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Absorption of volatile organic compounds by different wool types

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This paper summarises the quantitative analysis of the absorption of volatile organic compounds (VOCs), namely gaseous formaldehyde, toluene, limonene and dodecane, by different wool types. VOCs are of increasing concern due to their role as accumulating indoor air contaminants, and this paper demonstrates the potential of wool as a sustainable and natural solution to this problem. Building on previous data, different wool types were tested by way of two different methods to assess their absorption ability with regard to these VOCs. For formaldehyde analysis, the samples were subjected to cycles of exposure to excess formaldehyde gas while the weight gain was measured. For the other VOCs, a modified microchamber was used to flow the gases through the samples, followed by trapping and quantification of the non-absorbed VOCs using Tenax TA tubes. The data presented indicate that wool is able to absorb a range of VOCs in differing amounts. The data also show that the amount and the type of VOCs absorbed by wool were dependent on the sheep breed and the processing of the wool.

1. Introduction

Indoor air quality (IAQ) has intrigued scientists since the mid 1800s[1] and continued in the 1930s and the 1940s, when the main concern was the spread of microbial agents within dwellings and public buildings.[2,3] Historical developments such as the London smog of 1952 instigated substantial air pollution investigations, and differences in the health of people working indoors and outdoors were explored.[4] There has been a mild interest in the capacity of construction materials to contribute to a better atmospheric environment,[5] but the main studies investigating volatile organic compounds (VOCs) in buildings did not start until relatively recently, with at least 50 studies conducted between 1978 and 1990.[6] Unfortunately, indoor air pollution remains a recognised socio-economic problem,[7,8] potentially causing the loss of a projected $10 billion to $20 billion annually of projected savings and productivity gains in the USA alone.[9] Based on further scientific findings, the World Health Organisation (WHO) compiled a set of statements emphasising the right to breathe healthy indoor air and the obligations of responsible authorities.[10]

WHO define VOCs as organic compounds with boiling points from 50 to 260°C, and all other organic compounds with boiling points below 50°C as being very volatile organic compounds (vVOCs),[11] but this definition was based on analytical limitations. A working document supporting the European Mandate M/366 describes the technical specifications for horizontal measurement/test methods concerning indoor air emissions.[12] It defines VOCs according to their elution through a gas chromatography capillary column coated with 5% phenyl and 95% methyl-poly-siloxane; anything that elutes before *n*-hexane is classed as a vVOC and anything in between and including *n*-hexane and *n*-hexadecane as a VOC.

Keeping in mind that 99% of human exposure to VOCs results from direct inhalation,[13] a survey (performed in the USA with n = 9386) points out that the public spend 87% of their time in enclosed buildings and 6% of their time in enclosed vehicles.[14] According to the European Respiratory Society, pollutants 'may have an important biological impact even at low concentrations over long exposure periods'. They localised these pollutants

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mainly to homes, schools, congregating halls and residences and vehicles.[15] Figure 1 summarises the total VOC levels reported in the studies performed in different European countries.

The symptoms induced by these pollutants vary, but they can be briefly summarised as exacerbating known respiratory diseases, sensitising to airborne agents and reducing lung functionality. VOCs are frequently linked to what is termed sick building syndrome (SBS), which refers to a range of symptoms that include eye irritation, nasal congestion, dry skin, headache, fatigue and difficulty in concentrating. The first noticeable case of SBS was in the 1970s in Sweden, where SBS was observed in pre-schools; the cause was attributed to casein that was emitted from self-levelling cement. Several similar cases were subsequently reported; for example, an estimated cost of $1 million was incurred due to SBS at the Environmental Protection Agency's US headquarters due to decreased productivity.[19]

In response, the industry introduced a wide range of air-cleaning/treating products to the market, and the removal of both chemical and biological indoor contaminants remains a subject of interest.[20] However, such devices can be energy intensive, contribute to some other form of contamination and have a short operational lifespan compared to the building's life. It is possible that a passive solution can overcome such limitations.

Formaldehyde, as one of the vVOCs, is of importance for three main reasons: many building products emit it at significant rates;[21] it is a gas in its natural state, so occupants are easily exposed to it; and some studies suggest that it has possible adverse health effects at certain concentrations.[22,23] It has been classified as a category 1B carcinogen, which is a classification largely based on animal evidence and presumes to have carcinogenic potential for humans.[24]

Wool fibre is known to manage the problem when used as furniture, clothing or insulation.[25] Compared to previous studies, Curling *et al.*[26] proposed a quick and simple method to quantify gaseous formaldehyde absorption by sheep wool: They exposed wool to formaldehyde gas while observing its weight change using dynamic vapour sorption (DVS). The 4·9% gain in weight shows that wool absorbs this quantity of formaldehyde from the surrounding air. The sample is then placed in a formaldehyde-free environment for several cycles of low to high relative humidity (RH), allowing it to desorb the formaldehyde it contains. Interestingly, the weight of the wool sample does not drop down to its original weight but to 102·9% of its weight. This quantity of formaldehyde is permanently bound to the wool structure.

There are many different VOCs with different and unknown effects when inhaled at low concentrations. The aim of this study is to differentiate between the quantities of these VOCs absorbed by different wool types.

2. Experimental

To represent the widest range possible, four vVOCs were taken into account in this study covering boiling points from −19 to 216·2°C, a large polarity range and different chemical

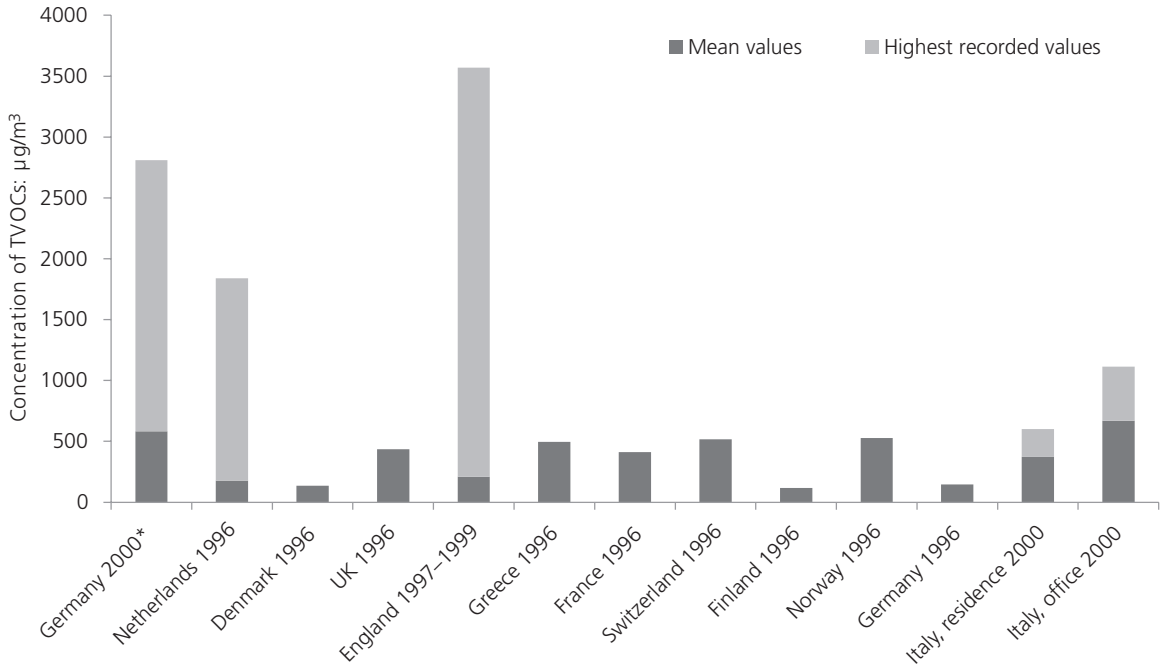

Figure 1. Total VOC (TVOC) measurements.[13,16–18] *Personal exposure, no constraints on individual activity

conformations: formaldehyde (simple and polar molecule), toluene (aromatic), limonene (cyclic and non-polar) and dodecane (straight chain and non-polar). Wools from a number of differing wool breeds were selected for use in the formaldehyde absorption study, with further comparison made to other species, as detailed below. All samples were obtained from commercially available sources.

- Sheep (*Ovis aries*) wool
  - Swaledale: a hardy UK hill sheep with a coarse durable wool predominately used for home furnishings and insulation.
  - Welsh Mountain: a hardy UK hill breed, and the wool has been commonly used for home furnishings.
  - Light Herdwick: a hardy UK mountain breed with the wool commonly used for home furnishing and insulation.
  - Drysdale: a New Zealand breed noted for its coarse wool that is used in home furnishings.
  - Blackface: a UK mountain breed with the wool used mostly for home furnishing and tweed cloth.
- Comparison species
  - Alpaca (*Vicugna pacos*): a llama-like camelid, with the hair in this case obtained from domestic animals raised in the UK.

In addition, the Swaledale and Herdwick samples were obtained and initially tested in their scoured and unscoured states. Scouring of wool is an alkali- and a detergent-based washing process used to remove contamination material, grease and lanolin that could affect the properties of the wool.

Based on the results of the formaldehyde study, further selections were made to reduce the number of wool types tested to Swaledale, Blackface and Herdwick for the other three VOCs.

2.1 Formaldehyde analysis

Formaldehyde sorption analyses were performed using the DVS system (Surface Measurement Systems, London, UK). Wool's ability to absorb formaldehyde was thus assessed by the use of DVS,[26] a method that shows good repeatability. A flow of formaldehyde gas was produced by bubbling nitrogen into a 9·25% solution of formaldehyde and water. This flow can be adjusted to give differing partial pressures of the formaldehyde in the test chamber – for example, the amount of exposure to gaseous formaldehyde increases with increasing partial pressure. A microbalance was used to detect any uptake of moisture and formaldehyde by the fibre. The sample was subjected to the following cycles to calculate the weight of formaldehyde that the wool was able to bind with chemically (Figure 2).

(*a*) The sample was left to equilibrate at 0% RH – that is, it was not exposed to moisture or formaldehyde. This sets its baseline weight. The equilibration at all steps was based on a weight change of less than 0·002% over 10 min.
(*b*) The sample was left to equilibrate at 90% RH – that is, it was exposed to high levels of moisture and formaldehyde where it sorbed both and gained weight.
(*c*) The sample was again equilibrated 0% RH; at this point, it lost all the water it had sorbed. Any weight gain relative to the sample's state at step 1 was therefore attributable to sorbed formaldehyde.
(*d*) Steps 1–3 were repeated several times to determine the total sorption capacity.

2.2 Limonene, toluene and dodecane analysis

The emissions generated from products can be tested using microchambers; but to study the absorption potential, however, certain modifications were applied to introduce gaseous toluene, limonene and dodecane. Due to differences in partial pressures, it was not possible to elute them from a highly compressed state. Therefore, the sources were prepared containing the VOCs in their liquid form in steel tubes, sealed on one side and stoppered with a flexible plastic cover on the other side; this allowed the slow release of the VOCs in their gaseous form even when the sources were put under slight pressure. Table 1 summarises the gaseous concentrations the samples were exposed to, which varied with external temperature.

A flow of nitrogen gas, cleaned of any VOCs already present, was passed through the ≈100 ml chamber containing the VOC sources. Thereafter the flow was controlled at 2·5 ± 0·1 ml/min, with an additional 2·5 ± 0·1 ml/min flow of clean nitrogen added. The controlled flow was fed into the microchamber (Markes Int.) for 2·5 h per run. A vertical sample holder where the wool was held is connected to the microchamber; this ensures that the VOCs pass through the whole sample and do not just interact with some of the surface of the sample. Any VOCs that were not absorbed by the sample were absorbed by 200 mg Tenax TA contained in 89 × 6·4 mm inert-coated stainless steel Tenax TA tubes (Markes Int.), which was in turn analysed using a thermal desorber coupled to gas chromatography coupled to a flame ionisation detector (GC-FID; PerkinElmer). Figure 3 summarises the connections. The GC-FID was previously calibrated using Tenax TA tubes injected with known amounts of the three VOCs (seven differing amounts for each VOC ran in triplicates covering a range of 3·9–312 ng were used to obtain a linear calibration fit forced through an intercept of 0 and having adjusted R^2 values of 0·9978 for toluene, 0·9989 for limonene and 0·9996 for dodecane). The injection of known amounts into the Tenax TA tubes was accomplished by injecting 0·5 µl of differing concentrations of the VOCs dissolved in methanol while a clean nitrogen flow of 100 ml/min was introduced for 15 min.

Blank runs and those for each type of wool were each run in triplicate. The difference in the amounts detected between the blank runs and the sample runs corresponds to the amount of VOCs absorbed by the sample (Figure 4). Note that in the case of

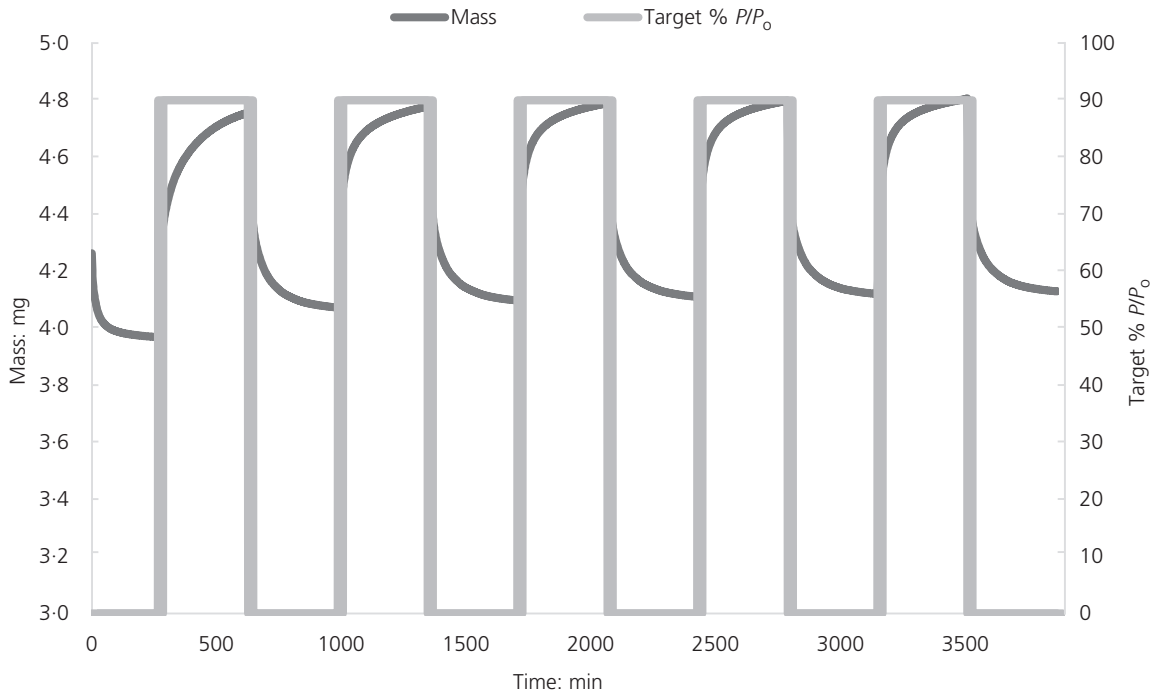

Figure 2. DVS mass plot of Swaledale wool exposed to formaldehyde gas, where P/P_o is the partial pressure of formaldehyde gas

Sample	Temperature: °C	Toluene: ng/l	Limonene: ng/l	Dodecane: ng/l
Swaledale Light Herdwick (2 repeats) Blackface Light Herdwick (1 repeat) Unscoured Swaledale	21·5 ± 1 17·5 ± 1	191·26 ± 32·60 138·88 ± 11·46	325·20 ± 13·66 216·47 ± 1·64	186·56 ± 14·78 113·03 ± 5·56

Table 1. Gaseous concentrations the different samples were exposed to from sources (total flow of ≈5 ml/min over 120 min)

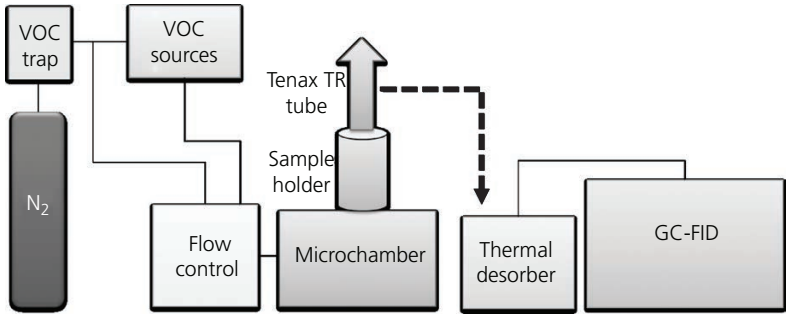

Figure 3. Schematic diagram of modified microchamber used in conjunction with a thermal desorber coupled with GC-FID

toluene, where no absorption was observed, the slightly higher amounts detected in a sample run was due to experimental error and not emissions from the sample (which had been previously tested for), specifically the volume of the wool sample that it takes out of the sample holder.

3. Results and discussion

In comparing the uptake of the VOCs, it should be remembered that two different methods were used. The formaldehyde sorption by DVS utilised an excess of formaldehyde and measured the cumulative uptake throughout multiple cycles of absorption/desorption – that is the wools' total capacity to absorb gaseous formaldehyde; while, however, the microchamber approach utilised a constant flow of relatively low concentrations of limonene, toluene and dodecane (in the nanogram of VOC per gram of wool range) and does not represent the wools' total capacity to absorb these three VOCs but simulates real-life situations. Figure 5 shows the amount of formaldehyde absorbed per kilogram of different wool types. It is evident that both wool type and condition (scoured or unscoured) have an effect on the wool's ability to absorb formaldehyde. It was also noticed that there is a general trend that the more darkly pigmented the wool fibre is, the higher its sorption capacity. Further research will determine if there is a correlation between fibre pigmentation of the same wool source.

Figure 6 shows the amounts of toluene, limonene and dodecane absorbed per gram of some wool types. In the case of formaldehyde, it was evident that both wool type and condition (scoured or unscoured) had an effect on absorption. It is noteworthy that in the case of unscoured wool, the total amount of limonene and dodecane that it was subjected to was completely absorbed, unlike the case of its scoured counterpart (Table 2).

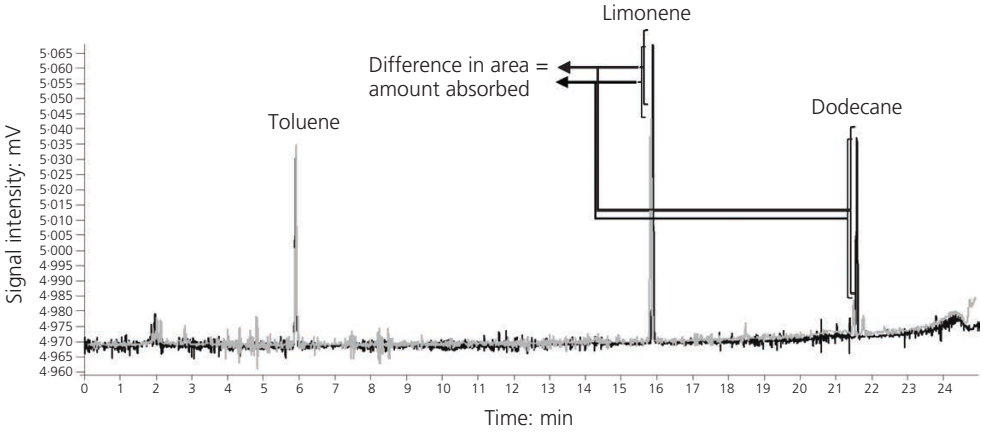

Figure 4. Chromatograms of a blank run (black) and a Swaledale run (grey) showing the detected amounts of toluene, limonene and dodecane that were not unabsorbed by the sample and collected on the Tenax TA tube

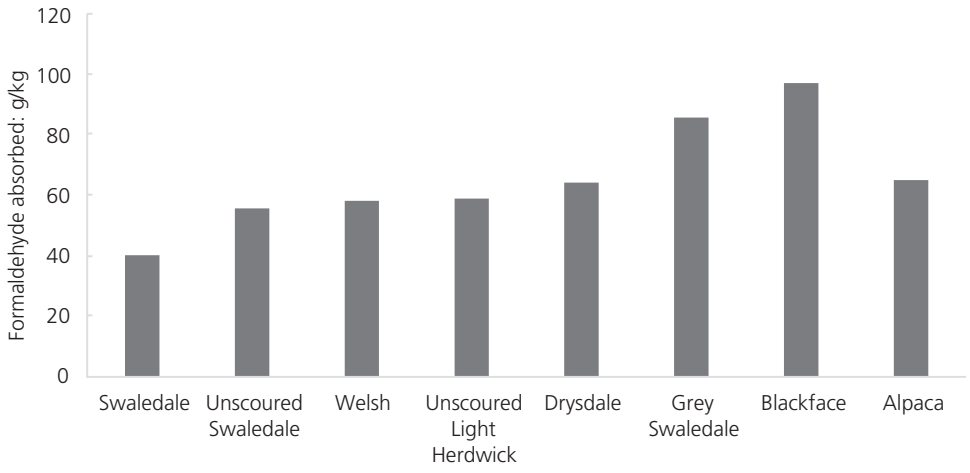

Figure 5. Masses of formaldehyde chemically bound by different wool types per kilogram of wool

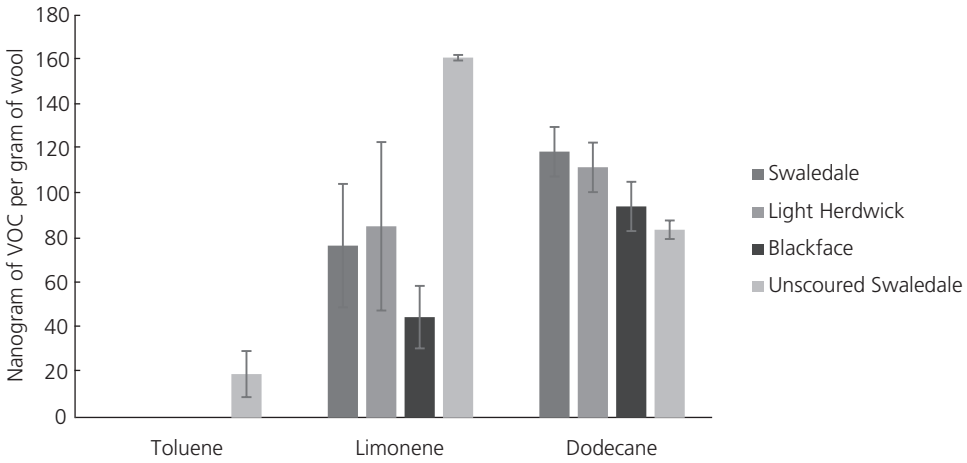

Figure 6. Masses of toluene, limonene and dodecane absorbed by different wool types

Sample	Toluene absorbed: %	Limonene absorbed: %	Dodecane absorbed: %
Swaledale	0·00	31·66 ± 11·35	85·31 ± 7·29
Light Herdwick	0·00	39·99 ± 4·20	93·25 ± 7·92
Blackface	0·00	18·52 ± 5·67	67·77 ± 7·92
Unscoured Swaledale	18·87 ± 9·78%	99·50 ± 0·76	99·50 ± 4·92

Table 2. Percentages of used masses of toluene, limonene and dodecane absorbed by different wool types

When the absorption of the studied VOCs is compared across the range of different wool types, a trend can be observed based on the polarity of the VOC. For example, in the case of formaldehyde absorption, Swaledale wool absorbs significantly less than Blackface. However, looking at the increasingly non-polar VOCs, Swaledale is seen to absorb more limonene and significantly more dodecane than Blackface does. This indicates that the polarity of the surface may be different between the wool types, leading to different levels of interactions between different VOCs depending on their polarity. Wool product producers may be able to take advantage of this phenomenon and create tailored products that absorb a specific range of those VOCs, which the air in a certain type of building is known to contain high levels of.

Unscoured wool was observed to absorb more of the tested VOCs than its scoured counterpart. This could be due to the presence of lanolin or contaminants that are removed during the scouring process, but it could also be due a modification of the wool surface due to the scouring process.

4. Conclusion

The data presented in this paper show that wool, a natural and sustainable material, is able to absorb a range of potentially harmful chemicals from the indoor environment. This has important considerations for the prevention or the reduction of SBS at a time when this issue is becoming more prevalent. The data indicate that the breed of sheep that provided the wool may have an important effect on the absorption of VOCs. The use of wool in building design may therefore have an important role not only in imparting thermal efficiency but also in the improvement of IAQ.

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