ANALYSIS OF RESIDUAL CONCENTRATIONS AND ACCUMULATION PROFILES OF CHLORINATED BENZENES IN ASH SAMPLES FROM INDUSTRIAL FACILITIES IN VIETNAM

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TÓM TẮT

PHÂN TÍCH HÀM LƯỢNG VÀ ĐẶC TRƯNG TÍCH LŨY CỦA CHLORINATED BENZENES TRONG MẪU TRO THU THẬP TẠI MỘT SỐ CƠ SỞ CÔNG NGHIỆP Ở VIỆT NAM

Chlorinated benzenes (CBzs) là nhóm chất hữu cơ bao gồm 12 chất, được hình thành khi thay thế 1 đến 6 nguyên tử hydro của phân tử benzene bằng số lượng tương ứng các nguyên tử clo. CBzs được coi là các chất ô nhiễm hữu cơ khó phân hủy với những tác động xấu đến sức khỏe môi trường và con người. Trong nghiên cứu này, hàm lượng của 7 chất CBzs (bao gồm 1,2-DCB, 1,3-DCB, 1,2,4-TCB, 1,2,4,5-TeCB, 1,2,3,4-TeCB, PeCB và HCB) được xác định trong mẫu tro bay và tro xỉ thu thập tại một số cơ sở công nghiệp sử dụng nhiệt độ cao ở miền Bắc Việt Nam. Mẫu tro được chiết Soxhlet với hỗn hợp dung môi acetone/hexane (1:1). Dịch chiết được cô đặc và chuyển vào dung môi hexane, sau đó được xử lý với acid sulfuric đặc, bột đồng kim loại và cột sắc ký đa lớp silica gel. CBzs được tách và phân tích trên hệ thống sắc ký khí ghép nối detector khối phổ (GC/MS) ở chế độ ion hóa va đập electron và quan sát chọn lọc ion. Hàm lượng của Σ7CBzs trong các mẫu tro giảm theo thứ tự sau: lò đốt rác thải > nhà máy luyện kim > nhà máy sản xuất gạch. Hàm lượng CBzs trong mẫu tro bay nhìn chung cao hơn so với các mẫu tro xỉ, phản ánh sự hình thành CBzs trong điều kiện xúc tác ở nhiệt độ thấp sau khu vực thiêu đốt. Đặc trưng tích lũy của CBzs có sự dao động lớn giữa các loại mẫu, các cơ sở công nghiệp và thậm chí giữa các ngày lấy mẫu khác nhau của cùng một cơ sở, cho thấy cơ chế hình thành và các yếu tố ảnh hưởng phức tạp. Các nghiên cứu tổng thể về mức độ ô nhiễm và đặc trưng tích lũy của CBzs trong nguồn phát thải và môi trường tiếp nhận ở Việt Nam cần tiếp tục được thực hiện.

Từ khóa: *Chlorinated benzenes, tro bay, tro xỉ, quá trình công nghiệp nhiệt độ cao, Việt Nam.*

1. INTRODUCTION

Chlorinated benzenes (CBzs) comprise 12 congeners, which contain one to six chlorine atoms attached to the benzene ring. There are six homologs, including mono-, di-, tri-, tetra-, penta-, and hexa-CB with numbers of congeners as 1, 3, 3, 3, 1, and 1, respectively [3]. CBzs were produced for multiple applications such as solvents, intermediates, dye carriers, industrial fluids, pesticides, etc. Besides, CBzs are also unintentionally formed as impurities in chlorinated chemicals and during thermal processes such as waste incineration and biomass

combustion [1,2]. These compounds have relatively high boiling points and *n*-octanol/air partition coefficients, resulting in particle/air distribution characteristics and bioaccumulation potentials [9]. The boiling points of CBzs increase with molecular weights, while water solubility decreases with molecular weights. Due to evaporation potentials and hydrophobic properties, CBzs can be subjected to long-range transport and accumulation in organic-rich media. Hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) have been classified as persistent organic pollutants (POPs) under the Stockholm Convention. Accordingly, these two compounds are originated from both agricultural, industrial, and unintentional sources.

In Vietnam, CBzs (notably HCB) have been detected in environmental and biota samples (e.g., soil, sediment, biota, human breast milk) from Vietnam since the late 1980s, reflecting the use of organochlorine pesticides [7,8,10,13]. HCB and PeCB were found in flue gas, fly ash, bottom ash, and soil samples collected from some industrial facilities in northern Vietnam, suggesting their industrial emission sources [4,15]. However, a comprehensive and continuous monitoring dataset about CBzs in this country is still lacking, especially for congeners other than HCB.

In this study, concentrations of CBzs at different chlorination degrees were determined in bottom ash and fly ash samples obtained from various industrial sectors such as brick making, metallurgy, and waste incineration in northern Vietnam. The analytical results will provide updated information about the residual levels and accumulation profiles of multiple CBz congeners in solid waste generated from Vietnamese industrial facilities.

2. METHODS

2.1. Sample collection

The bottom ash (BA) and fly ash (FA) samples were collected during 2017 and 2019 from various industrial facilities including brick making plant (BR), metallurgy plants (ML), incinerators for municipal waste (MU), medical waste (ME), and industrial waste (IN). These facilities are located in northern cities and provinces in Vietnam such as Hanoi (HN), Hai Phong (HP), Hai Duong (HD), and Thai Nguyen (TN). Detailed numbers of ash samples are presented in Table 1. A total of 57 samples, including 33 bottom ash samples and 24 fly ash samples, were collected.

Table 1: Ash samples analyzed in this study

Category	Location	Bottom ash	Fly ash
BR	TN	2	0
ML	TN	3	6
MU	TN	4	1
MU	HP	6	6
ME	HP	9	10
IN	TN	1	0
IN	HP	5	0
IN	HD	3	0
IN	HN	0	1

2.2. Chemical analysis

The analytical procedure generally followed Method 8212 (Chlorinated hydrocarbons by gas chromatography: capillary column technique) by US Environmental Protection Agency. The samples were homogenized by passing through 1-mm sieve. After spiking with surrogate standard (13C12-PCB-209), about 10 g sample was Soxhlet extracted with 450 mL acetone/hexane (1:1) for 16 h. The extract was then concentrated and solvent-exchanged into hexane. Extract clean-up was performed by concentrated sulfuric acid treatment (to remove most nonpersistent interferences), acid-washed copper treatment (to remove elemental sulfur), and multilayer silica gel column (for additional clean-up and fractionation). The eluate was concentrated and spiked with pentachloronitrobenzene (PeCNB) as internal standard before quantification analysis.

2.3. Instrumental analysis

Seven CBz congeners, including 1,2-dichloro (1,2-DCB), 1,3-dichloro (1,3-DCB), 1,2,4-trichloro (1,2,4-TCB), 1,2,3,4-tetrachloro (1,2,3,4-TeCB), 1,2,4,5-tetrachloro (1,2,4,5-TeCB), pentachloro (PeCB), and hexachloro (HCB) benzenes, were analyzed by using a 6890N gas chromatograph with 5973N mass spectrometer with a DB-5 column (30 m × 0.25 mm × 0.25 μm) (Agilent Technologies). Oven temperature program was initially set at 50 °C, increased to 120 °C (7 °C/min, hold 2 min), and to 280 °C (10 °C/min, hold 5 min). Temperature

of injection port, interface, and ion source was 220, 280, and 230 °C, respectively. The samples were injected to the GC/MS system with splitless mode and injection volume of 1 μL. The MS was operated at positive electron impact ionization mode and selected ion monitoring mode.

3. RESULTS AND DISCUSSION

3.1. Concentrations of CBzs in fly ash

CBzs were detected in all fly ash samples of this study at concentrations ranging from 6.98 to 404 (mean 101) ng/g (Fig. 1). The highest level was found in a sample collected from an industrial waste incinerator, while the lowest levels were measured in a medical waste incinerator. In general, average CBz concentrations decreased in the order: IN (404), MU (183; 59.1–391), ML (92.2; 24.2–234), and ME (19.2; 6.98–34.4) ng/g. Among CBzs, average concentrations in fly ash samples decreased in the order: HCB (29.6; 0.565–267); 1,2,4-TCB (19.2; 0.130–138); 1,2,4,5-TeCB (19.0; not detected–280); PeCB (14.7; not detected–66.2); 1,2,3,4-TeCB (9.94; not detected–48.4); 1,3-DCB (6.74; not detected–86.4); 1,2-DCB (1.96; not detected–9.74) ng/g. Elevated levels of tri- and tetra-chlorinated congeners suggest the need for full congener analysis of CBzs.

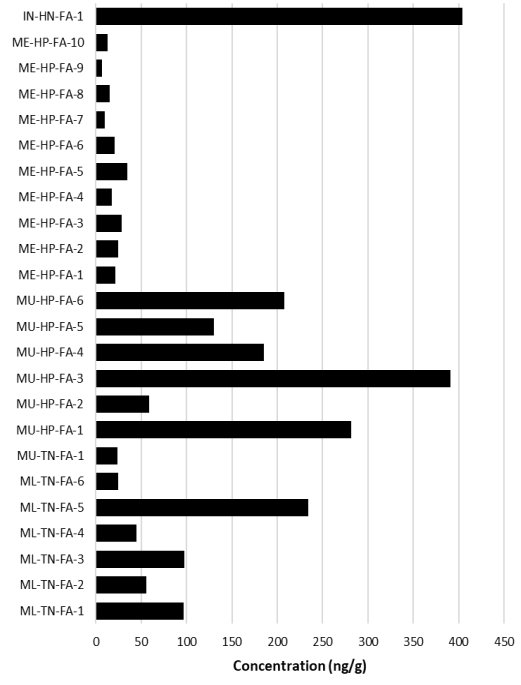

Fig. 1: Concentrations of Σ7CBzs in fly ash samples of this study

Levels of CBzs in our fly ash samples were comparable to the range reported for municipal waste incinerators in China (6.74–358 ng/g) [6], but still lower than those measured in municipal waste incinerators in Japan (870–1900 ng/g) [14]. Concentrations of CBzs in Vietnamese ash samples were generally higher than those of polychlorinated dibenzo-*p*-dioxins (PCDDs: mean 3.76; range 0.0006–12.4 ng/g) and polychlorinated dibenzofurans (PCDFs: mean 10.8; range 0.0001–40.3 ng/g) [12], but much lower than levels of polycyclic aromatic hydrocarbons (PAHs: 215000; 430–785000 ng/g) [11]. Concentration ranges of HCB (0.56–266 ng/g) and PeCB (0.01–66.2 ng/g) in our fly ash samples were also higher than levels of HCB (0.05–18.4 ng/g) and PeCB (0.18–15.5 ng/g) found in soil samples collected around industrial facilities in Vietnam [4].

3.2. Concentrations of CBzs in bottom ash

CBzs were detected in all bottom ash samples of this study at concentrations ranging from 1.53 to 125 (mean 26.1) ng/g (Fig. 2).

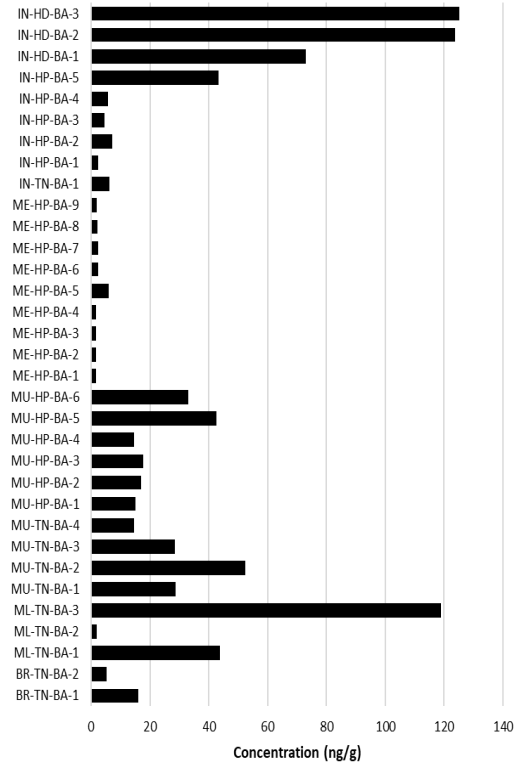

Fig. 2: Concentrations of Σ7CBzs in bottom samples of this study

These levels were markedly lower than those measured in the fly ash samples, partially indicating the low-temperature catalytic formation of these pollutants in post-combustion zone [6,14]. The highest levels were found in some samples collected from a metallurgy plant (119 ng/g) and an industrial waste incinerator (124–125 ng/g), while the lowest levels were observed in a medical waste incinerator. In general, average CBz concentrations decreased in the order: ML (55.0; 1.99–119), IN (43.4; 2.38–125), MU (26.4; 14.5–52.5), BR (10.6; 5.17–16.0), and ME (2.32; 1.53–5.98) ng/g. Among CBzs, average concentrations in bottom ash samples decreased in the order: HCB (5.62; not detected–29.2); 1,2-DCB (4.85; not detected–44.3); 1,2,3,4-TeCB (4.67; not detected–45.8); PeCB (2.92; not detected–35.6); 1,2-DCB (2.69; not detected–48.4); 1,3-DCB (6.74; not detected–86.4); 1,2-DCB (1.96; not detected–9.74) ng/g.

Levels of CBzs in our bottom ash samples were exceeded the range documented for municipal waste incinerators in China (2.23–2.99 ng/g) [6]. CBzs concentrations in Vietnamese ash samples (1.53–125 ng/g) were markedly higher than those of PCDDs (mean 0.21; range 0.0005–1.04 ng/g) and PCDFs (mean 0.47; range 0.0001–2.77 ng/g) [12], but much lower than levels of PAHs (mean 2380; range 52–6040 ng/g) [11]. Concentration ranges of HCB (0.01–29.2 ng/g) and PeCB (0.01–35.6 ng/g) in our bottom ash samples were comparable to or generally greater than levels of HCB (0.05–18.4 ng/g) and PeCB (0.18–15.5 ng/g) found in soil samples collected around industrial facilities in Vietnam [4].

3.3. Profiles of CBzs in ash

Accumulation profiles of CBzs in fly ash and bottom ash samples of this study are presented in Fig. 3. In general, CBzs patterns varied greatly between sample types (fly ash and bottom ash), categories (brick, metallurgy, and incinerator), and facilities. HCB was major compound detected in both bottom ash and fly ash from a municipal waste incinerator in Hai Phong, accounting for 40% to 60% of Σ7CBzs. Meanwhile, PeCB was important contributor to Σ7CBzs in Hai Phong medical waste incinerator fly ash (60%) and Hai Duong industrial waste incinerator bottom ash (25%). Elevated proportions of some di- to tetra-CBzs were found in Thai Nguyen brick bottom ash (1,3-DCB 50%), Thai Nguyen industrial bottom ash (1,3-DCB 50%), Thai Nguyen municipal fly ash (1,3-DCB 35%), Thai Nguyen metallurgy fly ash (1,2,4-TCB 50%), Hai Phong industrial waste incinerator bottom ash (1,2,3,4-TeCB 55%), Hanoi industrial waste incinerator fly ash (1,2,4,5-TeCB 70%), Hai Phong medical bottom ash (1,2,4,5-TeCB 33%). Complicated accumulation profiles of CBzs in our ash samples suggest that these compounds have been produced under different formation pathways and influencing factors (e.g., compositions of input materials, temperatures, combustion/production technologies, and types of pollution control devices).

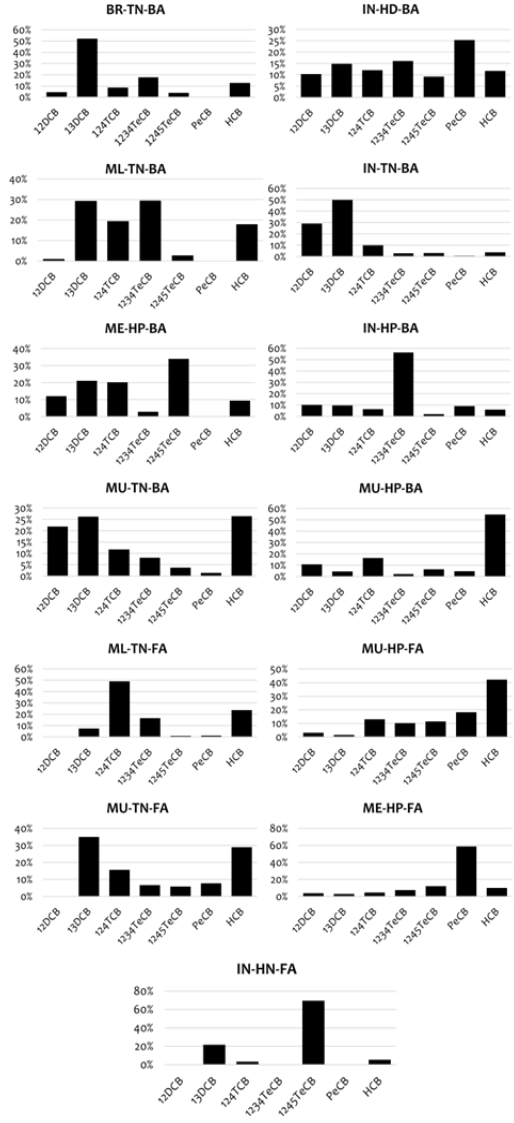

Fig. 3: Profiles of Σ7CBzs in fly and bottom ash samples of this study

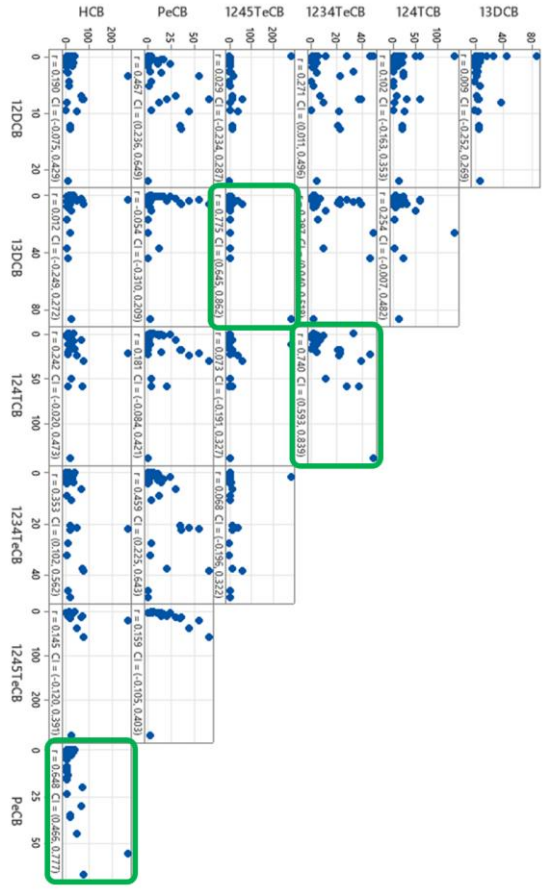

Fig. 4: Correlation analysis of CBzs in fly and bottom ash samples of this study

Pearson correlation analysis was applied to the whole dataset to estimate potential relationship between CBzs (Fig. 4). The statistical results indicated moderate correlations between 1,3-DCB and 1,2,4,5-TeCB (r = 0.775), between 1,2,4-TCB and 1,2,3,4-TeCB (r = 0.740), between PeCB and HCB (r = 0.648) (p < 0.05). Meanwhile, insignificant correlations were found for the remaining compound pairs (r < 0.5). The correlations between some compounds suggest the similarity in formation pathways, origins, or behaviors. Hue and Nguyen (2021) also reported significant correlations between PeCB and HCB in fly ash (R^2 = 0.7747) and bottom ash (R^2 = 0.5423) samples collected from multiple industrial sectors in northern Vietnam [5]. Dechlorination process of highly chlorinated CBzs (notably HCB) has also been considered as potential formation pathway of lower chlorinated congeners [1,2].

4. CONCLUSIONS

A CBzs of different chlorination degrees were measured in fly ash and bottom ash samples collected from various industrial sectors in northern Vietnam, providing updated information about this pollutant class. Levels of CBzs were generally higher in fly ash than in bottom ash, but accumulation profiles did not exhibit clear trends between ash types. Elevated CBz concentrations were found in some metallurgy plants, municipal waste incinerators, and industrial waste incinerator. Levels of CBzs in Vietnamese ash samples were comparable to or lower than those found in other countries like China and Japan. Correlations were found between some compound pairs (e.g., 1,3-DCB/1,2,4,5-TeCB; 1,2,4-TCB/1,2,3,4-TeCB; PeCB/HCB), suggesting similar formation pathways or effects of dichlorination processes. More comprehensive studies should be conducted for CBzs, for example, development of analytical methods for full congener analysis of CBzs in both waste and environmental samples, evaluation of CBz emissions from multiple industrial sectors and informal waste processing sites in different areas along the country, and assessment of CBzs in Vietnamese environment (e.g., air, soil, dust, water, sediment, biota) and their impacts on environmental and human health.

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