

Occupational Safety During the Remediation of a Contaminated Site: Monitoring of PCDD/PCDF Levels in Blood of Employees

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Introduction

In connection with road construction activities a dioxin contaminated site was discovered during the 1990's in a German city, containing residues of early industrial activities. PCDD/PCDF levels up to 41 ng I-TEQ/g dry matter could be detected in the material with a 1,2,3,4,7,8-HxCDF dominated pattern (Figure 1a). This pattern is very similar to samples related to the production and use of chlorine¹ in the early 20th century. Furthermore, sandy material showing a deviating and 1,2,3,7,8-PeCDF dominated pattern with an at least a factor of 10 lower concentrations was found (Figure 1b).

A remediation program was initiated including removal of contaminated soil and installing a drainage layer below the final asphalt layer sealing the site. Occupational safety for employees involved in any on-site activities was of primary importance following regulations for work in contaminated areas² and for preventive occupational medicine³.

Hygiene was strictly obeyed. On-site monitoring via chromatographic dust analysis was performed by surveying engineers. Employees working in contaminated areas wore Air-Filters A2P3 with motor support. The mandatory personal safety equipment included dust-proof protective suits for single use, chemical-proof gloves and boots.

In this context, it was the task of the Employer's Liability Insurance Association (Tiefbau-Berufsgenossenschaft, TBG) to strictly control compliance of occupational safety measures. The occupational medical service of this association was commissioned monitoring the health situation of the employees involved. Among other parameters, the corresponding control program included monitoring of PCDD/PCDF blood levels to identify possible alterations.

Methods and Materials

Monitoring Design and Sampling: In total 28 employees planned to be involved in on-site activities were checked for their dioxin levels in advance (2003-1). For 12 on-site employees (P1 – P12) control analyses have been executed after remediation activities were finished (2004-1), for five of them an interim control during on-site work had been included (2003-2). In total 45 samples for dioxin analyses have been collected. The blood was sampled in 5 EDTA-coated 9 ml monovettes per employee. These EDTA-stabilized blood portions were immediately combined to one 45 ml sample per employee by filling into a pre-cleaned and blank-level controlled glass vessel. After cooling in a refrigerator the samples have been sent to the laboratory within 24-h together with cooling elements and in an insulated packaging.

Analysis: Analyses of dioxins were executed in the Oekometric laboratory accredited according to ISO 17025 standard using isotope dilution method with $^{13}\text{C}_{12}$ -labelled dioxin standards. Blood was mixed with Na_2SO_4 in a ratio of 1:25 (w:w) and dioxins were extracted with hexane:iso-propanole 2:3 (v:v). Lipid content was determined by weight after evaporation of the solvent. Cleanup was based on mixed silica column method and aluminium oxide method and dioxins were eluted from the aluminium oxide column using hexane:dichloromethane 1:1.

Measurement of dioxins were performed using high resolution capillary gas chromatography on a Varian 3400 series unit (DB-Dioxin column) and high resolution mass spectrometry (HRMS) on a Finnigan MAT 90 system. Usual achievable limits of quantification (LOQ) for the dioxins were 2 pg I-TEQ/g lipid. Results are reported as upper bound levels including LOQ for not quantified congeners.

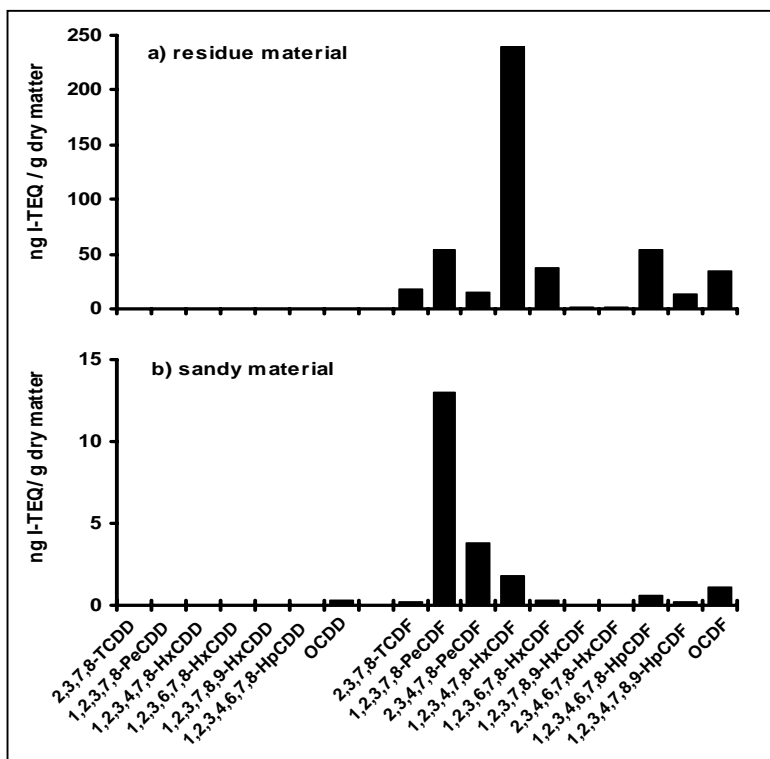


Figure 1: Typical PCDD/PCDF isomer patterns identified on the contaminated site.

Results and Discussion

The check of possible employees identified three person out of 28 with a level above 20 pg I-TEQ/g lipid (one level 32.9 pg I-TEQ/g lipid). The 12 monitored on-site employees showed a median levels of 12.2 pg I-TEQ/g lipid and a 90 percentile of 15.4 pg I-TEQ/g lipid (Figure 2). These levels are generally in good agreement with other data from Germany and Europe^{4,5} and thus, no increased PCDD/PCDF levels in employees blood could be identified. Between the two subgroups of employees according to their age, employees about 40 years old (P2 – P6) and employees about 50 years old (P7 – P12), no significant difference was observed.

Furthermore, with three exceptions (P2, P8, P9) all levels decreased within the one year monitoring period, for some employees quite significant. No significant correlation could be found for this decrease with the lipid content.

As the contaminated material on-site are dominated by PCDFs – especially by PeCDFs and HxCDFs - the isomer patterns of the individual blood samples have

been evaluated in view of variations in the relative PCDF pattern after on-site activities. With the exception of P7, no significant variation within relative PCDF patterns could be identified on an individual employee level (Figure 3). Only for employee P7 a slight increase of the relative contribution of 1,2,3,7,8-PeCDF could be observed (Figure 3), however, not combined with an increase of the I-TEQ level (Figure 2).

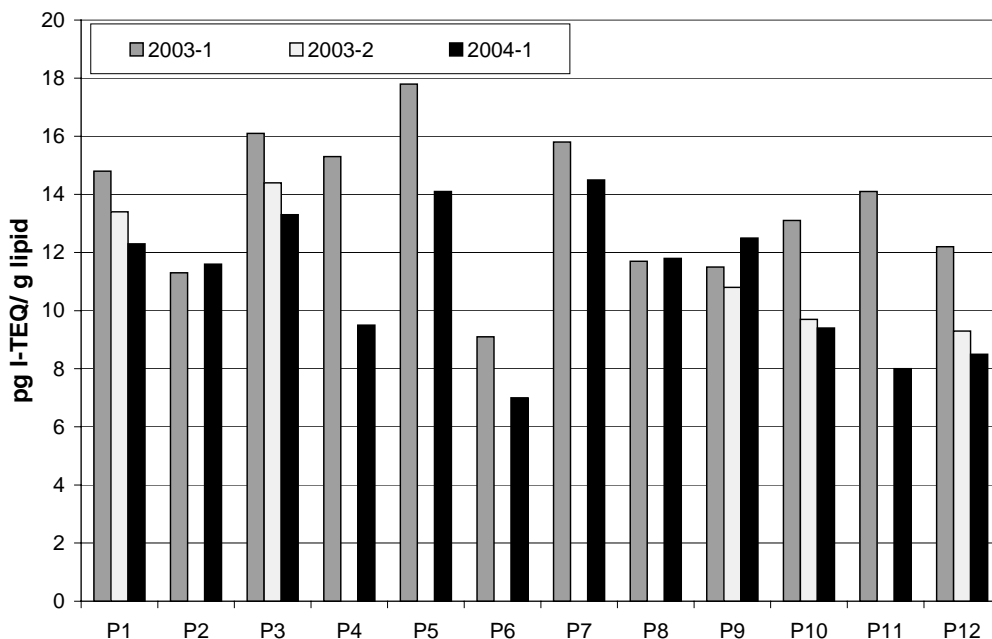


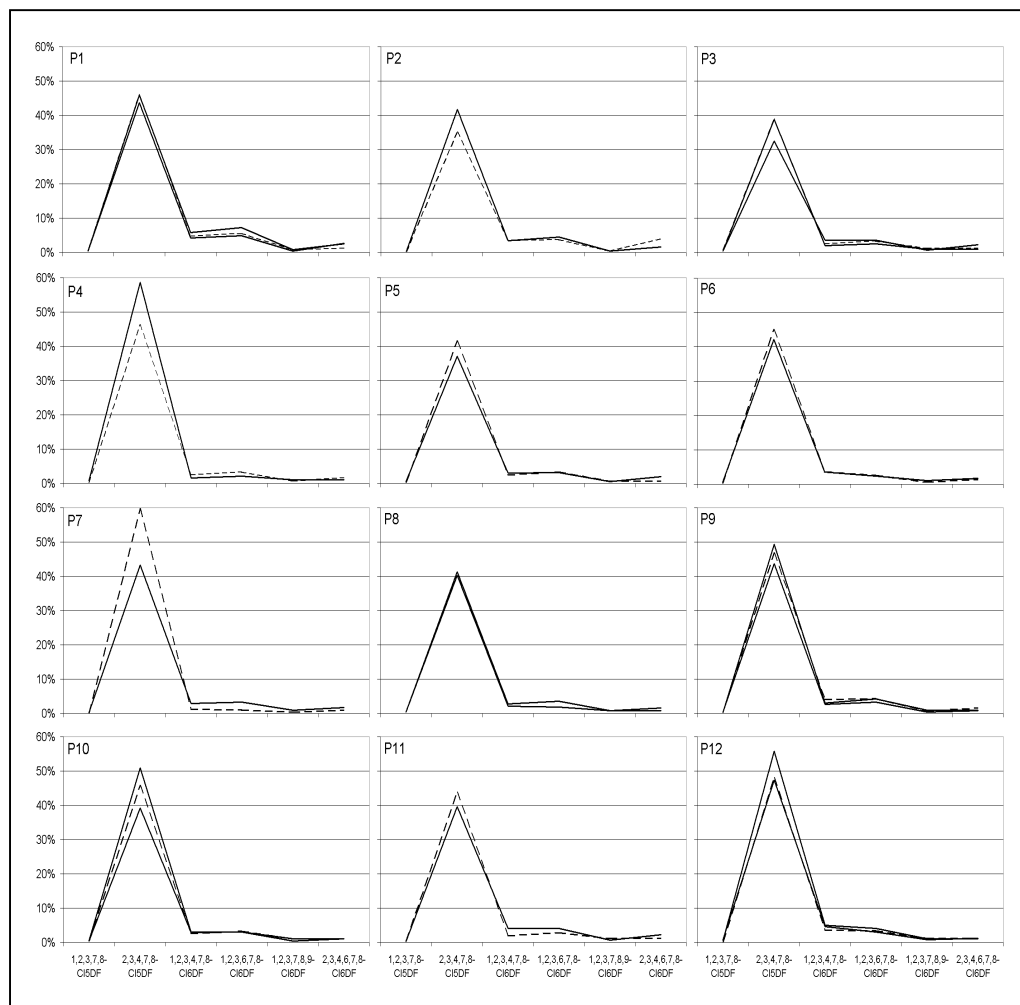
Figure 2: Dioxin levels (pg I-TEQ/g lipid) in human blood of employees.

The monitoring of employees PCDD/PCDF levels in blood during remediation of a contaminated site found no evidence for a significant additional dioxin burden due to working on-site and could confirm effectiveness of applied occupational safety measures.

References

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4. Wittsiepe J., Schrey P., Ewers U., Selenka F., Wilhelm M. (2000):
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Figure 3: Variation in relative PCDF patterns (PeCDF, HxCDF) after on-site activities

(2003 = — ; 2004 = - - -)