

PCDD/Fs EMISSIONS IN FLUE GAS FROM THERMAL TREATMENT OF HEAVY METALS HYPER ACCUMULATORS

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Introduction

Phytoextraction has become one of the most promising, cost-effective, and environmentally sound remediation techniques for shallow and moderate heavy metal (HM) contaminated soils¹⁻⁵. However, the technique invariably produces large amounts of HM-enriched hyper accumulators, which need further safe disposal. Incineration as a kind of thermal treatments is presently deemed as the most feasible, economically acceptable, and environmentally sound approach^{2,6-8}. Additionally, Keller et al. demonstrated that pyrolysis was a better method than incineration to increase volatilization and would allow the recycling of bottom ash as fertilizer⁶. During the incineration of HM-enriched hyperaccumulators, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) emissions from flue gas, fly ash and bottom ash were also be found⁹. Copper and iron chlorides catalyze the synthesis of PCDD/Fs¹⁰, so heavy metals in hyper accumulators may increase the generation of PCDD/Fs. In this study, experiments were conducted to investigate and control PCDD/Fs emissions from incineration of HM-enriched hyper accumulators on a laboratory scale using a fluidized bed tube furnace, other than heavy metal emissions. The emission characteristics of heavy metals and PCDD/Fs into flue gas were investigated by the Cd and Zn hyper accumulators *Sedum alfredii*. The PCDD/F concentrations in flue gas samples were analyzed and compared using the CALUX assay and HRGC/HRMS.

Materials and methods

The flue gas samples were collected from HM-enriched hyper accumulators incineration experiments using laboratory scale fluidized bed tube furnace. The absorption method of heavy metals in flue gas samples was according to USEPA Method 29, and that of PCDD/Fs was according to Specifications for Continuous Emissions Monitoring of Flue Gas Emitted from Stationary Sources (P.R. China).

For heavy metals analysis, the Cd, Zn, Pb, and Cu concentrations in flue gas absorption solution were determined by Inductively Coupled Plasma Emission Spectrometer (Thermo Fisher iCAP-6300, USA). Two standard analysis methods were used to determine the four heavy metals concentrations. The determine wavelengths of Cd, Zn, Pb, and Cu were 2144, 2138, 2203, and 2247, respectively.

For PCDD/Fs analysis, the absorption solution and XAD-2 resin of flue gas samples were soxhlet extracted for 24 hrs for HRGC/HRMS analysis. Each sample was spiked with a mixture of ¹³C-labelled PCDD/Fs compound stock solution (10 μ l, 100 ng/ μ l) before extraction. The extracts were subsequently passed through multilayer silica gel column and aluminum oxide column following USEPA Method 23. The extracts were blow down to 25 μ l by nitrogen (N₂), and 5 μ l (200 ng/ μ l) internal standard solution were added before sample were subjected to PCDD/Fs analysis by using HRGC/HRMS (JEOL JMS-800D, Japan) with a DB-5MS column (60 m \times 0.25 mm \times 0.25 μ m).

Same as HRGC/HRMS analysis, the absorption solution and XAD-2 resin of flue gas samples were soxhlet extracted for 24 hrs for CALUX bioassay. After the rotary evaporation, the extraction was loaded onto an acid-silica gel and XCARB (XDS Inc., USA) bigeminal columns. The DL-PCBs and PCDD/Fs fractions were then eluted with different solution only onto XCARB column respectively, and the PCDD/Fs fraction was selected for CALUX assay in this study. The CALUX assay was carried out using a recombinant H1L6.1 cell line. The cells were seeded on 96-well microplates, and after 24 hrs of incubation, cells were exposed in duplicate to the purified sample extracts and 2,3,7,8-TCDD standard solution for 20-24 hrs of incubation. The luciferase activity was measured using a Lucy I luminometer (Antos, Salzburg, Austria).

Results and discussion

The concentrations of PCDD/Fs and HMs in flue gas generated from incineration of *Sedum alfredii* in fluidized

bed tube furnace are shown in Figure 1. PCDD/Fs concentrations in flue gas increases with increasing temperature, from 0.14 ng-TEQ/Nm³ to 0.87 ng-TEQ/Nm³, during 750 °C~900 °C. At 850 °C, PCDD/Fs emissions are 0.57 ng-TEQ/Nm³ with no additives, 0.08 ng-TEQ/Nm³ with activated carbon injection in flue gas, and 1.43 ng-TEQ/ Nm³ with the additive of kaolin in *Sedum alfredii*. Activated carbon absorbs the PCDD/Fs in flue gas because of its large specific area. However, with the additive of kaolin, the PCDD/Fs value in flue gas was significantly increased, which may be cause by the component of kaolin (mainly Al₂O₃ and SiO₂). As shown in Figure 1, in general, Zn levels in flue gas are approximately one or two orders of magnitude higher than those of Cu, Pb and Cd. Differences between Zn and Cd and Cu on this scale were also found in *Sedum alfredii* (the data were not shown in the paper). Temperature has a significant impact on the HM volatilization process. Increasing the temperature could enhance vaporization by raising the vapor pressure of HM chlorides and enhancing the rates of diffusion^{11,12}, although vaporization rate is not linearly proportional to incineration temperature. However, previous studies showed that the influence of temperature on volatilization of HMs is complex without a clear understanding. In this study, the levels of Cu and Pb in flue gas almost increase with the increasing temperature, from 750 °C to 900 °C, but the level of Cd and Zn fluctuates with the increasing temperature, and the fluctuate rules of the two HMs are just opposite. The additives of activated carbon and kaolin could can the emissions of HMs, and the control effect of activated carbon is better. In addition, during 750 °C~900 °C, the emission rules of PCDD/Fs and Cu are just the same, that is the concentrations are increasing with the increasing temperature. Copper chloride may catalyze the formation of PCDD/Fs during the combustion, and increasing addition of copper chloride may effectively enhanced the formation of PCDD/Fs¹³.

PCDD/Fs values in flue gas samples were analyzed by both HRGC/HRMS and rapid bioassay CALUX. The toxic equivalents (TEQ) for PCDD/Fs determined by CALUX bioassay and HRGC/HRMS are written as “CALUX-TEQ” and “I-TEQ”, respectively. Though CALUX-TEQs are higher than I-TEQs as shown in Figure 2 (the average ratio of CALUX-TEQs to I-TEQs is 2.41), the results show that CALUX-TEQs and I-TEQs are highly correlated (R=0.999), which validates that the CALUX bioassay can be an suitable screening method or semi-quantitative detection method for PCDD/Fs determination of flue gas samples. The higher CALUX-TEQs for PCDD/Fs could be ascribed to various factors including (i) the difference between toxic equivalence factors (I-TEFs) and CALUX relative potency (REP) values, (ii) the presence of the congeners concentrations in CALUX-TEQs, which are not quantified with I-TEFs and not included in I-TEQs, and (iii) the presence of other AhR ligands that are not quantified during HRGC/HRMS analysis, for example, polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs), polybrominated biphenyls (PBBs), polyhalogenated dibenzo-p-dioxins and dibenzofurans (PXDD/Fs; X=Br/Cl) and a few polychlorinated naphthalene (PCNs) congeners, but also less persistent pollutants like polyaromatic hydrocarbons (PAHs), and even natural compounds¹⁴.

In general, the ratio of [PCDDs]:[PCDFs] is suggestive of the route by which PCDD/Fs is produced. The ratios of [PCDDs]:[PCDFs] for all the conditions are below 1 (0.11-0.51), which means that PCDD/Fs probably are formed mainly via the de novo route. PCDD/Fs congener profiles of flue gas samples are shown in Figure 3. 2,3,4,7,8-PeCDF is the predominant congener of all the seventeen toxic congeners, which may be the characteristics of flue gas samples from HMs hyper accumulators fluidized bed incinerator. The second group of abundant congeners in samples from the incineration conditions of 850 °C, 900 °C and 850 °C with kaolin are 2,3,4,6,7,8-HxCDF and 1,2,3,6,7,8-HxCDF, but from the conditions of 750 °C, 800 °C and 850 °C with activated carbon, the congeners are 2,3,4,7,8-PeCDD and 2,3,7,8-TCDD. Additionally, the values of first group samples are much higher than those of second group, and the ratios of [PCDDs]:[PCDFs] of first group samples (0.11-0.14) are much lower than those of second group (0.29-0.51). Therefore, these three characteristics may make the flue gas samples into two distinct groups.

Acknowledgements

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References

1. Raskin I, Smith RD, Salt DE. (1997) *Curr. Opin. Biotech.* 8 (2): 221–226.
2. Sas-Nowosielska A, Kucharski R, Malkowski E, Pogrzeba M, Kuperberg JM, Krynski K. (2004) *Environ.*

Pollut. 128 (3): 373–379.

3. Kumar PBAN, Dushenkov V, Motto H, Raskin I. (1995) *Environ. Sci. Technol.* 29 (5): 1232–1238.
4. Brooks RR, Chambers MF, Nicks LJ, Robinson BH. (1998) *Trends Plant Sci.* 3 (9): 359–362.
5. Lu SY, Du YZ, Zhong DX, Zhao B, Li XD, Xu MX, Li Z, Luo YM, Yan JH, Wu LH. (2012) *Environ. Sci. Technol.* 46: 5025–5031.
6. Keller C, Ludwig C, Davoli F, Wochele J. (2005) *Environ. Sci. Technol.* 39 (9) : 3359–3367.
7. Xing QG, Pan WB. (2004) *Ecol. Envir.* 13 (4) : 585–586, 600.
8. Xiao WL. (2007) *Master's thesis.* Nanchang University: Nanchang, P.R.China.
9. Meawad AS, Bojinova DY, Pelovski YG. (2010) *Waste Manage.* 30:2548–2559.
10. Nganai S, Lomnicki S, Dellinger B. (2009) *Environ. Sci. Technol.* 43:368–373.
11. Sun S, Abanades S, Lu JD, Flamant G, Gauthier D. (2004) *J. Environ. Sci.* 16 (4) : 635–639.
12. Liu J, Falcoz Q, Gauthier D, Flamant G, Zheng CZ. (2010) *Chemosphere* 80 (3): 241–247.
13. Wang DL, Xu XB, Zheng MH, Chiu CH. (2002) *Chemosphere* 48: 857–863.
14. Hasegawa J, Guruge KS, Seike N, Shirai Y, Yamata T, Nakamura M, Handa H, Yamanaka N, Miyazaki S. (2007) *Chemosphere* 69: 1188–1194.

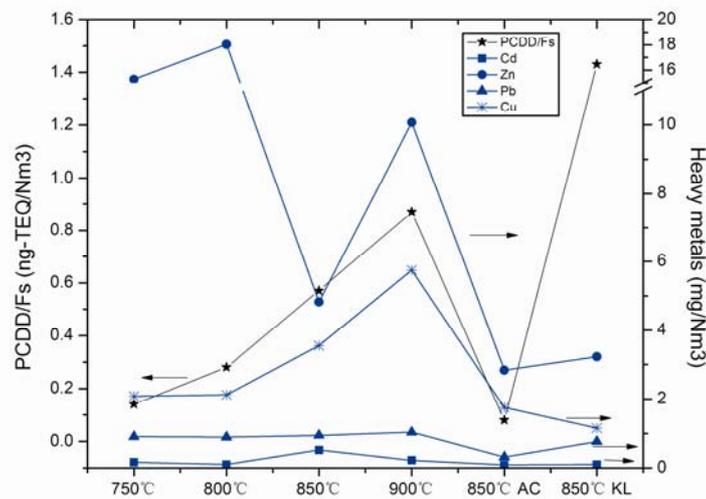


Figure 1 Concentrations of HMs and PCDD/Fs in flue gas under different experiment conditions. AC represents for activated carbon, and KL represents for kaolin.

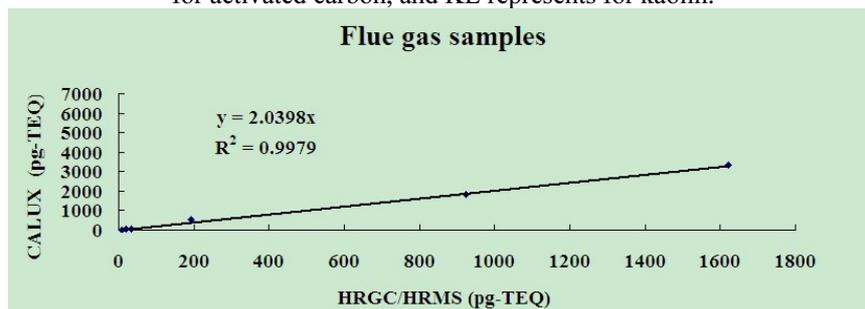


Figure 2 Correlation relationship of CALUX and HRGC/HRMS values for six flue gas samples

