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Hair: A Matrix for Non-Invasive Biomonitoring of Organic Chemicals in Mammals

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Human and environmental monitoring of organic chemicals has become increasingly important for exposure and risk assessment. Body fluids and tissues were commonly in use (Schaller et al. 1993) to characterise human exposure. Unfortunately this approach results in integrative description of exposures (long-term) in the past without enabling us to identify distinct body burdens. Hair has been identified as suitable alternative and overall bioindicator for short- and long-term exposure of organic xenobiotics (Schramm et al. 1991, 1992, 1993).
Recently, protected mammals as icebears or seals were epidemiologically affected by diseases of more or less unknown natural or chemical origin. Hair as the substantial part of the definition of mammals can serve as bioindicator for human monitoring and observation of xenobiotic impact of protected populations (Schramm 1995). It has to be acknowledged that commonly invasive monitoring with animals proceeds by often unlicensed killing a lot of individuals. In contrast non-invasive instruments of biomonitoring allow repeated sampling of the same individual. A scheme of the exposure paths for organic chemicals as polychlorinated Dibenzo-p-dioxins and Dibenzofurans (PCDD/F) or polychlorinated Biphenyls (PCB) are shown in Fig. 1. PCB- and PCDD/F - pharmacodynamics in animals and man result in congeners present which are not readily excreted or metabolised and thus can be highly accumulated. Therefore, the presence of non-persistent congeners must be attributed to external gaseous or particulate exposure. So far a differentiation of external and internal pathways of exposure becomes possible. Ingested and inhaled tetrachlorinated PCDDs are completely metabolised, except the 2,3,7,8-tetrachlorodibenzo-p-dioxin which is persistent and accumulates in the mammalian body. An external exposure of hair leads to a congener pattern that also contains the non-persistent isomers. Using the information from the PCDD/F-pattern the source and pathway of exposure can be identified.

MATERIALS AND METHODS

In the experiment on the partition of gas and hair, hair was exposed to gaseous PCB (Clophen A 40) in a closed system. Adsorption traps in the outflow allowed the semicontinous measurement of the gas concentrations. The gasbulk flow

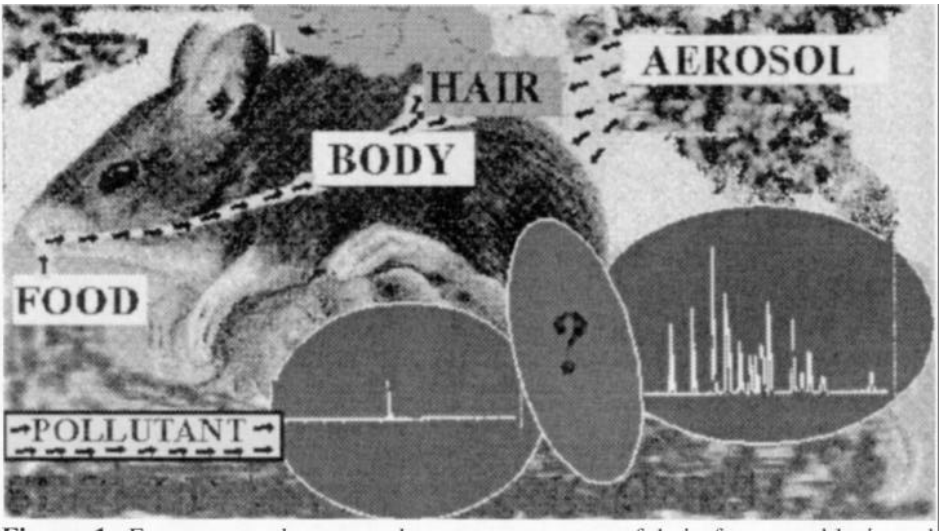

Figure 1. Exposure pathways and system response of hair for tetrachlorinated Dibenzo-p-dioxins.

applied was measured by two flowmeters in the in- and outflow. At certain times samples of hair in the exposure chamber were taken to resolve the kinetics of accumulation and elimination. The concentrations of PCB in hair and air were analysed applying a simple clean-up followed by isotope dilution and measurement with high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS).

The fire experiment was performed in a large hall, where furniture was burned and fire fighting exercised. Hair was exposed in an open glass vessel (500 ml) during the fire event. A wipe sample was taken from a 1 m^2 stainless steel platform. Wiping was done with toluene and cotton wool until the steel was free of soot again. Air sampling was performed according to the VDI 3498 Blatt 1 with a high volume sampler during the fire event (about 1 h).

Dry hair was cut in a usual manner to achieve a normal dressing and a sample between 1 and 5 g was taken. The hair was wrapped in aluminium foil and additionally stored in polyethylene bags and closed by melting.
For the analytical determination of PCDD/F and PCB a $^{13}C_{12}$-labeled internal standard mixture of sixteen 2,3,7,8-substituted PCDD/F, eleven PCB and HCB was added to the sample. After 'Soxhlet'-extraction of the sample with toluene for 24 hours the raw extract was treated with multi-column chromatography method (Schramm et al. 1992). This clean-up for PCDD/F combines a set of 4 established chromatographic steps in series, first chromatography on silica, secondly activated alumina, thirdly sulfuric acid coated silica gel and last deactivated florisil™. Before quantification by high-resolution GC/MS the sample was spiked with a recovery standard. After splitless injection the sample was separated on a Rt_x-2330 GC

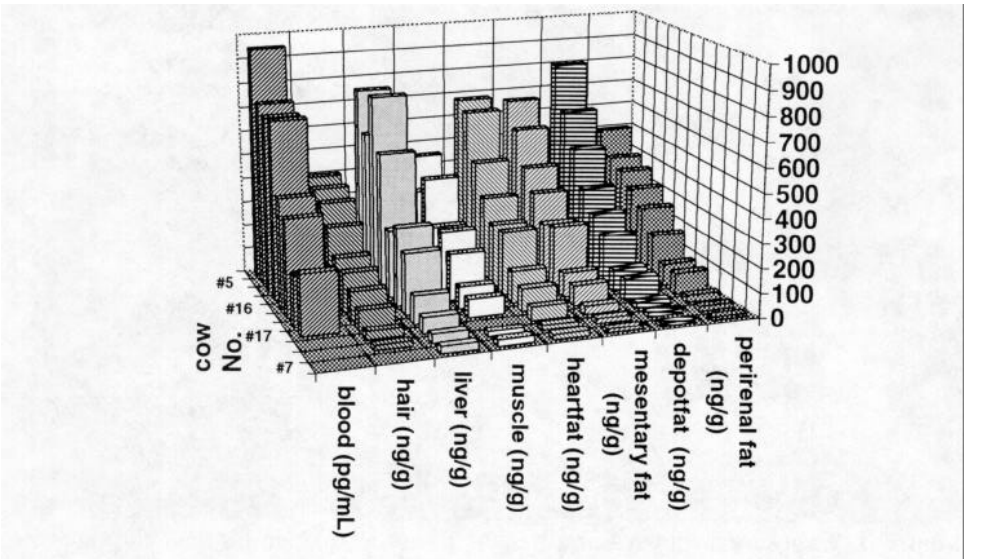

Figure 2. PCB 153 in tissues, blood and hair of 11 individual cows after ingestive exposure (Klein et al. 1992)

column (60m x 0.25mm x 0.25pm) and quantified by Finnigan MAT 95 mass spectrometer at resolution of 10000. The fraction of PCB was separated in the PCDD/F clean-up (activated alumina column chromatography, benzene and n-hexane/dichloromethane (98/2 v/v) fraction) (Wu et al. 1995). Further PCB clean-up includes: first size exclusion chromatography (GPC), second chromatography on sulfuric acid coated silica gel and at last C_{18} RP silica gel for removal of long chain hydrocarbons. The extracts were spiked with a recovery standard and analyzed by GC/MS. After splitless injection the sample was separated on a DB-5 MS (60m x 0.25mm x 0.1µm) and quantified by Finnigan SSQ 7000 mass spectrometer at resolution of 1000 in EI mode. For better sensitivity non-ortho PCBs were quantified in negative chemical ionization mode (NCI).

RESULTS AND DISCUSSION

In 1991 the occurrence of PCDD/F on hair was reported for the first time (Schramm et al. 1991). At that time partition coefficients between ambient air and hair were estimated, which were confirmed by simple partition experiments for PCB (Schramm and Kettrup 1995). At the same time Klein and coworkers (Klein et al. 1992) reported about relationships between milk, depotfat and hair concentrations of PCB in cows. The values for PCB 153 after ingestive exposure are shown in Fig. 2.

The elimination of PCB congeners is very similar in the different body compartments. Thus, the authors emphasize hair as a matrix of non-invasive monitoring purposes for xenobiotics as PCB.

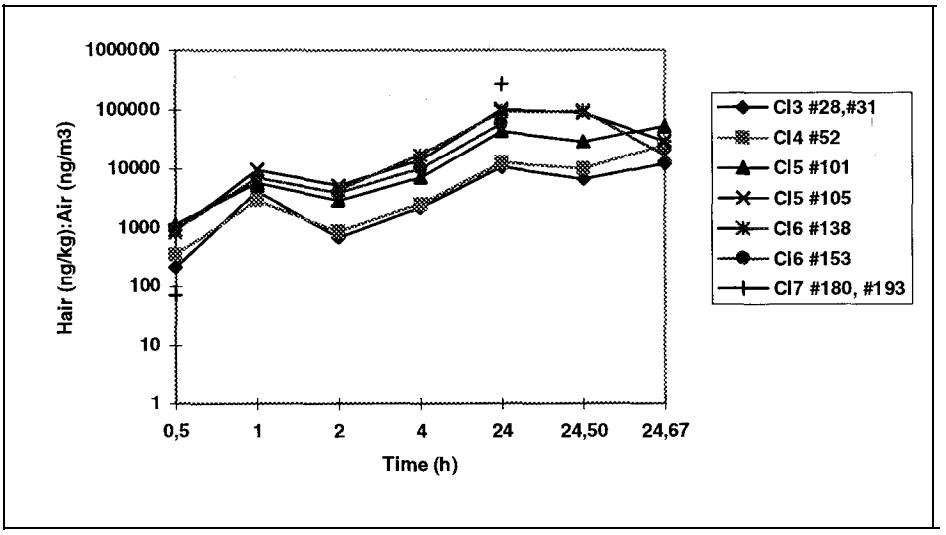

Figure 3. Partition coefficients hair-air of different chlorinated biphenyls (C13 to C17-PCB) after several durations of exposure.

The analysis of heavy metals and drugs in hair has been investigated more intensively in the past and is used as evidence in judgement. In some cases the analytical investigation of drug metabolites became necessary to enlarge safety of decisions (Fey 1993). The interpretation of element concentrations in hair for exposure and hazard assessment is lacking due to difficulties in differentiating between internal and external exposure (Chatt 1988).

After showing the presence of chemicals such as PCDD/F in hair, an important question was asked about the dynamics of adsorption and desorption of relevant compounds on hair. A fast adsorption and a slow desorption are of importance to rule out exposure before the next hair washing.

First investigations (Fig. 3) have shown that the main part of accumulation had been finished very quickly (< 1h). It is obvious that the partition between hair and air is completed fast. In addition a relationship between vapour pressure of the chemical and partition coefficient can be shown. The order of magnitude of the partition coefficients leads to a detectable accumulation of such chemicals caused by ambient air concentrations. These findings guarantee the detection of the outcoming exposition and the estimation of corresponding air concentrations. Similar results are expected for chemicals with similar physicochemical properties (PCDD/F, PAH, and some pesticides).

The obtained results of PCB and PCDD/F in hair show asymmetric frequency distributions (Fig. 4). However, the number of measurements is currently too small to evaluate general conclusions. Pooled samples will be a cheap approach in the future to detect regional or time dependent influences.

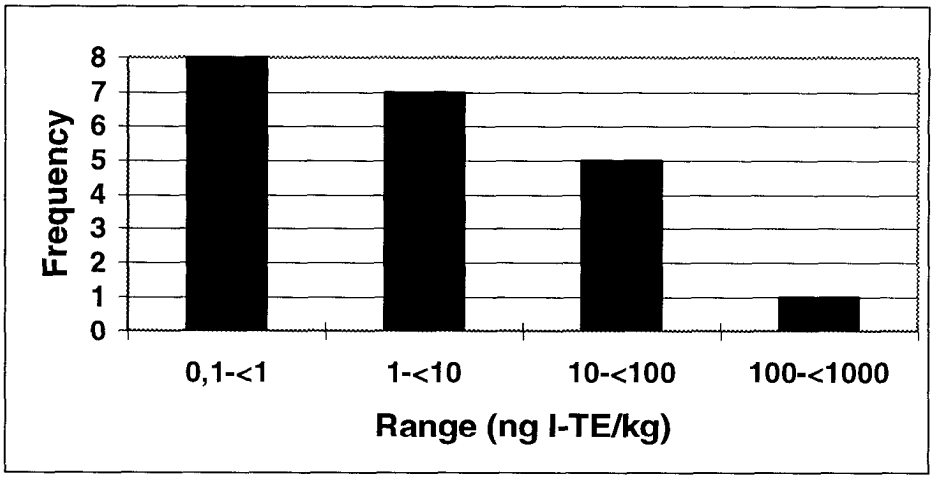

Figure 4. Frequency of PCDD/F I-TE-values in human hair

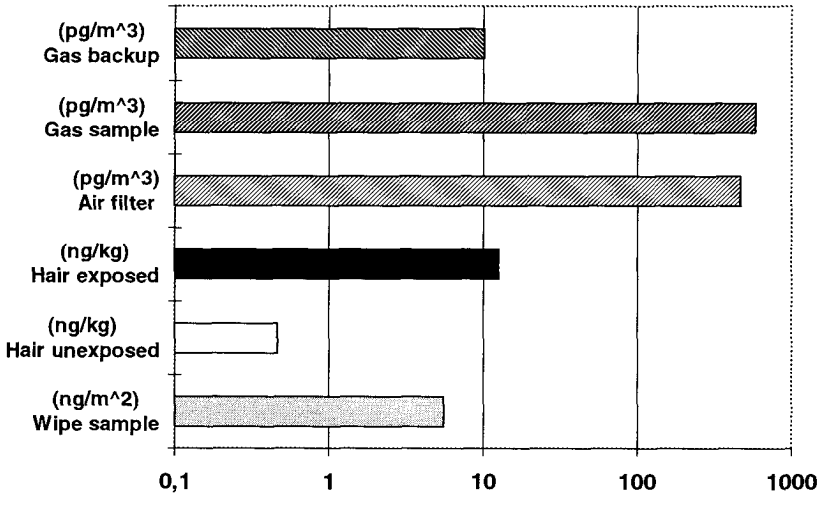

Figure 5. Concentrations of PCDD/F (I-TEQ) on hair before and after a 30 min fume exposure and corresponding air conditions

Firehouse experiments with exposed hair result in a high accumulation of polychlorinated Dibenzofurans (PCDF) after burning of PCB as by-product (Fig. 5). A similarity of fume PCDF pattern and hair pattern was obvious.
These investigations promise the applicability of hair biomonitoring in human residences and working places.

Hair analysis of PCDD/F and similar compounds is a cheap and fast, and analytically simple biomonitoring system to detect short- and long-term exposure. A method for short-term exposure studies of PCDD/F and related chemicals has not been available before.

Selenka et al. (1993) was not able to differentiate between firefighters and a reference group measuring PCDD/F in blood. Such results are not expected using hair as bioindicator.

Future research has to focus on partition between blood, tissues and hair for different exposure scenarios (Working place, indoor, urban and rural areas etc.) to characterise cohorts epidemiologically. Experiments and results from different types of hair will rule out intra- and inter-species relationships. Hair biomonitoring will overcome ethical problems and difficulties due to availability, cost and labour of exposure monitoring and risk assessment.

Hair monitoring will provide:
1. an ethically acceptable, cheap and easily applicable monitoring system for human and animal samples especially for protected animals.
2. a first system for elaborating the **short-term** and long-term exposure of individuals by ruling out the relationships between hair and body liquids and tissues (worst case exposure)

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