

Inorganic Composition and Environmental Impact of Biomass Feedstock

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ABSTRACT: Knowledge of the inorganic components of biomass feedstock is important for process control and for handling coproducts and wastes resulting from energy and fuel utilization of biomass. Analytical survey of forestry thinnings (wood chips), agricultural residues (rice straw, wheat straw, corn stover), and dedicated perennial grass crops (switchgrass, wheatgrass, and miscanthus) shows that, potentially, the whole periodic table may be present in biomass. The main effect of ashing is bonding of oxygen in the ash mainly as silicate, oxides, hydroxides, phosphates, and carbonate residual minerals. Carbon is partially retained as carbonates and graphite (char). Nitrogen is dominantly released to the flue gas, while sulfur is mostly retained in the ash as sulfates. Small losses (~19%) for both sulfur and chlorine were detected during ashing at 575 °C. The majority of the alkali metals (Li, Na, K, and Rb) will substantially modify soil if applied as a fertilizer. Only Mg, Ca, and Sr of the alkali earth metals, Mn, Cu, and Zn of the period 4 transition metals, and Mo and Cd of the period 5 transition metals may exceed regulatory limits if used as a fertilizer. The heavy elements occur in concentrations too low to cause concern with the exception of Se. The high alkali content of some biomass ash thus makes them good candidates for use as fertilizers provided that they are applied in low proportions (<50%) to soil. Ash of wood material is a carrier of many of the alkali elements (Li, K, Rb, Mg, Ca, Sr, Ba) and some transition elements (Mn, Cu, Zn, Mo, Ag, Cd). In contrast, ash of herbaceous plant material is in addition to K only variably enriched: Li, Na, Se, and Mo in wheatgrass, Mg, and Ca in switchgrass, Mg, Ca, and Cd in corn stover, Mn in rice straw, Mo in wheat straw, and Mn and Cd in miscanthus. Water leaching results in significant losses for anionic chlorine and sulfur as well as for most of the alkali metals, thus making resulting ash from such treated feedstock less attractive as K fertilizers although fuel properties are enhanced for thermal conversion.

1. INTRODUCTION

Process quality control and environmental monitoring of combustion and gasification reactors for energy and fuel synthesis require knowledge of metals and other inorganic components in high temperature process streams as well as in co- and waste products. Since inorganic components may constitute over 20% of some potential feedstock materials (as ash on a dry weight basis), knowledge of their composition and behavior are thus critical for successful applications.^{1,2} Thermal treatments are integral procedures for many fuel and energy applications of biomass,^{3–5} for coproduct development and waste reduction and control, as well as for many analytical procedures used to characterize inorganic products.⁶ The inorganic products are typically left as part of a residue after thermal or biochemical deconstruction. Following combustion, the residual inorganic ash or slag components are, depending on temperature, variously composed of silicates, carbonates, halides, phosphates, sulfates, oxides, hydroxides, as well as other hydrated components, either amorphous or crystalline, and often together with minor char.^{7–11} The entire periodic table may in fact potentially appear in major to trace concentrations in such residual ash and slag components^{11–16} with the result that the products may be highly detrimental to process streams and toxic to the workforce, environment, and livestock. The residual inorganic components thus need to be known, controlled, treated, utilized, or eventually safely disposed of as waste, if not recovered for economic value and use.^{10,17}

As part of a broad feasibility study of feedstock for syngas generation, we here characterize the inorganic components in some potential and common agricultural, forestry, and energy crop sources in California. We use the results to evaluate potential shortcomings or benefits for thermochemical processing and environmental control. The effects of batch water leaching are also briefly examined, although more detailed results from this type of processing are presented in an accompanying study.¹⁸

2. FEEDSTOCK SELECTION

Feedstock selection for this study was focused on appropriate materials readily available in California and other feedstock types such as purpose-grown crops and agricultural wastes with potential for large-scale utilization. Some of the selected feedstock materials (wood chips and rice and wheat straw) are already well-characterized.^{11,15,19} A 2007 assessment of biomass in California estimated that 29 million dry metric ton per year would be available on a sustainable basis,²⁰ nearly equally distributed among agricultural residues (26%), forest residues and thinnings (44%), and municipal wastes (30%). Growth of dedicated energy crops was in 2007 of minor importance but was estimated to rise to about 10% in 2020.²⁰

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Table 1. Quality Control of Feedstock Ash Compositions

analyte symbol	anal. method	unit symbol	detection limit	blank	standards		rice straw ash (Thy et al., 2008)				upper continental crust ^a	NIST 2709 San Joaquin soil
					meas.	certified	date	date	date	date		
SiO ₂	XRF ^b	% ^c	0.01	<0.01 ^d	47.95	49.20	69.02	68.42	67.58	68.34	0.72	63.45
TiO ₂	XRF	%	0.01	<0.01	1.26	1.32	0.02	0.02	0.03	0.02	0.01	0.57
Al ₂ O ₃	XRF	%	0.01	<0.01	27.67	28.40	0.42	0.31	0.37	0.37	0.06	14.17
Fe ₂ O ₃ ^{g,f}	XRF	%	0.01	<0.01	10.96	11.10	0.2	0.18	0.19	0.19	0.01	5.00
MnO	XRF	%	0.001	<0.001	0.017	0.020	0.324	0.295	0.312	0.310	0.015	0.069
MgO	XRF	%	0.01	<0.01	0.76	0.80	1.74	1.69	1.61	1.68	0.07	2.50
CaO	XRF	%	0.01	<0.01	2.11	2.11	1.84	1.74	1.74	1.77	0.06	2.64
Na ₂ O	XRF	%	0.01	<0.01	0.26	0.27	3.39	3.06	3.23	3.23	0.17	1.56
K ₂ O	XRF	%	0.01	<0.01	2.27	2.35	8.25	8.80	8.27	8.44	0.31	2.45
P ₂ O ₅	XRF	%	0.01	<0.01	0.55	0.53	11.37	13.36	13.47	12.73	1.18	0.14
LOI ^g	XRF	%	0.01	<0.01			97.9	99.22	98.07	98.38		
total												
Cl	INAA ^h	%	0.01	<0.01	3.03	3.10	1.94	2.10	1.96	2.00	0.09	0.04
Li	ICPMS ⁱ	ppm ^k	0.5	<0.5			1.7	1.3	1.2	1.4	0.3	2.1
Be	ICPMS	ppm	0.005	<0.005	0.63	0.46	0.03	<0.005	<0.005	2.1	2.1	2.94
B	ICPMS	ppm	5	<5	50	70	<5	16	25	21	17	12.4
Sc	ICPMS	ppm	0.5	<2		0.6	<0.5	0.9	<0.5		14	
Ti	ICPMS	ppm	1	<0.2	125	122	22	37	24	28	8	3836
V	ICPMS	ppm	1	<0.01	4	4	2	2	2	2	0	112
Cr	ICPMS	ppm	1	<0.1	2	3	4	4	4	4	0	130
Mn	ICPMS	ppm	0.1	<0.5	35.1	37.5	2040	1650	1850	1847	195	538
Co	ICPMS	ppm	0.01	<1	0.71	0.67	1.63	1.80	2.17	1.87	0.28	13.4
Ni	ICPMS	ppm	5	<1			5	<5	5	5	0.0	88
Cu	ICPMS	ppm	0.2	<0.1	4.3	3.8	8.2	8.4	8.8	8.5	0.3	34.6
Zn	ICPMS	ppm	1	<0.01	4.3	5.0	83	87	94	88	6	106
Ga	ICPMS	ppm	0.1	<0.01	1.0	0.9	0.2	0.4	0.3	0.3	0.1	14
Ge	ICPMS	ppm	0.1	<5		0.1	<0.1	<0.1	<0.1		1.4	
As	ICPMS	ppm	1	<0.2		1.0	5	5	5	5	0	17.7
Se	ICPMS	ppm	1	<1		1.0	<1	<1	<1		0.09	1.57
Rb	ICPMS	ppm	0.01	<0.1	0.28	0.34	190	184	216	197	17	96
Sr	ICPMS	ppm	0.1	<0.1	122	128	62	64	69	65	4	231
Y	ICPMS	ppm	0.001	<1	2.04	1.98	0.19	0.20	<0.001	0.20	21	18
Zr	ICPMS	ppm	0.5	<1	1.6	3.1	<0.5	<0.5	<0.5		193	160
Nb	ICPMS	ppm	0.005	<0.01	0.441	0.418	<0.005	<0.005	<0.005		12	
Mo	ICPMS	ppm	0.1	<0.01	0.2	0.2	2.9	2.5	2.4	2.6	0.26	2
Ag	ICPMS	ppm	0.2	<0.001		0.1	<0.2	<0.2	<0.2		0.05	0.41
Cd	ICPMS	ppm	0.01	<0.5	0.08	0.04	0.04	<0.01	0.10	0.07	0.09	0.38
In	ICPMS	ppb ^j	1	<0.005	7	7	<1	<1	<1		0.056	
Sb	ICPMS	ppm	0.02	<0.1		0.05	<0.02	<0.02	<0.02		0.4	7.9
Te	ICPMS	ppm	0.01	<0.2	0.07	0.05	0.03	<0.01	0.07	0.05	0.05	
Cs	ICPMS	ppm	0.001	<0.01		0.04	0.11	0.10	0.10	0.10	0.01	5.3

Table 1. continued

analyte symbol	anal. method	unit symbol	detection limit	blank	standards		rice straw ash (Thy et al., 2008)				upper continental crust ^a	NIST 2709 San Joaquin soil	
					meas.	certified	date	date	date	date			avg. N = 3
Ba	ICPMS	ppm	3	<1	317	330	40	42	43	43	42	624	968
La	ICPMS	ppm	0.002	<0.02	2.1	2.0	0.2	0.2	<0.002	<0.002	0.2	31	23
Ce	ICPMS	ppm	0.01	0.02	4.0	3.9	0.4	0.4	<0.01	<0.01	0.4	63	42
Pr	ICPMS	ppm	0.002	0.002	0.48	0.44	0.1	0.1	<0.002	<0.002	0.1	7.1	4.4
Nd	ICPMS	ppm	0.002	<3	1.8	1.6	0.2	0.2	<0.002	<0.002	0.2	27	19
Sm	ICPMS	ppm	0.001	<0.002	0.351	0.351	0.0	0.1	<0.001	<0.001	0.1	4.7	1.2
Eu	ICPMS	ppm	0.001	<0.01	0.082	0.066	0.012	<0.001	<0.001	<0.001	0.1	1.0	0.9
Gd	ICPMS	ppm	0.01	<0.002	0.37	0.34	0.05	0.10	<0.01	<0.01	0.08	4.0	
Tb	ICPMS	ppm	0.001	<0.002	0.076	0.051	0.008	<0.001	<0.001	<0.001		0.7	
Dy	ICPMS	ppm	0.001	<0.001	0.294	0.278	0.033	<0.001	<0.001	<0.001		3.9	3.5
Ho	ICPMS	ppm	0.001	<0.001	0.079	0.054	0.007	<0.001	<0.001	<0.001		0.83	0.54
Er	ICPMS	ppm	0.001	<0.01	0.184	0.159	0.018	<0.001	<0.001	<0.001		2.3	1.82
Tm	ICPMS	ppm	0.001	<0.001	0.021	0.003	0.003	<0.001	<0.001	<0.001		0.3	
Yb	ICPMS	ppm	0.001	<0.001	0.177	0.146	0.017	<0.001	<0.001	<0.001		2.0	1.6
Lu	ICPMS	ppm	0.001	<0.001	0.03	0.03	0.002	<0.001	<0.001	<0.001		0.31	0.23
Hf	ICPMS	ppm	0.01	<0.001	0.09	0.10	<0.01	<0.01	<0.01	<0.01		5.3	3.7
Ta	ICPMS	ppm	0.001	<0.001	0.023	0.023	<0.001	<0.001	<0.001	<0.001		0.9	
W	ICPMS	ppm	0.5	<0.001			<0.5	<0.5	<0.5	<0.5		1.9	2
Re	ICPMS	ppb	0.1	<0.001			0.6	0.5	<0.1	<0.1	0.6		
Tl	ICPMS	ppm	0.001	<0.01	0.08	0.06	0.004	<0.001	<0.001	<0.001		0.9	0.74
Pb	ICPMS	ppm	0.1	<0.001	2.1	2.1	0.2	0.3	<0.1	<0.1	0.3	17	18.9
Bi	ICPMS	ppm	0.05	<0.5	0.04	0.04	<0.05	<0.05	0.20	0.20		0.16	
Th	ICPMS	ppm	0.001	<0.1	0.754	0.56	0.07	0.20	<0.001	<0.001	0.14	10.5	11
U	ICPMS	ppm	0.001	<0.001	0.295	0.29	0.03	<0.001	<0.001	<0.001		2.7	3

^aUpper continental crust is average composition estimated by Rudnick and Gao. ³¹XRF: X-ray fluorescence. ⁶%; percentage on a oxide weight basis, except Cl on an atomic basis. ^d<: below detection limit. ⁶NIST 1633b: NIST certified standard Trace Elements in Coal Fly Ash. ⁷Fe₂O₃*: total iron as Fe₂O₃. ⁸LOI: loss on ignition at 950 °C. ⁹INAA: instrumental neutron activation analysis. ¹⁰MAG-1: USGS recommended values for standard Marine Sediment. ¹¹ICPMS: induced coupled plasma mass spectrometry. ¹²ppm: parts per million weight basis. ¹³ppb: parts per billion weight basis. ¹⁴Coal Ash-2: internal ActLab coal ash standard.

Table 2. Feedstock Compositions (on 105 °C Dry Basis, Except Moisture Content on an Air Dried Basis)

	Douglas fir		rice straw		wheat straw		Jose tall wheat grass		corn stover		switchgrass		miscanthus	
	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached
Proximate and Ultimate Compositions														
moisture content wt %	9.2	^a	8.0		9.0		11.1		7.7		8.9		7.3	
ash content wt % (575 °C)	0.20	0.12	18.5	18.3	8.3	6.3	8.5	4.5	8.4	4.0	5.9	4.5	8.3	5.1
volatile matter wt %	83.8	85.0	66.3	70.0	74.0	80.3	74.3	80.2	74.1	81.4	77.2	80.4	78.1	82.5
fixed carbon wt %	16.0	14.9	15.2	11.7	17.7	13.4	17.2	15.3	17.4	14.6	16.9	15.1	13.6	12.4
leaching mass loss wt %		1.7		10.8		9.9		20.9		17.0		8.4		3.1
C wt %	50.0	49.9	38.8	39.7	43.5	44.9	44.8	46.4	43.5	45.8	45.5	46.0	45.0	45.7
H wt %	6.1	6.0	5.2	5.2	5.7	5.7	5.9	6.0	5.7	5.8	5.9	5.9	5.8	5.9
N wt %	0.44	0.20	1.04	0.70	0.47	0.32	0.65	0.71	0.62	0.33	1.09	0.16	0.14	0.06
S wt %			0.07	0.04	0.11		0.23	0.06	0.05	0.03	0.06	0.03	0.03	0.01
O wt % ^b	43.3	43.8	36.4	36.1	41.9	42.8	39.9	42.3	41.7	44.0	41.6	43.4	40.7	43.2
Cl wt %	<0.01 ^c		0.46		0.85		1.73		0.78		0.21		0.02	
Volatile Compositions of Ash (wt %) ^d														
C wt %	6.28	7.04	2.12	1.97	2.27	2.25	1.98	1.96	1.90	1.32	1.10	1.24	1.26	1.36
H wt %	0.33	0.69	0.36	0.27	0.29	0.25	0.15	0.10	0.90	0.34	0.05	0.07	0.21	0.36
N wt %			0.61	0.37	0.50	0.35	0.58	0.49						
S wt %	1.14		0.24	0.19	0.73	0.57	2.24		0.43	0.69	0.89	0.69	0.34	0.29
Cl wt %	0.15	0.08	1.94		7.72		16.80	1.74	6.58	1.95	2.09	0.27	0.06	0.02
Major and Minor Oxide Composition of Ash														
SiO ₂	4.32	4.08	69.02	85.43	46.32	79.23	35.6	71.53	39.12	60.64	53.28	76.63	75.58	78.45
TiO ₂	0.16	0.12	0.02	0.04	0.04	0.05	0.08	0.07	0.24	0.20	0.08	0.04	0.48	0.31
Al ₂ O ₃	2.12	1.52	0.42	0.38	0.08	0.56	0.28	1.10	4.68	2.88	0.68	0.32	6.03	3.55
Fe ₂ O ₃ ^{**e}	2.44	2.72	0.20	0.26	0.24	0.28	0.48	0.48	2.27	1.76	0.60	0.36	2.20	1.45
MnO	1.130	1.260	0.320	0.220	0.050	0.030	0.100	0.100	0.125	0.120	0.084	0.095	0.286	0.345
MgO	5.52	5.88	1.74	0.72	2.56	1.58	1.84	1.42	6.15	4.48	6.96	6.49	1.35	1.19
CaO	28.40	32.92	1.84	2.16	1.96	2.10	4.48	4.76	3.95	4.36	4.08	5.66	2.73	3.78
Na ₂ O	1.68	1.40	3.39	1.55	3.12	1.72	20.12	6.47	1.37	1.00	0.84	1.11	0.73	0.55
K ₂ O	11.36	6.00	8.25	1.99	25.12	5.85	11.72	4.21	12.44	13.08	16.00	5.07	3.63	1.87
P ₂ O ₅	6.44	4.64	1.28	0.49	0.64	0.28	1.64	1.41	2.04	1.44	2.20	1.23	1.00	0.62
LOI ^f	24.36	25.66	11.37	5.82	7.75	6.67	2.49	5.57	24.65	4.80	9.81	2.79	3.93	6.68
total	87.93	86.20	97.85	99.06	87.88	98.35	78.83	97.12	97.05	94.80	94.65	99.82	97.95	98.83
Elemental Ash Compositions (wt %)														
Si	2.02	1.91	32.26	39.93	21.65	37.04	16.64	33.44	18.29	28.35	24.91	35.82	35.33	36.67
Ti	0.10	0.07	0.01	0.02	0.02	0.03	0.05	0.04	0.14	0.12	0.05	0.02	0.29	0.19
Al	1.12	0.80	0.22	0.20	0.04	0.30	0.15	0.58	2.48	1.52	0.36	0.17	3.19	1.88
Fe	1.71	1.90	0.14	0.18	0.17	0.20	0.34	0.34	1.59	1.23	0.42	0.25	1.54	1.01
Mn	0.88	0.98	0.25	0.17	0.04	0.02	0.08	0.08	0.10	0.09	0.07	0.07	0.22	0.27
Mg	3.33	3.55	1.05	0.43	1.54	0.95	1.11	0.86	3.71	2.70	4.20	3.91	0.81	0.72
Ca	20.30	23.53	1.32	1.54	1.40	1.50	3.20	3.40	2.82	3.12	2.92	4.05	1.95	2.70
Na	1.25	1.04	2.51	1.15	2.31	1.28	14.93	4.80	1.02	0.74	0.62	0.82	0.54	0.41
K	9.43	4.98	6.85	1.65	20.85	4.86	9.73	3.49	10.33	10.86	13.28	4.21	3.01	1.55

Table 2. continued

	Douglas fir		rice straw		wheat straw		Jose tall wheat grass		corn stover		switchgrass		miscanthus	
	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached
P	2.81	2.02	0.56	0.21	0.28	0.12	0.72	0.62	0.89	0.63	0.96	0.54	0.44	0.27
C (as C)			1.79	1.97	1.15	2.23	1.98	1.37	0.26	1.32		1.24	1.15	1.36
C (as CO ₂)	6.28	7.04	0.33		1.12	0.02		0.59	1.64		1.10		0.11	
H	0.33	0.69	0.36	0.27	0.29	0.25	0.15	0.10	0.90	0.34	0.05	0.07	0.21	0.36
N			0.61	0.37	0.50	0.35	0.58	0.49						
S	1.14		0.24		0.73		2.24		0.43	0.69	0.89	0.69	0.34	0.29
Cl	0.15	0.08	1.94	0.19	7.72	0.57	16.80	1.74	6.58	1.95	2.09	0.27	0.06	0.02
O	44.28	49.47	49.56	53.04	40.17	50.29	33.01	48.07	48.84	50.11	41.61	49.22	50.80	52.59
total	95.11	98.06	100.00	101.34	100.00	100.00	101.69	100.00	100.00	103.77	93.52	101.36	100.00	100.29
Trace Elements (ppm)														
Li	52	205	1.7	0.8	9	12	95	32	32	28	19	14	6	7
Be	0.11	0.19	0.03	0.03	0.05	0.03	0.08	0.06	0.18	0.23	0.09	0.07	0.53	0.30
B	636	1380	<5	<5	61	<5	2160	750	70	55	21	26	<5	<5
Sc	2.3	3.3	<0.5	<0.5	<0.5	0.6	0.8	0.8	3.8	3.2	1.0	0.8	3.0	2.0
Ti	208	310	22	15	21	20	65	71	158	144	58	27	160	89
V	10	14	2	1	2	2	4	6	26	22	6	3	24	16
Cr	74	216	4	4	18	31	10	26	39	43	12	12	19	39
Mn	7730	10400	2040	1150	252	176	442	456	880	766	489	515	2020	2400
Co	9.8	76	1.6	1.7	0.8	2.3	1.3	3.1	9.4	6.3	4.2	2.3	8.3	8.2
Ni	41	135	5	<5	10	10	20	16	50	41	33	16	15	25
Cu	301	2030	8	5	16	9	21	18	57	41	31	17	21	31
Zn	1900	3070	83	51	78	73	82	118	321	475	147	175	181	234
Ga	1.3	1.8	0.2	0.2	0.2	0.2	0.6	0.7	3.0	2.4	0.6	0.3	3.2	1.9
Ge	0.2	0.3	<0.1	<0.1	<0.1	<0.1	0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
As	31	18	5	2	<1	1	<1	3	3	2	<1	<1	5	4
Se	7	11	<1	<1	<1	<1	6	15	<1	<1	<1	<1	<1	<1
Rb	225	123	190	48	149	35	33	16	51	33	65	21	29	16
Sr	1690	2170	62	81	214	225	238	236	367	422	219	283	56	74
Y	8.6	9.0	0.19	0.20	0.19	0.23	0.57	0.72	3.5	3.2	0.73	0.44	5.9	5.0
Zr	<0.5	1.7	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.7	<0.5	<0.5	2.4	2.5
Nb	0.09	0.07	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.27	0.06
Mo	9	16	2.9	1.2	8	5.1	33	33	2.6	4.3	1.9	1.8	1.2	2.3
Ag	6	8	<0.2	<0.2	<0.2	<0.2	0.3	0.4	0.4	0.4	<0.2	<0.2	<0.2	<0.2
Cd	67	57	0.04	0.11	0.33	0.27	0.33	0.4	0.79	0.58	0.08	0.07	1.9	2.6
In ppb	15	21	<1	1	<1	<1	2	6	12	10	3	2	15	10
Sb	1.3	0.82	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Te	0.07	0.07	0.03	0.05	<0.01	0.03	0.05	<0.01	0.06	0.06	0.01	<0.01	0.08	0.14
Cs	0.57	0.40	0.11	0.06	0.22	0.09	0.26	0.27	0.72	0.58	0.24	0.11	0.87	0.51
Ba	946	379	40	49	424	725	19	25	236	288	132	142	291	383
La	11.7	12.8	0.227	0.222	0.200	0.295	0.771	1.08	3.80	3.53	0.821	0.418	11.6	8.5
Ce	10.9	12.0	0.44	0.45	0.41	0.57	1.55	2.19	7.97	7.60	1.70	0.90	24.5	18.2

Table 2. continued

	Douglas fir		rice straw		wheat straw		Jose tall wheat grass		corn stover		switchgrass		miscanthus	
	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached
	Trace Elements (ppm)													
Pr	2.53	2.84	0.052	0.056	0.051	0.071	0.180	0.249	0.987	0.905	0.211	0.114	2.73	2.08
Nd	9.2	10.3	0.203	0.223	0.192	0.264	0.649	0.926	3.94	3.67	0.872	0.445	10.00	7.78
Sm	2.1	2.3	0.047	0.053	0.044	0.058	0.146	0.192	0.924	0.819	0.191	0.114	2.00	1.55
Eu	0.56	0.71	0.012	0.011	<0.001	<0.001	0.031	0.041	0.23	0.20	0.039	0.022	0.41	0.31
Gd	2.1	2.6	0.05	0.04	0.04	0.06	0.13	0.18	0.85	0.79	0.18	0.11	1.67	1.34
Tb	0.312	0.359	0.008	0.007	0.006	0.008	0.020	0.024	0.125	0.110	0.027	0.014	0.232	0.188
Dy	1.60	1.81	0.033	0.040	0.031	0.041	0.105	0.135	0.667	0.609	0.142	0.081	1.19	0.93
Ho	0.288	0.324	0.007	0.006	0.006	0.008	0.019	0.025	0.124	0.109	0.025	0.015	0.210	0.166
Er	0.748	0.879	0.018	0.021	0.018	0.021	0.05	0.07	0.322	0.286	0.063	0.041	0.570	0.449
Tm	0.091	0.104	0.003	0.002	0.002	0.003	0.007	0.009	0.040	0.034	0.008	0.005	0.074	0.060
Yb	0.595	0.692	0.017	0.013	0.016	0.015	0.050	0.056	0.255	0.230	0.047	0.028	0.474	0.374
Lu	0.084	0.094	0.002	0.002	0.002	0.002	0.006	0.009	0.034	0.031	0.007	0.004	0.065	0.052
Hf	0.05	0.09	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.05	0.07	0.01	<0.01	0.11	0.09
Ta	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
W	1.9	10.5	<0.5	0.8	<0.5	1.0	<0.5	1.6	<0.5	1.6	<0.5	1.2	<0.5	0.5
Re ppb	9.5	4.7	0.6	<0.1	2.7	0.7	1400	415	5.9	2.4	0.9	<0.1	0.3	<0.1
Tl	0.030	0.048	0.004	0.008	0.003	0.005	0.008	0.017	0.056	0.027	0.007	0.003	0.214	0.126
Pb	26	60	0.2	0.5	0.4	0.6	1.0	1.4	6.8	5.2	4.8	2.1	20	20
Bi	0.05	0.12	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.08	<0.05	<0.05	0.10	0.09
Th	0.286	0.273	0.072	0.063	0.058	0.071	0.389	0.511	0.901	0.714	0.219	0.099	2.86	1.77
U	0.109	0.159	0.029	0.032	0.299	0.469	0.753	1.44	0.155	0.143	0.051	0.036	0.753	0.529
trace total wt % (2) ^g	1.40	2.08	0.25	0.14	0.13	0.13	0.32	0.11	0.22	0.23	0.13	0.13	0.29	0.34

^a empty; not analyzed or detected. ^b Calculated by balance to 100%. ^c below detection limit. ^d %; for ash composition always as percentage on an oxide weight basis, except Cl on an atomic basis. ^e Fe₂O₃; total iron as Fe₂O₃. ^f LOI: loss on ignition at 950 °C in air. ^g (2): The total of the trace elements plus Mn and Ti.

In this study, we will discuss forestry thinnings (wood chips), agricultural residues (rice straw, wheat straw, corn stover), and dedicated perennial grass crops (switchgrass, wheatgrass, and miscanthus). Brief descriptions of the examined feedstock are given below.

2.1. Wood Chips (w). Clean Douglas fir wood chips (*Pseudotsuga menziesii*) were obtained from Mallard Creek Inc., Rocklin, California, in November 2008 from trees harvested on the western slopes of the Sierra Nevada between Chico and Grass Valley, California. The trees were debarked and delimited prior to chipping.

2.2. Rice Straw (r). Rice straw (*Oryza sativa* variety M206) was harvested and collected from the Natomas region north of Sacramento, California, in October 2008.

2.3. Wheat Straw (wh). Bales of Yolo County wheat (*Triticum* spp.) straw were obtained from Windmill Feed, Woodland, California, in October 2008 and stored outside elevated under cover prior to sampling.

2.4. Corn Stover (c). Bales of corn (*Zea mays*) stover were obtained from Broken Box Ranch, Williams, California, in February 2009 from corn grown at Colusa, California, and harvested in early October 2008.

2.5. Switchgrass (s). Bales of switchgrass (*Panicum virgatum*) were provided by U.C. Davis Cooperative Extension, Davis, California, from plots in Davis harvested in July 2008 and June 2009.

2.6. Wheatgrass (j). Jose tall wheatgrass (*Agropyron elongatum*), a saline irrigated crop from the San Joaquin Valley, was harvested and baled at Red Rock Ranch, Five Points, California in October 2008.

2.7. Miscanthus (m). Bales of *Miscanthus x giganteus* were supplied by Mendel Biotechnology Inc. (Hayward, California). Miscanthus was harvested by Idaho National Laboratory at the University of Illinois "SoyFACE" farm, Savoy, Illinois, in January 2008.

3. METHODS

3.1. Treatment and Preparation. The biomass materials discussed in this study were collected for a laboratory-scale gasification study that required a total amount of 100 to 800 kg per type of feedstock. The majority of feedstock was obtained as air-dried field bales (wheat straw, wheatgrass, miscanthus, and corn stover) each of a total of about 800 kg. The remaining materials were obtained fresh in the field in batches of 100–250 kg (rice straw, wood chips, switchgrass) and were air-dried in the laboratory. The air-dried rice straw, corn stover, switchgrass, wheatgrass, wood chips, and miscanthus were stored indoor as bales or in open plastic bags. Bales of wheat straw were stored outdoors under cover and elevated above the ground.

The characterization of each feedstock was performed on secondary samples from 20 to 100 kg randomly selected from individual bales and bags or, in one case (switchgrass), representing the entirety of the primary sample as obtained. Representative samples of each feedstock were first hammer-milled through a 25-mm square-hole screen. About two-thirds of each feedstock was further knife-milled through a 2-mm screen (Pulverisette 19, Fritsch, Germany). These milled samples were stored dry at room temperature in airtight plastic bags for 20 to 30 days before leaching experiments were performed. The leaching procedure used 20 g of air-dried, 2-mm milled powders that were batch-leached with deionized water in a 500 mL beaker at room temperature using a 1/20 dry kg/L ratio.¹⁸ The mass loss during leaching was reported on a dry basis. About 200 g each of the air-dried, 2-mm-sized materials (untreated or leached) were milled to pass a 40-mesh sieve (<0.4 mm) using a Wiley Mill (A.H. Thomas Co., Philadelphia, PA). These powders were dried at 105 °C to determine

moisture content (ASTM D4442²¹) and were stored in airtight plastic bags for subsequent characterization.

3.2. Analytical Methods. The compositional and chemical characterizations are reported on a dry basis, unless otherwise specified. The ash content was determined by ignition at 575 °C for 3 h of oven-dried samples in an air-muffle furnace (Fisher Model 750-58, Fisher Scientific, Pittsburgh, PA) (ASTM E1755²²). Volatile matter was determined in covered crucibles to 950 °C in accordance with ASTM D3175²³ and fixed-carbon calculated as the difference of ash and volatile matter from 100% total.

The ultimate compositions (C, H, N, S) were determined with infrared spectroscopy or thermal conductivity cells (ASTM D5373²⁴) by heating to 950 °C using a LECO TrueSpec CHN elemental analyzer and infrared spectroscopy to 1300 °C (ASTM D4239²⁵) using a LECO TruSpec Sulfur add-on module (LECO, St. Joseph, Michigan). The relative standard deviation (% RSD) is typically 0.5–1%, and the lower limits of detection are 5–100 ppm. The oxygen content is calculated by difference to 100% assuming that the inorganic content is equivalent to the ash content. The chlorine contents were determined on both the feedstock and the ash by nondestructive, short duration irradiation, instrumental neutron activation analysis (INAA).

The effect of temperature on ashing content was investigated using a Diamond TA/DTA analyzer (PerkinElmer, Waltham, MA) calibrated against the melting of indium and gold. Open alumina containers, 20–50 mg of powder with a grain-size below 40 mesh for the raw feedstock, ramping temperature of 10 °C/min, and gas flow rate of 200 mL/min were used with air as the purge gas. Both the untreated feedstock and the corresponding ashes were studied.

The compositions of the ash after burning at 575 °C were determined using X-ray fluorescence (XRF) for the major and minor elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P).^{26,27} The ashes were heated to 950 °C to determine the loss-on-ignition (LOI) and were subsequently used for the XRF analyses. The analytical results were calibrated using a collection of certified standards similarly prepared and ideally similar in the compositional range and material structure to the unknown samples.²⁸ To eliminate matrix effects, both unknowns and standards were melted with a flux at about 950 °C and quenched to a glass tablet on which the analyses were performed. The total of the oxides and the LOI may ideally sum to 100%. The residual volatile components (C, H, N, S, Cl) of the ashes were analyzed as for the untreated and leached feedstock. The trace elements were determined using inductively coupled plasma mass-spectrometry (ICPMS),^{29,30} based on an acid solution technique using the 575 °C ashes.

Quality control measures for the analytical inorganic results are summarized in Table 1. The accuracy is evaluated by analyzing well-known or certified standards as unknowns. The standards used are NIST 1633b (fly ash from a coal fired power plant) for the major and minor elements, USGS MAG2 (marine sediment) for chlorine, and an internal laboratory coal ash standard (Actlab Coal Ash-2) for all trace elements (see Table 1). The precision has been evaluated by triplicate analyses of an ash of rice straw that was analyzed together with the ashes in this study and previous studies.¹⁵ The results for the major and trace elements are given as weight % oxides with a typical detection limit of 0.01 wt % and an uncertainty of 0.7–0.01 wt % (1 σ). The result for chloride is given on an elemental weight basis with a detection limit of 0.01% and an uncertainty of 0.1% (1 σ). The results for the trace elements are mostly given as parts per million (ppm) on a weight basis with detection limits of 1–0.001 ppm and uncertainties often below 10–0.01 ppm (1 σ) or 30–2% RSD. The results for In and Re are given as parts per billion mass (ppb).

3.3. Data Reduction and Presentation. The analytical results are summarized in Table 2. The ash compositions are reported on either an elemental basis for the volatile elements or as conventional oxides, all as weight %. The selection of oxides is reasonable considering that the ash was produced in an environment of excess air. The volatile elements as well as the LOI were determined on the 575 °C ash powder by heating to 950 °C and thus record the 575 °C ash composition. The chlorine was determined using nondestructive INAA methods on the untreated ash powder. Sulfur was analyzed by heating the ash powder to 1300 °C but is known to be partially retained in the

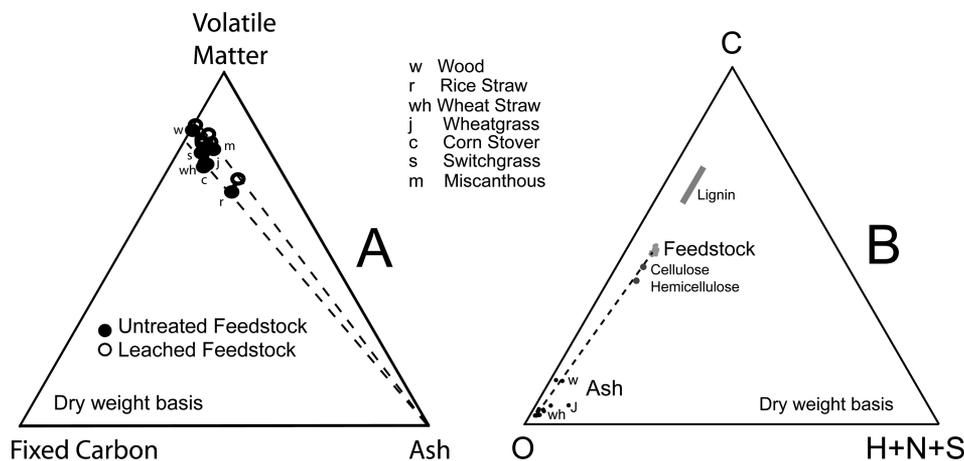


Figure 1. Summary of proximate and ultimate compositions on triangular diagrams. (A) The proximate feedstock compositions showing the fixed carbon/volatile matter/ash ratio. (B) The ultimate O–C–[H+N+S] compositions of untreated and leached raw feedstock and corresponding ashes. Comparisons are cellulose, hemicellulose (xylose), and lignin. Plotting the data on an atomic basis will only shift the variation toward higher hydrogen.

solid as sulfates at typical 575 °C ashing temperatures or at higher temperatures as sulfate melts.³² Thus, both Cl and S also record the 575 °C ash composition. The trace elements were determined on the 575 °C ashes. The major and minor oxides were in contrast determined on ash powder heated to 950 °C and thus could reflect unquantified elemental releases between the 575 °C ashing and the 950 °C reashing temperatures. This is particularly a concern for the alkali metals (K, Na, Rb, Cs), which are known to be partially lost during reheating of ash.^{6,11,15,19} This issue is from a mass balance point of view further complicated by the possibility of release of, specifically, Cl and K at temperatures well below typical ashing temperatures of 500–600 °C.^{6,32–35} It must thus be taken into account that the various parts of a typical ash analysis record the compositions of two different ashes (575 and 950 °C) with different loss patterns and that restoring ash compositions to raw feedstock compositions may underestimate specifically the alkali metals and halogen elements. An artifact of this is that chemical ash analyses may not always sum to an ideal 100%, due to elemental losses and mismatch between the two ashing temperatures.

The original ash compositions in Table 2 have been reduced to elemental compositions (on a weight basis), and oxygen is estimated based on simple assumptions of metal–oxygen bonding. Because the volatile elements (C, N, H, S, Cl) are given on an elemental basis, assumptions about their structural bonding to oxygen are required. The chlorine is assumed to appear as a salt mixture (e.g., [K,Na]Cl), requiring oxygen to be adjusted for the oxygen equivalent of chloride. The sulfur is assumed to appear as a sulfate mixture (e.g., [Na,K]₂SO₄ or [Na,K]₂O·SO₃), and oxygen is calculated based on a SO₃ unit. The nitrogen is assumed to occur as a nitrate mixture (e.g., [K,Na]NO₃ or [K,Na]₂O·NO_{2.5}), and oxygen calculated is based on a NO_{2.5} unit. The hydrogen is assumed to occur as hydroxyl groups (HO[−]), and oxygen calculated based on a HO[−] unit. The carbon is assumed to appear as either char/graphite (C) or carbonates (e.g., CaCO₃ or CaO·CO₂), and oxygen is calculated based on a CO₂ unit. The choice between graphite and carbonate is based on the best fit to a total of 100%. The assumptions are based on the direct determinations of sylvite and calcite or by thermodynamically modeling. The results of the elemental reduction of the oxides and the estimate of total oxygen are summarized in Table 2. The closeness of the totals to 100% testifies to the robustness of the assumptions in the calculation scheme.

4. RESULTS

4.1. Proximate and Ultimate Compositions. The proximate compositions on a dry basis are illustrated in Figure 1A as the fixed carbon/volatile matter/ash content ratio. The

main variability is in the 575 °C ash content, while the fixed carbon/volatile matter ratio is relatively constant. The ash content varies from below 1% for wood to about 18% for rice straw. There is further a tendency for the ash content and fixed carbon/volatile matter ratio to depend on whether the feedstock was pretreated by leaching, with lower ratios for leached (0.17) as compared to unleached (0.22), and, in general, a lower ash content for the leached feedstock.¹⁸ The ultimate compositions of the feedstock and the corresponding ashes are illustrated in Figure 1B, showing that the feedstock compositions are relatively constant in terms of O–C–H, reflecting similarly constant ratios of the organic composition (lignin, cellulose, and hemicellulose).

4.2. Major and Minor Element Ash Compositions. The general effect of ashing (or combustion/oxidation) is a bonding of oxygen in the ash mainly as oxides, silicate, and carbonate residual minerals. The overall result is thus a relative enrichment of oxygen in the ash and depletion in carbon and hydrogen compared to the crude biomass (Figure 1B). The dispersion in the ash compositions reflects the stabilization of carbonates and/or sulfates for some ashes (carbonate in wood and sulfate in some grasses). Sulfur is partially retained in the ash (Figure 2) as salts or quenched sulfate melt.

Two elements (S, Cl) were analyzed both on the untreated feedstock and the corresponding ash and thus permit an evaluation of losses during ashing. By comparing the measured concentrations with the calculated feedstock concentrations using the ash compositions and the ash content (Figure 3), a strong linear correlation is observed that suggests an average loss of 19% for both S and Cl. Thy et al.¹¹ presented similar data for Cl and K using wood and straw biomass and demonstrated a Cl loss of 20% for wheat straw and a 26% loss of K for wood. However, significantly increasing losses for both Cl and K with increasing ashing temperature were detected for all feedstocks, and it is thus possible that the contrast to the present results may reflect the 50 °C higher ashing temperature used here.

The ash compositions recast on a dry elemental weight basis vary widely across the types of feedstock (Table 2). The major elements, defined as above 2% weight concentration in ash on a volatile-free basis, are for the herbaceous feedstock ash generally O, Si, K, Cl, Mg, and Ca. Sodium appears in high

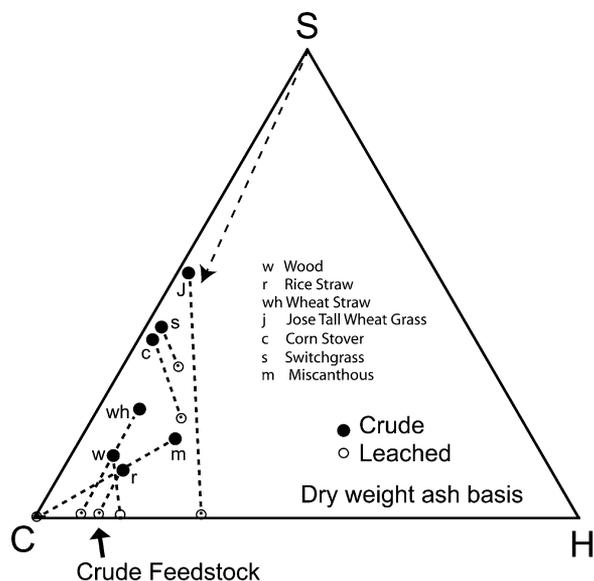


Figure 2. C–S–H compositions of untreated (filled dots) and leached (open dots) feedstock ashes. The arrow marked ‘crude’ indicates the position of feedstock on or near the binary C–H join. All data are from Table 1, on a dry weight basis.

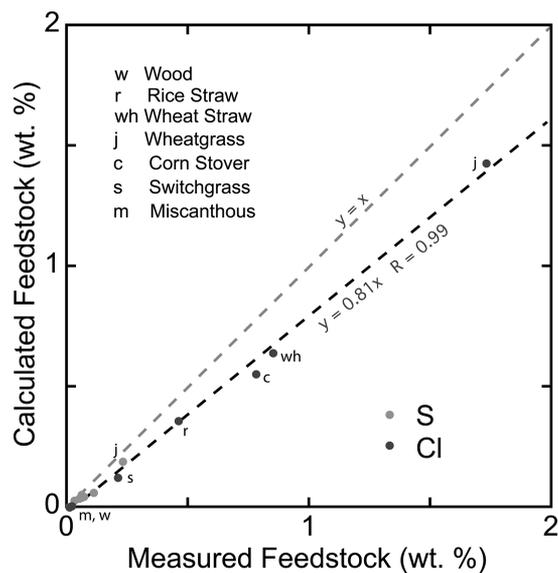


Figure 3. Calculated versus measured Cl and S in untreated feedstock (wt %). Linear regression through the whole data set indicates a loss of 19%.

concentration in the wheatgrass (~15%) attributed to saline irrigation and may in part have accumulated in the plant during growth in ionic form and probably also occurs as adhering sodium sulfates and halides to plant surfaces and root structure. The elements in smaller and variable concentrations are Ti, Al, Fe, Mn, P, S, and Na, part of which can be related to the incorporation of soil in the feedstock material (switchgrass, corn stover, and miscanthus). Calcium replaces silicon as the dominating element in wood ash compared to the herbaceous materials. An exception to this classification is sodium that appears in high concentration in the wheatgrass (~15%), a result attributed to the saline irrigation used with this crop and accumulation in the plant during growth. Sodium may also

occur as adventitious sodium sulfates and halides adhering to plant surfaces and roots.

The ash concentrations of chlorine, sulfur, and the alkali metals, as a result of water leaching of the feedstock, are illustrated in Figure 4 with the variables selected to simulate

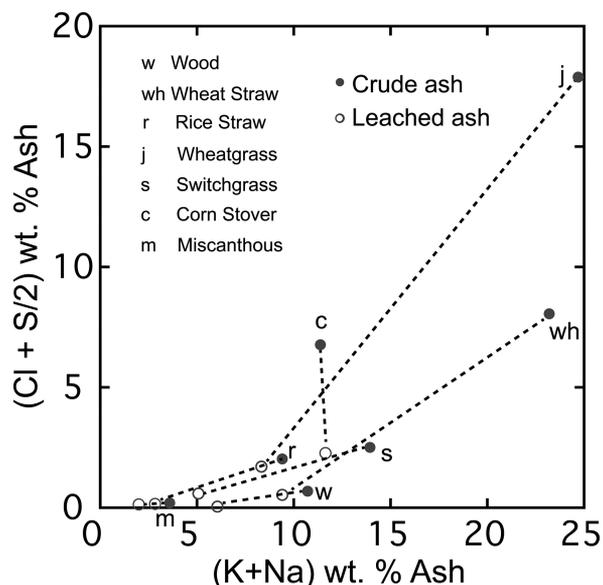


Figure 4. Compositions of the feedstock ashes in terms of (Cl + S/2) as a function of (K + Na) (all in wt %). The variables have been selected to simulate leaching of sulfates and halides from the raw feedstock during water leaching. Tie-lines connect untreated and leached concentrations for each feedstock.

leaching in the concentrations of the main halides and sulfates. Three groups are seen. The first is wood and miscanthus that show variations in the alkali metals largely unrelated to systematic low Cl and S concentrations. Corn stover comprises the second group that shows large variation in chlorine independent of the alkali concentrations. The third group, comprised of the remaining straws and grasses, suggests covariation between chlorine and the alkali metals. These groupings can only, in part, be related to the leaching of the halide and sulfate salts from the feedstock and suggest more complex bonding in the organic structure.

Figure 5 provides a visual display of the major and minor element concentrations for each feedstock (Table 2), normalized to rice ash (Table 1). The patterns reveal strong depletion in Na, K, S, and Cl resulting from water leaching for the herbaceous feedstock, with the exception of corn stover and miscanthus that are little affected. The elements Ti, Al, and Fe show a pronounced depletion from leaching for switchgrass, corn stover, and miscanthus attributed to partial removal of a soil component. Other elements, such as Si, Mn, Mg, Ca, and P, are largely unaffected by leaching due to their structural bonding in the organic structure.³⁶

4.3. Trace Element Compositions of Ash. Selected elemental concentrations (Table 2) reported for the ash are organized according to the main groups of the periodic table and ordered with increasing atomic number on semilog diagrams. In order to aid visual interpretation, the analytical concentrations have mostly been normalized to a central California, San Joaquin Valley soil (NIST SRM 2709^{37,38}) with a few elemental concentrations from NIST SRM 2709a or 2710a.³⁹ Changing the normalizing composition to an

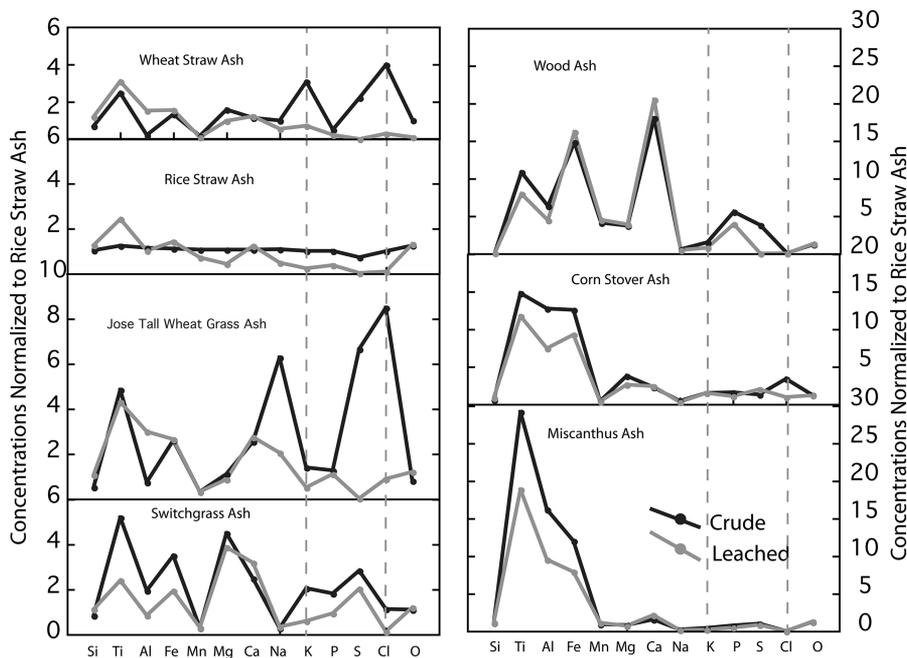


Figure 5. Summary of the major and minor element compositions of feedstock ashes normalized to the average rice straw ash of Table 1.

estimated composition of average upper continental crust³¹ will not substantially modify the trace element patterns. The normalizing compositions are summarized in Table 1. The enrichment factors for individual elements are defined relative to the normalizing compositions with a factor of 2-times enrichment taken for this study to be noteworthy. Elements at or below their detection limits are shown at their detection limits.

4.3.1. *Alkali Metals (Li, Na, K, Rb, Cs).* The alkali metal elements show wide variations with potassium systematically enriched in ash for all feedstock by up to 20-times the San Joaquin soil composition (Figure 6, Table 2). The absolute

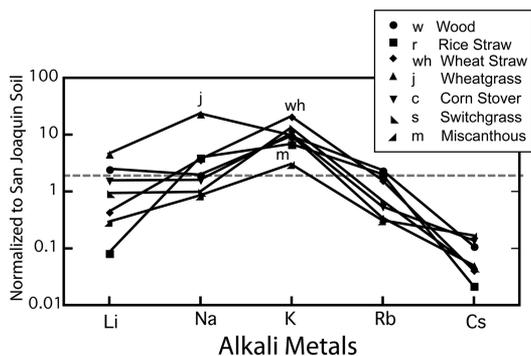


Figure 6. Alkali metal elements in feedstock ashes normalized to California soil on a log scale and arranged by increasing atomic number. The normalizing composition is a central San Joaquin Valley soil (NIST SRM 2907) as given in Table 1. The horizontal stippled line is the two-times San Joaquin soil.

concentration of Li varies from 2 to 95 ppm and is enriched in wood and wheatgrass ashes (>42 ppm, two-times the San Joaquin soil), Rb varies from 29 to 225 ppm and is only enriched in wood ash (>192 ppm), and Cs varies from 0.1 to 0.9 ppm without being enriched in any of the feedstock ash (<11 ppm) (Table 2). The concentration of Na varies from 0.5 to 15 wt % and is only enriched in wheatgrass ash (>2.4%).

Potassium varies from 3 to 21 wt % and is systematically enriched in all feedstock ash (>2.0%). The wheatgrass ash is enriched for both K (20-times) and Na (23-times), the latter enrichment related to the saline irrigation during feedstock production.

4.3.2. *Alkali Earth Metals (Be, Mg, Ca, Sr, Ba).* The alkali earth elements are variably enriched compared to the San Joaquin soil, specifically for Ca and Sr in wood ash (Figure 7,

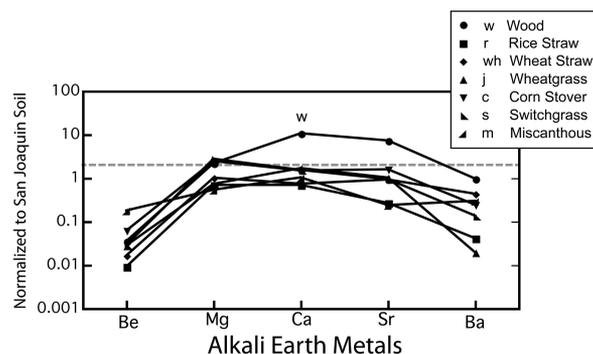


Figure 7. Alkali earth elements in feedstock ashes normalized to California soil on a log scale and arranged by increasing atomic number. The normalizing composition is a central San Joaquin Valley soil (NIST SRM 2907) as given in Table 1. The horizontal stippled line is the two-times San Joaquin soil.

Table 2). The absolute concentration of Be varies from 0.03 to 0.50 ppm without being enriched in any of the feedstock ash (<6 ppm), Sr varies from 60 to 1700 ppm with strong enrichment only in wood ash (>460 ppm), and Ba varies from 20 to 1000 ppm without being significantly enriched in any of the feedstock ash (<2000 ppm). The major element Mg varies from 1.0 to 4.2% and is enriched in wood, corn stover, and switchgrass ashes (>3.0%). Calcium varies from 1.3 to 20.0% and is also enriched in wood, corn stover, and switchgrass ashes (>3.8%). The strong enrichment of Ca is characteristic for

wood ash, reaching 10-times the San Joaquin soil concentration.

4.3.3. Period 4 Transition Metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn). The transition metals of period four elements with some notable exceptions occur systematically in concentrations below significance (Figure 8, Table 2). The exceptions are Mn,

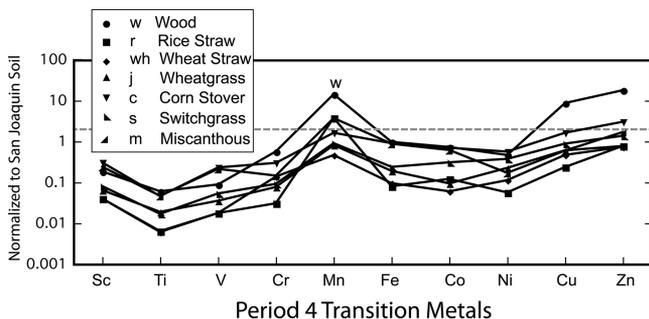


Figure 8. Period 4 transition metals in feedstock ashes normalized to California soil on a log scale and arranged by increasing atomic number. The normalizing composition is a central San Joaquin Valley soil (NIST SRM 2907) as given in Table 1. The horizontal stippled line is the two-times San Joaquin soil.

Cu, and Zn. Manganese occurs in concentrations between 250 and 7700 ppm and is enriched in wood, rice straw, and miscanthus ashes (>1800 ppm). Copper occurs in concentrations between 8 and 300 ppm, being only enriched in wood (>70 ppm). Zinc occurs in concentrations between 80 and 1900 ppm and is likewise only enriched in wood ash (>210 ppm) compared to the San Joaquin soil. The strong enrichments in Mn (14-times), Cu (9-times), and Zn (18-times) for wood ash are characteristic features for this group of elements. Manganese serves as a known reaction center in photosynthesis⁴⁰ and is essential for oxygen evolution and is a key plant catalyst for water oxidation and atmospheric oxygen production.⁴¹ Copper is a constituent of plant proteins that are involved in, or at higher concentrations can interfere with, photosynthesis and is important for maintaining membrane fluidity in electron transfer between the two photosystems (I and II).⁴² Zinc is a cofactor for a number of plant enzymes and involved in chlorophyll formation through the regulation of nutrients in the cytoplasm.⁴³

4.3.4. Period 5 Transition Metals (Y, Zr, Nb, Mo, Ag, Cd). The transition metals of period five elements occur with the exception of Mo, Ag, and Cd in concentrations below significant levels for all feedstock ash (Figure 9, Table 2). Molybdenum occurs in concentrations between 2 and 30 ppm and is enriched in wood, wheat straw, and wheatgrass (>4 ppm). Silver occurs in concentrations between the detection limit (0.2 ppm) and 6 ppm with enrichment only in wood ash (>1 ppm). Cadmium occurs in concentrations from near the detection limit of 0.04 ppm to 70 ppm and is significantly enriched in wood, corn stover, and miscanthus ashes (>0.8 ppm). The strong enrichment of Mo in wood ash (16-times) and Cd (175-times) compared to the San Joaquin soil are characteristic for this group of elements.

4.3.5. Rare Earth Elements (La–Lu). The rare earth elements occur systematically in low concentrations for all feedstock ash reaching a maximum of 12 ppm for La (Table 2). Normalized to the San Joaquin valley soil (Figure 10), only wood, corn stover, and miscanthus ashes show systematic patterns well above the background defined by the other

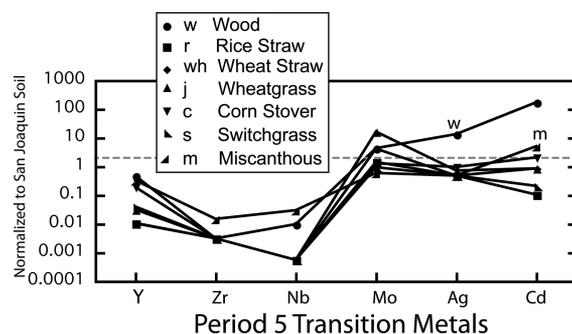


Figure 9. Period 5 transition metals in feedstock ashes normalized to California soil on a log scale and arranged by increasing atomic number. The normalizing composition is a central San Joaquin Valley soil (NIST SRM 2907) as given in Table 1 (with Nb from NIST SMR 2710a). The horizontal stippled line is the two-times San Joaquin soil. The wood concentration of Cd with a 67-ppm is enriched 175 times compared to San Joaquin soil.

feedstock ashes. The consistent and similar patterns are defined as a flat plateau throughout the rare earth elements (with the exception of an anomalous result for Ce in miscanthus and a detection limit result for Eu in wheatgrass). A marked relative enrichment for Sm is seen for all feedstock ash. It is possible that the high relative level for the rare earths in corn stover and miscanthus in part may reflect the inferred high soil component in these feedstock ashes; however, this cannot be the case for wood where the rare earth elements must be incorporated into the organic plant structure.

4.3.6. Toxic Elements (Be, Cr, Ni, Cu, As, Se, Cd, Sb, Ba, (Hg), Tl, Pb). Figure 11 summarizes the concentrations of potential toxic elements again normalized to the San Joaquin soil. The selection is the series of elements as defined by the U.S. Federal Safe Drinking Water Act of 1974 (with later amendments) potentially being able to cause adverse public health effects. The elements Be, Cr, Ni, Cu, As, Se, and Cd, already presented, are here amended with the heavy elements As, Se, Sb, Tl, and Pb in Figure 11. Mercury was analyzed by Thy and Jenkins¹⁶ in many biomass materials and ash showing that Hg was, as expected, volatilized during ashing being at or near the detection limit in all ash analyzed (<3–5 ppb).

With the exception of Cu, Se, and Cd, the potential toxic elements occur always in concentrations below significance as defined in this discussion (Figure 11, Table 2). Copper occurs in concentrations between 6 and 300 ppm and is only enriched in wood ash (>70 ppm). Selenium occurs in concentrations between the detection limit and 7 ppm with enrichment only in wood and wheatgrass ashes (>3 ppm), the latter reflecting the known high Se concentrations in soils and plants from the west side of the San Joaquin Valley, a region of higher concentrations than the standard soil used for comparison here. Cadmium occurs in concentrations from the detection limit to 70 ppm and is significantly enriched in wood, corn stover, and miscanthus ashes (>0.8 ppm). Of the remaining heavy metals, none appears in concentrations significantly enriched. Antimony appears in concentrations from the detection limit to 1 ppm (<16 ppm, wood). Barium appears in concentrations between 20 to 950 ppm, with the high value in wood ash, but does not reach concentrations above 2-times the San Joaquin soil (<2000 ppm). Thallium occurs in concentrations to 0.2 ppm (<1.5 ppm). Lead appears in concentrations between 0.2 to 26 ppm, with the high value in

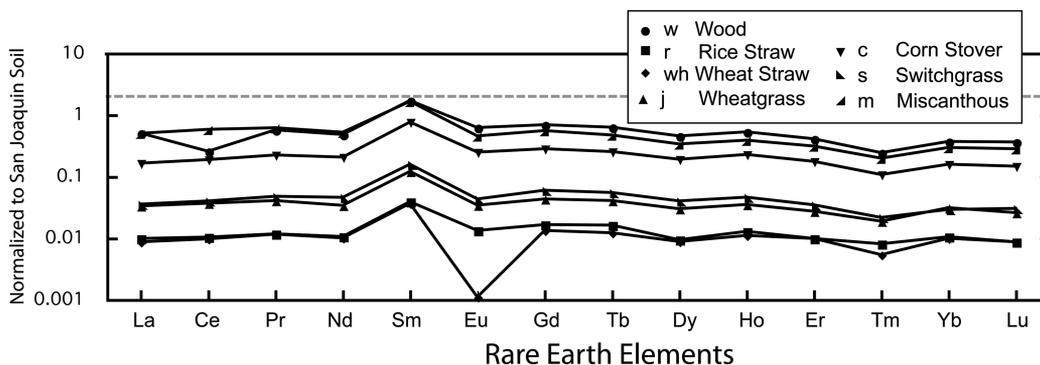


Figure 10. Rare earth elements in feedstock ashes normalized to California soil on a log scale and arranged by increasing atomic number. The normalizing composition is a central San Joaquin Valley soil (NIST SRM 2907) as given in Table 1 (with Nb from NIST SMR 2710a). The horizontal stippled line is the two-times San Joaquin soil.

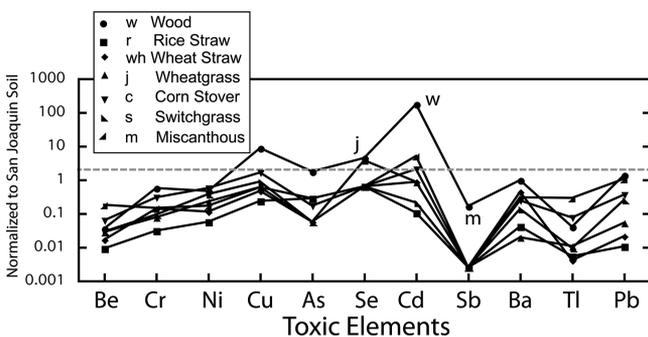


Figure 11. Selection of toxic elements (as defined by the Safe Drinking Water Act) in feedstock ashes normalized to California soil on a log scale and arranged by increasing atomic number. The normalizing composition is a central San Joaquin Valley soil (NIST SRM 2907) as given in Table 1. The horizontal stippled line is the two-times San Joaquin soil.

wood ash, but without reaching above two-times the San Joaquin soil (<40 ppm).

4.4. Effects of Ashing Temperature. The ash content as a function of temperature was determined in air for the raw feedstock. There is a reasonable correspondence, on a dry basis, between the ash content determined at 575 °C using the thermal analyzer (Figure 12A) and the content determined also at 575 °C following ASTM E1755²² (Table 2). The drying (<105 °C) and decomposition of the organic feedstock are seen with cellulose breakdown at 250–350 °C and lignin at 375–450 °C (Figure 12A). After about 500 °C, the ash content appears to remain stable with the lowest value for wood (~0%) and the highest for rice straw (17%). In order to more definitively evaluate the effects of ashing temperature, ash samples were heated using the same procedures as for the untreated feedstock. The results are shown in Figure 12B and are, in general, consistent with the results for the feedstock. The initial pattern suggests drying proceeding to ~180–200 °C resulting from the removal of some crystal bound water; the presence of which was implied by the compositional analysis of the ashes (Table 2). All ashes, to various degrees, subsequently reveal a downward sloping plateau until marked declines in mass loss occur at high temperature. Wood ash contains ~23% calcite (Table 2) that decomposes to CO₂ and lime (CaO) at temperatures between 600 and 800 °C,¹¹ as recorded by a CO₂ loss of mass of a corresponding magnitude (Figure 12B). Jose tall wheat grass, wheat straw, and corn stover contain high amounts of chloride of 7–16% Cl by weight (Table 2) that is

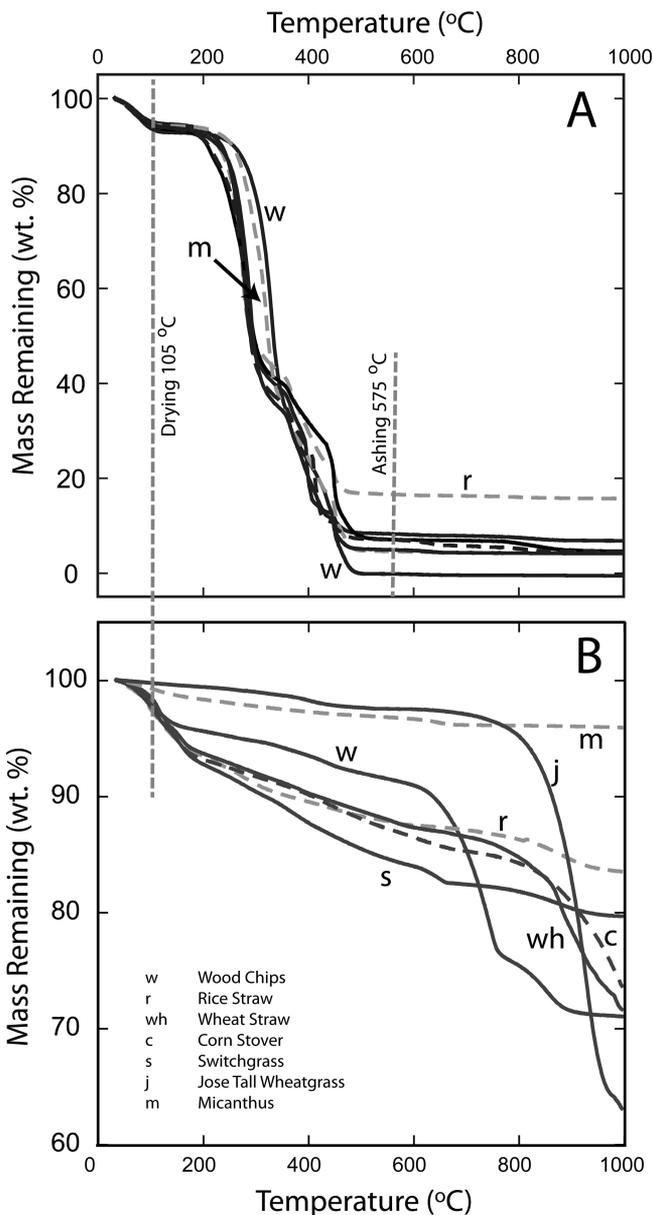


Figure 12. Mass remaining (wt %) as a function of temperature (°C) determined in air and a heating ramp of 10 °C/min. (A) Raw air-dried fuel. (B) Ash produced at 575 °C.

Table 3. Summary of Feedstock Composition and Elemental Losses for Selected Elements (Dry Weight Basis)

	Douglas fir		rice straw		wheat straw		Jose tall wheat grass		corn stover		switchgrass		miscanthus	
	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached
ash content %	0.20	0.12	18.5	18.3	8.3	6.3	8.5	4.5	8.4	4.0	5.9	4.5	8.3	5.1
leaching mass loss %		1.7		10.8		9.9		20.9		17.0		8.4		3.1
Ash Concentrations														
Cl %	0.15	0.08	1.94	0.19	7.72	0.57	16.80	1.74	6.58	1.95	2.09	0.27	0.06	0.02
S %	1.14	0.00	0.24	0.00	0.73	0.00	2.24	0.00	0.43	0.69	0.86	0.69	0.34	0.29
Li ppm	52	205	1.7	0.8	9	12	95	32	32	28	19	14	6	7
Na %	1.25	1.04	2.51	1.15	2.31	1.28	14.93	4.80	1.02	0.74	0.62	0.82	0.54	0.41
Mg %	3.33	3.55	1.05	0.43	1.54	0.95	1.11	0.86	3.71	2.70	4.20	3.91	0.81	0.72
K %	9.43	4.98	6.85	1.65	20.85	4.86	9.73	3.49	10.33	10.86	13.28	4.21	3.01	1.55
Ca %	20.30	23.53	1.32	1.54	1.40	1.50	3.20	3.40	2.82	3.12	2.92	4.05	1.95	2.70
Mn ppm	7730	10400	2040	1150	252	176	442	456	880	766	489	515	2020	2400
Cu ppm	301	2030	85	16	9	21	18	57	41	31	17	21	31	
Zn ppm	1900	3070	83	51	78	73	82	118	321	475	147	175	181	234
Rb ppm	225	123	190	48	149	35	33	16	51	33	65	21	29	16
Sr ppm	1690	2170	62	81	214	225	238	236	367	422	219	283	56	74
Mo ppm	9	16	2.9	1.2	8	5.1	33	33	2.6	4.3	1.9	1.8	1.2	2.3
Cd ppm	67	57	0.04	0.11	0.33	0.27	0.33	0.4	0.79	0.58	0.08	0.07	1.9	2.6
Cs ppm	0.57	0.40	0.11	0.06	0.22	0.09	0.26	0.27	0.72	0.58	0.24	0.11	0.9	0.5
Ba ppm	946	379	40	49	424	725	19	25	236	288	132	142	291.0	383.0
Leached Ash Concentration Adjusted for Mass Loss														
Cl %		0.08		0.17		0.51		1.38		1.62		0.25		0.02
S %		0		0		0		0		0.57		0.63		0.28
Li ppm		202		0.7		10		25		23		12.37		7
Na %		1.02		1.03		1.15		3.80		0.62		0.75		0.40
Mg %		3.49		0.39		0.86		0.68		2.24		3.58		0.70
K %		4.90		1.47		4.38		2.76		9.01		3.86		1.50
Ca %		23.13		1.38		1.35		2.69		2.59		3.71		2.62
Mn ppm		10223		1026		159		361		636		472		2326
Cu ppm		1995		5		8		14		34		15		30
Zn ppm		3018		45		66		93		394		160		227
Rb ppm		121		43		31		13		28		20		16
Sr ppm		2133		72		203		187		350		259		72
Mo ppm		16		1.1		4.6		26		3.6		1.6		2.2
Cd ppm		56		0.10		0.24		0.3		0.48		0.06		2.5
Cs ppm		0.39		0.05		0.08		0.2		0.48		0.10		0.49
Ba ppm		373		44		653		20		239		130		371
Feedstock Composition														
Cl ppm	3		3585		6392		14297		5527		1233		50	
S ppm	23		444		604		1906		361		507		282	
Li ppm	0.103		0.31		0.75		8		2.7		1.1		0.50	
Na ppm	25		4648		1916		12702		854		368		449	
Mg ppm	67		1939				944		3115		2476		676	
K ppm	189		12656		1278		8280		8675		7837		2501	
Ca ppm	406		2430		1160		2725		2371		1720		1619	
Mn ppm	15		377		21		38		74		29		168	
Cu ppm	0.60		1.5		1.3		1.8		5		1.8		1.73	
Zn ppm	3.8		15		6		7		27		9		15	
Rb ppm	0.45		35		12		2.8		4.3		3.8		2.42	
Sr ppm	3.4		11		18		20		31		13		4.61	
Mo ppm	0.017		0.54		0.70		2.8		0.22		0.11		0.100	
Cd ppm	0.13		0.007		0.027		0.028		0.066		0.005		0.161	
Cs ppm	0.0011		0.020		0.018		0.022		0.060		0.014		0.072	
Ba ppm	1.9		7.4		35		1.6		20		8		24	
Leached Feedstock Composition														
Cl ppm		0.9		310		322		618		647		111		10
S ppm		0		0		0		0		229		284		143
Li ppm		0.242		0.13		0.65		1.1		0.94		0.56		0.34
Na ppm		12		1876		721		1705		246		339		202
Mg ppm		42		708		538		304		897		1613		355

Table 3. continued

	Douglas fir		rice straw		wheat straw		Jose tall wheat grass		corn stover		switchgrass		miscanthus	
	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached	raw	leached
Ash Concentrations														
K ppm		59		2695		2743		1241		3605		1735		767
Ca ppm		278		2519		848		1208		1035		1667		1335
Mn ppm		12		188		9.94		16		25		21		119
Cu ppm		2.4		0.86		0.51		0.62		1.4		0.69		1.5
Zn ppm		3.6		8		4.12		4		16		7		12
Rb ppm		0.145		8		1.97		0.58		1.11		0.88		0.81
Sr ppm		2.6		13		12.71		8		14		12		4
Mo ppm		0.019		0.20		0.29		1.2		0.14		0.074		0.114
Cd ppm		0.068		0.018		0.015		0.014		0.019		0.003		0.13
Cs ppm		0.0005		0.010		0.005		0.010		0.019		0.005		0.025
Ba ppm		0.447		8		41		0.89		10		6		19
Elemental Gains (Negative) or Losses (Positive) from Leaching (Air-Dried Feedstock Basis)														
	abs	percent	abs	percent	abs	percent	abs	percent	abs	percent	abs	percent	abs	percent
Cl ppm	2.1	69	3275	91	6070	95	13679	96	4880	88	1122	91	40	80
S ppm	23	100	444	100	604	100	1906	100	132	37	223	44	139	49
Li ppm	-0.139		0.18	58	0.10	13	7	86	1.8	35	0.58	51	0.157	32
Na ppm	13	51	2772	60	496	62	10997	87	607	29	28	8	248	55
Mg ppm	25	37	1231	63	685	58	640	68	2218	29	863	35	321	48
K ppm	130	69	9961	79	13397	84	7038	85	5070	42	6102	78	1734	69
Ca ppm	128	32	-88		417	27	1517	56	1337	44	53	3	284	18
Mn ppm	3.192	21	189	50	11	52	21	57	48	34	8	26	49	29
Cu ppm	-1.793		0.65	43	0.84	62	1.17	65	3.4	29	1.13	62	0.219	13
Zn ppm	0.179	5	7.02	46	2.3	36	2.8	40	11	58	1.46	17	3.5	23
Rb ppm	0.305	68	27.30	78	10	84	2.19	79	3.2	26	3.0	77	1.61	67
Sr ppm	0.820	24	-1.85		5	28	12	59	17	45	1.26	10	0.96	21
Mo ppm	-0.002		0.340	63	0.41	59	1.6	58	0.076	65	0.038	34	-0.014	
Cd ppm	0.065	49	-0.011		0.012	44	0.014	49	0.047	29	0.002	39	0.034	21
Cs ppm	0.0007	59	0.011	52	0.013	72	0.013	57	0.041	32	0.010	68	0.047	65
Ba ppm	1.445	76	-0.602		-5.9		0.73	45	10	48	1.9	25	5.2	22

present dominantly as 11–28% halite (NaCl) or 15–35% sylvite (KCl), or mixtures of these and related salts in the ash. There is a good correlation between the original chloride content of the ash and the amount of mass loss (16.6% Cl and 37% mass loss for Jose tall wheat grass; 7.7% Cl and 27% mass loss for wheat straw; 6.6% Cl and 26% mass loss for corn stover). The total high temperature mass loss to 1000 °C from the 575 °C ashes amounts to 4.8% for miscanthus, 19.0% for rice straw, 22.6% for switchgrass, 29–31% for wood, 30.5% for wheat straw, 28.5% for corn stover, and 37.2% for Jose tall wheat grass (all on a dry basis). These mass losses affect the content of trace elements and offer maximum estimates of the elemental concentration, but they have limited effect on the major and minor elements that were determined on ash produced at the similar temperature of 950 °C.

4.5. Effects of Water Leaching. The elemental losses or gains from batch leaching are evaluated in Table 3 showing only the alkali metals, alkali earth elements, selected transition elements, and the most common anions. The concentrations have, for direct comparison, been corrected for mass loss during leaching as well as the ash content and are given as absolute values and as percentages with positive numbers reflecting losses and negative gains, relative to the original untreated compositions.

The calculations mostly show highly variable losses. Sodium is systematically depleted with losses from 8 to 87% of the original content. Potassium shows more restricted losses

between 42 and 85%, and Rb similarly shows losses between 42 and 84%. The effects on the remaining alkali metals, Li and Cs, mostly suggest losses, but with some mixed results probably attributable to the very low total concentrations in some of the original feedstock. Of the alkali earth elements, Mg shows more restricted losses between 29 to 68% and Ca, Sr, and Ba again indicate variable losses but also some very small gains or losses. The transition metals Mn, Cu, Zn, and Mo likewise point toward highly variable losses for most feedstock. The anions Cl and S show both strong depletions of 69–98% for Cl and 37–100% for S with the low values mostly for corn stover, switchgrass, and miscanthus.

More work is required to better understand many of these highly variable results that may not always be significant considering major factors contributing to the uncertainties during handling and leaching (contamination, leaching, duration, sampling). In addition, the differences between batch equilibrium and fractional leaching may become important for understanding contrasting leaching results.⁴⁴ The principal observation of this study is nevertheless that the majority of alkali and transition elements suffer strong depletion during leaching.

4.6. Feedstock Compositions. Provided that the ash content and the ash composition are known, the concentrations of many trace elements in the biomasses, however, can be evaluated based on the assumption that elemental losses do not occur during combustion and decomposition. The result of

such an evaluation for selected elements is given in Table 3, obtained by calculating feedstock compositions (untreated and leached) from the ash compositions adjusted for ash content and leaching mass loss and given as parts per million (ppm) on a dry weight basis for a selected group of elements of special interest. It is particularly noteworthy that the feedstock with the lowest concentrations of most alkali and transition elements is the wood. The only elements in concentrations above 20 ppm are, in general, Na, Mg, K, Ca, and Mn with concentrations in the straw feedstock up to 500-times the concentrations in wood. This is a reflection of the strong effects of the ash content in determining the concentrations of ash residuals. As noted, mercury was determined by Thy and Jenkins¹⁶ to be below 50 ppb for a selection of untreated California biomass feedstock similar to those studied here.

5. DISCUSSION AND CONCLUSIONS

The whole periodic table may potentially be present in biomass feedstock, including elements that can be highly beneficial and elements that can have strong adverse effects on process streams or have potential environmental toxicity. In addition to the importance to combustion systems, the control of inorganic materials in biomass gasification and the removal of inorganic contaminants from syngas are critical to reactor operations and to the prevention of catalyst deactivation in downstream synthesis. The waste and coproducts from feedstock treatment and fuel and energy generation need to be controlled, treated, utilized, or eventually safely disposed. Additional consideration must also be directed toward monitoring coproducts and waste from pretreatment of feedstock including leaching and thermal processing such as torrefaction and higher temperature pyrolysis.

5.1. Ash Compositions. A principal requirement for monitoring biomass processing is accurate and precise measurement of the inorganic composition of feedstock products. Multielement instrumental spectroscopic analyses (XRF, INA, and ICPMS) were used in this study to determine inorganic elemental compositions following mass reductions (dewatering and ashing). The results show a strong correlation between the type of feedstock, ash content, and the composition of the residual ash.

The feedstock is principally grouped as wood and herbaceous energy crops or agricultural plant residues. The herbaceous plant ashes are typically dominated by silica, potassium, and oxygen, while the wood ash is dominated by calcium, potassium, and oxygen. The perhaps trivial observation that the relative oxygen content in the combustion ashes (40–53%) is higher than in the raw biomasses (36–44%) is nonetheless interesting in reflecting the changes in compound structure occurring during combustion/oxidation. The remaining carbon in the ash occurs dominantly either as carbonates in wood or as residual graphite (char) in the herbaceous materials, the latter resulting from unintended incomplete oxidation (or burning) under standard ashing conditions. Sulfur is dominantly retained in the ash fraction as either sulfate minerals or melt. Small amounts of hydrogen are systematically detected in the ashes suggesting its presence as hydroxyl groups in silicate minerals, amorphous components, or glasses. An additional complication is that many ashes are hygroscopic and thus show increases in hydrogen even if nominally stored in sealed containers. The content of nitrogen in biomass is for these samples below 1% (although it can be higher in other types of biomass) and is

further depleted during ashing to concentrations often below detection limit.

The ash content of the crude feedstock is the principal variable with the proximate (volatile matter and fixed carbon content) and ultimate variables (O–C–H–N–S) occurring in relatively fixed ratios (Table 2). The mass (or volume) of the inorganic residual ash needing handling or disposal is, of course, directly proportional to the ash content of the original feedstock. Thus, burning 1 ton of rice straw will generate 185 kg of ash, but burning 1 ton of clean wood chips will only generate 2 kg of ash (on a dry basis). The contrast is much more pronounced if converted to a volume basis because of a very high porosity of straw ashes. The concentrations of minor and trace elements are similarly directly proportional to the ash fraction. Thus, for specific trace elements, the concentration in the wood ash will be enriched by a factor of nearly 100 times compared to that of rice straw ash, representing the extreme ash compositions evaluated here.

The element concentrations are of primary concern from an environmental perspective for beneficiary utilization of ash. The total mass of the trace elements and some minor elements, such as Ti and Mn, amounts to between 2.0 wt % in wood ash and 0.1 wt % in the straw ashes; thus, wood ash will have a stronger modifying effect despite being available in volumetric smaller amounts. The high alkali content of biomass ash typically makes them useful as fertilizers and at present they often are sold for such purpose. It is thus important to consider if the minor and trace elements in biomass ash will significantly change agricultural soil composition for the better or worse. This has been an issue of concern for existing biomass power stations where exclusion of painted wood has been a priority to avoid elevated lead in ash both for regulatory and coproduct value considerations. In this study, we have normalized the ash compositions to the composition of an agricultural soil (NIST SMR 2709),^{37,39} being a baseline soil composition of a fallow field from California's central San Joaquin Valley. We are further focusing our attention on normalized concentrations above a background double that of the San Joaquin soil. This background is justified by an analytical relative standard deviation of up to 20% for many elements in low concentrations, but it principally takes into account a substantial mixing ratio between ash and soil (<50/50%). The normalizing graphical procedure serves principally as an aid in comparing multicomponent analyses with distinct differences in ash compositions. The choice of normalizing composition may not necessarily have generic implications.

Against the standard soil used here, the majority of the alkali metals (Li, Na, K, and Rb) are able to substantially modify the composition under ash fertilizer applications. Only Mg, Ca, and Sr of the alkali earth metals, Mn, Cu, and Zn of the period 4 transition metals, Mo and Cd of the period 5 transition metals, and only Se of heavier elements may exceed the target background for the feedstocks examined. Only K is systematically enriched in all feedstock ash. Ash of wood material is the main carrier of many of the alkali elements (Li, K, Rb, Mg, Ca, Sr, Ba) and some transition elements (Mn, Cu, Zn, Mo, Ag, Cd). In contrast, ash of herbaceous plant materials are, in addition to K, only variably enriched: wheatgrass in Li, Na, Se, and Mo, switchgrass in Mg and Ca, corn stover in Mg, Ca, and Cd, rice straw in Mn, wheat straw in Mo, and miscanthus in Mn and Cd.

Some ash compositions suggest that an adventitious soil component may have contributed to high Al and Fe contents in

the ashes (corn stover and miscanthus). The concentrations in the ash are too high (5–6 wt % Al_2O_3) to be attributed to active uptake by the plant. The wood ash, however, also shows high concentrations of both Al and Fe due to direct uptake but the overall concentrations are small due to the low ash contents in comparison with the herbaceous feedstock. It is also possible that these elements in part may have been incorporated passively into the wood with soil dust particles during growth.⁴⁵ The concentrations of the rare earth elements (REE) in all ashes show generally consistent flat patterns. In general, the REEs suggest little fractionation during uptake in the plant material, possibly with the exception of Sm that is always systematically enriched relatively to the other REEs. Wheatgrass contains unusually high Na exceeding the content of K in the ash due to the saline irrigation employed for this crop as part of phytoremediation efforts on salt-affected lands. Some of the sodium may also be associated with halides and sulfates adhering to plant surfaces, but passive accumulation of sodium is known to occur in wheatgrass and similar plants grown under these conditions and active accumulation occurs in halophytes. The presence of some adventitious sodium is supported by the stronger depletion of preferentially Na compared to K during water leaching.

5.2. Effects of Ashing Temperature. The ashes analyzed as part of this study were produced at 575 °C as specified by ASTM E1755.²² This is a reasonable temperature, as seen in Figure 12A, showing that the organic components are decomposed between 250 and 450 °C with the ash contents stabilizing above 4–500 °C. A high-resolution study, using the corresponding ashes to 1000 °C, better simulates typical oxidizing commercial boiler conditions and reveals that substantial mass loss often occurs at high temperatures (Figure 12B). The mass losses above the decompositions of the organic framework are related to reaction and decomposition of inorganic components (mainly hydroxides, carbonates, halides, and sulfates). The first components expected to breakdown are the hydroxides, but they are not predicted to occur in large amounts in the ashes of this study (Table 2). The next group is carbonates, which predominantly as calcite are seen to decompose in wood ash from 600 to 850 °C (Figure 12B). The halogen salts may melt, react with the silicate matrix, or evaporate at temperatures above the decomposition of carbonates forming gaseous HCl, KCl, and/or Cl_2 mixtures, dependent on ash composition and temperature.^{32,46,47} Thy et al.¹¹ showed that loss of chlorine from wheat straw persisted to temperatures above 950 °C and partially related the loss of potassium to the breakdown of sylvite. Potassium has further been demonstrated to be released from ash of rice straw and urban wood at temperatures above their respective liquidus temperatures without the presence of chlorine,⁴⁸ although the type of chemical release species are unknown. The strong mass loss from about 800 °C can thus mainly be related to the release of chlorine and potassium to the vapor phase.⁴⁹

The substantial mass losses occurring to high temperatures may markedly raise the trace element concentrations by 5–37% dependent on feedstock type mainly due to the decomposition of carbonates and halides. Such values are nevertheless maximum estimates and may for the critical toxic elements only reach noteworthy values for wood (Cu 393 ppm; Se 9 ppm; Cd 87 ppm), corn stover (Cd 1.0 ppm), and miscanthus (Cd 2.0 ppm) ash. The effect of high-temperature mass loss may increase the toxicity of particularly the wood ash potentially raising the concentrations only for Cd. Typical

commercial boiler temperature varies widely from 500 to 1000 °C, dependent on boiler-type and process.^{4,5,50} Thus, only for some operations will temperatures reach calcite and halite breakdown and cause marked increases in trace element concentrations. Additionally, power stations typically burn a mix of wood fuels with ash contents well above the clean wood chip tested here, and conclusions may vary in respect to potential toxicity and other effects for these types of feedstock.⁵¹

5.3. Effects of Water Leaching. The highest depletion percentages, after correction for leaching mass loss, are observed for Cl with between 69 and 96% lost after water leaching, with the low value seen for wood that contains very low chlorine. Sulfur shows variable depletion between 37 and 49% for corn stover, switchgrass, and miscanthus, but it is strongly depleted for the remaining samples. High depletion percentages are also recorded, with few exceptions, for the alkali metals (Na, K, Rb, Cs). The depletion percentages for K vary between 69 and 85% of the original content and for Rb between 68 and 84%. Sodium shows systematically lower losses compared to K, with typical losses between 29 and 60%, with the exception of the lowest values recorded for switchgrass (8%). An exceptionally high Na loss is recorded for wheatgrass (87%) that can be attributed to saline irrigation and an inferred high halite (NaCl) content. The remaining alkali metal, Cs, also shows systematic depletion, but it is often present in concentrations too low ($\ll 0.5$ ppm) to give reliable measurements of depletion.

If the elemental depletions are recast into molecular ratios assuming general halide ($[\text{Na},\text{K}]\text{Cl}$) and sulfate ($[\text{Na},\text{K}]_2\text{SO}_4$) salt formulas, we observe systematic lower depletion in the alkali metals compared to Cl and S for most feedstock. This suggests that only part of the alkali metal is removed by dissolution of adhering salts. Switchgrass, miscanthus, and rice straw record a depletion ratio of 0.27, wheat straw 0.50, and wheatgrass 0.67 (as $[\text{Cl}+\text{S}/2]/[\text{Na}+\text{K}+\text{Cl}+\text{S}/2]$, atomic ratio). Only corn stover suggests, with a 0.93 ratio reasonably close to an ideal ratio of 1.00, the removal of all alkali metals by dissolution of adhering salts. In general, however, significant amounts of alkali metals can be retained in the feedstock probably mostly bound in the organic structure after water leaching.

The batch water leaching used in this study was intended to simulate any similar industrial process that might be employed for pretreatment. Liaw and Wu⁴⁴ have recently pointed out that changes to the solution properties in batch leaching may alter the extraction compared with semicontinuous or flow-through processes better reflecting the water solubilities of the solutes. In general, batch processes might be expected to dissolve more of the inorganic constituents due to acidification of the solution over time,⁴⁴ although earlier results on batch versus flow-through techniques are mixed.⁵³ Simultaneous organic matter extraction during leaching can also affect inorganic concentrations in the leached or leached-dewatered product, and removal of organic matter can constitute a loss in fuel value with economic implications.^{44,52,53} In some cases, recovery of inorganic and organic products may be possible from leachate.^{52,54,55}

5.4. Feedstock Compositions. The crude feedstock compositions have more than an academic interest by allowing evaluation of long-term storage and the effects of decomposition paths other than combustion. Sample reduction by combustion (or other decomposition techniques) of organic

material is a necessary part of most analytical methods for determining the inorganic composition, specifically the major and minor alkali elements and many trace elements (beneficiary or adverse). Some nondestructive techniques such as neutron activation may, however, allow direct determination of the trace element concentrations in biomass if the concentrations are sufficiently high to be above the instrumental detection limits. Provided that the ash content and the ash composition are known, the concentrations of many trace elements in the biomass can be estimated based on the assumption that elemental losses do not occur during combustion and decomposition. The result of such an evaluation for selected elements is given in Table 3, obtained by calculating the dry feedstock compositions from the ash compositions adjusted for ash content and leaching mass loss and given as parts per million (ppm) on a dry weight basis. The results show that most of the alkali metal and alkali earth elements are systematically present in concentrations readily detectable using nondestructive analytical methods. An unavoidable drawback is much higher detection limits and analytical uncertainties using nondestructive analytical methods compared to the standard analytical methods after burning and mass-reduction.

Both Cl and K occur in plant material in ionic form³⁶ and are thus easily removed by leaching (Table 3; Jenkins et al.;⁵² Bakker et al.⁵³). Both elements are further well-known to be partially lost to the flue gas during combustion. Knudsen et al.³² reported a sharp and near complete release of chlorine from wheat and rice straw between temperatures of 700–800 °C corresponding to a moderate release of potassium to 50% and followed by a steady release of the remaining potassium with increasing temperatures. Similar results were obtained by Thy et al.¹¹ confirming the decoupling of the release of Cl and K during combustion from temperatures above 800 °C. Both studies by Knudsen et al.³² and Thy et al.¹¹ show that neither K nor Cl are markedly depleted at ashing temperatures to 800 °C, well above the ashing temperature of 575 °C using in this study. Thy et al.,⁶ nevertheless, demonstrated a small loss of K between the initial ashing temperature of 525 °C and the 950 °C burning during X-ray fluorescence analysis amounting to 5–6% on a K₂O weight basis for wheat and rice straw ashes. It is thus very possible that the raw fuel concentration for potassium is underestimated by a similar amount of 5–6%, well above the analytical uncertainty.

By convention (ASTM E1755²²), ashing of biomass is conducted at temperatures of 500–600 °C in air and thus properties such as ash fraction and ash composition derived from these techniques may mainly only be conducive to understanding combustion processes. A combustion study of Thy et al.¹¹ showed that Cl was progressively released with increasing temperature above 700 °C from wheat and rice straw in accord with the expected decomposition of salts. It is generally believed that the release of K during combustion is facilitated by the presence of Cl and suppressed by Si leading to preferential bonding in silicate melt and/or minerals.^{11,32,46,56–58} Potassium is thought to be released as KCl or for hydrous systems also as KOH.^{56,57}

The behavior of the inorganic components of biomass is less well understood at low oxygen levels of pyrolysis and gasification decompositions. Enders et al.³⁵ examined the effect of temperature and oxygen fugacity (f_{O_2}) on the composition of coal slag at 1350–1450 °C. The results showed that K had the highest retention in air and that with decreasing oxygen

levels (to $f_{O_2} = 10^{-2}$), the loss of K would increase to about 30%. The loss of K can thus be positively related to decreases in the polymerization resulting from decreasing oxygen levels³⁵ as well as temperature and composition of the slag.⁴⁸ The effects of low oxygen pressure, or pyrolysis-types of decompositions, are undoubtedly to change the decomposition of the organic material, the mineralogy of the inorganic char or ash fraction, and the release patterns as a function of temperature. Björkman and Strömberg⁵³ discovered that Cl was prone to be lost at temperatures as low as 400 °C (20–50% loss) during pyrolysis of various straw biomass materials. The study by Enders et al.³⁴ showed that low oxygen pressure favored the release of K until intermediate f_{O_2} levels ($\sim 10^{-2}$), but not at very low levels ($\sim 10^{-3}$) that lead to an increased retention in the ash/slag. Olsson et al.⁵⁸ and Davidsson et al.⁵⁹ demonstrated experimentally that in inert atmospheres (Ar, N₂) with low oxygen content, the release of K and Na were dependent on the composition of the biomass, temperature, and fuel particle size. Jensen et al.⁴⁶ demonstrated that during straw pyrolysis (furnace purged by N₂), Cl was released to the gas phase already from 200 °C and that only limited K was released between 700 and 1050 °C (to 25% loss). Most recently, Okuno et al.⁶⁰ has demonstrated that during fast pyrolysis (He as the carrier gas) of pinewood the alkali earth elements (Ca, Mg) would be affected by an up to 30% release to a temperature of 900 °C.

This review of gas release during pyrolysis of straw and wood suggests that the behavior of Cl and K are decoupled during char formation and that the behavior patterns are dependent on the partial oxygen pressure. The ash fraction from pyrolysis markedly increases compared to combustion. This reflects a change in the mineralogy from mostly oxygen (oxides and silicates) as the dominating anionic component during combustion to an increase in oxocarbon anionic components during pyrolysis (e.g., carbonates). The partial oxygen pressure may thus have an important effect on the mineralogy of the ash/slag and on the retention or release of many alkali elements. Direct measurements of the elemental releases as a function of oxygen fugacity are, however, not well-known. It is nevertheless promising that the release patterns for both the alkalis and Cl are reduced for high oxygen levels and thus support the use of the combustion ash compositions for estimating the elemental contents of the feedstock biomass.

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Notes

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REFERENCES

- (1) Baxter, L. L. Ash deposition during biomass and coal combustion: A mechanistic approach. *Biomass Bioenergy* **1993**, *4*, 85–102.
- (2) Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vasileva, C. G. An overview of the chemical composition of biomass. *Fuel* **2010**, *89*, 913–933.
- (3) Miles, T. R.; Miles, T. R. Jr.; Baxter, L. L.; Bryers, R. W.; Jenkins, B. M.; Oden, L. L. *Alkali Deposits Found in Biomass Power Plants. A Preliminary Investigation of Their Extent and Nature*, Summary Report; National Renewable Energy Laboratory: Golden, CO, 1995.
- (4) Huber, G. W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. *Chem. Rev.* **2006**, *106*, 4044–4098.
- (5) Mohan, D.; Pittman, C. U.; Steele, P. H. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels* **2006**, *20*, 848–889.
- (6) Thy, P.; Grundvig, S.; Jenkins, B. M.; Shiraki, R.; Leshner, C. E. Analytical controlled losses of potassium from straw ash. *Energy Fuels* **2005**, *19*, 2571–2575.
- (7) Olanders, B.; Steenari, B.-M. Characterization of ashes from wood and straw. *Biomass Bioenergy* **1995**, *8*, 105–115.
- (8) Blander, M. The inorganic chemistry of the combustion of aspen wood with added sulfur. *Biomass Bioenergy* **1997**, *12*, 289–293.
- (9) Blander, M.; Pelton, A. D. The inorganic chemistry of the combustion of wheat straw. *Biomass Bioenergy* **1997**, *12*, 295–298.
- (10) Steenari, B.-M.; Lindqvist, O. Stabilization of biofuel ashes for recycling to forest soil. *Biomass Bioenergy* **1997**, *13*, 39–50.
- (11) Thy, P.; Jenkins, B. M.; Grundvig, S.; Shiraki, R.; Leshner, C. E. High temperature elemental losses and mineralogical changes in common biomass ashes. *Fuel* **2006**, *85*, 783–795.
- (12) Werkelin, J.; Skrifvars, B. J.; Hupa, M. Ash-forming elements in four Scandinavian wood species. Part 1: Summer harvest. *Biomass Bioenergy* **2005**, *29*, 451–466.
- (13) Richaud, R.; Herod, A. A.; Kandiyoti, R. Comparison of trace element contents in low-temperature and high temperature ash from coal and biomass. *Fuel* **2004**, *83*, 2001–2012.
- (14) Baerenthaler, G.; Zischka, M.; Haraldsson, C.; Obernberger, I. Determination of major and minor ash-forming elements in solid biofuels. *Biomass Bioenergy* **2006**, *30*, 983–997.
- (15) Thy, P.; Leshner, C. E.; Jenkins, B. M.; Gras, M. A.; Shiraki, R.; Tegner, C. *Trace Metal Mobilization during Combustion of Biomass Fuels*, PIER Final Report, CEC-500-2008-014; California Energy Commission, PIER Energy-Related Environmental Research Program: Sacramento, CA, 2008. <http://www.energy.ca.gov/2008publications/CEC-500-2008-014/CEC-500-2008-014.PDF>
- (16) Thy, P.; Jenkins, B. M. Mercury in biomass feedstock and combustion residuals. *Water, Air, Soil Pollut.* **2010**, *209*, 429–437.
- (17) Obernberger, I.; Biedermann, F.; Widmann, W.; Riedl, R. Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions. *Biomass Bioenergy* **1997**, *12*, 211–224.
- (18) Yu, C.; Thy, P.; Jenkins, B. M.; Wang, L.; Anderson, S.; VanderGheynst, J. S.; Upadhyaya, S. K. Influence of leaching pretreatment on chemical properties of biomass. *Fuel Process. Technol.*, submitted, **2013**.
- (19) Thy, P.; Jenkins, B. M.; Leshner, C. E.; Grundvig, S. Compositional constraints on slag formation and potassium volatilization from rice straw blended wood fuel. *Fuel Process. Technol.* **2006**, *87*, 383–408.
- (20) Williams, R. B. *An Assessment of Biomass Resources in California*, 2007, Final Report, PIER Collaborative Report (Contract 500-01-016); California Energy Commission, PIER Program: Sacramento, CA, 2008.
- (21) ASTM D4442. *Standard Test Methods for Direct Moisture Content Measurement of Wood and Wood-Base Materials*; ASTM International: West Conshohocken, PA, Nov. 15, 2007.
- (22) ASTM E1755. *Standard Test Method for Ash in Biomass*, Version 01; ASTM International: West Conshohocken, PA, Nov. 5, 2007.
- (23) ASTM D3175. *Standard Test Methods for Volatile Matter in the Analysis Sample of Coal and Coke*, Version 07; ASTM International: West Conshohocken, PA, March 1, 2007.
- (24) ASTM D5373. *Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal*, Version 08; ASTM International: West Conshohocken, PA, March 1, 2008.
- (25) ASTM D4239. *Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion*, Version 10; ASTM International: West Conshohocken, PA, May 1, 2010.
- (26) Norrish, K.; Hutton, J. T. An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. *Geochim. Cosmochim. Acta* **1969**, *33*, 4431–4453.
- (27) Potts, P. J. A. *Handbook of Silicate Rock Analyses*; Blackie: Glasgow, 1987.
- (28) Govindaraju, K. 1994 Compilation of working values and sample description for 383 geostandards. *Geostandards Newslett.* **1994**, *18* (Special Issue), 1–158.
- (29) Jenner, G. A.; Longerich, H. P.; Jackson, S. E.; Fryer, B. J. ICP-MS—A powerful tool for high-precision trace-element analysis in Earth sciences: Evidence from analysis of selected U.S.G.S. reference samples. *Chem. Geol.* **1990**, *83*, 13–148.
- (30) Lachas, H.; Richaud, R.; Herod, A. A.; Dugwell, D. R.; Kandiyoti, R. Determination of trace elements by inductively coupled plasma mass spectrometry of biomass and fuel oil reference materials using milligram sample sizes. *Rapid Commun. Mass Spectrom.* **2000**, *14*, 335–343.
- (31) Rudnick, R. L.; Gao, S. Composition of the continental crust. In *Treatise on Geochemistry*, Vol. 3, *The Crust*; Rudnick, R. L., Ed.; Elsevier and Pergamon: Amsterdam, 2003; pp 1–90.
- (32) Knudsen, J. N.; Jensen, P. A.; Dam-Johansen, K. Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass. *Energy Fuels* **2004**, *18*, 1385–1399.
- (33) Björkman, E.; Strömberg, B. Release of chloride from biomass at pyrolysis and gasification conditions. *Energy Fuels* **1997**, *11*, 1026–1032.
- (34) Salo, K.; Mojtahedi, W. Fate of alkali and trace metals in biomass gasification. *Biomass Bioenergy* **1998**, *15*, 263–267.
- (35) Enders, M.; Willenborg, W.; Albrecht, J.; Putnis, A. Alkali retention in hot coal slag under controlled oxidizing gas atmospheres (air–CO₂). *Fuel Process. Technol.* **2000**, *68*, 57–73.
- (36) Marschner, H. *Mineral Nutrition of Higher Plants*; Academic Press: London, 1986.
- (37) May, W. E.; Rumble, J. *Certificate of Analysis NISTSMR 2709 San Joaquin Soil*; National Institute of Standards and Technology: Gaithersburg, MD, 2003.
- (38) *GeoRem, Geological and Environmental Reference Materials*; MPI für Chemie, Mainz, Germany, <http://georem.mpch-mainz.gwdg.de> (accessed March 2013).
- (39) Mackey, E. A.; Christopher, S. J.; Lindstrom, R. M.; Long, S. E.; et al. *Certification of Three NIST Renewal Soil Standard Reference Materials for Element Content: SRM 2709a San Joaquin Soil, SRM 2710a Montana Soil I, and SRM 2711a Montana Soil II*, NIST Special Publication 260-172; National Institute of Standards and Technology: Gaithersburg, MD, 2010.
- (40) Gavalas, N. A.; Clark, H. E. On the role of manganese in photosynthesis. *Plant Physiol.* **1971**, *47*, 139–143.
- (41) Haddy, A. Mn and photosynthetic systems. *Encyclopedia of Metalloproteins*; Springer, New York, <http://www.springerreference.com/docs/html/chapterdbid/313088.html> (accessed June 3, 2013).
- (42) Droppa, M.; Horvath, G. The role of copper in photosynthesis. *Crit. Rev. Plant Sci.* **2008**, *9*, 111–123.
- (43) Kosesakal, T.; Unal, M. Role of zinc deficiency in photosynthetic pigments and peroxidase activity of tomato seedlings. *IUFES J. Biol.* **2009**, *68*, 113–120.
- (44) Liaw, S. B.; Wu, H. Leaching characteristics of organic and inorganic matter from biomass by water: Differences between batch and semi-continuous operations. *Ind. Eng. Chem. Res.* **2013**, *52*, 4280–4289.
- (45) Schiegl, S.; Lev-Yadun, S.; Bar-Yosef, O.; El Goresy, A.; Weiner, S. Siliceous aggregates from prehistoric wood ash: A major component

of sediments in Kebara and Hayonim caves (Israel). *Isr. J. Earth Sci.* **1994**, *43*, 267–278.

(46) Jensen, P. A.; Frandsen, F. J.; Dam-Johansen, K.; Sanfer, B. Experimental investigation of the transformation and release to gas phase of potassium and chlorine during straw pyrolysis. *Energy Fuels* **2000**, *14*, 1280–1285.

(47) Novakovic, A.; van Lith, S. C.; Frandsen, F. J.; Jensen, P. A.; Holgersen, L. B. Release of potassium from the systems K–Ca–Si and K–Ca–P. *Energy Fuels* **2009**, *23*, 3423–3428.

(48) Thy, P.; Leshner, C. E.; Jenkins, B. M. Experimental determination of high temperature losses from biomass fuel ashes. *Fuel* **2000**, *79*, 693–700.

(49) Arvelakis, S.; Jensen, P. A.; Dam-Johansen, K. Simultaneous thermal analysis (STA) on ash from high-alkali biomass. *Energy Fuels* **2004**, *18*, 1066–1076.

(50) Bartels, M.; Lin, W.; Nijenhuis, J.; Kapteijn, F.; van Ommen, J. R. Agglomeration in fluidized beds at high temperatures: Mechanisms, detection, and prevention. *Prog. Energy Combust. Sci.* **2008**, *34*, 633–666.

(51) Jenkins, B. M.; Baxter, L. L.; Miles, T. R., Jr.; Miles, T. R. Combustion properties of biomass. *Fuel Process. Technol.* **1998**, *54*, 17–46.

(52) Yu, C. W.; Zheng, Y.; Cheng, Y.-S.; Jenkins, B. M.; Zhang, R.; VanderGheynst, J. S. Solid–liquid extraction of alkali metals and organic compounds by leaching of food industry residues. *Bioresour. Technol.* **2010**, *101*, 4331–4336.

(53) Bakker, R. R.; Jenkins, B. M.; Williams, R. B. Fluidized bed combustion of leached rice straw. *Energy Fuels* **2002**, *16*, 356–375.

(54) Jenkins, B. M.; Bakker, R. R.; Wei, J. B. On the properties of washed straw. *Biomass Bioenergy* **1996**, *10*, 177–200.

(55) Jenkins, B. M.; Mannapperuma, J. D.; Bakker, R. R. Biomass leachate treatment by reverse osmosis. *Fuel Process. Technol.* **2003**, *81*, 223–246.

(56) Dayton, D. C.; French, R. J.; Milne, T. A. Direct observation of alkali vapor release during biomass combustion and gasification. 1. Application of molecular beam mass spectrometry to switchgrass combustion. *Energy Fuels* **1995**, *9*, 855–865.

(57) Dayton, D. C.; Jenkins, B. M.; Turn, S. Q.; Bakker, R. R.; Williams, R. B.; Belle-Oudry, D.; Hill, L. M. Release of inorganic constituents from leached biomass during thermal conversion. *Energy Fuels* **1999**, *13*, 860–870.

(58) Olsson, J. G.; Jäglid, U.; Pettersson, J. B. C.; Hald, P. Alkali metal emission during pyrolysis of biomass. *Energy Fuels* **1997**, *11*, 779–784.

(59) Davidsson, K. O.; Stojkava, B. J.; Pettersson, J. B. C. Alkali emission from birchwood particles during rapid pyrolysis. *Energy Fuels* **2002**, *16*, 1033–1039.

(60) Okuno, T.; Sonoyama, N.; Hayashi, J.-I.; Li, C.-Z.; Sathem, C.; Chiba, T. Primary release of alkali and alkaline earth metallic species during pyrolysis of pulverized biomass. *Energy Fuels* **2005**, *19*, 2164–2171.