

Pressurised hot water extraction (PHWE) of PCDFs from industrial soil.

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Introduction

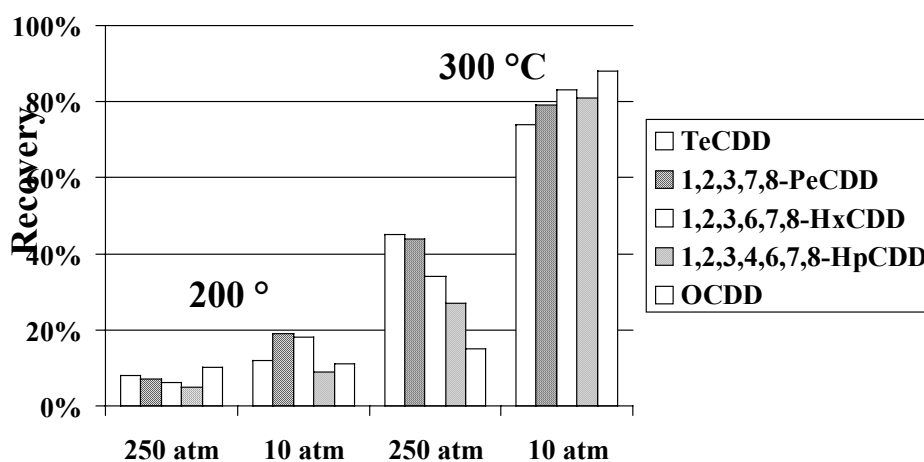
Water under pressure and at temperatures above 100°C changes from being a polar solvent into a solvent with non-polar characteristics^{1,2,3,4}. For example the dielectric constant (ϵ) of water under pressure drops from around 80 at room temperature to below 10 at temperatures above 300°C. The dielectric constant of steam⁵ is close to 1 and it is increased slightly when approaching the critical point. This capacity of water together with enhanced thermal desorption and compounds vapour pressures theoretically and in practise opens the way to extract non-polar pollutants from environmental samples using Pressurised Hot Water Extraction (PHWE) also referred to as subcritical water extraction. In this study, PHWE results of the PCDDs and PCDFs are presented. The extraction of model compounds from sand as well as the extraction of PCDFs and PCNs from an aged industrial sample is described.

Material and Methods

Soil from a chlor-alkali facility was air-dried and ground by using a planetary micro mill. After grinding the soil it was homogenised and stored in closed glass bottles until analysis or PHWE experiments. PHWE was performed at different conditions using two slightly different systems, which are described in detail elsewhere.^{4,6} The extraction cells were filled with 3 g of toluene-washed sea sand or 2 grams of sea sand and 0.5 or 1.0 g of the sample. After addition of a mixture of ¹³C labelled standards on top of the soil or sand sample the extraction was started. Extractions were performed at pressures of 10, 50 and 250 atmospheres and at temperatures between 200 and 400 °C. The extraction was started by first pumping water through the extraction cell at constant velocity of around 1ml/min, and the variable pressure regulator was adjusted to meet the desired pressure. The extraction temperature was set after the system was found leak free. After cooling down the water the extracted analytes were collected into 4 ml of heptane. Drying the tubings with nitrogen and rinsing them with heptane finished extraction. The total extraction time was around 30 minutes resulting in a volume of around 30 ml (28-35 ml) of water. This 30 ml of water was extracted with 3 times 10 ml of heptane. All heptane fractions were combined and concentrated to 1 ml and a recovery standard containing ¹³C labelled 1,2,3,4,7,8-PeCDF and 1,2,3,4,7,8,9-HxCDF in tetradecane was added. Before GC/MS analysis the samples were eluted through a pipette filled with Na₂SO₄ to remove water. Recoveries of the ¹³C-labelled PCDFs from both the sand and the soil samples were calculated against the recovery standards (¹³C-labelled 1,2,3,4,7,8-PeCDF and 1,2,3,4,7,8,9-HxCDF). Also quantification was done against the recovery standard, in order to calculate the PHWE efficiencies of the 'native' PCDFs for the aged industrial soil.

Results and discussion

Results from the PHWE of ^{13}C -labelled PCDDs are given in Figure 1. Water is in the gas phase at 10 atm and in the liquid phase at 250 atm. Extraction of ^{13}C labelled PCDDs from sand was much more efficient at 300 °C than at 200 °C. This is in agreement with a lower dielectric constant (in liquid phase) and thus polarity at the higher temperature. From Figure 1 it can also be concluded that extracting in the gas phase at 10 atm is more efficient than extracting in the water phase. This is again in agreement with even lower dielectric constant of steam reflecting a non-polar solvent. With steam, however, a dielectric constant can not explain the difference in extraction behaviour between 200 °C and 300 °C especially when the difference in dielectric constants at 10 atm is very small ($\Delta\epsilon = 0.013$). Due to enhanced thermal desorption and compounds vapour pressures, faster extraction kinetics at higher temperatures is achieved and these thermal effects play a major role in the extraction of normally hydrophobic compounds like PCDDs and PCDFs. With respect to the fact that both PCDDs and PCDFs are hydrophobic and practically insoluble in water,⁷ 80 %



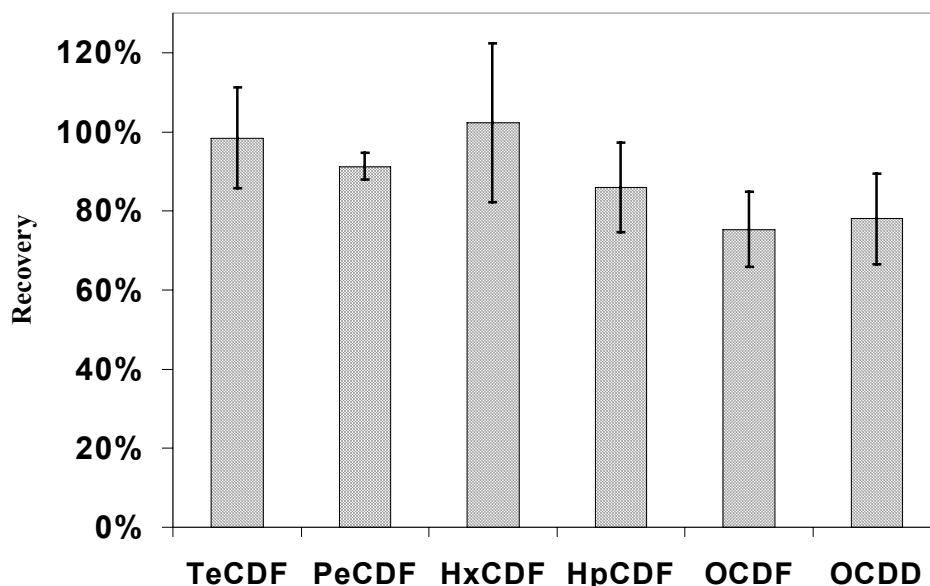
extraction efficiency in the preliminary PHWE experiments is very promising.

Figure 1. Recovery of ^{13}C -labelled model compound from sand extracted by using water under different conditions. At 250 atm water is present in the liquid phase and at 10 atm water is present in the gas phase.

After the initial experiments the PHWE system⁴ was modified by changing the oven to an old HP 5790A GC oven and the water pump to new Jasco PU-980 HPLC pump. This set-up was used for further experiments and with this system it was possible to control the flow-rate, pressure and temperature during the extraction more accurately and thus more reproducible results were obtained. From the initial results it was concluded that water in the gas phase at higher temperature resulted the highest extraction efficiencies. Therefore, additional experiments were done in the gas phase but at a slightly higher pressure (50 atm) than the initial experiments. The sand was replaced by a real soil sample from an industrial facility. The recoveries for the added ^{13}C PCDFs from the soil are shown in Figure 2 for five subsequent extractions. Again, surprisingly high extraction

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efficiencies (62-120 %) were achieved at 50 atm and at 300 °C. Also the repeatability of the experiments was good with a RSD between 3 and 20 %. The larger PCDFs e.g. OCDF seems to



be somewhat more difficult to extract from the soil.

Figure 2. Recovery of added ^{13}C labelled PCDFs from an industrial soil with PHWE at 300 °C and 50 atm. The standard deviation ($n = 5$) is represented by the error bars.

Although, PHWE of standard solutions from environmental samples does give important information about the behaviour of PCDDs and PCDFs, they hardly reflect a 'real life' situation. Most environmental samples have been weathered and aged since exposure to the contaminants. This means that the extraction can be much more difficult. Results for PHWE at 300 °C and 50 atm of a real aged industrial soil sample are given in Figure 3. This industrial soil was used in an international laboratory comparison study⁸ and within this study relatively high levels of PCDFs were reported. The reported levels were compared with the amounts extracted using PHWE. As can be seen from Figure 3, both tetra- and penta-PCDFs are efficiently extracted from the soil. Especially the most toxic 2,3,7,8- substituted tetra- and penta- congeners are nearly quantitatively removed (67-107 %). The extraction efficiency of OCDF was much lower (26%), indicating a different extraction behaviour for this congener. However, the low concentration of this congener in the soil in addition to the low TEF value assigned to OCDF results only in a minor contribution of this congener from a risk assessment point of view. The total TEQ of the soil was reduced with more than 90% by PHWE.

The conclusion that PCDDs and PCDFs, in contrast to common knowledge, are soluble in pressurised hot water has major impact on the analytical and environmental chemistry of this compound class. The discovery that non-polar environmental pollutants can be extracted by using

water is especially interesting in the development of remediation techniques for contaminated soil. PHWE at moderate temperatures is able to clean the soil and makes the target compounds available for further chemical and biological degradation.

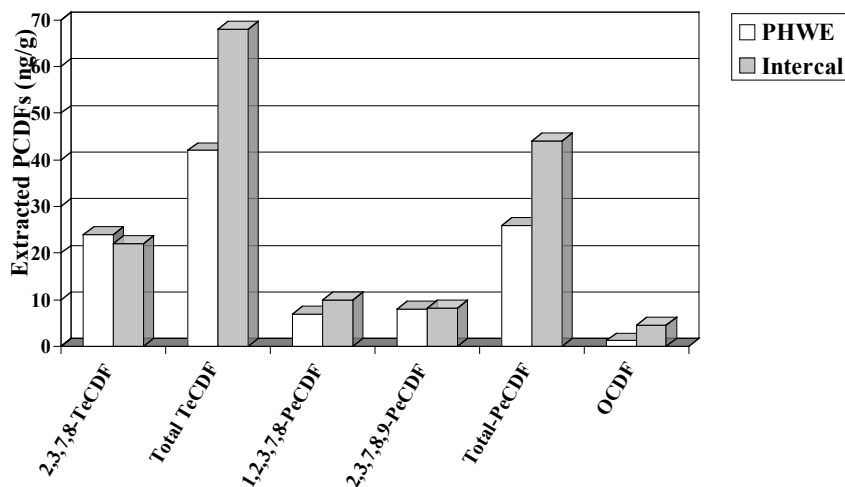


Figure 3. PHWE efficiency for PCDFs at 300 °C and 50 atm compared to the data obtained from an international laboratory comparison study.⁸

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