Measurements of saturation vapour pressure for estimating biocide concentrations in indoor air

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ABSTRACT
The vapour pressure is an important parameter for estimating the fate of chemicals in the indoor environment. For compounds of low volatility, a combination of the Knudsen effusion method and the Langmuir free evaporation method enables the precise measurement of vapour pressures over a wide temperature range. This is demonstrated for the compounds dichlofluanid, tolylfluanid and α-endosulfan. Saturation concentrations were estimated and compared with results from test chamber experiments carried out under indoor conditions.

INDEX TERMS
Biocides; Vapour pressure; Emission; Indoor air quality; Test chambers

INTRODUCTION
For many years, materials for indoor use were treated with preservatives containing fungicides and/or insecticides. Such compounds may contribute to the pollution of the indoor environment by accumulation in indoor air and house dust (Salthammer, 1999). With regard to possible adverse effects on human health and comfort, exposure levels must be evaluated. In Germany, a combination of the fungicide pentachlorophenol (PCP) and the insecticide lindane was applied in most products for protection of wood. When PCP was banned by law in 1989, it was substituted by dichlofluanid and later tolylfluanid. Endosulfan has been used for wood protection as insecticide, but is now widely substituted by other agents. The evaporation rate of a specific compound is dependent on its physical properties and on the climatic conditions in the indoor environment. It was previously shown that the vapour pressure is an important parameter for estimating the volatilization process (Müller *et al.*, 1998) and the distribution in the indoor environment (Weschler, 2002a). However, for many biocides, which are low volatile compounds, the precise determination of the vapour pressure is a sophisticated process. In many cases the saturation vapour pressures for room temperatures are not measured directly but extrapolated from high temperature measurements. As a consequence, the values reported in the literature show differences over several magnitudes as has been demonstrated for lindane (Boehncke *et al.*, 1996). In this work, data from vapour pressure measurements on dichlofluanid, tolylfluanid and α-endosulfan according to the methods of Knudsen and Langmuir are presented. For dichlofluanid and tolylfluanid, the results of test chamber experiments were compared with calculated saturation concentrations in the gas phase.

METHODS
The compounds under investigation were two fungicides (dichlofluanid, tolylfluanid) and one insecticide (α-endosulfan) (see Industrieverband Agrar (2000) for physical and toxicological properties). The insecticide lindane has been the subject of previous work (Boehncke *et al.*, 1996). All compounds were of technical quality and purified by sublimation and/or zone refining. The determination of vapour pressures requires purities >99.95%.

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If the saturation vapour pressure p_s of a specific compound is known, the maximum emission rate can be calculated from the kinetic theory of gases. For a pure substance, the vapour pressure p_s, which is only dependent on temperature T and enthalpy of evaporation ΔH_v, can be described by Eqn (1):

$$\ln p_s = \frac{\Delta H_v}{RT} + \text{const.} \qquad (1)$$

For an accurate determination of small vapour pressures, the dynamic methods of Knudsen (Boehncke *et al.*, 1996) (1–10^{-4} Pa) and Langmuir (Cammenga *et al.*, 1981) (10^{-4}–10^{-6} Pa) can be applied.

Vapour pressure measurements at low vapour undersaturation were performed by a variation of the Knudsen effusion method. A more detailed description of the apparatus and procedure has been described by Cammenga *et al.* (1977). The substance under investigation is placed in cylindrical cells of cross-sectional area A made from Duran glass. For effusion measurements the cells have an interchangeable cap, which carries the circular effusion orifice of area a in the centre of a thin molybdenum foil, and which is connected to the cell body by a short, thoroughly polished ground glass joint. The distance from sample surface to the foil carrying the effusion hole is made equal to the cell inner diameter, as demanded by theory. By using various combinations of orifices of effective area Wa and cells of area A, the ratio Wa/A can be varied from 5.0×10^{-4} to 5.4×10^{-2}. Here, W is the calculated penetration probability of the orifice (Clausing factor). For measurement, a high vacuum is maintained for a period of 3–18 h, while the vapour effusing from the hole is collected on a condenser cooled with liquid nitrogen. From the kinetic theory of gases, the pressure inside the cell, p', is given by:

$$p' = -\frac{1}{Wa}\left(\frac{\Delta m}{\Delta t}\right)_T \left(\frac{2\pi RT}{M}\right)^{0.5} \qquad (2)$$

p' is close to the saturation vapour pressure p_s and the relation between p' and p_s is:

$$p_s = \left(1 + \frac{1}{\alpha\gamma}\frac{Wa}{A}\right) p' \qquad (3)$$

where α is the evaporation coefficient, γ the surface roughness, $(\Delta m/\Delta t)_T$ the rate of mass loss by effusion, R the universal gas constant, T the absolute temperature and M the molar mass. To obtain the saturation vapour pressure p_s from p' it is necessary to perform a series of measurements at constant temperature with various combinations of cells and orifices. Then $1/\alpha\gamma$ can be calculated from the measured quantities:

$$p' = p_s - \frac{1}{\alpha\gamma}\frac{Wap'}{A} \qquad (4)$$

Measurements of the free evaporation rate are performed by the Langmuir method using cells without any cap. The substance to be studied is pressed into the cells by a tightly fitting piston and a briquetting press to form a disc, which is then lifted by raising the adjustable cell bottom until the sample surface is at the same level as the cell rim. A more detailed description of the apparatus and procedure may be found in Cammenga *et al.* (1977, 1981). The rate of free evaporation into vacuum is given by the Hertz–Knudsen–Langmuir equation:

$$p_s = -\frac{1}{\alpha\gamma A}\left(\frac{\Delta m}{\Delta t}\right)_T \left(\frac{2\pi RT}{M}\right)^{0.5} \qquad (5)$$

The investigated products A–C are described in Table 1. Each paint was applied on pine board with 200 g m^{-2}. All emission experiments were carried out in self-constructed 1 m^3 glass chambers. Technical details of the chamber design have been described elsewhere

(Salthammer and Wensing, 2000). The test conditions are also summarized in Table 1. The chambers were loaded immediately after preparation of the test specimen. Before each test the chamber was heated for 48 h to reduce memory effects and keep the chamber blank low. The effectiveness of thermal cleaning process was controlled by measuring a blank value. Sampling was performed on polyurethane (PUR) foam. Chemical analysis was carried out by GC/ECD after extraction using a solvent mixture of acetone and hexane.

Table 1 Investigated products and test chamber conditions (r.h. = relative humidity, N = air exchange rate; L = loading)

Product	Type	Ingredients	T (°C)	r.h. (%)	N (h^{-1})	L (m^{-1})
A	Solvent based paint; no pigment; thin film	0.60% tebuconazole; 0.01% cyfluthrin; 0.57% tolylfluanid	23	45	1.00	1.0
B	Solvent based paint; no pigment; thin film	0.60% tebuconazole; 0.55% dichlofluanid; 0.01% cyfluthrin	23	45	1.00	1.0
C	Solvent based paint; no pigment; thick film	0.55% dichlofluanid	23	45	0.35	1.0

RESULTS

The parameters A and B listed in Table 2 are obtained from a straight line fit to the data with $\ln p = A - B/T$. Then the enthalpy of evaporation ΔH_v was calculated from Eqn (1) according to $\Delta H_v = B\mathrm{R}$. Within the framework of the measuring accuracy, the determined saturation vapour pressures for all substances according to the two effusion methods showed a good correlation. As demonstrated in Table 2, at 20°C the values deviate by 3 and 6%, respectively, for dichlofluanid and tolylfluanid, for α-Endosulfan the deviation is about 15%. Moreover, the obtained evaporation enthalpies only differ by a maximum of 5%.

Table 2 Fit parameters A and B (see also Figure 1) with calculated enthalpies of evaporation ΔH_v and saturation concentrations C_s

Compound	M (g mol^{-1})	Method	A	B (K)	ΔH_v (kJ mol^{-1})	p_s (293 K) (10^{-5} Pa)	C_s (293 K) (μg m^{-3})
Dichlofluanid	333.2	Knudsen	40.0	14 420	119.9	10.2	14.0
		Langmuir	37.3	13 648	113.5	9.6	13.1
Tolylfluanid	347.3	Knudsen	39.0	14 218	118.2	7.5	10.7
		Langmuir	40.8	14 739	122.5	7.7	11.0
α-Endosulfan	406.9	Knudsen	34.8	11 810	98.2	414	691.5
		Langmuir	36.2	12 179	101.3	477	797.8
Lindane[a]	290.8	Knudsen	34.5	11 754	97.7	383	457.2

[a]Data from Boehncke *et al.* (1996).

A comparison with literature data—only individual values were available and no vapour pressure curves—showed a very irregular appearance. For dichlofluanid, the measured values are partially clearly higher than the probably extrapolated vapour pressure data. For 20°C Perkow and Ploss (1994) indicate p_s to be $<10^{-7}$ Pa, the publication of the Industrieverband

Agrar (2000) stipulates 1.4×10^{-5} Pa for the same temperature. In contrast, these authors, according to their corresponding values obtained for dichlofluanid, classify tolylfluanid as clearly more volatile (1.6×10^{-4} and 1.6×10^{-6} Pa, respectively). According to our investigations guided by the vapour pressure curves (see Figure 1) it is obvious that the saturation vapour pressures of the two substances deviate only slightly from each other, particularly at relevant indoor temperatures. Consequently, these substances might show similar volatilization behaviours. When it comes to the vapour pressure of endosulfan, literature values do not differentiate between the α- and β-isomers, although their melting points clearly differ from each other (α, 108°C; β, 207°C; technical isomer mixture, consisting up to 70–80% of the α-isomer, 70–100°C). For 20°C it is indicated: $p_s < 1 \times 10^{-3}$ Pa and $p_s = 1 \times 10^{-3}$ Pa, respectively. The value of approximately 4.5×10^{-3} Pa is in that order of magnitude, but it was determined only for the α-isomer. Up to now it was not possible to measure the vapour pressure curve for the corresponding β-isomer of endosulfan since the necessary purification of the samples could not be realized.

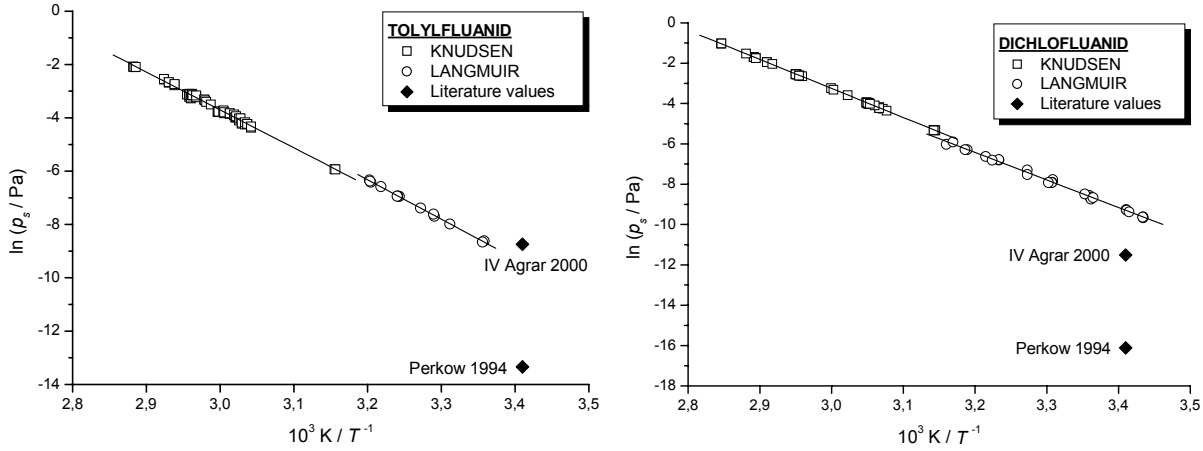

Figure 1 Plot of the vapour pressure of dichlofluanid and tolylfluanid measured according to the methods of Knudsen and Langmuir.

We have also performed vapour pressure measurement of a non-purified compound (dichlofluanid). The results are presented in Figure 2 and clearly indicate the dependence of p' from the evaporated mass.

For the investigated compounds, saturation concentrations C_s in air were calculated from the perfect gas equation $pV = nRT$ and are summarized in Table 2. As shown in Figure 3 for dichlofluanid and tolylfluanid, the calculated C_s values are in very good agreement with experimental data. However, in the initial phase (<15 days) the measured chamber concentrations of dichlofluanid exceeded the theoretical values. This effect might result from particle bound molecules emitting from the test specimen. Wet paints, which are suspensions, may easily form volatile aerosols and particles. Weschler (2002b) suggested that in the beginning of the experiment the emission rate is large enough to exceed the saturation vapour pressure. The biocide then starts to condense on pre-existing ultrafine particles as well as chamber walls (sink-effect). These biocide aerosols grow in size and soon the surface of these aerosols is primarily biocide and subsequent associations are dominated by absorption rather than condensation. Biocide concentrations in excess of the vapour pressure concentration probably result from sampling a mixture of biocides in the gas phase and in the condensed phase.

Over time, the emission rate decreases and the concentration in the chamber falls below that corresponding to the saturation vapour pressure.

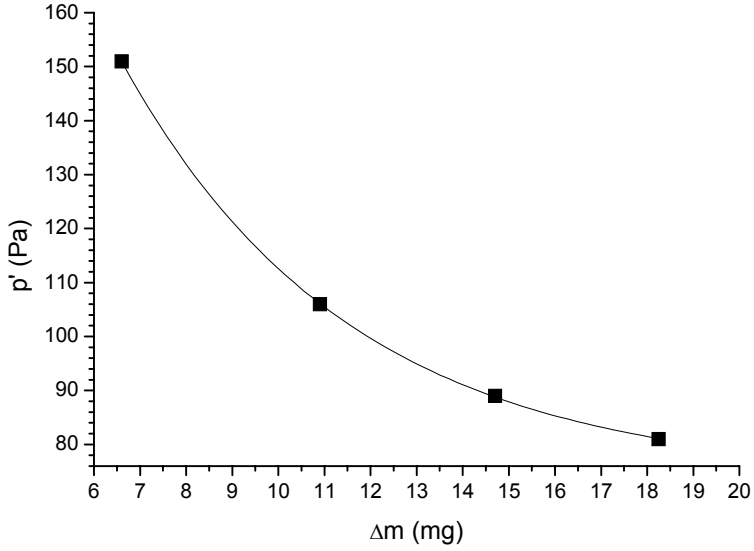

Figure 2 Dependence of p' from evaporated mass for dichlofluanid of technical quality (not purified).

Chamber air or indoor air concentrations in the range of C_s can be observed if the drag-out via air exchange is small compared to the area specific emission rate SER_A (µg m^{-2} h^{-1})). In the steady state, SER_A can be calculated by use of the simple equation $SER_A = CN/L$ (Salthammer and Wensing, 2000). High SER_A values might be achieved for freshly produced samples when the emission process is controlled by evaporation rather than diffusion.

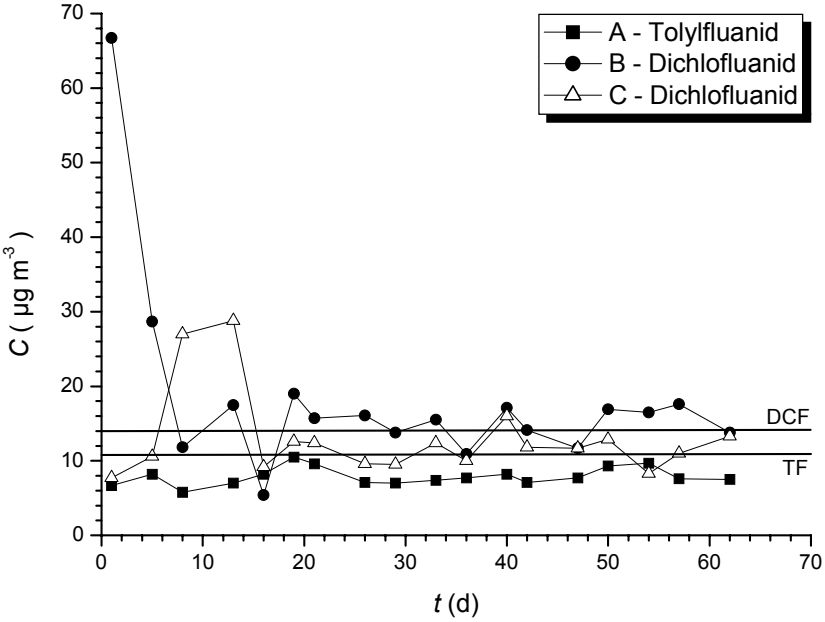

Figure 3 Concentration versus time curves for dichlofluanid and tolylfluanid in the test chamber (see Table 1 for test conditions). The horizontal lines represent the C_s-values.

However, for most biocides (including dichlofluanid and tolylfluanid), measured chamber and indoor concentrations are far below the saturation values (Zimmerli *et al.*, 1979; Petrowitz, 1986). This might be due to low emission rates and strong sink effects. Boehncke *et al.* (1996) have compared their results on vapour pressure measurements of lindane (see also Table 2) with previously published values. They observed considerable scatter, especially at temperatures of indoor living conditions (typically 18–23°C).

Nevertheless, the vapour pressure is a helpful parameter for estimation of possible concentrations of pollutants in indoor air (Müller *et al.*, 2003). This is important for calculation of exposures and risk assessment. Moreover, it was demonstrated that many processes with relevance to indoor sciences correlate with a compound's vapour pressure (Weschler, 2002a).

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