AMBIENT MONITORING AND BIOMONITORING OF PENTACHLOROPHENOL AFTER INDOOR EXPOSURE

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ABSTRACT
Background: The suspected carcinogen, pentachlorophenol (PCP), has been widely used as a wood preservative. Because PCP has the tendency to leach out for a long time, treated products may constitute a long-term health hazard. Methods: Case 1: A family of four that resided in a PCP-treated block house built in 1978. Case 2: A male adult who had resided in a PCP-treated wooden frame house since 1975. Regular ambient monitoring and biomonitoring of PCP was carried out before and after renovation. Results: Before renovation, PCP levels in air were 0.28-0.6 µg/m^3. PCP in serum before renovation was 60-200 µg/L and after renovation 50-100 µg/L (case 1) and 18 µg/L (case 2), respectively. PCP in urine (case 1) was 25-60 µg/L before and 20-40 µg/L after renovation. No adverse effects were observed in the exposed individuals. Conclusions: Current HBM-II values were successfully applied in judging the 2 case studies.

INDEX TERMS
Pentachlorophenol, ambient monitoring, human biomonitoring, renovation, health effects

INTRODUCTION
The fungicide pentachlorophenol (PCP) is a man-made substance that has widely been used as a wood preservative. Traditionally, PCP has been used in block houses. In a study by the National Toxicology Program in1991, pure PCP showed oncogenic activity in mice. The American Conference of Governmental Industrial Hygienists (ACGIH) has classified PCP in category A3: “Confirmed animal carcinogen with unknown relevance to humans“ (2001). The classification of the German Commission for the investigation of health hazards due to chemical compounds in the work area is category 2: “Substances that are considered to be carcinogenic for man because of sufficient data from long-term animal studies, substantiated by evidence from epidemiological studies“ (2001). Mainly because of its carcinogenicity, U.S. Environmental Protection Agency (EPA) banned PCP for all non-wood products in 1987. In Germany, the use of PCP was generally banned by law in 1989 (PCP-Verbotsverordnung). Because PCP is released into the air by evaporation from treated wood surfaces for a considerable period of time, PCP-treated wood manufactured before prohibition by law may still constitute a health hazard for exposed persons.

In 2 case studies carried out in block houses treated with PCP it was attempted to quantify the exposure by ambient monitoring of PCP in air and dust samples as well as in samples of wood and furniture before and after renovation of contaminated material. In addition, the PCP-

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uptake of the inhabitants was recorded in urine and serum samples during this period of time. A careful attempt was also made to screen for adverse health effects in the inhabitants after years of exposure.

METHODS

Case 1

A family of four (father *1945, mother *1954, daughter *1985, son *1988) that had resided in a block house in southern Germany since 1978. The wood of the house had been thoroughly treated by the adults with the PCP-containing wood preservative „Xyladecor“ (Desowag-Bayer, Germany). The investigations were initiated because of non-specific health disorders, e. g. fatigue, exhaustion, lack of concentration, and digestive disorders (father). No other conspicuous disease was reported. Over a period of more than 10 years all family members were examined physically; in addition, special laboratory tests were carried out.

Case 2

A male adult, born in 1936, who had been living in a wooden frame house in western Germany since 1975. The house had been treated with the PCP-containing wood preservative „Xyladecor“, containing 4.8% PCP (Desowag-Bayer, Germany). The otherwise healthy patient was suffering from symptoms such as fatigue, exhaustion and digestive disorders.

Quantitative determination of PCP

In both cases, ambient monitoring of wood (mixed sample obtained from three different areas in the house in case study 1), dust (case 1: passively deposited, suspended particulate; case 2: sample from a vacuum cleaner bag) and indoor air was carried out before, during, and after renovation. Quantitative determination was undertaken according to analytical procedures described elsewhere (Butte, 1987 a), (Walker *et al*., 1999). Biomonitoring was performed using serum (Angerer and Schaller, 1998) and morning urine (Meissner and Schweinsberg, 1996) (case 1) or serum specimens (Butte, 1987 b) (case 2) before, during, and after renovation.

Methods of renovation

Two different methods were applied. In case 1 the block house, which was constructed entirely of solid wood (approximately 600 m^2 indoor area), was treated twice with „EX Schadstoffvernichter“ (Baden-Chemie, Germany)**,** a water-based product with a pH-value of approx. 9.6. It contains hydrolyzing components (sodium hydroxide and amino acid buffer). This mixture degrades PCP, as has been demonstrated by the determination of PCP in wood and in test chamber air before and after treatment in various test reports (unpublished data). Approx. 90 % of PCP is degraded after treatment of wooden panels with this coating (see also patent specification DE 195 17 811 A 1). The furniture was not treated, the carpets were removed later. In case 2 all wooden material (ca. 500 m^2) was grinded off, followed by masking of the treated wood with “Biophil”-products of Imparat (Glinde, Germany). The “Biophil” system consists of two components: a liquid containing quarternary ammonium salts to bind PCP and a varnish (not diffusible) to coat the wood.

RESULTS

Ambient monitoring

Table 1 illustrates the results of ambient monitoring before renovation. In both cases, a high level of PCP was found in treated wood, confirming the long persistence of PCP in this material. PCP levels found in the air emphasize clearly that an indoor application of PCP has occurred. To quantify a secondary contamination, several samples of carpet material from

different rooms and from leather were analyzed. PCP levels ranged from 38 to 324 mg/kg, indicating a strong source of additional exposure. In both cases, the degree of indoor exposure to PCP was quite similar.

Table 1. PCP levels from ambient monitoring in two case studies before renovation

Material	Case study 1	Case study 2	Unit
Wood	1200	810 / 3100	mg/kg
Air	0.6[1] / 0.28[2]	0.4[3]	µg/m³
Dust	145[4]	32[5]	mg/kg
Carpet	38 – 324 (n = 6; mean = 184)	51	mg/kg
Leather	140	39	mg/kg
Blanket/Wool carpet	11	11	mg/kg

[1] 8 h sampling; [2] 1 week sampling; [3] 2 h sampling; [4] sample of passively deposited, suspended particulate; [5] sample of vacuum cleaner bag

Human biomonitoring (HBM)

Table 2 reveals that in case study 1 there were distinct differences between the PCP levels in serum in the children and the adults during the whole period of examination. The PCP-levels before and during renovation remained constant, in contrast to an increase in case 2. Following renovation, the PCP concentrations decreased slowly. At the end of the investigations, however, they were still around the HBM-II value of 70 µg/L. HBM-II was defined by the Human Biomonitoring Commission of the German Federal Environmental Agency as the concentration of an environmental toxin in a human biological material above which there is - according to the knowledge and judgement of the commission - an increased risk of adverse health effects in susceptible individuals of the general population (Ewers *et al*., 1999). On the other hand, successful renovation could clearly be seen in case study 2, as indicated by the clear decrease in the PCP concentration in serum.

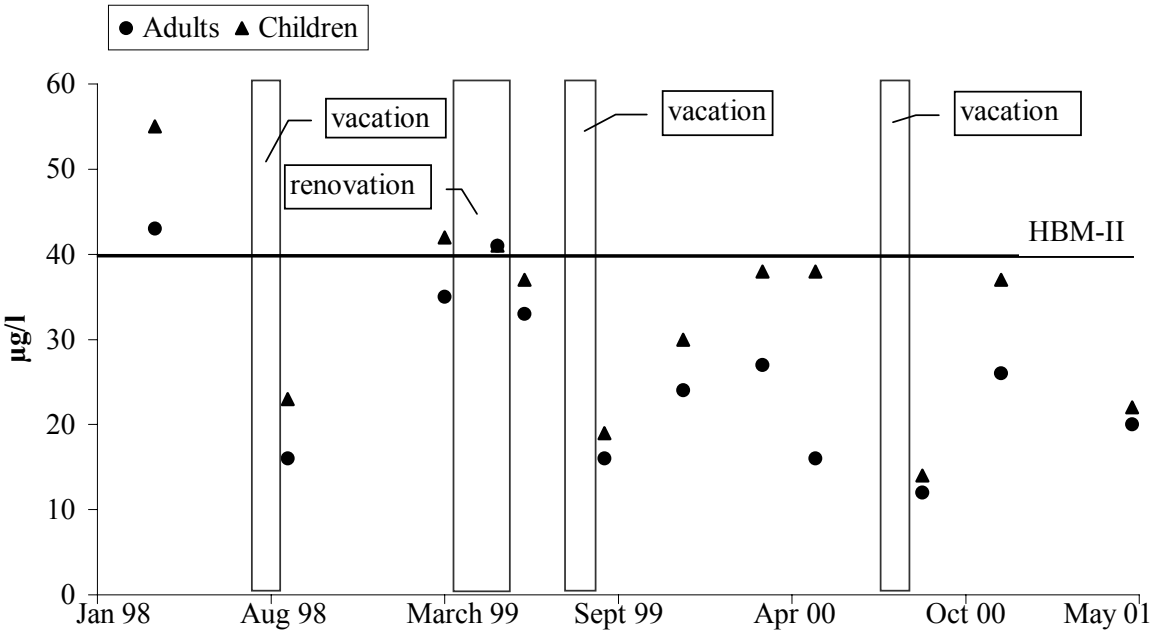
Table 2. Mean PCP concentrations in serum (µg/l) from both case studies before, during, and after renovation; n = number of analysis

		Renovation											
		Before			During			After					
		Date	n	PCP	Date	n	PCP	Date	n	PCP	Date	n	PCP
Case study 1	Adults	3/98	2	102	5-8/99	6	103	12/99	2	73	2/01	2	69
	Children		2	175		4	143		2	133		2	71
Case study 2	Adult	3/96	1	71	6/96	1	114	5/97	1	12	2/98	1	18

Figure 1 demonstrates that the PCP levels in urine in the children were distinctly higher than those of the parents, with a margin of ca. 10 µg/l. This can be satisfactorily explained by the presence of the children in the house for longer periods of time. Before renovation, the levels in urine before and after vacation allow a half-life of PCP of approx. 20 days to be deduced.

This is in good agreement with published data for long-lasting exposure (Cline *et al*.,1989), (Heinzow, 1992), (Heudorf *et al*., 2000). The PCP levels during this period were found to exceed the HBM-II value for urine of 40 µg/l.

During renovation, PCP in urine of both adults and children (case 1) was nearly equal because in this period of time the adults participated in renovation activities. A clear increase of PCP in serum was also recorded in case 2.



After renovation in case 1 only a small decrease in the PCP level in urine was noted. However, the levels determined at this point were below the HBM-II value.

Figure 1. PCP in urine (µg/l) of adults and children living in a PCP-treated block house before and after annual vacations and renovation of the wood (case study 1).

Physical examinations and laboratory tests

In both case studies, the reason for initiating a specific examination for PCP in serum were non-specific health disorders such as fatigue, exhaustion and lack of concentration. Additional adverse effects caused by PCP, e. g. irritation of skin, mucous membranes and tonsils, alopecia, neuralgia, rheumatism, irritability, depression, sweating and increase of body temperature, have been reported in the literature (Heinzow, 1992). These symptoms were not observed in either of the two case studies at all, even though the adults and children in case study 1 had been undergoing regular physical examinations by their general practitioner for over 10 years. In the children, the usual prophylactical check-ups had been carefully documented by a pediatrician from birth to the age of six and normal development had been described. However, the boy was found to be prone to eczema. Table 3 shows the results of examinations carried out by the general practitioner and different medical specialists (neurologist, internist) and the results of special laboratory tests which were performed after the high, long-lasting exposure of PCP became apparent. Because micro-albumin was detected in the urine by reagent strips, a quantitative determination of albumin, alpha-1-microglobulin, and IgG in 24 h-urine sample had been carried out. The results of all four samples demonstrate a normal kidney function. Arrhythmia had occurred occasionally in the

mother since 1995, and was diagnosed as a typical AV-nodal reentry-tachycardia, which was cured by modulation in 2000. A slight increase of eosinophils, which might be connected with exposure to PCP, can still be seen.

Table 3. Results of medical examinations of the family in case study 1 (father = f, mother = m, daughter = d , son = s)

Organ	Examination	Pathological findings	Person
Skin	Inspection	proneness to eczema	s
Kidney	urine test, creatinine	microalbumin detectable	f, m, d, s
Liver	GGT, GOT, GPT, GLDH	normal	
Pancreas	lipase, cholinesterase	normal	
Thyroid gland	TSH, T3, T4	normal	
Heart	ECG	arrhythmia	m
Blood	blood cell count, immunoelectrophoreses	increase in eosinophils	f, m, d, s
Digestive system	Endoscopy	sporadic diarrhoea	f
Nervous system	neurologic and psychiatric examination, EEG, CT	normal	

DISCUSSION

Following the ban of PCP in 1989 a decrease in the average level of PCP in serum and urine was observed in Germany. The reference values (95. percentile) for the general German population as defined by the Human Biomonitoring Commission of the German Federal Environmental Agency decreased from 20 µg/L serum and 15 µg/L urine in 1997 to 12 µg/L serum and 8 µg/L urine respectively in 1999. A further decrease for PCP determined in plasma (6.1 µg/L) was reported in 2000 (Heudorf *et al*., 2000). As demonstrated in the case studies described here, this is not the case for PCP-treated wooden houses, which might subject the residents to a high and long-lasting exposure. From the results of study 1, especially as regards PCP levels in the air after renovation, it has to be concluded that (a) an abatement of PCP has principally not been achieved or (b) that sources of secondary contamination contribute essentially to exposure or (c) that both mechanisms have to be considered. On the other hand, the effectiveness of method 1 was clearly demonstrated when analyzing PCP of a wooden board after renovation according to the instructions in a test chamber. In addition, after renovation of the block house in study 1, the PCP level of a wooden board decreased dramatically (before: 1200 mg/kg; after: 50 mg/kg), as well as the level in dust samples (before: 145 µg/kg; after 4.7 µg/kg). As can be seen from Table 1, secondary contamination, especially from the carpets, is likely to be responsible for the poor success of renovation in case 1. In addition it must be stated that some parts of wooden material were not renovated at all. For effective renovation, the replacement of contaminated furnishings must be drawn into consideration. In the five persons included in this study no adverse health effects which could be related to PCP exposure were observed (Cline *et al*., 1989), (Hill *et al*., 1989). Therefore, with respect to the high level of PCP contamination (> HBM-II values) that persisted for over one decade it can be concluded that there is no necessity to lower these HBM values.

CONCLUSION AND IMPLICATIONS

The results described in this study do not support a reduction in the human biological monitoring values for PCP as laid down by the Human Biomonitoring Commission of the German Federal Environmental Agency in 1999; this applies in particular to the HBM-II value for PCP in urine of 40 µg/L and in serum of 70 µg/L. The application of appropriate

measures to remove PCP from indoor wood constructions will help to lower exposure significantly. But secondary contamination of indoor accessories such as carpets must also be considered as a source of human exposure.

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REFERENCES

Angerer J, and Schaller KH. 1998. Pentachlorophenol. In: *Analyses of Hazardous Substances in Biological Materials*. Deutsche Forschungsgemeinschaft, ed. Weinheim: Wiley-VCH, pp 189-192.

Butte W. 1987 a. Simultaneous determination of pentachlorophenol and γ-hexachlorocyclohexane in indoor air. *Fresenius Journal of Analytical Chemistry*. Vol. 327, pp 33-34.

Butte W. 1987 b. The determination of pentachlorophenol (PCP) in human serum and urine using triethylsulfoniumhydroxide for pyrolytic ethylation. *Fresenius Journal of Analytical Chemistry*. Vol. 326, pp 449-452.

Cline RE, Hill RH, Phillips DL, *et al*. 1989. Pentachlorophenol measurements in body fluids of people in log homes and workplaces. *Archives of Environmental Contamination and Toxicology*. Vol. 18, pp 475-481.

Ewers U, Krause C, Schulz C, *et al*. 1999. Reference values and human biological monitoring values for environmental toxins. Report on the work and recommendations of the Commission on Human Biological Monitoring of the German Federal Environmental Agency. *International Archives of Occupational and Environmental Health*. Vol. 72, pp 255-260.

Heinzow B. 1992. Organische Verbindungen/Pentachlorphenol. In *Handbuch Umweltmedizin*, Wichmann R, Schlipköter U, and Fülgraff G, eds. Landsberg: ecomed Verlag, pp 1-22.

Heudorf U, Letzel S, Peters M, *et al.*. 2000. PCP in the blood plasma: Current exposure of the population in Germany, based on data obtained in 1998. *International Journal of Hygiene and Environmental Health*. Vol. 203, pp 135-139.

Hill RH, To T, Holler JS, *et al*. 1989. Residues of chlorinated phenols and phenoxy acid herbicides in the urine of Arkansas children. *Archives of Environmental Contamination and Toxicology*. Vol. 18, pp 469-474.

Meissner T, and Schweinsberg F. 1996. Pentachlorophenol in the indoor environment: Evidence for a correlation between pentachlorophenol in passively deposited suspended particulate and in urine of exposed persons. *Toxicology Letters*. Vol. 88, pp 237-242.

Walker G, Hostrup O, Hoffmann W, *et al*. 1999. Biozide im Hausstaub: Ergebnisse eines repräsentativen Monitorings in Wohnräumen. *Gefahrstoffe- Reinhaltung der Luft*. Vol. 59, pp 33-41.