

Emissions of major gaseous and particulate species during experimental burns of southern African biomass

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[1] Characteristic vegetation and biofuels in major ecosystems of southern Africa were sampled during summer and autumn 2000 and burned under semicontrolled conditions. Elemental compositions of fuels and ash and emissions of CO₂, CO, CH₃COOH, HCOOH, NO_x, NH₃, HONO, HNO₃, HCl, total volatile inorganic Cl and Br, SO₂ and particulate C, N, and major ions were measured. Modified combustion efficiencies (MCEs, median = 0.94) were similar to those of ambient fires. Elemental emissions factors (EF_{el}) for CH₃COOH were inversely correlated with MCEs; EF_{el}s for heading and mixed grass fires were higher than those for backing fires of comparable MCEs. NO_x, NH₃, HONO, and particulate N accounted for a median of 22% of emitted N; HNO₃ emissions were insignificant. Grass fires with the highest EF_{el}s for NH₃ corresponded to MCEs in the range of 0.93; grass fires with higher and low MCEs exhibited lower EF_{el}s. NH₃ emissions for most fuels were poorly correlated with fuel N. Most Cl and Br in fuel was emitted during combustion (median for each = 73%). Inorganic gases and particulate ions accounted for medians of 53% and 30% of emitted Cl and Br, respectively. About half of volatile inorganic Cl was HCl indicating significant emissions of other gaseous inorganic Cl species. Most fuel S (median = 76%) was emitted during combustion; SO₂ and particulate SO₄²⁻ accounted for about half the flux. Mobilization of P by fire (median emission = 82%) implies large nutrient losses from burned regions and potentially important exogenous sources of fertilization for downwind ecosystems.

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1. Introduction

[2] Biomass burning is a major source for atmospheric pollutants [e.g., Crutzen *et al.*, 1979; Crutzen and Andreae, 1990; Andreae and Merlet, 2001]. The amount of carbon emitted to the atmosphere from the combustion of biomass is similar to that from fossil fuels [Crutzen and Andreae, 1990]. Currently, Africa accounts for about 35% of biomass burning globally (J. A. Logan and R. Yevich cited by Lobert *et al.* [1999]). The most abundant compounds emitted during

biomass burning are water vapor, carbon dioxide (CO₂) and carbon monoxide (CO). However, thousands other gaseous and particulate species have been detected in exhaust plumes [e.g., Johnson and Plimmer, 1959] with significant implications for atmospheric and biogeochemical cycles. In addition, chemical reactions rapidly (<1 hour) transform the compositions of fresh plumes [e.g., Trentmann *et al.*, 2005]; consequently, quantification of primary biomass-burning emissions is essential for resolving the chemical evolution of plumes and predicting associated environmental influences. Despite intense scientific study over the past three decades, however, global and regional emissions of many compounds are still poorly constrained.

[3] Emissions from open burning are controlled by a small number of highly variable factors including fuel moisture, physical size and arrangement of the fuel, and wind conditions. These factors regulate overall burning efficiency (e.g., the ratio of CO₂ emitted to total C emitted [e.g., Lobert and Warnatz, 1993]). Thus, as burning efficiency decreases, emissions of CO and organic C-containing compounds increase relative to CO₂. The elemental contents of biomass also influence corresponding emissions of N- [Hao *et al.*, 1991; Lobert *et al.*, 1991], S- [Delmas, 1982; Bingemer *et al.*, 1991], and halogen-containing compounds [e.g., Rasmussen *et al.*, 1980; Andreae *et al.*, 1996;

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Figure 1. Sampling locations in southern Africa, depicted in white.

Blake *et al.*, 1996; Lobert *et al.*, 1999]. Most N and S in biomass is associated with organic constituents whereas halogens exist primarily as electrolytes. During high-temperature combustion, these species often form reactive, short-lived intermediates that are emitted directly or recombine with carbon-containing fragments or hydrogen atoms to form more stable secondary products that are subsequently emitted [Lobert and Warnatz, 1993].

[4] Available evidence indicates that biomass-burning emissions represent major fluxes in regional or global budgets of nitrogen [e.g., Lobert *et al.*, 1991], sulfur [e.g., Bingemer *et al.*, 1991], chlorine [e.g., Lobert *et al.*, 1999], bromine, and iodine [Andreae *et al.*, 1996; Blake *et al.*, 1996; Ferek *et al.*, 1998]. Relative to those of C, however, our knowledge of speciated emissions of N-, S-, and halogen-containing compounds from different types of biomass burning is limited and, consequently, regional and global flux estimates are considerably more uncertain. In particular, the general lack of coupled data for the elemental composition of fuels and the corresponding speciated emissions during combustion seriously constrains current predictive capabilities [e.g., Lobert *et al.*, 1999].

[5] Under the auspices of the Southern Africa Regional Science Initiative during austral winter 2000 (SAFARI 2000), biomass-burning emissions were investigated in the savanna and Miombo ecosystems of Southern Africa [Swap *et al.*, 2003]. Multiple integrated approaches including semicontrolled experimental burns, prescribed burns, ambient burns of opportunity, measurements at surface sites and from aircraft, satellite imagery, and model calculations were employed to characterize the burned area, quantify local and regional fluxes, and evaluate environmental implications. In this paper, we report emission fluxes of CO₂, CO, NO_x (NO + NO₂) soluble reactive trace gases (CH₃COOH, HCOOH, NH₃, HONO, HNO₃, HCl, SO₂), total volatile inorganic Cl and Br, and particulate species (total C, CH₃COO⁻, HCOO⁻, (COO)₂⁻, total N, NH₄⁺, NO₃⁻, Cl⁻,

Br⁻, SO₄²⁻, PO₄²⁻, K⁺, Ca²⁺, Na⁺, and Mg²⁺) as functions of fuel composition and combustion conditions during 48 semicontrolled experimental burns of representative biomass types from the major ecosystems of southern Africa and of cow dung from India. Individual data for all experimental burns together with images of the sampling sites, fuels, and fires and related ancillary data are available for further evaluation through the project web site at <http://science.jurgenlobert.net/>.

2. Methods

2.1. Biomass Collection and Processing

[6] During August through October, 2000, characteristic vegetation and biofuels including grasses, shrubs, branches, litter, agricultural waste (maize stalks), and locally produced charcoal were sampled at multiple sites within the savanna grasslands of Etosha National Park, Namibia (ENP) and Kruger National Park, South Africa, (KNP); in the Miombo woodlands of Malawi (MAL); and in the Miombo dambos (grasslands) in the Zambezi River valley west of Mongu, Zambia (ZAM) (Figure 1 and Table 1). Fuels were collected by or in consultation with collaborating park rangers and scientists who worked in each region and were knowledgeable about local burning practices and conditions. Typically, 3 to 5 kg (wet weight) of major grasses and leafy material and 6 to 9 kg of branches were sampled at any given site. Fresh vegetation was weighed, air dried for 2 to 4 days, and reweighed on location; loosely packed in polyethylene-lined cardboard boxes; and express shipped to the Max Planck Institute (MPI) in Mainz, Germany. The packing procedure represented a compromise between the competing needs to minimize potential alteration of fuel composition during shipment via microbial activity versus contamination. The interior liners were left open to air exchange, which allowed samples to equilibrate with variations in temperature and relative humidity during shipment and thereby minimize microbial and fungal growth and associated alteration of chemical composition. The edges of the boxes were sealed with polyethylene tape, which minimized direct air exchange and associated contamination. Inspection upon receipt revealed no obvious signs of biological deterioration or contamination of samples. Samples were stored in an environmental chamber at ambient temperature and humidity until burned. Cow dung that had been sampled previously in India (IND) and similarly processed was also analyzed as part of this study.

2.2. Experimental Burns and Exhaust Sampling

[7] Between 11 November 2000 and 16 January 2001, biomass samples were reweighed at MPI; most were rehydrated to near ambient water contents by spraying with a fine mist of >18 MΩ cm⁻¹ deionized water (DIW) and incubating in sealed plastic bags for 1 to 2 days prior to combustion (Table 1). Samples were subsequently weighed and burned under semicontrolled conditions at the MPI burn facility; fresh exhaust for chemical analysis was sampled from the stack (approximately 2 m above the burn table) (see Lobert *et al.* [1990, 1991] for detailed description of the facility). Ambient air was similarly characterized. Fuel and residual ash were subsampled and analyzed for elemental constituents. In addition to the species described in more

Table 1. Biomass and Fire Characteristics^a

ID ^b	Fuel Type	Sampling Location	Burn Condition ^c	MCE, gC gC ⁻¹	CC, g g ⁻¹	Moisture, %	Elemental Content, g kg ⁻¹										Elemental Emission, %									
							C	N	Cl	Br	S	P	K	Ca	Na	Mg	C	N	Cl	Br	S	P	K	Ca	Na	Mg
<i>Etosha National Park, Namibia</i>																										
4	grass	Dungaries	heading	0.91	0.97	10.4	435	6.16	4.34	<0.0000	1.24	0.081	5.70	0.45	0.125	0.155	98	95	69	>100	59	81	71	73	77	85
8	grass	Okondeka	backing	0.93	0.99	10.0	415	7.02	9.86	0.0048	2.33	0.256	5.73	0.63	4.13	0.113	96	93	<0	98	35	82	19	65	<0	89
12	grass	Ombika	backing	0.93	0.98	9.5	422	7.52	6.68	0.0105	1.83	0.150	12.7	2.42	2.21	1.46	97	92	18	37	42	84	49	96	75	98
16	grass	DolomietP	heading	0.94	1.00	10.2	450	5.46	1.24	0.0039	0.87	0.715	7.00	1.53	0.084	0.826	95	86	<0	>100	43	87	54	92	82	92
20	grass	Okaukuejo	flat mixed	0.93	0.99	8.0	420	10.4	6.85	0.0074	2.78	0.339	11.5	0.78	0.878	0.328	94	89	46	17	30	95	55	89	63	96
7	shrubs	Okondeka	10° heading	0.91	0.93	20.2	412	16.5	19.4	0.0086	4.09	0.316	13.8	3.35	45.4	1.33	95	36	99	67	78	38	95	71	93	
15	shrubs	DolomietP	10° heading	0.90	0.92	20.2	471	11.5	2.91	0.0068	2.45	0.645	13.9	3.69	0.240	1.14	88	81	<0	<0	<0	96	<0	93	23	97
19	shrubs	Okaukuejo	10° heading	0.92	0.98	8.0	437	12.6	1.91	0.0030	1.01	0.021	6.68	4.24	1.16	1.03	95	96	<0	<0	<0	96	<0	93	<0	69
14	branches 4–6 cm	DolomietP	10° heading	0.94	0.99	2.5	452	6.80	1.00	0.0006	0.61	0.007	5.31	5.29	0.035	1.06	98	88	67	44	33	9	94	82	99	
18	branches <2 cm	Okaukuejo	10° heading	0.95	0.97	9.5	476	8.55	1.29	0.0047	0.91	0.190	5.79	7.06	0.503	1.12	99	98	71	57	40	99	3	99	66	99
17	litter	DolomietP	10° backing	0.92	0.60	9.1	444	9.94	1.52	0.0009	1.12	0.189	8.50	7.36	0.106	1.34	90	79	60	<0	58	82	76	91	83	93
<i>Miombo Woodlands, Malawi</i>																										
1	grass	Chimaliro	backing	0.95	0.98	16.7	451	3.39	1.57	0.0029	0.15	0.279	2.19	0.63	0.034	0.160	98	97	76	71	79	20	84	25	76	63
5a	grass	Chimaliro	heading	0.85	0.99	13.5	435	3.12	1.36	<0.0000	0.19	0.224	1.72	0.61	0.036	0.122	97	92	77	>100	82	83	85	86	86	87
5b	grass	Chimaliro	heading	0.97	0.98	13.5	435	3.12	1.36	<0.0000	0.19	0.224	1.72	0.61	0.036	0.122	98	96	89	>100	90	70	88	74	89	74
15	grass	Chimaliro	backing	0.96	0.98	10.6	450	2.84	0.98	0.0029	0.34	0.061	1.11	0.41	0.020	0.080	99	97	93	42	85	65	93	82	91	91
3	shrub	Chimaliro	10° heading	0.94	0.98	9.8	488	5.19	1.17	0.0061	0.26	0.698	7.24	3.74	0.041	1.062	99	98	71	88	83	99	-	-	-	-
11	shrub	Chimaliro	10° heading	0.93	0.90	11.8	472	4.64	1.14	0.0015	0.21	0.373	5.37	3.37	0.028	0.728	99	98	91	77	84	99	49	99	85	100
2	branches <2 cm ^d	Chimaliro	flat mixed	0.96	1.00	4.1	445	4.26	0.10	0.0039	0.27	0.106	1.91	7.93	0.074	0.682	97	97	95	>100	88	49	<0	93	21	63
6	branches <2 cm ^d	Chimaliro	10° mixed	0.95	0.98	4.8	455	4.42	0.14	0.0030	0.35	0.028	1.00	2.46	0.028	0.456	97	98	94	93	78	71	89	91	92	91
14	branches <2 cm ^d	Chimaliro	10° heading	0.95	0.91	3.6	468	4.91	0.17	0.0018	0.33	0.079	3.22	6.20	0.031	1.473	97	96	94	>100	85	94	24	95	78	99
9+5	litter+grass	Chimaliro	10° backing	0.86	0.94	12.7	468	7.87	0.70	0.0006	0.46	0.467	5.01	3.98	0.085	0.520	91	89	<0	<0	75	91	86	96	91	96
12a	ag waste, maize ^d	Chimaliro	25° backing	0.94	0.99	3.4	444	4.07	1.41	0.0017	0.32	0.281	12.50	0.88	0.030	0.358	98	98	70	<0	92	94	<0	99	94	99
12b	ag waste, maize ^d	Chimaliro	25° backing	0.93	0.91	3.4	444	4.07	1.41	0.0017	0.32	0.281	12.50	0.88	0.030	0.358	98	98	70	<0	92	94	<0	99	94	99
19	ag waste, maize ^d	Mpilisi	flat mixed	0.97	1.00	2.9	441	3.32	0.72	0.0028	0.24	0.079	5.17	0.64	0.062	0.264	99	96	67	>100	77	99	80	78	88	73
20	ag waste, maize ^d	Mpilisi	10° heading	0.96	0.98	3.3	417	3.89	0.84	0.0034	0.33	0.086	4.90	0.39	0.104	0.146	98	92	78	82	80	74	95	85	92	84
17a	charcoal ^d	Mpilisi	flat oven	0.81	0.97	3.8	824	4.42	0.83	0.0014	0.27	0.427	5.65	3.63	0.049	0.910	99	99	87	77	99	44	99	80	80	100
17b	charcoal ^d	Mpilisi	flat oven	0.85	1.00	3.8	824	4.42	0.83	0.0014	0.27	0.288	5.65	3.63	0.049	0.910	97	95	100	>100	<0	79	20	78	55	78
<i>Miombo Dambos (Grasslands), Zambia</i>																										
2	grass ^d	Site 2	mixed	0.95	0.99	4.4	441	6.10	0.50	0.0026	0.46	0.022	1.17	0.10	0.045	0.032	96	92	82	69	78	41	90	31	87	77
3	grass ^d	Site 2	backing	0.96	1.00	7.2	432	3.97	0.51	0.0043	0.55	0.025	2.62	0.12	0.202	0.042	99	98	88	65	76	90	90	66	85	84
7	grass	Site 2	backing	0.90	0.96	40.1	421	4.17	2.21	0.0041	0.91	0.032	2.11	0.24	0.242	0.034	99	96	69	62	68	16	64	<0	60	<0
8	grass	Site 2	backing	0.91	0.97	38.9	434	4.37	1.47	0.0045	1.11	0.033	2.28	0.27	0.523	0.060	99	98	81	66	70	71	81	20	82	47
9	grass	Site 2	heading	0.89	0.99	33.1	435	4.16	2.14	0.0053	0.88	0.028	2.84	0.20	0.238	0.048	98	96	83	80	66	94	82	55	72	75
<i>Kruger National Park, South Africa</i>																										
2a	grass	Skukuza	backing	0.92	0.99	43.9	438	6.90	2.09	0.0022	1.68	0.212	1.60	0.44	0.536	0.124	97	94	65	2	63	87	80	74	83	89
2b	grass	Skukuza	backing	0.88	0.96	43.9	438	6.90	2.09	0.0022	1.68	0.212	1.60	0.44	0.536	0.124	98	95	62	21	59	82	76	60	83	86
3	grass	Skukuza	backing	0.95	0.98	32.9	426	5.93	1.50	0.0050	1.07	0.170	0.77	0.15	0.141	0.037	97	94	53	64	58	70	57	<0	1	36
5	grass ^d	Skukuza	heading	0.96	0.99	3.3	440	5.23	1.32	0.0038	1.11	0.170	1.09	0.23	0.117	0.028	96	88	73	97	59	84	85	27	71	<0
6	grass ^d	Skukuza	heading	0.95	0.99	2.5	430	8.57	1.39	0.0040	1.58	0.176	1.68	0.40	0.422	0.113	96	91	70	68	59	83	87	51	88	63
7	grass ^d	Skukuza	mixed	0.95	0.99	5.4	422	9.22	1.75	0.0026	1.76	0.192	2.09	0.30	0.310	0.086	96	91	58	>100	61	87	81	57	82	84
9	grass	Skukuza	backing	0.94	0.99	40.7	432	7.78	1.51	0.0041	1.38	0.120	2.31	0.55	0.286	0.112	96	91	52	55	63	58	80	58	87	78
10	grass	Skukuza	backing	0.96	0.99	24.3	433	5.89	1.24	0.0002	1.19	0.297	1.63	0.22	0.243	0.070	98	95	78	<0	82	75	90	<0	89	28
12	grass	Satara	backing	0.93	0.98	26.2	419	7.58	1.33	0.0036	1.17	0.717	2.75	0.60	0.569	0.222	96	94	44	55	77	11	79	<0	69	<0
13	grass	Satara	backing	0.98	0.98	14.9	421	6.51	1.37	0.0027	1.29	0.675	2.20	0.58	0.294	0.222	93	93	77	73	88	50	68	50	78	42

Table 1. (continued)

ID ^b	Fuel Type	Sampling Location	Burn Condition ^c	MCE, gC gC ⁻¹	CC, g g ⁻¹	Moisture, %	Elemental Content, g kg ⁻¹										Elemental Emission, %									
							C	N	Cl	Br	S	P	K	Ca	Na	Mg	C	N	Cl	Br	S	P	K	Ca	Na	Mg
15	grass ^d	Satara	mixed	0.96	0.99	2.7	416	4.19	1.37	0.0016	1.01	0.654	1.57	0.17	0.514	0.060	98	91	75	31	81	39	80	<0	61	<0
16a	grass	Satara	25° backing	0.95	0.97	37.6	424	5.83	1.60	0.0049	0.96	0.284	1.86	0.33	0.454	0.122	98	95	56	75	78	51	82	5	81	65
16b	grass ^d	Satara	heading	0.90	0.99	3.4	424	5.83	1.60	0.0049	0.96	0.284	1.86	0.33	0.454	0.122	98	94	59	83	77	49	77	17	80	69
18	grass	Satara	heading	0.97	0.96	17.7	428	3.93	0.69	0.0036	0.73	0.677	1.27	0.48	0.067	0.111	95	92	80	>100	83	59	55	64	53	18
20	grass	Satara	25° backing	0.98	0.99	15.1	436	5.83	0.87	0.0044	0.76	0.700	2.52	0.46	0.055	0.113	91	90	81	>100	89	31	54	25	53	25
22	grass	Satara	backing	0.96	0.96	23.9	428	4.88	1.00	0.0071	0.72	0.673	2.16	0.21	0.051	0.088	94	91	74	87	82	44	66	<0	28	<0
23	grass	Satara	backing	0.97	0.97	24.1	436	4.48	0.75	0.0033	0.68	0.827	2.28	0.30	0.079	0.081	90	87	54	57	75	34	46	<0	<0	<0
4a	branches <1 cm	Skukuza	10° heading	0.95	0.94	4.5	477	6.27	1.12	0.0039	0.54	0.133	4.22	7.37	0.288	0.784	99	99	91	94	90	100	37	100	87	97
4b	branches <1 cm	Skukuza	10° heading	0.94	0.94	4.5	477	6.27	1.12	0.0039	0.54	0.133	4.22	7.37	0.288	0.784	98	99	91	98	94	100	-	-	-	-
11	branches <1 cm	Skukuza	10° heading	0.94	0.96	7.8	481	8.53	0.82	0.0026	0.62	0.056	2.01	7.01	0.197	0.503	98	99	92	86	93	99	<0	87	72	99
17	branches <2 cm	Satara	10° heading	0.95	0.94	8.7	464	7.01	1.07	0.0022	0.62	0.256	5.20	5.18	0.215	0.598	97	99	85	92	90	100	9	86	62	99
19	branches <2 cm	Satara	10° mixed	0.94	0.91	13.9	471	7.12	1.64	0.0041	0.55	0.242	5.16	9.19	0.413	1.043	98	99	86	92	73	100	15	96	63	100
8	litter/leaves	Skukuza	backing	0.91	0.97	27.4	453	13.5	0.63	0.0020	1.13	0.138	2.00	3.60	0.365	0.687	96	95	82	<0	76	100	77	84	93	93
1a	cow dung ^d		flat oven	0.82	1.00	4.5	326	16.7	2.38	0.0087	3.02	0.976	3.19	0.87	0.640	0.355	99	97	39	30	67	36	9	<0	2	<0
1b	cow dung ^d		10° open	0.85	1.00	1.9	326	16.7	2.38	0.0087	3.02	0.976	3.19	0.87	0.640	0.355	96	88	7	<0	45	<0	33	<0	2	<0
75th percent				0.95	0.99	20.19	453	7.58	1.64	0.0045	1.19	0.373	5.65	3.63	0.454	0.784	98	97	85	97	83	94	81	93	86	96
Median				0.94	0.98	9.78	437	5.89	1.36	0.0034	0.87	0.224	2.75	0.63	0.202	0.222	97	95	73	73	76	82	66	74	78	84
25th percent				0.91	0.96	4.36	426	4.37	0.87	0.0020	0.35	0.106	1.86	0.39	0.051	0.112	96	92	56	37	59	51	29	26	62	55

^aBranches refer to woody plant material of indicated diameter. Elemental contents are based on oven dry weights; moisture contents were at time of burn. Emitted percentages correspond to total dry mass of volatilized fuel (excluding unburned residual). Values below detection limits are included to provide reliable sample statistics; individual negative values and percentages >100 reflect relatively large accumulated measurement uncertainties; see text. Dashes depict missing data.

^bThe letters a and b indicate independent experimental burns of the same biomass sample.

^cUnless otherwise noted, the burn table was set at an angle of 30°.

^dBiomass sample not rehydrated prior to burn.

detail below, collaborating investigators analyzed the exhaust for CH₄ and N₂O with gas chromatography (GC), methyl halides with GC mass spectrometry (GC-MS), SO₂ and volatile organics with atmospheric pressure chemical ionization (AP) MS [Jost, 2002], volatile organics with proton transfer reaction (PTR) MS, and speciated particulate organic and elemental carbon. Hg was also measured in a subset of paired fuel and ash samples [Friedli *et al.*, 2003]. Wet weight of fuels burned during individual fires ranged from about 0.5 to 0.7 kg for grasses to about 2 kg for branches. Fire durations ranged from about 5 min for dryer savanna grasses to several hours for larger branches, charcoal, and dung; typically, two experimental burns were conducted each day. Combustion temperature, emitted biomass (via weight loss), and the mass flux of exhaust through the stack were monitored continuously during each experiment. The angle of the burn table and the initial ignition point of the fire were varied to simulate a range of different burn conditions (Table 1). Three basic fire types were evaluated. Backing fires were ignited on the downwind (top) elevation of the table, heading fires were ignited on the upwind (bottom) elevation of the table, and mixed fires that include both backing and heading components were ignited in the center or on the side. To qualitatively evaluate the influence of regional stoves on emission fluxes from the combustion of charcoal and dung, a small brick oven was assembled on the burn table for some experiments and preheated prior to igniting the fuel.

2.3. Elemental Contents of Biomass and Ash

[8] At MPI, representative air-dried subsamples of biomass and fresh subsamples of ash were milled to pass through a 1 mm screen and then through a 0.08 mm screen yielding a mean particle size of about 60 μm [Lobert, 1989]. Samples were then weighed, dried at 72°C for 48 hours [e.g., McKenzie *et al.*, 1996] cooled in a desiccator, reweighed, stored in sealed glass containers, and transported to the University of Virginia (UVA) for analysis. At UVA, subsamples of approximately 100 mg each were analyzed in triplicate for C and N on a Thermoquest CE (Carlo Erba) Model NA Elemental Analyzer. The instrument was calibrated with atropine (C = 70.6%; N = 9.39%) at the beginning and end of each analytical run. Methionine (C = 40.3%; N = 9.39%), atropine, and blanks were analyzed as unknowns between each set of approximately 10 samples. Results indicate that the data are unbiased. Average analytical detection limits (DLs; defined here as twice the average standard deviation for replicate sets of analyses of samples) for biomass were 0.0056 kg C kg_{dry wt}⁻¹ and 0.28 g N kg_{dry wt}⁻¹ and for ash were 0.0054 kg C kg_{dry wt}⁻¹ and 0.13 g N kg_{dry wt}⁻¹.

[9] One gram of each sample was oxidized at 25 atm O₂ in a Parr bomb containing 10 mL of 5 mN Li₂CO₃ and extracted with deionized water to a final volume of approximately 50 mL. The Parr bomb was blanked with benzoic acid. H₂O₂ was added to extracts prior to analyzing SO₄²⁻ and PO₄³⁻ and H₄N₂ was added prior to analysis of Br⁻ and I⁻ [e.g., Smith *et al.*, 1977; Butler *et al.*, 1979; Rubin, 1987]. Extracts were subsequently analyzed for the above anions and for base cations (K⁺, Ca²⁺, Na⁺ and Mg²⁺) by ion chromatography (IC) on a Dionex 4000 series instrument. Performance was verified by analysis of standard additions

and audit solutions traceable to the National Institute of Standards and Technology. Average DLs (estimated as twice the average standard deviation for replicate analyses of low-concentration standard solutions) for S, P, Cl, Br, and I content of biomass were 9.1, 6.6, 21, 4.3, and 30 mg kg_{dry wt}⁻¹, respectively, and those of ash were 2.4, 5.1, 33, 2.2, and 39 mg kg_{dry wt}⁻¹, respectively. The I contents of all samples were below the DL. Average DLs for K, Ca, Na and Mg in biomass and ash were 74, 2.5, 13, and 15 mg kg_{dry wt}⁻¹, respectively. Replicates and splits were routinely processed and analyzed. Data for field replicates (paired subsamples of biomass that were processed independently, N = 3), field splits (paired subsamples of biomass that were partitioned after grinding and subsequently processed independently; N = 5), and lab splits of biomass (N = 6) and ash (N = 7) were averaged for evaluation of associated emissions from individual fires.

2.4. CO₂, CO, and NO_x

[10] Subsamples of exhaust streams for analysis of CO₂ and CO were continuously pumped through a cold trap (-20°C), a glass fiber filter (Alltech) and a stainless steel sinter filter (Valco). Streams were then split and dynamically diluted into the analytical ranges of the instrument. Sampling rates were regulated with mass flow controllers. Both gases were quantified using two nondispersive infrared analyzers (model BINOS, Heraeus) each of which operated at two different concentration ranges. The CO₂ instrument contained two separate cells with ranges of 0–1500 ppmv and 0–6 Vol-%, respectively; the CO instrument contained a single cell that was electronically split into ranges of 0–100 ppmv and 0–2000 ppmv. The DL for both instruments was about 5 ppmv.

[11] Subsamples of the exhaust stream for analysis of NO_x (NO + NO₂) were continuously pumped through a heated, 6.3 mm OD by 8-m long Teflon tube followed by a Teflon filter (0.5 μm, Supelco) and a cold trap (-20°C). NO_x was quantified by chemiluminescence using a Thermo Electron Model 14A analyzer equipped with a stainless steel converter maintained at 600°C to minimize interference by acetonitrile and other nitrogen-containing compounds [Lobert *et al.*, 1991]. The detection limit was about 50 ppbv. All three instruments were routinely calibrated with commercial standard gas mixtures (Steininger) in the measured concentration ranges.

2.5. Water-Soluble Reactive Trace Gases

[12] Soluble carbon- (CH₃COOH, HCOOH), nitrogen- (NH₃, HONO, HNO₃), chlorine- (primarily HCl), and sulfur- (SO₂) containing gases in the exhaust were sampled at a nominal rate of 20 L min⁻¹ with tandem mist chambers (MCs) each of which contained 20 mL of DIW [e.g., Russell *et al.*, 2003; Keene *et al.*, 2004]. All air volumes reported herein were measured with mass flowmeters normalized to 0°C and 1 atm. Sample exhaust was pulled through a 47 mm quartz filter (Pallflex QAT-UP 2500) mounted in a stainless steel housing attached to the stack followed by an insulated 4.76 mm ID by 1.5-m long Teflon tube and a 47 mm Teflon filter (Gelman, 2 μm pore size) before entering the first chamber. The residence time of sample air in the inlet was approximately 0.1 second. Evaporative losses of mist solutions were manually replaced during

operation to minimize variability in collection efficiencies [e.g., Keene *et al.*, 1993]. Dissolved ions in exposed mist solutions were measured on site (generally within a few hours after recovery) by IC using Dionex 4000 series instruments. Testing during the initial stages of the experiment revealed significant condensation of analytes, water, and other species on the walls of the insulated Teflon inlet and the Teflon filter. Consequently, condensed analytes upstream of the first mist chamber were quantitatively (>95%) extracted by flushing exposed surfaces of the tube, filter, and housing with two sequential 5 mL DIW rinses. These rinses were subsequently analyzed and included in the calculation of concentrations in the exhaust; associated analytical uncertainties were also incorporated in estimating overall precisions and detection limits (reported below). Median recoveries of CH₃COOH, HCOOH, NH₃, HONO, HCl, and SO₂ from the inlet corresponded to 21%, 25%, 28%, 3%, >98%, and 16%, respectively, of total concentrations. It is evident that reliable measurement of such rapidly condensing gases in fresh biomass-burning exhaust requires quantitative extraction and analysis of exposed surfaces upstream of sampling media or detectors. Dynamic blanks were collected prior to each sample by loading chambers with DIW and pulling clean air [Keene *et al.*, 1993] through the system for approximately 10 seconds. Thereafter blanks were processed using the same procedures as samples. Ambient air was sampled over 1-hour intervals prior to the first experimental burn each day and characterized for soluble trace gases (and for volatile inorganic halogens and particulate species, described below) using similar procedures.

[13] Performance characteristics of the standard MC-IC technique for most of these compounds in ambient air have been critically evaluated [see Keene *et al.*, 2004, and references therein]; those for HONO are discussed below. Collection efficiencies for all species in ambient air are greater than 95%. To our knowledge, however, performance of this approach when sampling fresh biomass-burning emissions have not been critically evaluated previously. Comparison of measured concentrations of analytes in the upstream and downstream mist solutions indicated somewhat lower collection efficiencies for some analytes in biomass-burning emissions relative to ambient air. On the basis of the assumption that a given compound was sampled with equal efficiency in both tandem chambers, the collection efficiencies and original mixing ratios in the burn exhaust were calculated directly. Median collection efficiencies for the tandem system ranged from a low of 74% for SO₂ to a high of >98% for NH₃ and HCl.

[14] Fresh mist solutions that were analyzed immediately after recovery contained significant concentrations of NO₂⁻ (presumably from HONO dissolution) but virtually no NO₃⁻ (from HNO₃ dissolution). However, sequential, time series analyses of stored samples revealed that NO₂⁻ was quantitatively oxidized to NO₃⁻ over periods of 5 to 48 hours. We infer that HONO was the primary source for both NO₂⁻ and NO₃⁻ in mist solutions and that HNO₃ was produced by secondary reactions. Reported fluxes of HONO correspond to the measured sum of NO₂⁻ plus NO₃⁻ in exposed mist solutions and inlet flushes. Performance characteristics of the MC-IC technique for HONO have not been rigorously characterized. However, HONO in polluted coastal air at

Appledore Island, MA, USA (43.0°N, 70.6°W) during July 2004 was measured in parallel by both MC-IC and long-path differential optical absorption spectroscopy (DOAS) with a path length of 4.6 km [Stutz *et al.*, 2002; J. Stutz, University of California, Los Angeles, unpublished data, 2005]. The mist chamber samplers were deployed on a tower (~43 m asl) and configured and operated using established procedures [e.g., Keene *et al.*, 2004]; the DOAS telescope and spectrophotometer were positioned approximately 8 m below. Individual DOAS measurements were averaged over each MC sampling interval. A reduced major axis regression (RMA [Hirsch and Gilroy, 1984]) of all paired MC-IC (Y axis) versus DOAS (X axis) data yielded a significant linear correlation (slope = 1.2, intercept = 49, r² = 0.57, N = 22, range <45 to 730 pptv); the slope and intercept were not significantly different from 1 and 0, respectively. About half of the DOAS observations were below DLs and thereby constrained resolution of the inter-comparison. Although these results indicate reasonable agreement with an established technique, fluxes reported herein are considered semiquantitative (because of limited testing) and upper limits (based on published evidence that HONO may be produced via artifact reactions [e.g., Zhou *et al.*, 2002]).

[15] Average DLs for NH₃, HONO, CH₃COOH, HCOOH, HCl, and SO₂ in burn exhaust were 0.80, 6.2, 47, 5.6, 3.2, and 1.2 ppbv, respectively. The average mixing ratios of all analytes in ambient air were less than 0.5% of those in fire emissions and, consequently, were ignored in calculating fluxes.

2.6. Volatile Inorganic Halogens

[16] Volatile, inorganic Cl, Br, and I in burn exhaust were sampled at an average flow rate of 95 L min⁻¹ immediately downstream of the stack using a filter pack [e.g., Li *et al.*, 1994; Pszenny *et al.*, 2004, and references therein]. Particles were removed by drawing sample air through a 142-mm-diameter quartz fiber filter (Pallflex QAT-UP 2500) mounted in a stainless steel housing attached to the stack and gases were sampled quantitatively downstream on tandem 90 mm Rayon filters (Schleicher and Schuell 8S) impregnated with 10% K₂CO₃ -10% glycerol and mounted in a Delrin housing. Flow was measured with a mass flowmeter.

[17] Exposed quartz fiber and impregnated rayon filters were transferred to sealed polyethylene bags, placed in airtight Mason jars to prevent gas exchange, and stored frozen until analysis. At UVA, entire impregnated filters were extracted under sonication in 20 mL DIW and analyzed for halogen ions by IC. Average DLs for volatile inorganic Cl and Br in the burn exhaust were 2.0 and 0.4 ppbv, respectively; volatile I was undetectable. Analysis of tandem filters indicated collection efficiencies greater than 97% for both Cl and Br gases.

2.7. Particulate Species

[18] In a clean bench at UVA, two or three strips (approximately 6 × 67 mm each) were cut from exposed portions of the quartz filters described above, measured and independently analyzed for total particulate C and N on a Thermoquest CE (Carlo Erba) Model NA Elemental Analyzer. Calibration procedures were similar to those de-

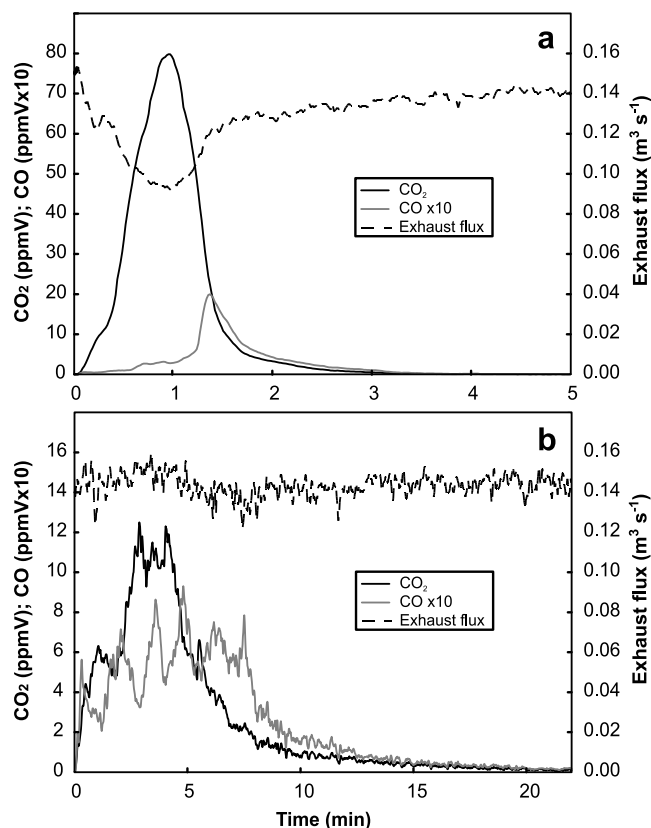


Figure 2. Molar mixing ratios of CO₂ (solid line) and CO (shaded line) and the mass flux of exhaust through the stack normalized to standard temperature (0°C) and pressure (1 atm) (dashed line) during typical experimental burns of (a) grass (Kruger sample 13) and (b) shrubs (Etosha sample 7).

scribed for biomass and ash samples and average detection limits were 0.25 mmol C m⁻³ and 8.4 μmol N m⁻³. Half sections of each quartz filter were extracted under sonication in DIW and analyzed for soluble ionic constituents [including total (dissociated + undissociated) NH₄⁺, NO₃⁻, CH₃COO⁻, HCOO⁻, (COO)⁻², Cl⁻, Br⁻, SO₄²⁻, PO₄³⁻, K⁺, Ca²⁺, Na⁺, and Mg²⁺] by IC. Corresponding DLs were <0.001, 0.038, 0.15, 0.028, <0.001, 0.075, 0.013, 0.017, 0.030, 0.037, 0.058, 0.18, and 0.046 μmol m⁻³, respectively.

2.8. Measurement Uncertainties

[19] In addition to random analytical errors summarized above, two other important sources of uncertainty constrain interpretation of results reported herein. A detailed evaluation of chemical variability within components of individual biomass samples (e.g., seeds, leaves, and stems of a given grass sample) was beyond the scope of this study. The representativeness of biomass subsampled for chemical analysis and for experimental burns was based on visual inspection. Elemental data for paired field replicates of grass samples generally agreed within ±15% suggesting that subsamples of such fairly homogeneous fuels were representative. The consistency in percentage emissions of elemental constituents from paired independent burns of

separate subsamples of the same fuels (Table 1) also indicate that subsampling was generally representative. However, some elemental components (including P, Br, and base cations) of paired subsamples of Indian dung varied by greater than a factor of two. On the basis of these results, we infer that nonrepresentative subsampling contributed to divergence in emissions of some analytes during independent burns of dung (Table 1). Data for other more heterogeneous fuel types may be similarly impacted. We return to this issue below.

[20] With the exception of CO₂, CO, and NO_x, data reported herein correspond to integrated samples collected at near-constant rates over entire durations of individual fires. Because the density of the exhaust varied as a function of temperature, the mass flux of exhaust through the stack varied (typically by about 5% to 40%) during most burns (e.g., Figure 2). Some compounds (e.g., CO₂) are emitted preferentially under hotter, flaming conditions whereas others (e.g., CO) are emitted preferentially under cooler, smoldering conditions. Consequently, concentrations and associated emission fluxes of individual compounds did not always vary in direct proportion with the mass flux of burn exhaust. To evaluate the corresponding potential magnitude of error in emission fluxes estimated from integrated samples, we calculated and compared the integrated emission fluxes of CO₂ and CO depicted in Figure 2 using two different approaches: (1) The individual paired measurements of concentrations and mass fluxes during the course of each burn and (2) the average concentration of each compound in the exhaust and the corresponding total mass flux through the stack over the entire burn. The latter approach is analogous to estimating fluxes on the basis of integrated samples collected at constant rates. Relative to those based on the individual paired measurements, the emission fluxes of CO₂ and CO calculated from average concentrations over the durations of the burns were 24% and 6% higher, respectively, for the grass fire and 2% lower and <1% higher, respectively, for the shrub fire. Comparisons based on data from other experimental burns yielded similar results. These comparisons suggest that integrated sampling for compounds emitted primarily during the flaming stage of high-temperature grass fires overestimated emission fluxes by 15% to 25%. For lower-temperature fires and for compounds emitted primarily under smoldering conditions, integrated sampling yielded representative emission fluxes. Given the relatively large accumulated uncertainties in quantifying biomass-burning emissions, our analysis will focus primarily on sample statistics for central tendencies including median values and the middle 50th (i.e., 25th through 75th) percentile of results.

2.9. Calculations

[21] Emission fluxes are reported using three common conventions.

[22] 1. The standard emission factor (EF_{st-x}) for species (x) is defined as

$$EF_{st-x} = \frac{M_x}{M_{biomass}}$$

where M_x is the integrated mass (molecular, ionic, or elemental) in grams of species X measured in the exhaust

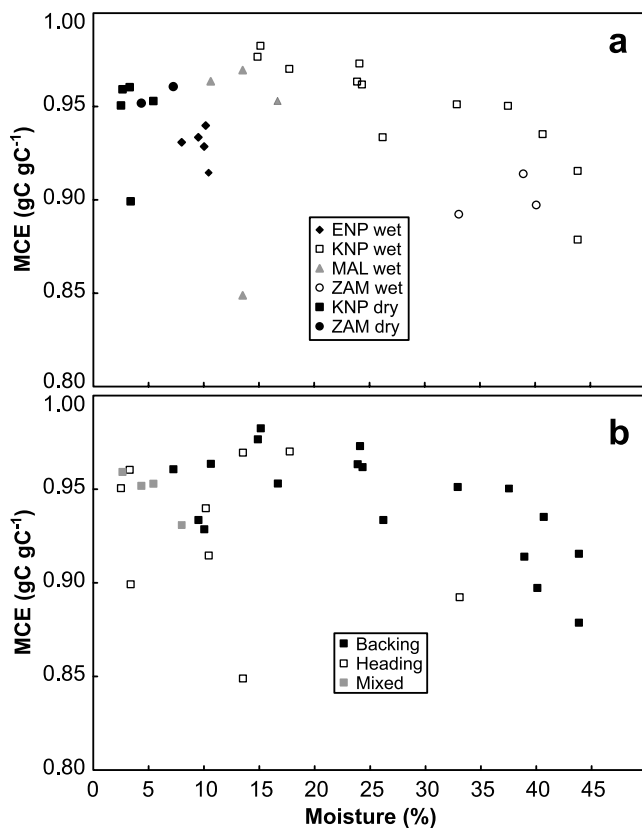


Figure 3. MCE versus moisture content for experimental burns of grass as functions of (a) region and rehydration and (b) type of burn.

over the course of a fire and M_{biomass} is the corresponding mass in kilograms dry weight of biomass that is burned and emitted (i.e., excluding ash and any unburned fuel).

[23] 2. The elemental emission factor (ER_{el}) is defined as

$$EF_{el-X} = \frac{M_{el-X}}{M_{el-biomass}}$$

where M_{el-X} is the integrated mass in grams of a given element associated with species X measured in the exhaust and $M_{el-biomass}$ is the corresponding mass in kilograms of that element associated with the biomass that is burned and emitted.

[24] 3. Molar emission ratios relative to CO (ER_{CO}) and CO₂ (ER_{CO_2}) are defined as (using CO as an example)

$$ER_{CO} = \frac{Mol_X}{Mol_{CO}}$$

where Mol_X is the integrated molar mixing ratio of species X measured in the exhaust and Mol_{CO} is the corresponding integrated molar mixing ratio of CO. The following analysis focuses primarily on interpretation of $EF_{el,s}$ and $EF_{st,s}$ for soluble reactive trace gases and particulate species.

[25] The modified combustion efficiency (MCE) is an important diagnostic of corresponding emission fluxes.

$$MCE = \frac{CO_2}{CO_2 + CO}$$

where all units are based on g C.

3. Results and Discussion

3.1. Fire Characteristics

[26] MCEs for most burns fell within a fairly narrow range (Table 1 and Figure 3). The middle 50th percentile range for all burns (0.91 to 0.95 g C g C⁻¹) was very similar to the reported range for ambient savanna fires in southern Africa (e.g., 0.90 to 0.95 g C g C⁻¹ [Ward *et al.*, 1996]). Both the moisture content of fuel and the nature of the burn (backing, heading, or mixed) influenced MCE. For the subset of experimental burns involving grasses, as moisture contents increased from about 20% to 44%, corresponding MCEs decreased from greater than 0.95 to less than 0.90 (Figure 3). Although the MCEs for some heading fires fell within the range of those for backing fires involving grasses of comparable moisture content, others were substantially lower. The four lowest MCE values for the subset of fires involving grasses with moisture contents less than 35% (N = 25) were all associated with heading fires (Figure 3b). Results also suggest regional differences in these relationships. Backing fires involving grasses from ENP were systematically lower than those of comparable moisture contents from other regions (Figure 3a). Relative to other fuels, the two processed biofuels (charcoal and dung) exhibited lower MCEs ranging from 0.81 to 0.85 g C g C⁻¹. Dung burned on an open platform and within a brick oven yielded similar values suggesting that the lower MCEs for this biofuel (and perhaps for charcoal) were primarily a function of fuel characteristics rather than the nature of combustion. Combustion completeness [CC = (initial dry wt. of biomass – the dry wt. of residual unburned biomass)/initial dry wt. of biomass] for most fires during this investigation (Table 1) were generally higher than those for ambient fires in southern Africa (e.g., 0.87 to 0.94 [Ward *et al.*, 1996]; 0.30 to 0.95 [Hély *et al.*, 2003]).

3.2. Carbon

[27] With the exception of charcoal and cow dung, the carbon contents of fuels fell within a relatively narrow range and virtually all (median = 97%) was emitted during combustion (Table 1). On the basis of median values, CO₂ and CO accounted for greater than 99% of the estimated carbon flux (Tables 2a–2d) and median $EF_{st,s}$ for these compounds generally fell within the ranges of reported values (Table 3). On the basis of median values, total particulate C accounted for about 1% and gaseous carboxylic acids about 0.2% of the C emission flux. Particulate CH₃COO⁻, HCOO⁻, and (COO)₂⁻ typically accounted for <1% of total particulate C (Table 2). $EF_{st,s}$ for particulate C during these experimental burns were generally within the range of values reported in the literature but those for gaseous carboxylic acids tend to be somewhat lower (Table 3). Most previously published emission factors for the carboxylic acids were based on measurements in plumes from ambient fires. Carboxylic acids are produced rapidly (<1 hour) as emissions age [Yokelson *et al.*, 2003; Trentmann *et al.*, 2005] and, consequently, measurements in ambient plumes reflect contributions from both primary emissions and secondary production. Relative differences in the ages of sampled plumes thereby contribute to the somewhat lower EF_{el,s} for carboxylic acids measured in fresh emissions during this study. The nature of the burn also influenced $EF_{el,s}$ for carboxylic acids. For example, during

Table 2a. Summary Statistics for Standard Emission Factors (EF_{st})^a

Analyte	Grass			Shrub			Branches			Litter			Agricultural Waste			Charcoal		Cow Dung		
	75th	50th	25th	N	75th	50th	25th	N	75th	50th	25th	N	75th	50th	25th	N	50th	N		
CO ₂	1729	1626	1552	31	1967	1641	1562	5	1755	1664	1628	10	1566	1532	1319	4	2755	2	899	2
CO	77.4	53.1	41.6	31	103	86.2	84.3	5	69.0	62.9	58.2	10	108	106	97.4	4	351	2	106	2
CH ₃ COOH	2.16	1.34	0.82	28		0.85		2	1.07	0.87	0.62	7	8.15	5.49	3.44	3	0.49	1	7.85	2
HCOOH	0.262	0.164	0.089	28		0.085		2	0.094	0.079	0.054	7	0.778	0.471	0.246	3	0.079	1	0.497	2
Part. CH ₃ COO ⁻	0.165	0.026	<DL	30		0.013		2	0.002	<DL	<DL	8	2.14	1.45	1.02	3	0.008	2	0.758	2
Part. (COO) ₂ ²⁻	0.007	<DL	<DL	30		0.006		2	<DL	<DL	<DL	8	0.005	<DL	<DL	3	0.0003	2	0.018	2
Part. C	11.2	5.3	2.8	30		4.2		2	2.0	1.5	1.4	7	39.6	26.8	21.6	3	0.3	1	22.9	2
NO _x ^b	2.02	1.80	1.52	31	3.92	0.65	0.58	5	1.89	1.81	1.69	10	2.09	2.03	1.25	3	1.27	2	0.50	2
NH ₃	0.119	0.056	0.031	28		0.639		2	0.476	0.403	0.279	7	1.37	0.973	0.701	3	0.224	1	3.543	2
HONO	0.198	0.135	0.098	28		0.239		2	0.225	0.188	0.107	7	0.407	0.345	0.203	3	0.205	2	0.238	2
Part. NH ₄ ⁺	0.099	0.049	0.029	30		0.126		2	0.019	0.014	0.010	8	0.403	0.392	0.294	3	0.0003	2	0.445	2
Part. NO ₃ ⁻	0.013	0.007	0.004	30		0.030		2	0.017	0.015	0.013	8	0.053	0.044	0.040	3	0.004	2	0.025	2
Part. N	0.371	0.192	0.137	30		0.385		2	0.063	0.058	0.051	7	1.61	1.59	1.30	3	0.029	2	2.08	2
HCl	0.265	0.188	0.107	17		0.023		2	0.032	0.017	0.010	7	0.005	<DL	<DL	2	0.035	2	0.002	2
Inorg. Cl _g	0.518	0.316	0.239	30	0.079	0.047	0.029	3	0.056	0.032	0.018	8	0.001	<DL	<DL	3	0.056	2	0.001	2
Part. Cl ⁻	0.666	0.305	0.215	30		0.911		2	0.425	0.214	0.038	8	0.582	0.391	0.311	3	0.164	2	0.493	2
Inorg. Br _g	0.0053	0.0032	<DL	30	<DL	<DL	<DL	3	<DL	<DL	<DL	8	<DL	<DL	<DL	3	0.0002	2	<DL	2
Part. Br ⁻	0.0040	0.0017	0.0008	30		0.004		2	0.0010	0.0008	0.0005	8	0.0036	0.0020	0.0010	3	0.0015	2	0.0011	2
SO ₂	1.00	0.786	0.675	28		0.257		2	0.287	0.206	0.162	7	0.170	0.142	0.111	3	0.193	2	0.064	2
Part. SO ₄ ²⁻	0.240	0.140	0.066	30		0.156		2	0.075	0.041	0.018	8	0.460	0.371	0.339	3	0.028	2	1.08	2
Part. PO ₄ ³⁻	0.0031	<DL	<DL	30		0.0003		2	0.0007	0.0001	<DL	8	0.0081	0.0050	0.0031	3	0.0021	2	<DL	2
Part. K ⁺	0.541	0.242	0.135	30		0.524		2	0.507	0.250	0.066	8	0.285	0.158	0.118	3	0.292	2	0.038	2
Part. Ca ²⁺	0.0244	0.0162	0.0109	30		0.0169		2	0.0326	0.0130	0.0092	8	0.0386	0.0338	0.0245	3	0.0069	2	0.0049	2
Part. Na ⁺	0.0246	0.0101	0.0029	30		0.0229		2	0.0102	0.0043	<DL	8	<DL	<DL	<DL	3	<DL	2	<DL	2
Part. Mg ²⁺	0.0053	0.0041	0.0028	30		0.0037		2	0.0039	0.0020	0.0013	8	0.0080	0.0074	0.0053	3	0.0029	2	0.0010	2

^aUnits are (g species emitted) (kg dry wt. fuel emitted)⁻¹. Particulate HCOO⁻ was undetectable in all samples.^bBased on assumption that all NO_x was in the form of NO.

Table 2b. Summary Statistics for Elemental Emission Factors (EF_{el})^a

Analyte	Grass			Shrub			Branches			Litter			Agricultural Waste			Charcoal		Cow Dung	
	75th	50th	25th	N	75th	50th	25th	N	75th	50th	25th	N	75th	50th	25th	N	50th	N	
CO ₂	992	946	899	31	1121	938	871	5	962	940	921	10	907	896	748	3	816	2	521
CO	69.9	49.1	38.1	31	85.8	74.2	73.8	5	61.0	55.4	51.4	10	93.5	92.7	88.4	3	165	2	96.4
CH ₃ COOH	1.81	1.14	0.68	28	0.70	0.70	0.51	7	0.88	0.72	0.51	7	6.71	4.83	2.98	3	0.20	1	6.73
HCOOH	0.143	0.092	0.050	28	0.045	0.045	0.028	7	0.050	0.043	0.028	7	0.417	0.271	0.141	3	0.021	1	0.278
Part. CH ₃ COO ⁻	0.138	0.022	<DL	30	0.010	0.010	<DL	2	0.002	<DL	<DL	8	1.77	1.28	0.879	3	0.001	1	0.649
Part. (COO) ₂ ²⁻	0.0040	<DL	<DL	30	0.0031	0.0031	<DL	2	<DL	<DL	<DL	8	0.0031	<DL	<DL	3	<DL	1	0.0105
Part. C	23.5	11.1	6.0	30	8.6	8.6	2.8	7	4.0	3.1	2.8	7	81.7	59.0	46.2	3	0.3	1	49.2
NO _x ^b	175	141	117	31	160	52	50	5	164	146	117	10	93	70	48	3	153	2	10
NH ₃	16.4	9.77	4.86	28	59.9	59.9	40.0	7	52.9	51.1	40.0	7	108.9	55.9	49.4	3	99.6	1	128.4
HONO	12.9	6.7	5.0	28	10.5	10.5	6.4	7	8.8	8.2	6.4	7	10.6	9.8	6.0	3	9.8	1	3.1
Part. NH ₄ ⁺	12.5	6.32	3.84	30	7.54	7.54	1.16	8	2.51	1.66	1.16	8	36.5	34.1	22.3	3	<DL	1	15.2
Part. NO ₃ ⁻	0.544	0.283	0.220	30	1.1	1.1	0.449	8	0.573	0.492	0.449	8	1.40	1.11	0.838	3	1.88	1	0.252
Part. N	66.1	32.3	24.6	30	31.7	31.7	6.9	7	11.7	7.5	6.9	7	187	178	124	3	<DL	1	91.5
HCl	219	145	80	17	9.4	9.4	19.1	7	46.2	27.8	19.1	7	0.6	<DL	<DL	2	<DL	1	9.17
Inorg. Cl _g	455	260	185	30	54.8	5.7	<DL	3	161	91.4	49.0	8	0.6	<DL	<DL	3	169	1	0.4
Part. Cl ⁻	487	260	184	30	<DL	<DL	<DL	2	354	253	160	8	568	396	41.8	3	31.8	1	873
Inorg. Br _g	150	11	<DL	30	<DL	<DL	<DL	3	<DL	<DL	<DL	8	<DL	<DL	<DL	3	<DL	1	<DL
Part. Br ⁻	1534	649	123	30	832	832	251	8	672	251	193	8	<DL	<DL	<DL	3	<DL	1	<DL
SO ₂	815	627	430	28	<DL	<DL	240	7	290	260	240	7	170	96	69	3	<DL	1	14
Part. SO ₄ ²⁻	104	59	34	30	<DL	<DL	22	8	53	33	22	8	250	248	188	3	<DL	1	147
Part. PO ₄ ³⁻	7.70	<DL	<DL	30	0.2	0.2	<DL	2	2.8	0.8	<DL	8	8.2	7.3	4.8	3	<DL	1	<DL
Part. K ⁺	224	123	88	30	<DL	<DL	4.4	2	4.9	2.4	1.5	8	50	45	38	3	<DL	1	66
Part. Ca ²⁺	84.8	47.5	5.5	30	4.4	4.4	2.4	8	7.1	4.5	4.4	3	8.6	8.6	4.4	3	<DL	1	<DL
Part. Na ⁺	121.3	59.4	27.0	30	10.5	10.5	24.0	8	43.4	24.0	<DL	8	<DL	<DL	<DL	3	<DL	1	<DL
Part. Mg ²⁺	54.7	31.9	8.6	30	4.7	4.7	2.9	8	6.5	2.9	1.5	8	9.9	5.2	4.9	3	3.8	1	<DL

^aUnits are (g element emitted) (kg fuel element emitted)⁻¹. Particulate HCOO⁻ was undetectable in all samples.^bBased on assumption that all NO_x was in the form of NO.

Table 2c. Summary Statistics for Molar Emission Ratios Relative to CO (ER_{CO})^a

Analyte	Grass			Shrub			Branches			Litter			Agricultural Waste			Charcoal		Cow Dung					
	75th	50th	25th	N	75th	50th	25th	N	75th	50th	25th	N	75th	50th	25th	N	50th	N					
CO ₂	2.5E+1	1.9E+1	1.2E+1	31	1.3E+1	1.2E+1	1.0E+1	5	1.8E+1	1.7E+1	1.5E+1	10	1.0E+1	9.7E+0	8.0E+0	3	2.7E+1	2.5E+1	2.1E+1	4	5.0E+0	5.1E+0	2
CO	1.0E+0	1.0E+0	1.0E+0	31	1.0E+0	1.0E+0	1.0E+0	5	1.0E+0	1.0E+0	1.0E+0	10	1.0E+0	1.0E+0	1.0E+0	3	1.0E+0	1.0E+0	1.0E+0	4	1.0E+0	1.0E+0	2
CH ₃ COOH	2.1E-2	1.1E-2	6.2E-3	28	4.8E-3	4.8E-3	8.1E-3	7	8.1E-3	7.0E-3	5.6E-3	7	3.7E-2	2.9E-2	1.7E-2	3	3.4E-3	3.4E-3	3.4E-3	2	6.5E-4	4.3E-2	2
HCOOH	3.2E-3	1.5E-3	8.7E-4	28	6.3E-4	6.3E-4	9.1E-4	7	4.6E-3	3.2E-3	1.7E-3	3	4.6E-3	3.6E-4	3.6E-4	2	1.4E-4	1.4E-4	1.4E-4	2	1.4E-4	3.7E-3	2
Part. CH ₃ COO ⁻	1.1E-3	2.3E-4	<DL	30	7.1E-5	<DL	1.8E-5	2	1.8E-5	<DL	<DL	8	9.9E-3	7.7E-3	5.2E-3	3	6.2E-5	6.2E-5	6.2E-5	2	4.7E-6	4.0E-3	2
Part. (COO) ₂ ²⁻	4.7E-5	<DL	<DL	30	2.1E-5	<DL	<DL	2	<DL	<DL	<DL	8	1.6E-5	<DL	<DL	3	<DL	<DL	<DL	2	<DL	7.8E-5	2
Part. C	4.4E-1	2.1E-1	1.0E-1	30	1.2E-1	1.2E-1	6.8E-2	7	6.8E-2	6.3E-2	5.6E-2	7	9.0E-1	7.0E-1	5.3E-1	3	4.0E-2	4.0E-2	4.0E-2	2	1.7E-3	6.5E-1	2
NO _x ^b	4.0E-2	3.0E-2	2.0E-2	31	3.6E-2	7.2E-3	6.3E-3	5	3.0E-2	2.8E-2	2.5E-2	10	1.8E-2	1.7E-2	1.1E-2	3	2.7E-2	2.0E-2	1.4E-2	4	4.3E-3	5.3E-3	2
NH ₃	3.3E-3	2.2E-3	9.3E-4	28	1.3E-2	1.3E-2	1.2E-2	2	1.2E-2	1.1E-2	8.6E-3	7	2.4E-2	1.5E-2	1.1E-2	3	8.6E-3	8.6E-3	8.6E-3	2	3.0E-3	6.8E-2	2
HONO	2.4E-3	1.5E-3	8.0E-4	28	1.8E-3	1.8E-3	2.0E-3	2	2.0E-3	1.9E-3	1.1E-3	7	2.5E-3	2.3E-3	1.3E-3	3	2.6E-3	2.6E-3	2.6E-3	2	2.9E-4	2.4E-3	2
Part. NH ₄ ⁺	2.5E-3	1.5E-3	8.5E-4	30	2.3E-3	2.3E-3	5.1E-4	8	5.1E-4	3.5E-4	2.4E-4	8	6.3E-3	5.8E-3	4.3E-3	3	1.6E-5	1.6E-5	1.6E-5	2	<DL	9.7E-3	2
Part. NO ₃ ⁻	9.3E-5	6.0E-5	5.1E-5	30	1.7E-4	1.7E-4	1.2E-4	2	1.2E-4	1.0E-4	9.8E-5	8	2.4E-4	2.2E-4	1.9E-4	3	4.1E-5	4.1E-5	4.1E-5	2	5.6E-5	1.3E-4	2
Part. N	1.4E-2	8.4E-3	4.3E-3	30	9.2E-3	9.2E-3	2.2E-3	2	2.2E-3	1.9E-3	1.6E-3	7	3.2E-2	2.9E-2	2.4E-2	3	1.3E-3	1.3E-3	1.3E-3	2	<DL	5.3E-2	2
HCl	4.9E-3	2.3E-3	1.8E-3	17	2.2E-4	2.2E-4	4.3E-4	2	4.3E-4	2.0E-4	1.3E-4	7	3.1E-5	3.1E-5	2.4E-2	2	7.2E-4	7.2E-4	7.2E-4	2	<DL	1.1E-5	2
Inorg. Cl _g	8.1E-3	5.1E-3	2.7E-3	30	7.2E-4	3.1E-4	2.1E-4	3	6.3E-4	5.1E-4	2.3E-4	8	5.4E-6	<DL	<DL	3	1.2E-3	1.2E-3	1.2E-3	2	3.9E-4	8.6E-6	2
Part. Cl ⁻	8.1E-3	5.3E-3	3.7E-3	30	8.8E-3	8.8E-3	4.7E-3	2	4.7E-3	2.8E-3	5.0E-4	8	4.8E-3	2.8E-3	2.3E-3	3	2.4E-3	2.4E-3	2.4E-3	2	7.4E-5	5.9E-3	2
Inorg. Br _g	4.0E-6	2.5E-6	<DL	30	<DL	<DL	<DL	3	<DL	<DL	<DL	8	<DL	<DL	<DL	3	2.4E-7	2.4E-7	2.4E-7	2	<DL	<DL	2
Part. Br ⁻	1.7E-5	1.3E-5	7.6E-6	30	1.6E-5	1.6E-5	6.4E-6	2	6.4E-6	4.3E-6	3.5E-6	8	1.3E-5	7.7E-6	<DL	3	8.7E-6	8.7E-6	8.7E-6	2	<DL	6.6E-6	2
SO ₂	9.4E-3	5.8E-3	4.6E-3	28	1.4E-3	1.4E-3	2.1E-3	2	2.1E-3	1.3E-3	1.2E-3	7	7.4E-4	7.0E-4	5.1E-4	3	2.1E-3	2.1E-3	2.1E-3	2	6.0E-5	2.9E-4	2
Part. SO ₄ ²⁻	1.1E-3	7.5E-4	4.6E-4	30	5.5E-4	5.5E-4	3.7E-4	2	3.7E-4	2.0E-4	1.1E-4	8	1.4E-3	1.0E-3	9.2E-4	3	1.6E-4	1.6E-4	1.6E-4	2	8.1E-5	4.3E-3	2
Part. PO ₄ ³⁻	1.7E-5	<DL	<DL	30	9.9E-7	9.9E-7	3.4E-6	2	3.4E-6	9.3E-7	<DL	8	2.3E-5	1.6E-5	9.8E-6	3	1.2E-5	1.2E-5	1.2E-5	2	8.7E-6	<DL	2
Part. K ⁺	6.2E-3	4.1E-3	2.5E-3	30	4.7E-3	4.7E-3	5.2E-3	2	5.2E-3	3.0E-3	8.1E-4	8	2.2E-3	1.0E-3	7.7E-4	3	3.6E-3	3.6E-3	3.6E-3	2	2.9E-4	3.7E-4	2
Part. Ca ²⁺	3.0E-4	2.0E-4	1.2E-4	30	1.5E-4	1.5E-4	3.4E-4	2	3.4E-4	1.8E-4	1.2E-4	8	2.7E-4	2.6E-4	1.8E-4	3	9.2E-5	9.2E-5	9.2E-5	2	4.9E-5	4.8E-5	2
Part. Na ⁺	3.9E-4	2.2E-4	8.5E-5	30	3.3E-4	3.3E-4	1.9E-4	2	1.9E-4	9.0E-5	<DL	8	<DL	<DL	<DL	3	<DL	<DL	<DL	2	<DL	<DL	2
Part. Mg ²⁺	1.2E-4	8.2E-5	5.1E-5	30	5.2E-5	5.2E-5	6.9E-5	2	6.9E-5	4.6E-5	2.6E-5	8	9.2E-5	8.9E-5	6.2E-5	3	6.6E-5	6.6E-5	6.6E-5	2	1.1E-5	1.3E-5	2

^aUnits are (mol analyte emitted) / (mol CO emitted)⁻¹. Particulate HCOO⁻ was undetectable in all samples.

^bBased on assumption that all NO_x was in the form of NO.

Table 2d. Summary Statistics for Molar Emission Ratios Relative to CO₂ (ER_{CO2})^a

Analyte	Grass			Shrub			Branches			Litter			Agricultural Waste			Charcoal		Cow Dung		
	75th	50th	25th	N	75th	50th	25th	N	75th	50th	25th	N	75th	50th	25th	N	50th	N		
CO ₂	1.0E+0	1.0E+0	1.0E+0	31	1.0E+0	1.0E+0	1.0E+0	10	1.0E+0	1.0E+0	1.0E+0	3	1.0E+0	1.0E+0	1.0E+0	4	1.0E+0	2	1.0E+0	2
CO	8.5E-2	5.2E-2	4.0E-2	31	9.6E-2	8.5E-2	7.4E-2	5	6.6E-2	5.7E-2	5.4E-2	10	1.3E-1	1.0E-1	9.8E-2	3	4.9E-2	4	2.0E-1	2
CH ₃ COOH	9.5E-4	5.9E-4	3.6E-4	28	3.9E-4	3.9E-4	4.0E-4	2	4.7E-4	4.0E-4	2.7E-4	7	4.9E-3	2.6E-3	1.6E-3	3	1.4E-4	2	1.2E-4	1
HCOOH	1.5E-4	9.8E-5	5.4E-5	28	5.1E-5	4.6E-5	3.0E-5	2	5.5E-5	4.6E-5	2.9E-4	3	6.2E-4	2.9E-4	1.5E-4	3	1.5E-5	2	2.5E-5	1
Part. CH ₃ COO ⁻	8.4E-5	1.2E-5	<DL	30	6.1E-6	<DL	<DL	2	9.6E-7	<DL	7.1E-4	3	1.3E-3	4.9E-4	3.7E-6	2	8.5E-7	1	8.4E-4	2
Part. (COO) ₂ ²⁻	2.7E-6	<DL	<DL	30	1.8E-6	<DL	<DL	2	<DL	<DL	<DL	3	1.7E-6	<DL	1.0E-7	2	<DL	1	1.7E-5	2
Part. C	2.8E-2	1.1E-2	6.5E-3	30	9.7E-3	3.5E-3	2.9E-3	7	4.3E-3	3.5E-3	6.4E-2	3	1.2E-1	6.4E-2	1.7E-3	2	3.1E-4	1	1.4E-1	2
NO _x ^b	1.9E-3	1.7E-3	1.4E-3	31	3.8E-3	6.1E-4	4.4E-4	5	1.7E-3	1.6E-3	1.5E-3	10	2.3E-3	2.0E-3	1.2E-3	3	1.2E-3	4	9.4E-4	2
NH ₃	1.9E-4	1.2E-4	5.5E-5	28	1.0E-3	6.3E-4	4.2E-4	7	7.5E-4	6.3E-4	1.6E-3	3	2.3E-3	1.6E-3	1.3E-3	3	5.3E-4	1	1.4E-2	2
HONO	1.1E-4	8.3E-5	5.8E-5	28	1.4E-4	1.0E-4	6.1E-5	7	1.3E-4	1.0E-4	2.1E-4	3	2.4E-4	2.1E-4	1.3E-4	3	1.2E-4	2	5.2E-5	1
Part. NH ₄ ⁺	1.8E-4	7.5E-5	4.0E-5	30	2.0E-4	2.1E-5	1.4E-5	8	7.7E-4	6.3E-4	4.6E-4	3	7.7E-4	6.3E-4	5.4E-7	2	<DL	1	2.1E-3	2
Part. NO ₃ ⁻	6.1E-6	3.3E-6	2.1E-6	30	1.3E-5	1.3E-5	5.2E-6	8	7.4E-6	6.5E-6	5.2E-6	8	3.0E-5	2.0E-5	1.8E-5	3	1.9E-6	2	2.8E-5	2
Part. N	7.8E-4	4.3E-4	2.7E-4	30	7.7E-4	1.7E-5	1.9E-5	2	1.2E-4	1.1E-4	9.6E-5	7	3.9E-3	3.3E-3	2.6E-3	3	5.7E-5	2	<DL	1
HCl	3.3E-4	1.3E-4	8.0E-5	17	1.7E-5	1.2E-5	6.8E-6	7	2.3E-5	1.2E-5	4.9E-6	2	5.0E-7	<DL	<DL	3	2.7E-5	2	1.1E-2	2
Inorg. Cl _g	3.8E-4	2.4E-4	1.7E-4	30	5.7E-5	3.0E-5	1.9E-5	3	4.0E-5	2.4E-5	1.3E-5	8	5.0E-7	<DL	<DL	3	4.5E-5	2	1.9E-6	2
Part. Cl ⁻	6.8E-4	2.7E-4	1.6E-4	30	7.1E-4	1.6E-4	2.8E-5	8	3.1E-4	1.6E-4	4.4E-4	3	5.3E-4	4.4E-4	3.1E-4	3	1.3E-4	2	1.3E-5	2
Inorg. Br _g	1.9E-7	1.1E-7	<DL	30	<DL	<DL	<DL	3	<DL	<DL	<DL	8	<DL	<DL	<DL	3	8.4E-9	1	<DL	2
Part. Br ⁻	1.4E-6	6.3E-7	3.4E-7	30	1.3E-6	2.4E-7	1.7E-7	8	3.4E-7	2.4E-7	7.0E-7	3	1.3E-6	7.0E-7	4.9E-7	2	<DL	1	1.5E-6	2
SO ₂	4.4E-4	3.6E-4	2.8E-4	28	1.1E-4	8.5E-5	6.8E-5	7	1.2E-4	8.5E-5	6.4E-5	3	9.4E-5	6.4E-5	4.9E-5	3	8.4E-5	2	1.1E-5	1
Part. SO ₄ ²⁻	8.9E-5	4.0E-5	2.0E-5	30	4.5E-5	1.1E-5	5.0E-6	8	2.2E-5	1.1E-5	1.3E-4	3	1.5E-4	1.3E-4	1.2E-4	3	8.0E-6	2	1.5E-5	1
Part. PO ₄ ³⁻	9.1E-7	<DL	<DL	30	7.4E-8	4.0E-8	<DL	8	1.9E-7	4.0E-8	1.5E-6	3	3.1E-6	9.1E-7	6.1E-7	2	1.6E-6	1	<DL	2
Part. K ⁺	4.3E-4	1.9E-4	9.8E-5	30	3.6E-4	1.7E-4	4.5E-5	8	3.4E-4	1.7E-4	1.6E-4	3	2.3E-4	1.6E-4	2.0E-4	2	2.0E-4	2	5.3E-5	1
Part. Ca ²⁺	1.8E-5	1.1E-5	7.8E-6	30	1.1E-5	8.5E-6	6.1E-6	8	2.2E-5	8.5E-6	2.4E-5	3	3.4E-5	2.4E-5	4.7E-6	2	4.7E-6	2	8.8E-6	1
Part. Na ⁺	3.0E-5	1.2E-5	3.8E-6	30	2.8E-5	5.1E-6	<DL	8	1.1E-5	5.1E-6	<DL	3	<DL	<DL	<DL	3	<DL	1	<DL	2
Part. Mg ²⁺	6.3E-6	4.9E-6	3.3E-6	30	4.2E-6	2.3E-6	1.4E-6	8	4.3E-6	2.3E-6	8.8E-6	3	1.1E-5	8.8E-6	6.2E-6	2	2.0E-6	1	2.8E-6	2

^aUnits are (mol analyte emitted) (mol CO₂ emitted)⁻¹. Particulate HCOO⁻ was undetectable in all samples.

^bBased on assumption that all NO_x was in the form of NO.

Table 3. Comparison of Standard Emission Factors (EF_{st}) With Previously Published Values

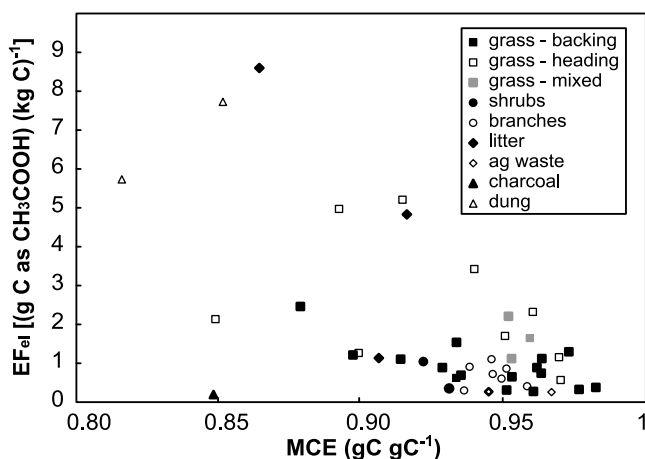
Species	Median Values for This Study						Literature Values Summarized by <i>Andreae and Merlet</i> [2001]					
	Grass	Shrubs	Branches	Litter	Ag Waste	Charcoal	Dung	Savanna and Grassland	Tropical Forests	Biofuel	Agricultural Waste	Charcoal Burning
CO ₂	1626	1641	1664	1532	1524	2755	899	1613 ± 95	1580 ± 90	1550 ± 95	1515 ± 177	2611 ± 241
CO	53	86	63	105	38	351	106	65 ± 20	104 ± 20	78 ± 31	92 ± 84	200 ± 38
CH ₃ COOH	1.34	0.85	0.87	5.49	0.31	0.49	7.85	1.30	2.1	1.4–0.4	0.8	4.1
HCOOH	0.16	0.08	0.08	0.47	0.03	0.08	0.50	0.70	1.1	0.13	0.22	2.0
Total particulate C	5.3	4.2	1.5	26.8	0.7	0.3	22.9	3.7 ± 1.3	6.6 ± 1.5	5.2 ± 1.1	4.0	6.3
NO _x	1.8	0.7	1.8	2.0	1.2	1.6	0.5	3.9 ± 2.4	1.6 ± 0.7	1.1 ± 0.6	2.5 ± 1.0	3.9
NH ₃	0.06	0.64	0.40	0.97	0.22	0.63	3.54	0.6–1.5	1.30	1.30	1.30	1.30
SO ₂	0.79	0.26	0.21	0.14	0.19	0.05	0.06	0.35 ± 0.16	0.57 ± 0.23	0.27 ± 0.30	0.40	0.40
Particulate K ⁺	0.24	0.52	0.25	0.16	0.29	0.14	0.04	0.34 ± 0.15	0.29 ± 0.22	0.05 ± 0.01	0.13–0.43	0.40

the combustion of savanna grasses, most heading and mixed fires exhibited systematically higher EF_{el} s for CH₃COOH relative to backing fires of comparable MCEs (Figure 4). An RMA regression of EF_{el} versus MCE for heading and mixed fires ($N = 10$ excluding 2 outliers) yielded a slope of -64.7 , an intercept of 63.7 and a r^2 of 0.85 ; the corresponding regression for backing fires ($N = 16$) yielded a slope of -19.3 , an intercept of 19.1 , and a r^2 of 0.24 . The highest EF_{el} s for CH₃COOH were associated with dung, litter, and heading burns of savanna grasses (Figure 4).

[28] The median integrated exhaust flux of carbon via all species reported herein was 101% of the corresponding emission flux of fuel C during combustion (Table 4). Although these integrated exhaust fluxes do not include minor additional contributions from other volatile organic compounds (maximum of a few percent [*Andreae and Merlet, 2001*]), the agreement between the sum of carbon-containing species measured in the exhaust and total fuel C emitted during the burns is well within the overall combined uncertainty of the associated measurements.

3.3. Nitrogen

[29] With the exception of dung, the N contents of fuels fell within a fairly narrow range and, like carbon, most (median = 95%) was emitted during combustion (Table 1). Grasses in Miombo ecosystems generally contained less N than those in the Kruger and Etosha savannas (Table 1), which is consistent with their relatively lower fertility [e.g.,

**Figure 4.** EF_{el} for CH₃COOH versus MCE.

Hély et al., 2003]. In contrast to carbonaceous species, measured N-containing analytes in the exhaust corresponded to relatively minor fractions (median = 22%) of the emitted N (Table 4). Available evidence indicates that molecular N accounts for 35% to 60% of the total N flux from biomass burning [e.g., *Kuhlbusch et al., 1991*]; HCN, CH₃CN, other nitriles, N₂O, and higher-molecular weight organic gases are also emitted and thereby contribute to the observed imbalances between emitted N and corresponding sums of measured N-containing analytes.

[30] The relative contributions of species reported herein varied substantially among fuel types (Tables 2a–2d). For example, on the basis of median values of measured analytes, NO_x was the most important N-containing species emitted during the combustion of grass, branches, agricultural waste, and charcoal; particulate N dominated emissions during combustion of litter; and NH₃ was the single most important species emitted during the combustion of dung. NH₄⁺ and NO₃⁻ generally accounted for less than half of total particulate N suggesting that organic N-containing species dominated particulate N emitted from most burns. As plumes age and cool, the composition and pH of particles evolve in response to the condensation of water and other primary emissions, the gas-phase production and subsequent condensation of acids, chemical reactions in bulk solutions and on surfaces, and phase partitioning of compounds with pH-dependent solubilities such as NH₃ and HNO₃ [e.g., *Gao et al., 2003*; *Li et al., 2003*; *Magi and Hobbs, 2003*]. Although generally lower relative to fluxes of other N-containing species, model calculations indicate that HONO significantly influences the cycling of HO_x and O₃ in aging biomass-burning plumes [*Trentmann et al., 2005*].

[31] EF_{st} s for NO_x for these experimental burns were generally within the range of values reported by *Andreae and Merlet* [2001] but those for NH₃ emitted during the combustion of savanna grasses were lower by an order of magnitude or more (Table 3). However, EF_{st} s for NH₃

Table 4. Percentage of Emitted Elements Recovered From the Sum of all Analytes Reported Herein

Statistic	C	N	Cl	Br	S	P	K	Ca	Na	Mg
75th percentile	105	25	74	146	75	0.7	23	6.5	8.1	3.9
Median	101	22	53	30	51	0.1	11	0.8	3.8	1.0
25th percentile	99	19	36	6	32	0.0	7	0.2	<DL	0.3
N	45	45	45	45	45	48	48	48	48	48

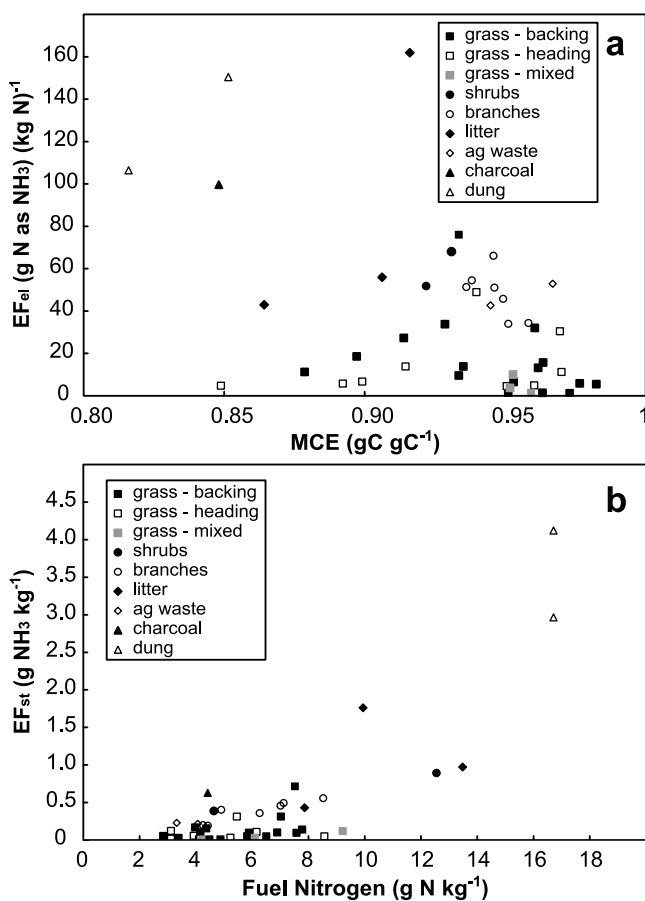


Figure 5. (a) EF_{el} for NH_3 versus MCE and (b) EF_{st} for NH_3 versus the N content of fuel.

during our grass burns fell within the lower end of the range of EF_{st} s based on measurements in ambient plumes from savanna fires in southern Africa during SAFARI 2000 (0.28 ± 0.14 g/kg [Yokelson *et al.*, 2003]) and were similar to EF_{st} for NH_3 reported for a savanna fire in Ivory Coast [Delmas *et al.*, 1995]. To evaluate these data further, we compared EF_{el} s for NH_3 measured during this study with results from a previous set of experimental burns of African savanna grasses and agricultural waste at the same facility [Lobert *et al.*, 1990]. The average EF_{el} for all burns during the previous study (40 ± 31 g kg⁻¹, $N = 15$) encompasses the range of average values for savanna grasses (15 ± 17 g kg⁻¹, $N = 28$) and agricultural waste (48 g kg⁻¹, $N = 2$) measured during our experiments. We conclude that NH_3 emissions from savanna fires in southern Africa are quite variable and generally lower than those associated with other extratropical fires. Variability in the moisture and N contents of fuels, burn conditions, and perhaps volatilization from soils and subsurface roots upon heating by ambient fires contribute to the wide range in reported values.

[32] Most NH_3 is emitted during the smoldering stage of fires [Griffith *et al.*, 1991; Lobert *et al.*, 1991] and, consequently, as for CH_3COOH , we would expect an inverse relationship between EF_{el} and MCE. Fuels associated with relatively lower MCEs (dung, charcoal, and litter) exhibited generally higher EF_{el} s and those for branches were significantly correlated (Figure 5a). In contrast, EF_{el} s

for grass fires did not exhibit a consistent pattern. The three highest EF_{el} s for individual grass fires were associated with MCEs around 0.93 but two other grass fires with similar MCEs exhibited substantially lower EF_{el} s (Figure 5a). Most EF_{el} s for NH_3 that corresponded to MCEs greater than 0.95 were relatively low and those associated with MCEs less than 0.92 decreased with decreasing MCE (Figure 5a). EF_{el} s for heading fires tended to be less than those for backing fires of similar MCE. Standard emission factors for NH_3 corresponding to ambient savanna fires during SAFARI 2000 were also poorly correlated with MCE [Yokelson *et al.*, 2003]. Fuels with the highest N contents (dung, litter, and one shrub sample) exhibited systematically higher EF_{st} s relative to other fuels (Figure 5b). With the exception of those for branches, however, the poor correlations between EF_{st} s and the corresponding N contents of these other fuels (Figure 5b) indicate that N content had a minor to negligible influence on the corresponding NH_3 emissions during combustion.

[33] In India where dung is widely burned as fuel, the substantial associated NH_3 emissions (Tables 2a–2d and Figure 5b) have potentially important implications for the multiphase chemical processes. For example, enhanced titration of atmospheric acidity relative to other regions should result in higher aerosol pHs, which could sustain efficient S(IV) oxidation in aerosol solutions but quench halogen activation chemistry [e.g., Keene *et al.*, 1998]. In addition, high NH_3 mixing ratios may enhance aerosol nucleation [e.g., Korhonen *et al.*, 1999; Kulmala *et al.*, 2000] and efficient atmospheric deposition would contribute to eutrophication of ecosystems [e.g., Russell *et al.*, 2003]. Additional research is needed to critically evaluate the environmental implications of large NH_3 emissions from dung burning in India.

3.4. Halogens

[34] Compared to C and N, the Cl and Br contents of vegetation were more variable and relatively smaller fractions were emitted during combustion (median for all fuels = 73% for both Cl and Br, Table 1). Similar amounts of gaseous inorganic Cl and particulate Cl⁻ were emitted during the combustion of savanna grass (Tables 2a–2d). With the exception of charcoal and shrubs, however, particulate Cl⁻ was the primary Cl-containing analyte measured in the exhaust from combustion of other fuel types (Tables 2a–2d). Particulate Br⁻ typically dominated inorganic Br emissions from all fuel types (Tables 2a–2d). EF_{st} s for volatile inorganic and particulate halogens associated with most fuel types generally increased with increasing halogen content of biomass (Figure 6). These relationships illustrate that fuel composition partially controls the corresponding pyrogenic emissions of inorganic halogens. The greater scatter in the EF_{st} versus fuel Cl for volatile inorganic Cl (Figure 6a) compared to that for particulate Cl⁻ (Figure 6b) suggests that other factors including type of fuel are relatively more important in regulating emissions of volatile inorganic Cl. We infer from these results that regional variability in the halogen contents of fuels (e.g., relatively high in grasses of Etosha and relatively low branches of Malawi, Table 1) would contribute to systematic regional variability in the corresponding emissions from biomass

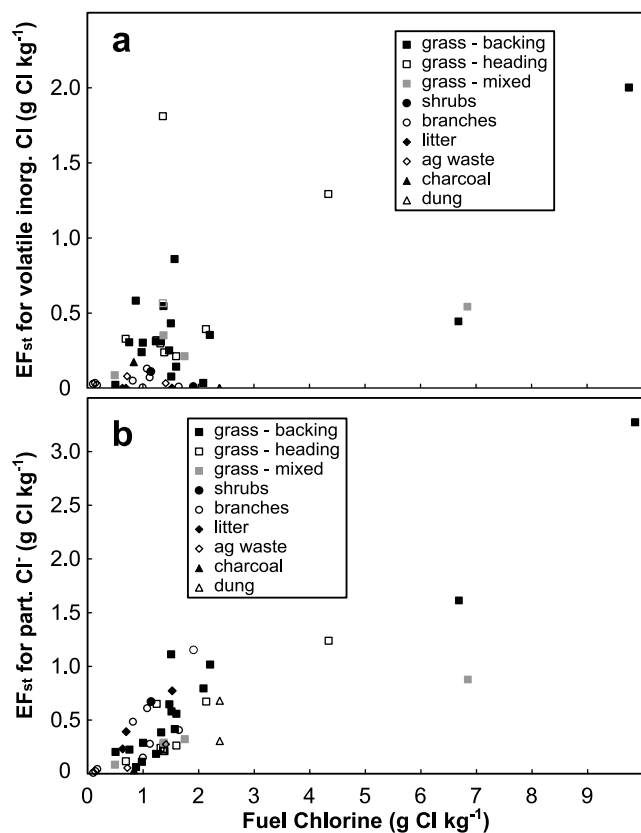


Figure 6. EF_{st} for (a) volatile inorganic Cl and (b) particulate Cl^- versus the Cl content of fuel. Figure 6a excludes one litter sample with a high fuel Cl content of $19.4 \text{ g Cl kg}^{-1}$ and a corresponding EF_{st} for volatile inorganic Cl of $0.05 \text{ g Cl kg}^{-1}$.

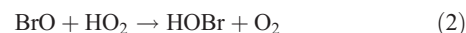
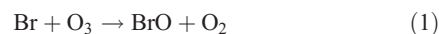
burning and associated influences on the chemical processing of plumes. On the basis of median values for all fires, inorganic gases and particulate ions accounted for 53% of the emitted Cl and 30% of the emitted Br (Table 4). Organic Cl- and Br-containing gases and particulate species composed the balance of total Cl and Br emitted during the experimental burns.

[35] The role of reactive inorganic halogens in the chemical evolution of biomass burning plumes is poorly constrained. On the basis of median values, HCl accounted for about half of total volatile inorganic Cl in fresh exhaust (Tables 2a–2d), which suggests that other, more reactive inorganic Cl gases such as Cl_2 , HOCl, and BrCl were emitted in significant concentrations. Rapid photolysis of these compounds in sunlight generates atomic Cl, which subsequently reacts rapidly with hydrocarbons (primarily alkanes) via H abstraction to produce HCl [e.g., Graedel and Keene, 1995]. At high HCl mixing ratios ($>1 \text{ ppbv}$), the gas-phase reaction of HCl and OH also contributes significantly to Cl-atom production [e.g., Singh and Kasting, 1988]. At high NO_x , the enhanced supply of odd hydrogen radicals from hydrocarbon oxidation by Cl contributes to O_3 production [e.g., Tanaka et al., 2000]. On the basis of its thermodynamic properties, HCl partitions with aqueous aerosols as a function of pH. In acidic solution, reaction of HOCl

and HOBr with Cl^- produces Cl_2 and BrCl, respectively, that subsequently volatilize and photolyze [e.g., Sander et al., 2003]. These multiphase pathways (e.g., $HCl \rightarrow Cl^- \rightarrow Cl_2 \rightarrow Cl \rightarrow HCl$) recycle the relatively less reactive product species (HCl and particulate Cl^-) to photochemically active forms. Because Cl atoms react with hydrocarbons primarily via H abstraction to produce HCl, such recycling would be required to sustain significant Cl-radical chemistry in aging plumes.

[36] The potential importance of oxidation by atomic Cl was evaluated in a biomass-burning plume during SAFARI 2000 on the basis of concentration changes in C_2H_2 relative to CO, a conservative tracer [Tabazadeh et al., 2004]. Because C_2H_2 is oxidized rapidly by atomic Cl but not by OH, decreasing ratios of $\Delta C_2H_2/\Delta CO$ with time would indicate significant Cl-atom concentrations. However, ratios based on measurements over a period of about 1 hour following emission were relatively constant indicating negligible oxidation by atomic Cl. Our results indicate that volatile inorganic Cl and particulate Cl^- were present at high concentrations in plumes from savanna fires in this region. In addition, emission ratios for major acids (CH_3COOH , $HCOOH$ and HCl) and acid precursors (SO_2 , NO_x , volatile inorganic Cl other than HCl) exceeded those for NH_3 in all fires suggesting that condensed solutions in evolving plumes were either acidic or rapidly acidified. However, the low ambient relative humidity (RH, $\sim 40\%$) and associated liquid water may have limited multiphase recycling leading to the accumulation of relatively unreactive HCl and particulate Cl^- and thus little Cl-atom production in the aging plume. High concentrations of condensed organics on surfaces and in bulk solution may have also influenced HCl phase partitioning and corresponding rates of Cl recycling. At higher RH and associated liquid water (e.g., exhaust from temperate wildfires), Cl-radical chemistry may be relatively more important in the chemical evolution of plumes.

[37] The measured emission fluxes of gaseous, inorganic Br and particulate Br^- in association with acids and particles suggests that Br radicals may also influence the chemical evolution of biomass-burning plumes. Analogous multiphase pathways involving sea-salt aerosol impact the cycling of NO_x , O_3 , S, and other constituents of marine air [e.g., Sander et al., 2003; Pszenny et al., 2004, and references therein]. On the basis of the measured speciation of volatile inorganic Cl, we hypothesize that a significant fraction of volatile inorganic Br was emitted in photochemically active forms including Br_2 , BrCl, and HOBr. Photolysis of these compounds generates atomic Br that catalytically destroys ozone via:



Because biomass-burning plumes also contain high concentrations of HCHO and other oxygenated organic

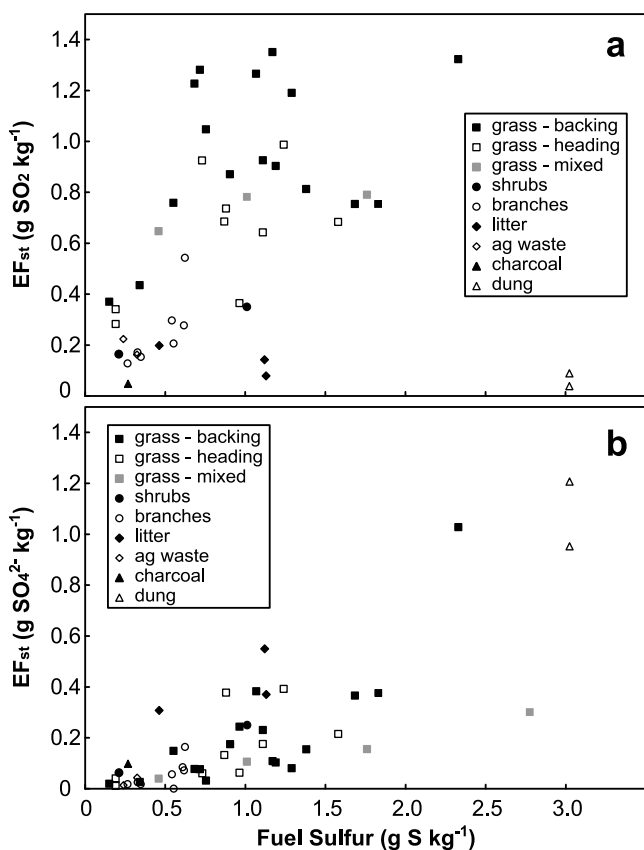
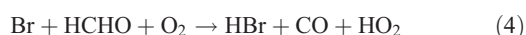


Figure 7. EF_{st} for (a) SO₂ and (b) particulate SO₄²⁻ versus the S content of fuel.

compounds [e.g., Yokelson *et al.*, 2003], important side reactions such as



may limit gas-phase recycling of Br radicals [e.g., Dickerson *et al.*, 1999] and lead to accumulation of particulate Br⁻ via condensation of HBr. Like Cl, activation of particulate Br⁻, which dominated inorganic Br emissions during the experimental burns (Tables 2a–2d), requires aqueous media. As may be the case for inorganic Cl, the low RHs and associated liquid water perhaps coupled with the high concentrations of condensed organic compounds may limit active Br-radical chemistry in biomass-burning exhaust over southern Africa. Focused experiments over a wider range of RH are needed to resolve the potentially important influences of halogen radicals in the chemical evolution of biomass-burning plumes.

3.5. Sulfur

[38] The S contents of vegetation varied significantly across the region with highest values in Etosha and lowest in the Miombo woodlands (Table 1). On the basis of median values for all burns, 76% of this S was emitted (Table 1) and 51% of the emitted S was in form of SO₂ and particulate SO₄²⁻ (Table 4). Presumably, the balance was composed primarily of H₂S, COS, other organic S-containing gases, and particulate species. Like inorganic Cl, inorganic S emissions were correlated with S contents (Figure 7) and the relative impor-

tance of gaseous versus particulate emissions varied substantially as a function of fuel type (Tables 2a–2d). SO₂ typically dominated inorganic S emissions during the combustion of grass, branches, and agricultural wastes whereas particulate S was the major inorganic S species emitted during the combustion of litter and dung. The low EF_{st}s for SO₂ and particulate SO₄²⁻ from charcoal fires (Tables 2a–2d) reflects the relatively low S content of the fuel (Table 1). Heterogeneity in S content of the charcoal sample (as inferred from large variability in S associated with ash from replicate burns) precluded reliable quantification of corresponding EF_{st}s. Median EF_{st}s for SO₂ during the combustion of most fuel types evaluated during this study were within a factor of two of the corresponding values recommended by *Andreae and Merlet* [2001]; the EF_{st} for charcoal based on our results was a factor of 8 lower (Table 3).

3.6. Phosphorous

[39] The P contents of vegetation varied substantially among the same fuel type within a given region (e.g., factor of 8 among grasses in Etosha), between different fuel types in the same region (e.g., branches were generally factors of 2 to 10 lower than grasses), and between the same fuel type in different regions (e.g., grasses of the Miombo Dambos were about a factor of 10 lower than most of those in other regions, Table 1). Like those for N, the low P contents of Miombo grasses reflects the relative infertility of these ecosystems [e.g., Hély *et al.*, 2003]. On the basis of median values for all burns, 82% of the P was emitted during combustion but only 0.1% was recovered in the form of particulate PO₄³⁻. These results suggest that most P in biomass is emitted during combustion in association with organic, probably particulate species. To our knowledge, a satisfactory chemical mass balance for P during biomass burning does not exist. However, results from this investigation imply substantial mobilization associated with large net losses of P from burned ecosystems and potentially important exogenous sources of nutrient P for downwind ecosystems. To resolve the potential importance of this large biogeochemical flux, experiments should be conducted to determine the total P content of emitted particles and its associated bioavailability.

3.7. Base Cations

[40] The base cation contents of fuels varied substantially among regions (those in Etosha were relatively high and in Zambia relatively low) and fuel types (e.g., shrubs were more concentrated in K and branches in Ca; Table 1). On the basis of median values, most K, Ca, Na, and Mg (66%, 74%, 78%, and 84%, respectively) were emitted during combustion (Table 1). However, only minor fractions were recovered as soluble particulate K⁺, Ca²⁺, Na⁺, and Mg²⁺ (median values of 11%, 0.8%, 3.8%, and 1.0%, respectively, Table 4). On the basis of these results, we infer that most base cations in fuels were emitted during combustion in association with insoluble particulate compounds. EF_{st}s for K⁺ were within the range previously published values (Table 3).

4. Conclusions

[41] 1. The middle 50th percentile range of MCEs for all burns (0.91 to 0.95 g C g C⁻¹) was similar to the reported

range for ambient savanna fires in southern Africa. Lower MCEs were generally associated with higher moisture contents, heading versus backing fires, and processed fuels (dung, charcoal).

[42] 2. Virtually all (median = 97%) fuel C was emitted during combustion primarily as CO₂ and CO (median = 99%). EF_{el} for CH₃COOH was negatively correlated with MCE; during the combustion of savanna grasses, most heading and mixed fires exhibited systematically higher EF_{el}s for CH₃COOH relative to backing fires of comparable MCEs.

[43] 3. Measured analytes in the exhaust (NO_x, NH₃, HONO, and particulate N) accounted for relatively minor fractions of the emitted N (median = 22%); on the basis of Kuhlbusch *et al.* [1991], we infer that N₂ contributed most of the unmeasured balance. Significant HONO but virtually no HNO₃ were emitted during the experimental burns. Savanna grass fires with the highest EF_{el}s for NH₃ were associated with MCEs around 0.93; fires with higher and lower MCEs exhibited lower EF_{el}s. Fuels with the highest N contents (dung and litter) exhibited the highest EF_{el}s for NH₃. With the exception of branch fires, however, NH₃ emissions during combustion of other fuels were poorly correlated with the N content.

[44] 4. Most Cl and Br in fuel (median for both = 73%) was emitted during the experimental burns. On the basis of median values, volatile inorganic species and particulate ions accounted for 53% of emitted Cl and 30% of the emitted Br. HCl accounted for about half of volatile inorganic Cl suggesting that other, more reactive, species (including Cl₂, HOCl, BrCl) were also emitted in significant concentrations. The halogen contents of fuels partially regulated corresponding pyrogenic emissions.

[45] 5. On the basis of median values for all burns, 76% of fuel S was emitted during combustion and 51% of the emitted S was in form of SO₂ and particulate SO₄²⁻.

[46] 6. On the basis of median values for all burns, 82% of fuel P was emitted during combustion but only 0.1% was recovered in the form of particulate PO₄³⁻. These results imply large net losses of P from burned ecosystems and potentially important exogenous sources of nutrient P for downwind ecosystems.

[47] 7. On the basis of median values, most K, Ca, Na, and Mg in fuel (66%, 74%, 78%, and 84%, respectively) was emitted during combustion but little (11%, 0.8%, 3.8%, and 1.0%, respectively) was recovered as soluble particulate K⁺, Ca²⁺, Na⁺, and Mg²⁺.

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