Characteristics of residual organics in municipal solid waste incinerator bottom ash

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ABSTRACT

Although heavy metals in bottom ash have been a primary issue in resource recovery of municipal solid waste incinerator residues in past decades, less studied are potentially toxic and odorous organic fractions that exist as they have not been completely oxidized during the mass burn process. Using supercritical fluid extraction (SFE) and soxtec extraction (SE) techniques, this study investigated the characteristics of un-oxidized organic residues contained in bottom ash from three municipal solid waste incinerators in Taiwan during 2008–2009. All together 99 organics were identified in bottom ash samples using gas chromatography-mass spectrometry (GC-MS). Among the identified organics, aromatic compounds were most frequently detected. No polycyclic aromatic hydrocarbons were extracted by SFE or SE. Several phthalates (e.g., phthalic acid isobutyl tridec-2-yn-1-yl ester, dibutyl phthalate and 2-butoxyethyl butyl benzene-1,2-dicarboxylate), organic phosphates (e.g., octicizer and phosphoric acid isodecyl diphenyl ester), and aromatics and amines including pyridine, quinoline derivatives, chloro- and cyano-organics were successfully extracted. Aromatic amines (e.g., 1-nitro-9,10-dioxo-9,10-dihydro-anthracene-2-carboxylic acid diethylamide and 3-bromo-N-(4-bromo-2-chlorophenyl)-propanamide) and aromatic compounds (other than amines) (e.g., 7-chloro-4-methoxy-3-methylquinoline and 2,3-dihydro-N-hydroxy-4-methoxy-3,3-dimethyl indole-2-one) are probably the major odorous compounds in bottom ash. This work identifies organic pollutants in incinerated bottom ash that have received far less attention than their heavy metals counterpart.

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1. Introduction

Incineration has been widely used to treat municipal solid waste (MSW) in many countries. Incineration has advantages such as reduction in waste volume, pathogen inactivation and potential energy recuperation; but it also has disadvantages such as release of gaseous pollutants and generation of wastewater and ash residues [1]. In 2008 three incinerators of Taipei County (Taiwan) treated a total of 1 M tons of MSW and produced approximately 140,000 tons of bottom ash [2]. These bottom ashes were mainly used as controlled low-strength materials (CLSM) in trench construction.

The bottom ash from municipal incinerators has to be treated and examined with toxicity characteristics leaching procedure (TCLP) prior to reuse [3]. The TCLP test normally includes analysis of leachate for heavy metals and chlorinated organics [4–6]. The MSW often contains various synthetic materials, from which numerous organics may be released during the incineration process. Since incineration cannot achieve complete mineralization of

wastes, organics such as phthalates, organic phosphates, pyridine and quinoline derivatives, poly-aromatic hydrocarbons and chlorinated organics may be present in the ashes and enter into the environment as micro-pollutants. Only a few studies have reported the presence of organics in bottom ash [7,8]. Phthalates, organic phosphates, pyridine and quinoline derivatives might pose various carcinogenic, endocrine-disrupting and toxic effects on aquatic life and mammals [9–12]. The US environmental protection agency (USEPA) lists phthalates and organic phosphates as priority pollutants. The presence of toxic organic chemicals and foul odor of bottom ash may limit its reuse as a secondary material in many practical applications such as substitutes for road base materials.

Existing data on bottom ash are largely limited to heavy metals and specific groups of organics such as polycyclic aromatic hydrocarbons [6,7,13]. With the potential presence of toxic organics in bottom ash, studies are needed to characterize and quantify these residual organics or organic byproducts. As such, effective extraction methods are required to extract these organics from bottom ash for analysis. Soxhlet extraction and SFE are two feasible techniques to extract organics from solid matrixes [14–16]. The supercritical fluid has unique properties including low viscosity, high coefficient of diffusion and low toxicity [17,18]. SFE
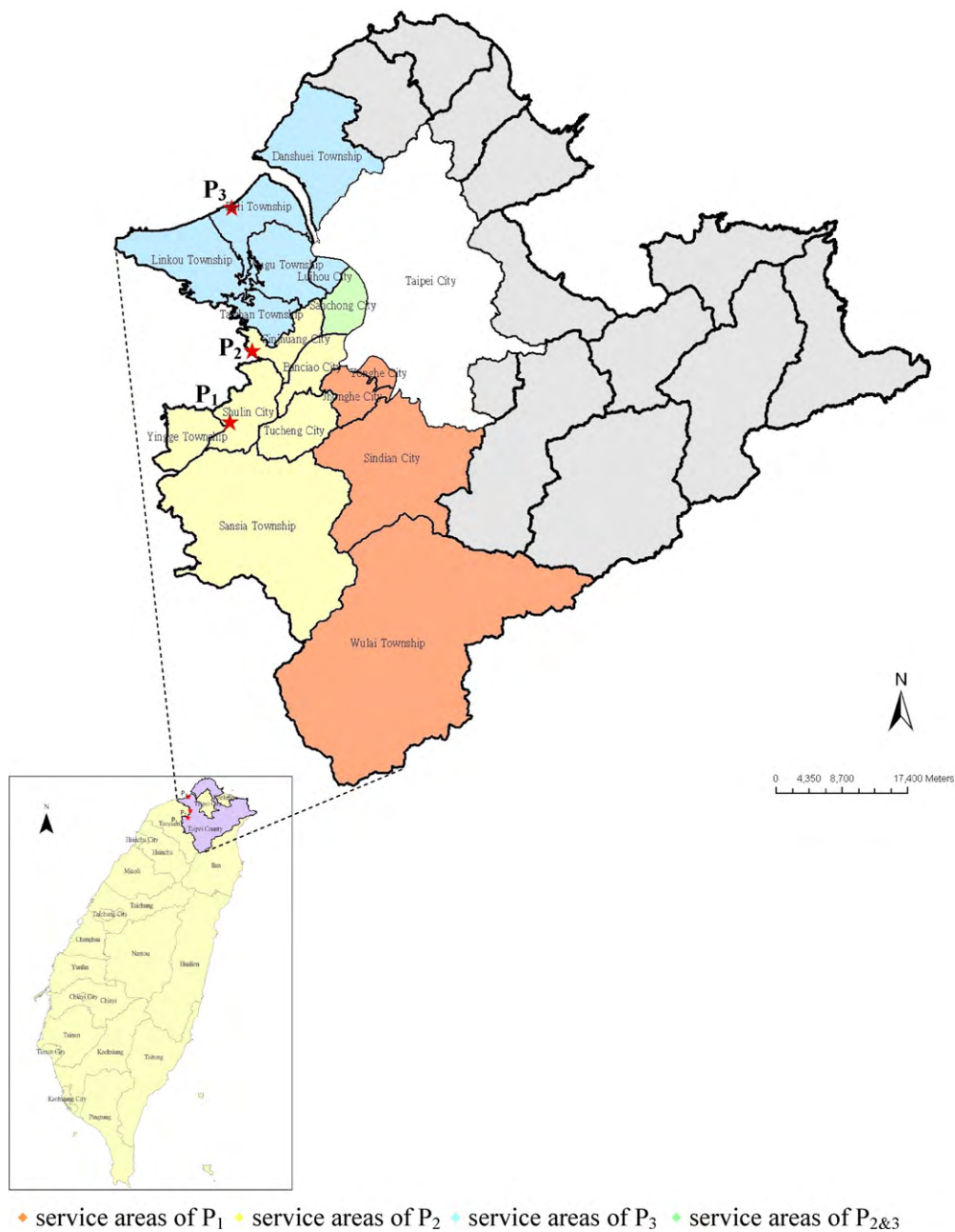
Fig. 1. Taipei County and locations of study incinerators (P_1, P_2 and P_3) in Taiwan.
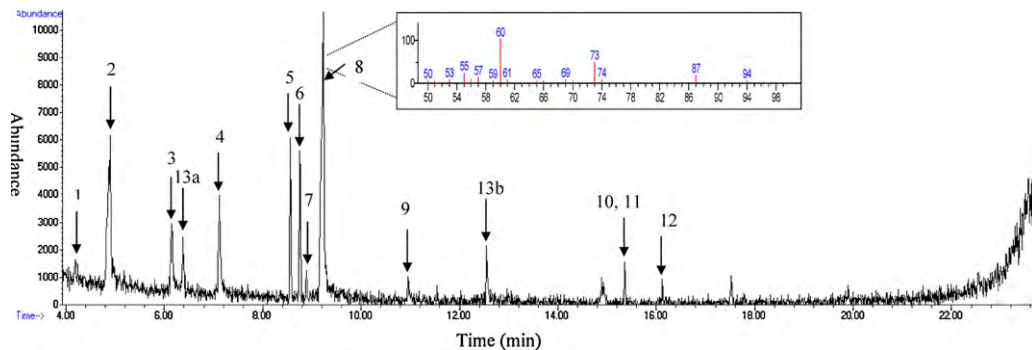

Fig. 2. Gas chromatogram of SFE extract of bottom ash from P_1 incinerator in S_2 season. (1) 2,2-dimethylpropanol, (2) pentanoic acid, (3) 3-methylpentanoic acid, (4) propylpropanedioic acid, (5) 1-ethylbutylhydroperoxide, (6) 1-methylpentyl hydroperoxide, (7) benzaldehyde, (8) hexanoic acid, (9) 2-aminooxypentanoic acid, (10) 3-hydroxybenzaldehyde, (11) 4-hydroxybenzaldehyde, (12) 2,6-diamino-8-azapurine, (13a) and (13b) are impurities form column. Mass spectrum of hexanoic acid is shown in box.
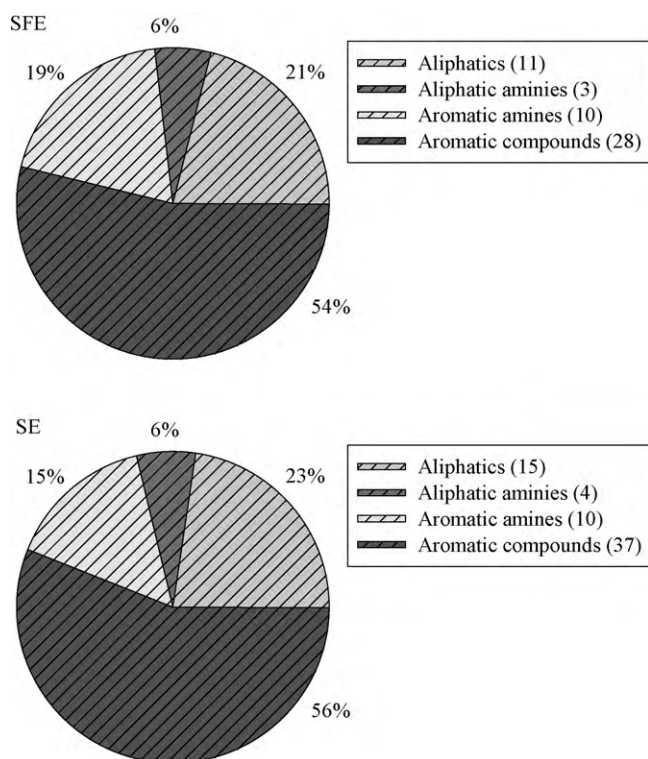
Fig. 3. Comparison of supercritical fluid extraction (SFE) and soxtec extraction (SE) on extraction of organics in various categories.

using pure CO_2 is able to extract a wide range of organics including non-polar and less polar compounds. SE is a rapid, reliable and economical technique preferred over the classic Soxhlet method. This study used both SFE and SE to extract organics from bottom ashes of three MSW incinerators. The objectives of the study were to (1) identify the organic compounds that were extractable by these two methods, (2) compare the relative occurrences of

the extracted organics, (3) compare the seasonal variations caused by varying compositions of the raw waste materials, and (4) identify the types of organics responsible for foul odors from bottom ash.

2. Experimental

2.1. Sample collection

Bottom ash samples were collected from three mass-burning incinerators (P_1, P_2 and P_3) in Taipei County (Taiwan) during three consecutive seasons of fall (S_1), winter (S_2) and spring (S_3) from November 2008 to July 2009. Fig. 1 shows the locations of the three study incinerators in the northern part of Taiwan. The plants are located in the Taipei County of northern Taiwan; one plant (P_3) is at the northern end of Taiwan and two others are about 19 km (P_2) and 13 km (P_1) south of P_3. Bottom ash samples were collected from the bottom ash treatment plant which treated bottom ashes from the three mass-burning incinerators (P_1, P_2 and P_3) in Taipei County (shaded in purple). The service areas of the three study incinerators were shown with different colors in Taipei County. The operation conditions of incinerators are given in Table 1, with a feedstock supply rate of 13.1–18.8 tons/h and incineration temperature reaching 1050 °C using diesel as an auxiliary fuel. These incinerators are equipped with air pollution control and water quenching equipments. Bottom ashes have been typically collected over 13–15 days and pretreated, which includes magnetic separation, crushing and screening at room temperature for removal of metals. Thus, the collected samples were composite samples with negligible loss of organic matter during pretreatment. A random sampling method was applied in which batches of approximately 100–150 g of bottom ash were collected from different parts of an ash pile. The collected samples were randomly combined to make up a sample of 2 kg that represents one incinerator in one season; this was performed in triplicate. Incinerators P_1 and P_2 mainly treated municipal solid wastes and incinerator P_3 received both municipal and industrial solid wastes at a ratio
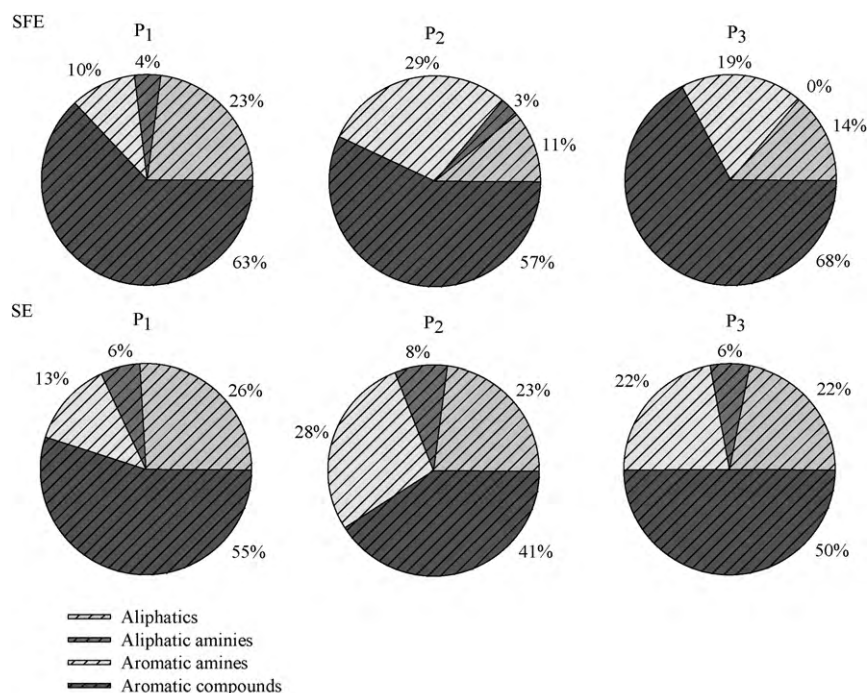

Fig. 4. Frequency of detection of different kinds of organics extracted from bottom ash by SFE and SE.

of 3:1. The bottom ash samples were sieved (2 mm) in the laboratory and stored in airtight metal containers at room temperature. These sieved samples were then subjected to SFE and SE extraction.

2.2. Supercritical fluid extraction

SFE was performed using an ISCO Model 260D (ISCO Inc., USA) equipped with syringe pumps and connected to an extraction unit model SFX2-10, which was placed into a tube heater for temperature control. A sieved bottom ash sample of 10 g was placed in a 10 mL cell in the extractor which was immediately pressurized to a prescribed pressure and kept in a static mode for 10 min. The extraction process was performed in the dynamic mode for 20 min at 2.7–2.9 mL/min flow of compressed CO_2. All extractions were performed with pure CO_2. The extracted mixture was col-

lected by inserting a restrictor into a vial which contained 10 mL of n-hexane.

A preliminary study was conducted to determine the optimal operating parameters based on odor strength of the bottom ash residue after extraction. SFE was carried out at 40, 50 or 60 °C at 2.0×10^7, 3.1×10^7 or 4.1×10^7 Pa with an extraction time of 10, 20 or 30 min. Thereafter the ash residue was collected and sniffed for odor. The optimal conditions were set when the residual bottom ash showed no foul odor. The optimal SFE conditions of 50 °C, 3.1×10^7 Pa, and 20 min extraction period were used for all subsequent experiments.

2.3. Soxtec extraction

SE was performed using the FOSS Soxtec System model 2043 (FOSS. Tecator Technology, Sweden). This soxtec system required
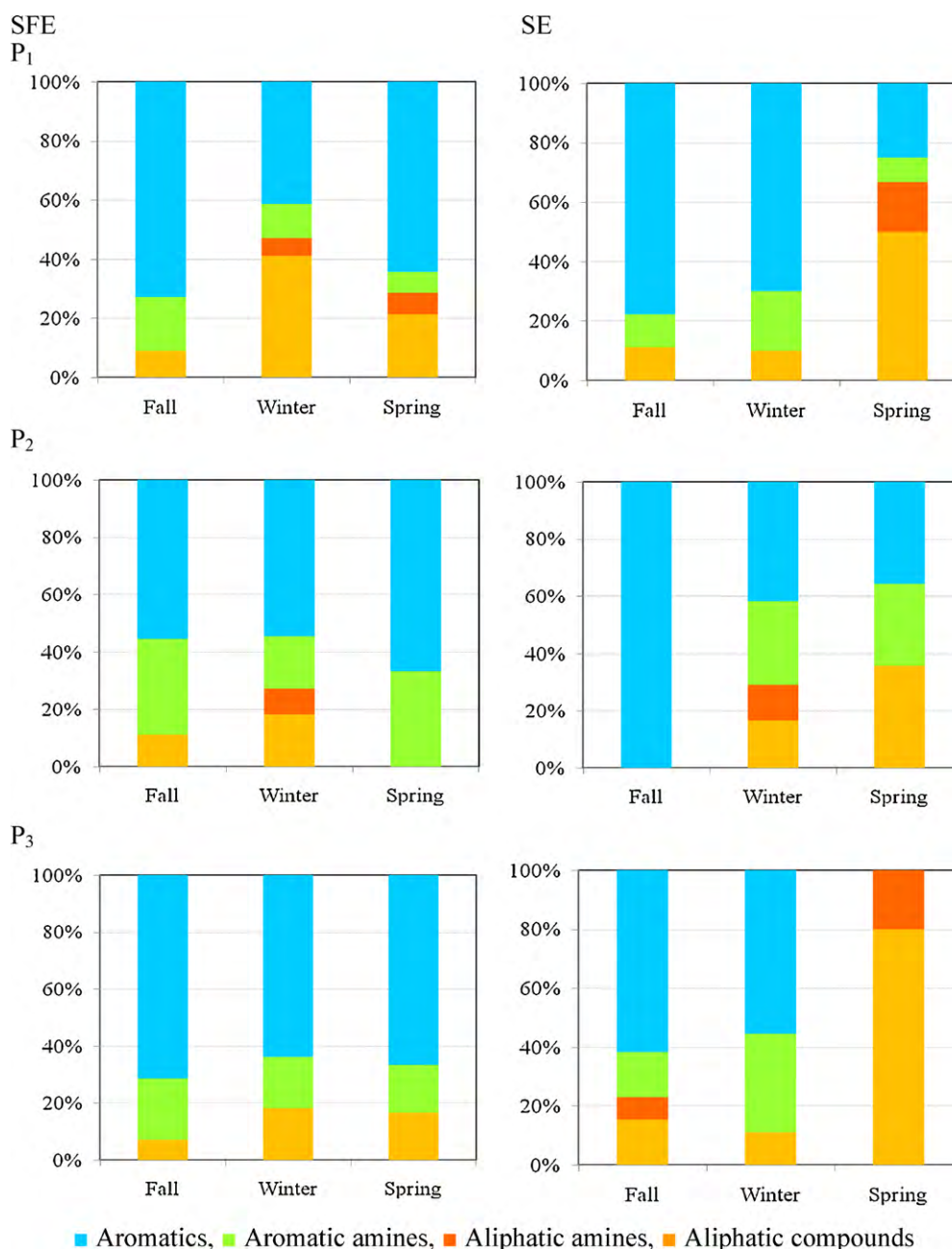

Fig. 5. Distribution of various categories of organics by extraction methods, incineration plants and seasons.

less solvent and time in comparison with conventional Soxhlet extraction. Operation of SE required 3 g of bottom ash sample and 40 mL of n-hexane/acetone (1:1) under continuous reflux for 75 min (boiling time 50 min and rinsing time 25 min) at 140 °C. After extraction, the thimble and the container were rinsed with solvent and the extract was added with solvent to 10 mL.

Control experiments (recovery) for PAH analysis were carried out by spiking of 1 mL of PAH standard (PAHs mix 64 from Merck) containing 2 μg of each PAH in hexane into 10 and 3.0 g of bottom ash in triplicates, which were extracted by SFE and SE, respectively. The spiked samples thus contained 0.2 and 0.67 mg kg^{-1} of each PAH. After extraction and concentration steps, GC/MS method of USEPA 8270D (US EPA, 1998) was used for quantification of PAHs.

2.4. GC/MS analysis

Agilent GC/MS Model 6890 PLUS (Agilent, USA) equipped with a DB-5ms column (0.25 mm I.D. × 30 m column length, 0.25 μm film
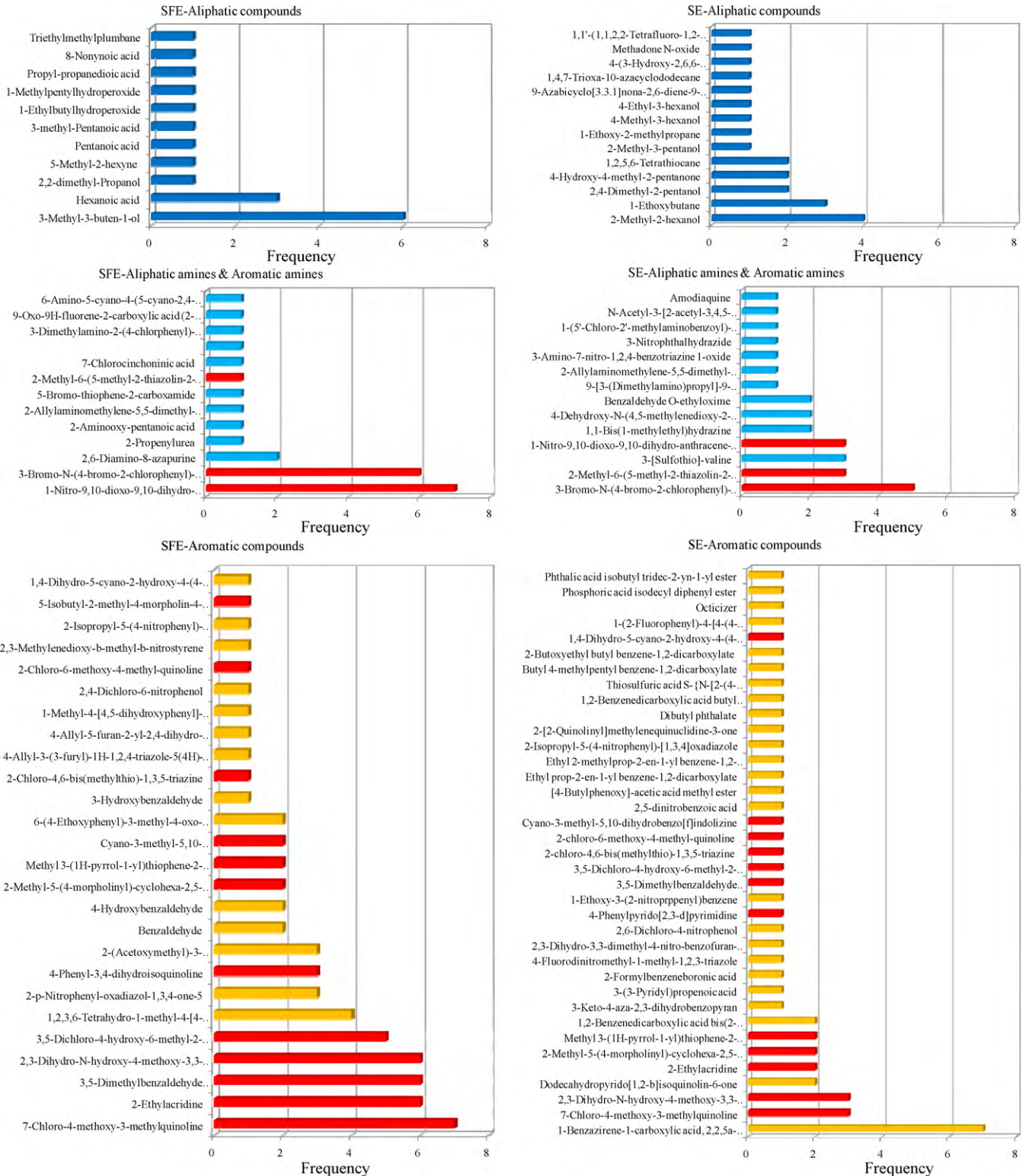

Fig. 6. Frequency of detection of different organics by extraction methods and categories.

thickness) was employed for analysis of extracts from SFE and SE. A sample volume of 1 μL was injected into the injection port maintained at 230 °C. The oven temperature program was held at 50 °C for 4 min followed by a 10 °C/min ramp to 300 °C. The temperature was held at 160, 280 and 300 °C for 1, 4 and 10 min, respectively. Pure helium gas was used as the carrier at 0.8 mL/min. Mass spectra was obtained using a full scan mode (m/z 50–550 at a scan rate of 2.92 scan/s).

An electron ionization voltage of 70 eV and a source temperature of 230 °C were used. Compound identification was based on similarity of mass spectrum and retention index (RI) within certain thresholds (i.e., mass spectral match > 650 and RI deviation < 10). Wiley 275.1 and NIST/USEPA/NIH mass spectral library (NIST 05) with the above thresholds were used for identifying residual organics in bottom ash. Probability-based matching (PBM) was also used for comparison with the possible target organics.

2.5. Total organic carbon (TOC) measurement

The TOC of bottom ash before and after extraction was determined with an IO Analytical TOC analyzer (USA) coupled with a non-dispersive infrared (NDIR) detector. About 210 mg of raw bottom ash and 400 mg of extracted bottom ash were weighed in duplicate and used for TOC analysis. The sample was acidified and subjected to heating at 250 °C to remove inorganic carbon, and continued to combustion at 950 °C. Carbon dioxide generated from the sample was quantified by a non-dispersive infrared detector that was calibrated with glucose with a detection limit of 0.5 mg carbon.

3. Results and discussion

TOC results show organic carbon contents of the bottom ash samples from the study incinerators to be in the range of 0.69–4.01% over three seasons, which are in compliance with Taiwan EPA regulations (4–7%) [19]. This suggests high burn-out efficiency in all three incinerators. Similarly the TOC values (supporting information in Table S1) of extracted bottom ash are below detection of SE and are 0.67–1.9% using SFE. The recoveries using SE and SFE were found to be >99% and 33%, respectively.

Fig. 2 is a typical gas chromatogram for a SFE extract of the bottom ash. For all bottom ash samples, a total of 99 compounds were found by GC/MS. These compounds could be grouped into four categories: aliphatics (other than amines), aliphatic amines, aromatic amines and aromatic hydrocarbons (other than amines) based on

their aliphatic and aromatic properties and the general odor nature of organic amines.

Table 2 lists all the organic compounds identified in the SFE and SE extracts of the bottom ash samples. Certain thresholds, such as mass spectral match > 650 and RI deviation < 10 from the database, were used in identification of these organics. The identification of organic compounds also followed the procedure of semivolatile organic compounds by GC/MS (USEPA Method 8270C), and only those compounds with more than 50% similarity were matched and listed. From Table 2, it is clear that several phthalates, organic phosphates, chloro- and cyano-organics were identified but no PAHs were extracted by SFE or SE. The absence of PAHs should be viewed with factors such as limitation in mass spectral match thresholds, relatively low PAH recovery, high combustion temperature, long detention time, time lapse of sampling after discharge of bottom ash from incinerator and quenching of bottom ash with water. Control experiments revealed wide variations in recovery (69–105%) for most PAH compounds (supporting information Fig. S1). Extraction of the spiked PAH mixture showed a wide range of recovery results (Fig. S1) – from 0% to 50% recovery such as for naphthalene, fluorine and carbazole to 125–174% recovery for pyrene, acenaphthalene and benzo[a]pyrene. These results show that PAHs are extractable by SE and SFE, albeit with varied effectiveness among them.

Fig. 3 compares the numbers of organics extracted by SFE and SE. SE extracted more organic compounds than SFE, which was corroborated by control experiments that showed far higher recovery with SE (>99% recovery of TOC). SE extracted more or at least similar kinds of organics in various categories: 37 vs. 28 in aromatics, 15 vs. 11 in aliphatics, and about equal in aromatic amines (10 vs. 10) and aliphatic amines (4 vs. 3). Among all organics extracted by both SE and SFE, aromatic compounds were most abundant (>50%). No foul odor was detected in samples after extraction with SFE while a weak odor was detected in SE-extracted samples. It indicates the effectiveness of SFE in extracting odor-causing organics. Phthalates (i.e., phthalic acid isobutyl tridec-2-yn-1-yl ester, dibutyl phthalate and 2-butoxyethyl butyl benzene-1,2-dicarboxylate) and organic phosphates (i.e., octicizer and phosphoric acid isodecyl diphenyl ester), which were categorized as aromatic compounds, were extracted only by SE. The use of both polar and non-polar solvents in SE may be a possible reason for its capability in extraction of a large number of organics including phthalates and organic phosphates. Generally, the non-polar nature and low dielectric constant of CO_2 may hinder the capability in extracting polar organics [20]. On the contrary, a larger number of aliphatic carboxylic acids were

Table 1
Operating conditions of three study incinerators.

Operating conditions	P_1	P_2	P_3
Feeding rate			
Feedstock (max.) tons/day	900	1350	1350
Feedstock (tons/h)	13.125–18.75	13.125–18.75	13.125–18.75
Type of auxiliary fuel	Super diesel	Super diesel	Super diesel
Air pollution control devices	Dry, AC, BH	SD, AC, BH	CYC, SD, AC, BH
Combustion temperature (°C)			
First combustion chamber	850–1050	850–1050	850–1050
Second combustion chamber	-	-	-
Actual measurement	950–1050	900–950	950
Combustion condition			
Detention time (min/batch)	30	30	60
Combustion efficiency (%)	92–95	92–95	98
Humidity range (%)	20–21	20–21	21
Fuel used in co-combustion	Super diesel	Super diesel	Super diesel
Water quenching process	Yes	Yes	Yes
Retention time of water in quenching process (min)	10–15	10–15	10
Quantity of water in quenching process (m³/day)	5	5	10–13

Dry: dry scrubber, AC: activated carbon, BH: bag house, SD: semi-dry scrubber, CYC: cyclone. P_1, P_2 and P_3 are the three incinerators in the present study.

Table 2
Compounds identified in extracts of bottom ash by supercritical fluid (SFE) and soxtec extraction (SE) methods.

S. no.	Compound name	Molecular weight	SE	SFE
Aliphatics (other than amines)				
1	3-Methyl-3-buten-1-ol	86	$P_1/S_2,P_2/S_3,P_3/S_2$[a]	$P_2/S_{1,2},P_3/S_{1,2,3}$
2	2,2-Dimethylpropanol	88		P_1/S_2
3	5-Methyl-2-hexyne	96		P_3/S_3
4	Pentanoic acid	102		P_1/S_2
5	1-Ethoxybutane	102	$P_1/S_3,P_2/S_{2,3}$	
6	2-Methyl-3-pentanol	102	P_1/S_3	
7	1-Ethoxy-2-methylpropane	102	P_3/S_3	
8	2-Methyl-2-hexanol	116	$P_1/S_3,P_2/S_{2,3},P_3/S_3$	
9	2,4-Dimethyl-2-pentanol	116	$P_2/S_2,P_3/S_3$	
10	4-Hydroxy-4-methyl-2-pentanone	116	$P_1/S_3,P_3/S_2$	
11	4-Methyl-3-hexanol	116	P_1/S_3	
12	3-methyl-Pentanoic acid	116		P_1/S_2
13	Hexanoic acid	116		$P_1/S_2, P_2/S_2, P_3/S_2$
14	1-Ethylbutylhydroperoxide	118		P_1/S_2
15	1-Methylpentylhydroperoxide	118		P_1/S_2
16	4-Ethyl-3-hexanol	130	P_1/S_3	
17	Propyl-propanedioic acid	146		P_1/S_2
18	9-Azabicyclo[3.3.1]nona-2,6-diene-9-carboxaldehyde	149	P_3/S_1	
19	8-Nonynoic acid	154		P_2/S_1
20	1,4,7-Trioxa-10-azacyclododecane	175	P_2/S_3	
21	1,2,5,6-Tetrathiocane	184	$P_2/S_2,P_3/S_1$	
22	4-(3-Hydroxy-2,6,6-trimethylcyclohex-1-enyl)pent-3-en-2-one	222	P_2/S_3	
23	Triethylmethylplumbane	310		P_1/S_1
24	Methadone N-oxide	325	P_3/S_2	
25	1,1′-(1,1,2,2-Tetrafluoro-1,2-ethanediyl) bis[2-chloro-2,3,3-trifluorocyclobutane	386	P_1/S_1	
Aliphatic amines				
26	2-Propenylurea	100		P_2/S_2
27	1,1-Bis(1-methylethyl)hydrazine	116	$P_1/S_3,P_2/S_2$	
28	2-Aminooxy-pentanoic acid	133		P_1/S_2
29	9-[3-(dimethylamino)propyl]-9-Borabicyclo[3.3.1]nonane	207	P_2/S_2	
30	2-Allylaminomethylene-5,5-dimethyl-cyclohexane-1,3-dione	207	P_2/S_2	P_1/S_3
31	3-[Sulfothio]-valine	229	$P_1/S_3,P_3/S_{1,3}$	
Aromatic amines				
32	Benzaldehyde O-ethyl-oxime	149	$P_1/S_1,P_3/S_1$	
33	2,6-Diamino-8-azapurine	151		$P_1/S_2,P_2/S_3$
34	5-Bromo-thiophene-2-carboxamide	205		P_2/S_1
35	3-Amino-7-nitro-1,2,4-benzotriazine-1-oxide	207	P_3/S_2	
36	3-Nitrophthalhydrazide	207	P_3/S_2	
37	2-Methyl-6-(5-methyl-2-thiazolin-2-ylamino)pyridine	207	$P_2/S_{2,3},P_3/S_1$	P_3/S_3
38	7-Chlorocinchoninic acid	207		P_3/S_1
39	2-Nitro-benzaldehyde diaminomethylidenhydrazone	207		P_2/S_1
40	3-Dimethylamino-2-(4-chlorphenyl)-thioacrylamide	240		P_2/S_1
41	1-(5′-Chloro-2′-methylaminobenzoyl)-cyclohex-1-ene	249	P_2/S_2	
42	9-Oxo-9H-fluorene-2-carboxylic acid (2-hydroxyethyl)(methyl)amide	281		P_2/S_1
43	4-Dehydroxy-N-(4,5-methylenedioxy-2-nitrobenzylidene)tyramine	298	$P_2/S_2,P_3/S_2$	
44	N-Acetyl-3-[2-acetyl-3,4,5-trimethoxyphenyl]-n-propylamine	309	P_1/S_2	
45	6-Amino-5-cyano-4-(5-cyano-2,4-dimethyl-1H-pyrrol-3-yl)-2-methyl-4H-pyran-3-carboxylic acid ethyl ester	326		P_2/S_2
46	3-Bromo-N-(4-bromo-2-chlorophenyl)-propanamide	339	$P_1/S_{2,3},P_2/S_{2,3},P_3/S_2$	$P_1/S_1,P_2/S_{1,3},P_3/S_{1,2}$
47	1-Nitro-9,10-dioxo-9,10-dihydro-anthracene-2-carboxylic acid diethylamide	352	$P_2/S_{2,3},P_3/S_2$	$P_1/S_{1,3},P_2/S_{1,2},P_3/S_{1,2,3}$
48	4-[(7-chloroquinolin-4-yl)amino]-2-[(diethylamino)methyl]phenol (amodiaquine)	355	P_3/S_2	
Aromatic compounds (other than amines)				
49	Benzaldehyde	106		$P_1/S_2, P_2S_3$
50	3-Hydroxybenzaldehyde	122		P_1/S_2
51	4-Hydroxybenzaldehyde	122		P_1/S_2
52	3-Keto-4-aza-2,3-dihydrobenzopyran	149	P_3/S_1	
53	3-(3-Pyridyl)propenoic acid	149	P_3/S_1	
54	2-Formylbenzeneboronic acid	150	P_3/S_2	
55	4-Fluorodinitromethyl-1-methyl-1,2,3-triazole	205	P_1/S_2	
56	2,3-Dihydro-3,3-dimethyl-4-nitro-benzofuran-2-one	207	P_1/S_3	
57	Dodecahydro-pyrido[1,2-b]isoquinolin-6-one	207	$P_1/S_2,P_3/S_2$	
58	2,6-Dichloro-4-nitrophenol	207	P_2/S_2	
59	4-Phenyl-pyrido[2,3-d]pyrimidine	207	P_3/S_1	
60	1-Ethoxy-3-(2-nitroprppenyl)benzene	207	P_1/S_3	

Table 2 (*Continued*)

S. no.	Compound name	Molecular weight	SE	SFE
61	7-Chloro-4-methoxy-3-methylquinoline	207	$P_2/S_{2,3}, P_3/S_2$	$P_1/S_3, P_2/S_{1,2,3}, P_3/S_{1,2,3}$
62	2-Ethylacridine	207	$P_1/S_2, P_2/S_2$	$P_1/S_3, P_2/S_{1,3}, P_3/S_{1,2,3}$
63	3,5-Dimethylbenzaldehyde thiocarbamoyl hydrazone	207	P_2/S_3	$P_1/S_{1,3}, P_2/S_2, P_3/S_{1,3}$
64	2,3-Dihydro-N-hydroxy-4-methoxy-3,3-dimethyl indole-2-one	207	$P_1/S_2, P_2/S_2, P_3/S_2$	$P_1/S_{1,3}, P_2/S_{1,3}, P_3/S_2$
65	1,2,3,6-Tetrahydro-1-methyl-4-(4-chlorophenyl)-pyridine	207		$P_1/S_3, P_2/S_1, P_3/S_1$
66	2-p-Nitrophenyl-oxadiazol-1,3,4-one-5	207		$P_1/S_{1,3}, P_3/S_1$
67	3,5-Dichloro-4-hydroxy-6-methyl-2-pyridinemethanol	207	P_1/S_2	$P_1/S_3, P_2/S_2, P_3/S_{1,2,3}$
68	4-Phenyl-3,4-dihydroisoquinoline	207		$P_2/S_1, P_3/S_{1,2}$
69	2-Methyl-5-(4-morpholinyl)-cyclohexa-2,5-diene-1,4-dione	207	$P_1/S_2, P_2/S_2$	$P_1/S_1, P_3/S_1$
70	Methyl 3-(1H-pyrrol-1-yl)thiophene-2-carboxylate	207	$P_2/S_{2,3}$	$P_1/S_{1,3}$
71	2-Chloro-4,6-bis(methylthio)-1,3,5-triazine	207	P_2/S_3	P_3/S_3
72	4-Allyl-3-(3-furyl)-1H-1,2,4-triazole-5(4H)-thione	207		P_3/S_3
73	4-Allyl-5-furan-2-yl-2,4-dihydro-[1,2,4]triazole-3-thione	207		P_2/S_1
74	1-Methyl-4-[4,5-dihydroxyphenyl]-hexahydropyridine	207		P_2/S_2
75	2,4-Dichloro-6-nitrophenol	207		P_3/S_2
76	2-Chloro-6-methoxy-4-methyl-quinoline	207	P_2/S_2	P_3/S_2
77	4-(2-Nitropropenyl)benzo[1,3]dioxole	207		P_2/S_1
78	Cyano-3-methyl-5,10-dihydrobenzo[f]indolizine	208	P_3/S_2	$P_1/S_2, P_2/S_1$
79	2,5-Dinitrobenzoic acid	212	P_1/S_1	
80	[4-Butylphenoxy]-acetic acid methyl ester	222	P_2/S_2	
81	Ethyl prop-2-en-1-yl benzene-1,2-dicarboxylate	234	P_3/S_1	
82	Ethyl 2-methylprop-2-en-1-yl benzene-1,2-dicarboxylate	248	P_1/S_1	
83	2-Isopropyl-5-(4-nitrophenyl)-[1,3,4]oxadiazole	249	P_3/S_2	P_1/S_1
84	2-[2-Quinolinyl]methylenequinuclidine-3-one	264	P_2/S_3	
85	1-Benzazirene-1-carboxylic acid, 2,2,5a-trimethyl-1a-[3-oxo-1-butenyl] perhydro- methyl ester	265	$P_1/S_{2,3}, P_2/S_{1,2,3}, P_3/S_{1,2}$	$P_1/S_3, P_2/S_1, P_3/S_{1,3}$
86	1,2-Benzenedicarboxylic acid bis(2-methylpropyl) ester	278	$P_1/S_1, P_3/S_1$	
87	Dibutyl phthalate	278	P_1/S_1	
88	5-Isobutyl-2-methyl-4-morpholin-4-ylmethyl-furan-3-carboxylic acid	281		P_1/S_1
89	2-(Acetoxymethyl)-3-(methoxycarbonyl) biphenylene	282		$P_1/S_1, P_2/S_1, P_3/S_3$
90	1,2-Benzenedicarboxylic acid butyl cyclohexyl ester	304	P_1/S_1	
91	Thiosulfuric acid S-{N-[2-(4-methoxyphenyl)ethyl]carbamimidoylmethyl}ester	304	P_3/S_1	
92	Butyl 4-methylpentyl benzene-1,2-dicarboxylate	306	P_1/S_1	
93	2-Butoxyethyl butyl benzene-1,2-dicarboxylate	322	P_3/S_1	
94	5-Cyano-2-hydroxy-4-(4-isopropylphenyl)-6-methyl-1,4-Dihydro-pyridine-3-carboxylic acid ethyl ester	326	P_3/S_2	P_2/S_2
95	6-(4-Ethoxyphenyl)-3-methyl-4-oxo-4,5,6,7-tetrahydro-1H-Indole-2-carboxylic acid isopropyl ester	355		$P_2/S_2, P_3/S_1$
96	1-(2-Fluorophenyl)-4-[4-(4-fluorophenyl)thiazol-2-yl]-piperazine	357	P_2/S_2	
97	2-Ethylhexyl diphenyl phosphate (Octicizer)	362	P_3/S_2	
98	Phosphoric acid isodecyl diphenyl ester	390	P_3/S_2	
99	Phthalic acid isobutyl tridec-2-yn-1-yl ester	400	P_1/S_1	

[a] P_1, P_2 and P_3 are the three incinerators; S_1, S_2 and S_3 indicate fall, winter and spring seasons, respectively.

extracted by SFE than by SE. This might be due to the use of higher pressure in SFE which increases the solubility of aliphatic carboxylic compounds in CO_2 [21] and hence more aliphatic carboxylic acids were extracted. Niki et al. [22] reported that the dielectric constant of solvent decreased at higher temperatures and hence the extractable aliphatic carboxylic acids were less. In this study we also tentatively located a few aliphatic carboxylic acids in the SE extracts.

To compare the occurrences of the four categories of compounds in the extracts, the frequency of occurrence of each category in each incinerator was calculated using Eq. (1) and the results are shown in Fig. 4.

$$\text{Frequency}\,(\%) = \frac{\sum_{x=1}^{3} N_{kx}}{\sum_{x=1}^{3}\sum_{k=1}^{3} N_{kx}} \times 100\% \tag{1}$$

where k is the number of samples from incinerator P_k (P_1, P_2, P_3) and x is the number of samples from season S_k (S_1, S_2, S_3). The SFE extracts of the third incinerator (P_3) deviate from the other

two incinerators (P_1 and P_2). It may be attributable to the source difference in waste incinerated.

Fig. 5 depicts the distribution of various categories of organics in different seasons. The percentage of distribution was calculated by dividing the number of organics identified in one category with the total number of organics identified in that season. As expected, the percentages of organics differ in three seasons for each extraction method likely because of different storage temperatures in different seasons, different incineration temperatures, variations in characteristics of wastes produced in seasonal festivals of tradition, as well as small amounts of industrial waste included. Considerable seasonal differences in TOC measurements have been found to vary from 4.09% in S_1 to 0.69% in S_3 that indicate seasonal variations in temperature and incineration processes. Variations were more noticeable in the SE extracts during spring, when aliphatics were predominant. Analyses of bottom ashes have exhibited temporal variations in the characteristics of their organic constituents; this is significant for managing environmental risks in engineering applications of the recycled MSWI bottom ashes.

Fig. 6 shows frequencies of detection of the identified organic compounds. The frequency of each compound was calculated using Eq. (2).

$$\text{Frequency} = \sum_{x=1}^{3} \sum_{y=1}^{3} N_{PxSy} \qquad (2)$$

where N_{PxSy} is the number of occurrence of each compound that was identified in incinerator Px in season Sy. For example, 3-methyl-3-buten-1-ol was found in P_1/S_3, P_2/S_1, P_2/S_2, P_3/S_1, P_3/S_2 and P_3/S_3; thus the frequency was calculated to be six. Many organics were extracted less than five times, which reflects the non-homogeneous nature of bottom ash.

It is difficult to identify the critical odorants because of the complex matrix and the presence of numerous organics. The absence of foul odor in the residues after SFE, the effectiveness of SFE in extracting aromatic amines and aromatic compounds, and the identification of a larger number of aromatic compounds and aromatic amines with relatively higher frequencies in SFE extracts have provided indirect evidences that these categories of organics are responsible for the foul odor in bottom ash. SE is successful to a smaller extent in the extraction of odorous compounds, thus a weak odor remains in the extracted ash residues.

The results of this study confirm the presence of numerous organics in various categories in bottom ash. Aromatic compounds were identified more frequently. From the toxicity data of organics listed by USEPA, several phthalates, organic phosphates, pyridine and quinoline derivatives including chloro- and cyano-organics show toxicities of various levels. Removal of toxic organic compounds from bottom ash to acceptable levels is necessary before its beneficial reuse. Our study therefore suggests a need for control of organics prior to reuse of bottom ash and for further development of economically feasible pretreatment methods such as leaching of bottom ash with water to remove or reduce organics of environmental and health concerns.

4. Conclusions

Extraction methods SFE and SE successfully extract a total of 99 organics from bottom ash from three MSW incinerators including phthalates, organic phosphates, aromatics and amines consisting of several pyridines, quinoline derivatives, chloro- and cyano-organics which are considered toxic. Among the identified organics, aromatic compounds were most frequently detected. No polycyclic aromatic hydrocarbons were extracted by either SFE or SE. Aromatic amines and other aromatic compounds were compounds likely responsible for emission of foul odor from bottom ash. The distributions of various categories of organics in three different seasons were different for each extraction method because of variations in waste characteristics, incineration and storage temperatures.

SFE and SE are demonstrated as very useful techniques for the extraction of organic compounds in bottom ash. SFE is effective for extraction of aromatic compounds and aromatic amines while SE is effective for extraction of aliphatics and aromatics. Additional studies are necessary particularly on creating qualitative and quantitative databases for organic residues in bottom ash from different municipal solid waste incinerators. These databases are useful in reducing environmental risks due to residual organics in bottom ash and should be available when large-scale reuses are planned.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.06.037.

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