BIOCIDE EMISSIONS FROM MATERIALS INTO INDOOR AIR

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ABSTRACT
The European biocides directive (98/8/EG) demand the control of emissions into the environment like soil, water and air. In this study a method for measuring the input of biocides into the indoor air from materials should be developed. The emission of two products containing biocides (plastic foil, wool carpet) and six different types of biocide containing formulations applied on wood or ceramic tiles were investigated in 20 or 23 l glass emission chambers. Each chamber test was performed over a period of 100 up to 200 days. SVOC show totally different emission curves in chamber tests compared to volatile organic compounds (VOC). They reach their maximum value after some days or weeks. Thus a period of 3 months is sometimes necessary for exact measurements. Area specific emission rates (SER_a in µg/m²h) for permethrin (0.006), propiconazole (0.2), dichlofluanid (1.5), tolylfluanid (1.2), octylisothiazolinone (2.5) and for iodpropinylbutylcarbamat (1.7) were determined.

INDEX TERMS
SVOC, Biocide, Chamber test, Polyurethane foam, Testing method

INTRODUCTION
Each material that contains organic compounds might be damaged through fungi, microbes or insects. Therefore, biocides are widely used to protect materials against such an attack. The aim of this study is to develop suited methods for measuring the input of biocides in the environment from materials. The directive of the European parliament and of the council (EC) No 98/8 on the placing of biocidal products on the market demands the consideration of emissions of biocides from products during their lifetime, when estimating their environmental impact (EC, 1998). However, standard methods for measuring these emissions into water or air do not exist. So the aim of this investigation was to prepare such test procedures. The complete results were presented in an UBA-Text (Schoknecht, Wegner, Horn *et al.*, 2002). One part of this report, the emission of biocide into indoor air, is presented in this paper.

Typical biocides on the European market used to protect products are dichlofluanid, tolylfluanid, iodpropinylbutylcarbamat (IPBC), permethrin, octylisothiazolinone (OIT), propiconazole and others. In the past also pentachlorophenol (PCP) and lindane were important biocides and so most of the publications dealt with this both compounds and even the VDI guideline 4301 part 2 (VDI, 2000) was developed to measure these compounds in indoor air during field studies. The sampling procedure is based on polyurethane foam as adsorbent, which had been introduced by the first version of the ASTM guideline D4861 (ASTM, 2000).

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The majority of biocides belong to the group of semi volatile organic compounds (SVOC). Their detection in emission chambers is more difficult than the detection of VOC, because sink effects are very important and can reduce the concentrations. Emissions of biocides in emission chambers were presented only in a few investigations (e.g. Horn and Marutzky, 1993, Marchal, Ozanne and Vasseur, 1997, Jann and Wilke, 1999, 1999a). The present paper continues the investigations of Jann and Wilke (1999, 1999a) and applies and advances their method for the measurement of emissions from many different products.

MATERIAL AND METHODS

Products

The European directive of biocidal products classifies many industrial products that might contain biocides. The present investigation deals with 4 different types of products mentioned in annex V under main group 2, preservatives: type 7, film preservatives, type 8, wood preservatives, type 9, fibre, leather and polymerised materials preservatives, and type 10, masonry preservatives. However, in these different types of products often the same biocide is used, for example permethrin in carpets and in wood preservatives. Some of these preservative agents were applied during the production process (carpet, foil). The other formulations were applied in the laboratory in accordance with the instructions of the producer. The cutting edge of the timber and the edge of the other materials were separated from the chamber air with self-adhesive aluminium foil. Additionally, with this foil the emitting surface can be adjusted to the size that is needed for an exact loading. In the present study the emissions of permethrin, dichlofluanid, tolylfluanid, iodpropinylbutylcarbamat (IPBC), octylisothiazolinone (OIT) and propiconazole were investigated.

Table 1. Biocide products and treated materials. (*Number of samples in brackets)

Product No	*Biocide (content)*	*Tested material*	*Emitting surface * in mm*	*Used quantity*
Type 7: Film preservatives				
0701	tolylfluanid (0.45 %)	wood	312 x 20 x 20 (x5)	78 g/m²
0702	dichlofluanid (0.5 %)	wood	312 x 20 x 20 (x5)	50 g/m²
0703	IPBC (0.3 %)	wood	312 x 20 x 20 (x5)	88 g/m²
0707	propiconazole (0.4 %)	wood	312 x 20 x 20 (x5)	69 g/m²
Type 8: Wood preservatives				
0803	propiconazole (1.2 %), permethrin (0.1 %)	wood	312 x 20 x 20 (x5)	56 kg/m³
Type 9: Fibre, leather, rubber and polymerised material preservatives				
	Carpet			
0901	permethrin	carpet	250 x 200 (x2)	40 mg/m²
	Foil			
0909	OIT (0.2 %)	foil	177 x 177 (x4)	3.5 g/m²
Type 10: Masonry preservatives				
1002	IPBC (1 %)	ceramic tile	177 x 177 (x4)	500 g/m²

Chambers

For the investigation described here 20 l or 23 l exsiccators, made of glass (Jann and Wilke, 1999a) were used (see Figure 1). These chambers are very suited for investigations of SVOC emissions from materials (Jann and Wilke, 1999). In the present paper the investigations were conducted under the following conditions: temperature of 23 ± 0.3 °C, relative humidity of 50 ± 5 %, area specific air flow rate of q = 1 m³/m²h or q = 1.25 m³/m²h (carpet), respectively,

and air velocity was in the range of 0.1 to 0.3 m/s on the surface of the material. In the present study a loading of 6.25 or 5.43 m²/m³ (0.125 m² material surface in 20 or 23 l chamber) was used with an airflow rate of $\dot{V}$ = 0.125 m³/h.

The area specific emission rates (SER_a) can be easily calculated from concentrations as can be seen in the equation 1.

$$SER_a = C * \frac{\dot{V}}{A} = C * \frac{n}{L} = C * q \qquad (1)$$

where C is the concentration (µg/m³), A is the material surface (m²), $\dot{V}$ is the air flow rate (m³/h), n is the air exchange rate (1/h), L is the loading factor (m²/m³) and q is the area specific air flow rate (m³/m²h).

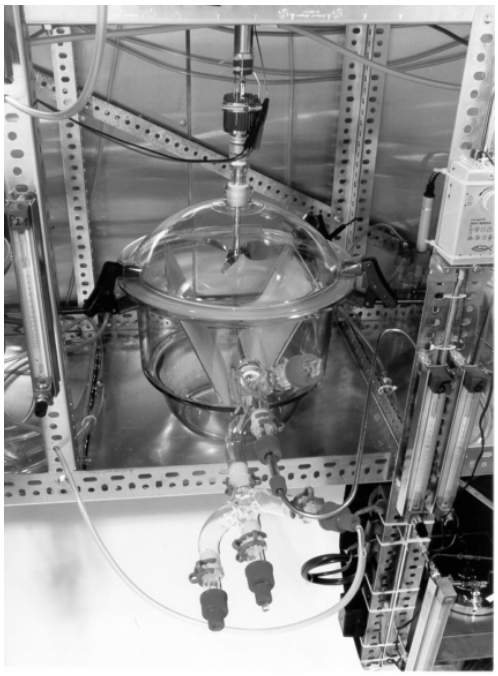

Figure 1. 20 l glass chamber with the technical equipment and loaded with two plates.

Sampling

For sampling of biocides polyurethane (PU) foam is proven to be the best adsorbent for many biocides (ASTM, 2000, VDI, 2000). In the present study PU-foam plugs with a diameter of 13 mm and a length of 50 mm in glass tubes were used. Up to 15 m³ of chamber air were sucked through the PU-foam, equipped with a second foam to exclude a break through of the biocides. Sampling were done for up to 7 days with a maximum sampling velocity of 100 litres per hour. Subsequently, the PU-foam was desorbed with acetone or hexane (OIT) for 45 minutes in an ultrasonic bath. Before it was concentrated to 1 ml, internal standard (4-(4'-chlorobenzoyl)-pyridine) was added to the extract. Identification and quantification with GC/MS followed. The results were calculated using the internal standard method in comparison with calibration curves. The limits of determination are shown in Table 2 (calculated with a sampling volume of 15 m³).

Table 2. Limits of determination of the biocides investigated.

	IPBC	tolylfluanid	dichlofluanid	OIT	propiconazole	permethrin
ng/m³	15	2	5	0.5	5	0.5

RESULTS

The courses of emission curves of the biocide chamber measurements received in this study were quite different in comparison to VOC measurements. VOC curves normally increase to high point levels in the first few hours, followed by a decrease over few days to much lower levels and than a period of time follows where the curve ran low. In contrast to that the SVOC curves increased slowly until it reached a concentration that was constant for a long time (Figure 2). Most of the biocides investigated here show such curves. Table 3 gives the SER_a of the biocides investigated in this study. This SER_a represent the mean values reached after some weeks, when equilibrium between the concentration in the air and at the walls is expected and sink effects can be neglected. In contrast to these results the emission curves of IPBC from film-coated wood (product No. 0703, Figure not shown here) corresponded with

those of VOC. In these test series the emission started at 3 µg/m²h and after nearly 20 days the SER_a of 1.5 µg/m²h was reached. The preservative for the protection of masonry also containing IPBC showed a totally different run of the emission curve (Figure 3). In the test series 1002 IPBC started at a level of about 1 µg/m²h and decreased sharply to 0.2 µg/m²h within 20 days. Starting at that point the concentration then increased slowly up to 0.4 µg/m²h in the remaining 120 days of the test series. However, it seemed that at that time the equilibrium concentration was not reached already and the rise of concentration might be observed for an additional time.

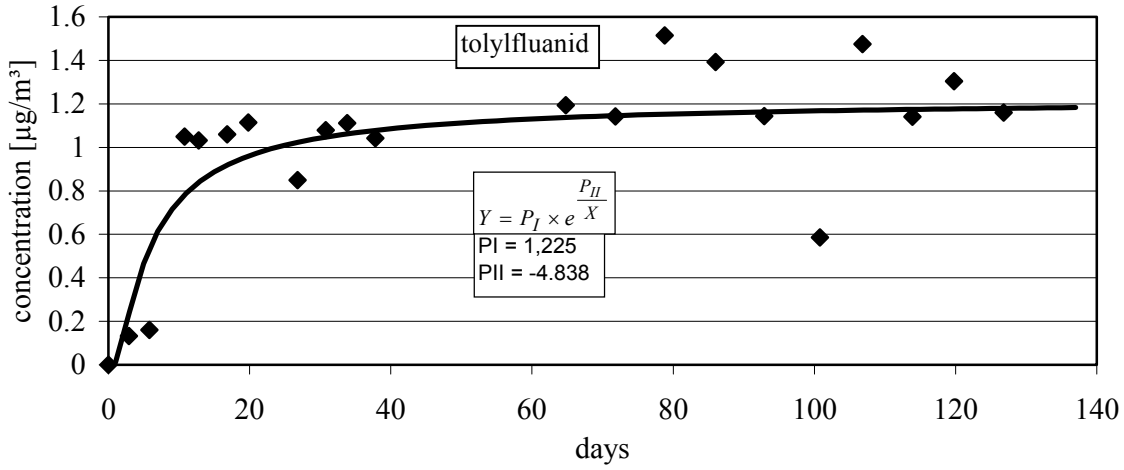

Figure 2. Concentration of tolylfluanid from film preservative applied on wood (0701).

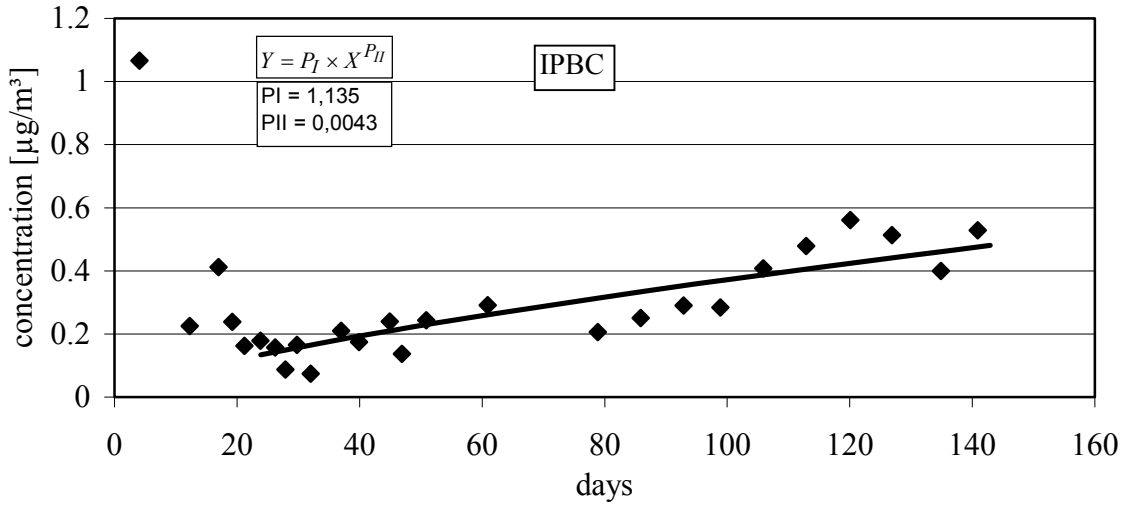

Figure 3. Concentration of IPBC from masonry preservatives applied on ceramic tiles (1002).

Table 3. SER_a [µg/m²h] reached after some days or weeks in the chamber tests and the approximate number of days to reach this value under equilibrium conditions.

	0701	*0702*	*0703*	*0709*	*0803*	*0803*	*0901*	*0909*	*1002*
Biocide	tolyl	dichl	IPBC	prop	prop	per	per	OIT	IPBC*
SER_a	1.2	1.5	1.7	0.02	0.2	0.03	0.06	2.5	1
Days to reach	7	1	10	30	40	30	30	10	3

tolyl: tolylfluanid, dichl: dichlofluanid, prop: propiconazole, per: permethrin.
* for IPBC 1002 no equilibrium is measured, highest value is given here

In Table 4 the complete loss in µg of the biocides from the materials during the test series is listed. How it was expected, biocides showed only a slight loss into air. Additionally, the loss for 20 day-segments is listed and it can be seen that for most components this values stayed at one level. However, the 20 day-values of some compounds vary, because this values were the sum of all measurements made in this period of time in the test series. In between that time some values are not available and so some 20 day-values are incorrect.

Table 4. Biocides emitted into the chamber air: Starting amount (biocide content of the material sample) in the chamber test, loss of biocides for the whole time and loss separated in values of 20 days. Values are in µg.

	0701	*0702*	*0703*	*0709*	*0803*	*0803*	*0901*	*0909*	*1002*
Biocide	tolyl	dichl	IPBC	prop	prop	per	per	OIT	IPBC
Starting amount	44000	31000	33000	35000	5.6 E5	69000	4000	440000	625000
Complete loss	360	620	540	7.5	84	1.4	1.8	570	108
Number of days	129	176	144	139	195	195	178	135	143
Loss in %	0.8	2	1.6	0.02	0.01	0.002	0.05	0.13	0.001
Days 0 - 20	41	59	92	0.5	3.5	0.09	0.09	123	21
Days 20 - 40	46	60	56	1.4	4.6	0.08	0.17	87	6.6
Days 40 - 60	64	83	82	1.1	11	0.15	0.15	126	11
Days 60 - 80	78	64	84	1.3	17	0.24	0.23	84	8
Days 80 - 100	60	73	76	1.5	7.8	0.12	0.24	66	10
Days 100 - 120	68	85	90	1.2	7.7	0.13	0.26	49	26

tolyl: tolylfluanid, dichl: dichlofluanid, prop: propiconazole, per: permethrin,

It can be seen in the test series 0703 and 1002 the same compound applied on different materials can emit completely different. IPBC applied on masonry (1002) might penetrate in deeper layers of the material and emit much slower. The concentrations increased for more than 120 days and the end was not observed. Losses of 0.001 % indicate that there is a high potential of biocide remaining in the material. Otherwise, IPBC applied on wood (0703) loose nearly 2 % of its content in 120 days and the value after 10 days remains on a constant level.

DISCUSSION

In the present paper some of the same biocides were investigated as in the study of Jann and Wilke (1999, 1999a). They received emission rates of dichlofluanid and permethrin from treated timber, which were up to 10 times higher, than they were measured in the present study. They had found concentrations of 10 µg/m³ and 0.02 µg/m³ for dichlofluanid and for permethrin, respectively. If the area specific air flow rate of q = 5 m²/m³h of their test series is taken into account the values must be multiplied with 5 to be compared with those from the present study. However, the main differences between both investigations are the formulations used to treat the timbers. In the present study original formulations received from the producers were used in contrast to solutions of biocides in organic solvents in the study of Jann and Wilke (1999, 1999a). Especially, if binders and other ingredients like e.g. pigments or additives are used in the formulation a layer is formed at the surface of the sample. This is expected to reduce diffusion of the biocides, thus lower concentrations and emission rates are observed.

The loss of biocides into indoor air is not very high. The emission was observed for 200 days in maximum and 2 % was the highest value for the biocide loss. In contrast a loss of 20 up to 50 % can be measured in aquatic systems (Schoknecht, Wegner, Horn et al., 2002). The run of

biocide emission curves into the air indicates that the reached concentrations will stay for a longer time at the same level. Consequently, the emission of biocides into indoor air on a low level results in a long time pollution of the inhabitant's direct environment.

CONCLUSION AND IMPLICATIONS

The described method was proved to be suited for the determination of biocide emissions in emission chambers. Each test should be performed for more than 50 days, because equilibrium or no change of emission should be reached and the period of time for air sampling is quite long with 2 to 7 days for one sample. The calculation of SER_a may not be done from the concentration values as long as no equilibrium between the biocide concentration in the air and the biocide concentration at the chamber walls (sinks) is established. Otherwise, due to a permanent loss to the chamber walls, the calculated SER_a is underestimated. SER_a observed in the study showed mostly more or less constant values for some months, so the long time SER_a for several years might be predictable from these results.

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