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Organic Micropollutants in Roof Runoff – A Study of the Emission/Retention Potential of Green Roofs

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ABSTRACT

The incidence of extensive roof greening structures in the contamination of roof runoff has been analysed for three families of organic micropollutants (polycyclic aromatic hydrocarbons [PAHs], alkylphenols [APs], and bisphenol A [BPA]) by means of both laboratory leaching tests and field experiments. For PAHs, which do not have any local source on the green roof and originate only from atmospheric fallout, the green roof behaves as a sink and reduces by a factor 10 the emitted loads compared to a conventional flat roof. APs and BPA however can be emitted by the synthetic materials that constitute the roofing structure (e.g., roof sealing, drainage material, filter, evacuation pipes). Potential emissions of BPA and nonylphenol (NP) from the geotextile, the sealing membrane and PVC pipes have especially been identified. Field results confirm increased NP and octylphenol (OP) emissions in the green roof runoff. However, the concentrations and loads remain within the range of values observed for other types of urban surfaces.

KEYWORDS

Alkylphenols, bisphenol A, green roofs, construction materials, organic micropollutants, sources

INTRODUCTION

Green roofs are of growing interest for urban stormwater managers. They are considered for their capacity to reduce annual runoff volumes, both at roof and catchment scale, and to mitigate peak flow stormwater discharges. Some focus has also been given to the quality of runoff waters from vegetated roofs. Whereas some authors noted a phenomenon of filtration and retention of atmospheric contaminants, especially metals, others underlined the emission of nutrients (Berndtsson 2010; Gregoire et Clausen 2011; Seidl et al. 2013). The presence of organic micropollutants in green roof runoff, and the behaviour of these contaminants in the roofing structure is less documented. However, previous research underlined that roof sealing membranes used on vegetated roofs could be an important source of biocides and also emit other organic micropollutants (Bucheli 1998, Burkhardt et al. 2008).

Green roofing systems are composed of several layers of either natural or synthetic materials that are in contact with stormwaters: vegetation, substrate, filter layer, drainage layer, roof sealing layer, runoff evacuation pipes. These layers could act either as a source or as a sink of micropollutants. In the present study, 3 families of organic micropollutants were considered: alkylphenols (APs), bisphenolA (BPA) and Polycyclic Aromatic Hydrocarbons (PAHs). The

first two families are known to be used in a wide range of urban materials and their presence in urban runoff at significant concentration levels has been documented (Bressy et al. 2012, Gasperi et al. *in press*). APs are used as a stabilizer in plastics (ECB 2002), as well as emulsifiers or dispersant additives in the manufacture of polymers. BPA is an additive in PVC manufacturing and is also used as a monomer in polymer production (ECB 2010). Their potential emission from green roof layers was therefore suspected. PAHs are not likely to be emitted at significant levels by roofing materials but are mainly tracers of atmospheric contamination. Their potential of retention in the green roof structure was thus considered.

METHODS

Field experiments

Within the frame of the TVGEP research project (a 4 years French research project coordinated by CSTB on “vegetated roofs for stormwater management”), an experimental green roof test bench was set up in Paris conurbation. An existing 300 m² flat roof was transformed into 6 extensive green roofs (35 m², 7x5 m) and 2 reference roofs (21 m², 7x3 m), each green roof consisting of a specific combination of the 3 main layers : drainage, substrate and vegetation. A complete description of this experimental roof setup can be found in Gromaire et al. (2013).

Data presented in this paper were collected from two of these roofs:

- a conventional flat roof (code: BI), covered with a self-protected (slate chippings) SBS elastomeric bitumen waterproofing membrane;
- an extensive green roof structure (code: SE3Y), overlying the same SBS elastomeric bitumen waterproofing membrane, and composed of an expanded polystyrene drainage layer, a non woven polypropylene geotextile filter layer, a 3 cm thick substrate layer (natural pumice, lava, bark compost and green compost, 3.4 % in mass of organic matter) and a mix of *sedum* (*S.album*, *S. sexagularer*, *S. reflexum*, *S. kamchatikum*, *S. spurim*, *S. Acre*) vegetation layer.

Runoff/percolation water from each roof was collected at the outlet of the PVC downspout pipe. Tipping bucket flow meters were used to measure continuously the flow at the outlet of each experimental roof. Event mean samples were collected with a flow divider and a sampling line entirely made of aluminium and PTFE ending in 20 L glass recipients. An 1 m² stainless steel rectangular funnel was placed nearby the roof to collect total atmospheric fallout over the rain event and the preceding dry weather period.

Atmospheric fallout, runoff from the conventional flat roof and runoff from the extensive green roof were collected simultaneously over 10 rain events, during the period 25/01/2012 to 05/12/2012. Table 1 summarises the main characteristics of the sampled rain events as well as the range of runoff coefficients observed for both roofs. Rain event depth range from 5.8 to 21.1 mm per event, while maximal rainfall intensities cover a wide range from 4 to 52 mm/h. Due to the minimal sample volume of 5 litres needed for analyses, small rain events (< 5 mm) were not sampled. Most samples were collected during relatively wet periods, and shortly follow a previous rain event.

Table 1. Characteristics of sampled rain events (n=10)

	Rain depth (mm)	Previous dry weather period (days)	Max intensity over 3 mn (mm/h)	runoff coefficient	
				BI	SE3Y
Minimum	5.8	0.13	4	0.63	0.10

Median	11.1	0.71	12	0.76	0.65
Maximum	21.1	3.26	52	0.90	0.86

Samples were analysed for:

- 13 PAHs¹ deriving from the US EPA list, excluding naphthalene, acenaphthene and acenaphthylene, which are too volatile to be correctly quantified;
- bisphenol A (BPA) and 7 alkylphenolic compounds (APs): nonylphenol (NP), nonylphenol mono- (NP1EO) and diethoxylates (NP2EO), nonylphenol acetic acid (NP1EC), octylphenol (OP) and octylphenol mono- (OP1EO) and diethoxylates (OP2EO).

Laboratory experiments

Leaching tests were performed on a selection of green roof materials representative of the materials commonly used in extensive green roof structures, in order to identify the presence or not of alkylphenols and bisphenol A and, if present in the material, the potential of release into water.

The following materials were selected:

- 3 substrates for extensive or semi-intensive roof greening (among which the substrate used on the experimental green roof bench);
- 3 types of new SBS polymeric bitumen sealing membranes (among which the waterproofing membrane used on the experimental roof),
- 3 types of drainage materials: 1 expanded polystyrene layer (PSe - used on the experimental roof), 1 extruded polypropylene layer (PP), 1 polyamid / polyethylene layer (PO/PE),
- 1 polypropylene filtering layer geotextile (same as used on the experimental roof),
- 5 types of PVC gutters (among which the PVC pipe used on the experimental roof).

Substrates were crushed, sieved at 2 mm, and microwave extracted in a mixture of dichloromethane/methanol (40/60, v/v).

The other materials were first cleaned successively with deionised water and methanol and then cut into small pieces (size reduction to < 4 mm). A leaching test into methanol was performed, in order to identify if extractable APs or BPA were present in significant amounts. 10 g of material (SBS membranes, PVC gutters, PP drainage) were stirred over a 24 h period in 100 ml methanol at room temperature. For some materials with very low densities this liquid over solid ratio L/S= 10 could not be applied: a ratio L/S = 80 was applied for expanded polystyrene (1 g PSe in 80 ml MeOH) and L/S = 20 for the PO/PE drainage material (5 g PO/PE in 100 ml MeOH) and the geotextile filter (1 g geotextile in 20 ml MeOH).



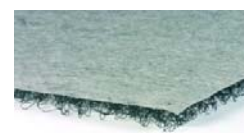
SBS bitumen sealing membrane



Polystyrene drainage layer (PSe)



Polypropylene drainage layer (PP)



Polyamide/ polyethylene drainage layer (PO/PE)



¹ Polycyclic Aromatic Hydrocarbons: Fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3]pyrene, di-benzo[a,h]anthracene, and benzo[g,h,i]perylene

Geotextile

Substrates

PVC gutters

Figure 1. Roofing materials selected for laboratory experiments

The materials used on the experimental green roof (geotextile filter, PSe drainage, SBS bitumen membrane and PVC gutter) were further analysed. A leaching test in distilled water was performed in order to identify if the contaminants present in the material could leach into water. For SBS membrane and PVC gutter, 50 g of material were stirred in 500 ml ultra pure water over 48 h at room temperature (L/S = 10). The ratio was of 9 g in 527 ml water for PSe (L/S=59) and 20 g in 1000 ml for the geotextile (L/S = 50).

In order to quantify potential contaminations during the leaching and the analysis procedures, blanks were performed. Results are presented as ng of pollutant leached per g of extracted material, after deduction of the blank concentration.

The SBS modified membrane and the PVC gutter, which appeared as potential sources of runoff contamination, were further tested under simulated rainfall. The aim was to identify potential releases into runoff under conditions similar to real exposure i.e. very short contact time between the runoff and the material and contact limited to the surface of the material. A continuous rainfall generated with a spinning disk droplet generator (Sprai SAS) was applied at a constant rain intensity of approximately 10 mm/h during 2h, in duplicate, on a 0.07 m² SBS membrane sample, a 0.02 m² PVC gutter sample and an aluminium plate used as blank. Synthetic rainwater, with a ionic composition similar to runoff was used (Seidl et al. 2013).

Analytical methods

The samples were filtered on 0.7 µm glass fibre filter (GF/F, Whatman). The solid phase of field runoff samples was microwave extracted in a mixture of dichloromethane/methanol (40/60, v/v). For APs and BPA analysis, filtrates were preconcentrated and purified on OASIS HLB SPE cartridges (6 cc, Waters) after addition of internal standards (deuterated compounds BPA-d6, NP1EO-d2 and n-OP-d17). The extracts were analysed using UPLC-MSMS (Acquity UPLC–TQD, Waters). Detection and quantification were performed with 2 transitions per compound and matrix effects were corrected using internal standard addition (4-nNP, nNP1EO and nNP2EC). For PAHs analyses, the filtrates were extracted on C18 SPE cartridges (6 cc, Macherey Nagel) after addition of internal standards (naphthalene D8, acenaphthene D10, phenanthrene D10, chrysene D12, perylene D12). Extracts were purified on silica columns before analysis in GC-MS (Focus-DSQ, Thermo).

RESULTS AND DISCUSSION**Potential emissions from construction materials**

Substrates extractions. The only compounds that were quantified at levels superior to the blank are NP in two of the substrates and BPA in the third one, concentrations remain low.

Methanol leaching tests. APs and BPA are detected in most materials at levels above blanks, but the leached masses vary in a wide range from one sample to another and from one pollutant to another (Figure 2).

The highest methanol lixiviation levels are observed for 4-nonylphenol and bisphenol A whereas NP1EC, OP1EO and OP2EO are hardly quantified. SBS polymeric bitumen membranes show significant BPA leaching (14 to 23 ng/g), very high NP leaching (400 to 2400 ng/g) and 100 times lower OP leaching (3 to 13 ng/g). These values have however to be considered with caution as analytical extraction yields were not satisfactory for the bitumen membranes due to interferences with other compounds leached. PVC gutters mainly leach

BPA (9 to 70 ng/g), and lower quantities of AP and APnEO (NP: 1 to 11 ng/g, NP1EO: 1 to 6 ng/g). The emission profile of drainage and filter layers varies from one material to another, but NP is the compound leached at the highest level for all 4 materials (12 to 240 ng/g).

Deionised water leaching tests. Leaching tests into deionised water (Figure 3) lead to much lower emissions (< 10 ng/g). The highest emissions are observed for BPA from the geotextile filter (8.5 ng/g) and the PVC gutter (9 ng/g), followed by NP emissions from the SBS membrane and the PVC gutter (6 ng/g). Alkylphenol ethoxylates (NP1EO, NP2EO, OP1EO, OP2EO) are quantified only for the PVC gutter.

Simulated rainfall. Figure 4 allows a comparison of the concentrations measured for the SBS membrane and the PVC gutter during either static leaching into water or simulated rainfall. The emission profiles observed under both types of tests appear to be quite different. While concentrations are much lower under simulated rainfall for almost all contaminants, due to much lower values of both surface of contact and contact time, one can notice the very high NP concentration emitted during simulated rain by the SBS membrane (≈ 600 ng/l). These results suggest the presence of a stock of easily available NP at the surface of the new bitumen membranes, whereas BPA would rather be present in the mass of the PVC gutter and thus less rapidly but more durably leach into runoff. Simulated rainfall leads to BPA concentrations of 64 ng/l for the SBS membrane and 34 ng/l for the PVC gutter, and OP concentration of 26 ng/l for the SBS membrane. Ethoxylated alkylphenols do not show significant concentrations compared to the blank.

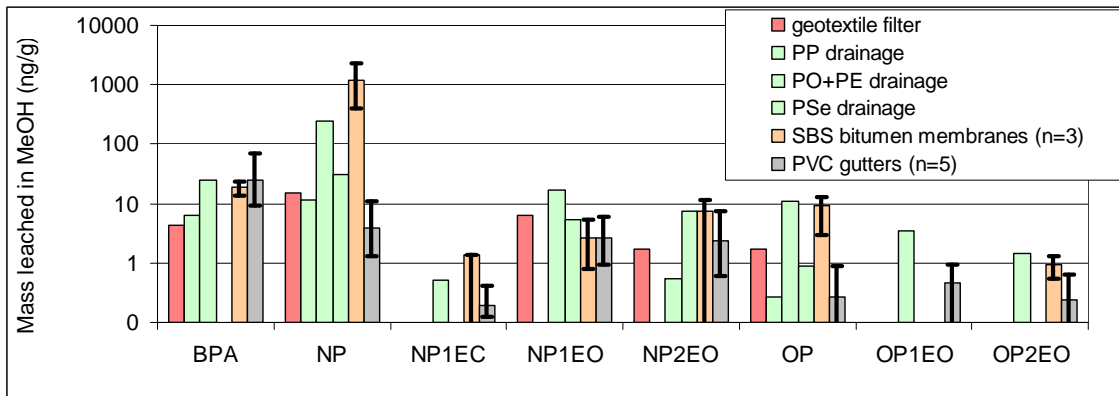


Figure 2: APs and BPA masses leached into methanol

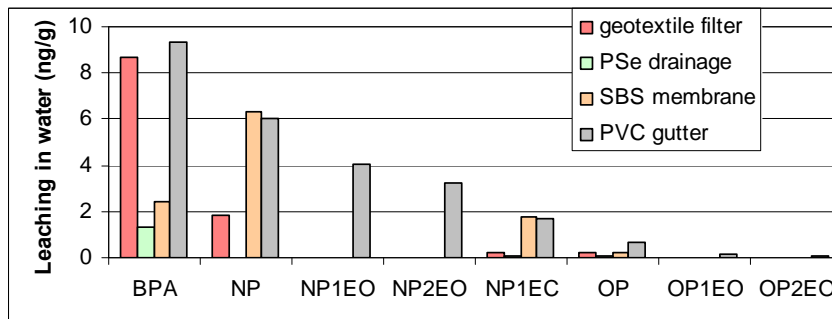


Figure 3: APs and BPA masses leached into deionised water

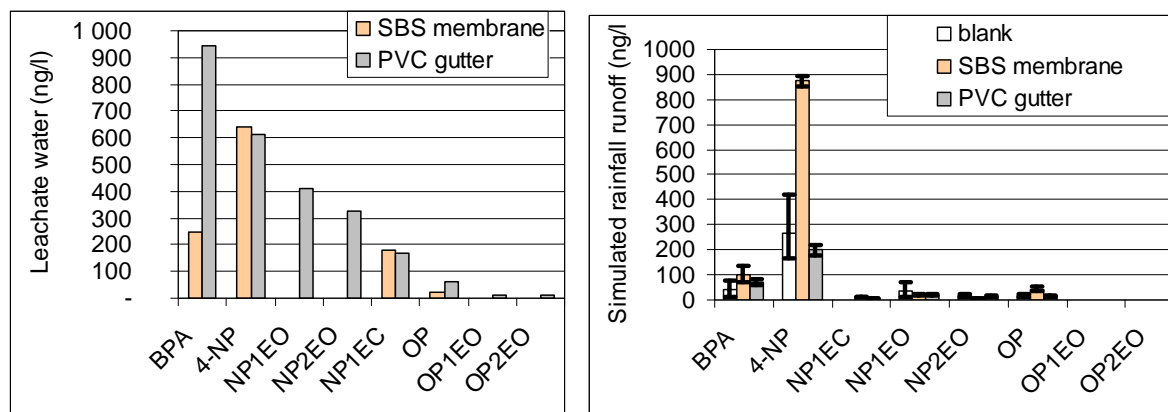


Figure 4: comparison of the concentrations measured during leaching experiment and during simulated rainfall for the SBS bitumen membrane and the PVC gutter

Micropollutants loads in the runoff from the experimental roofs

Field results on atmospheric fallout and runoff from conventional and vegetated flat roofs are summarised in Figure 5, for the sum of the 13 PAHs, the sum of the 4 nonylphenolic compounds ($\Sigma 4 \text{ NP} = \text{NP} + \text{NP1EO} + \text{NP2EO} + \text{NP1EC}$), the sum of the 3 octylphenolic compounds ($\Sigma 3 \text{ OP} = \text{OP} + \text{OP1EO} + \text{OP2EO}$) and for bisphenol A (BPA).

The comparison between atmospheric fallout and roof runoff confirms the atmospheric origin of PAHs whereas an endogenous production of APs and BPA is observed on the experimental roofs.

For PAHs, a significant and systematic filtration effect is observed on the vegetated roof, with median runoff concentrations inferior by a factor 3 to those of atmospheric fallout and conventional flat roof runoff. PAHs concentrations (fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene and benzo(k)fluoranthene) at the outlet of the green roof remain far inferior to European EQS² values.

For nonylphenols ($\Sigma 4 \text{ NP}$), much higher concentrations are observed in the green roof runoff compared to the conventional flat roof runoff, with a median concentration twice that of the conventional roof. This is also observed for median octylphenol concentrations ($\Sigma 3 \text{ OP}$), though it is not systematic for all rain events. The higher green roof concentrations are attributable to NP and OP, while alkylphenol ethoxylates do not show significant concentration shifts between the reference roof and the green roof and are 10 times inferior to NP or OP concentrations. The higher concentrations on the green roof are surprising as APs were expected to originate mainly from the sealing membrane and the PVC gutter which are the same in both roofs (much lower contents were measured during laboratory experiments for substrates, drainage and filter). It can be supposed that the stock of APs available on the top of the membrane has been rapidly washed off on the conventional flat roof where it is directly exposed to rain without any protection, and that hydrologic conditions (longer wet periods, smaller runoff flows) on the green roof are more favourable to slow diffusion emission processes. However, the concentrations of nonylphenol measured downstream of the green roof remain below European EQS values (EQS = 300 ng/l for NP and 100 ng/l for OP) for most rain events. They are slightly superior to the values reported by Gasperi et al. (this proceeding) for roof runoff but in the lower range of stormwater concentrations at catchment scale.

² Environmental Quality Standards given by the EU water framework directive 2013/39/UE

For BPA the behaviour of the two roofs is even different. While the median runoff concentration from the bituminous flat roof is 4 times higher than the median atmospheric fallout, and superior to concentrations reported for zinc or slate roofs (Gasperi et al., this proceedings), the concentrations measured for the green roof runoff vary in a wide range from one rain event to another but with a median value comparable to the atmospheric fallout. The SBS waterproofing membrane was identified as the main potential source of bisphenol A during simulated rainfall experiments. The lower emissions from the green roof might be explained by the protective effect of the vegetation layers, which could prevent photodegradation and thermodegradation of the roofing membrane.

The pollutants loads emitted by the green roof are dependent on its water retention capacity, which can vary in a wide range from one rain event to another as a function of the initial wetness of the substrate, but leads to lower runoff coefficients than the reference roof (Table 1). These lower runoff coefficients partly offset the increased NP and OP concentrations as it can be seen on Figure 6 which compares the loads emitted per m² and per mm of rain on both roofs.

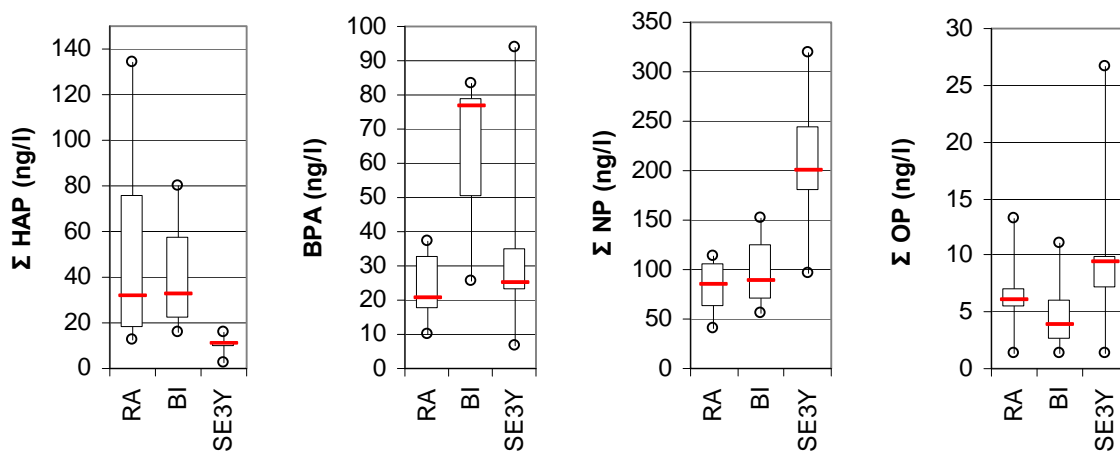


Figure 5: distribution of runoff concentrations measured for atmospheric fallout (RA), bitumen reference roof (BI) and vegetated roof (SE3Y). The box plots indicate median, Q25-Q75 and minimum - maximum values.

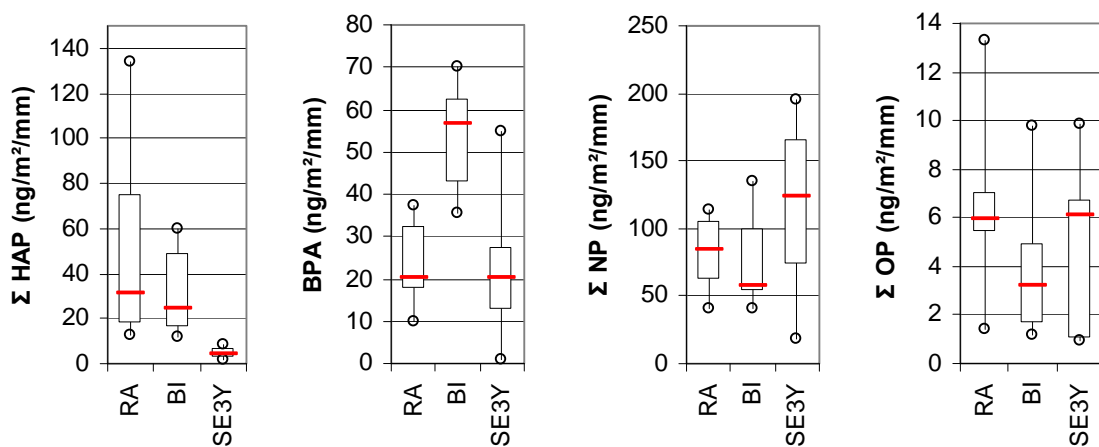


Figure 6: distribution of pollutant loads measured, per mm of rain event, for atmospheric fallout (RA), bitumen reference roof (BI) and vegetated roof (SE3Y). The box plots indicate median, Q25-Q75 and minimum - maximum values.

CONCLUSIONS

The experimental follow up of 3 families of organic contaminants (alkylphenols, bisphenolA and PAHs) with different origins proved complex interactions between green roof layers and pollutants:

- some pollutants like PAHs that mainly originate from atmospheric fallout are retained in the structure, and much lower loads are issued from the green roof compared to a conventional flat roof;
- other organic micropollutants might however be released by the various materials used in the green roof structure. This is the case of APs or BPA which enter in the composition of numerous polymeric materials. Thus one should be very cautious when choosing the materials of roof greening layers.

The level of these emissions is influenced by the hydrologic behaviour of the roof :

- the loads emitted are limited by the low runoff coefficients of green roofs compared to standard roofs. For APs and BPA they remain within the range of other urban surfaces;
- the leaching of some micropollutants contained in the construction materials may be favored by the humidity of the substrate which can enhance hydrolysis or diffusion processes;
- the substrate layer may offer protection against photo and thermodegradation of underlying layers, especially the roof waterproofing membrane, and thus reduce the emission of some contaminants.

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