CHLORINATED AND BROMINATED POLYCYCLIC AROMATIC HYDROCARBONS IN E-WASTE OPEN BURNING SOILS IN VIETNAM, THE PHILIPPINES, AND GHANA

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Introduction

Chlorinated polycyclic aromatic hydrocarbons (ClPAHs) are substituted PAHs that are produced during the combustion of solid wastes. ClPAHs have been reported to be carcinogenic and mutagenic, and they have a similar toxic potency as chlorinated dioxins such as polychlorinated dibenzo-p-dioxins and dibenzofurans, (PCDD/Fs)[1,2]. The open burning of electronic waste (e-waste), which is a primitive e-waste recycling activity, has become a serious source of environmental pollution in ecosystems near recycling areas. Previous studies have reported high concentrations of PCDD/Fs, PCBs, and chlorobenzenes in e-waste open-burning soils (EOBS)[3]. However, their percentage contribution to the total organic chlorine (TOCl) was small[3]. There were many unidentified chlorinated compounds (more than 99.3% of the total) generated by open-burning activities. In addition, a higher concentration of PAHs than chlorinated dioxins has been detected in EOBS[4]. This suggests that high concentrations of ClPAHs (i.e., substituted PAHs), could be detected among the unidentified chlorinated compounds. Because brominated flame-retardants are present in e-waste, brominated polycyclic aromatic hydrocarbons (BrPAHs) can also be emitted when the waste is burned. Although ClPAHs have been identified in the dust from workshop-floors, soils from e-waste recycling facilities,[5] and in municipal solid waste incineration ash[6], there are currently no records of their presence in soils from e-waste open-burning sites. This is the first study to investigate the level of ClPAHs and BrPAHs (Cl/BrPAHs) in EOBS collected from three countries: Vietnam, the Philippines, and Ghana.

Materials and methods

Sample collection and sample preparation. Soil samples were collected in Vietnam (Jan. 2011), in the Philippines (Aug. 2010), and in Ghana (Aug. 2013). EOBS samples were collected from directly beneath combusted residue at each site using a shovel, packed in plastic bags, and stored in a cooler. A reference soil sample (VN-1) was collected in Duong Quang, Hanoi, Vietnam, where e-waste recycling is not conducted. Two surface soils (VN-2 and VN-3) were collected at an informal site for the open burning of wires and cables in Bui Dau, Hanoi, Vietnam, a town known for e-waste recycling activities. Two surface soils (PHI-1 and PHI-2) were collected from an e-waste open-burning site on the bank of the Marilao River in Caloocan, Metro Manila, the Philippines. The other two surface soils were collected from Agbogbloshie market, Accra, Ghana, which is a primitive e-waste recycling site in Ghana (GH-1 and GH-2). Samples were stored in a refrigerator prior to analysis.

Table 1. Target PAHs.

Abbreviation of PAHs	
Nap	Naphthalene
Ace	Acenaphthene
Fle	Fluorene
Phe	Phenanthrene
Ant	Anthracene
Flu	Fluoranthene
Pyr	Pyrene
Chr	Chrysene
BaA	Benzo[*a*]anthracene
BbkF	Benzo[*b*]fluoranthene
	Benzo[*k*]flooranthene
BaP	Benzo[*a*]pyrene
DA	Dibenz[*a,h*]anthracene
IP	Indeno[*1,2,3-cd*]pyrene
BP	Benzo[*g,h,i*]perylene

Sample preparation and analysis for Cl/BrPAHs. We analyzed 26 ClPAHs, 14 BrPAHs, and 15 PAHs. The abbreviations of target PAHs and parent PAHs of Cl/BrPAHs are given in **Table 1**. Cl/BrPAHs were analyzed following a previously described method with some modifications[7]. Each soil sample (1 g) was homogenized with 10 g of anhydrous sodium sulfate and extracted for 18 h in a

Soxhlet apparatus using 360 mL of a mixture of dichloromethane (DCM) and n-hexane (3:1, v/v). A 2.5 ng amount of each ^{13}C-labeled PAH standard (^{13}C-labeled PAH, 16PAH mix, Cambridge Isotope Laboratory, Tewksbury, MA, USA) was spiked onto an aliquot of each sample after extraction. The extracts were concentrated and replaced by hexane. The solutions were purified, and fractionated using an activated carbon cartridge column (Carboxene 1016, 200 mg, Supelco, Bellefonte, PA, USA) connected to a silica gel cartridge column (Supelclean LC-Si, 2 g, Supelco). The cartridge columns were eluted with 20 mL of 10% DCM/hexane. The silica gel cartridge was removed and the active carbon cartridge was reversed, and then eluted with 120 mL of toluene. The toluene fraction including theCl/BrPAHs was concentrated and spiked with 2.5 ng of d12-Chrysene as a recovery standard to make a total volume of 100 µL. The concentrations of Cl/BrPAHs were determined by HRGC-HRMS (JMS-800D, JEOL, Tokyo, Japan).

Sample preparation and analysis for PAHs.

Each soil sample (1 g) was extracted with ultrasonic extraction after adding 5 mL of acetone. The extracts were centrifuged at 2500 rpm for 5 min in a centrifugal separator and then dissolved into 500 mL of ultra-pure water. This extraction process was conducted twice. The solution was cleaned up and concentrated through a cartridge (InterSep RP-1, GL Sciences, Eindhoven, Netherlands) at 7 mL/min. After dehydration, the cartridge was eluted with 10 mL of DCM. The elute was concentrated to less than 1 mL with a stream of nitrogen and diluted to 1.0 mL with acetonitrile. The analysis of 15 PAHs was conducted using HPLC-FL (GL-7400 Series, GL science).

Results and discussion

Concentrations of ClPAHs, BrPAHs, and PAHs. The sum of the concentrations of 26 ClPAHs (ΣClPAHs), 14 BrPAHs (ΣBrPAHs), and 15 PAHs (ΣPAHs) in each soil sample are shown in **Fig.1a**. The trend in all the soil samples was generally ΣPAHs > ΣClPAHs > ΣBrPAHs, and the concentrations of all PAHs, ClPAHs, and BrPAHs was considerably higher in EOBS than in the reference soil (VN-1). The concentration of ΣClPAHs in GH-1 and GH-2 varied from 21 to 29 ng/g, which was 200-fold higher than in VN-1. The concentration of ClPAHs in PHI-1 and PHI-2 varied from 110 to 250 ng/g, which was three orders of magnitude higher than in VN-1. In VN-2 and VN-3 the concentration of ClPAHs varied from 1800 to 2800 ng/g, which was four orders of magnitude higher than in VN-1. The mean concentration of ΣClPAHs (8700 ng/g) in EOBS was higher than in other e-waste recycling samples; 14-fold higher than in electronic shredder waste, 8-fold higher than in dust from the floor of e-waste recycling facilities, and 31-fold higher than in soil around similar facilities in China[5]. This suggests that open-burning activities are potentially a larger emission source of ClPAHs than other primitive recycling activities. Moreover, the concentrations were two orders of magnitude higher than in bottom ash and were comparable to fly ash from a waste incinerator[6]. BrPAHs were not detected in VN-1. The concentration of BrPAHs concentrations varied from 5.8 to 530 ng/g in the EOBS. This suggests that BrPAHs were generated anthropogenically in the EOBS. The mean concentration of ΣBrPAHs (120 ng/g) was also two orders of magnitude higher than that in bottom ash and comparable to that in fly ash from a waste incinerator[6]. The concentration of ΣPAHs was 30 ng/g in VN-1 and varied from 480 to 7100 ng/g in the EOBS. The mean ΣPAHs

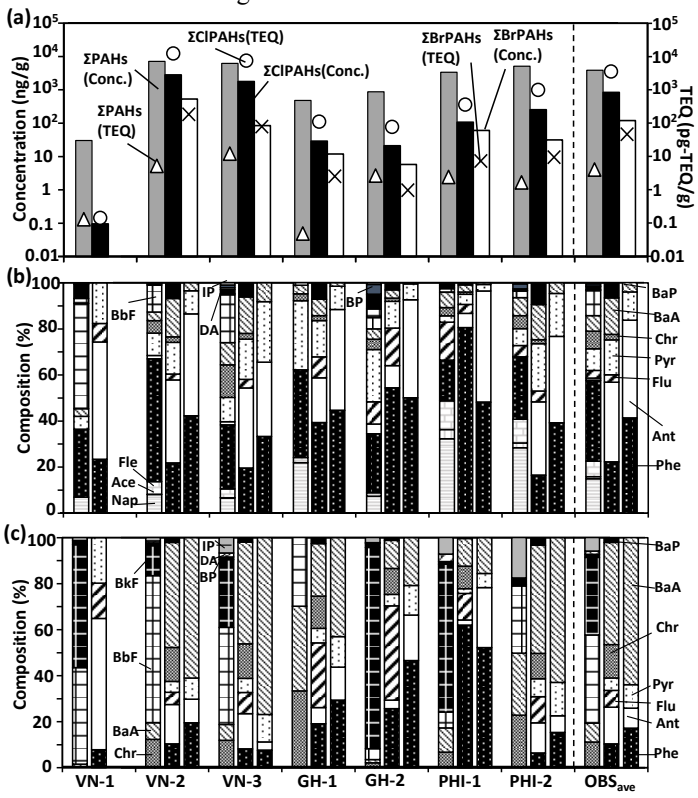

Figure 1. (a) The concentrations and toxic equivalency (TEQ) values of ΣPAHs, ΣClPAHs, and ΣBrPAHs in soils. (b) Compositions of individual PAHs, Cl/BrPAHs among the ΣPAHs, ΣClPAHs and ΣBrPAHs in soils. (c) Compositions of the TEQ concentrations for individual PAHs, Cl/BrPAH among the ΣTEQ_{PAHs}, ΣTEQ_{ClPAHs}, and ΣTEQ_{BrPAHs}.

concentration (3900 ng/g) was not more than one-fifteenth of that in fly ash and was ninefold higher than in bottom ash[6]. This was the same order of magnitude as in EOBS in China[4].

Toxic equivalency quotients of ClPAHs, BrPAHs, and PAHs. The AhR-mediated activities of 17 ClPAHs, nine BrPAHs, and their corresponding parent PAHs have been reported using a YCM3 cell bioassay[1]. We estimated the TEQ concentrations of Cl/BrPAHs and PAHs in soil samples using the following equation: TEQ = $\Sigma\ [C_i]\times REP_{BaP,\ i}/60$, where C_i is the concentration of an individual ClPAH or BrPAH and $REP_{BaP,\ i}$ is their potency relative to BaP (REP_{BaP}; based on EC_{50})[8]. Seven dioxin-like PAHs and their potencies (REP_{PAHs}) relative to TCDD were used to calculate the TEQ concentrations of PAHs[9]. The calculated TEQ concentrations are shown in the second axis of **Fig. 1a**. The calculated TEQ concentrations of ClPAHs (ΣTEQ_{ClPAHs}) were 0.14 pg-TEQ/g in VN-1. In EOBS, ΣTEQ_{ClPAHs} varied from 78 to 110 pg-TEQ/g in GH, from 360 to 1000 pg-TEQ/g in PHI, and from 7600 to 12000 pg-TEQ/g in VN-2 and VN-3. The mean ΣTEQ_{ClPAHs} in EOBS was one-fifth that in fly ash and fivefold higher than the maximum value in the bottom ash of a waste incinarator[6]. In VN-2, VN-3, and PHI-2, the ΣTEQ_{ClPAHs} concentrations exceeded the Environmental Quality Standard of Japan. In the EOBS, the calculated TEQ concentrations of BrPAHs (ΣTEQ_{BrPAHs}) varied from 0.90 to 160 pg-TEQ/g and the calculated TEQ concentrations of PAHs (ΣTEQ_{PAHs}) varied from 0.048 to 12 pg-TEQ/g. The TEQ concentrations in the EOBS generally followed the order: $\Sigma TEQ_{ClPAHs} > \Sigma TEQ_{BrPAHs} > \Sigma TEQ_{PAHs}$. Although the concentrations of ΣClPAHs and ΣBrPAHs were considerably lower than the concentration of ΣPAHs, the concentrations of ΣTEQ_{ClPAHs} and ΣTEQ_{BrPAHs} were several hundred-fold higher than the concentration of ΣTEQ_{PAHs} in the EOBS, and accounted for 3.9-54% of the TEQ concentration due to dioxins (i.e., the sum of the TEQ concentrations of PCDD/Fs and DL-PCBs) in the same soil samples[3]. This suggests that Cl/BrPAHs in EOBS have a toxic potency equivalent to dioxins.

Profiles of ClPAHs, BrPAHs, and PAHs. The composition of individual ClPAHs, BrPAHs, and PAHs to each ΣClPAHs, ΣBrPAHs, and ΣPAHs, are shown in **Fig. 1b**. In general, similar ClPAH profiles were found in all EOBS samples. Among the individual ClPAHs, three-ring ClPAHs (ClPhe, ClAnt, and ClFlu) were the predominant components. The sum of these accounted for 52-91% (68% on average) of the ΣClPAHs. Four ring ClPAHs (ClPry, ClChr, and ClBaP) accounted for 8.5-38% (26% on average), while five-ring ClPAHs (ClBaP) accounted for only 5.6% (on average) of the ΣClPAHs. This profile differed from those of samples from e-waste shredding recycling facilities[5] and fly ash[6], in which four- and five-ring ClPAHs were more dominant than three-ring ClPAHs. The BrPAH profiles were also similar in all EOBS. The collective sum of BrPhe and BrAnt accounted for 84%, BrPyr accounted for 12%, and five-ring BrBaP accounted for only 3.2% of the ΣBrPAHs. These profiles were different from those in fly ash in which BrPyr or BrBaA were the predominant constituents. This suggests that these profiles are intrinsic to EOBS. The composition of the TEQ concentrations of individual PAHs, ClPAHs, and BrPAHs to each ΣTEQ_{PAHs}, ΣTEQ_{ClPAHs}, and ΣTEQ_{BrPAHs} are shown in **Fig. 1c**. Although the proportional concentration of potent ClPAHs among the ΣClPAHs was very low, the proportional TEQ concentration among ΣTEQ_{ClPAHs} was high. For example, the proportional concentration of 3,8-Cl_2Flu, the most potent ClPAH ($REP_{BaP} = 5.7$), among ΣClPAHs was only 0.58%, the proportional TEQ concentration was 13%. As another example, although BrBaA (including 7-BrBaA and 4,7-Br_2BaA, which have the highest and second highest REP_{BaP} at 0.84 and 0.77, respectively) were the least dominant BrPAHs among ΣBrPAHs, they were the most dominant BrPAHs in the ΣTEQ_{BrPAHs}.

Source implications of ClPAH concentrations. To identify the source of ClPAHs, concentration ratios for selected ClPAHs normalized to 1-ClPyr and 3-ClFlu (6-ClBaP/1-ClPyr, 3-ClFlu/1-ClPyr, 7-ClBaA/1-ClPyr, 6-ClBaP/3-ClFlu, 1-ClPyr/3-ClFlu, and 7-ClBaA/3-ClFlu) were calculated for soils the EOBS and samples around e-waste recycling facilities[5], fly ash samples[6], and the atmosphere within road tunnels[10] as reported in previous studies. The ratio of 6-ClBaP to 3-ClFlu was used as a more suitable indicator of sources of ClPAHs, because 3-ClFlu has a higher photostability than the other ClPAHs[11,12]. It has been previously reported that there are four potential emission sources of ClPAHs; e-waste recycling facilities (EF), including e-waste shredder dust; municipal solid waste incineration (MSWI), including fly ash; chemical industrial activities involving chlorine; and automobile exhaust (AE), including the air within road tunnels[6]. EF samples included the dust from workshop floors and soils from e-waste recycling facilities. Urban air samples can indicate the influence of MSWI because incineration facilities have been reported to be stationary sources of ClPAHs in urban air[12]. Leaf samples from the e-waste recycling facilities were categorized as AE sources because automobile exhaust gases can be considered to have environmental partitioning properties for ClPAHs[6]. In our study, principal component analysis (PCA) was performed on the previous data set[5,6,10] and our data set containing information on the six ratios concentration ratios for the selected ClPAHs normalized to 1-ClPyr and 3-ClFlu. The soil sample positions on the PCA-score plot are shown in **Fig. 2**. Two factors explaining 88.0% of the original data variance governed

the distribution of the concentration ratios as follows: PC1 (accounting for 53.8% of the total variance) was influenced mainly by e-waste recycling activity because almost all of the EOBS samples and e-waste recycling facility samples were located in the positive region; PC2 (34.2%) was influenced mainly by industrial activity because industrial complex samples, such as fly ash and industrial soils, were located in the positive region. The results for VN-1 are not shown in Fig. 2 because four of the concentration ratios (6-ClBaP/1-ClPyr, 7-ClBaA/1-ClPyr, 6-ClBaP/3-ClFlu, and 7-ClBaA/3-ClFlu) were not calculated. In terms of 3-ClFlu/1-ClPyr and 1-ClPyr/3-ClFlu values, the values in VN-1 were most similar to those for urban air. The previous categorization generally applies to our PCA results. The results showed that there were four distinct clusters and that most of the EOBS samples were located in close proximity to each other, with the exception of GH-2 and PHI-1. EOBS samples were located in an individual cluster far from EF and MSWI sources, but close to AE sources. The difference between most EOBS samples and two specific samples (GH-2 and PHI-1) was due to the difference in the composition of the waste materials burned. For example, at open-burning sites in Vietnam, wires and cables were burned to extract metals (especially copper). However, in Ghana, other waste materials (e.g., plastics) were also mixed with wires and cables and burned. Among the e-waste recycling activities, open-burning activities and non-burning processes, such as e-waste shredding and dismantling, were in different clusters. This suggests that the combustion process is an important source of ClPAHs. Among the samples generated through combustion processes, EOBS samples were located in a different cluster from fly ash. This suggests that the formation of ClPAHs may be related to not only the composition of the waste materials burned but also the combustion temperature. Because oil was usually used to initiate and maintain the fires when open-burning activities were conducted, EOBS samples were located near to AE sources on the PCA plot.

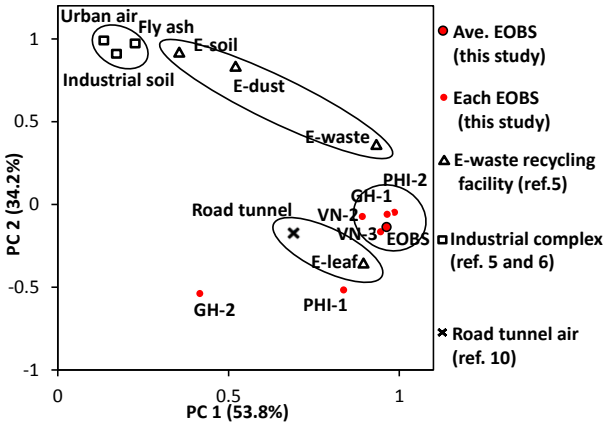

Figure 2. Score plot of two principal components from the data set containing information on the concentration ratios for the selected ClPAHs normalized to 1-ClPyr and 3-ClFlu in this study and for previous studies.

Conclusion

This is the first study to report concentrations of Cl/BrPAHs in EOBS. The results indicated different concentrations in EOBS samples from three developing countries. The highest concentrations of Cl/BrPAHs were detected in EOBS samples from Vietnam. We found that concentrations of Cl/BrPAHs in EOBS samples were higher than in samples from other e-waste recycling activities and in waste incineration bottom ash, and were comparable to waste incineration fly ash. The Cl/BrPAHs in EOBS samples had a toxic potency equivalent to dioxins, and each group had its own intrinsic profile. An investigation of the formation mechanisms of Cl/BrPAHs during the burning of e-waste materials and the influence of combustion temperature is needed.

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