

## A Sampling and Analysis Scheme for Risk Analysis of a Highly PCDD/PCDF-Contaminated Sports Field

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### 1. Introduction

Slag from the mining of copper ore in North-Rhine-Westfalia/Germany during the 1930s and 1940s at an estimated total amount of 800,000 tons has been marketed as covering material for public play- and sports fields as well as for road construction. The common trading name for this copper slag was "Kieselrot" because of the reddish colour of the silicious material <sup>1</sup>.

It was only in 1991 when a survey of German playgrounds revealed very high concentrations of PCDD/PCDF. By tracing back the origin of the covering material, it could be shown that the former use of "Kieselrot" was the source of contamination. For total dioxins and furans more than 5,000,000 ng/kg (equivalent to > 100,000 ng TEQ/kg) and PCBs in the upper  $\mu\text{g}/\text{kg}$  range were measured <sup>2</sup>. Subsequently, many play- and sports grounds have been analysed and up to now more than 300 of these sites in Germany are known to be contaminated with "Kieselrot".

The presence of public areas, highly contaminated with PCDD/PCDF, poses a major problem not only to human health and environmental quality but also to the disposal of this large amount of material. Communities and sports clubs as owners of affected sites are concerned about the future use of their contaminated play- and sports grounds, while the problems of remediation or disposal still remain unclear. According to German laws ("Gefahrstoffverordnung" - Hazardous Substances Act <sup>3</sup> and "Gefahrgutverordnung Straße" - Act on Road Transport of Hazardous Material <sup>4</sup>), material which contains more than 5  $\mu\text{g}/\text{kg}$  of eight 2,3,7,8-chlorine substituted PCDD/PCDF must not be handled or transported without special precautions and legal permission.

### 2. Experimental

#### 2.1 Sampling

The site consists of two sports fields (Fields II and III) and one sprint-course. Prior qualitative and quantitative analyses of PCDD/PCDF indicated that "Kieselrot" had been used as covering material on considerable parts of the Field II and possibly on the sprint-course as well. Total PCDD/PCDF exceeded 1,000,000 ng/kg d.w. (dry weight) on some spots, especially on Field II and 100,000 ng/kg on the adjacent sprint-course,

# RISK

while Field III showed only relatively low contamination (total PCDD/PCDF <30,000 ng/kg d.w.).

Combining these preliminary results with the information available about the history of the site, a sampling scheme was developed, suitable to reveal the horizontal and vertical distribution of the PCDD/PCDF-contamination. Additionally we proposed the sampling of the drainage system, the sediment of the nearby river and private gardens in the vicinity in the prevailing wind direction.

From the surface of Field II and III (approx. 100 m x 60 m each) composite samples were taken from six grids (approx. 20 m x 30 m each). In vertical profiles composite samples were taken in layers of 5-10 cm down to a depth of 50 cm. The same procedure was applied to the sprint-course (approx. 60 m x 7 m).

Soil samples from the private gardens and the river sediment were refrigerated immediately after sampling and stored in glass bottles in the dark. A total number of 234 single samples were combined to 45 composite samples and prepared for chemical analysis.

## 2.2 Analysis

Prior to extraction 10 g of "Kieselrot" (or 100 g of soil or sediment, respectively) were dried for 15 hours at 105°C. Then the material was ground, spiked with a <sup>13</sup>C-labelled standard mixture of PCDD/PCDF (one isomer for each homologue) and extracted with toluene in a soxhlet apparatus for 24 hours. Clean-up was performed with column chromatography using different adsorbents (silica-gel and aluminum oxide). Finally the purified extract was concentrated to about 100 µL. Determination of PCDD/PCDF was done either with GC/LRMS (Hewlett Packard 5890 coupled with a HP 5970) or HRGC/HRMS (Varian 3000 coupled with a Finnigan MAT 90), respectively. To determine the recovery rate of 2,3,7,8-Cl<sub>4</sub>DD, an additional <sup>13</sup>C-labelled Cl<sub>4</sub>DD surrogate standard was added prior to injection.

Knowing that the upper layer of the sports fields contained high amounts of PCDD/PCDF, analysis with GC/LRMS (detection limit 1 ng/kg d.w. for each congener) was sufficient to detect all 2,3,7,8-substituted PCDD/PCDF congeners. In deeper layers of the site as well as in sediments and the vicinity of the sports fields significantly lower PCDD/PCDF-concentration were expected. Therefore analysis of these samples was done exclusively with HRGC/HRMS, which allowed a detection limit of 0.01 ng/kg d.w. for each congener.

## 3. Results

"Kieselrot" shows a characteristic homologue pattern dominated by the dibenzofurans. The most abundant congener is Cl<sub>8</sub>DF, which contributes about 50% of the total PCDD/PCDF-concentration. Concentrations increase from Cl<sub>4</sub>DD to Cl<sub>6</sub>DD and Cl<sub>4</sub>DF to Cl<sub>8</sub>DF and the ratio of Cl<sub>8</sub>DF/Cl<sub>6</sub>DD varies from 5:1 to 7:1 (see Figure 1).

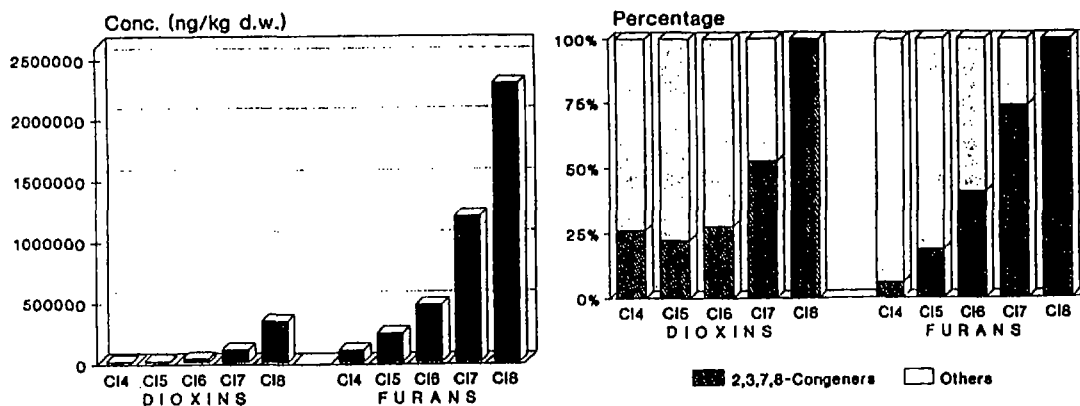


Figure 1: Homologue pattern (left) and percentage of 2,3,7,8-substituted congeners of the homologue (right) of a "Kieselrot"-sample from Field II.

Also the percentage of the 2,3,7,8-substituted congeners within the homologue features a relatively constant portion with 2,3,7,8-substituted PCDD contributing about 25% of the homologue for tetra- to hexa-chlorinated dibenzo-*p*-dioxins and about 50% for the Cl<sub>7</sub>-DD.

Table 1: Location and total number of samples analysed

Location	Number of Samples
Field II (vertical & horizontal)	14
Field III (horizontal)	3
Sprint-course (vertical & horizontal)	5
River sediment	5
Vicinity	5

Of a total number of 45 samples, 32 were analysed to investigate (Table 1) the site. This was regarded as sufficient to determine the vertical and horizontal distribution PCDD/PCDF-contamination. The rest of the samples were stored for reasons of quality control.

Highest concentrations were detected at the surface layer of Field II with  $\Sigma$  PCDD/PCDF of 4,767,000 ng/kg, resulting in a TEQ of 43,700 ng/kg. Concentrations decreased rapidly with increasing depth, and in the layer 18-23 cm PCDD/PCDF-concentrations fell to 728 ng I-TEQ/kg (Table 2).

Results indicate a contamination of Field II and the sprint-course originating from the use of "Kieselrot" as covering material. Furthermore, it could be shown that the original structure of the different layers according to German standards was still preserved. The contamination of Field III may be secondary due to transfer of copper slag particles by various processes, e.g. wind erosion and abrasion, or through maintenance. Very similar homologue patterns were found in "Kieselrot", soil and sediment samples. Thus, the transport of dioxin contaminated particulates from the sports fields to the drainage system via water and to the house gardens via air could be deduced.

# RISK

Table 2: PCDD/PCDF-concentration and TEQ of selected samples (ng/kg d.w.)

Location	Depth	$\Sigma$ PCDD/PCDF	TEQ
Field II	0-5 cm	4,767,000	4,700
	5-12 cm	648,900	7,450
	12-18 cm	170,100	1,720
	18-23 cm	85,100	728
Field III	0-7 cm	6,808	85
	0-7 cm	27,960	245
	0-7 cm	22,580	181
Sprint-course	0-10 cm	289,600	2,350
	10-17 cm	526,300	3,950
River Sediment (4 samples)		142-605	0.8-7.7
Soil (5 samples)	surface	208-2,880	2.2-58

## 4. Conclusions

The sampling and analysis scheme used in this case provided a powerful tool to locate vertical and horizontal distribution of the PCDD/PCDF-contamination of the sports fields. Furthermore the influence of "Kieselrot"-contamination in river sediments and adjacent private gardens could be shown. The data base obtained by the sampling and analysis scheme applied can be used for subsequent risk assessment.

## Acknowledgements

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## References

- 1 Stock, H.D., P. Fürst, W. König, and G.H.M. Krause (1991): Dioxinbelastung durch das Röstverfahren in der Marsberger Kupferhütte. *Organohalogen Compounds* 7, 97-122, ECOINFORMA Press, Bayreuth, Germany
- 2 Theisen, J., A. Maulshagen, and J. Fuchs (1993): Organic and Inorganic Substances in the Copper Slag "Kieselrot". *Chemosphere* 26, 881-896
- 3 Gefahrstoffverordnung (GefStoffV) vom 26.08.1986. *BGBI. I S.* 1931
- 4 Gefahrgutverordnung Straße (GGVS) vom 22.07.1985. *BGBI. I S.* 1326