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Multielement analysis using PIXE for beneficial use of ashes from a biomass power plant

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Abstract Elemental analysis of wood fuels and ashes from a biomass power plant was carried out using particle induced X-ray emission (PIXE) to confirm that the ashes can be utilized safely. The power plant produced four types of ash: one cinder and three fly ashes. Ignition loss tests revealed that the cinder included little unburned carbon, while the unburned carbon concentrations in the fly ashes were considerably higher. From PIXE analysis, more than 20 elements were found in all the ashes and it was shown that aluminum, silicon, calcium, potassium, and iron were the major elements in the ashes. In the fly ash collected in a bag filter, sodium, sulfur, and chlorine were also classified as major elements. Although chromium, arsenic, and lead were detected in all the ashes, leaching tests indicated that there were no potential problems associated with landfill treatment of the ashes. It was assumed that temporal fluctuation in the concentrations of major elements in the ashes was not significant. Nine kinds of waste wood fuels were analyzed by PIXE and 24 elements were determined. Lead was detected in all the woody fuels, but arsenic was not detected.

Key words Ash · Biomass power generation · Elemental analysis · PIXE · Waste wood

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Introduction

Careful use of fossil fuels is now believed to be essential for the prevention of global warming. From the viewpoint of carbon neutrality, wood resources are now being examined with keen interest as alternative energy sources to petroleum and coal. In recent years, many research studies have been conducted on obtaining energy from direct combustion, gasification, and liquefaction of woody biomass. Above all, biomass power generation by burning wood chips will enter the commercial stage in due course. In Japan, the use of biomass power plants has increased progressively and most of the facilities have been located near wood product factories. However, serious problems have arisen in the administration of these facilities and these need to be resolved.

One of the problems is the disposal of ash from biomass power plants. Wood fuel is not completely gasified by burning, and a biomass power plant discharges a considerable amount of ash that contains unburned carbon and inorganic components such as metal oxides. The ash is required to be cleared out lawfully because it is industrial waste, and the disposal cost is covered by the operating budget of the facility. Thus, it is important to reduce the amount of ash, and beneficial use of the ash undoubtedly contributes toward zero-emission power generation.

The utilization of ash from coal-fired power plants is well established, and includes manufacture of cement materials, fill materials, ground improvement materials, or construction boards. Moreover, it can be expected that the demand for the coal ash will increase vastly for use as pavement base materials. Although the utilization of wood fuel ash would be analogous to that of coal ash, it is necessary for the utilization to correctly evaluate the composition and safety of wood fuel ash. In other words, wood fuel ash needs thorough analysis of the elements and hazardous materials before a beneficial use can be identified.

Although the ash from wood fuels is likely to consist mainly of unburned carbon and inorganic components from wood, it is possible to detect other unexpected elements if

construction waste wood is included in wood fuels. Timber treated with chromated copper arsenate (CCA) contains arsenic (As), chromium (Cr), and copper (Cu) at high concentrations, and painted waste wood may contain lead (Pb). It is extremely difficult to fully exclude materials other than wood from construction waste wood, and therefore analysis of the wood fuel ash is required to be highly sensitive and with multielement capability. Moreover, the analytical method should be suitable for solid-state samples because unburned carbon in the ash, which absorbs various substances, is very difficult to dissolve completely. Particle induced X-ray emission (PIXE) is an analytical method that can sensitively determine multiple elements from sodium (Na) to uranium (U).

We have applied this method to many real samples and published several environmental chemical and geochemical reports.[1–4] There is only one report[5] on the analysis of ash from woody waste by PIXE as far as we know, whereas PIXE has been frequently used for analyzing elements in coal ash[6–8] and wood.[9–11] Hence, PIXE provides a powerful technique for determining multiple elements in the ash from biomass fuels.

We have already reported a preliminary study[12] of elemental analysis of ashes from a biomass power plant using PIXE. The aim of the present work was to explore chemical compositions of the ashes from wood fuels in more detail. We elementally analyzed the raw wood fuels and ashes from a relatively large-scale biomass power facility by using PIXE. Moreover, a leaching test of elements, an ignition test, and Raman spectroscopic measurements for the ashes were carried out. In this article, we report the characteristics of the elemental composition of the ashes.

Materials and methods

Sampling of ashes and raw wood fuels

The biomass power facility that we explored in this study produced four kinds of ashes. The first ash (ash-1) was cinder sinking under a fluidized bed combustor, which contained clinker that fell down from the furnace wall. The second ash (ash-2) was fly ash ejected at a cyclone separator. The third ash (ash-3) was fly ash dissociated by the cyclone separator, and the last ash (ash-4) was fly ash collected in a bag filter. All the ash samples were extracted from ash in a stockyard using stainless steel beakers and kept hermetically sealed in aluminum bags. Two samplings of the ashes were performed on 7 June 2004 and 8 October 2004. Nine kinds of raw wood samples were selected from a mixture of wood fuels in a stockyard at the biomass power facility on 21 January 2005. The wood samples were dried in air for 2 months and then broken up to powder. The powder samples were kept in an aluminum bag.

Loss-on-ignition of ashes

An ash sample of about 6 g in a porcelain evaporation pan was dried at 110°C for 2 h, and then the dry weight of the sample was measured. The dry samples were ignited at 300°C, 600°C, and 900°C for 2 h in air by using an electric oven.

Raman measurements of ashes

Raman spectra of the ashes were obtained at room temperature using a Renishaw Raman imaging microscope system 1000 equipped with an air-cooled CCD detector. A He–Ne laser (632.8 nm) was employed as the excitation source. Back-scattered Raman signals were collected through a microscope and holographic notch filters with a spectral resolution of 2 cm^{-1}. The laser power was kept at about 20 mW. The laser beam was focused to a diameter in the range of several microns on the sample surface. The wavenumber was calibrated using the 520-cm^{-1} line of a silicon wafer and the 1332-cm^{-1} line of diamond. Raman spectra were measured at more than 20 points for each ash sample.

Leaching test of ashes

In order to use the ashes as construction materials or as landfill, the amount of designated elements, arsenic, lead, chromium, cadmium (Cd), mercury (Hg), etc., in the leaching test solution must be less than the legal criteria. Leaching tests of the four ashes were performed, and the concentrations of the elements were determined by PIXE analysis.

In a leaching test of ashes, rainwater passed through a disposable cellulose acetate membrane filter (diameter: 25 mm, pore size: 0.45 μm) was used as a solvent. The pH and electrical conductivity of the rainwater were 5.24 and 18.21 μS/cm, respectively. Two milligrams of an ash sample was put in a 50-ml Erlenmeyer flask together with 20 ml of the rainwater in accordance with Notification No. 13 of the Ministry of Environment of Japan. The flask was shaken at 200 rpm for 6 h.

PIXE analysis

Ash samples were prepared using the method developed by Sera et al.,[13] where 100 mg of sample was ground into fine powder in an agate mortar, and 20 mg palladium (Pd)-on-carbon (C) powder (5% Pd) was added as an internal standard, after which they were mixed uniformly in the agate mortar. The thinnest target was prepared by taking ca. 0.1 mg of the powder and putting it onto a 4-μm thick polypropylene film, and dropping 1 μl of 10% collodion solution diluted with ethanol onto it for fixing and smoothing. This process was carried out on a clean bench.

To prepare the ash sample for the leaching test, 50 μl of nitric acid was added to leachate of approximately 5 ml filtered with the membrane filter. Indium solution (1000 mg/l) was added as an internal standard and indium concentration in the sample solution was adjusted to 5 μg/ml. The thinnest targets were prepared on a clean bench by drop-

ping 20 μl of the sample solution onto a 4-μm-thick polypropylene film, after which it was dried in clean air.

The raw wood samples thus prepared were decomposed with nitric acid using a microwave oven,[14] where nearly 50 mg of the sample was put in a polytetrafluoroethylene (PTFE) vessel together with 1 ml of nitric acid, and indium concentration in the sample was adjusted to 1000 μg/g by adding standard indium solution. This PTFE vessel was tightly sealed with a polypropylene jacket, and then heated twice for 2 min at low power corresponding to 170 W. The thinnest targets were prepared by the same method as the target of the leaching test.

Elemental concentrations were determined by the PIXE system at the Nishina Memorial Cyclotron Center (NMCC), Japan Radioisotope Association. The thinnest target was used for PIXE analysis. The target sample was bombarded with 2.9-MeV protons from a baby cyclotron[15] and the inner diameter of the beam duct was 6 mm. X-Ray spectra were analyzed using the SAPIX program.[15] Quantitative analysis of elemental concentrations was performed based on a powdered internal standard method[13] for the ash sample, and on an internal standard method[14] for the leaching test sample and raw wood sample.

Results and discussion

Loss-on-ignition of ashes

Data for loss-on-ignition at 300°C, 600°C, and 900°C of ashes sampled on 7 June 2004 and 8 October 2004 are summarized in Table 1. Ash-1 was pale-gray coarse grains and the other ashes were dark-gray soot-like particles. Microscope observations revealed that particle size decreased in the order, ash-1 > ash-2 > ash-3 > ash-4.

Table 1 shows the wide variations in weight loss-on-ignition among the four ashes. Weight loss-on-ignition up to 600°C is likely to depend primarily upon unburned carbon in the ash. Thus, the values of weight loss at 600°C suggest considerable differences in the unburned carbon contents among the ashes. The losses-on-ignition of ash-1 and ash-2 were almost independent of the sampling day, while there were appreciable differences in losses-on-ignition of ash-3 and ash-4 between the two sampling days.

The weight losses of ash-1, ash-2, and ash-3 at 300°C displayed low values, but the losses-on-ignition at 600°C, with the exception of ash-1, increased greatly and the weight losses in ash-3 and ash-4 ranged from 18% to 27%. In general, carbon atoms lost up to 300°C and from 300°C to 600°C are considered to be organic carbon and inorganic carbon, respectively. The proportion of organic carbon in total carbon in ash-3 ranged from 13% to 24%, while that in ash-4 ranged from 54% to 70%. Hence, it can be assumed that the physicochemical characteristics of unburned carbon in ash-3 are entirely different from those in ash-4. The results of loss-on-ignition at 600°C indicate that carbon is a major element in ash-2, ash-3, and ash-4.

Although the weight loss from 600°C to 900°C of ash-1, ash-2, and ash-3 ranged from 1% to 3%, ash-4 showed weight loss of 8%–12%. This thermogravimetric behavior of ash-4 was noticeably anomalous. The large differences in loss-on-ignition at 600°C of ash-3 and ash-4 between the two sampling days suggest that the unburned carbon content in these ashes was strongly affected by burning conditions of wood in the combustor.

Raman spectra of ashes

Figure 1 shows the typical Raman spectra of the ashes. Each ash showed various Raman spectral patterns. There were, however, few distinguishable differences in spectral features among the four ashes. The only positive difference was the presence or absence of Raman bands due to unburned carbon. Although several sharp Raman bands presumably due to inorganic components were clearly observed, no Raman band assigned to unburned carbon was detected in the ash-1 sample, as expected from the results of loss-on-ignition. However, for ash-2, ash-3, and ash-4, two broad Raman bands attributed to unburned carbon appeared at about 1325 and 1590 cm^{-1} as shown in spectra a, b, c, and d in Fig. 1. These Raman bands are characteristic of charcoal, which are called the D-band (1325 cm^{-1}) and the G-band (1590 cm^{-1}).

We have analyzed charcoal using Raman spectroscopy and already reported that the line shape of Raman bands due to charcoal is highly dependent upon heat-treatment temperature.[16,17] Based on our previous works, all the line shapes of D-bands and G-bands observed in this study were

Table 1. Loss-on-ignition of ash from a biomass power plant

Temperature (°C)	Samples collected 7 June 2004				Samples collected 8 October 2004			
	Ash-1[a]	Ash-2[b]	Ash-3[c]	Ash-4[d]	Ash-1	Ash-2	Ash-3	Ash-4
300	0.6	2.7	4.5	10.6	0.8	1.5	3.4	18.5
600	2.2	12.8	18.7	19.6	3.0	11.5	25.7	26.3
900	3.1	13.5	21.4	27.8	3.1	12.7	26.7	38.5

Data given as percent loss
[a] Cinder
[b] Cyclone ash
[c] Ash dissociated by cyclone separator

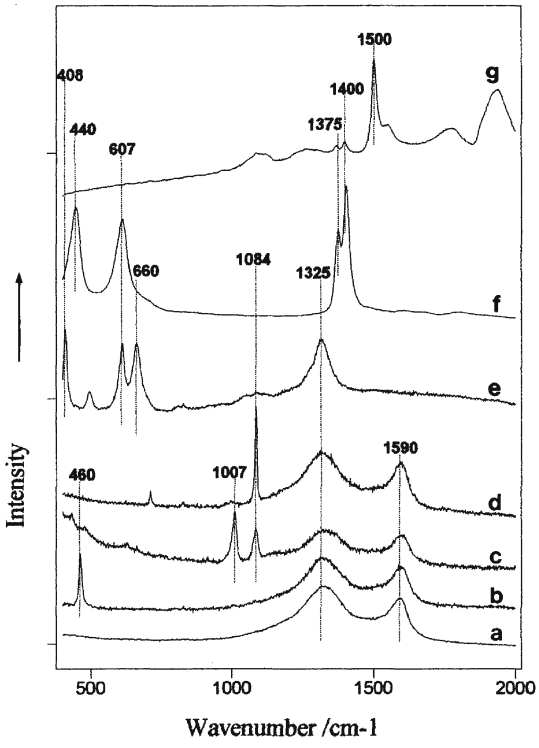

Fig. 1. Typical Raman spectra of ashes from a biomass power plant. See text for discussion of spectra *a–g*

attributable to those of charcoal treated at a temperature higher than 800°C. Therefore, it was concluded that the combustor in the power plant was heated by the burning of wood fuels to temperatures over 800°C.

In all the ashes, the bands attributable to titanium dioxide (rutile type) and crystallized silicon dioxide were detected at 440 and 607 cm^{-1} (spectrum f), and about 460 cm^{-1} (spectrum b), respectively. A sharp Raman band was also observed at about 1084 cm^{-1} (spectra c and d) in the spectra of all the ashes, indicating the presence of calcium and other metal carbonates. In addition, a band at 408 cm^{-1} (spectrum e), which is probably due to zinc oxide, was ascertained in ash-1. From the Raman measurements, it was expected that a substantial amount of oxygen (O) was included in all the ashes. In addition, spectrum g shown in Fig. 1 is a spectral pattern that was frequently observed for all the ashes, although there are no Raman band assignments for the spectrum.

PIXE analysis of ashes

Elemental analysis data of the ashes obtained on 7 June 2004 and 8 October 2004 are summarized in Table 2. More than 20 elements were detected in all the ashes from sodium to lead. Aluminum (Al), silicon (Si), potassium (K), calcium (Ca), and iron (Fe) were detected in all the ashes and the contents were in the weight percentage order. Thus, these elements are considered as principal elements, while sodium, magnesium (Mg), sulfur (S), chlorine (Cl), and tita-

Table 2. Elemental concentration (dry weight) in ash samples

Element	Samples collected 7 June 2004				Samples collected 8 October 2004			
	Ash-1	Ash-2	Ash-3	Ash-4	Ash-1	Ash-2	Ash-3	Ash-4
Na[a]	2.80 ± 0.30	6.73 ± 0.85	6.51 ± 0.20	20.6 ± 1.91	3.93 ± 0.79	6.16 ± 0.47	9.84 ± 0.92	17.6 ± 4.27
Mg[a]	1.70 ± 0.39	2.92 ± 0.35	3.00 ± 0.65	5.44 ± 1.13	2.03 ± 0.60	2.68 ± 0.31	3.55 ± 0.27	6.92 ± 1.65
Al[a]	11.2 ± 2.23	16.8 ± 1.08	11.2 ± 1.44	11.9 ± 0.48	15.3 ± 1.75	12.7 ± 1.59	12.8 ± 1.82	9.54 ± 1.54
Si[a]	51.5 ± 0.78	71.1 ± 8.41	40.3 ± 5.98	37.5 ± 1.49	74.5 ± 3.22	54.0 ± 6.70	47.0 ± 6.48	25.3 ± 4.24
P[a]	<LOQ	0.54 ± 0.06	0.70 ± 0.11	2.17 ± 0.14	<LOQ	<LOQ	1.58 ± 0.14	2.63 ± 0.52
S[a]	2.35 ± 0.24	4.46 ± 0.29	9.93 ± 1.44	30.6 ± 0.10	2.12 ± 0.46	9.11 ± 1.70	13.5 ± 2.05	29.8 ± 2.56
Cl[a]	0.44 ± 0.03	2.15 ± 0.02	6.08 ± 1.03	64.2 ± 9.01	0.57 ± 0.12	4.48 ± 1.10	17.5 ± 0.98	77.0 ± 14.4
K[a]	7.33 ± 0.68	14.3 ± 1.59	19.4 ± 2.34	75.8 ± 2.78	9.16 ± 0.43	17.0 ± 1.33	28.7 ± 1.68	73.6 ± 9.71
Ca[a]	34.6 ± 1.21	62.6 ± 1.08	92.2 ± 8.38	120 ± 2.65	48.0 ± 6.13	70.9 ± 5.97	126 ± 13.8	123 ± 9.05
Ti[a]	3.21 ± 0.41	6.27 ± 0.64	3.83 ± 0.26	3.54 ± 0.27	3.41 ± 0.12	4.88 ± 0.45	5.07 ± 0.26	4.22 ± 0.62
Cr[a]	0.12 ± 0.02	0.10 ± 0.01	0.27 ± 0.04	0.39 ± 0.04	0.21 ± 0.07	0.36 ± 0.25	0.57 ± 0.06	0.28 ± 0.06
Mn[a]	0.71 ± 0.04	1.48 ± 0.08	2.22 ± 0.26	3.46 ± 0.37	0.53 ± 0.05	1.38 ± 0.16	2.27 ± 0.36	3.43 ± 0.50
Fe[a]	22.1 ± 1.08	38.0 ± 3.43	31.4 ± 1.55	28.3 ± 1.64	26.0 ± 2.08	30.5 ± 3.77	30.2 ± 3.50	17.9 ± 1.77
Cu[a]	0.13 ± 0.00	0.12 ± 0.01	0.33 ± 0.04	0.80 ± 0.10	0.12 ± 0.02	0.28 ± 0.02	0.44 ± 0.04	0.93 ± 0.07
Zn[a]	0.31 ± 0.03	0.68 ± 0.05	3.21 ± 0.25	9.42 ± 0.46	0.43 ± 0.03	1.46 ± 0.25	3.05 ± 0.19	9.67 ± 0.51
Ga[b]	6.5 ± 1.1	17.6 ± 0.3	16.1 ± 5.7	67.2 ± 4.0	9.5 ± 1.3	14.9 ± 4.0	25.6 ± 2.9	79.9 ± 9.9
As[b]	12.0 ± 0.6	10.9 ± 4.0	53.7 ± 5.4	318 ± 60.0	10.6 ± 1.8	26.6 ± 2.4	73.8 ± 8.7	323 ± 53.8
Br[b]	4.1 ± 0.4	19.2 ± 0.9	99.5 ± 6.7	562 ± 29.4	6.3 ± 2.4	34.3 ± 3.5	209 ± 12.7	866 ± 121
Rb[b]	33.1 ± 4.3	34.6 ± 0.6	42.5 ± 3.5	142 ± 2.1	18.3 ± 5.4	31.1 ± 6.8	53.5 ± 2.3	142 ± 1.8
Sr[a]	0.20 ± 0.02	0.26 ± 0.01	0.46 ± 0.03	0.59 ± 0.03	0.18 ± 0.01	0.34 ± 0.04	0.53 ± 0.04	0.55 ± 0.05
Zr[b]	74.0 ± 6.1	<LOQ	70.6 ± 3.1	59.7 ± 11.4	72.6 ± 12.1	98.3 ± 15.5	87.6 ± 8.0	61.9 ± 11.9
Ba[a]	0.43 ± 0.04	0.56 ± 0.03	0.45 ± 0.03	<LOQ	0.42 ± 0.03	0.55 ± 0.09	0.66 ± 0.08	0.61 ± 0.14
Pb[a]	0.23 ± 0.02	0.21 ± 0.02	0.94 ± 0.05	3.65 ± 0.21	0.14 ± 0.01	0.44 ± 0.03	1.03 ± 0.07	3.25 ± 0.20

Data given as mean ± standard deviation, $n = 5$
LOQ, Limit of quantification
[a] Concentration given in milligrams per gram
[b] Concentration given in micrograms per gram

nium (Ti) are subprincipal elements. The nails and bolts included in waste wood are likely to play the role of iron supplier. For ash-4, sodium, sulfur, and chlorine can also be regarded as major elements. The concentrations of sodium, sulfur, chlorine, and potassium distinctly increased in the order of ash-1 < ash-2 < ash-3 < ash-4. In particular, the concentration of chlorine in ash-4 was much larger than those in other ashes. Like sodium and sulfur, the concentration of many minor elements increased in the order of ash-1 < ash-2 < ash-3 < ash-4, and arsenic and bromine (Br) had a clear-cut tendency to concentrate in ash-4.

The detection of copper, chromium, and arsenic indicates that timber treated with CCA preservative was included in whole waste wood fuels. The behavior of arsenic in the furnace and exhaust gas line was presumably entirely different from that of copper and chromium, because the increase in arsenic concentration from ash-1 to ash-4 was much greater than those for copper and chromium concentrations. Moreover, the paint used on waste wood may contribute to the high lead concentration.

Table 3 shows the ratios of the elemental concentrations on 7 June 2004 to those on 8 October 2004. The fluctuations of principal elemental concentrations between the two sampling days were relatively small except for sulfur and chlorine in ash-2 and chlorine in ash-3. For other elements, the fluctuations of copper, chromium, arsenic, zinc (Zn), and lead in ash-2, and chromium and bromine in ash-3 seemed to be slightly larger, but there were no elements showing distinct fluctuations in ash-1 or ash-4. Thus, it is expected that temporal changes in elemental composition of the ashes are not large. In this respect, the ashes are likely to be easy to use.

Leaching test of ashes using PIXE

Table 4 shows the concentrations of elements that dissolved in rainwater during the leaching tests. The concentrations were determined by PIXE measurements. As expected, both cadmium and mercury, which were not observed in the ashes, were not detected in the leaching test solutions. The concentrations of arsenic were below the limit of quantification. All the leaching test solutions contained no lead or small amounts thereof. For chromium, there was no problem for landfill disposal.

The ratios of the leaching concentration of the two sampling days are listed in Table 5. The leaching concentrations fluctuated between the two sampling days much more widely than the elemental concentrations in the ashes, especially for silicon and sulfur in ash-1, calcium in ash-2, bromine in ash-3, and chlorine and bromine in ash-4. Com-

Table 3. Ratios of elemental concentration of ash collected on 7 June 2004 to elemental concentration of ash collected on 8 October 2004

Element	Ash-1	Ash-2	Ash-3	Ash-4
Na	0.71	1.09	0.66	1.17
Mg	0.84	1.09	0.85	0.79
Al	0.73	1.32	0.88	1.25
Si	0.69	1.32	0.86	1.48
P	–	–	0.44	0.83
S	1.11	0.49	0.74	1.03
Cl	0.77	0.48	0.35	0.83
K	0.80	0.84	0.68	1.03
Ca	0.72	0.88	0.73	0.98
Ti	0.94	1.28	0.76	0.84
Cr	0.57	0.28	0.47	1.39
Mn	1.34	1.07	0.98	1.01
Fe	0.85	1.25	1.04	1.58
Cu	1.08	0.43	0.75	0.86
Zn	0.72	0.47	1.05	0.97
Ga	0.68	1.18	0.63	0.84
As	1.13	0.41	0.73	0.98
Br	0.65	0.56	0.48	0.65
Rb	1.81	1.11	0.79	1.00
Sr	1.11	0.76	0.87	1.07
Zr	1.02	–	0.81	0.96
Ba	1.02	1.02	0.68	–
Pb	1.64	0.48	0.91	1.12

Table 4. Elemental concentration in leachates of ashes

Element	Samples collected 7 June 2004				Samples collected 8 October 2004			
	Ash-1	Ash-2	Ash-3	Ash-4	Ash-1	Ash-2	Ash-3	Ash-4
Na	12.6 ± 2.30	80.2 ± 6.90	40.6 ± 12.8	77.7 ± 7.76	9.00 ± 1.72	35.4 ± 4.27	17.8 ± 1.77	51.7 ± 9.28
Mg	<LOQ	4.83 ± 1.05	6.07 ± 0.72	12.5 ± 2.51	<LOQ	<LOQ	<LOQ	<LOQ
Al	1.42 ± 0.25	<LOQ	<LOQ	1.83 ± 0.90	<LOQ	1.15 ± 0.22	0.34 ± 0.13	0.92 ± 0.07
Si	5.35 ± 0.73	3.72 ± 0.52	1.89 ± 0.38	1.28 ± 0.59	0.58 ± 0.17	9.21 ± 1.15	1.47 ± 0.30	0.50 ± 0.04
P	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.01 ± 0.09	0.64 ± 0.12	0.94 ± 0.16
S	96.9 ± 14.1	564 ± 63.3	205 ± 38.3	398 ± 37.2	10.49 ± 0.52	132 ± 6.10	165 ± 21.5	162 ± 46.0
Cl	<LOQ	<LOQ	<LOQ	524 ± 25.9	0.45 ± 0.04	<LOQ	<LOQ	24.3 ± 2.39
K	91.7 ± 9.53	452 ± 15.9	549 ± 47.1	1470 ± 108	93.3 ± 7.67	357 ± 13.3	285 ± 34.1	518 ± 73.0
Ca	115 ± 13.4	231 ± 18.4	132 ± 36.4	184 ± 25.6	113 ± 11.9	14.7 ± 1.96	92.1 ± 13.7	102 ± 28.1
Cr	0.18 ± 0.01	0.38 ± 0.06	0.22 ± 0.04	0.39 ± 0.04	0.15 ± 0.02	0.52 ± 0.01	0.36 ± 0.05	0.39 ± 0.09
Mn	0.02 ± 0.01	0.04 ± 0.02	<LOQ	0.04 ± 0.01	<LOQ	<LOQ	<LOQ	<LOQ
Fe	<LOQ	<LOQ	<LOQ	0.08 ± 0.04	<LOQ	<LOQ	<LOQ	<LOQ
Zn	<LOQ	<LOQ	<LOQ	0.04 ± 0.01	<LOQ	<LOQ	<LOQ	0.11 ± 0.01
As	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Br	<LOQ	0.06 ± 0.01	0.21 ± 0.08	9.53 ± 0.82	<LOQ	0.03 ± 0.01	0.02 ± 0.01	0.36 ± 0.09
Rb	0.13 ± 0.01	0.96 ± 0.04	2.43 ± 0.08	11.9 ± 0.90	0.16 ± 0.02	0.83 ± 0.07	1.80 ± 0.29	5.66 ± 0.74
Sr	0.41 ± 0.04	2.24 ± 0.11	4.75 ± 0.25	5.66 ± 0.33	0.47 ± 0.02	0.71 ± 0.04	4.01 ± 1.27	5.37 ± 1.48
Pb	<LOQ	<LOQ	<LOQ	0.08 ± 0.01	0.02 ± 0.01	0.02 ± 0.02	0.02 ± 0.01	0.26 ± 0.02

Table 5. Ratios of elemental concentration in leachate from ash collected on 7 June 2004 to elemental concentration in leachate from ash collected on 8 October

Element	Ash-1	Ash-2	Ash-3	Ash-4
Na	1.40	2.27	2.28	1.50
Mg	–	–	–	–
Al	–	–	–	1.99
Si	9.22	0.40	1.29	2.56
P	–	–	–	–
S	9.24	4.27	1.24	2.46
Cl	–	–	–	21.56
K	0.98	1.27	1.93	2.84
Ca	1.02	15.71	1.43	1.80
Cr	1.20	0.73	0.61	1.00
Mn	–	–	–	–
Fe	–	–	–	–
Zn	–	–	–	0.36
As	–	–	–	–
Br	–	2.00	10.50	26.47
Rb	0.81	1.16	1.35	2.10
Sr	0.87	3.15	1.18	1.05
Pb	–	–	–	0.31

parison of Tables 3 and 5 suggests that there is no close correlation between the concentrations of elements leached into water and those in the solid ashes. This is a remarkable result that suggests the leaching concentration is strongly affected by small variations in combustion conditions.

PIXE analysis of raw wood fuels

The elemental analysis results obtained from PIXE measurements of nine kinds of wood fuels are given in Table 6. Twenty-four elements were detected in the range from sodium to lead, but no element was classified as a principal element. Potassium and calcium were present as 0.1% (w/w) in all the wood fuel samples, and sodium, magnesium, aluminum, silicon, sulfur, and iron were also observed in all the samples, although their concentrations were considerably lower than those of potassium and calcium. The results can be expected from the fact that most wood species possess these elements as trace elements. As mentioned above, these elements were analyzed as principal or relatively high concentration components in the ashes, and

Table 6. Elemental concentrations (dry weight) in wood fuels of a biomass power plant

Element	Sample								
	Wood-1[a]	Wood-2[b]	Wood-3[c]	Wood-4[d]	Wood-5[e]	Wood-6[f]	Wood-7[g]	Wood-8[h]	Wood-9[i]
Na[j]	0.777 ± 0.057	0.099 ± 0.020	0.094 ± 0.017	0.131 ± 0.020	0.135 ± 0.029	0.163 ± 0.009	0.112 ± 0.013	0.215 ± 0.053	0.173 ± 0.02
Mg[j]	0.212 ± 0.021	0.104 ± 0.008	0.148 ± 0.016	0.136 ± 0.017	0.038 ± 0.016	0.282 ± 0.065	0.262 ± 0.032	0.297 ± 0.035	0.260 ± 0.04
Al[j]	0.108 ± 0.006	0.066 ± 0.024	0.050 ± 0.010	0.081 ± 0.003	0.372 ± 0.034	0.053 ± 0.008	0.134 ± 0.016	0.149 ± 0.007	1.57 ± 0.01
Si[j]	0.370 ± 0.088	0.205 ± 0.028	0.242 ± 0.007	0.233 ± 0.031	0.197 ± 0.040	0.218 ± 0.022	0.214 ± 0.028	0.457 ± 0.006	1.58 ± 0.10
P[j]	0.159 ± 0.023	<LOQ	0.027 ± 0.007	0.445 ± 0.013	0.055 ± 0.012	0.175 ± 0.015	0.081 ± 0.012	0.208 ± 0.033	0.040 ± 0.009
S[j]	0.431 ± 0.013	0.123 ± 0.005	0.080 ± 0.010	0.073 ± 0.015	0.109 ± 0.014	0.386 ± 0.049	0.163 ± 0.016	0.341 ± 0.026	0.150 ± 0.006
Cl[k]	92 ± 28	15 ± 4	26 ± 12	62 ± 12	<LOQ	<LOQ	<LOQ	22 ± 5	29 ± 11
K[j]	1.94 ± 0.06	1.17 ± 0.14	0.319 ± 0.055	0.566 ± 0.012	0.250 ± 0.031	1.49 ± 0.17	0.409 ± 0.062	1.86 ± 0.01	0.372 ± 0.022
Ca[j]	2.51 ± 0.11	1.16 ± 0.15	1.87 ± 0.04	1.28 ± 0.03	0.530 ± 0.032	3.21 ± 0.32	4.04 ± 0.18	8.71 ± 0.15	2.70 ± 0.18
Ti[k]	15.4 ± 3.0	5.1 ± 0.7	11.8 ± 1.6	83.7 ± 15.7	12.0 ± 2.8	14.7 ± 1.6	7.3 ± 3.7	9.3 ± 1.7	80.0 ± 2.1
V[k]	<LOQ	1.0 ± 0.1	<LOQ	<LOQ	<LOQ	2.2 ± 0.2	1.4 ± 0.1	<LOQ	2.6 ± 0.5
Cr[k]	2.1 ± 0.7	1.2 ± 0.2	1.3 ± 0.9	1.2 ± 0.1	1.0 ± 0.2	<LOQ	<LOQ	1.3 ± 0.2	5.4 ± 0.3
Mn[k]	19.7 ± 1.5	11.5 ± 0.7	1.4 ± 0.2	26.9 ± 1.9	11.3 ± 0.7	11.5 ± 1.0	26.0 ± 1.1	12.3 ± 0.7	22.1 ± 2.0
Fe[j]	0.138 ± 0.030	0.050 ± 0.004	0.081 ± 0.006	0.075 ± 0.014	0.074 ± 0.004	0.057 ± 0.004	0.063 ± 0.027	0.153 ± 0.007	0.335 ± 0.072
Co[k]	<LOQ	<LOQ	<LOQ	<LOQ	0.7 ± 0.2	<LOQ	<LOQ	1.7 ± 0.1	1.9 ± 0.2
Ni[k]	1.1 ± 0.2	0.4 ± 0.0	0.7 ± 0.5	0.9 ± 0.2	1.3 ± 0.2	1.3 ± 0.1	<LOQ	1.7 ± 0.5	0.6 ± 0.2
Cu[k]	5.8 ± 0.6	3.5 ± 0.6	3.2 ± 0.7	2.5 ± 0.3	2.7 ± 0.5	3.1 ± 0.3	4.7 ± 0.4	4.4 ± 0.2	6.9 ± 0.6
Zn[k]	44.6 ± 0.8	25.5 ± 5.1	7.1 ± 1.4	6.4 ± 2.0	5.8 ± 1.7	23.3 ± 3.9	17.1 ± 0.3	7.5 ± 0.6	35.1 ± 2.4
Ga[k]	<LOQ	<LOQ	<LOQ	<LOQ	0.3 ± 0.1	<LOQ	0.4 ± 0.1	<LOQ	<LOQ
Br[k]	1.9 ± 0.1	0.3 ± 0.1	<LOQ	0.5 ± 0.2	0.5 ± 0.1	1.0 ± 0.3	0.4 ± 0.1	0.7 ± 0.2	18.2 ± 10.0
Rb[k]	1.7 ± 0.4	0.8 ± 0.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.2 ± 0.1	<LOQ
Sr[k]	23.0 ± 0.1	4.8 ± 0.3	12.6 ± 1.1	7.8 ± 0.2	2.4 ± 0.1	25.1 ± 2.1	18.4 ± 0.9	14.2 ± 1.4	6.5 ± 0.4
Hg[k]	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.5 ± 0.3	2.0 ± 0.4	<LOQ
Pb[k]	10.8 ± 1.3	3.9 ± 0.4	8.2 ± 2.1	6.8 ± 1.3	8.3 ± 0.5	7.9 ± 0.3	7.2 ± 0.9	12.8 ± 3.2	13.2 ± 0.1

Data given as mean ± standard deviation ($n = 5$)
[a] Construction waste wood (plywood)
[b] Construction waste wood (square wood)
[c] Waste wood from woodworking industry (solid board)
[d] Waste wood from woodworking industry (fancy plywood)
[e] Waste wood from woodworking industry (hardboard)
[f] Wood from trees damaged by strong winds (false acacia)
[g] Wood from trees attacked by pinewood nematode
[h] Japanese cedar bark
[i] Insulation fiberboard
[j] Concentration in milligrams per gram
[k] Concentration in micrograms per gram

therefore it was elucidated that they were concentrated in the ashes by combustion. Moreover, titanium, chromium, manganese (Mn), nickel (Ni), copper, zinc, bromine, strontium (Sr), and lead were detected at ppm levels in all the fuel samples.

Clear evidence for arsenic and barium (Ba) was clearly observed in the ashes as shown in Table 2, but these elements were not detected in all waste wood samples. No detection of arsenic indicates that timber treated with CCA was not included in the nine kinds of raw wood fuels. On the other hand, although nickel, vanadium (V), and mercury were not detected in the ashes, they were detectable in the waste wood samples.

Titanium was highly concentrated in fancy plywood (wood-4) and insulation fiber board (wood-9) as compared with other waste wood samples, suggesting that the two wood samples contained titanium dioxide that was used as bulking filler of an adhesive. For wood-9, the concentrations of aluminum and silicon also showed fairly high values, and thus it seems likely that these elements were added to adhesive as filler. In addition, it is presumed that lead derived from paint was not contained in any wood samples used for PIXE measurements, because fluctuations of lead concentration among the samples were relatively small.

Conclusions

From the PIXE, Raman, and loss-on-ignition analyses, we have obtained a substantial amount of chemical information on the ashes from a biomass power plant. Unburned carbon included in the ash increased in the order of ash-1 < ash-2 < ash-3 < ash-4, and carbon was one of the principal elements in ash-2, ash-3, and ash-4. Ash-4 showed a large weight loss for the ignition temperature range from 600°C to 900°C when compared with other ashes. It was elucidated from PIXE analysis that the principal elements common to all the ashes were aluminum, silicon, potassium, calcium, and iron. Moreover, sodium, sulfur, and chlorine in ash-4 were classified into the principal element group. Based on Raman measurements, it was assumed that a considerable amount of oxygen was included in all the ashes. Many elements, especially arsenic and bromine, showed a tendency to increase in the order of ash-1 < ash-2 < ash-3 < ash-4. For the principal elements in the ashes, the differences in concentration were relatively small between the two sampling days, suggesting that the temporal fluctuation of the elemental concentration was not large. This is an important point in terms of utilization of the ashes. Chromium, arsenic, and lead were detected in all the ashes, whereas in the leaching test arsenic was undetectable and the concentrations of chromium and lead were much lower than the legal requirements for landfill disposal of combustion products.

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References

1. Saitoh K, Sera K, Hirano K, Shirai T (2002) Chemical characterization of particles in winter-night smog in Tokyo. Atmos Environ 36:435–440
2. Saitoh K, Sera K, Shirai T, Sato T, Okada M (2003) Determination of elemental and ionic compositions for diesel exhaust particle induced X-ray emission and ion chromatography analysis. Anal Sci 19:525–528
3. Saitoh K (2003) Study on atmospheric environment at Shirakami-sanchi world heritage area: concentration of atmospheric gaseous substance and change of elemental composition in beech leaves with development (in Japanese). J Jpn Soc Atmos Environ 38:145–161
4. Saitoh K, Sera K, Futatsugawa S, Kitagawa M (2005) Simultaneous multi-element analysis of atmospheric particles collected on a quartz-fiber filter by PIXE (in Japanese). Radioisotopes 54:115–121
5. Smolik J, Schwarz J, Vesely V, Puncochar M, Kugler J, Sykorova I, Havranek V (1999) Composition of particulate emissions from fluidized bed combustion of charcoal. J Aerosol Sci 30:783–784
6. Vijayan V, Ramamurthy VS, Behera SN (1995) Particle-induced X-ray emission (PIXE) analysis of coal fly ash. Int J PIXE 5:211–219
7. Cereda E, Marcazzan GMB, Grime GW, Mattachini F (1996) Macroscopic and microscopic approach to the study of enrichment phenomena in the electrostatic precipitation of coal fly ash particles. Nucl Instrum Methods Phys Res B 109/110:696–700
8. Alamin MB, Spyrou NM (1997) Elemental characterization of different matrices including coal, sawdust, fly-ash and landfill waste samples using INAA and PIXE analyses. J Radioanal Nucl Chem 216:41–45
9. Hall GS (1990) Sample preparation methods of tree-rings for PIXE-PIGE multielemental analysis. Nucl Instrum Methods Phys Res B 49:60–64
10. Saarela K-E, Harju L, Lill J-O, Rajander J, Lindoos A, Heselius S-J (2002) Thick-target PIXE analysis of trace elements in wood incoming to a pulp mill. Holzforschung 56:380–387
11. Saarela K-E, Harju L, Rajander J, Lill J-O, Heselius S-J, Lindoos A, Mattsson K (2005) Elemental analyses of pine bark and wood in an environmental study. Sci Total Environ 343:231–241
12. Yamauchi S, Saitoh K, Sera K, Wada Y, Kuwahara M (2007) Elemental composition characteristics of ashes from biomass power facility: multi-elemental analysis by particle induced X-ray emission (in Japanese). Mokuzai Kogyo 62:157–162
13. Sera K, Futatsugawa S, Ishiyama D (1999) Application of a powdered-internal-standard method combined with correction for self-absorption of X-ray to geological, environmental and biological samples. Int J PIXE 9:63–81
14. Futatsugawa S, Hatakeyama S, Saitou S, Sera K (1993) Present status of NMCC and sample preparation method for bio-samples. Int J PIXE 3:319–328
15. Sera K, Yanagisawa T, Tsunoda H, Hutatukawa S, Saitoh Y, Suzuki S, Orihara H (1992) Bio-PIXE at the Takizawa facility (Bio-PIXE with a baby cyclotron). Int J PIXE 2:325–330
16. Yamauchi S, Kikuchi Y, Kurimoto Y (2000) Raman spectral changes of sugi bark during thermal degradation and carbonization. Mater Sci Res Int 6:227–228
17. Yamauchi S, Kurimoto Y (2003) Raman spectroscopic study on pyrolyzed wood and bark of Japanese cedar: temperature dependence of Raman parameters. J Wood Sci 49:235–240