

Polychlorinated dibenzo(p)dioxins and dibenzofurans in ambient air; concentration and deposition measurements in Hessen, Germany

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At the end of 1989 the Hessische Landesanstalt für Umwelt, Wiesbaden, Germany started extensive measurements of polychlorinated dibenzo(p)dioxins and dibenzofurans in ambient air at which those compounds were - respectively are - measured as suspended particulate matter ("concentration measurement") and as part of the bulk deposition ("deposition measurement"). The collection of the suspended particulate matter samples is carried out in a way which guarantees the sampling of the gaseous portion as well.

Methods

The collection of the suspended matter is carried out by use of so-called LIB filter devices, which are equipped with glas fibre filters for the sampling of particulate PCDD/F and an additional unit (PU-foam spiked with $^{13}\text{C}_{12}$ -1234-TetraCDD standard for controlling of the sampling efficiency) for the adsorption of the gaseous PCDD/F portion.

The collection refers to an air volume of 1000 m³ for each sample being taken over a time of 72 hours. The later reported yearly means correspond to 21 of those samples, which are collected nearly every 18 days.

The deposition samples are taken by the Bergerhoff method. This method uses cylindrical glas containers with a volume of 1500 cm³ and an efficient sampling cross section of about 62 cm². The sampling devices are exposed for about 30 days to the ambient air. Each deposition sampling field covers a region of about 1 km². To get enough mass for the later laboratory analysis, for one analysis result the contents of 10 sampling containers are joined together in the laboratory.

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For the PCDD/F analysis the above mentioned samples are extracted with toluene in a soxhlet apparatus (before soxhlet extraction the deposition samples are divided into a solid phase and a water phase of which the water phase is preextracted with that toluene used for soxhlet extraction). Prior to extraction ten $^{13}\text{C}_{12}$ -labelled PCDD/F standards are added to the toluene (one compound for each homolog group). The extract is purified several times by column chromatography. Recovery rates of $^{13}\text{C}_{12}$ -labelled compounds are determined by adding further standards prior to GC/MS analysis.

After separation by capillary gas chromatography on a polar stationary phase (SP 2331) the PCDD/F are detected by high resolution mass spectrometry.

The laboratory analysis as well as the preparation of the sampling devices and the collection of the suspended particulate matter samples are carried out by the GfA - Gesellschaft für Arbeitsplatz- und Umweltanalytik mbH Otto-Hahn-Str. 22, D-4400 Münster, Germany².

Sampling places

During the years 1990 to 1992 "concentration measurements" were performed on ten locations of different pollution character to get a first rough survey over the pollution situation by polychlorinated organic compounds in Hessen. Longterm measurements are carried out on the four places

Riedstadt-Crumstadt	(rural region with some industry)
Frankfurt-Griesheim	(industrial / living area)
Hanau	(industrial area)
Hünfelden-Kirberg	(rural area, "background-situation")

For "deposition measurements" the three of the above mentioned locations **Crumstadt**, **Griesheim** and **Kirberg** have been selected and there are provided longterm measurements as well.

Results

The results (summarized as yearly means) are plotted in figure 1 for the concentration measurements and in figure 2 for the deposition measurements.

As figure 1 shows the concentration measurements indicate a variation of I-TEq-values about a factor of two between rural and industrial regions in a range of 0.04 to nearly 0.15 pg/m^3 at which the 0.15 pg/m^3 in Hanau are due to a direct local industrial influence. Furthermore the measurements show a reduction of the PCDD/F-content in air on nearly all stations in the range of about 25% to 40% during the measuring period from 1990 to 1992. Even at the Hünfelden-Kirberg location, which lies in a rural region far away from any industrial area or bigger city we found a reduction in PCDD/F concentration of about 25% from the year 1990

to 1992. The reason for this reduction is not investigated up to now, may be technical improvements in processes concerning any kind of energy production or waste incineration in the last years. Up to now we got no indication that the PCDD/F-reduction is caused by changes for

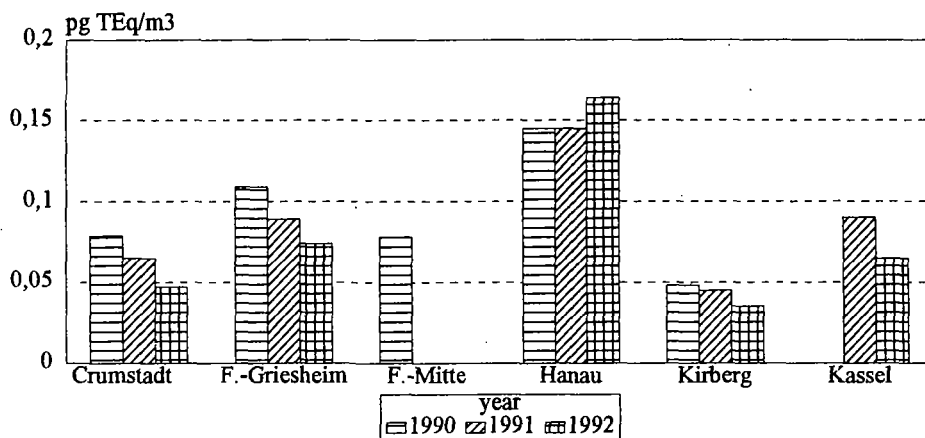


Figure 1: Dioxin-/Furan-concentration in Hessen, annual I-TEq-means 1990 - 1992

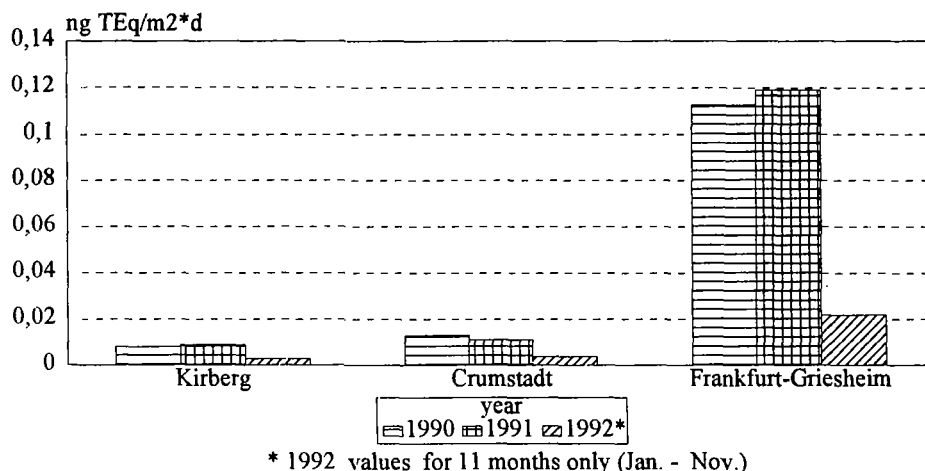


Figure 2: Dioxin-/Furan-deposition in Hessen, annual I-TEq-means 1990 - 1992

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example in the yearly meteorological conditions. Nevertheless the long-term measurements have to be carried on to get further results which confirm or - may be - which refute our above given interpretation.

Similar to the concentration measurements the deposition measurements indicate a reduction of PCDD/F-I-TEq-values during the last three years. The annual means vary between 0,003 and 0,013 ng/m²·d in rural areas and up to 0,12 ng/m²·d in an industrial region; the higher values in Frankfurt-Griesheim during the years 1990 and 1991 are due to erosion effects from an industrial landfill near the location of the sampling device. At the end of 1991 the problem was solved by covering this landfill with "clean" soil, so that the spreading of PCDD/F-containing dust could be stopped. In both cases (increased PCDD/F-concentrations in Hanau and increased PCDD/F-depositionrates in Frankfurt-Griesheim) the responsible sources could be identified by comparison of the characteristic congener pattern. The profiles from the emission source and the ambient air samples in our two cases had been compared in the sense of a "finger-print" study with very clear results identifying the responsible sources. In the case of Hanau an analysis of the wind directions confirmed the results of the "finger-print" study.

The hessian PCDD/F-results indicate clear annual variations with higher values during the winter months. This annual trend is more pronounced in the air concentration than in the deposition values.

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