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Study on the assessment of dioxin emissions in some non-ferrous metal recycling craft villages in Bacninh province

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Introduction

1. The urgency of the dissertation

Dioxins are persistent organic pollutants (POPs) that degrade very slowly in the environment and have the ability to bioaccumulate in living organisms. Dioxins are harmful to human health, with 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD) being the most toxic compound among the 210 congeners. Dioxins and furans are included in the list of substances targeted for elimination under the Stockholm Convention. The International Agency for Research on Cancer (IARC) has classified 2,3,7,8-TCDD as a Group 1 carcinogen, meaning it is "carcinogenic to humans," and there is no safe exposure threshold for dioxins [1, 2]. In ecosystems, dioxins persist in soil, sediment, and the food chain for long periods, and even at extremely low doses, they can be lethal to test animals [3]. Therefore, dioxins not only pose risks to human health but also threaten the existence and development of ecosystems.

Dioxins and furans are unintended by-products formed during combustion processes, such as metal smelting, cement production, municipal waste incineration, and industrial waste burning. Among these, the metal recycling industry, particularly in non-ferrous metal recycling, is one of the most concerning sources of dioxin emissions into the environment [2]. However, the 2008 National Environmental Report on Vietnamese Craft Villages by the Ministry of Natural Resources and Environment and the Report on Dioxin Contamination in Vietnam's Environment did not address dioxin pollution in craft villages [4]. This indicates that dioxin pollution in craft villages has not been adequately considered in Vietnam's environmental reports.

The concentration of dioxins in the environment is very low, making their monitoring in environmental components challenging. Currently, the most common analytical method for determining dioxins in environmental samples involves Soxhlet extraction followed by analysis using high-resolution gas chromatography-mass spectrometry (HRGC-MS). While Soxhlet extraction is the standard method, it requires significant time and chemical consumption. Accelerated solvent extraction (ASE), which provides high extraction efficiency while saving time and chemicals, is a promising alternative to overcome the limitations of Soxhlet extraction.

Traditional craft villages in Vietnam have existed for hundreds of years, serving not only as a source of income for local communities but also as an important part of the nation's cultural heritage. One type of craft village with the potential for dioxin emissions is the non-ferrous metal recycling village in Bac Ninh Province, Vietnam. Therefore, the study titled *"An analytical study and preliminary evaluation of dioxin emissions from some metal recycling craft villages in Bac Ninh Province"* was conducted with the following objectives and scope:

2. Research Objectives

First, to study the optimal parameters and the most appropriate analytical conditions for determining dioxins/furans in various types of samples, including soil, sediment, fly ash, and bottom ash, collected from craft villages, by applying accelerated solvent extraction (ASE) in chemical analysis.

Second, to conduct the analysis and assessment of the concentrations and pollution characteristics of dioxins/furans in environmental samples collected from the craft villages, thereby evaluating the potential ecological risks in the study area..

3. Scientific and Practical Significance of the Study

This dissertation has successfully investigated and optimized the extraction conditions for dioxins/furans in various environmental matrices, including soil, sediment, fly ash, and bottom ash, meeting the analytical requirements for trace-level determination of these compounds. The findings contribute to the advancement of extraction techniques for persistent organic pollutants (POPs) at trace levels in environmental samples. The study establishes a scientific foundation for the application of modern analytical technologies in accurately determining ultra-trace concentrations (in ng/kg) of environmental contaminants, while ensuring high analytical efficiency and reliable accuracy.

The research outcomes provide essential data to policymakers and environmental managers, enabling the development of effective control measures for pollutants originating from industrial activities in traditional craft villages. This supports efforts to protect the environment, preserve ecosystem health, and safeguard the well-being of local communities residing and working in and around these villages.

4. Novel Contributions of the Study

The study successfully optimized several conditions for accelerated solvent extraction (ASE), combined with quantitative analysis using HRGC/HRMS, to determine dioxin concentrations in soil, fly ash, bottom ash, and sediment samples. The results confirmed that ASE offers comparable extraction efficiency to the traditional Soxhlet method, while significantly reducing solvent consumption and extraction time, making it a more environmentally friendly approach.

The research identified the presence of dioxins/furans in environmental samples affected by industrial activities in metal recycling craft villages and assessed their contamination levels. The ecological risk assessment indicated that dioxins/furans in soil, sediment, fly ash, and bottom ash from the studied areas may pose potential threats to the local ecosystems in these craft villages.

Chapter 1: Overview

1.1 Overview of Dioxins/Furans

1.1.1. Polychlorinated dibenzo-p-dioxins (PCDDs)

1.1.2. Polychlorinated dibenzofurans (PCDFs)

1.1.3. Physicochemical properties

1.1.4. Toxicity of dioxins/furans

1.2 Sources and formation of dioxins/furans

1.3 Research on dioxins/furans in Vietnam

1.3.1. Current status of dioxin/furan contamination in the Vietnamese environment

1.3.2. Emissions of dioxins/furans into the environment

1.3.3. Regulations on dioxins/furans in the environment

1.4 Analysis of dioxins/furans

1.4.1. Extraction, cleanup, and enrichment methods

1.4.2. Analytical method using HRGC/HRMS

1.5 Metal recycling craft villages

1.5.1. Aluminum recycling villages

1.5.2. Bronze casting villages

1.5.3. Metalworking villages

1.6 Ecological risk assessment of dioxins at craft villages

1.6.1. Ecological risk assessment

1.7 Green analytical chemistry in dioxin analysis

Chapter 2: Research Methodology

2.1 Research object

The toxic dioxin/furan congeners studied: 17 representative compounds from the PCDD and PCDF groups, each containing at least four chlorine atoms substituted at the 2,3,7,8-positions on the benzene rings.

Method of dioxin/furan extraction: Application of accelerated solvent extraction (ASE) technique for the extraction of dioxins/furans from soil, sediment, fly ash, and bottom ash samples.

Sampling locations: Fly ash, bottom ash, soil, and sediment samples were collected from selected metal recycling craft villages in Bac Ninh Province, Vietnam

2.2 Chemicals, equipment

2.3 Research Content

2.3.1 Investigation of Analytical Method Conditions

First, the study investigates and selects appropriate analytical conditions to optimize the processes of extraction, clean-up, and analysis of dioxins/furans. Determining suitable technical parameters forms the basis for ensuring the accuracy and efficiency of the entire procedure. This task includes examining ASE extraction conditions as well as optimizing analytical conditions on the HRGC/HRMS system. The ASE extraction conditions are compared with the Soxhlet extraction technique according to EPA Method 1613B to ensure that ASE extraction meets the requirements for identification and quantification of toxic dioxin/furan congeners.

2.3.2 Validation of the Analytical Method for Dioxins/Furans

Based on the optimal parameters selected in the previous section, the study proceeds with validating the analytical method for dioxins/furans using ASE extraction combined with quantification by HRGC/HRMS. Method validation is carried out through key performance indicators, including accuracy, precision, repeatability, limits of detection and quantification

(LOD/LOQ), recovery, and linearity. This is a critical step to demonstrate that the method meets both scientific and practical requirements.

2.3.3 Evaluation of the "Green" Efficiency of the Analytical Method

In addition to accuracy, the study also considers the "green" efficiency of the method, focusing on minimizing solvent use, reducing hazardous chemicals, lowering energy consumption, and shortening analysis time. This approach ensures that the method not only holds scientific value but also aligns with sustainable development trends in environmental analysis.

2.3.4 Assessment of Pollution Levels and Distribution

The assessment of pollution levels for the 17 target congeners is expressed through the concentrations of each congener and their total concentration in the environment. Furthermore, the study distinguishes between dioxin and furan concentrations to highlight the separate pollution levels of these two groups. The distribution of congeners in the environment is also examined in this section.

2.3.6 Ecological Risk Assessment

Essential information used for ecological risk assessment of pollutants such as dioxins/furans in sediment includes: accumulation factor, accumulation index, pollution index (PI), potential ecological risk factor (Er), and comprehensive ecological risk index (RI). These indicators were originally proposed by Hakanson and later refined by Brady to better suit practical conditions.

2.4 Research methodology

2.4.1 Sampling method

Soil Sample: Soil samples were collected following the Vietnamese Standard TCVN 7538-2:2005: Technical guidelines for soil sampling.

Sediment Sample: Sediment samples were collected according to TCVN 6663-15:2004: Guidelines for sediment sampling.

Fly Ash and Bottom Ash Samples: Approximately 1 kg of ash was scooped using a shovel at the base of the chimney

2.4.2 extraction method

The sample extraction steps on the ASE device include the following:

- Step 1 (B1): Weigh approximately 5 g of sample and place it into the extraction cell; add 100 pg of 13C-labeled internal standard (P/N: EDF – 8999) to the sample, then transfer into a 34 mL extraction cell and perform extraction on the ASE 350 system.
- Step 2 (B2): Raise the extraction cell temperature to the selected extraction temperature of 150°C, pump toluene into the cell to reach 1500 psi pressure.
- Step 3 (B3): Maintain the sample at high temperature and pressure for 7 minutes to extract the analytes.
- Step 4 (B4): Collect the extract into a collection vial.

Repeat steps B1 to B4 three times to ensure complete extraction of dioxins from the sample.

The Soxhlet extraction method was used to analyze dioxins in environmental samples.

2.4.3 Optimization of HRGC/HRMS operating conditions

Inject 2 µL of the sample extract using an automatic sample injector. Use a TG-Dioxin column to separate dioxin compounds on a high-resolution GC/MS system. The MS detector is tuned to achieve a minimum resolution of 1000, with an ion source temperature set at 250°C.

2.4.4 Sample preconcentration method

2.4.5 Analytical method using HRGC/MS instrument

2.5.6 Data analysis method

2.4.7 Method for evaluating "green" performance

2.4.8 Ecological risk assessment method

Chapter 3: Results and Discussion

3.1 Optimize the analysis conditions

3.1.1 Confirm the mass of dioxins

The study has identified the mass fragments of congeners with 4 to 8 chlorine atoms in the PCDD/F molecules, as shown in table 3.1 below.

Table 3.1: Mass fragments of the tetra- to octa-congeners of dioxins/furans.

Name	Mass			
	Ion quanlifier			
	m/z 1	Type	m/z 2	Type
TCDF	303,9016	M+	305,8987	M+2
TCDD	319,8965	M+	321,8936	M+2
PCDF	339,8597	M+2	341,8568	M+4
PCDD	355,8546	M+2	357,8516	M+2
HxCDF	373,8207	M+2	375,8178	M+4
HxCDD	389,8157	M+2	391,8127	M+4
HpCDF	407,7818	M+2	409,7788	M+4
HpCDD	423,7767	M+2	425,7737	M+4
OCDD	457,7377	M+2	459,7378	M+4
OCDF	441,7428	M+2	443,7398	M+4

3.1.2 Optimize the GC temperature program

The results of the survey on temperature programs TP1, TP2, TP3, and TP4 show that the tested programs have relatively well separated the dioxin and furan compounds with different carbon atom counts into distinct time windows. The results of programs TP1 and TP4 both gave a resolution of <1.5, while program TP3 provided the highest resolution. Therefore, the TP3 temperature program was selected for dioxin analysis due to its effective separation of dioxin/furan congeners. The program is as follows: initial temperature of 160°C, held for 1 minute, then increased to 220°C at a rate of 20°C/min, held for 11 minutes, then increased to 280°C at a rate of 10°C/min and held for 10 minutes, and finally increased to 300°C at a rate of 10°C/min, held for 25 minutes.

Table 3.3: Retention time resolution of HxCDD and HxCDF isomers in temperature programs TP1, TP2, TP3, and TP4.

Temperature programs	TP1	TP2	TP3	TP4
Compounds	Resolution			
1,2,3,4,7,8/1,2,3,6,7,8-HxCDD	2,21	2,34	4,12	3,45
1,2,3,4,7,8/1,2,3,6,7,8-HxCDF	0,98	1,82	3,36	1,21

3.1.3 Construct the calibration curve

The calibration curve for PCDD/Fs was established by analyzing standard solutions CS1, CS2, CS3, CS4, and CS5 using the optimized method. The results showed that all 17 calibration curves of the 17 congeners of 2,3,7,8-PCDD/Fs had correlation coefficients (R^2) > 0.9999, indicating excellent linearity and meeting the requirements for sample analysis.

3.2. Results of the Accelerated Solvent Extraction Method Survey

3.2.1 Soil sample

Dioxins/furans in soil samples were extracted using the accelerated solvent extraction (ASE) method. Certified reference material (CRM) soil samples were used to evaluate the efficiency of different extraction solvents in the accelerated solvent extraction (ASE) method, based on US EPA Method 1613B. The solvents investigated included toluene, hexane, and a hexane:dichloromethane mixture (95:5, v:v). Each solvent was tested in triplicate, and the deviation, ME, and RMSE between the mean dioxin/furan concentrations obtained and the manufacturer's reference values were calculated.

The analytical results of the 17 toxic dioxin congeners obtained using toluene were the closest to the reference values provided by the supplier, compared with the other two extraction solvent systems.

3.2.2 Fly ash sample

Fly ash samples were collected from an aluminum recycling furnace in Man Xa, and extracted using the ASE device with solvents including toluene, hexane, and a hexane: DCM mixture. The findings show that toluene was the most effective solvent for extracting dioxins from the fly ash samples.

In summary, the survey results of various solvents used for dioxin extraction from different sample matrices consistently indicate that toluene is the most effective solvent for extraction.

3.3. Evaluation of the Efficiency of Accelerated Solvent Extraction

To compare the extraction efficiency of dioxins/furans from samples using the Soxhlet extraction and Accelerated Solvent Extraction (ASE) methods, several environmental samples and certified reference materials (CRMs) were selected for parallel extraction using both techniques. After extraction, the samples were cleaned up and analyzed using high-resolution gas chromatography/mass spectrometry (HRGC/MS), and the results were compared. Specifically, the tested samples included: certified reference soil samples (CRM), sediment samples, fly ash, and bottom ash collected from an aluminum recycling facility. Each sample type was extracted using both the Soxhlet and ASE methods. The analytical results were compared to evaluate the extraction efficiency of each method for different sample matrices. The results showed that, in this study, the ASE method provided dioxin/furan extraction efficiencies from soil, sediment, fly ash, and bottom ash that were comparable to those obtained with the Soxhlet extraction method.

3.4. Method Validation and Summary of Analytical Procedure

Summary of analysis method

In this study, dioxins were extracted from soil, sediment, fly ash, and bottom ash samples using the Accelerated Solvent Extraction (ASE) technique. The dioxin/furan analytical procedure comprises the following steps: first, the sample is extracted using the ASE method; second, the extract is purified using a multilayer silica gel column followed by an activated carbon column; third, the sample is concentrated by vacuum rotary evaporation and solvent evaporation under a nitrogen stream; and finally, the analysis is performed using high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC/HRMS).

Figure 3.6: Diagram of the Analytical Procedure for PCDD/F

The procedure was validated for its usability using parameters such as the determination of the detection limit and quantification limit of the method, accuracy, repeatability, reproducibility, and measurement uncertainty of the method.

3.4.2 Method detection limit, quantification limit

The results for the MDL and LOQ for the 17 congeners are shown in table 3.5The Method Detection Limit (MDL) of the method is defined as the concentration value corresponding to the concentration where the signal-to-noise ratio for each dioxin congener in the spiked sample is 3. The Quantification Limit (LOQ) of the method is calculated as 10/3 times the MDL.. The MDL and LOQ results are suitable for analyzing PCDD/Fs in samples collected from metal recycling villages.

3.4.3 Accuracy

A standard sample containing 17 dioxin congeners with concentrations ranging from 1.0 µg/L to 10 µg/L, as shown in Table 3.7, was processed and analyzed to assess the accuracy of the method. The accuracy results for the 17 congeners ranged from 98% to 102%, meeting the requirements for analyzing samples collected from the recycling villages.

3.4.4 Recovery

The recovery results for 17 toxic congeners at three concentration levels—low, medium, and high—were in the ranges of 42.6–85.5%, 42.6–99.1%, and 44.9–106%, respectively. All values fall within the acceptable recovery ranges defined by AOAC [103], generally classified as medium to high. Overall, the recovery tended to increase as the concentration of the analytes increased.

3.4.5 Repeatability and Reproducibility

The repeatability was calculated by the relative standard deviation (RSD) of the results from 7 replicate experiments conducted on the same day. The reproducibility was calculated by the standard deviation of the results obtained over 7 different days. The repeatability results at low, medium, and high concentrations ranged from 3.76% to 6.23%, 3.67% to 7.02%, and 2.66% to 6.61%, respectively. The reproducibility results for the same concentrations ranged from 6.35% to 8.29%, 5.49% to 7.30%, and 3.85% to 7.05%, respectively. These repeatability and reproducibility results meet the required standards for chemical analysis methods.

3.4.6 Uncertainty

The expanded uncertainty was calculated based on the results of repeatability, reproducibility, and accuracy of the method at low, medium, and high concentrations, as previously mentioned. The expanded uncertainty of the method at low, medium, and high concentration levels ranged from 15.3% to 19.4%, 9.21% to 18.7%, and 14.9% to 20.3%, respectively. The results of the expanded uncertainty indicate that the method meets the necessary criteria for analyzing dioxin concentrations in environmental samples collected from metal recycling villages.

3.4.7 International interlaboratory test results

A sediment sample from an international interlaboratory testing program was used to evaluate the extraction efficiency of Accelerated Solvent Extraction (ASE) and subsequent analysis by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS). The Z-score results indicate that the analytical method for PCDD/F congeners using ASE extraction provides high accuracy.

3.5. Dioxin results in various sample matrices from the metal craft village

3.5.1 Dioxin results in fly ash, bottom ash, soil, and sediment samples

The concentrations, ranges, and total toxic equivalent (TEQ) of dioxin/furan (PCDD/F) in soil, sediment, fly ash, and bottom ash samples from metal recycling villages in Bac Ninh province are summarized in Table 3.19. Fly ash exhibited the highest average PCDD/F concentrations (2065–4754 ng/kg d.w.), followed by bottom ash (48.8–101 ng/kg d.w.), soil (6.66–234 ng/kg d.w.), and sediment (11.0–323 ng/kg d.w.). TEQ values were significantly higher in fly ash (60.8–359 ng TEQ/kg d.w.) compared to bottom ash (2.59–6.16 ng TEQ/kg d.w.), attributed to the high surface area of fly ash particles enhancing dioxin adsorption. Soil TEQ ranged from 0.067–8.64 ng TEQ/kg d.w., higher than rice fields but lower than open-burning sites. Sediment TEQ (2.39–15.6 ng TEQ/kg d.w.) was comparable to electronic waste recycling areas but higher than downstream sites and the Cau River. Overall, dioxin/furan contamination in Bac Ninh's recycling villages is notable, particularly in fly ash, and exceeds levels in less impacted areas but is lower than open-burning sites.

Table 3.15. Concentrations of PCDD/Fs in different matrices

Type	Location	quan	Mass Concentration PCDD/F (ng/kg d.w)			TEQ
			Average	Min	Max	PCDD/F
Bottom ash	Aluminum	3	72,7	45,8	91,9	6,16
	Copper	3	101	44,8	164	4,90
	Metal	3	48,8	33,5	74,4	2,59
Fly ash	Aluminum	3	4754	4522	5166	359
	Copper	3	2066	2008	2131	60,8
	Metal	3	3278	3002	3491	125
Soil	Aluminum	3	234	107	441	8,64
	Copper	3	6,66	2,20	11,0	0,230
	Metal	3	13,9	7,61	23,1	0,067
Sediment	Aluminum	5	323	6,40	676	15,6
	Copper	5	11,0	8,21	98,6	2,39
	Metal	5	244	100	434	10,8

3.5.2 Bottom and fly ash samples

a, Aluminum recycling village

The analytical results of 17 dioxin/furan congeners (PCDD/Fs) in fly ash and bottom ash samples from an aluminum recycling craft village in Bac Ninh (Table 3.20) showed that: In the collected ash samples, there was a clear difference in PCDD/F and TEQ levels between fly ash and bottom ash. Specifically, fly ash had total PCDD/F concentrations ranging from 4522–5166 ng/kg d.w., with an average of 4571 ng/kg d.w.; TEQ values ranged from 284–423 ng TEQ/kg d.w., with an average of 359 ng TEQ/kg d.w. These values were generally higher than those of bottom ash, lower than values reported for some aluminum recycling plants in Vietnam, Korea, and China, but higher than those reported in Taiwan.

In contrast, bottom ash exhibited much lower total PCDD/F concentrations, ranging from 45.9–91.9 ng/kg d.w. (average 72.7 ng/kg d.w.), with TEQ values ranging from 3.68–7.93 ng TEQ/kg d.w. (average

6.32 ng TEQ/kg d.w.). These findings indicate that fly ash is a more concerning source of PCDD/F emissions compared with bottom ash.

The higher PCDD/F and TEQ levels in fly ash can be attributed to its finer particles, larger surface area, and greater tendency to adsorb dioxins. PCDFs were dominant over PCDDs, with de novo synthesis as the primary formation mechanism. Among congeners, 2,3,4,7,8-PeCDF contributed the most to TEQ, followed by 1,2,3,7,8-PeCDD, while 2,3,7,8-TCDD made negligible contributions. Therefore, fly ash requires careful management due to its high potential for dioxin release.

b, Copper casting village

At the bronze casting craft village in Bac Ninh, the analysis of 17 dioxin/furan congeners (PCDD/Fs) (Table 3.21) revealed the following: The results showed a marked difference in PCDD/F and TEQ concentrations between fly ash and bottom ash. Fly ash contained PCDD/F concentrations ranging from 2008–2131 ng/kg d.w., with an average of 2065 ng/kg d.w.; TEQ values ranged from 47.7–77.2 ng TEQ/kg d.w. (average 60.8 ng TEQ/kg d.w.), which were approximately 300–700 times higher than those of bottom ash. In contrast, bottom ash had much lower PCDD/F concentrations, ranging from 44.8–164 ng/kg d.w. (average 101 ng/kg d.w.), with TEQ values in the range of 2.84–6.08 ng TEQ/kg d.w. (average 4.90 ng TEQ/kg d.w.).

Congener profiles indicated that PCDFs were predominant, formed mainly through the de novo synthesis mechanism. Among congeners, 2,3,4,7,8-PeCDF contributed the most to TEQ, followed by 1,2,3,7,8-PeCDD, whereas 2,3,7,8-TCDD was almost negligible. The higher concentrations and TEQ values in fly ash can be attributed to its finer particle size and greater capacity to adsorb dioxins compared with bottom ash..

c, Metal craft village

Analysis of 17 dioxin/furan (PCDD/F) congeners in fly ash and bottom ash from the metalworking village in Bac Ninh (Table 3.22) shows: The analytical results showed that fly ash had an average PCDD/F concentration of 3278 ng/kg d.w. and an average TEQ of 125 ng TEQ/kg d.w., which were significantly higher than those of bottom ash. These values were lower than those reported for some steel plants in Vietnam but higher than those recorded in Korea. In contrast, bottom ash had much lower levels, with an average PCDD/F concentration of only 48.8 ng/kg d.w. and an average TEQ of 2.59 ng TEQ/kg d.w., although still higher than values reported for steel furnaces in northern Vietnam.

In terms of congener profiles, PCDFs predominated over PCDDs, formed mainly through the de novo synthesis mechanism. The congeners OCDD, OCDF, and 1,2,3,4,6,7,8-HpCDF were present at relatively high concentrations, while 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were the main contributors to TEQ. In contrast, 2,3,7,8-TCDD was found at very low levels and contributed negligibly to TEQ.

3.5.3 Soil sample

a, Aluminum recycling village

Analysis of 17 PCDD/F congeners in soil samples from the aluminum recycling village in Bac Ninh (Table 3.23) shows: The soil analysis results showed significant differences in total PCDD/F concentrations across different locations, with average values of 441 ng/kg d.w. in the village, 107 ng/kg d.w. outside the industrial cluster, and 155 ng/kg d.w. in farmland; the corresponding TEQ values were 10.9, 3.01, and 12.0 ng TEQ/kg d.w., respectively. Overall, soils within the village and farmland near the village had higher PCDD/F and TEQ levels compared with soils outside the industrial cluster; however, all values remained below the regulatory limits set by QCVN 45:2012/BTNMT.

Regarding congener profiles, OCDD, OCDF, and 1,2,3,4,6,7,8-HpCDF predominated in village and industrial cluster soils, reflecting dry deposition processes; whereas 1,2,3,7,8-PeCDF and 2,3,7,8-TCDF were more prominent in farmland soils, possibly associated with wet deposition. In terms of TEQ contribution, 1,2,3,7,8,9-HxCDD and 1,2,3,7,8-PeCDD were the main contributors, while 2,3,7,8-TCDD was present at low levels and made negligible contributions.

b, Bronze casting village

Analysis of 17 PCDD/F congeners in soil samples from the copper casting village in Bac Ninh (Table 3.24) shows: The analysis results showed that the total PCDD/F concentrations in soils at the surveyed sites were 11.0 ng/kg d.w. in the village, 6.75 ng/kg d.w. in cropland soil, and 2.20 ng/kg d.w. in paddy soil; the corresponding TEQ values were 0.326, 0.305, and 0.061 ng TEQ/kg d.w., respectively. All these values were below the regulatory limits set by QCVN 45:2012/BTNMT.

In terms of congener composition, highly chlorinated compounds such as OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, and OCDF predominated, reflecting the characteristic accumulation of persistent congeners. Meanwhile, 2,3,4,7,8-PeCDF was the largest contributor to TEQ, followed by 1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-HxCDF; notably, although 2,3,7,8-TCDD was present at low concentrations, it still contributed significantly to TEQ values. An international comparison indicated that the TEQ levels in soils from this area were approximately 26–32 times lower than those in soils near copper smelting plants in Iran and China.

c, Metal craft village

Analysis of 17 PCDD/F congeners in three soil samples from the metalworking village in Bac Ninh (Table 3.25) shows: The analysis results showed that total PCDD/F concentrations in the soil samples ranged from

7.61–23.1 ng/kg d.w., with TEQ values between 0.027–0.131 ng TEQ/kg d.w., all of which were far below the regulatory limit set by QCVN 45:2012/BTNMT (40 ng TEQ/kg d.w. for agricultural soils).

Regarding congener composition, OCDD was the most abundant, followed by OCDF, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,6,7,8-HpCDD, whereas 2,3,7,8-TCDD was detected at very low levels. In terms of TEQ contribution, samples 3.Đ1 and 3.Đ2 were dominated mainly by 1,2,3,7,8-PeCDF, while sample 3.Đ3 was primarily influenced by 1,2,3,7,8-PeCDD, followed by 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, and 2,3,7,8-TCDD. These results reflect the differences in the congener profiles contributing to TEQ across the sampling sites.

3.5.4 Sediment sample

a, Aluminum recycling village

At the aluminum recycling village, analysis of 17 PCDD/F congeners in sediment samples (Table 3.26) shows: The sediment analysis results showed that total PCDD/F concentrations ranged from 4.43 ng/kg d.w. in the canal outside the industrial cluster to 243–676 ng/kg d.w. in the village and waste ponds, with corresponding TEQ values ranging from 0.171–23 ng TEQ/kg d.w. Notably, sediment within the village had values 55–153 times higher than those outside the cluster. Among the five samples analyzed, four were below the regulatory threshold of QCVN 43:2017/BTNMT (21.5 ng TEQ/kg d.w.), except for sample 1.TT3 (waste pond), which slightly exceeded the limit. In terms of congener composition, village sediments were dominated by OCDF, 1,2,3,4,6,7,8-HpCDF, and 2,3,4,6,7,8-HxCDF, whereas sediments outside the cluster were characterized by 1,2,4,6,7,8-HpCDF, 2,3,4,6,7,8-HxCDF, and 1,2,3,7,8,9-HxCDF. This congener profile indicates that sediments in the village have a distinct composition compared with fly ash, bottom ash, and soil. Regarding

TEQ contributions, 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were the main contributors, while 2,3,7,8-TCDD was present at low concentrations and contributed negligibly.

b, Bronze casting village

Analysis of PCDD/F in sediment samples (Table 3.27) shows: The analysis of PCDD/Fs in sediment samples from the bronze casting village (Table 3.27) showed that total PCDD/F concentrations ranged from 8.34–98.6 ng/kg d.w., with an average of 41.29 ng/kg d.w.; the highest level was recorded in the village canal sample (2.TT2), while the lowest was found in pond sample 1 (2.TT3). Total TEQ values ranged from 0.319–6.99 ng TEQ/kg d.w., all of which were below the regulatory limit set by QCVN 43:2017/BTNMT (21.5 ng TEQ/kg d.w.).

In terms of congener composition, highly chlorinated compounds such as OCDD, OCDF, and 1,2,3,4,6,7,8-HpCDF predominated in concentration, whereas 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were the major contributors to TEQ. In contrast, 2,3,7,8-TCDD was present at very low levels and made negligible contributions.

c, Metal craft village

The analysis of 17 PCDD/F congeners in five sediment samples from the metalworking craft village in Bac Ninh (Table 3.28) showed that total PCDD/F concentrations ranged from 257–344 ng/kg d.w., with an average of 289 ng/kg d.w.; the average TEQ was 10.8 ng TEQ/kg d.w., all of which were below the regulatory limit of QCVN 43:2017/BTNMT (21.5 ng TEQ/kg d.w.). Among congeners, OCDD was predominant (>40%), followed by 1,2,3,4,7,8,9-HpCDF, OCDF, and 1,2,3,4,6,7,8-HpCDD, whereas 2,3,7,8-TCDD was present at very low levels. In terms of TEQ contribution, 2,3,4,7,8-PeCDF was the dominant congener (~30%), followed by 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, and

2,3,4,6,7,8-HxCDF (all in the range of 10–20%); notably, 2,3,7,8-TCDF was prominent in sample 3.TT3. Meanwhile, OCDD and OCDF contributed little to TEQ, and 2,3,7,8-TCDD accounted for about 5%.

A comparison of PCDD/F concentrations in sediments from the three craft villages (bronze casting, aluminum recycling, and metalworking) in Bac Ninh with other sites showed that the lowest level was observed in the bronze casting village (41.3 ng/kg d.w.), followed by the Cau River (266 ng/kg d.w.), the metalworking village (289 ng/kg d.w.), and the aluminum recycling village (322 ng/kg d.w.). These values were all lower than that of Truc Bach Lake (390 ng/kg d.w.) and, in particular, much lower than that of Bien Hung Lake (8590 ng/kg d.w., 27–208 times higher).

With respect to TEQ, all samples were below the QCVN 43:2017/BTNMT threshold, where 2,3,4,7,8-PeCDF was the dominant contributor in the craft villages, whereas at Bien Hung Lake, TEQ was mainly driven by 2,3,7,8-TCDD. International comparison indicated that PCDD/F levels in Bac Ninh craft villages were lower than those in the Kankazi River in Osaka, Dongting Lake (China), and Shihwa Lake (Korea, 941 ng/kg d.w.), but comparable to or lower than suburban areas of Osaka.

3.6 Ecosystem Risk Assessment

In this study, the health and ecological risk assessment caused by dioxins was applied to soil and sediment environments due to the wide scope and significant impact of these two environmental components.

3.6.1 Ecological impacts caused by dioxins in sediments in craft villages

In this study, the Hakanson method was applied to assess the ecological risk posed by dioxins/furans in craft village ecosystems. The accumulation factor of dioxins in sediment from the aluminum recycling village reached 47.4, which is classified as very high according to Hakanson's reference scale.

Similarly, PCDD/F accumulation levels in sediments from the bronze casting and metalworking villages were also in the very high category.

The ecological risk index (RI) derived from toxic PCDD/F congeners in sediments collected across the craft village catchments in Bac Ninh is presented in Figure 3.31. The results indicate that the ecological risk posed by dioxins/furans was very high (RI > 600) in both the aluminum recycling and metalworking villages, whereas the bronze casting village showed a moderate risk level (RI = 150–300).

The analysis results revealed the presence of dioxins/furans in sediment samples collected from several metal recycling craft villages in Bac Ninh province, which are identified as contributing factors to ecological risks in the local aquatic ecosystems. The accumulation coefficients of PCDD/Fs ranged from high at the bronze casting and metalworking villages to very high at the aluminum recycling village. In terms of ecological risk index (RI), the bronze casting village was classified at a low–moderate level, whereas the aluminum recycling and metalworking villages were both at high levels, indicating considerable potential risks that require close attention and control.

3.7 Evaluation of the environmental friendliness of the two methods

3.7.1 Comparison of the environmental friendliness of two extraction techniques

The results show that ASE performs the extraction process 27 times faster, uses 4 times less solvent, and reduces electricity consumption by 36 times compared to the Soxhlet method. In addition, ASE can process up to 12 samples per run, nearly double the Soxhlet system, which can only process 6 samples. The solvents used for PCDD/Fs extraction, such as dichloromethane (DCM) and toluene, are all environmentally harmful solvents. However, the ASE system helps to minimize the release of toxic solvents into the laboratory environment thanks to its completely closed design. The higher level of automation of ASE compared to Soxhlet also reduces manual labor and limits the risk of chemical exposure during extraction

3.7.2 Evaluation of the green score of the method

Figures 3.32 and 3.33 present the green scores of two analytical methods for dioxin/furan in fly ash and bottom ash, obtained using ASE and Soxhlet extraction, as calculated by the AGREE Prep software. The results show that the ASE-based method achieved a higher green score (0.50) compared to the Soxhlet-based method (0.31), with advantages in sample preparation time, level of automation, and energy consumption. However, this score does not fully reflect the environmental benefits of ASE over Soxhlet, since the evaluation considers the entire analytical procedure—including extraction, cleanup, and final analysis—while the present study only compares the extraction step, keeping other factors constant. In summary, ASE extraction is a greener and more efficient alternative to Soxhlet extraction.

However, this score does not fully capture the environmental advantages of ASE over Soxhlet, as the evaluation considers the entire analytical process—including extraction, cleanup, and final determination—whereas this study only compares the extraction step while keeping other factors constant. In summary, the extraction method based on ASE technology represents a greener alternative to Soxhlet extraction.

CONCLUSION

The study successfully optimized and established the analytical procedures and technical parameters for the determination of dioxins/furans in soil, sediment, fly ash, and bottom ash matrices, using Accelerated Solvent Extraction (ASE) combined with High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS). All parameters met the required criteria, ensuring the reliability of dioxin/furan analysis.

The validated method was applied to environmental samples collected from metal recycling craft villages in Bac Ninh province, including aluminum recycling, bronze casting, and metalworking. The results showed that the total TEQ of toxic PCDD/F congeners ranged from 60.8 to 359 ng TEQ/kg d.w. in fly ash, and was considerably lower in bottom ash (2.59–6.16 ng TEQ/kg d.w.). In soils, TEQ values ranged from 0.067 to 8.64 ng TEQ/kg d.w., while in sediments, the total TEQ was 15.6, 2.39, and 10.8 ng TEQ/kg d.w. for the three respective villages.

Sediment analysis further revealed high to very high accumulation factors of dioxins/furans, with ecological risk indices reaching high levels at the aluminum recycling and metalworking villages, indicating potential adverse impacts on aquatic ecosystems.

Compared to Soxhlet extraction, ASE required less solvent, energy, and time, thereby reducing emissions and improving efficiency. Assessment using the AGREE Prep software confirmed a higher “green” score for ASE, highlighting its sustainability and environmental advantages in dioxin/furan analysis.

Proposal

The results of this study on the characteristics of PCDD/Fs at several representative metal recycling craft villages in Bac Ninh province have provided valuable information on the levels of dioxin/furan contamination in soil, sediment, fly ash, and bottom ash, as well as their impacts on ecosystem health. However, the study still has certain limitations, such as the relatively small number of analyzed samples and the fact that not all environmental components, such as water and air, were included.

Below are some recommendations for further research in the future:

Expansion of sampling scope: Future studies should further expand the scope and number of samples collected from other types of craft villages in Bac Ninh as well as from other regions with similar production characteristics. This will allow a more comprehensive and complete assessment of dioxin/furan contamination levels in soil and sediment, while also enabling comparisons with areas that are either uncontaminated or less contaminated. In addition, other environmental components such as water and air should be collected and analyzed to provide a more holistic view of dioxin/furan status in the environment of traditional craft villages in Bac Ninh and nationwide.

Application of ASE technique: The Accelerated Solvent Extraction (ASE) technique should be further studied and incorporated into the analytical process for dioxins/furans in particular and for other organic pollutants in environmental samples in general, as it is a more environmentally friendly ("green") alternative compared to Soxhlet extraction.

References

Appendix

LIST OF PUBLICATIONS RELATED TO THE THESIS

1, A Comprehensive Evaluation of Dioxins and Furans Occurrence in River Sediments from a Secondary Steel Recycling Craft Village in Northern Vietnam, Authors: **Hung Xuan Nguyen**, Xuyen Thi Nguyen, Hang Thi Hong Hang, Huong Thi Nguyen, Nam Duc Vu, Thao Thi Phuong Pham, Trung Quang Nguyen, Dat Tien Nguyen, Nam Thanh Duong, Anh Le Tuan Hoang, Tung Ngoc Nguyen, Nhan Van Le, Ha Viet Dao, Minh Truong Ngoc, Minh Quang Bui, Journal: Molecules 2024; Volume 29, Issue 8, 1788. Doi: 10.3390/molecules29081788. SCIE- Q2.

2, Occurrence and Contamination Levels of Polychlorinated Dibenzo-p-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) in Soil and Sediment in the Vicinity of Recycle Waste Metal Casting Villages: Case Study in Vietnam. Authors: **Hung Nguyen Xuan**, Quang Phan Dinh, Xuyen Nguyen Thi, Hang Mai Thi Hong, Anh Nguyen Phuc, Nhan Le Van, Minh Bui Quang, Trung Nguyen Quang, Binh Chu Dinh , Dat Nguyen Tien , Tuan Anh Le Hoang, Nam Vu Duc. Soil and Sediment Contamination: International Journal; https://doi.org/10.1080/15320383.2024.2407643. SCIE- Q2.

3, Comparative efficiency of soxhlet and accelerated solvent extraction (ASE) methods for dioxin/furan analysis in ash samples: A green chemistry perspective. Authors: **Xuan Hung Nguyen**, Duc Nam Vu, Quang Minh Bui, Quang Trung Nguyen, Anh Tuan Nguyen. Tạp chí Green Analytical Chemistry, 12 (2025) 100227. https://doi.org/10.1016/j.greeac.2025.100227. ESCI – Q1

4, Comparison of the Efficiency of Dioxin/Furan Extraction in Soil and Sediment Samples Using Accelerated Solvent Extraction and the Soxhlet Extraction Method. Authors: **Nguyen Xuan Hung**, Vu Duc Nam, Bui Quang Minh, Nguyen Quang Trung, Nguyen Anh Tuan. Journal of Science and Technology, Volume 66, Special Issue 10 ĐB-HH, https://doi.org/10.31276/VJST.66(10DB-HH).50-55.