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ABSTRACT

Two methods used to determine stored VOC (volatile organic compounds) in concrete slabs has been compared. These methods are frequently used in investigating indoor environment problems where emissions from moisture damaged floorings are suspected.

Comparative measurements were made in situ, and the results show good agreement with expected values, especially in measurements of a profile at several levels in the concrete floor, or at several different places in one and the same damaged floor.

The comparative measurements have been used in evaluating the partition coefficient (K) and the diffusion coefficient (D, δ) for n-butanol and 2-ethyl-1-hexanol in concrete.

Key words: VOC, measurement methods, stored degradation products, partition coefficient (K), diffusion coefficient (D, δ)

1. INTRODUCTION

A common outcome in investigations of indoor environment problems in Scandinavia is that structures with damp concrete floors may be a considerable source of VOC to the indoor air.

Two of the methods frequently used among investigators are examined and compared in this paper.

The deterioration of flooring materials is well known as a plausible cause of indoor air problem. Emissions from floor constructions may contribute considerable quantities of volatile organic compounds (VOC) to the indoor air, Gustavsson and Lundgren /1/, Wiglusz et al /2/, Cox et al /3/, Saarela et al /4/, Sjöberg /5,6/, Wilke et al /7/. For example, building materials of polyvinyl chloride (PVC) are known to degrade in damp alkaline conditions and the degradation products have been related to upper respiratory symptoms and signs of inflammation, Wieslander G, et al /8/ and to asthma symptoms, Norbäck et al, /9/, Bornehag et al, /10/.

According to Sjöberg /6, 11/, the moist alkaline environments that a concrete slab may provide enhance the risk that plasticizers in flooring materials and acrylate based copolymers in adhesives will be hydrolysed. In alkaline hydrolysis the alcohols 2-ethyl-1-hexanol (EtHx) and n-butanol (BuOH), and other compounds, may be formed and emitted from the material, Alexandersson /12, 13/, Björk et al /14/, Persson /15/, Sjöberg /11/ and Wilke et al /7/. These specific degradation products have been found to correlate with increased SBS symptoms in damp buildings, Nordström et al /16/, and cause irritation of the human mucous membrane, Podlekareva et al /17/, and they are good tracers of the decomposition of flooring materials due to alkaline hydrolysis.

In addition to the emission from the flooring surface the volatile degradation products may also migrate down into the concrete substrate and be stored there for a long time, Sjöberg /6, 11, 18/. Since concrete is a porous substrate with ca 15 % pore volume there may be space for a considerable amount of those organic compounds to be stored. If the concrete surface condition later on changes, e g the flooring is removed or replaced, the stored degradation products may start to migrate upwards again and be emitted through the surface into the indoor air.

This paper describes and assesses two different methods used to determine the extent of stored decomposition products in concrete slabs, namely the flask headspace method (FHM) and the vial headspace method (VHM). The methods are often used by damage investigators who investigate indoor air problems and moisture damage in floor constructions. From the results of these types of measurements, the damage investigators often draw different conclusions regarding the condition of the floor constructions. At times it is a matter of deciding whether the moisture damage is still active, so that the source of moisture also must be dealt with, or whether it is only an old moisture damage which has now dried out, in which case only the remaining stored pollutants must be considered. In both cases it is of critical importance to determine how extensive the dispersion of the pollutants has been and to what depth they have penetrated into the concrete slab. This information can then be used in determining how extensive and effective the methods applied to decontaminate and restore the floor construction must be.

In view of this objective, it is of great importance to understand all the phenomena that govern the stored VOC transport within the concrete slab. Consequently, stored VOC concentration gradients in the concrete slab of five buildings were measured using both the FHM and the VHM methods. Apart from comparing the data and discussing the practical advantages and shortcomings of the two methods, the data were also used to derive the partition and diffusion coefficients of the VOC and concrete systems. The partition coefficients represent the storage capacities of the concrete for the VOCs. On the other hand, the diffusion coefficients determine the VOC kinetics of diffusion within the concrete slab. These two coefficients are typical inputs of physically-based sink or emission models that can be used to define adequate strategies for remediation. Here, particular emphasis is put on discussing their variations as a function of the

moisture content of the concrete (relative humidity in the air-phase of the pores), another parameter that was measured at each sampling point.

2.   METHODS

2.1   VOC concentration in the gas phase

The equilibrium concentration of VOC in the gas phase (c_{air}, g_{voc}/m^3_{air}) was measured with the flask headspace method (FHM). This method was based on determination of the concentration of VOC in the air in the headspace of a flask, in equilibrium with a sample of the contaminated material.

The flask headspace method (FHM) was devised by Sjöberg /11/ and has been frequently used by the scientific community and practitioners in Sweden. Sjöberg /5/ Engström & Sjöberg /19/, Sjöberg & Engström /20/ Engström et al /21/. The FHM method consists of three stages; the first stage is sample preparation of the contaminated material, followed by headspace sampling of VOC on an adsorbent tube and finally analysis of the adsorbent tube by gas chromatography (GC-FID),

In the frame of the present study, the first stage of the FHM method was preparation of samples from the contaminated concrete slab. Samples were taken from several different depths in the substrate in order to determine the range of the penetration profile of contamination in the concrete slab. Moreover, samples were collected from a number different locations in order to determine the range of the problem area. A hammer drill was used to drill and chisel out the samples from different depths in the floor substrate. No cooling water was used in the process since there may be a risk of washing away water soluble organic compounds. It was also important to work quickly and not to warm up the material with the drill since the stored VOC may otherwise be emitted from the heated pieces of the sample.

The concrete samples at every depth were broken up into fragments of about 1 cm^3 size and about 5 - 10 pieces (ca 50 gram total) were quickly placed in a 250 ml glass flask, see Fig. 1. The flask was immediately sealed with a tightly fitting Teflon sealed cap and kept at room temperature (22°C) for three days before headspace sampling. The intention was to enable the VOC in the concrete sample to attain equilibrium with the headspace air in the flask at room temperature. It was therefore important not to raise the temperature of the sample before or during the conditioning period or at the time the headspace air was sampled. In a previous study, a conditioning period of three days had been found enough for equilibrium to be reached in the flask under these conditions. The achievement of an equilibrium state represents a situation where diffusion is completed: VOC concentrations in the air-phase of the pores are uniform throughout the concrete sample and the same as in the headspace of the flask. Therefore, the measured concentration is representative of the local pore air-phase concentrations that characterise the sorption equilibrium within the pores of the concrete samples. Furthermore, it is important to note that 1) the measured concentration embeds the contributions of adsorption / desorption processes at the pore surfaces, but also absorption / desorption processes in the liquid water filling some pores, and 2) not all the VOCs contained in the concrete samples have been diffused to the headspace of the flask at equilibrium: the main part of molecules are remaining at the pores surfaces and in the aqueous phase as a result of the air-phase, solid phase and aqueous phase partitioning.

Figure 1. Flask with two concrete pieces during sampling. Connected via Teflon tube to a TENAX tube and a plastic syringe.

In the second stage an adsorbent tube consisting of TENAX TA was used to sample the VOC in the air of the headspace. In a pre study Solid Phase Micro Extraction (SPME) was used with unsatisfactory results. On the occasion when the headspace air was sampled a carbon filter was attached to one of the gas proof connections in the cap, the air inlet tube (Figure 1). To the other connection a TENAX tube for air sampling was attached. During sampling a 20 ml plastic syringe was used to slowly draw a 20 ml volume of air through the TENAX tube. In order to prevent short circuiting, the air inlet was lowered via a Teflon tube to the bottom of the flask and the outlet was placed at the top. Since only 8% of the air in the flask was replaced during the sampling of the headspace the concentration in the air was not noticeably diluted. Pre studies of repeated samplings from a flask have shown that this dilution effect may hardly be measurable with this method.

The third and final stage in this method was analysis of the TENAX tube by gas chromatography and flame ionisation detector (GC-FID). In a pre study mass spectrometry (MS) had been used to identify the main peaks in the chromatogram.

The absorber tube was desorbed thermally. During the thermal desorption, the adsorbed VOCs were driven off from the adsorber and transported by the carrier gas to the stationary phase of the column. The column was kept refrigerated during the whole desorption phase. After the desorption phase the temperature in the column was raised according to a predetermined scheme; see Sjöberg /11/. No split of the gas stream was performed. When the temperature in the column increases, the VOCs begin to move through the column at different rates according to their characteristics such as e.g. molecule size. When the VOCs pass through the FID, in order, the electrical conduction increases and a higher current is produced as the amount of hydrocarbon radicals is increased. The variation in current was plotted as a function of time in a chromatogram, where each peak in the chromatogram represents an organic compound with a specific retention time. The total concentration or the concentration of the individual VOCs could be calculated with reference to the sampling volume for the analysed TENAX tube and the integrated area below the peaks.

2.2   VOC concentration in the material phase

The second method used in this study was the vial headspace method (VHM). Unlike, the FHM method, this method evaluates directly the total mass of a certain VOC that is contained in a concrete sample (C_{mtrl}, g_{voc}/m^3_{mtrl}).

The VHM method was devised by a commercial company which specialises in laboratory analysis of buildings. This company has in readiness a broad range of methods that any external consultant who needs to investigate a building with indoor air problems or moisture damage may use. The consultants receive instructions and may even borrow some of the needed equipment from the laboratory, and then take all the samples in the building. The samples are then sent to the laboratory through the post. The laboratory performs analyses on the sample and sends the result and some guidelines for the evaluation of the building's condition back to the consultant.

The VHM method consists basically of the same stages as the FHM method since it was a development and adaptation of the latter. All stages have nevertheless been developed and simplified in order to be safely handled by consultants without special training and to fit in better with the laboratory's selection of analysis methods.

In the first stage of the VHM method the drill cuttings from a hammer drill are sampled, which is an important simplification from the larger specimens used in the FHM method. A normal 12 mm hammer drill was used to drill a single hole and the drill cuttings were continuously collected from different depths in glass vials. About 3 g of the concrete cuttings was placed in each vial of 21 ml and quickly sealed by a cap. The only required condition of the concrete sample was that the pieces should be smaller than the opening of the vial (Øint = 12 mm). The vials were packed in a shock absorbent parcel and sent by normal post to the laboratory.

The second stage of the VHM method was extraction of the VOC in the sample and equilibrium with the headspace. When the sample arrived at the laboratory it was weighed for evaluation purposes and 5 ml of an extraction solution was added into each vial. The extraction solution basically consists of 90 % purified and deionised water (milliQ water), 10% ethanol and several internal standards. The vial was sealed with an aluminium cap with a rubber septum and placed in a shaking machine at 85°C for 30 minutes. According to internal studies performed by the method developer at the laboratory this was sufficient to extract the VOC in the concrete cuttings and reach equilibrium with the headspace.

The third stage of the VHM method was to analyse the headspace by gas chromatography and mass spectrometry (GC-MS). The sampling of the headspace was performed while the vial was still at the high temperature. The vials were placed on a turntable, an injection needle from a GC-MS instrument penetrated the septum and injected the overpressure of the headspace directly into the column. The VOCs in the headspace were separated in the GC column and identified by the MS, and the total amounts of different VOCs were quantified with reference to the external standard used and the mass of the concrete sample.

2.3   Moisture measurements

The moisture level in the concrete substrate was measured as relative humidity (RH) in the air in the pores of the material. The procedure used in this study is the common standard in Scandinavia for moisture measurements in most porous building materials. Regulations and critical values are also mostly expressed as a RH value.

Samples of the concrete were removed according to the FHM method and placed in test tubes made of silicate glass. Samples were taken from the concrete at several levels so that a moisture profile may be determined. In most cases the moisture samples were taken at exactly the same places and depths as the samples for FHM and VHM. The test specimens were broken up with a hammer and chisel, and pieces from each level were quickly taken and placed in test tubes which were sealed with rubber plugs. It was essential that the samples should be broken up and placed of in the test tubes quickly so that no moisture would be lost from the samples.

The next day RH probes were inserted into the test tubes. The measuring instrument was read when the system of samples, air in the test tubes and probe had reached equilibrium. The probe will relatively quickly reach equilibrium with the moisture level in the air in the test tube; what took the longest time was for the moisture to leave the concrete samples and reach equilibrium with the air in the test tube. It usually took about 24 hours before equilibrium was reached and the instrument could be read. The values obtained from the instrument were then converted into RH with reference to calibration curves. For this method, RH-probes HMP 36 and hand instrument HMI 31 from Vaisala were used.

3. MEASUREMENT RESULT

The measurements described in this paper were made in a number of buildings in central and southern Sweden during investigations of poor indoor environments. The main objective of the measurements was to demonstrate abnormal moisture levels and the presence of stored VOC in the concrete floor structure, i.e. to show whether there is moisture damage which has produced and stored degradation products in the floor, with the potential consequence of adversely affect indoor air quality at longer times.

3.1 Partition coefficient K

In situ measurements
Measurements A and B were made in situ in 2004 on the concrete slab in an office building in Sweden, built in 1979. During a renovation in 2001, bonded PVC flooring was laid on all floors in the building; this was also done in those areas of the building in which the concrete slab had had no flooring previously. Some time after the renovation, staff complained that they suffered from building related health problems of the SBS type when they were in the building. In a preliminary investigation, VOC from degraded adhesive was identified by the working environment engineer as a likely source of pollution in the indoor air.

Five rooms of the building were investigated. At all locations, RH and VOC contents in the concrete were determined using the methods presented above (both the VHM and FHM methods were used to measure the VOC concentrations).
When holes were made in the floor construction, it was found that at points A1 and A2 parts of the concrete slab were ca 100-130 mm thick and were laid on expanded plastics insulation. At these points the measurements showed that the moisture level in the concrete was ca 77-84% RH throughout, as shown in Tables 1 and 2; this is below the critical limit of 85% RH which is usually specified for bonded PVC flooring. In other parts of the concrete slab there was no such insulation and the slab rested directly on damp gravel without any moisture barrier. At measurement point B1 the concrete slab was ca 400 mm thick, and at the other two points (B2, B3) it was ca 110-120 mm thick. Moisture levels in the concrete where it had been laid directly on the gravel were very high, around 93 - <95% RH.

The results of measurements at all measurement points, A1 – B3, by both the FHM and VHM methods, are set out in Tables 1 and 2. It is evident from these results that there is a high concentration of VOC at all points near the surface, and that concentration diminishes with depth. This behaviour is, in general, the same for both n-butanol and 2-ethyl-1-hexanol, and is reflected in the same way in the results from both measurement methods. At a depth of ca 100 mm, the concentration of VOC in the concrete is much lower than at the surface, but in most cases it had penetrated even to this depth.

Before the renovation in 2001, the floor had been covered by PVC flooring in the area around measurement point A1. Around points A2 and B1 the concrete floor had had no covering at all. The floor around point B2 had previously had an application of clear epoxy varnish, and around point B3 there had been a rubber mat.

Table 1. Content of n-butanol and 2-ethyl-1-hexanol stored in a moisture damaged concrete slab. Moderate moisture level, about 80 % RH in the concrete subfloor.

Label	Depth	RH	1-butanol			2-etyl-1-hexanol		
			VHM $\cdot 10^{-3}$	FHM $\cdot 10^{-6}$	K	VHM $\cdot 10^{-3}$	FHM $\cdot 10^{-6}$	K
	mm	(%)	kg/m^3_{mtrl}	kg/m^3_{air}	$\cdot 10^3$	kg/m^3_{mtrl}	kg/m^3_{air}	$\cdot 10^3$
A1-1	0-15	77.0	12.0	1.4	8.54	66.7	0.79	84.4
A1-2	25-40	78.0	3.0	1.4	2.14	34.5	0.6	57.5
A1-3	50-70	80.0	3.2	1.3	2.48	25.3	1.4	18.1
A1-4	80-100	79.0	3.0	0.9	3.32	16.1	0.46	35.0
A2-1	0-15	78.5	4.4	1.3	3.36	110	1.1	100
A2-2	25-40	80.5	2.8	1.2	2.30	25.3	0.6	42.2
A2-3	50-70	83.0	-	0.8	-	9.9	0.23	43.0
A2-4	80-100	83.5	-	0.6	-	-	0.18	-
mean		79.9			3.96			54.4
std dev		2.3			2.43			28.9

Table 2. Content of n-butanol and 2-ethyl-1-hexanol stored in a moisture damaged concrete slab. High moisture level, about 95 % RH in the concrete subfloor.

Label	Depth	RH	1-butanol			2-etyl-1-hexanol		
			VHM $\cdot 10^{-3}$	FHM $\cdot 10^{-6}$	K	VHM $\cdot 10^{-3}$	FHM $\cdot 10^{-6}$	K
	mm	(%)	kg/m^3_{mtrl}	kg/m^3_{air}	$\cdot 10^3$	kg/m^3_{mtrl}	kg/m^3_{airl}	$\cdot 10^3$
B1-1	0-15	93.5	43.7	31	1.41	214	9.0	23.8
B1-2	25-40	93.5	22.1	19	1.16	101	4.2	24.1
B1-3	50-70	93.0	15.2	12	1.27	57.5	2.4	24.0
B1-4	80-100	94.0	5.30	6.3	0.84	14.7	1.1	13.4
B2-1	0-15	95.0	48.3	47	1.03	172	13	13.3
B2-2	25-40	95.0	36.8	32	1.15	85.1	3.6	23.6
B2-3	50-70	95.0	25.3	36	0.70	34.5	2.9	11.9
B2-4	80-100	>95	20.9	26	0.81	13.8	1.1	12.6
B3-1	0-15	94.0	46.0	48	0.96	71.3	4.8	14.9
B3-2	30-45	>95	32.2	29	1.11	8.30	0.55	15.1
B3-3	50-70	>95	18.9	22	0.86	-	0.40	-
B3-4	80-100	>95	32.2	19	1.69	-	0.18	-
mean		>94.4			1.08			17.6
std dev		>0.8			0.28			5.43

When the building was constructed in 1979, it was usual in Sweden to lay insulation only under certain parts of a building, the primary task of which was to save energy, but it also protected the concrete slab from rising damp from the soil. This was utilised later on in moisture resistant design. The fact that impervious PVC flooring was now laid at all places is decisive for the high moisture level in some parts of the floor. Soil moisture that rises up through the floor cannot now evaporate into the room air but remains below the flooring and creates a very high moisture level which, together with the alkaline environment in the concrete, decomposes the polymer chains in the floor adhesive and, to some extent, the plasticisers in the plastic flooring. Björk et al /14/, Sjöberg /6/.

Theoretical evaluation
Since measurements have been made of both the content of VOC in the concrete (VHM method) and the free concentration of VOC in air in equilibrium with the concrete (FHM method), the partition coefficient K [-] can be evaluated according to the equation

$$K = \frac{C_{mtrl}}{c_{air}} \qquad \left[\frac{g_{voc}/m^3_{mtrl}}{g_{voc}/m^3_{air}} \right] \Rightarrow [-] \qquad (1)$$

where C_{mtrl} [g_{voc}/m^3_{mtrl}] is the total content of a particular VOC per volume of material, and c_{air} [g_{voc}/m^3_{air}] is the concentration of a particular VOC per volume of air. As explained in paragraph 2.1, K embeds the contributions of adsorption at the pore surfaces, and absorption in the water filling some pores. In the field of indoor air quality, it is generally accepted that concentrations are low enough so that each of these sorption processes can be described through the definition of partition coefficients between the air-phase on the one hand, and the solid-phase or liquid phase on the other hand; Finally, K represents here the global binding capacity of the concrete for the measured moisture level (RH determines the amount of condensed water as well as the surface area available for VOC adsorption onto the pore walls).

In this study, this is done by calculating the ratio of pairs of values measured at the same point and at the same depth by the two methods VHM and FHM. These are set out in Tables 1 and 2.

It is shown that a moist concrete (ca 95 % RH) has a mean value of approximately $K = 1.1 \cdot 10^3$ [-] while a drier concrete (85%RH) has $K = 2.8 \cdot 10^3$ [-]. If the concrete evaluated above has a considerably lower moisture level, the higher values of the partition coefficient ($23 \cdot 10^3$) may very well be correct for the drier concrete.

3.2   Effective Diffusion coefficient D

In situ measurements
Measurements at points C-E were made in situ in a concrete slab laid on the ground in three different buildings. In all buildings the users had reported building related health complaints of the SBS type when they were present in the building. VOC from degraded floor adhesive was suspected to be a likely source of the pollutants in indoor air. These measurements were described for the first time in Sjöberg /11/.

Building C was a newly constructed hospital building where the staff, soon after moving in, began to experience symptoms of the SBS type in operating theatres etc where PVC flooring had been bonded to the floor for reasons of hygiene. This type of flooring is considered easy to keep clean in hospital premises since it can be laid with a portion drawn up along the wall and with welded joints which makes it possible for frequent wet cleaning to be carried out. Sampling

in this building was performed when emission damage was about 1 year old. Moisture level in the slab was ca 78% RH in the surface and ca 85% RH lower down in the slab. By making a back calculation of moisture transport, the investigating consultant could show that moisture level in the slab at the time the flooring was laid was considerably higher and exceeded the critical value of 85% RH for applying the adhesive for the PVC flooring.

Building D was a supervised accommodation building with the slab on the ground, with underlying insulation and underfloor heating. About 3.5 years after completion, the staff experienced such SBS and odour problems that the flooring was removed. The adhesive had lost almost all its tensile strength and was almost completely saponified. There was a strong pungent smell which the damage investigator identified as 2-ethyl-1-hexanol. At the time of the investigation, moisture levels were ca 91% RH at the concrete surface and 87% RH lower down. However, the investigation did not show whether or not the concrete had been much wetter earlier.

Building E was a school building constructed in the 1980s. The foundation construction was a slab on the ground with underlying insulation and PVC flooring bonded directly to the concrete floor. After about ten years, the users experienced building related health problems of the SBS type, and a damage investigator was called in. The preliminary assessment was alkaline hydrolysis of the floor adhesive. The investigation found that this was an old moisture damage which had been much wetter but has now "dried up". At the time of investigation the moisture level measured in the floor was ca 90% RH throughout the floor construction.

Pieces of concrete were taken from these concrete slabs at different depths and analysed with the FHM method for moisture level and VOC in the concrete. The results are shown in Figs. 2-4. In these results also it can be seen that there is a high concentration in the measurements nearest the surface, and a decrease in concentration with depth. In Buildings C and D the concentration of VOC at a depth of 100 mm is very near zero, while in building E which is much older penetration had also reached this depth. Distribution profiles of both n-butanol and 2-ethyl-1-hexanol have the same shape at all meassurement points. The spread of results at the same depth, which can be seen in Fig. 2-4, is probably due to the facts that samples had at times been taken from different places (cores) in the same room and sometimes from different places of the same core. If they originate from different parts of the same core, it is possible for the sample to have been taken from the area near the surface where it was exposed to an elevated temperature and may have lost some of its VOC content.
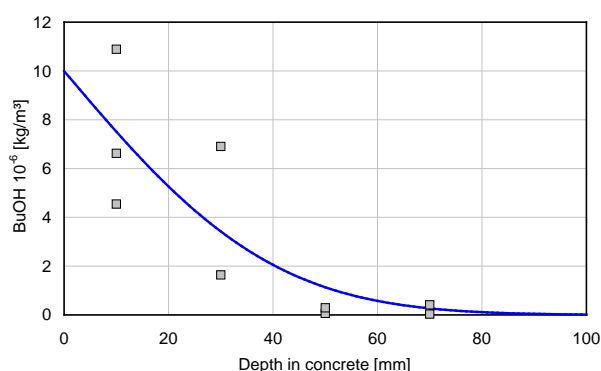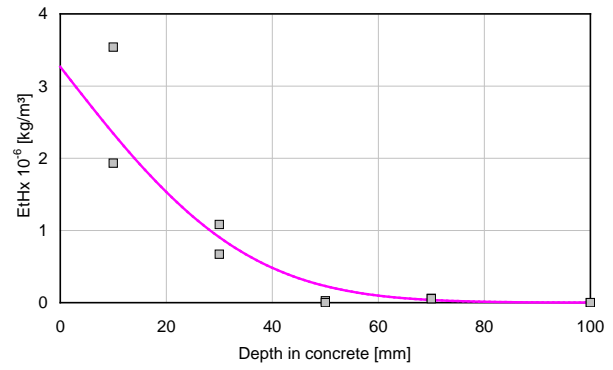

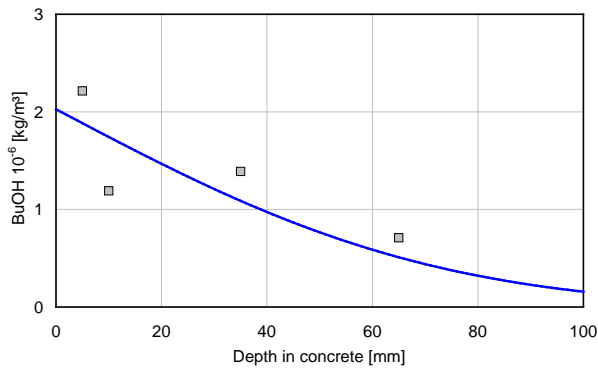*2a. Sample C. Distribution profile of n-butanol, ca 1 year old moisture induced damage.*
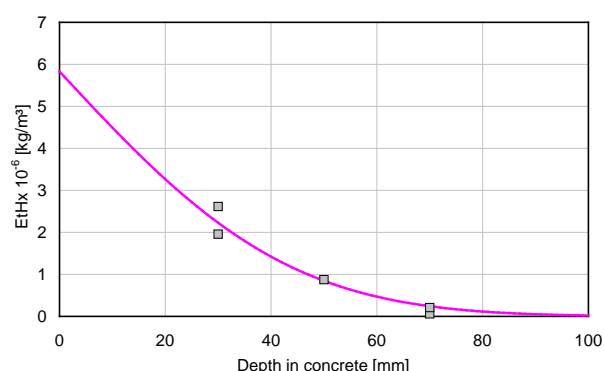
2b. Sample C. Distribution profile of 2-ethyl-1-hexanol, ca 1 year old moisture induced damage.
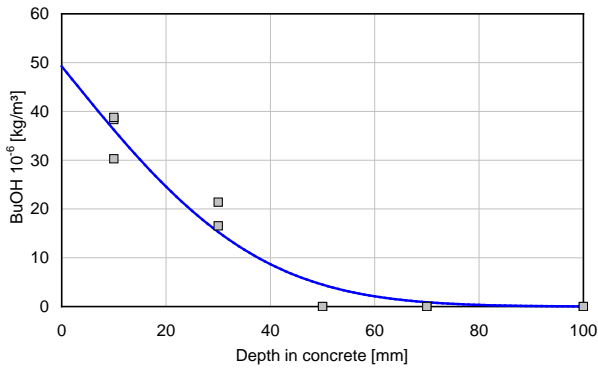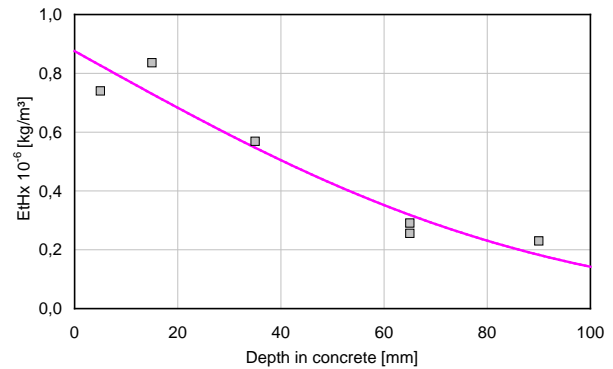
3a. Sample D. Distribution profile of n-butanol, ca 3.5 year old moisture induced damage.

3b. Sample D. Distribution profile of 2-ethyl-1-hexanol, ca 3.5 year old moisture induced damage.

4a. Sample E. Distribution profile of n-butanol, ca 10 year old moisture induced damage.

4b. Sample E. Distribution profile of 2-ethyl-1-hexanol, ca 10 year old moisture induced damage.

Figures 2-4. In situ measured distribution profiles of c_{air} in concrete substrate from three different buildings. The dots in the graphs are values measured with the FHM method and the curve is the best fit to the error function with the method of least squares.
Evaluation of D

The results of the measurements with method FHM on samples of the concrete slab from buildings C – D show that VOC from decomposition of the adhesive had penetrated deep into the concrete, about 50 – 100 mm. According to Crank /23/, the effective diffusion coefficient (D) can be evaluated with reference to Fick's second law. For such an evaluation it is necessary to know the penetration profile for a specific compound which has formed during incremental changes in a semi-infinite medium.

Under the assumption that the surface concentration c_S (g_{voc}/m^3_{air}) in the air-phase of the pores at the boundary layer between flooring and concrete surface had changed in stages from the initial value 0 to a constant value which then remained unchanged during the whole period, the fundamental incremental change requirement is satisfied. In view of the fact that the concentration at the bottom of the measured profiles, 100 mm from the surface, is very low, the depth of the slab may be considered infinite in this respect.

Fick's second law can then be solved with Equation 2 according to Crank /23/; this is the complement to the "error function".

$$c(x,t) = c_s \cdot \left[1 - erf\left(\frac{x}{2 \cdot \sqrt{D \cdot t}} \right) \right] \qquad \left[g_{VOC} / m^3_{air} \right] \qquad (2)$$

In Fig. 5, the complement to the error function has been calculated for a number of different combinations of D·t where t is the time during which the surface concentration was high after the incremental change.
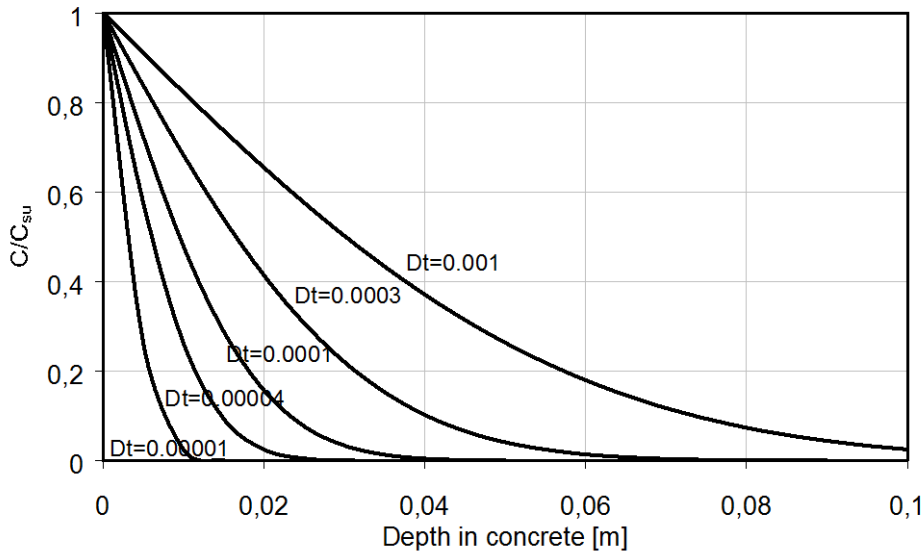

Figure 5. Solution of Fick's second law with the complement to the error function. The figures along the curves are the values of D · t; see Equation 2.

The best fit to the measured values for buildings C – E is plotted as a solid curve in Fig. 2 - 4. Curve fitting was performed by the method of least squares for differences in concentration at the different depths.

Surface concentration (c_s) for n-butanol was higher than for 2-ethyl-1-hexanol in all buildings, $2\text{-}49 \cdot 10^{-6}$ (kg/m^3) as against $0.9\text{-}5.8 \cdot 10^{-6}$ (kg/m^3). In spite of this the penetration depth and the shape of the distribution profiles were almost exactly the same, which means that D is of the same order of magnitude for n-butanol and 2-ethyl-1-hexanol in this study, see table 3. The effective diffusion coefficient D is in the range of $4\text{-}16 \cdot 10^{-12}$ (m^2/s) for n-butanol and $3\text{-}19 \cdot 10^{-12}$ (m^2/s) for 2-ethyl-1-hexanol.

Table 3. Measured and evaluated properties of n-butanol (BuOH) and 2-ethyl-1-hexanol (EtHx) in buildings C– E.

Building	Age (year)	RH [%]	C_S ($\cdot 10^{-6}$ kg/m$^3_{mtrl}$) BuOH	EtHx	D ($\cdot 10^{-12}$ m^2/s) BuOH	EtHx
C	1	78-84	10	5.8	16	19
D	3.5	87-91	49	3.3	4.1	3.6
E	10	ca 90	2.0	0.9	5.2	8.4

The assumption regarding incremental change may not fully be correct, the surface concentration (c_s) which has been calculated may be seen as an effective mean value. The test specimens were in the range of 1 – 10 years old when the samples were taken. The concentration below the flooring may have changed during these years. The concrete may have dried out through the flooring in some cases, so that the reaction and thus the production of VOC had ceased.

The effective diffusion coefficient (D) which has been evaluated may also be a mean value for variable moisture conditions. The rate of penetration of VOC down into the concrete has probably been affected by the redistribution and drying of moisture in the concrete.

4.   DISCUSSION

4.1   Measurement methods

As regards reliability, the results of measurements by the two methods appear to be of equal validity. Both methods gave relatively good agreement with expected values when profiles were measured at several levels or at several measurement points on the same damaged floor, although individual values may be different. To some extent, this provides confirmation that, physically, the gas-phase concentration is linearly correlated to the total VOC content of the material through the computed partition coefficient K. If the aim of the measurements is only to find whether there are elevated contents of VOC in the concrete, and to determine the penetration depth and the appearance of the profile, the methods may, on the whole, be regarded as equivalent. If, instead of this, the intention is to determine the partition coefficient (K), then it is necessary to apply the two methods..

Sampling in the field was considerably easier with the VHM method where it is possible to use drill cuttings of powder consistency which are produced when a hole ca 12 mm in diameter is cut with a normal hammer drill. It was easy to collect the cuttings from different depths and to put them into the small vials that are used for this method. On the other hand, the FHM method necessitates the use of a core drill and careful removal of a core without water cooling. This type of dry drilling is something that most operators want to avoid since it exposes the expensive equipment to hard wear.

Transport to the remote laboratory was also easier with the VHM method since these vials were only a fraction as large as the flasks used in the FHM method – 21 ml vials for VHM as against 250 ml flasks for FHM. This makes it much easier to pack the containers in such as way that there is no risk of breakage during transport by post. The FHM flasks also contain whole pieces of concrete which should preferably not rub against one another and crumble to powder, since the binding capacity of the material can then change markedly. With the VHM, the collected sample is preferably already in powder form since the subsequent extraction and analysis take place in a way that permits this.

Sample preparation in the laboratory and analysis of the headspace was much quicker with the VHM method, a few hours compared with several days for the FHM method. It can thus be concluded that the VHM method is the most practical and easy to use, especially for an unfamiliar user who only needs to make measurements in a few places.

4.2   Partition coefficient and storage capacity

The partition coefficient (K) for concrete is different for different gases; generally speaking, 2-ethyl-1-hexanol was found to have a value ca 10 times higher than n-butanol. This means that, for the same quantity of these compounds stored in the material, the concentration of n-butanol in the air in the concrete pores, under equilibrium conditions, is ca 10 times higher. Conversely, if the equilibrium concentration of these compounds in air is the same, there is about 10 times more ethylhexanol stored in the concrete under equilibrium conditions.

According to Sjöberg /11/ the partition coefficient may also be evaluated out of the diffusion coefficient in concrete for VOC in the gas phase, δ [m^2/s] together with the effective diffusion coefficient for VOC in concrete, D [m^2/s], Eq. 3. It is important that the same types of materials should have been evaluated in the different cases, since there are a large number of different concrete types with great variations in different types of material related properties.

$$K = \frac{\delta}{D} \qquad \left\lfloor \frac{m^2/s}{m^2/s} \right\rfloor \Rightarrow [-] \qquad (3)$$

The diffusion coefficient in normal house building concrete (water cement ratio approx 0.6 – 0.7) for n-butanol, δ is determined as $93 \cdot 10^{-9}$ m^2/s by Sjöberg /11/, Sjöberg & Nilsson /22/. The effective diffusion coefficient (D) for n-butanol in the same concrete is in the range of $4{-}16 \cdot 10^{-12}$ m^2/s according to Table 3.

This means that the partition coefficient (K) for n-butanol in concrete should be in the range of $5.8 – 23 \cdot 10^3$ [-]. Based on this assessment, the results presented in tables 1 and 2 seem to be reliable if it is borne in mind that there is probably a variation in the value of K between concretes of different moisture levels, as shown by Tables 1 and 2.

The moisture level in the concrete was also found to have great influence on the size of the storage capacity for these two compounds. At a moisture level of ca 80% RH (A1-A2), the mean value of K for n-butanol was 4.0 ± 2.4, with an outlier that distorts the standard deviation, and 54.4 ± 28.9 for ethylhexanol. At a moisture level of ca 95% RH (B1 – B3), the corresponding values of K for n-butanol were 1.1 ± 0.3 and for ethylhexanol 17.6 ± 5.4. On the other hand, the data presented in Table 1 and Table 2 indicate that the VOC contents of the concrete samples is from 3 to 3.5 times higher when the moisture level increases from ca 80 kg/m^3 to about 110 kg/m^3. In other words, the actual storage capacity of concrete (C_{mtrl}) increases with increasing humidity, although the intrinsic binding capacity of the material (K) is significantly lowered at higher humidity. The explanation most probably lies in the dual effects of moisture. When relative humidity is increased, both the water vapour concentration in the air-phase of the pores and the liquid water content of the material are increased. Consequently, the surface area available for gas adsorption at the pore surfaces is decreased and the competition between water vapour and VOC molecules for adsorption on the active sites of the pores is stronger. The combined effects of these two phenomena are reflected in lower K values. On the other hand, the increased water content favours the VOC absorption in the pores. Higher values of C_{mtrl} at high moisture levels indicate that this is probably the dominating process or, in other words, that the decrease in the amount of VOC adsorbed is largely offset by additional absorption in the aqueous phase.

This moisture related effect on K in concrete has also been demonstrated by Sjöberg /24/). The above values of the absolute moisture content of concrete, at different RH, are to be regarded as typical values that may however vary slightly depending on concrete type and quality.

4.3   Transport coefficient

In Table 3 there is an indication that the effective diffusion coefficient (D) for both n-butanol and 2-ethyl-1-hexanol is higher when the moisture level in concrete is lower. D for n-butanol is ca 3-4 times higher at about 80% RH than at ca 95% RH. For 2-ethyl-1-hexanol, the coefficient is of the order of 2-5 higher at the lower moisture level.

If a comparison is made instead of the difference in diffusion coefficient in concrete for VOC in the gas phase, δ [m^2/s], the difference between different moisture levels is even greater. For n-butanol at ca 90% RH, δ is ca $5 \cdot 10^{-9}$ (m^2/s) if the measured values are substituted into Equation 3. At ca 80% RH, the correspondiong value of δ is ca $64 \cdot 10^{-9}$ (m^2/s), i.e. about 13 times higher. For 2-ethyl-1-hexanol, the corresponding values are ca $110 \cdot 10^{-9}$ (m^2/s) at 95% RH and $1050 \cdot 10^{-9}$ (m^2/s) at 80% RH, i.e. the values are of about 9.5 higher.

This moisture dependent variation is probably related to the proportion of the pore system of concrete that is filled with liquid. Normally, concrete contains about 15% pores. As a rough estimate, two-thirds of these pores may be said to be filled at 95% RH if it is estimated that the concrete then contains 110 kg water per m^3, but to be only half filled at 80% RH when the concrete contains ca 80 kg water per m^3.

5. SUMMARY

All in all, the evaluated material coefficients K, D and δ show that when moisture damage occurs, the concrete is damp and has a low rate of moisture transport, which means that transport down into the concrete takes a long time. This is however compensated for by the high storage capacity of moist concrete which means that it can bind large quantities of VOC per unit volume, probably in some sort of liquid phase in the pores. When the moisture later on dries out, the moisture content of concrete decreases and the rate of transport increases. The probable result of this is that the decomposition products rapidly penetrate deeper into the concrete if there is an airtight flooring on top of the concrete slab. If, however, the flooring has been removed or replaced by a material that is more permeable, more of the stored decomposition products will instead be emitted from the floor surface and will be removed by the general ventilation system in the premises.

Under these conditions, it is of the greatest importance that the general ventilation should have a sufficient rate of flow to collect the emissions from the floor and remove them from the building. In buildings with stored pollutants in the floor, it is therefore highly inadvisable to make use of the extract air from rooms with emission damaged floors and to use this as part of the return air in the building in order to reduce running costs in this way.

In conclusion, it should be pointed out that this paper does not discuss what measures should be taken in buildings with stored pollutants in concrete floors. Great care should be instead be taken in selecting such measures, with reference to the quantity of stored pollutants, the rate of flow of general ventilation and the type of use of the building. The occupants of residential buildings, schools or offices often have greater demands regarding the quality of indoor air than workers in a factory or warehouse.

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