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INFLUENCE OF LINEAR ALKYLBENZENE SULFONATE (LAS) AS ORGANIC COSOLVENT ON LEACHING BEHAVIOUR OF PCDD/Fs FROM FLY ASH AND SOIL

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Abstract

The leaching of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) was measured in soil and standard fly ash column eluted with pure water and linear alkylbenzene sulfonate (LAS) - water. The data obtained were used to evaluate the leachability of PCDD/Fs from waste dump like incineration residual slag and fly ash deposition. The leaching rate was shown to be increased significantly by using LAS water. The leachate contents of PCDD/Fs were above their known water solubility. Concentration of PCDD/Fs in the leachates as well as the relative leaching (calculated on the fly ash content) increased with increasing chlorinating degree and decreasing water solubility. LAS above the critical micelle concentration (CMC) probably enhances PCDD/Fs solubility.

Key Words: PCDD/Fs, leaching, linear alkylbenzene sulfonate (LAS), soil, fly ash

Introduction

Millions of tons of municipal waste are incinerated every year worldwide producing a large amount of fly ash and slag will be produced in the incineration. Therefore, disposal of the incineration residues is a rapidly grown problem (Ballschmiter, Scholz, 1983; Hagenmaier, She, Lindig, 1992). Development of

decisive criteria to evaluate the environmental behaviour of fly ash deposition becomes very important. Leaching tests are often used to simulate mobility under dump conditions.

Currently, no reports have shown that PCDD/Fs can be transported significantly in soil or leached from fly ash or soil by water or rain. Solution experiments based on the instructions of the German DIN 38414 test showed only a more or less artificial solution of the high chlorinated congeners due to difficulties in separating the particles from the solvent phase (Fischer, Lorenz, Bahadir 1992). The main amount of PCDD/Fs was bound to particular organic carbon which were not centrifuged quantitatively. From recent research results, leaching experiments from fly ash and soil with fire-extinguishing water resulted in significant amounts of PCDD/Fs in the leachates (Schramm et al., 1995). The surfactant (fatty alcohol sulphate) as cosolvent present in the fire-extinguishing water can enhance PCDD/Fs solubility and leachability.

Linear alkylbenzene sulfonate (LAS) has been found to increase water solubility of chemicals (Pennell, Abriola, Weber, 1993). LAS is used primarily as an ionic surfactant in detergents and cleaning products. The commercial material consists of a complex mixture of homologues and isomers. Individual LAS homologues of isomers are identified by alkyl chain length and by the position of attachment of the benzene sulphate on the chain. The mixture frequently used in detergent formulations has an average chain length of 10-13 and a phenyl position between 2 and 6 (Hand, Williams, 1987). A large amount of LAS is disposed to sewage and removed during primary and secondary sewage treatment. Low but measurable concentrations of LAS have been reported in river and estuarine sediment. Therefore, the influence of LAS as eluent on the leaching of PCDD/Fs was investigated in this study. Whether the transport mechanism of PCDD/Fs is caused by adsorption on non-filterable fine particles is also checked and discussed.

Experimental

Chemicals and Soil

LAS: ALDRICH, tech. grade. Critical micelle concentration (CMC) is 0.5g/l, the concentration of the LAS water used for elution is 1.5g /l, three times the CMC. The properties of the soil are listed in Table 1. The investigated soil was a German reference material of the type Inceptisol Unbrett and was purchased from the Landwirtschaftliche Untersuchung sund Forschungsanstalt Speyer. The packing of the soil column was very homogeneous, thus wall effects or transport of liquid or solids through large pores could be excluded.

Table 1: Properties of the soil using in the leaching experiment

specifications of soil	characteristics	standard deviation
total carbon	0,6 %	0,2
clay	4,4 %	0,6
silt	4,8 %	0,9
sand	90,2 %	4,2
pH (H_2O, $CaCl_2$)	6,1	0,4
cation exchange capacity	36 mole charge/kg	0,5

Leaching tests

The leaching experiments are depicted in Figure 1. A storage vessel was connected with two glass columns (i.d. 50x300mm) in series. Both columns were equipped with glassfilter discs (16µm pore size). For column preparation fly ash and soil were always mixed with equal weights of seasand to improve the percolation.

The vessel supplied this leaching system with LAS from which percolated the two columns by gravity. The percolation flow rate was 20±5ml/h. The infiltration capacity of the soil was not overridden because a supernatant in soil columns could not be observed during leaching experiments.

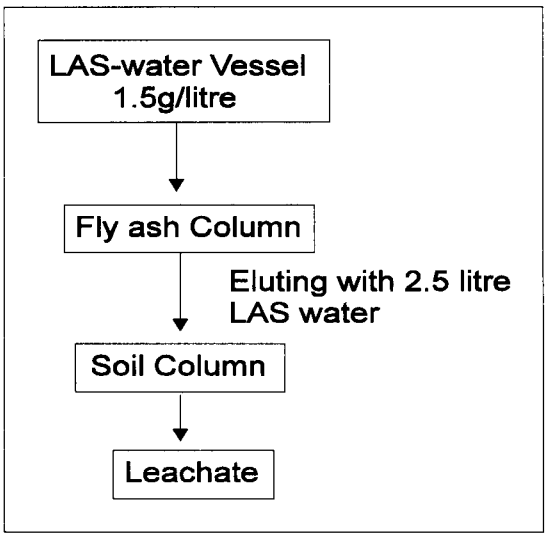

Figure 1: Schematic plot of the leaching experiments

(1) The first experiment was carried out according Figure 1. The second column only contained discs filter and 20g seasand without soil. The fly ash was eluted with pure water and LAS water.

(2) The second experiment was performenced with soil columns of 4cm and 18cm length, respectively. The column was eluted by LAS water.

After finishing the experiment the soil columns were frozen (-80^{0}C). The column of 18cm length was carefully cut into layers of 2cm depth, the column of 4cm length was mixed and analysed as a whole. The leachate was sampled in a glass vessel and analysed as a whole.

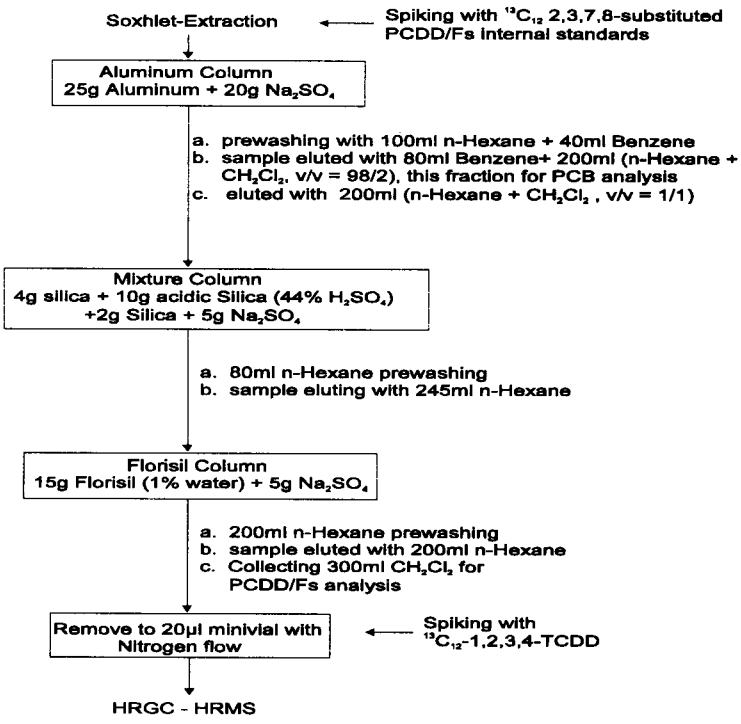

Figure 2: Clean-up procedure of PCDD/Fs analysis

PCDD/Fs Analysis

The PCDD/Fs analysis included the following steps:

1. Addition of labelled standards to the sample

(isotope dilution method)

Prior to extraction the sample is spiked with the $^{13}C_{12}$ labelled 2,3,7,8-substituted PCDD/Fs internal standards.

2. Quantitative extraction of 20 to 25g of lyophilised sample was carried out by Soxhlet extraction for 24 hours with toluene for the solids. Liquids were pre- conditioned with concentrated sulphuric acid and then stirred with toluene for 24 hours. After phase separation of the aqueous and the organic phase latter was subject to PCDD/Fs analysis, organic phase was passed through a Na_2SO_4 column.

3 Clean-up scheme is included in Figure 2.

4. Quantification

The identification and quantification were accomplished with capillary GC/MS systems where high resolution gas chromatography (HRGC) is obligatory. Capillary column (Restec RTx-2330, 60m in length, 0.25mm ID, 0.1μm df) was applied. The temperature program was: $90^{o}C$(1.5min) to $180^{o}C$(0min) with rate of $25^{o}C$/min, then to $260^{o}C$(30min) with rate of $2^{o}C$/min. The injection was done with a Gerstel system where the sample was injected as a liquid. The injector was programmed as follows: $120^{o}C$(0min) to $280^{o}C$(10min) with rate of $12^{o}C$/s, then to $300^{o}C$(10min) with rate of $12^{o}C$/s. The column head pressure was 24psi. The interface was heated at $260^{o}C$. The PCDD/Fs were commonly determined by mass spectrometry in the EI mode by tracing their M^{+}, $(M+2)^{+}$ ions or the most intensive ions of the isotope cluster. The measurement was conducted with high resolution (R=10000) at a Finnigan MAT 95 mass spectrometer.

Results and Discussion

The PCDD/Fs pattern of unleached fly ash is shown in Figure 3 and all homologues are present in sufficient amounts. It was suitable for the leaching experiment. The homologue profile of leachate from the fly ash without soil is plotted in Figure 4. Obviously all homologues have been leached by the LAS water at considerable amounts (Figure 4) much more than was leached by pure water. In fact the content of PCDD/Fs in the leachate by pure water is very low. This results indicate the transport of particles is not so important to the leaching of PCDD/Fs in the fly ash and soil. The suggested mechanism is that LAS above the critical micelle concentration (CMC) as cosolvent enhance the water solubility of PCDD/Fs.

From Figure 4, the pattern of PCDD/Fs congeners in the leachate is surprisingly shifted to high chlorinated PCDD/Fs which is in contrast to the corresponding water solubility of the PCDD/Fs. The concentrations of higher chlorinated PCDD/Fs are far above their water solubility (Fiedler, Schramm, 1990; Friesen, Sarna, Webster, 1985).

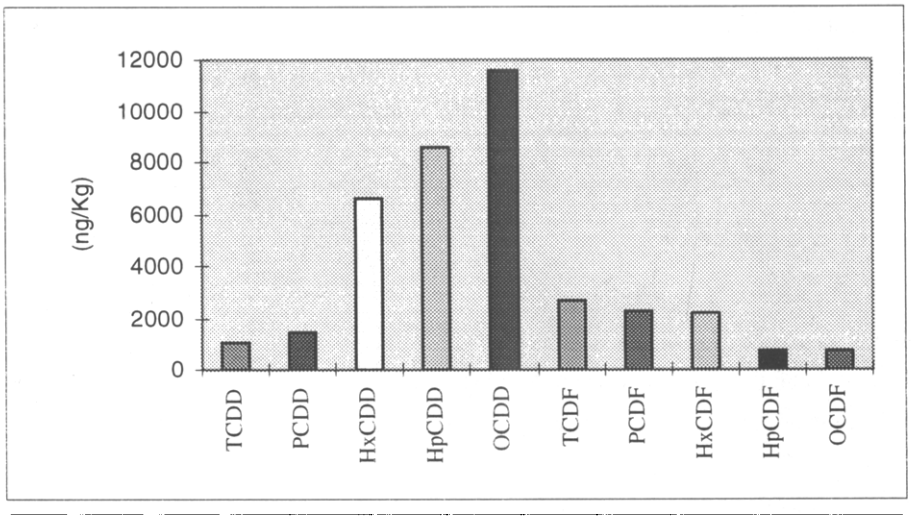

Figure 3: PCDD/Fs pattern of the unleached fly ash

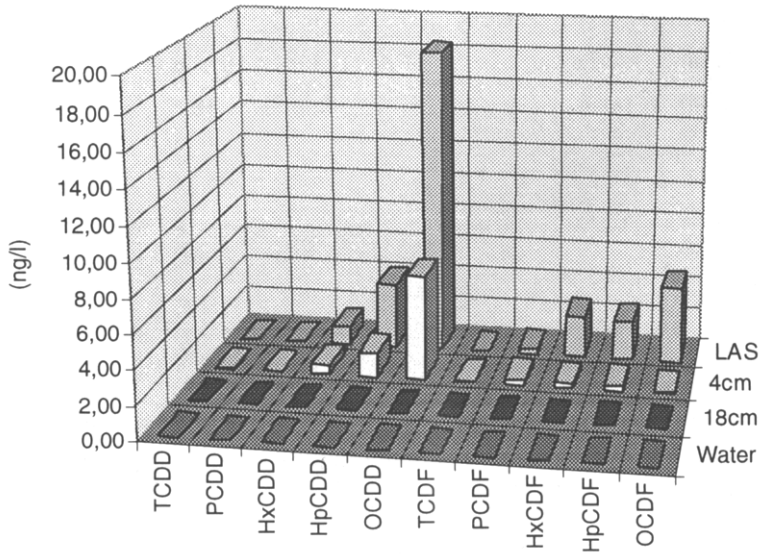

Figure 4: PCDD/Fs pattern of the leachate from the fly ash leached through the 4cm and 18cm soil column and leachate with LAS and pure water without soil

Figure 5 shows the results that a soil column of 4cm length was added following the fly ash

column. Again significant amounts of PCDD/Fs could be measured in the leachate. In the soil column of 18cm length, the content of PCDD/Fs is not so high, but the amount of the congeners is also higher than their solubility. This fact is also found in the leaching report by the fire-extinguishing water (Schramm et al, 1995). All of these leaching results for LAS water are different from the findings for leaching with distilled water (Carsch, Thoma, Hutzinger, 1986; Karasek, Charbonneau, 1987).

To measure the PCDD/Fs profile in the soil column, the leaching experiment using 18cm soil was performed. Figure 5 also shows the pattern of leachate and distribution of PCDD/Fs congeners in different soil depth. The high chlorinated PCDD/Fs like hexa-, hepta- and octa-CDD/Fs break through the column whereas the tetra- and penta- homologues are not leached to that extent. This finding is consistent with the results of the leachates.

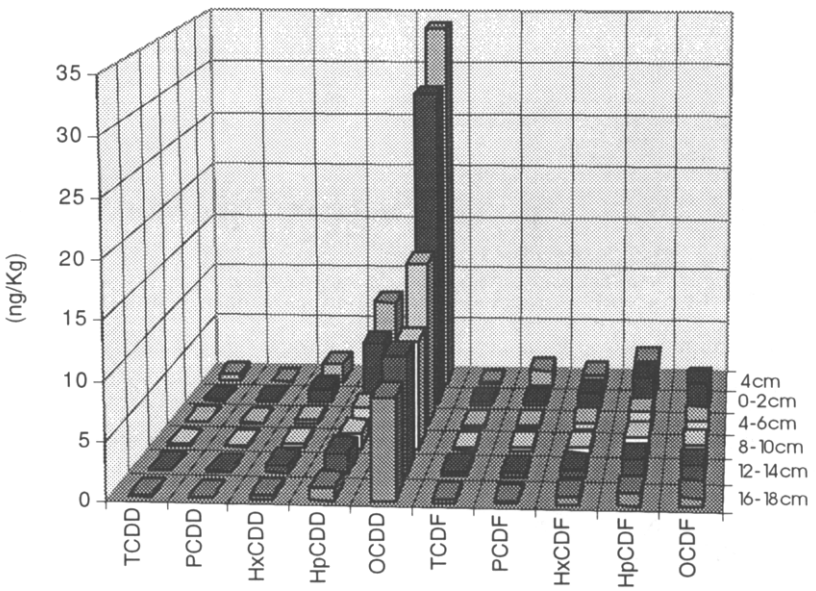

Figure 5: PCDD/Fs congeners in 4cm length column and the vertical distribution in the 18cm soil column.

The content of PCDD/Fs congeners in the column is decreasing from the top to the bottom. For the column of 4cm length, the content of PCDD/Fs is nearly same as that in the top of 18cm length column, but a

significant maximum in one layer could not be observed (Figure 5). An ultimate breakthrough could be postulated for these compounds.

In conclusion, the abnormal behaviour of the PCDD/Fs under leaching condition with LAS water in this study can be explained by the surfactant LAS enhancing the water solubility. Every year, a large amount of detergent containing LAS is being used and then discharged to soil, water and sediment, i.e. via sewage sluge. It must be mentioned that the solubility enhancement to the high toxic pollutants like PCDD/Fs and possibly other compounds with similar properties can result in a rapid transportation and lead to environmental problems.

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