

Plasma hexachlorobenzene and octachlorostyrene in aluminium foundry workers using hexachloroethane for degassing

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1. Introduction

Hexachloroethane (HCE) has been commercially available for more than half a century as a simple means for hydrogen removal (degassing) in molten aluminium¹. Previously considered fairly innocuous, recent studies of this process have shown that it may cause substantial emissions of persistent organochlorine compounds (OCC)²⁻⁴. Subsequently, HCE based degassing agents are no longer used in contemporary Swedish aluminium foundries or secondary aluminium smelters. The epidemiological aspects of these emissions remain to be elucidated, however, and this pilot study was designed to estimate retrospectively the contribution of occupational OCC exposure in aluminium degassing, if any, to the background level. Among the various OCC emitted⁴ hexachlorobenzene (HCB) and octachlorostyrene (OCS) were considered suitable and accurate for biological monitoring.

2. Material and methods

All invited HCE exposed male smelters (n=9; median age 50 years, range 26-64 years), employed at six aluminium foundries in central and southeastern Sweden and selected by the local management agreed to participate in the study. For each smelter, two local controls matched for sex, age and social class were selected (n=18; median age 51 years, range 28-62 years). Most of the controls were employed at the same company as the corresponding exposed subject, but the controls worked in buildings separated from the melting department. From questionnaires and from interviews with the smelters and their foremen several estimates of cumulative exposure were assessed. Plasma samples from the study subjects were collected while avoiding contamination, coded, and frozen at -20°C until analysis.

Analytical procedures

5 ml of plasma was pipetted into a Teflon centrifuge tube. 2.5 ml of methanol was added to the plasma and the tube was vortexed for 15 sek. The denatured plasma was extracted with 6.25 ml of n-hexane/diethylether 1:1 (v/v) by agitation for 10 min. The tube was centrifuged for 5 min. at 3 000 rpm and the organic layer was transferred to a tared glass container. The extraction procedure was repeated twice and the combined organic extracts were evaporated to dryness and the fat residue was determined gravimetrically.

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The fat residue was resolved in 1 ml of n-hexane and was applied on a 10 mm i.d glass column with a 50 ml reservoir packed with 10 mm of anhydrous sodium sulphate, 1 g of neutral silica gel, 4 g of sulphuric-acid impregnated silica gel, 2 g of basic silica gel, and 10 mm of anhydrous sodium sulphate. The column was eluted with 60 ml 20% methylene chloride in n-hexane. The eluant was collected and evaporated to about 1 ml and caution was taken to prevent the extract from going to dryness. 1 ng of $^{13}\text{C}_{12}$ -PCB IUPAC no. 101 was added as internal standard and 30 μl of tetradecane was added as keeper solution. A gentle steam of nitrogen was applied to concentrate the sample just to dryness. 1 μl of the sample was analysed on a HP-5890 gas chromatograph equipped with a capillary column (DB-5, 60 m, i.d. 0.32 mm) and coupled to a VG70SQ magnet sector instrument running in EI+/SIR mode, low resolution. GC injection temperature was 230°C. The initial column temperature of 160°C was held for 2 min, then programmed to 300°C at 10°C/min and held for 5 minutes. Quantification of HCB and OCS was carried out by the use of $^{13}\text{C}_6$ -HCB (99%), spiked to the sample before extraction. The recovery was found to be 70 to 90%. The detection limit of the analytical method was 0.8 ng/l for HCB and 0.6 ng/l for OCS.

Several aliquots of a pooled sample of reference plasma were analysed during the period of the study. The results obtained from a series of 7 separate analytical runs had a coefficient of variation less than 5%.

3. Results

The plasma HCB (P-HCB) level varied considerably among the exposed subjects (Figure 1) with a four-fold increase of the mean level compared to the controls (313.1 versus 66.7 ng/g lipid). The P-HCB data were considered approximately lognormally distributed and after logarithmic transformation the difference to the controls was statistically significant ($p < 0.05$; t-test for paired samples). A similar and even more pronounced difference between exposed and controls was observed for OCS (54.6 versus 0.7 ng/g lipid; $p < 0.05$ after logarithmic transformation). The HCB and OCS level in individual samples, respectively, was correlated to the various estimates of cumulative exposure as a smelter. The best correlation was found for the number of years with HCE exposure as an aluminium smelter (Figure 2).

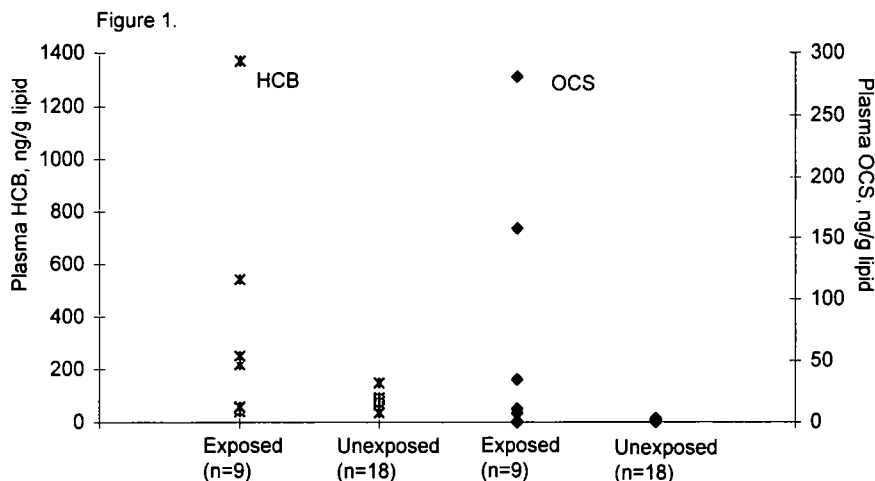
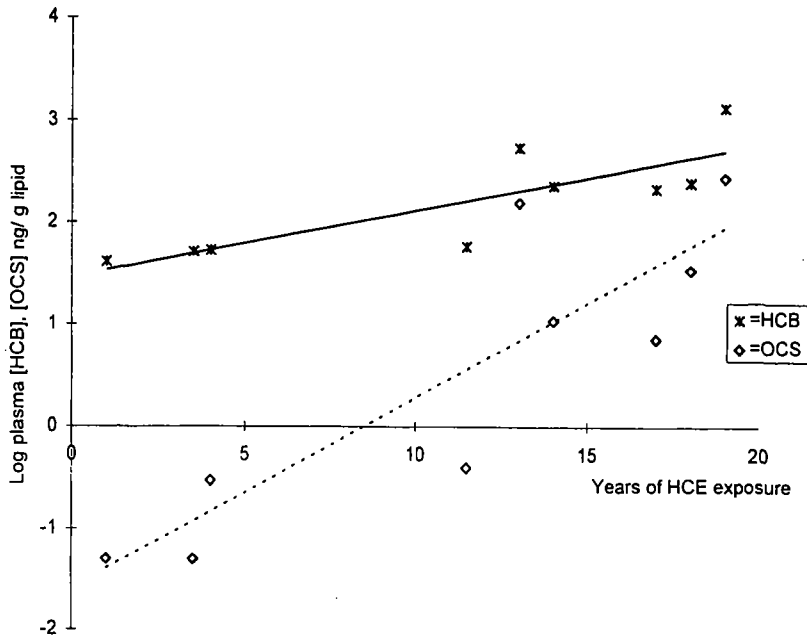


Figure 2.



4. Discussion

Recent restrictions imposed on HCE based aluminium degassing agents in Sweden substantially reduced the number of subjects eligible for this study. Some of the exposed subjects were quite young and inexperienced in HCE based degassing. Moreover, the plasma samples were obtained 2-4 years after discontinuance of this degassing technique. Still, five of the smelters had clearly increased plasma HCB/OCS levels in comparison to their pair of matched controls. In four of the exposed subjects the HCB/OCS levels were well within the control range, possibly reflecting a combination of the lagtime from last exposure and their work history. This small number of plasma samples also indicate that HCB and OCS levels several orders of magnitude higher than the general background may be reached in HCE based degassing. Considering the porphyrinogenic (HCB, OCS)^{5,6} and carcinogenic (HCB)⁵ potential of these chemicals and the future probable abolition of HCE,⁷ there is an urgent need to confirm, or refute, these findings in a larger and more recently HCE exposed population of aluminium foundry workers in order to obtain a basis for future epidemiological studies.

5. Conclusions

In addition to substantial emissions of OCC to the general environment, HCE based aluminium degassing may also imply an occupational hazard from the OCC exposure as indicated from this pilot study.

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6. References

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