

FORMATION AND SOURCES I -POSTER

CONCENTRATIONS OF POLYCHLORINATED DIBENZO-P-DIOXINS, DIBENZOFURANS AND BIPHENYLS IN TYRES

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Introduction

The abrasion of tyres on German roads amounts to about 60,000 - 65,000 t per year [1,2]. The fine dust is spread out into the environment, precipitates on soils and plants, and can be inhaled by humans.

Tyres are produced from a complex mixture of synthetic and natural components: appr. 70% rubber mixture (mostly synthetic), 15% steel, 15% textile fibres, mineral substances and others. The rubber mixture contains about 30% of soot, which is produced by incomplete combustion of hydrocarbons like colophony, naphthalene or tar oils.

Because polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF) and biphenyls (PCB) are formed during combustion processes in the presence of chlorine, it may be possible that the soot used in tyres is contaminated with these compounds. To investigate this we analyzed several car tyres from different manufacturers to get an impression whether the abrasion of tyres represents a remarkable entry path of PCDD/F and PCB into the environment.

Methods and Materials

Ten samples of used tires, each from a different manufacturer, were analyzed for PCDD/F and PCB. A part of the tread was cut out of each tyre and further was cut into small pieces. Then this was ground in a variable speed rotor mill "pulverisette 14" (Fritsch, Germany) by adding liquid nitrogen to get a fine powder. About 10 g of each sample was spiked with ¹³C-labelled PCDD/F and PCB standards and extracted in a Soxhlet apparatus with cyclohexane for 24 h. The following clean-up is shown in figure 1. The instrumental analysis for PCDD/F was performed with a high resolution mass spectrometer (Finnigan MAT 95S) coupled with an Agilent GC 6890. Chromatographic separation was achieved by splitless injection (temperature programmable injector KAS4, Gerstel, Germany) of 1 µl on a Restek Rtx-2330 column (60 m, ID 0.25 mm, ft 0.1 µm). The GC oven was programmed as follows: 90°C initial hold for 1.5 min, increase at a rate of 25°C/min to 180°C followed by an increase of 2°C/min to 260°C, final hold at 260°C for 15 min.

For PCB analysis a high resolution mass spectrometer (Finnigan MAT 95) was used coupled with an Agilent GC 5890 Series II. Chromatographic separation was achieved by splitless injection (temperature programmable injector KAS3, Gerstel, Germany) of 0.5 µl on a J&W DB-5ms column (60 m, ID 0.25 mm, ft 0.1 µm). The GC oven was programmed as follows: 90°C initial hold for 1.5 min, increase at a rate of 20°C/min to 170°C, hold for 7.5 min, followed by an increase of 3°C/min to 280°C, final hold at 280°C for 10 min.

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Both MS were operated in SIM mode at a resolution of 10000 (MAT 95S) or 8000 (MAT 95) and the two most intense ions of the molecular ion cluster were monitored for the unlabeled and labeled isomers.

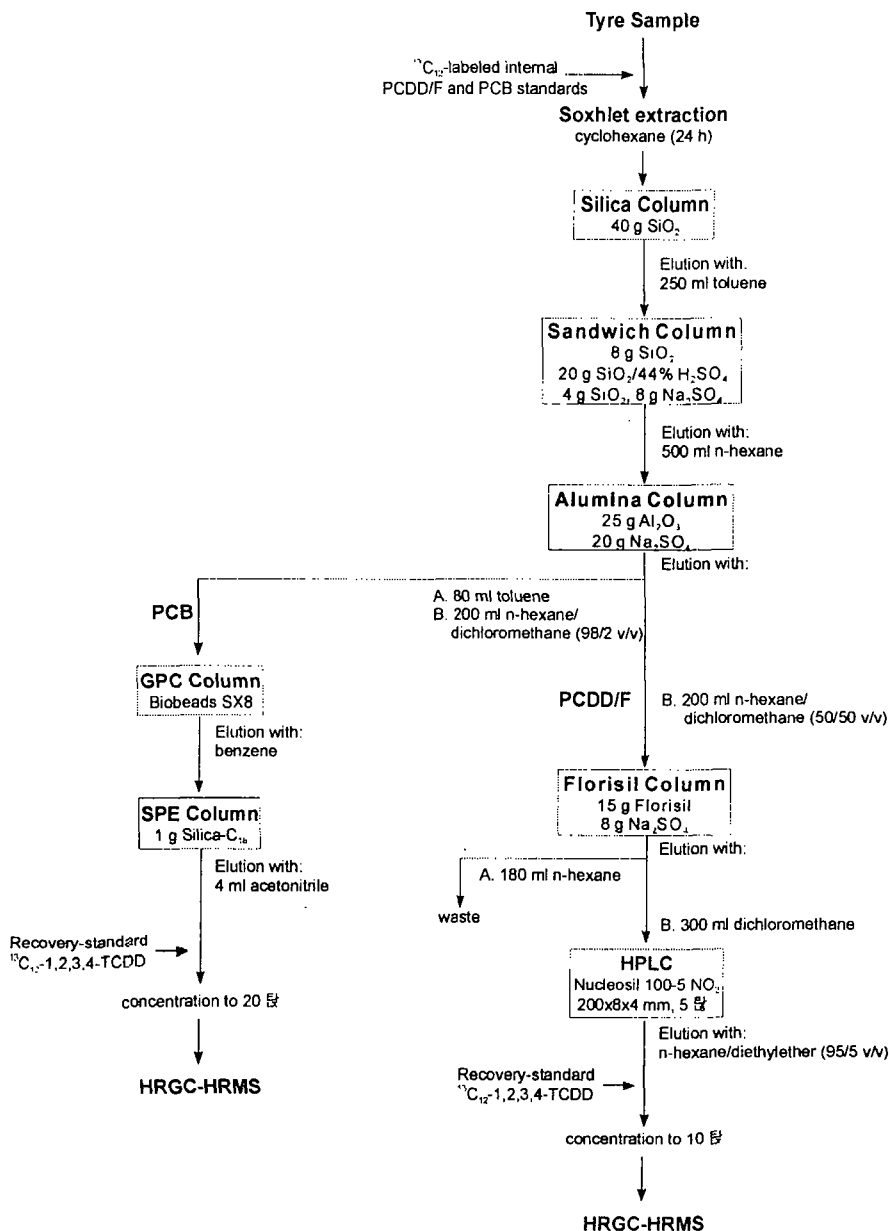


Figure 1: Clean-up procedure for the tyre samples

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Results and Discussion

Due to the complex mixture of components in the tyres, it was necessary to optimize the extraction solvent and to perform an extensive clean-up.

Toluene as a common extraction solvent for PCDD/F was not very suitable, because it nearly dissolves the complete rubber mixture. After evaporation of the solvent to 2-3 ml a very viscous residue was left, which was hard to handle and often plugged the chromatographic column of the first clean-up step. Cyclohexane was proven to be a good alternative and the results were in good agreement with those of toluene.

Another problem were the high amounts of polycyclic aromatic hydrocarbons and other aromatic compounds, which disturb the final chromatography on the GC column. It was not possible to completely separate them from the PCDD/F fraction with the first clean-up steps. Here a HPLC separation on a Nucleosil-NO₂ column was the method of choice.

The concentrations found in the tyre samples are listed in table 1. There is a wide variation in the WHO-TEQ values (for humans) for the PCDD/F (0.3 to 181 pg/g) and in a smaller extent also for the PCB (1.3 to 10.1 pg/g). Certainly an explanation for this is that we choose tyres from different manufacturers who likely have their own suppliers for the raw products.

Tab. 1: Concentrations of PCDD/F and PCB in tyre samples (in pg WHO-TEQ/g, "-" = not analyzed)

pg WHO-TEQ/g	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
PCDD/F	1.6	24.7	54.2	6.6	0.3
PCB	1.3	-	2.0	2.1	2.0
	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
PCDD/F	0.3	181	15.1	13.6	6.3
PCB	-	10.1	-	1.8	-

To estimate the total amounts of PCDD/F and PCB which are released to the environment by the abrasion of the tyres the median of the concentrations found is used (PCDD/F: 10.1 pg TEQ/g, PCB: 2.0 pg TEQ/g). Calculating with 60,000 – 65,000 t of abrasion this results in a load of 606 to 657 mg WHO-TEQ for the PCDD/F and 120 to 130 mg WHO-TEQ for the PCB per year.

Comparing this results for the tyres investigated with the estimated total annual PCDD/F emissions of about 70 g I-TEQ [3] or less in Germany, the abrasion of tyres seems not to be an important or underestimated source for PCDD/F and PCB until now. In addition there are about 5-10 g PCDD/F TEQ stored in the tyres that will undergo material turnover.

Conclusions

Although the percentage contribution of the tyre abrasion to the annual emission of PCDD/F-TEQ seems to be low, the very different concentrations of PCDD/F and PCB in the tyres may encourage the manufacturers still to minimize them to the lower end of the amounts we already found.

References

- [1] Stark, R., (1995) Kautschuk Gummi Kunststoffe 48, 448
- [2] Baumann, W. et al., (1998) Kautschuk Gummi Kunststoffe 51, 182
- [3] UNEP Chemicals (1999), Dioxin and Furan Inventories – National and Regional Emissions of PCDD/PCDF