

A SEVEN CONSECUTIVE YEAR OF INTERCALIBRATION EXERCISES ON ORGANOCHLORINE COMPOUNDS IN CHINA: RESULTS ON PCDD/Fs IN THE VARIOUS ENVIRONMENTAL SAMPLES

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Introduction

PCDD/Fs are highly toxic to humans, bioaccumulative in ecosystems and persistent in various environmental compartments. Analytical methods commonly used in analysis of PCDD/Fs in environment are time consuming, labor-intensive, costly and often dubious due to the fact that PCDD/Fs are present mostly at parts per billion (ppb) or even parts per trillion (ppt) levels in environmental compartments. The investigated pollutants have to be concentrated and separated from the matrix so that they can be identified and measured mainly by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) applied in monitoring programs. Applicability of monitoring data depends on their quality measured in terms of reliability, which relies on precision and accuracy. In order to give all Chinese domestic laboratories the possibility of intercomparing their analytical performances and thus improve the reliability and accuracy of the obtained monitoring data, National Research Center for Environmental Analysis and Measurement (CNEAC) attempted to initiate an intercalibration study by organizing the first China Intercalibration study for environmental PCDD/Fs on national level in the year 2012. Seven consecutive-year of intercalibration exercises have been carried out by CNEAC ever since then. The success of these studies is demonstrated by the steady increase in the number of participating laboratories growing from 14 in 2012 to 37 in 2018, which covers over 80% of PCDD/Fs laboratories in domestic China. Here are present and discussed results of intercalibration exercises from the seven year experience.

Materials and methods

Sample preparation

As displayed in Table1, different sets of standard solution, soil, fly ash or extracted ambient air samples were delivered to the laboratories for the analysis of PCDD/Fs every year. The standard solution samples were custom made by Wellington Laboratories Inc. (Guelph, Canada). Soil samples were taken from a real environmental matrix and collected from the surface soil of area adjacent to municipal or medical solid waste incinerators. Fly ash samples came from municipal solid waste incinerators. Soil samples were dried at room temperature after separating large debris, grinded and sieved through a 100 µm sieve subsequently. Fly ash samples were grinded and sieved through a 100 µm sieve. Air extracts were prepared by mixing several sample extracts, which were collected in polluted weather using high volume air sampler (HV-700F, Sibata, Japan) and extracted with accelerated solvent extractor (ASE-300, DIONEX, U.S.). The homogeneity and stability test were performed based on the rule of ISO1. The samples were stored in amber glass containers and distributed to the participants after passing the test.

Data evaluation

Raw data treatment, result description and evaluation were performed by the robust statistical method following the rule of China National Accreditation Service for Conformity Assessment (CNAS). The results presented in

this paper were obtained after a statistical treatment of the original data. The following statistical indexes were computed: mean, median, standard deviation, Interquartile Range, maximum, minimum and coefficient of variation, for each matrix and class of compounds. The performance of each participant result were estimated by means of z-scores coefficients.

Table 1 Sample matrix for China Intercalibration study for environmental PCDD/Fs

year	Sample description
2012	1 standard solution, 2 fly ash samples with different PCDD/Fs concentrations
2013	1 standard solution, 1 fly ash sample and 1 soil sample
2014	1 standard solution, 2 fly ash samples with different PCDD/Fs concentrations
2015	1 standard solution, 3 fly ash extracts with different PCDD/Fs concentrations
2016	1 standard solution, 1 air extract solution and 1 fly ash sample
2017	1 standard solution, 1 soil sample
2018	1 standard solution, 1 fly ash sample and 1 soil sample

Results

All participants that reported results used HRGC-HRMS(EI) and isotope-labeled standards for the determination of target compounds. The duplicate results from each laboratory were averaged, then the average concentrations and other statistical indexes were calculated and summarized for each congeners and total toxic equivalent quantity (TEQ). The z-scores based on the values of TEQ from each participant for each matrix from 2012 to 2018 are shown in Figure 1.

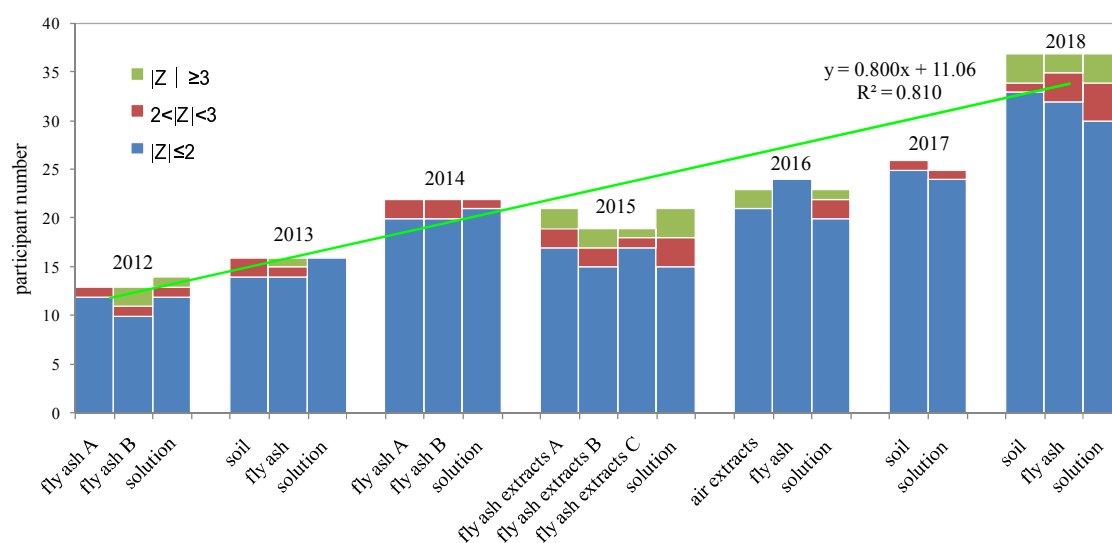


Figure 1 The corresponding z-scores for each matrix from 2012 to 2018 in China Intercalibration study. As is seen from figure 1, the number of participant laboratories is steadily increasing within seven-year period. And the laboratories cover those affiliated to ministry of ecology and environment, university or research institutes, and other industries and commercials. Moreover, the percentage of commercial laboratories rises from 14.3% in 2012 to 48.6% in 2018, indicating the rapid market growth for environmental PCDD/Fs analysis in China.

Taking the results in year 2018 as example, the relative standard deviation (RSD) for 17 congeners in different matrixes is displayed in figure 2. The results on standard solution revealed good agreement in both averaged concentration reported by the participants and designed values for almost all the compounds analyzed. The RSDs

for PCDD/Fs ranged from 12.4%-46.2%. The results on soil and fly ash are also reasonable with RSDs from 17.4%-28.3% and 23.9%-35.3%, respectively except for 1,2,3,7,8,9-HxCDF. Compared with standard solution, the RSDs for most of PCDD/Fs congeners were relatively high in the soil and fly ash samples, indicating possible errors in pretreatment of samples and/or interference by impurities in the GC-MS analysis. Particularly, higher variation of the concentrations of 1,2,3,7,8,9-HxCDD/F than the other isomers would be due to its poor separation from other isomer peaks. The general trends for both phenomena were observed in overall year exercises.

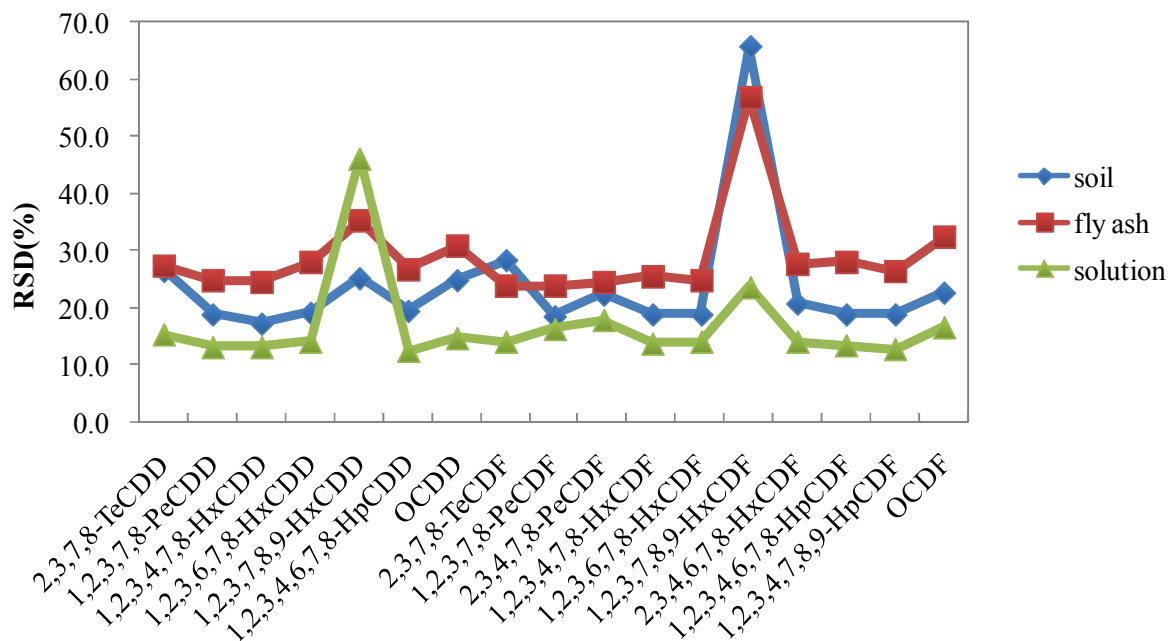
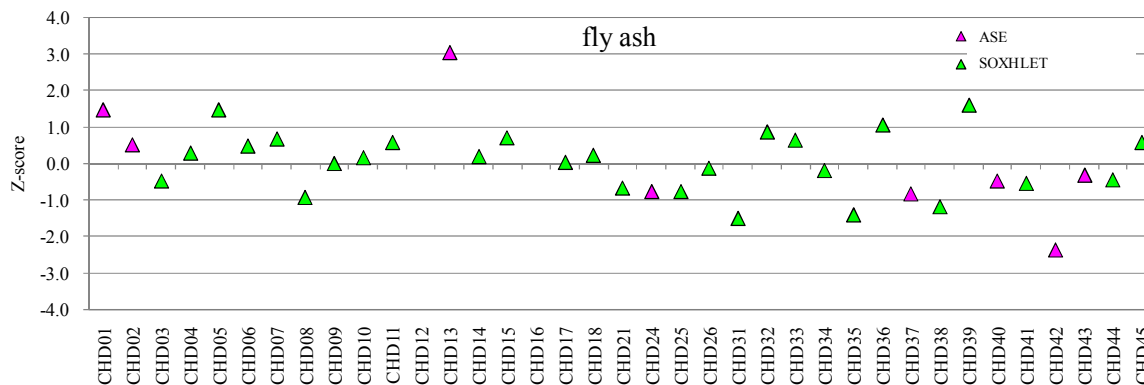


Figure 2 An example results in intercalibration of PCDD/Fs congeners in soil, fly ash and solution, 2018

Discussion

We tried to assess whether the differences in the extraction or pretreatment techniques could be a source of bias. A non-parametric statistical test, T-test, was used for comparing the z-scores obtained using different extraction techniques, "ASE" and "SOXHLET". The results of the test did not evidence any statistical difference at a level of 0.05. Similarly, no statistical differences were observed when the test was applied to the comparison of the z-score values by using HCl pretreatment vs those obtained not using HCl pretreatment although the results seem slightly higher for the former cases.



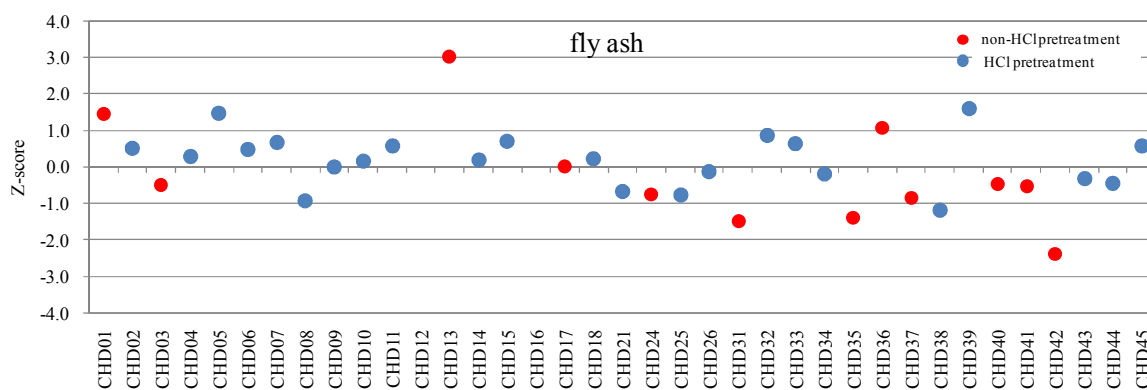


Figure 3 Comparison among the estimates of the z-score in relation to (a) the extraction methods and (b) the pretreatment methods for fly ash, 2018

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References

1. International Organization for Standardization(ISO,2010).*ISO/IEC 17043: 2010 "Conformity assessment - General requirements for proficiency testing"*. ISO,Geneva, Switzerland
2. China National Accreditation Service for Conformity Assessment (CNAS, 2006).*CNAS-CL03:2006 Accreditation Criteria for Proficiency Testing Providers*.CNAS,Beijing, China.
3. Zhang T, Liu A, Li N, et al. (2015) *Organohalogen Compounds* 77, 598-601.
4. Takahashi S, Sakai S, Watanabe I. (2004) *Organohalogen Compounds* 66, 541-545.
5. Picer M, Picer N, Kobasic H, et al. (2007) *Organohalogen Compounds* 69, 1265-1268.
6. Raccanelli S, Petrizzo A, Favotto M, et al.(2007) *Organohalogen Compounds* 69, 982-985.