Maffei, Germany) at 210 °C with an injection speed of 30 cm³ s⁻¹. Square samples of 100 × 100 × 2 mm³ were obtained. Vegetal fibers pellets were formulated by pressing them in prontopress-2 device (Strues, France) into 25-mm diameter pellets.

2.3. Weathering

Square samples were exposed in the South West of France (Pau) under flat windshield glass to simulate car interior environment according to ISO 877-2:2011 standard (Fig. 1). The exposition panels were oriented towards South at 45° with the ground. Interior environment was naturally ventilated thanks to holes located at the top and bottom of the stainless steel boxes 2 h per day. The exposure started in September 2015 and finished in September 2016 in order to study long-term ageing effects. Temperature T (°C) and relative humidity RH (%) were monitored (Fig. 2). The maximum temperature and relative humidity values reached over the weathering were respectively 89 °C and 95% whereas the minimum values were –5 °C and 3%. Three samples of each material PP, PP10 and PP30 taken after 1, 2, 3, 6, 9 and 12 months of exposition were analyzed at the laboratory.

2.4. Sampling and analytical methodology

VOCs were sampled according to a passive sampling method previously developed (Fig. 3). It consists of two steps: firstly, an emission 320-mL glass cell is deposited on the material in order to isolate its



Fig. 1. Under windshield glass exposure racks.

surface, the sampled area being 50 cm². Then, VOCs are emitted in the cell volume until reaching a constant air concentration. Two hours are required to reach material/air equilibrium [38]. This sampling step was carried out at two temperatures, 23 and 80 °C, in order to reflect ambient and extreme conditions found in cars. Then, a Solid Phase MicroExtraction (SPME) fiber is introduced via a septum in the glass cell

to extract emitted VOCs (Fig. 3). Then, the fiber was thermally desorbed in a Varian CP-3800 gas chromatograph (GC) injector. A 1200Q quadrupole mass spectrometer (MS) was used for identification whereas a flame ionization detector (FID) (Varian, Les Ulis, France) was used for quantification. Separation was achieved using a polydimethylsiloxane (PDMS) 5% phenyl capillary column of 60 m × 0.25 mm i.d. × 1 µm film thickness. The complete analytical procedure is detailed elsewhere [40].

Two different analyses were performed on non-weathered and weathered samples: VOCs screening to identify and quantify the widest range of emitted compounds, and specific analysis of formaldehyde and acetaldehyde which are classified as CMR [41]. For VOCs screening, a polydimethylsiloxane-divinylbenzene-carboxen fiber (PDMS/DVB/CAR, 50/30 µm) was selected. For formaldehyde and acetaldehyde, a polydimethylsiloxane-divinylbenzene (PDMS/DVB, 65 µm) fiber impregnated with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) (Fluka, Brucks, Switzerland) was used [40,42]. The two SPME fibers were purchased from Supelco (Bellefonte, USA). For the two fibers, for 23 °C sampling, an extraction time of 20 min was chosen from previous work [43]. At 80 °C, an extraction time of 5 min was determined as a good compromise between sensitivity and short-time sampling. All samplings were conducted in triplicates to evaluate the measurement repeatability.

This methodology allows determining the VOCs concentrations at the material/air interface (also called surface concentration) which is related to the emission rate through the First Fick law of diffusion [38,39].

In order to determine the contribution of vegetal fibers in major VOCs emissions from biocomposites, qualitative analysis of VOCs emission of vegetal fibers pellets was carried out. About 2 g of samples of non-weathered and two-month weathered pellets were analyzed by head-space-SPME in 250 mL glass vials (Entech Instruments, Simi Valley, USA). The sampling was carried out for 2 h at 80 °C and the analytical conditions were the same as for surface emission characterization.

2.5. Quantitative analysis

For the screening analysis using PDMS-DVB-CAR fiber, VOCs were quantified as toluene equivalent using FID response since it is proportional to the effective carbon atoms number in the molecule [20]. Standard gas of toluene was generated by a continuous syringe injection system supplied by Calibrage (Saint Chamas, France) equipped with a syringe pump (PHD 2000, Harvard Apparatus, Les Ulis, France) [43]. Covered toluene concentrations ranged from 17 to 388 µg m⁻³ for the 20 min-sampling and 67–1553 µg m⁻³ for the 5 min-sampling. Furfural and 2-furanmethanol, compounds specific to hemp fibers and listed as CMR substances [41] were specifically quantified. Standard gases were also generated by a continuous syringe injection, as described above. For the specific analysis of formaldehyde and acetaldehyde by PDMS/DVB fiber impregnated with PFBHA, standard gases were generated according to the permeation method [44]. The device used was supplied by Calibrage (Saint Chamas, France). For the two SPME methods, the Limits of Detection (LOD) are in the µg.m⁻³ order level for the 20-min sampling and are around 10 µg m⁻³ for 5-min sampling.

3. Results and discussion

The detailed results for surface concentrations of individual VOCs emitted by neat PP and biocomposites before and after weathering for the two sampling temperatures are presented in Table 2.

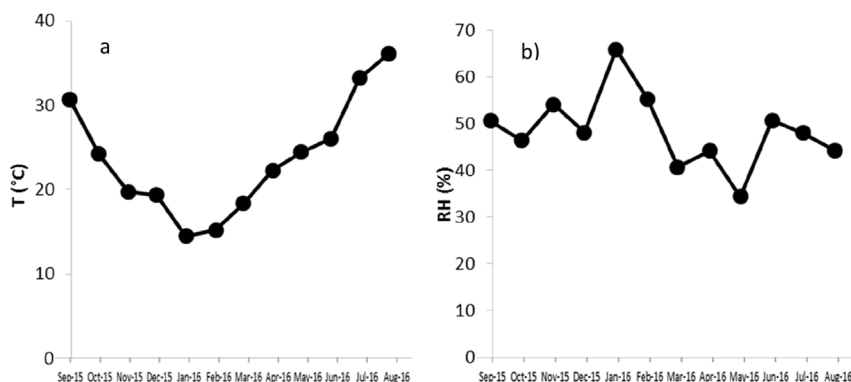


Fig. 2. Average monthly temperature (°C) (a) and relative humidity (%) (b) values in stainless steel boxes.

3.1. VOCs emissions at non-weathered state: impact of process and sampling conditions

For non-weathered PP, PP10 and PP30 analyzed at 23 °C by PDMS/DVB/CAR fiber, no VOC was detected. As the limits of detection for surface concentration are below the $\mu\text{g}\cdot\text{m}^{-3}$ level for these sampling conditions, this means that non-weathered PP, PP10 and PP30 can be considered as non-emissive materials at ambient temperature.

Contrary to 23 °C, some VOCs were detected at 80 °C (Fig. 4 and Table 2). Thus, as expected, a higher temperature promoted the emission of volatile products. Those compounds may be generated by the thermo-oxidative degradation during the extrusion and injection molding process and/or by the 2 h sampling at 80 °C. Indeed, it was reported that hemp fibers are sensitive even at 70 °C [31].

PP mainly emitted C_9 – C_{15} branched and linear aliphatic hydrocarbons arising from the PP chains (they are gathered into groups having same carbon atoms number in Table 2). These products were caused by either polymerization defects or thermal degradation of polymer chains during processing or sampling at 80 °C. A few oxygenated compounds (alcohols, ketones, aldehydes) were also identified due to the thermo-oxidation of polymer chains.

The global VOCs surface concentration increased with the hemp fibers loading from $6851 \pm 595 \mu\text{g}\cdot\text{m}^{-3}$ for neat PP to $9880 \pm 979 \mu\text{g}\cdot\text{m}^{-3}$ for PP30 (Fig. 4). So biocomposites were more subjected to thermal degradation than PP. The concentration of oxygenated products (alcohols, carboxylic acids, ketones and aldehydes) also increased with the fiber loading to the detriment of alkanes emitted by the polymer. Some of these oxygenated compounds originated from PP: for example, levels of acetone and 4-hydroxy-4-methyl-2-pentanone emitted by non-weathered PP, PP10 and PP30 are comparable (Table 2). Thus, it can be supposed that oxidized PP chains mainly contribute to the total level of these two ketones. However, oxygenated compounds specific to vegetal fibers decomposition are predominant in global VOCs emission from biocomposites. These VOCs are referred in Table 2 with asterisk symbols when they are detected in qualitative analysis of vegetal fibers pellets. For example, furanones were emitted

at the $\text{mg}\cdot\text{m}^{-3}$ level by PP30, but also phenolic and nitrogen containing products (azines) at $400 \mu\text{g}\cdot\text{m}^{-3}$ and $60 \mu\text{g}\cdot\text{m}^{-3}$ respectively (Table 2). All cyclic products are also known to be issued from vegetal fibers [45–47]. Moreover, several linear carboxylic acids and aldehydes (hexanoic acid, heptanoic acid, octanal and nonanal) were only identified for biocomposites and vegetal fibers pellets, which suggests that these VOCs only resulted from vegetal fibers. Some VOCs identified for biocomposites but non-identified for vegetal fiber pellets, such as 2-nonenal, can be issued from prodegrading effect of fibers which provokes depolymerization.

3.2. VOCs emissions during weathering: impact of climatic conditions

For all materials analyzed at a sampling temperature of 23 °C, the VOCs concentration increased after one-year weathering, but in a larger proportion for biocomposites. VOCs level reached $892 \pm 183 \mu\text{g}\cdot\text{m}^{-3}$ for PP30 whereas it only reached $73 \pm 14 \mu\text{g}\cdot\text{m}^{-3}$ for neat PP after one year (Table 2). This means that weathering affected more biocomposites stability than PP one. Ketones (acetone and 2,4-pentanedione) and carboxylic acids (acetic and propionic acids) were increasingly detected during the weathering (Table 2). These oxygenated products come from the polymer chains and hemp fibers oxidation under high temperatures and UV rays, key factors favoring free-radical mechanisms involving reactions with oxygen from the atmosphere [48]. Propionic acid was only emitted by biocomposites, suggesting that it was only issued from hemp fibers degradation. This will be confirmed in the following part.

In view of the higher number of VOCs detected after 80 °C sampling than at 23 °C one, the study all along the ageing is focalized to the analysis carried out at the highest sampling temperature. Hence, the evolution of concentrations of VOCs sampled at 80 °C all along the ageing for PP, PP10 and PP30 is illustrated by main chemical family in Fig. 5.

The global concentration of VOCs emitted by PP did not significantly vary. Thus, the weathering did not greatly influence the global level. C_9 – C_{15} alkanes were among the predominant VOC species sampled all along the weathering. However, C_9 , C_{10} and C_{11} short

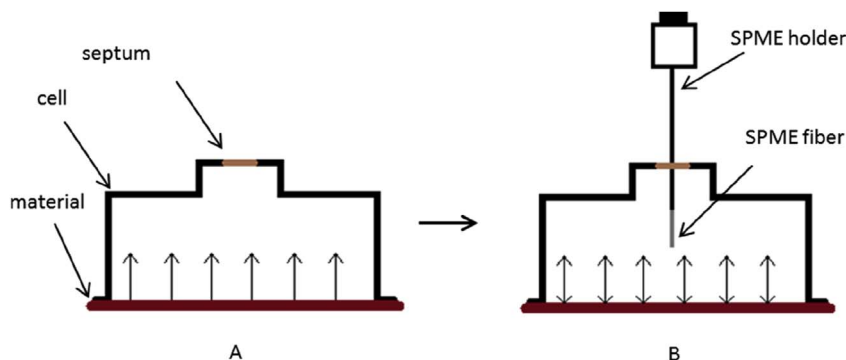


Fig. 3. Schematic representation of the emission cell-SPME system (A: establishment of the material/air equilibrium at 23 °C or 80 °C, B: SPME sampling of VOCs).

Table 2

VOCs emitted by PP, PP10 and PP30 before and after one-year weathering (sampling at 23 and 80 °C) (NW: Non-weathered, W: weathered, SD: Standard deviation, *: mostly identified for NW fibers pellets, **: mostly identified for W fibers pellets, ***: mostly identified for NW and W fibers pellets, n.d. NW: non-detected for NW fibers pellets but detected for NW PP30, n.d. W: non-detected for W fibers pellets but detected for W PP30).

	Surface concentration \pm SD ($\mu\text{g}\cdot\text{m}^{-3}$)								
	PP			PP30			PP10		
	W (23 °C)	NW (80 °C)	W (80 °C)	W (23 °C)	NW (80 °C)	W (80 °C)	W (23 °C)	NW (80 °C)	W (80 °C)
<i>Aliphatic hydrocarbons</i>									
C ₉	–	65 \pm 5	179 \pm 8	–	–	–	–	–	–
C ₁₀	–	786 \pm 14	1625 \pm 367	–	239 \pm 11	–	–	590 \pm 25	–
C ₁₁	–	550 \pm 64	1061 \pm 92	–	104 \pm 2	–	–	291 \pm 52	–
C ₁₂	–	820 \pm 27	692 \pm 116	–	114 \pm 8	–	–	575 \pm 8	–
C ₁₃	–	1768 \pm 50	1241 \pm 240	–	181 \pm 32	631 \pm 173	–	1230 \pm 136	833 \pm 39
C ₁₄	–	339 \pm 117	140 \pm 16	–	59 \pm 5	260 \pm 8	–	238 \pm 20	139 \pm 3
C ₁₅	–	1672 \pm 50	771 \pm 52	–	–	305 \pm 21	–	1388 \pm 26	–
<i>Ketones</i>									
Acetone*	24 \pm 5	25 \pm 8	333 \pm 34	45 \pm 5	36 \pm 15	1108 \pm 406	35 \pm 7	15 \pm 1	1074 \pm 22
1-hydroxy-2-propanone*	–	–	–	–	420 \pm 81	796 \pm 375	–	122 \pm 15	911 \pm 109
2,3-butanedione (n.d. NW)	–	–	–	–	84 \pm 7	–	–	31 \pm 5	–
2-pentanone (n.d. W)	–	–	–	–	–	426 \pm 273	–	–	453 \pm 28
3-hydroxy-2-butanone*	–	–	–	–	36 \pm 4	–	–	–	–
3-penten-2-one (n.d. W)	–	–	–	–	–	927 \pm 52	–	–	619 \pm 71
2(5H)-furanone (n.d. NW)	–	–	–	–	355 \pm 38	–	–	157 \pm 10	–
Butyrolactone***	–	–	–	–	230 \pm 10	324 \pm 125	–	123 \pm 9	295 \pm 5
Cyclopentene-1,3-dione (n.d. NW)	–	–	–	–	157 \pm 11	–	–	–	–
5-methyl-2(5H)-furanone (n.d. NW)	–	–	–	–	68 \pm 7	–	–	27 \pm 7	–
Cyclopentane-1,2-dione	–	–	–	–	89 \pm 7	–	–	42 \pm 1	–
5-methyl-2(3H)-furanone	–	–	–	–	40 \pm 14	–	–	53 \pm 16	–
Pentane-2,4-dione**	19 \pm 5	–	441 \pm 106	124 \pm 10	27 \pm 1	7399 \pm 4216	–	–	7368 \pm 211
4-hydroxy-2-pentanone (n.d. W)	–	–	–	–	–	255 \pm 161	–	–	275 \pm 21
1-(1H-pyrrol-2-yl)-ethanone (n.d. NW)	–	–	–	–	114 \pm 4	–	–	87 \pm 3	–
1-(2-furanyl)-ethanone	–	–	–	–	30 \pm 3	–	–	27 \pm 2	–
3-methyl-2,5-furandione	–	–	–	–	–	628 \pm 174	–	–	746 \pm 21
2,5-dihydro-3,5-dimethyl-2-furanone	–	–	–	–	–	267 \pm 149	–	–	218 \pm 8
3-methyl-1,2-cyclopentanedione (n.d. NW)	–	–	–	–	101 \pm 17	–	–	42 \pm 6	–
3-methyl-3-hexen-2-one	–	–	–	–	–	168 \pm 83	–	–	127 \pm 2
1-(3,3-dimethyloxiranyl)-ethanone**	–	–	–	–	–	663 \pm 27	–	–	872 \pm 5
3,4-epoxy-3-ethyl-2,3-butanone	–	–	–	–	–	361 \pm 53	–	–	313 \pm 6
2,5-hexanedione**	–	–	–	–	–	868 \pm 107	–	–	521 \pm 40
1-acetyloxy-2-propanone*	–	–	–	–	366 \pm 11	377 \pm 153	–	147 \pm 17	451 \pm 10
4-hydroxy-4-methyl-2-pentanone**	–	65 \pm 13	82 \pm 25	–	87 \pm 10	3125 \pm 137	–	79 \pm 15	3592 \pm 82
6-methyl-5-hepten-2-one	–	–	49 \pm 1	–	–	–	–	–	–
4-methoxy-2-heptanone**	–	–	–	–	–	162 \pm 64	–	–	189 \pm 6
Maltol	–	–	–	–	145 \pm 19	–	–	43 \pm 2	–
Levogluconone (n.d. NW)	–	–	–	–	97 \pm 4	–	–	68 \pm 9	–
3,4-dimethyl-2,5-furanedione	–	–	–	–	–	118 \pm 32	–	–	–
2,4,4-trimethylbut-2-enolide**	–	–	–	–	–	1314 \pm 20	–	–	1990 \pm 146
3-ethyl-2-hydroxy-2-cyclopenten-1-one	–	–	–	–	72 \pm 9	–	–	–	–
5-hydroxy-4,5-dimethyl-2,5-(2H)-furanone	–	–	–	–	–	754 \pm 118	–	–	968 \pm 44
3,3-dimethyl-2,4-pentanedione (n.d. W)	–	–	–	–	–	157 \pm 55	–	–	135 \pm 1
1-(2,4-dimethyl-furan-3-yl)-ethanone**	–	–	–	–	–	1063 \pm 243	–	–	1807 \pm 149
3-acetonylcyclopentanone***	–	–	–	–	–	1899 \pm 70	–	–	2324 \pm 120
2,4-dihydro-5-hydroxy-3,3,5-trimethyl-2-furanone**	–	–	–	–	–	303 \pm 48	–	–	330 \pm 18
4-acetonylcyclohexanone	–	–	–	–	–	277 \pm 63	–	–	333 \pm 5
4,6-dimethyl-2-heptanone**	–	–	–	–	–	361 \pm 81	–	–	278 \pm 2
2-methyl-3-nonanone (n.d. W)	–	–	–	–	–	110 \pm 9	–	–	85 \pm 11
3,6-dimethyloctan-2-one	–	–	–	–	–	265 \pm 56	–	–	344 \pm 4
6,10-dimethyl-5,9-undecadien-2-one*	–	–	–	–	48 \pm 0	–	–	–	–
4,4,5,5-tetramethyl-2,7-octanedione	–	–	–	–	–	172 \pm 48	–	–	212 \pm 26
<i>Carboxylic acids</i>									
Acetic acid*	30 \pm 4	26 \pm 1	542 \pm 61	667 \pm 152	397 \pm 62	18304 \pm 620	452 \pm 200	179 \pm 74	13008 \pm 874
Propionic acid*	–	–	–	56 \pm 16	–	1403 \pm 3	39 \pm 4	–	839 \pm 75
Crotonic acid* (n.d. W)	–	–	–	–	–	3332 \pm 612	–	–	3682 \pm 175
Methacrylic acid	–	–	120 \pm 70	–	–	–	–	–	–
Hexanoic acid*	–	24 \pm 8	81 \pm 25	–	130 \pm 8	213 \pm 48	–	69 \pm 15	199 \pm 17

(continued on next page)

Table 2 (continued)

	Surface concentration \pm SD ($\mu\text{g}\cdot\text{m}^{-3}$)								
	PP			PP30			PP10		
	W (23 °C)	NW (80 °C)	W (80 °C)	W (23 °C)	NW (80 °C)	W (80 °C)	W (23 °C)	NW (80 °C)	W (80 °C)
Benzoic acid	–	–	–	–	45 \pm 6	–	–	44 \pm 13	–
Heptanoic acid*	–	–	–	–	–	115 \pm 15	–	–	87 \pm 9
Octanoic acid*	–	25 \pm 7	62 \pm 4	–	70 \pm 10	201 \pm 14	–	43 \pm 22	238 \pm 1
7-oxooctanoic acid	–	–	–	–	–	271 \pm 26	–	–	389 \pm 2
Nonanoic acid*	–	–	–	–	–	266 \pm 27	–	–	304 \pm 2
Dehydroacetic acid	–	–	–	–	–	473 \pm 55	–	–	618 \pm 41
Aldehydes									
Methacrolein**	–	–	–	–	–	291 \pm 44	–	–	107 \pm 76
Furfural*	–	–	–	–	1611 \pm 20	–	–	703 \pm 15	–
Furfuryl formate	–	–	–	–	38 \pm 4	–	–	–	–
Furfuryl acetate*	–	–	–	–	43 \pm 4	–	–	–	–
5-methylfurfural*	–	–	–	–	660 \pm 30	–	–	245 \pm 14	–
Benzaldehyde*	–	–	–	–	93 \pm 0	77 \pm 10	–	28 \pm 11	–
Octanal***	–	26 \pm 6	51 \pm 1	–	29 \pm 7	54 \pm 15	–	27 \pm 5	41 \pm 3
Nonanal***	–	–	–	–	160 \pm 28	94 \pm 14	–	259 \pm 27	149 \pm 2
2,4-dimethyl-pentanal	–	–	–	–	–	64 \pm 1	–	–	89 \pm 9
2-nonenal (n.d. NW)	–	–	–	–	65 \pm 7	–	–	27 \pm 10	–
Decanal*	–	89 \pm 28	135 \pm 1	–	119 \pm 30	121 \pm 16	–	128 \pm 12	146 \pm 1
1-(1,1-dimethylethyl)methyl-2-propenal (n.d.W)	–	–	–	–	–	741 \pm 71	–	–	882 \pm 42
Dodecanal*	–	40 \pm 9	57 \pm 30	–	63 \pm 3	–	–	53 \pm 8	–
1H-pyrrole-2-carboxaldehyde*	–	–	–	–	121 \pm 22	–	–	79 \pm 6	–
Vanillin	–	–	–	–	159 \pm 27	–	–	–	–
Alcohols									
2-methyl-2-propen-1-ol (n.d. W)	–	–	–	–	–	602 \pm 110	–	–	293 \pm 41
2-furanmethanol*	–	–	–	–	2319 \pm 176	–	–	641 \pm 89	–
2-ethyl-1-hexanol*	–	52 \pm 11	52 \pm 4	–	79 \pm 9	176 \pm 17	–	101 \pm 7	148 \pm 1
2-isopropyl-5-methyl-1-heptanol	–	206 \pm 9	214 \pm 1	–	44 \pm 1	–	–	166 \pm 15	–
4-methyl-1,6-heptadien-4-ol	–	–	–	–	–	832 \pm 46	–	–	889 \pm 23
2-ethyldecanol	–	–	62 \pm 1	–	–	–	–	–	–
Tridecanol	–	63 \pm 6	50 \pm 4	–	–	–	–	–	–
2-methyltridecanol	–	89 \pm 50	26 \pm 1	–	–	–	–	59 \pm 9	–
Phenols									
3,5-dimethylphenol**	–	–	–	–	–	471 \pm 75	–	–	642 \pm 2
2-methoxy-4-vinylphenol*	–	–	–	–	195 \pm 28	–	–	–	–
2,6-bis(1,1-dimethylethyl)phenol	–	124 \pm 7	195 \pm 22	–	163 \pm 16	120 \pm 11	–	392 \pm 60	158 \pm 7
Furans									
2,4-dimethylfuran/2,5-dimethylfuran**	–	–	82 \pm 14	–	–	2462 \pm 143	–	–	990 \pm 82
Azines									
Methylpyrazine*	–	–	–	–	25 \pm 2	–	–	–	–
N-acetyl-4(H)-pyridine	–	–	–	–	38 \pm 4	–	–	–	–
Non-quantified (N.Q.)–									
C ₁₅ (1 VOC)	–	N.Q.	N.Q.	–	N.Q.	N.Q.	–	N.Q.	N.Q.
2,6-di-butyl-2,5-cyclohexadiene-1,4-dione	–	N.Q.	N.Q.	–	N.Q.	N.Q.	–	N.Q.	N.Q.
Total (sum of concentrations)	73 \pm 14	6854 \pm 490	8343 \pm 1260	892 \pm 183	9965 \pm 872	56526 \pm 9593	526 \pm 211	8618 \pm 797	51700 \pm 2700

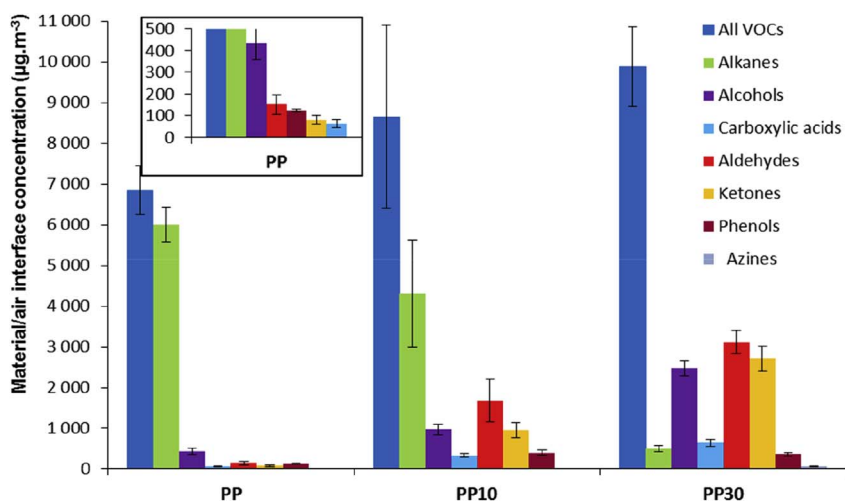


Fig. 4. Families of VOCs emitted by non-weathered PP, PP10 and PP30.

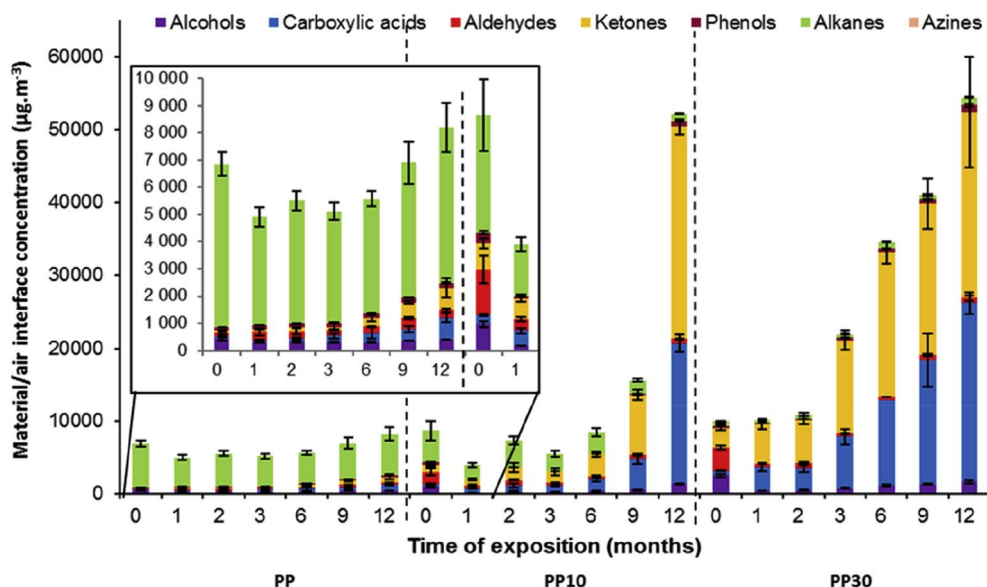


Fig. 5. Evolution of chemical families over the weathering (PDMS/DVB/CAR SPME fiber – sampling at 80 °C).

alkanes concentrations increased after the ageing to the detriment of C_{14} and C_{15} (Table 2). This result suggests that the weathering induced polymer chain scissions which favored shorter chains formation. Also, ketones, aldehydes and carboxylic acids proportion increased after one-year weathering of PP and represented 28% of VOCs surface concentration (Fig. 5). In addition, the substituted phenols detected in virgin PP identified as 2,6-bis(1,1-dimethylethyl)phenol and 2,6-di-*n*-butyl-2,5-cyclohexadiene-1,4-dione were derived from the Irganox L140[®] and Irganox 1010[®] antioxidants respectively probably incorporated during manufacturing process to stabilize the polymer and prevent its thermo-oxidation (Table 2) [31].

PP10 and PP30 emitted VOCs at higher concentrations than PP over the exposition (Fig. 5): their global surface concentration drastically increased by 6 and 5 times respectively (Table 2).

As shown in Fig. 5, PP10 presented a same VOCs emission profile as PP30 after 1 year whereas it mainly emitted alkanes from the polymer matrix at non-aged state. This suggests that hemp fibers proportion on PP10 surface increased with the weathering time to the detriment of polymer matrix. Moreover, studies reporting the surface topography evolution during an ageing showed a roughness increase on natural fillers composites surface caused by fillers proportion increase [23,30].

As at non-weathered state, PP30 emitted alkanes at lower concentrations than PP due to a lower proportion of virgin PP in the biocomposite. However, contrary to PP, C_{13} , C_{14} and C_{15} alkanes levels increased during the exposition of PP30 (Table 2). This can be due to hindrance of polymer derivatives emission at non-weathered state caused by the presence of physical entanglement of hemp fibers. Then, the degradation of vegetal fibers during the weathering led to fibers network overthrow inducing the increase of C_{13} , C_{14} and C_{15} alkanes emission with weathering time.

In addition to alkanes coming from polymer, oxygenated compounds were emitted by biocomposites. The main oxygenated compounds contributors are ketones and carboxylic acids. These latter represented 37% and 45% of total concentration for one-year weathered PP10 and PP30 respectively. As shown by the specific analysis of aged hemp fibers pellets (asterisks in Table 2), these compounds are mainly issued from the fibers decomposition. Some major substances such as pentane-2,4-dione, 1-(2,4-dimethyl-furan-3-yl)-ethanone and nonanal emitted by one-year weathered biocomposites were proved to come from fibers degradation since they were also identified after analysis of the aged fibers pellets. These results confirm that the drastic increase of oxygenated compounds over the weathering is mainly due to vegetal fibers oxidation. Indeed, the presence of chromophoric structures in

natural fibers enhances energy absorption in UV rays range so that their reactivity is favored [26,49], inducing hemp fibers degradation and by-products emission. As for non-weathered state, all cyclic compounds are known to originate from fibers decomposition [45–47]. However, some VOCs, such as crotonic acid, 2-pentanone, 4-hydroxy-2-pentanone, 3-penten-2-one, 2-methyl-2-propen-1-ol and 1-(1,1-dimethylethyl)methyl-2-propenal, present in one-year weathered PP30, were not identified in aged fibers pellets analysis. This demonstrates possible interactions between polymer and hemp fibers and/or prodegrading effect implying degradation mechanisms different from those specific to fibers and PP separately.

Among the oxygenated compounds specifically emitted by the biocomposites, furanic and phenolic substances are quantified at high concentration levels (almost $6900 \mu\text{g m}^{-3}$ and $470 \mu\text{g m}^{-3}$ respectively for one-year weathered PP30). They are of particular interest as they are known to be issued from holocellulose and lignin which compose the hemp fibers. Therefore, the next section (3.3) focuses on these compounds.

3.2.1. Cellulose and hemicelluloses by-products

Some furanic compounds are specifically emitted by the biocomposites both at non-weathered and weathered states. The evolution of these cyclic ketones issued from cellulose and hemicelluloses degradation was individually followed over the exposition. The surface concentration variations measured for the highest fiber loading biocomposite (PP30) analyzed at 80 °C are represented in Fig. 6 for furan and cycloketone products.

Some products like furfural ($1611 \pm 20 \mu\text{g m}^{-3}$) and 2-furanmethanol ($2319 \pm 219 \mu\text{g m}^{-3}$), emitted by unaged samples, were no longer detected after the weathering of biocomposites (Fig. 6a). These compounds originated from ring-opening of primary saccharides contained in holocellulose followed by further cyclization [45]. Other furans were emitted and mainly methyl substituted furanones appeared during weathering. After 6 months, their concentrations stagnated except for dimethylfuran, the lightest furan molecule, increasing all along the ageing. This last trend is explained by a reaction equilibrium favored towards short carbonyl fragments formation, continually increasing, rather than furanone derivatives formation. Also, the higher temperatures observed during the second half-year exposition (Fig. 2) favored low molecular weight compounds emissions due to long-term degradation. However, the rising release of dimethylfuran is due to the contribution of polymer matrix to this product emission in addition to hemp fibers [50]. As regards cyclic ketones, two acetyl substituted

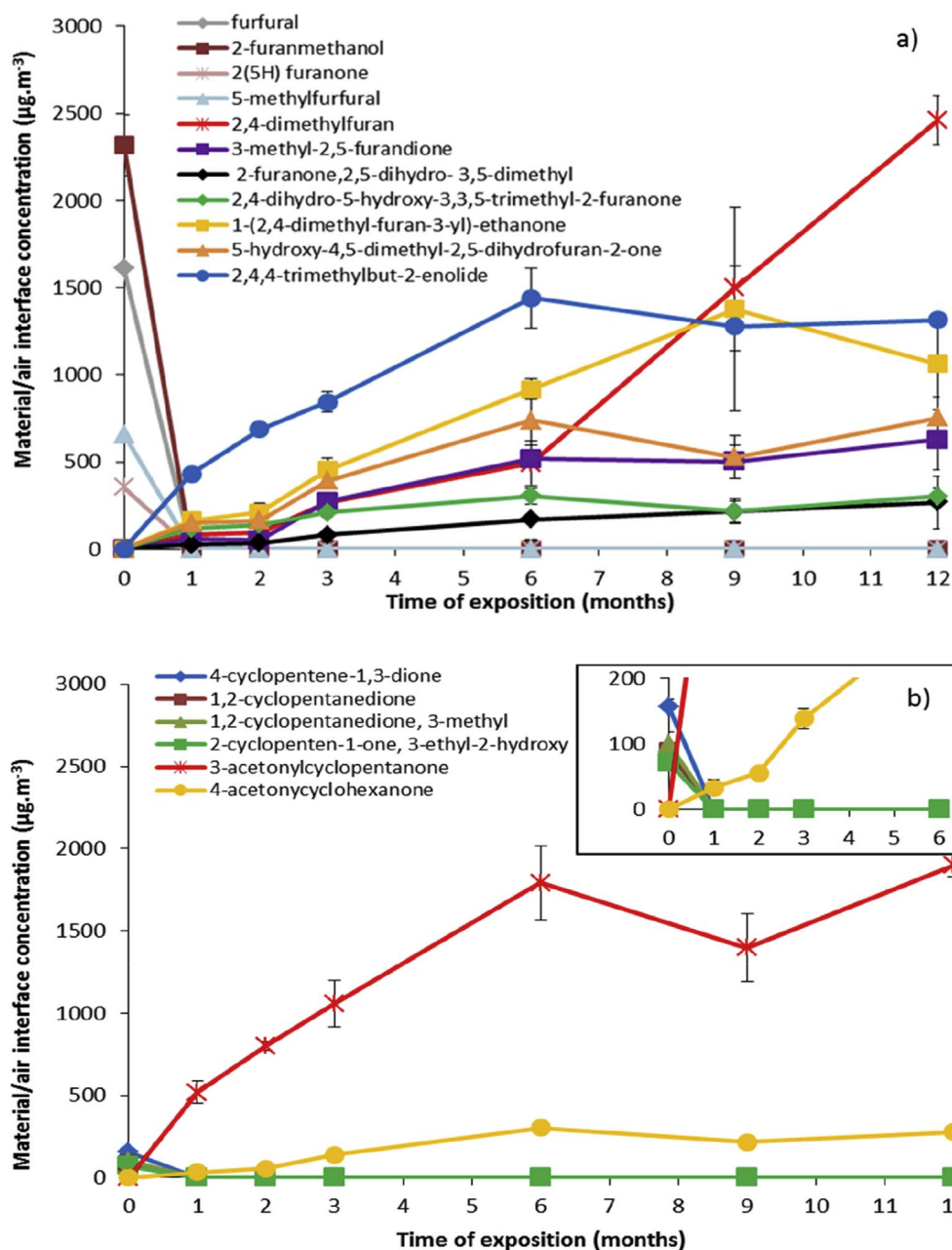


Fig. 6. Variations of major furan (a) and cyclic ketones (b) VOCs released by PP30 over the exposition (PDMS/DVB/CAR SPME fiber – sampling at 80 °C).

cyclic ketone substances were formed during the ageing (Fig. 6b): 3-acetonylcyclopentanone was predominant among all substances belonging to this group. This molecule present in great quantity ($1899 \pm 70 \mu\text{g}\cdot\text{m}^{-3}$ after 1 year) is supposed to mainly originate from cellulose source rather than hemicelluloses [46,47].

3.2.2. Lignin by-products

Phenolic monomeric products emitted by PP30 were linked to the thermal breakdown of lignin, amorphous cross-linked phenolic polymer contained in vegetal fibers (Fig. 7). Whatever the weathering duration, phenolic molecules concentrations are lower than carbohydrates derived VOCs. It is explained by the lower proportion of lignin present in hemp fibers, which approximately accounts for less than 10 wt% whereas the holocellulose part almost represents 85 wt% [51,52]. Moreover, hemp fibers having undergone a long retting time to facilitate separation of the fiber from the stem, it led to a lower lignin proportion since chromophores present in lignin are sensitive to retting parameters such as solar radiation [53–55].

Methoxy substituted phenols like 4-hydroxy-3-methoxybenzaldehyde (vanillin) and 2-methoxy-4-vinylphenol (4-vinylguaiacol) disappeared after weathering. These compounds were originated from a lignin primary decomposition implying primary reactions occurring in solid phase [56]. 3,5-dimethylphenol, which is an alkyl substituted aromatic ring, replaced them after ageing as secondary decomposition product. The last one involves reactions in vapor phase or heterogeneous gas/solid reactions. Indeed, bonds cleavage of pre-formed guaiacol structures can induce alkyl substituted phenols formation.

3.3. Impact on indoor air quality (IAQ)

Recently, the vehicle indoor air quality (VIAQ) has been getting extensive attention as a result of various hazardous substances detection. Hence, this part focuses on the possible toxicity or noxiousness of some identified products.

According to their well-known toxicity [21,57], formaldehyde and

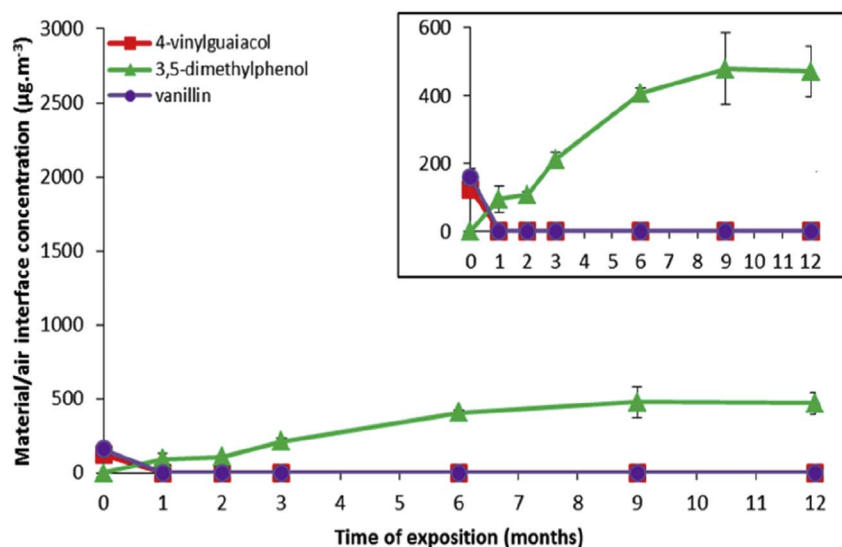


Fig. 7. Variations of phenolic VOCs released by PP30 over the exposition (PDMS/DVB/CAR SPME fiber – sampling at 80 °C).

acetaldehyde emissions were specifically monitored thanks to PDMS-DVB fiber impregnated with PFBHA. Indeed, formaldehyde is carcinogenic to humans whereas acetaldehyde is classified in C2 category in CLP regulation meaning that it is suspected of being carcinogenic [41] (Table 3). Concentrations were measured after 0, 6 and 12 months of weathering (Fig. 8).

As for the other aldehydes (see 3.1), the concentration of these two compounds increased for all materials during the exposition, especially for PP30, reaching $20.3 \pm 0.9 \mu\text{g m}^{-3}$ (formaldehyde) and $39.5 \pm 0.3 \mu\text{g m}^{-3}$ (acetaldehyde) after one year and a 23 °C sampling.

Furfural (2-furaldehyde) and 2-furanmethanol (furfuryl alcohol), emitted by biocomposites at high surface concentration in high-heat conditions ($1611 \pm 20 \mu\text{g m}^{-3}$ and $2319 \pm 219 \mu\text{g m}^{-3}$ respectively for PP30), are classified in C2 category (Table 3). Nevertheless, the biocomposites weathering induced their disappearance and would thus no longer have negative effects. However, other substituted furan compounds appeared and are of concern since furan molecule is presented as a C1B M2. Also, alkanes released at high level by the polymer heated at 80 °C are also classified in C1B category. Otherwise, phenols coming from lignin component are notified as impacting organic pollutants and are classified as of concern.

Table 4 resumes formaldehyde, acetaldehyde and TVOCs surface concentrations determined in this study. Limit values of indoor concentrations given by existing VIAQ guidelines and standards were gathered in Table 5. Only formaldehyde and acetaldehyde are concerned. It should be noticed that the data from Tables 4 and 5 cannot be directly compared. Indeed, the relationship between indoor air concentration and surface concentration of a pollutant is deduced from the first Fick's law of diffusion and is given by equation (1), considering that the studied indoor environment (e.g. the car cabin) behaves as a continuous stirred reactor operating in steady state conditions [38].

Table 3

CLP regulation of harmful substances (C1B: carcinogenic, M2: suspected to be mutagenic, C2: suspected to be carcinogenic, M3: substance of concern in reason of possible mutagenic effects).

Substances	CMR classification
Formaldehyde	C1B M2
Acetaldehyde	C2
Furan	C1B M2
2-furaldehyde	C2
Furfuryl alcohol	C2
C ₁₂ –C ₂₆ branched and linear alkanes	C1B
Phenols	M3

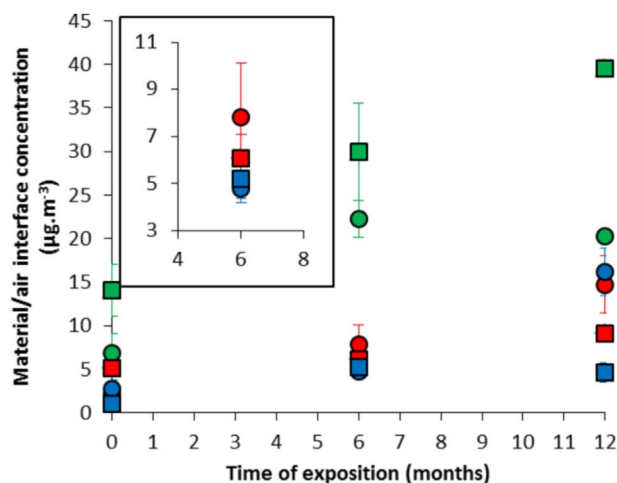


Fig. 8. Formaldehyde (spheres) and acetaldehyde (squares) surface concentrations over the weathering (blue: PP, red: PP10, green: PP30) (PDMS/DVB SPME fiber impregnated with PFBHA – sampling at 23 °C). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 4

Formaldehyde, acetaldehyde and TVOCs levels (ST: sampling temperature).

	ST (°C)	Surface concentration (µg.m ⁻³)					
		Before weathering			After weathering		
		PP	PP10	PP30	PP	PP10	PP30
Formaldehyde	23	2.8	2.24	6.9	16.2	14.7	20.3
Acetaldehyde	23	–	5.1	14.1	4.6	9.1	39.5
TVOCs	23	–	–	–	19	112	124
	80	6342	8322	9267	7676	35284	30849

Table 5

Guideline and recommended standard limit values.

	VIAQ limit values (µg.m ⁻³)		
	JAMA (Japan)	GB/T 27630 (China)	No 2007-539 (Korea)
Formaldehyde	100	100	250
Acetaldehyde	48	50	–
TVOCs	–	–	–

$$Q_{ij} = h_{ij} \frac{A_j}{V(C_{sij} - C_i)} \quad (1)$$

with h_{ij} the convective mass transfer coefficient of pollutant i through the boundary layer over the material j (m.s^{-1}), A_j the surface area of the material j (m^2), V the volume of the studied indoor environment (m^3), C_{sij} the concentration of the pollutant i at the material surface and C_i the average indoor air concentration of the pollutant i ($\mu\text{g.m}^{-3}$).

Table 4 shows that surface concentrations of aldehydes slightly increased over the weathering but they are always lower than their respective indoor concentration limits. Hence, the materials studied here are considered as very low emissive regarding these compounds and they would comply with the current VIAQ regulations.

Currently, no VIAQ standard or guideline has been found preconizing TVOCs limit concentration. However, as reported in the introductory part, TVOCs indoor concentration is an indicator of health effects. Relationship between TVOCs levels found in indoor air and discomfort felt by individuals has been investigated through epidemiological studies [58]. Four exposure ranges were proposed that are a comfort ($< 20 \mu\text{g m}^{-3}$), a multifactorial exposure ($20\text{--}300 \mu\text{g m}^{-3}$), a discomfort ($300\text{--}25000 \mu\text{g m}^{-3}$), and a toxic ($> 25000 \mu\text{g m}^{-3}$) ranges. Weathered PP10 and PP30 can imply possible irritation and discomfort if other exposures interact according to this dose-response model. However, all materials may potentially cause more severe effects when they are heated at 80°C . This assumption should be moderated by the fact that biocomposites are generally implemented with other materials (for example, door panels). Thus, linings and coatings can act as barrier and reduce biocomposite emission in indoor air, as observed for other material assemblies [59,60].

4. Conclusion

An original methodology for the analysis of emitted VOCs by materials was applied to the study of one-year weathering of biocomposites in comparison with neat polymer (PP). The weathering had a higher impact on the evolution of VOCs types and emitted concentrations of biocomposites than of neat PP. At non-weathered state, the greater the hemp fiber loading was, the higher the emitted VOCs amount was. Moreover, the VOCs emission drastically increased for the highest loading (PP30) after 12 months of weathering. Oxygenated products mostly contributed to the weathered biocomposites emission concentration, demonstrating an oxidative degradation due to UV radiation and high temperatures. A major part of these compounds was shown to originate from hemp fibers but some of them were only detected in biocomposites emissions (non-identified in the hemp fibers individual analysis), assuming possible prodegrading effect. VOCs emissions characterization can be thus a useful way for understanding degradation mechanisms explaining the formation of products issued from the polymer matrix and from the carbohydrates and lignin decomposition.

Regarding the application of these composites in car cabins, all VOCs toxicity was checked. A potential impact on VIAQ was noted because of the release of some products issued from both PP and vegetal fibers. Even if their concentrations satisfy with current VIAQ regulation, this emphasizes a drawback of these fibers reinforced polymers regarding their use in indoor environments because of the higher concentration of hazardous VOCs emitted by biocomposites than virgin PP. The TVOCs level, which considerably increased with weathering time, the temperature and the hemp fiber rate, indicated that health effects by exposition to heated aged biocomposites could become of greater concern. Nevertheless, biocomposites in vehicles are generally implemented in materials assemblies and possible barrier effects could reduce the impact on VIAQ.

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