

A MODULAR PRESSURIZED LIQUID EXTRACTION PROCEDURE FOR SIMULTANEOUS EXTRACTION, CLEAN-UP AND FRACTIONATION OF PCDD/Fs IN SOIL AND SEDIMENT SAMPLES

Lan T. Do*, Thong H. Xuan, Staffan Lundstedt, Peter Haglund

Department of Environmental Chemistry, Umea University, SE-901 87, Sweden

Introduction

Environmental monitoring of polychlorinated dibenzo-p-dioxins (PCDDs or dioxins) and polychlorinated dibenzofurans (PCDFs or furans) are of great interest due to their persistency and high potential of adverse health effects.[1, 2] However, the extensive sample preparation, including several steps of extraction and cleanup, followed by gas chromatography/high resolution mass spectrometer (GC/HRMS) is a drawback.[3, 4] The analysis is expensive (\$500-\$1000 USD per sample), time and solvent consuming.[5]

Recent developments indicate that there are many possibilities to modify pressurized liquid extraction (PLE) instrument, such as: in-cell cleanup, selective PLE, PLE with an integrated carbon trap or modular PLE (M-PLE).[6-11] The modification aims to improve the versatility of PLE. So far M-PLE is the most flexible PLE method that combines extraction, cleanup and fractionation in one step.[7] M-PLE is available from 2008 but the method has been encountered with many limitations. In this paper, we aimed to develop, optimize and validate a fully robust M-PLE procedure for PCDD/Fs analysis in contaminated solid samples.

Materials and methods

The M-PLE procedure consists of two cells: Cell 1 filled with sample and multi-layer silica and Cell 2 with carbon/Celite mixture, connected together by an in-house produced adaptor (Figure 1). In step 1, the modular is extracted, matrices are retained in the multi-layer silica while the planar PCDD/Fs and dioxin-like PCBs are trapped in the carbon/celite. The first fraction eluted from the M-PLE contains non-planar PCBs. In step 2, cell 1 is removed from the modular. In step 3, cell 2 is inverted with a new cap and extracted by toluene. The second fraction contained PCDD/Fs and other planar compounds are clean enough to be directly analyzed.

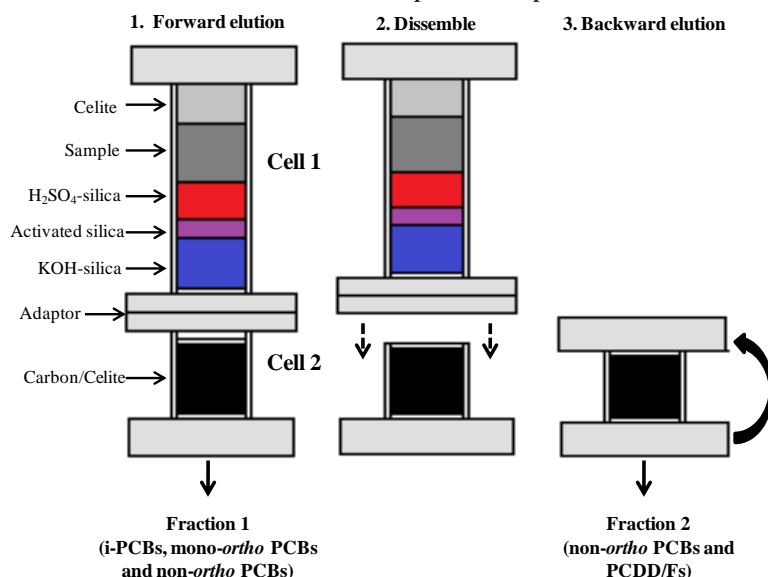


Figure 1. Packing strategy of modular pressurized liquid extraction (M-PLE).

The forward elution was studied on two solvent systems: DCM/Hp (1/1, v/v) at 100% flush, 110°C in 2 cycle x 11 min or DEE/Hp (1/2, v/v) at 140°C in 2 cycle x 12 min. While the backward elution was similar in all cases,

including 3 cycle x 7 min at 150°C, 60% flush with toluene. The composition of carbon/celite was evaluated to study the trapping / releasing capacities. The carbon/celite was varied from 0.5 to 15% carbon (w/w). Then full M-PLE performance was evaluated with certified reference materials (CRMs) and samples from International Intercalibration Studies.

The extracts were analyzed by an Agilent 6890GC coupled to an Autospec Ultima HRMS operated in the selected ion monitoring (SIM) mode at a resolution of 10 000. The analysis was performed on DB-5 MS and SP-2331 columns.

Results and discussion

Screening of the carbon trap: In general, PCBs appear at a concentration much higher than dioxins, which may overlap the small peaks of dioxins in the chromatogram. The purpose of the first trial is to optimize the most suitable composition of carbon on Celite for which major *ortho*-PCBs and coplanar PCBs are eliminated, providing 2,3,7,8-PCDD/Fs extracts free from interferences. As the planar structure of the activated carbon (AX21) facilitates the binding selectivity of carbon on planar compounds[12], such as: coplanar PCBs and PCDD/Fs will bind strongly to the carbon/Celite better than such non-planar PCBs.

From Figure 2, there were not any carbon contents or solvent mixtures providing a complete separation of labeled coplanar PCBs from Dioxins. The most ones were the traps filled with 0.5% or 1% carbon. Since the planar compounds will remain longer in the carbon than the non planar ones, if the carbon trap showed the most break-through of coplanar PCBs, one could ensure the non-planar PCBs were washed completely out from the carbon trap. Additionally there was no significant difference between the efficiencies of 0.5% and 1%. A trap containing 1% carbon was likely to be more robust than a trap containing 0.5% carbon due to its higher trapping capacity of PCDD/Fs, which might be important if dealing with highly contaminated samples. Therefore, the carbon trap comprising 1% of carbon on Celite was selected for further study in both mixtures DCM/Hp (1/1, v/v) and DEE/Hp (1/2, v/v).

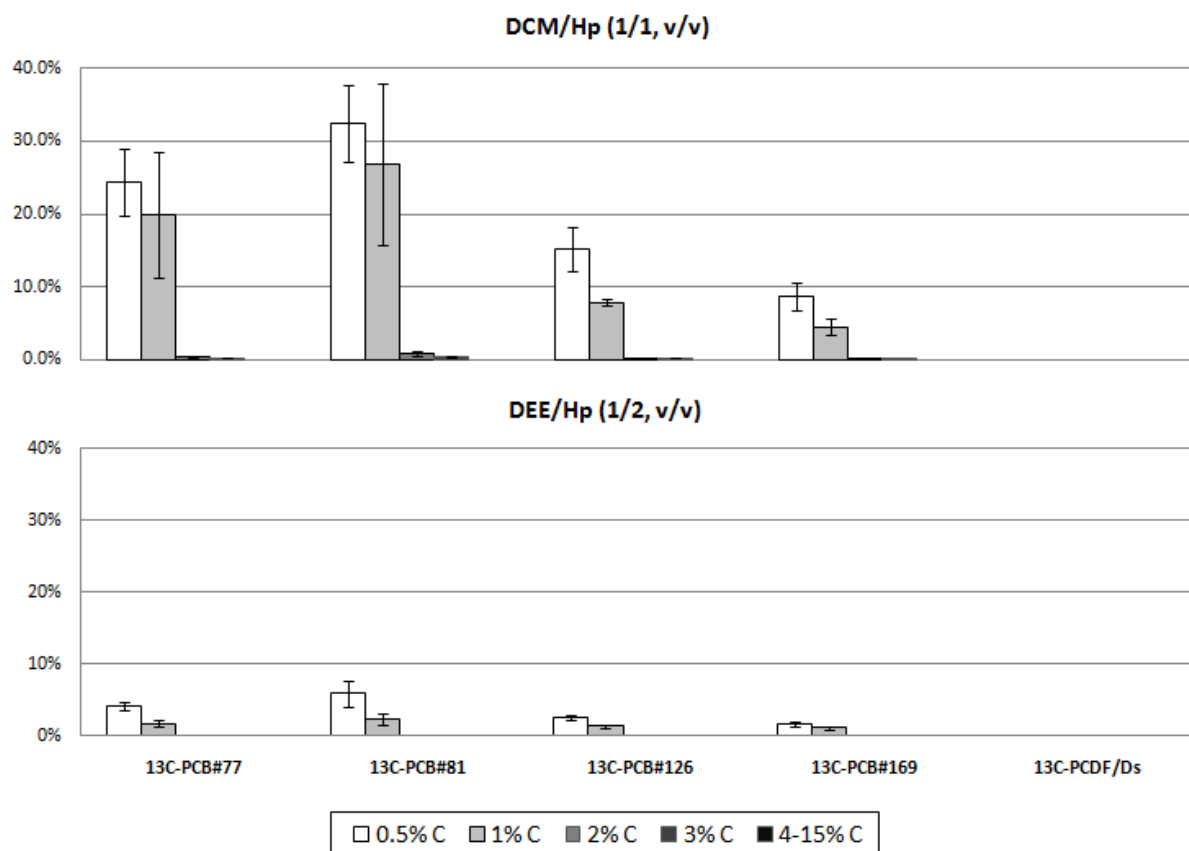


Figure 2. Relative distribution of ^{13}C -labeled coplanar PCBs and ^{13}C -labeled PCDD/Fs from the first fractions using ASE[®]200 M-PLE with a carbon trap filled with 2.5 g of 0.5, 1, 2, 3, 4-15 % carbon in Celite, respectively.

Performance of the modular-PLE using 1% carbon/Celite and low sample intake: The M-PLE method was developed using the certified lake sediment WMS-01 and two inter-calibration samples: Soil C, Sludge C. All samples were prepared approximately one-gram weight to maintain a low sample intake in order to not overloading the carbon trap. The extractions were performed on either ASE[®]200 or ASE[®]350 with two solvents DCM/Hp (1/1, v/v) and DEE/Hp (1/2, v/v). The average M-PLE concentrations are based on triplicate analyses and the TEQs have been calculated via the WHO-TEF values established in 2005 [2].

There were no significant differences in the PCDD/F concentrations (data not showed) determined by the two M-PLEs vs the reference, as manifested in overlapping 95% confidence intervals. Moreover, the TEQ values were in a good agreement with the reference values to both DCM/Hp and DEE/Hp mixtures (Figure 3). To each material, their mean TEQ values were similar and none of them exceeded the 95% confidence intervals. The recoveries were high, no significant breakthrough of the internal standard was detected. Therefore, the M-PLE_{1%} carbon trap methods were concluded to be well robust.

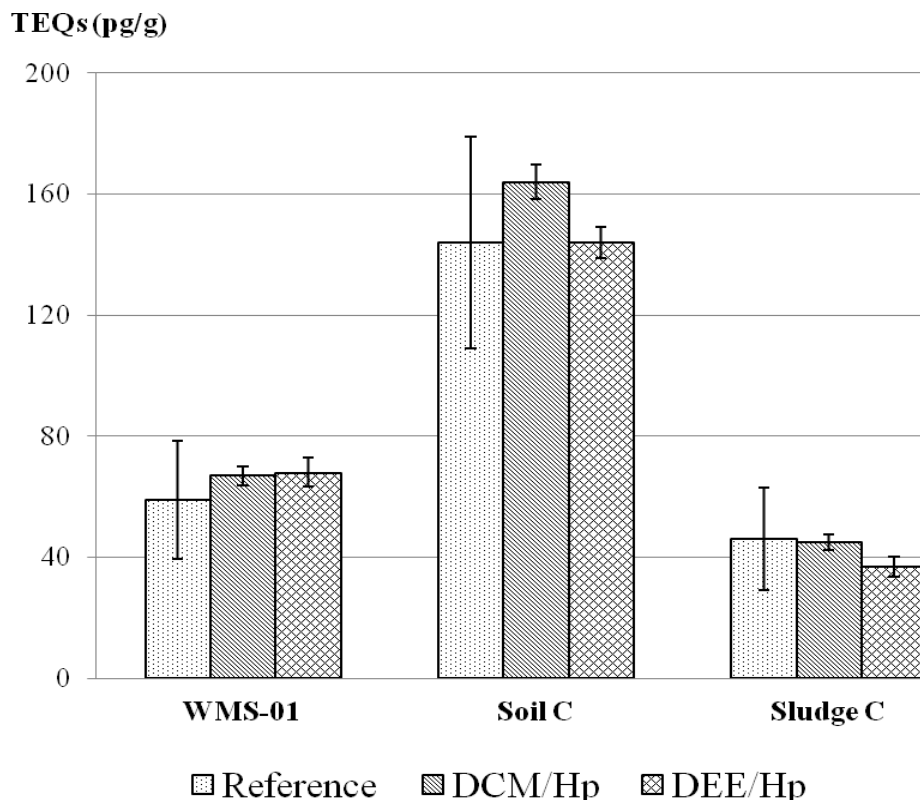


Figure 3. TEQ values (pg/g) of certified material WMS-01 and two inter-calibration samples Soil C, Sludge C.

Acknowledgements

We would like to acknowledge the support from the EU research network Soil Remediation Centre North and the Kempe foundation. We gratefully acknowledge Peter Wikström for his contribution in designing the modular approach.

References:

- Schechter A, Birnbaum L, Ryan JJ, Constable JD (2006) *Environ Res* 101:419-428
- Van Den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H, Hanberg A, Haws L, Rose M, Safe S, Schrenk D, Tohyama C, Tritscher A, Tuomisto J, Tysklind M, Walker N, Peterson RE (2006) *Toxicol Sci* 93:223-241
- US-EPA (1994) Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS.
- US-EPA (2007) SW-846 Method 8290A: Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS).
- Spinnel E, Fick J, Andersson PL, Haglund P (2008) *Environ Sci Technol* 42:9255-9261
- Richter BE, Jones BA, Ezzell JL, Porter NL, Avdalovic N, Pohl C (1996) *Anal Chem* 68:1033-1039
- Spinnel E (2008) PLE with Integrated Clean-up Followed by Alternative Detection Steps for Cost-effective Analysis of Dioxins and Dioxin-like compounds. Umea University,
- Haglund P, Sporning S, Wiberg K, Bjorklund E (2007) *Anal Chem* 79:2945-2951
- Lundstedt S, Haglund P, Oberg L (2006) *Anal Chem* 78:2993-3000
- Bjorklund E, Sporning S, Wiberg K, Haglund P, Von Hillist C (2006) *Trac-Trends in Anal Chem* 25:318-325
- Westbom R, Sporning S, Cederberg L, Linderöth LA, Bjorklund E (2008) *Anal Sci* 24:531-533

12. Spinnel E, Danielsson C, Haglund P (2008) *Anal Bioanal Chem* 390:411-417