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Chemical Composition of Wood Chips and Wood Pellets

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S Supporting Information

ABSTRACT: The chemical composition of 23 wood chip samples and 132 wood pellet samples manufactured in the United States and Canada were analyzed for their energy and chemical properties and compared to German standards for pellet quality. The pellet samples obtained from various locations across northern New York and New England included 100 different manufacturers and duplicate samples of some brands. The calorific value, moisture content, and ash content of the samples were determined according to the American Society for Testing and Materials (ASTM) methods. Sulfate and chloride samples were prepared using ASTM methods and analyzed by ion chromatography (IC). The elemental compositions of the ashed wood samples were determined using inductively coupled plasma mass spectrometry (ICP–MS). Mercury was measured by direct analysis of wood samples. The distributions of the sample characteristics, such as heating value, ash content, moisture content, ions, and heavy elements, are presented. Major ash-forming elements were Ca, K, Al, Mg, and Fe. Although heavy elements are found naturally in wood and bark, some pellet samples had unusually high concentrations of heavy elements. This contamination was likely because of inclusion of extraneous materials, such as scrap or painted wood, bark or leaves, and other possible contaminants, during pellet manufacturing processes. Most of the commercially available wood pellets of this study would meet German and European industrial standards. However, standards for elemental compositions of commercial wood pellets and chips need to be established in the United States to exclude extraneous materials. The promulgation of such standards would reduce environmental problems related to air emissions and ash used as fertilizers for agriculture soils, where there are limits on the allowable concentrations for many elements.

INTRODUCTION

Biomass combustion technology is gaining interest. Biomass is a renewable resource, and energy generation by biomass combustion can become cost-effective.¹ Biomass is generally considered as a renewable energy source, although a complete life cycle assessment (LCA) can identify environmental problems related to planting, harvesting, transporting, and processing that involve considerable energy use.^{2,3}

Woody biomass is an available residential and commercial source for space heating energy needs. Biomass combustion has variable emission factors depending upon the types and quality of fuel used, combustion technologies, and operating conditions.^{4,5} The quality of the fuel mainly depends upon its chemical composition, including its water content. The composition depends upon the nature of the plant species. The ability of plant species to uptake selectively specific compounds from soil, water, and air varies, dependent upon where it grows (origin), such as the geographic locations, climate, seasons, and soil, fertilizers and pesticides used, harvesting practices, transport, handling and processing, blending of plant species type, and contamination of waste wood by paints or chemically treated wood.^{6–17} The ash content varies with inorganic species present in the biomass. Generally, the ash content of woody biomass ranges from 0.5 to 3% dry weight (dw). However, a few studies reported high values of biomass fuel ash (10% dw).^{3,18}

Major constituents in wood are carbon (from 45 to 50% of the mass), followed by oxygen (about 40–50%), hydrogen (about 6%), and nitrogen (less than 1%). Other major ash-

forming elements in decreasing order are calcium (Ca), potassium (K), sodium (Na), magnesium (Mg), manganese (Mn), iron (Fe), and aluminum (Al). Minor ash-forming elements include cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), arsenic (As), mercury (Hg), and lead (Pb).^{17–19} However, plant uptake of elements from soils, including heavy elements, has been reported.¹⁹ For example, lead (Pb) is taken up by the plant root hairs and stored as lead pyrophosphate in cell walls. The degree of uptake is dependent upon the plant species. Some plants are protected against certain elements, while others are not.^{6,19} Apart from natural uptake, contamination in wood chips and pellets can occur during the manufacturing process by including waste wood materials that include paints or have been pressure-treated. Contamination might also occur with materials such as dust, dirt, and soil and entrained as inclusions during harvesting and processing. Combustion of contaminated wood poses potential environmental problems related to particulate emissions and ash disposal. The emissions mainly depend upon the combustion appliance and combustion condition. There is concern about elements in wood ash on the allowable concentrations defined for many elements to be used as fertilizers in agriculture soils, where individual states set limits on the allowable element concentrations.²⁸

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Table 1. Various Standards for Wood Pellets

specification	units	CEN/TS ^a	Austria	Germany	Sweden ^b	PFI (U.S.)
gross calorific value	MJ/kg	20.00–20.47	>18.00	17.45–19.54	>16.91	18.61
ash	%, dw	0.3	<0.5	<1.5	≤0.7	<1
moisture	%, as received	<10	<12	<12	≤10	<8
chlorides	ppm	<100–300	<200	<300	≤300	<300
sulfur	%	<0.01–0.005	<0.04	0.08	≤0.08	
nitrogen	%	<0.1–0.5	<0.30	0.3		
arsenic	mg/kg			0.8		
cadmium	mg/kg	0.1		0.5		
chromium	mg/kg	1		8		
copper	mg/kg	2		5		
mercury	mg/kg			0.05		
lead	mg/kg			<10		
zinc	mg/kg	10		<100		

^aEuropean Committee for Standardization as given in CEN/TS 14961 “Annex A” Examples of Specifications for High Quality Classes of Solid Biofuels Recommended for Household Usage. ^bSweden Group 1 (best) specification.

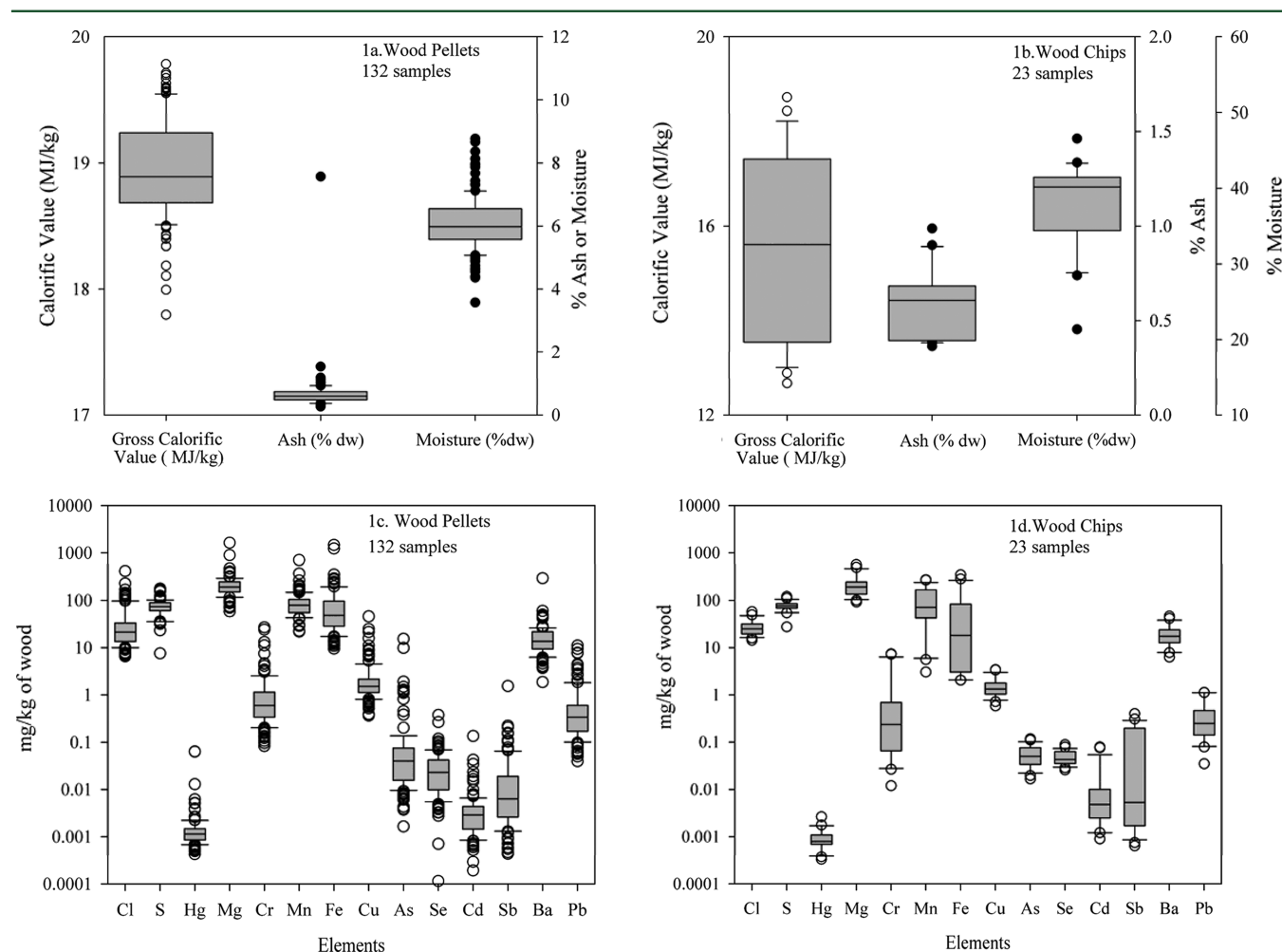


Figure 1. Basic characterization (gross calorific content, percent ash, and percent moisture) and heavy-element concentrations (dw basis) in wood pellets (left) and chips (right).

Standards have been established for wood pellets in some European countries and for the European industry (Table 1).²⁰ The Pellet Fuel Institute (PFI) in the United States (U.S.) has some limited voluntary standards for U.S. wood pellets. There have been a few small studies of the composition of woody biofuels.^{21,22} However, there has not been a large study of wood chips and pellets analyzed using the same methods. In this

study, 132 wood pellet samples and 23 samples of wood chips were analyzed for chemical and energy properties.

EXPERIMENTAL SECTION

Pellet samples were purchased across seven northeastern states: New York (NY), Vermont (VT), New Hampshire (NH), Connecticut (CT), Massachusetts (MA), Rhode Island (RI), and Maine (ME). The 132 wood pellet samples represented 100 different brands. Duplicate

Table 2. Variation in Pellet Elemental Concentration (mg/kg of Wood) with Mean, Standard Deviation, Minimum, and Maximum Concentrations

element	mean	median	standard deviation	minimum	maximum
Cl	36.6	21	48.9	6.5	413
SO ₄	0.222	0.22	0.076	0.02	0.53
S	73.9	73	25.5	7.6	175
Hg	0.00736	0.0012	0.0432	0.0004	0.44
Li	0.772	0.57	0.696	0.035	4.7
Na	60	30	113	8.4	973
Mg	216	188	155	58	1620
Al	60.2	31	127	4.9	1360
K	777	709	840	167	9833
Ca	1139	916	1399	303	16000
V	0.151	0.085	0.235	0.011	2.1
Cr	1.46	0.58	3.45	0.083	27
Mn	91.1	78	71.1	22	702
Fe	91.7	48	171	9.5	1460
Co	0.077	0.054	0.117	0.0044	1.2
Ni	0.52	0.36	0.823	0.017	8.3
Cu	2.72	1.5	5.01	0.36	46
Zn	9.28	7.2	8.92	1.2	90
As	0.31	0.04	1.58	0.0016	15
Se	0.034	0.023	0.0434	0.00011	0.37
Rb	2	1.7	1.92	0.29	18
Sr	8.38	6.5	9.21	2.9	101
Cd	0.00501	0.0029	0.0126	0.0000890	0.14
Sb	0.032	0.0063	0.137	0.00043	1.5
Ba	17.9	14	25.8	1.9	292
Tl	0.00111	0.00041	0.00171	0	0.011
Pb	0.81	0.34	1.65	0.04	11

Table 3. Variation in Wood Chip Elemental Concentration (mg/kg of Wood) with Mean, Standard Deviation, Minimum, and Maximum Concentrations

element	mean	median	standard deviation	minimum	maximum
Cl	27.6	24.7	10.7	14	57
S	76.1	75.5	19.4	27.3	120
Hg	0.00095	0.00079	0.00051	0.0003	0.0026
Li	0.399	0.235	0.33	0.081	1.51
Na	34.2	20.9	28.3	9.2	106
Mg	216	189	123	91	563
Al	68	14.4	107	0.85	399
K	839	745	380	381	2066
Ca	1184	1190	512	373	2639
V	0.114	0.022	0.168	0.004	0.574
Cr	1.31	0.24	2.28	0.012	7.36
Mn	97.5	70.6	78.8	3	272
Fe	64	18.1	98.2	2	345
Co	0.0456	0.029	0.0392	0.01	0.142
Ni	0.56	0.362	0.468	0.17	1.98
Cu	1.5	1.32	0.75	0.58	3.41
Zn	7.11	5.93	4.54	1.53	17
As	0.0554	0.05	0.0277	0.017	0.117
Se	0.0498	0.043	0.0168	0.026	0.088
Rb	1.83	1.55	1.04	0.59	4.57
Sr	6.67	5.83	3.7	2.39	17.9
Cd	0.0122	0.0048	0.0212	0.0009	0.079
Sb	0.0872	0.0053	0.122	0.00064	0.397
Ba	19	17.4	10.2	6.3	45.9
Tl	0.00056	0.00033	0.00064	0.0000747	0.0027
Pb	0.383	0.249	0.338	0.035	1.12

samples of some brands were purchased in different locations and at different times to examine the batch–batch variation of manufactured pellets. A total of 23 wood chip samples were collected at three different facilities that use wood chips for fuel from a single supplier. All of the samples were analyzed for calorific value, moisture, ash, chloride, sulfate, mercury, and trace elements.

Determination of the Gross Calorific Value. The gross calorific value was determined according to American Society for Testing and Materials (ASTM) E711-87. About 1 g of sample was combusted in an oxygen bomb calorimeter. Three replicates were analyzed for each sample.

Determination of Moisture and Ash. The moisture content was determined using ASTM E871-82, where about 5 g of sample was heated in an oven at 102 ± 2 °C for 16 h. Three replicates were analyzed for each sample. The wood pellets were ground in a cryogenic freezer mill. At least 2 g of the ground sample was ashed in a porcelain crucible for 2 h at 580 °C using a muffle furnace according to ASTM D1102-84. Three replicates were analyzed for each sample.

Determination of Chloride and Sulfate. Samples for chloride and sulfate analysis were prepared by a modified version of the bomb-washing method in ASTM E775 and the U.S. Environmental Protection Agency (EPA) SWP-846 Method 5050, respectively, and then analyzed by ion chromatography (IC).

Determination of Mercury. The mercury content was determined by direct analysis of ground wood samples because ashing wood might volatilize the mercury. A direct mercury analyzer (Milestone DMA-80) was used to analyze two replicates for each sample.

Determination of Trace Elements. The ground wood was ashed in a porcelain crucible according to ASTM D1102-84. The ash samples were microwave-digested (MARS Express, CEM Corp.) in 10 mL of 50% HNO₃ and analyzed for trace elements by inductively coupled plasma mass spectrometry (ICP–MS) using EPA Method IO-3.5. A total of 10% of the samples was subjected to duplicate analysis for quality control (QC) purposes, which also includes the sample preparation process.

Determination of the Carbon Content. A subset of wood samples was analyzed for the carbon content using a Shimadzu total organic carbon (TOC) analyzer model V_{CPH}. The analyses were performed on samples of six types of wood pellets and two types of the wood chips that included hardwood, softwood, and blended hardwood and softwood (two samples of each) from a single manufacturer.

RESULTS AND DISCUSSION

The basic analysis results (gross calorific value and ash and moisture contents) of all of the wood pellet and wood chip samples are reported in Tables S1 and S2 of the Supporting Information. The moisture content in the wood chips is about 5 times higher than in the wood pellets. The heating value of the wood chips is lower than that of the wood pellets as a result of their higher moisture content. There was limited variation in the wood chip ash content, although there was a relatively limited number of samples. In the wood pellets, the ash content ranged from 0.29 to 1.53% dw, with one outlier sample whose ash content was about 7.5% dw indicating the likely presence of extraneous materials. The concentration of Ca, Ni, Zn, and Pb was high in the sample, which might be due to inclusion of bark, where the element concentrations are generally high. The ground sample also had some coarse particles. Thus, a contamination might have occurred with materials such as dust, dirt, and soil and entrained as inclusions during harvesting and processing. On the basis of a mass closure analysis of the measured elements in the ash summed as their oxides, the Si concentrations in the pellet samples were insignificant, except for the few samples that had a high ash content. The distributions of the calorific value and ash and moisture

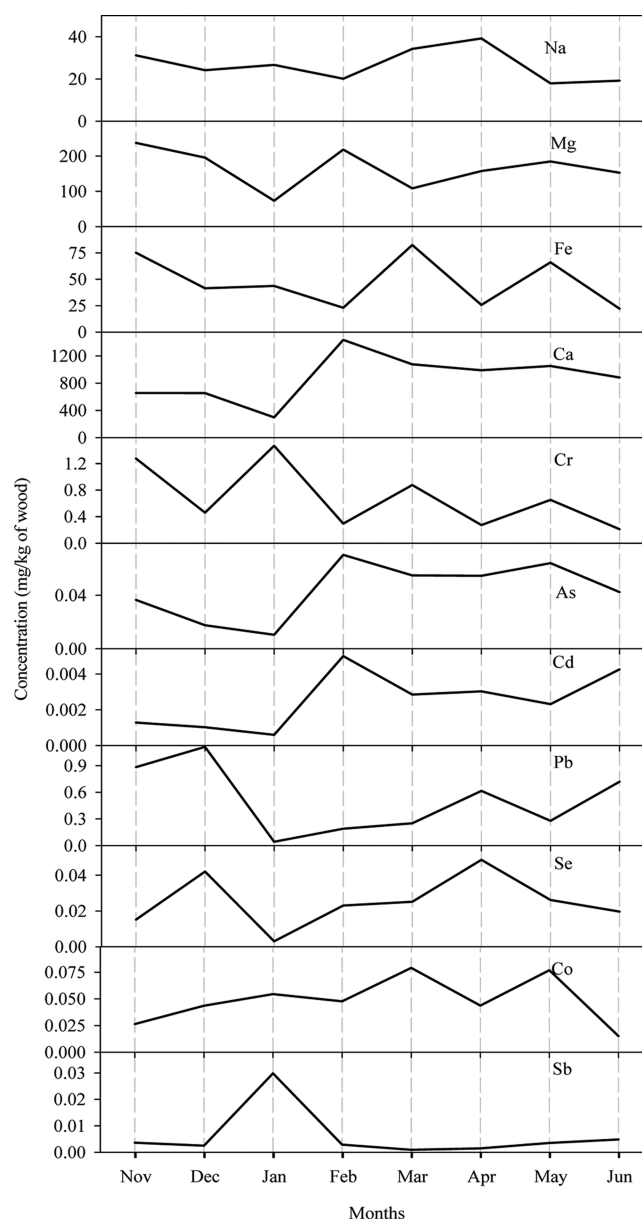


Figure 2. Variation in elemental concentration over time from manufacturer 1 on a dw basis.

contents are plotted in panels a (pellets) and b (chips) of Figure 1.

The presence of extraneous materials affected the pellet elemental composition. The elemental concentrations were analyzed in the ash and reported as mass per unit mass of ash. These values were then converted to the concentration in wood by multiplying with the ash mass obtained for the sample in grams. The elemental compositions of the wood pellets and wood chips are reported in Tables S3 and S4 of the Supporting Information. A total of 10% of the samples was subjected to duplicate analysis for QC purposes that also includes the sample preparation process. These results are summarized in Table S5 of the Supporting Information.

The distribution of the measured elemental concentrations in the wood pellets and chips are plotted in panels c and d of Figure 1, respectively. The mean, standard deviation, median, maximum, and minimum concentrations of the elements in the wood pellet and chip samples are summarized in Tables 2 and

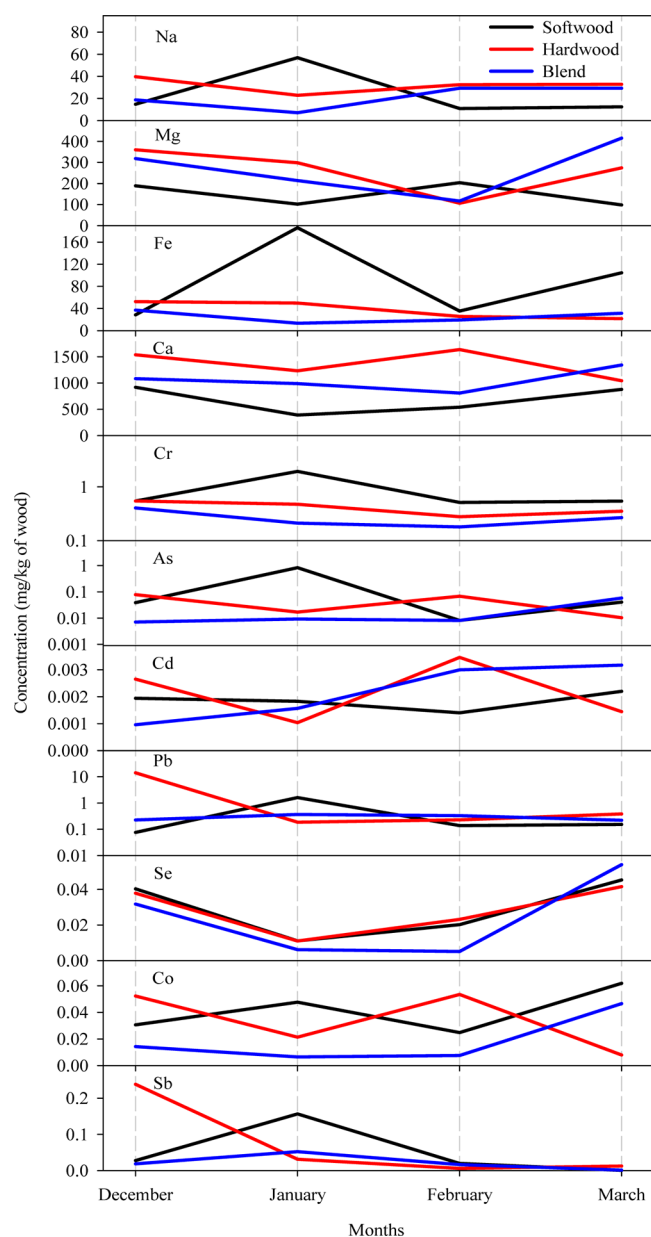


Figure 3. Variation in elemental concentration over time from manufacturer 2 on a dw basis.

3. There are substantial similarities to the distributions of elements between the pellets and chips. Large variations are observed in aluminum (Al) and iron (Fe) for the wood chips (Figure 1d). The major ash-forming elements in wood pellets and wood chips were identified to be Ca (45%), K (37%), and Mg (8%), expressed as percent dw of ash; other elements were Mn (4%), Fe (3%), Al (1%), and Na (1–2%). Some of the wood chip samples contained visible coarse sand particles, which lead to higher concentrations of Al and Fe. Generally, low vapor pressure compounds, alkali earth elements (Ca and Mg), alkaline earth oxides, phosphates, and silicates that are not volatilized easily remain in the bottom ash. Alkali chloride and sulfate and silicates are harmful to the combustion device because they cause fouling, slagging, and corrosion in the combustion appliances.²³ The reaction between the alkali elements, chloride, and sulfate depends upon the fuel composition and combustion conditions.^{5,23,24}

The concentrations of all other heavy elements, such as Cd, As, and Cr, were less than 0.1%. A few wood chip samples had elevated Cd and Cr concentrations. Those elements with relative standard deviations more than 100% likely represent wood that was adulterated by extraneous materials. Some heavy elements, such as arsenic, copper, and chromium, were found to be higher in some wood pellet samples. High concentrations of these heavy elements in wood pellets indicate the likely use of preservative-treated wood. There is a large variation for the elements Cu, Cr, and As in wood pellets (Table 2). It is possible that some scrap wood that was copper chromium arsenate (CCA)-treated might have been included. CCA treatment is used in a wide variety of applications, such as poles, piling, and retaining structures. There are few restrictions imposed by the U.S. EPA in using CCA for the treatment of residential timber. The information gathered from the manufacturers of the wood pellets suggested that some of them used recycled wood products, waste, and wood residues.

A subset of wood pellet samples (13 samples) was also analyzed for titanium (Ti). Four samples had higher Ti concentrations (up to 3000 ppm). The Ti contamination was likely from the inclusion of painted wood. High concentrations of lead in samples (see Table S3 of the Supporting Information) could be due to lead-based paint on old wood and/or the uptake of lead from lead arsenate pesticide contaminated soil.¹⁰

Cadmium concentrations have been found to be high in coniferous bark, pine, and willow.^{25,26} A few samples (both wood pellets and wood chips) that were very dark in color had higher cadmium concentrations, suggesting that they might include bark. Most of the high heavy-element concentrations were found in samples that were darker. In general, the heavy-element uptake in the bark is substantially higher than that in core wood.^{3,25} The concentration of mercury is lower in the ash than that in the wood itself. Mercury in wood is present mostly in organic form. It can be assumed that about 90% of mercury is lost to the atmosphere during the combustion process.²⁷

Wood pellet samples from two different manufacturers were acquired over a 6 month period to examine the variation in their properties over the season and between sample batches. Manufacturer M1 sent four samples each of hardwood, softwood, and blend (mixture of hardwood and softwood). Manufacturer M2 sent samples each month from November 2010 until June 2011. There were no observable trends in the elements over time from either manufacturer. However, the heavy-element concentration from softwood was higher than that in the hardwood from manufacturer M1 in all of the samples (Figure 2). The blend was hardwood and softwood in proportions that were not disclosed by the manufacturer. In general, the pure hardwood or the blends had lower heavy-element concentrations. There was little variation in elemental composition in pellets from manufacturer M2 over time (Figure 3). Pearson correlation coefficients were calculated to explore the time series correlations between the elements in the pellets from these two manufacturers. These results are presented in Tables S6 and S7 of the Supporting Information. There exist some significant correlations between elements, such as Al and Fe and Cr, Cu, and As. Given the low levels of these concentrations, the correlations are likely to be due to the use of wood harvested from similar locations, so that the wood composition reflects the tree species and location where the trees were grown.^{3,18}

■ CONCLUSION

Wood pellets were found to have higher variations in concentrations of heavy elements, such as Cu, Cr, As, and Pb, than wood chips, although the number of chip samples was substantially smaller than the number of pellet samples. In general, the element content of the wood samples was low. However, some samples were found to have unusually high concentrations of heavy elements. Although the wood pellet samples generally meet the quality standards presented in Table 1, there are some samples that would fail the ash content requirements. Only the German standards have extensive trace element limits. Most of the samples would meet these standards, but some samples would fail to meet these standards based on their arsenic, cadmium, and copper concentrations. It is likely that inclusion of extraneous materials, such as painted or pressure-treated lumber, led to the observed high concentrations.

Given the increasing use of pellets and chips as a renewable fuel, standards for the elemental composition of commercial wood pellets and chips are needed in the U.S. to avoid the inclusion of extraneous materials. Such standards would reduce the environmental impact of toxic species that would be released when the wood is burned.

■ ASSOCIATED CONTENT

● Supporting Information

Properties of wood pellet and chip samples (Tables S1–S7). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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