Do particleboards produced with recycled wood contribute to indoor air pollution with biocides?

W. Horn*, O. Hahn, O. Jann, S. Kalus

Federal Institute for Materials Research and Testing, Berlin, Germany

ABSTRACT
Biocides are widely used to protect wood against an attack of fungi, microbes or insects. After their lifetime wooden constructions are often recycled and used, e.g. for particleboards. In this study, the emissions of PCP, lindane, dichlofluanid and DDT from particleboards, which should contain only allowed traces of biocides, were investigated. From a quantity of 29 particleboards the emission and biocide content of three commercially produced and six self-manufactured boards (with defined biocide content) were tested. Each chamber test was performed over a period of 60–100 days. After more than 30 days SER_a for PCP, lindane, dichlofluanid, and DDT of 50, 20, 20 and 10 ng m^{-2} h^{-1}, respectively, were determined. But it can be concluded that boards containing only traces of biocides (below 5 mg kg^{-1}) show in the most cases no significant long term emission above 10 ng m^{-2} h^{-1}.

INDEX TERMS
SVOC; Biocide; Chamber study; Material emission; Wood

INTRODUCTION
In the past some organic biocides were often used to protect wood against fungal or insect attack. These products were mostly used to refresh wood protection, e.g. in attics or for preventative application in the indoor use. In 1970 and up to the beginning of the 1980s, pentachlorophenol (PCP) and γ-hexachlorocyclohexane (lindane) were the significant biocides in the western part of Germany and additionally up to the end of the 1980s dichlorodiphenyltrichloroethane (DDT) and also lindane in the eastern part. In the 1980s dichlofluanid was introduced and this biocide is still in use. So these four biocides were selected to be representative for the contamination of used wood and will be discussed in this paper.

The German Ordinance on the management of waste wood defines different fractions of waste wood (BMU, 2002) and demands a maximum content of 3 mg kg^{-1} for the biocide pentachlorophenol (PCP) in waste wood. In Germany, particleboards contain about 10% of waste wood.

Emissions of biocides from wood or other products in emission chambers were presented in a few investigations (e.g. Horn and Marutzky, 1993; Marchal *et al.*, 1997; Jann and Wilke, 1999, 1999a; Schoknecht *et al.*, 2002). The sampling procedure for biocides is based on polyurethane foam as adsorbent, which had been introduced by the first version of the ASTM guideline D4861 (ASTM, 2000). Emission of PCP from particleboards was described by Marutzky and Strecker (1999). They investigated the emissions from particleboards that were manufactured in a laboratory scale with defined concentrations of PCP in the chips. They found less than 10 ng m^{-3} for PCP in the chamber air emitted from boards with 15 mg kg^{-1} PCP.

In the present study, the emissions of PCP, lindane, DDT and dichlofluanid from particleboards were investigated. Boards obtained from manufacturers, testing institutes or

* Corresponding author. E-mail: wolfgang.horn@bam.de

from local dealers and additionally self-manufactured particleboards were tested in small emission chambers. Furthermore, the biocide content of the tested materials was analysed.

MATERIAL AND METHODS

Products

From manufacturers, the local market and from testing institutes 21 particleboards were received. Two different types of wood chip badges were obtained from a waste wood recycling company. Some other types were especially produced for this study from fresh wood out of the forest and some were made out of biocide treated timber. These last ones consisted of a DDT-treated beam and some other biocide treated shelves from a former investigation (Wilke and Jann, 1999). They were reduced to small pieces first with a mortise chisel and second with a cutting mill to chips of 1–3 mm diameter, approximately. With those chips of used wood together with fresh wood chips the A-board was manufactured (see Table 1). Additionally, 1 kg (~8 l) of the fresh wood chips was treated with a mixture of the four biocides in Acetone. These self-impregnated chips were used in different quantities to produce laboratory particleboards (MA, MB, MC, D). In the majority of cases two laboratory boards of the same type were produced. The composition of all self manufactured particleboards is shown in Table 1.

Table 1 Composition of the laboratory boards. Quantities given for the production of one particleboard with a dimension of 50 × 50 cm, approximately

Samples	Intermediate layer			Upper layer		
	Fresh chips, g	Chips treated with Biozide	g	Fresh chips, g	Chips treated with Biozide	g
0	1800			1200		
MA	1750	Self-impregnated	49	1200		
MB	1650	Self-impregnated	150	1200		
MC	1525	Self-impregnated	275	1200		
A	1575	Used wood[a]	225	1200		
D	1800			1150	Self impregnated	50

[a]Mixture of chips from used wood contaminated with different biocides.

The content of biocides in the material of all tested particleboards and wood chips was analysed. From those particleboards that were unload from the chamber tests samples were taken with a Forstner drill 35 mm on different spots. Approximately 1 g of the samples was extracted with 20 ml acidified toluene (0.5 ml H_2SO_4 (1 M)). The wood particles were separated from the extract with a filter and the extract was filled up to 25 ml. To 1 ml of this extract the internal standard solution (30 µl of 10 ng μl^{-1} $^{13}C_6$-PCP und $^{13}C_6$-lindane) and 50 µl of the derivatization solution (40 µl acetic anhydride, 40 µl pyridine in 920 µl hexane) were added followed by a treatment in an ultrasonic bath for 10 min. The qualification and quantification was made by GC/MS.

Chamber Measurements

For the investigation described here 20- or 23-l exsiccators, made of glass (Jann and Wilke, 1999a) were used. These chambers are very suited for investigations of SVOC emissions from materials, for detailed information see Schoknecht *et al.* (2002). Before chamber tests the cutting edge of the plates 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 and the part of open edges can be fixed to the tenth part of the hole area of the plates (DIN V ENV 717-1, 2002). The results of the chamber measurements are given in area specific emission rates (SER_a/ng/(m^2 h) (EN 13419-1).

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 20 m^3 of chamber air were sucked through the PU foam, equipped with a second foam to exclude a breakthrough of the biocides. Sampling was done for up to 7 days with a maximum sampling velocity of 100 l h^{-1}. Subsequently, the PU-foam was desorbed with acetone for 45 min in an ultrasonic bath. Before it was concentrated to 1 ml internal standard ($^{13}C_6$-PCP and $^{13}C_6$-lindane) 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 (LD) are shown in Table 2 (ng m^{-2} h^{-1} calculated with a sampling volume of 20 m^3 and mg kg^{-1} calculated with 1 g of wood).

Table 2 Limits of determination of the biocides investigated

	Lindane	PCP	Dichlofluanid	DDT
ng m^{-2} h^{-1}	4	0.7	3	1
mg kg^{-1}	0.1	0.1	0.1	0.1

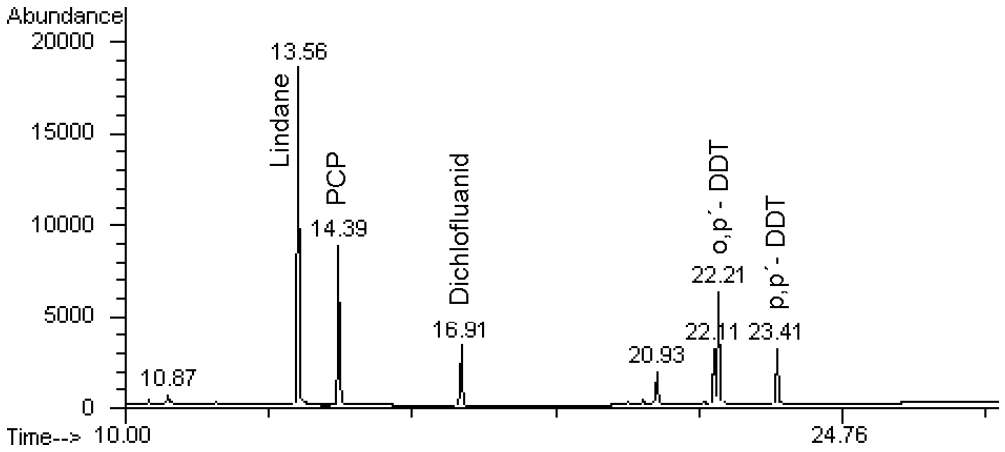

Figure 1 Chromatogram of a solution with biocide standards. The peaks represent an amount of 1.5 ng PCP, 1.1 ng lindane, 1.5 ng dichlofluanid und 0.8 ng *o,p'*-DDT and *p,p'*-DDT each.

RESULTS

The biocides concentrations of all particleboards being tested in emission chambers are listed in Table 3. From the knowledge of the biocide contents of the wooden material board MC, e.g., should contain 5 mg kg^{-1} PCP. However, only 1.4 mg kg^{-1} could be detected. The same problem of reduced recovery was ascertained for the other biocides. In the industrial produced boards $P_{4,12,14}$ only PCP and small amounts of lindane could be detected. The other particleboards MA, MB, MC, A and D contain all four biocides.

Table 3 Concentrations [mg kg^{-1}] in particleboards investigated

Biocide	Lindane	PCP	Dichlofluanid	DDT
MA	0.5	0.2	0.1	0.9
MB	0.7	0.7	1.0	1.8
MC	1.5	1.4	2.3	2.9
A	1.9	0.3	1.3	4.1
D	0.9	0.7	0.7	1.6
P_4	–	2.1	–	–
P_{12}	0.1	6.6	–	–
P_{14}	0.4	0.7	–	–

In Table 4, the SER_a of the biocides tested in emission test chambers are given after a period of 30 days. The industrial produced boards $P_{4,12,14}$ emitted only small amounts of lindane and also PCP except for P_{12} with the highest emission in this investigation.

Table 4 SER_a [ng m^{-2} h^{-1}] reached after 30 days in the chamber tests

Biocide	Lindane	PCP	Dichlofluanid	DDT
MA	6	0.7	3	4
MB	9	1	7	5
MC	15	3	13	7
A	20	1.5	13	7
D	16	4	20	9
P_4	6	3	-	-
P_{12}	6	50	-	-
P_{12}^a	5	30	-	-
P_{14}	6	8	-	-

Emission tests without sealed edges = a; and all other with sealed edges.

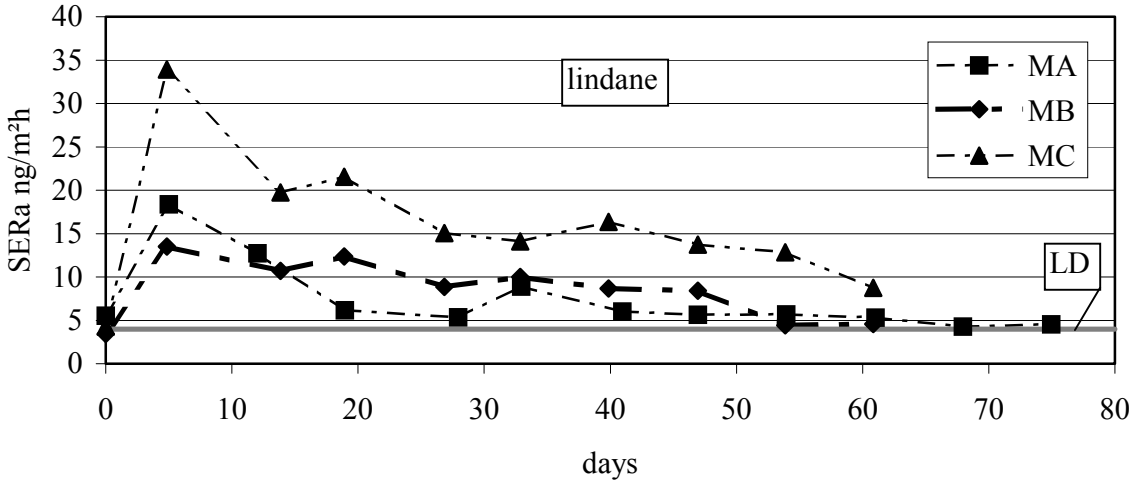

Figure 2 SER_a of lindane from self-manufactured particleboards MA, MB, MC.

The three boards MA, MB, MC were manufactured with different amounts of contaminated wood chips. MA has the lowest and MC the highest concentration. The courses of concentration for these boards are shown in Figure 2 for lindane. In all chamber tests the three emission curves showed for MC the higher and for MA the lower emissions, as it was

expected. Figure 3 shows the SER_a of the boards MA, MC and D. The theoretical PCP concentration calculated with the PCP concentration of the used wood chips of MA and D is nearly the same.

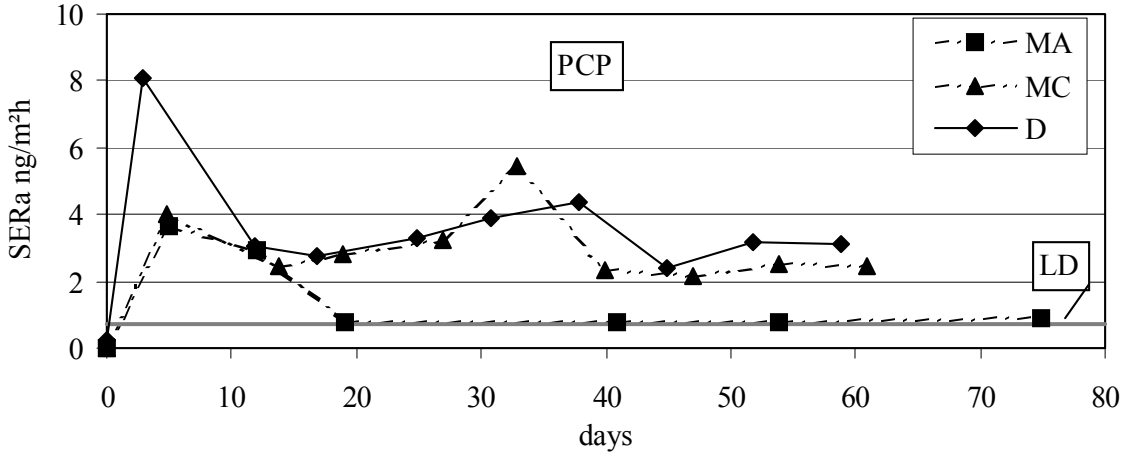

Figure 3 SER_a of PCP from self manufactured particleboards MA, MC, D.

DISCUSSION

Particleboards that contain small amounts of biocides (about 5 mg kg^{-1}) can emit these compounds up to concentrations of 50 ng m^{-2} h^{-1}. However, this is the maximum value reached from a single particleboard P_{12}. Typically, the emission rates decreased under 10 ng m^{-2} h^{-1} for DDT and PCP and under 20 ng m^{-2} h^{-1} for lindane and dichlofluanid after 30 days.

The PCP concentration of P_{12} with 6.6 mg kg^{-1} is the highest of all boards investigated and even higher than the limit value of the German prohibition of chemicals ordinance given with 5 mg kg^{-1}. These particleboards were tested with and without sealed edges. Surprisingly the SER_a for the board without sealing is lower than the SER_a for the other particleboard. This might be possibly caused by an irregular dispersion of the contaminated wood pieces in the board and or by a strong sink effect of the open edges. Additionally, the surface concentration of PCP might be important, so it is possible that P_2 has a high PCP concentration in the upper layer. Normally, the used wood is applied in the middle layer of the usual three layer particleboard. The self-manufactured board MC contains 1.4 mg kg^{-1} and emits only 3 ng m^{-2} h^{-1} PCP. This is nearly ten times lower in comparison to the board P_{12}. However, board MC is manufactured with PCP in the middle layer. Board D with lower content emits more PCP than MC. Particleboard D was composed with fresh chips in the middle layer and a small amount of biocide treated chips in the upper layer. As it was expected the concentration in the upper layer is very important for the emission. The theoretical PCP concentration calculated with the concentration of the used wood chips of MA and D is nearly the same.

CONCLUSION AND IMPLICATIONS

The biocide emission from particleboards containing only allowed traces of these compounds were low. If the contaminated material (5 or 3 mg kg^{-1}, respectively) is only used in the middle layer SER_a with a maximum of 20 ng m^{-2} h^{-1} were received. The German guide value (RWII) for PCP is 100 ng m^{-3} in indoor air (IRK/AGLMB, 1997). A PCP indoor air concentration higher than 100 ng m^{-3} might be possible in the case of board P_{12} in combination with unfavourable circumstances, like, e.g. high loading factor, lower air exchange rates.

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REFERENCES

ASTM (2000). *ASTM-D 4861-00*. Standard Practice for Sampling and selection of analytical techniques for pesticides and polychlorinated biphenyls in air. West Conshohocken: American Society for Testing and Materials.

Federal Environmental Ministry (BMU) (2002). Ordinance on the management of waste wood: http://www.bmu.de/english/download/waste/files/wastewood_ordinance.pdf.

Horn, W. and Marutzky, R. (1993). Measuring of organic wood preservatives in indoor air—sampling and 1-m^3 camber tests. *Proceedings of the 6th International Conference on Indoor Air Quality and Climate—Indoor Air '93,* Vol. 2, pp. 513–518. Helsinki: Indoor Air ´93.

Ad-hoc-Arbeitsgruppe aus Mitgliedern der Innenraumlufthygiene-Kommission (IRK) des Umweltbundesamtes und des Ausschusses für Umwelthygiene der AGLMB (1997). Richtwerte für die Innenraumluft: Pentachlorphenol. *Bundesgesundheitsblatt* **40**, 234–236. http://www.umweltbundesamt.de/uba-info-daten-e/daten-e/irk.htm

Jann, O. and Wilke, O. (1999). Sampling and analysis of wood preservatives in test chambers. In: Salthammer, T., *Organic Indoor Air Pollutants. Occurrence–Measurement–Evaluation*, pp. 31–43. Weinheim: Wiley-VCH.

Marchal, P., Ozanne, G. and Vasseur, P. (1997). Glass test chamber model to evaluate pesticide air emissions from treated wood. *Indoor Built Environment* **7**, 47–53.

Schoknecht, U., Wegner, R., Horn, W. and Jann, O. (2002). Emission of Biocides from Treated Materials - Test Procedures for Water and Air. *Environ Science and Poluttion Research* **10**, 154–161.

Marutzky, R. and Strecker, M. (1999). PCP-emissions of particleboards contaminated with PCP. WKI-Kurzbericht Nr. 27/1999, WKI, Braunschweig.

Verein Deutscher Ingenieure (VDI) (2000). *VDI-Guideline 4101 Part 2* Measurement of indoor air pollution—Measurement of pentachlorophenol (PCP) and γ-hexachloro-cyclohexan (lindane) GC/MS method. VDI-Handbuch Reinhaltung der Luft, Band 5, Berlin: Beuth Verlag GmbH.

DIN EN 717-1 (Norm-Entwurf) (2002). Wood-based panels—determination of formaldehyde release—Part 1: Formaldehyde emission by the chamber method.

DIN EN 13419-1 (Entwurf) 01-2003. Building products—Determination of the emission of volatile organic compounds—Part 1: Emission test chamber method.