

Emissions of Volatile Inorganic Halogens, Carboxylic Acids, NH₃, and SO₂ from Experimental Burns of Southern African Biofuels

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Introduction

Biomass burning in southern Africa is a major source of atmospheric pollution both regionally and globally [e.g. Crutzen et al, 1979; Crutzen and Andreae, 1990]. African burning currently accounts for about 35% of the global total [Logan and Yevich cited in: Lobert et al, 1999] and substantial absolute and percentage increases are projected for the future [Crutzen and Andreae, 1990, Lelieveld et al., 1998]. Consequently, quantification of biomass-burning emissions in Africa is essential for understanding and predicting associated environmental (including climatic) impacts. Despite intense study over the past two decades, however, regional and global emissions of some compounds are still poorly constrained.

As part of the SAFARI-2000 campaign, we conducted 60 semi-controlled burns of representative biofuels from 4 regions of southern Africa and measured emissions of CO₂; CO; CH₃Cl; CH₃Br; CH₃I; CH₄; CH₃COOH; HCOOH; CH₃COCH₃; CH₃CN; other non-methane hydrocarbons; NO_x (NO + NO₂); N₂O; NH₃; HNO₃; HONO; SO₂; HCl; total volatile inorganic Cl, Br and I; the ionic composition of particles including Cl⁻, Br⁻, NO₃⁻, NH₄⁺, SO₄²⁻, HCOO⁻, CH₃COO⁻; and the elemental composition of particles including C, N, S, Cl, Br, I, P, Ca, K. The above elemental contents and Hg were also measured in both biofuels and residual ash. Herein we report preliminary emissions of a subset of soluble reactive trace gases. Methyl halide emissions from these burns are reported in a companion paper by Lobert et al. [2001].

Methods

Sample Collection and Processing

During the dry season (August to October) 2000, representative biofuels were sampled in Etosha National Park, Namibia; Kruger National Park, South Africa; and the Miombo woodlands of Malawi and Zambia (Fig. 1). Cow dung samples from India were also processed. Samples were weighed, air dried, and reweighed on site; shipped to Germany in loosely packed cardboard boxes; reweighed; subsampled for elemental analysis; and burned at the Max Planck Institute for Chemistry (MPI) in Mainz (Fig 2, Table 1). Most samples were rehydrated with deionized water (DIW) before burning. Typically, 0.5 to 0.6 kg subsamples of grass and 1 to 4 kg subsamples of branches were burned for a given experiment. Burn durations ranged from several minutes for grasses to >1 hour for large branches, charcoal, and dung.



Fig. 1. Sampling locations in southern Africa.

Subsamples of biofuels and ash were ground in a Wiley mill, weighed, dried at 72° C for 48 hours, cooled in a desiccator, and reweighed. C and N contents were measured with a Carlo-Erba Elemental Analyzer. Halogens, S, P, Ca, and K were measured by ion chromatography (IC) following digest of subsamples via Parr Bomb [Butler et al., 1979].

Measurement Techniques for Soluble Gases

NH₃, HONO, HNO₃, HCl, SO₂, CH₃COOH, and HCOOH in ambient air and burn exhaust were sampled at 18 SLPM with tandem mist chambers [Keene and Savoie, 1998] containing DIW and analyzed by IC. A 45-mm quartz fiber filter (Pallflex QAT-UP 2500) removed particles at the stack. Analytes condensed onto inlet walls (1.2 m insulated 3/16 inch ID Teflon line) were extracted, analyzed, and included in calculating total concentrations. Inorganic volatile Cl, Br, and I were sampled at 100 SLPM on tandem 90-mm Rayon filters (Schleicher and Schuell 8S) impregnated with 10% K₂CO₃-10% glycerol [Bardwell et al., 1990] and positioned immediately downstream of a 142-mm quartz fiber filter (Pallflex QAT-UP 2500) that removed particles at the stack.

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Andreae, Pascal Guyon, Christof Jost, Olga Mayol-Bracero, and Detlev Sprung of the MPI Biogeochemistry Division; and Hans Friedli at the National Center for Atmospheric Research collaborated in the investigation. Champagne to toast the dung burn was graciously provided by Paul Crutzen. Financial support was provided by the National Science Foundation through awards ATM-0003865 to the University of Virginia and ATM-0001424 to Scripps Institution of Oceanography.

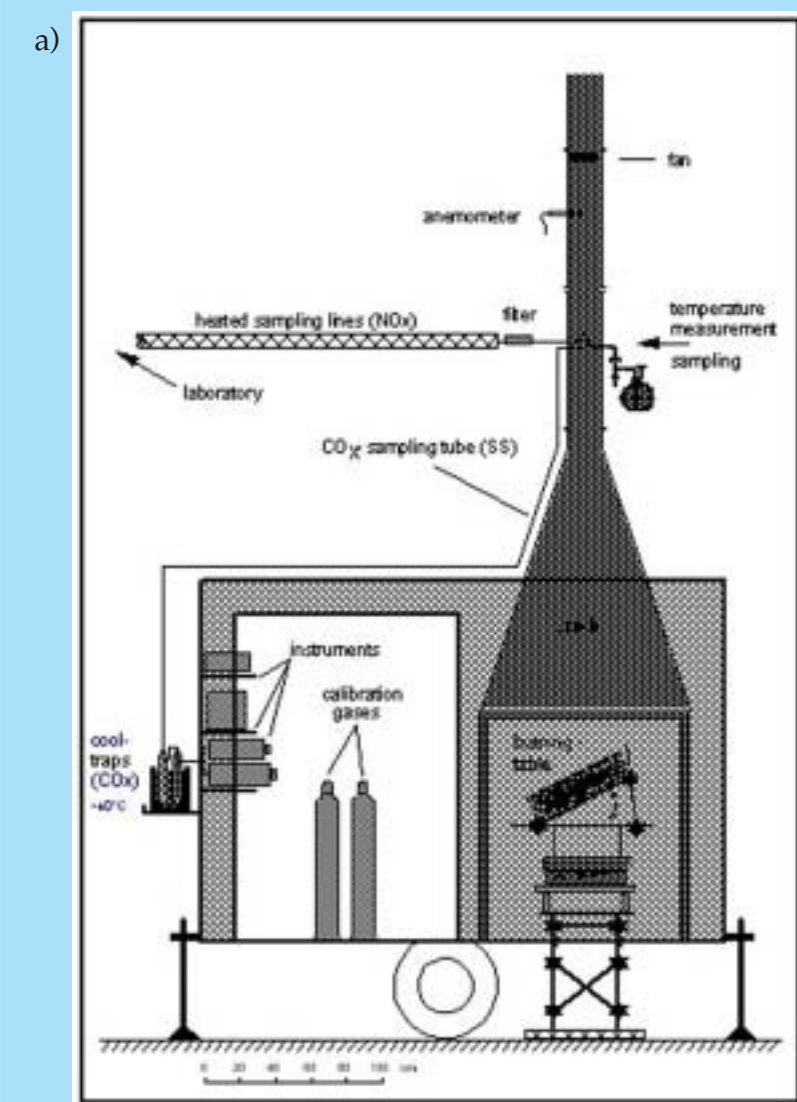


Fig. 2. a) Diagram of burning facility at MPI; b) technician igniting center of branch sample stacked on burn table positioned at 10°; and c) sampling equipment deployed on roof of facility.

Table 1. Fuel type and burn conditions.

ID	Fuel Type#	Burn Conditions*
Etosha National Park, Namibia		
4	Grass	Heading
7	Shrubs	10°, front ignite
8	Grass	Backing
12	Grass	Backing
14	Bush (>4cm)	10°, front ignite
16	Grass	Heading
17	Litter	10°, backing
19	Shrubs	10°, front ignite
20	Grass	Flat, center ignite
Kruger National Park, South Africa		
2	Grass	Backing
3	Grass	Backing
4	Branches (0.2-1cm)	10° front ignite
5	Grass#	Heading
6	Grass#	Heading
7	Grass#	Center ignite
8	Litter/leaves	Backing
9	Grass	Backing
10	Grass	Backing
11	Branches (0.1-1 cm)	10°, front ignite
12	Grass	Backing
13	Grass	Backing
15	Grass#	Side ignite
16a	Grass	25°, backing
16b	Grass#	Heading
17	Twigs (0.2-1.5 cm)	10°, front ignite
18	Grass	Heading
19	Branches (0.2-2 cm)	10°, top ignite
20	Grass	25°, backing
22	Grass	Backing
23	Grass	Backing
Miombo Woodlands of Malawi		
1	Grass	Backing
2	Branches (0.5-2 cm)#	Flat center ignite
5a	Grass	Heading
5b	Grass	Heading
6	Branches (1-2 cm)#	10°, center ignite
9+5	Litter+grass	10°, backing
11	Brush/shrub	10°, front ignite
12	Ag. waste – maize#	25°, backing
14	Branches#	10°, pyramid stack, front ignite
15	Grass	Backing
17	Charcoal#	Flat, preheated stove, front ignite
19	Ag waste – maize#	Flat, center ignite
Miombo Dambos (grasslands) of Zambia		
2	Grass#	Side ignite
3	Grass#	Backing
7	Grass	Backing
8	Grass	Backing
9	Grass	Heading
India		
1a	Cow dung#	Flat, stove
1b	Cow dung#	10°, open burn

#Designates samples that were not hydrated prior to burn
*Unless otherwise noted, burn table positioned at 30° and fuel loosely arranged.

Results

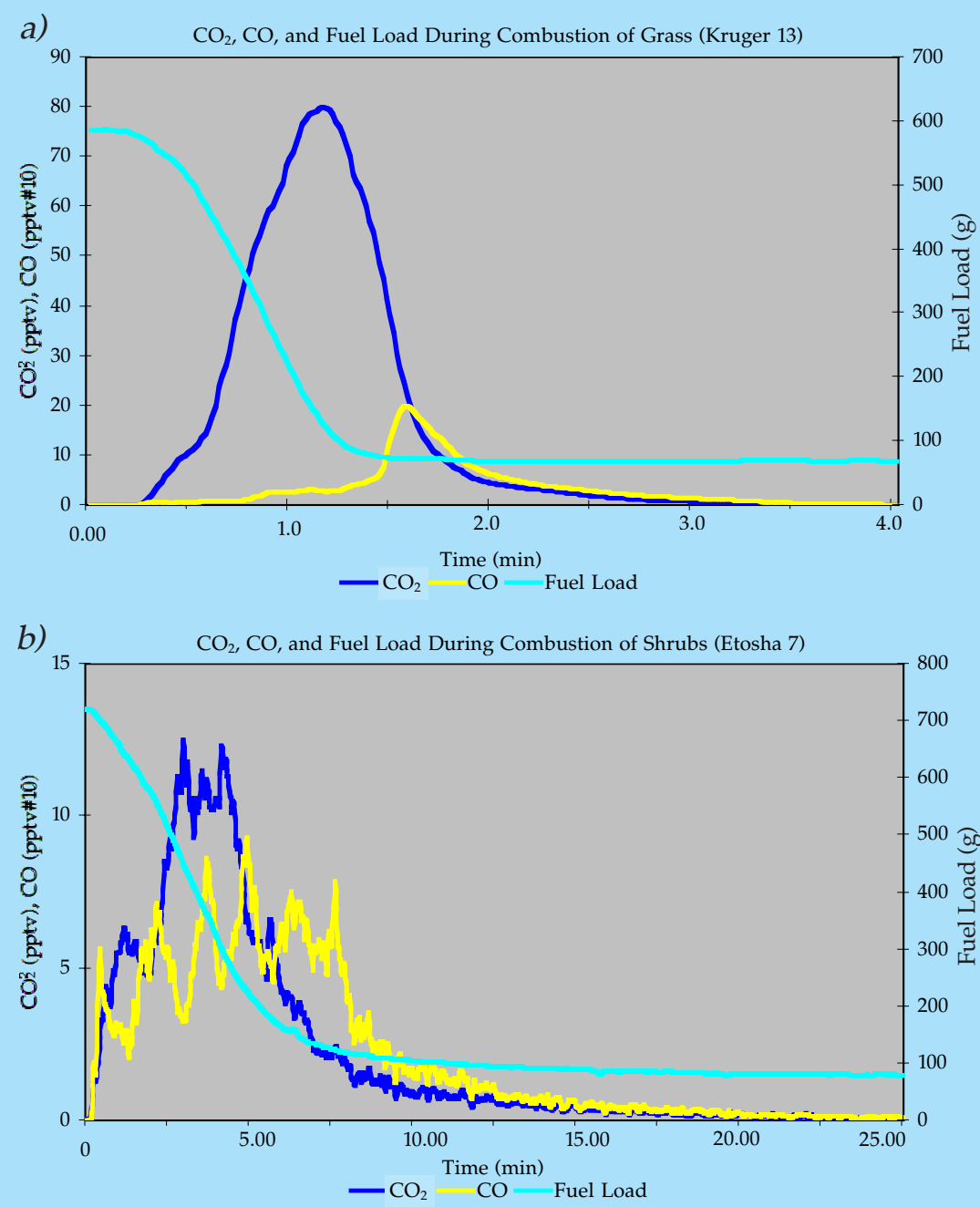


Figure 3. Time series of CO₂, CO, and fuel load for typical burns of a) savanna grass (Kruger 13) and b) shrubs (Etosha 7).

Discussion

CH₃COOH and HCOOH.

- CH₃COOH was the most abundant volatile acid emitted during all burns and accounted for large fractions of emitted C other than CO₂ and CO.
- Relatively larger fractions of C were emitted as carboxylic acids during heading fires and litter combustion (Fig. 4, Table 1).
- Mixing ratios of carboxylic acids exceeded those of NH₃ during 65% of burns suggesting that the multiphase chemical evolution of bioburn plumes is dominated by aqueous transformations involving acidic aerosol solutions.

NH₃, HONO

- NH₃ was the most abundant N gas other than NO_x measured during the experiment; typically 1% to 15% of emitted N was in the form of NH₃.
- Relatively larger fractions of N were emitted as NH₃ during the combustion of woody fuels, litter, and dung, which were associated with longer periods of smoldering conditions (Fig. 5, Table 1).
- Significant HONO was emitted during most burns (Fig. 4); time-series analyses of fresh samples indicate that virtually all measured HNO₃ in the burn exhaust was a secondary product of the aqueous-phase oxidation of HONO in mist solutions.

Total volatile inorganic Cl and HCl.

- Large fractions (20% to 70%) of emitted Cl was typically in the form of volatile inorganic Cl.
- Measured HCl accounted for <50% of volatile inorganic Cl in most burns suggesting that substantial fractions of emitted Cl were associated with Cl₂, HOCl, or other photochemically active, inorganic Cl gases.
- Transformations involving Cl radicals (e.g., alkane oxidation) may be important in the chemical evolution of bioburn plumes.

SO₂

- Typically 20% to 90% of emitted S was in the form of SO₂

Summary of work in progress

The above are preliminary results from a work in progress. Related activities currently underway include:

- Completing analyses of volatile Br and I and aerosol composition.
- Integrating results from all groups and calculating chemical mass balances.
- Integrating results with models to estimate regional bioburn emissions.

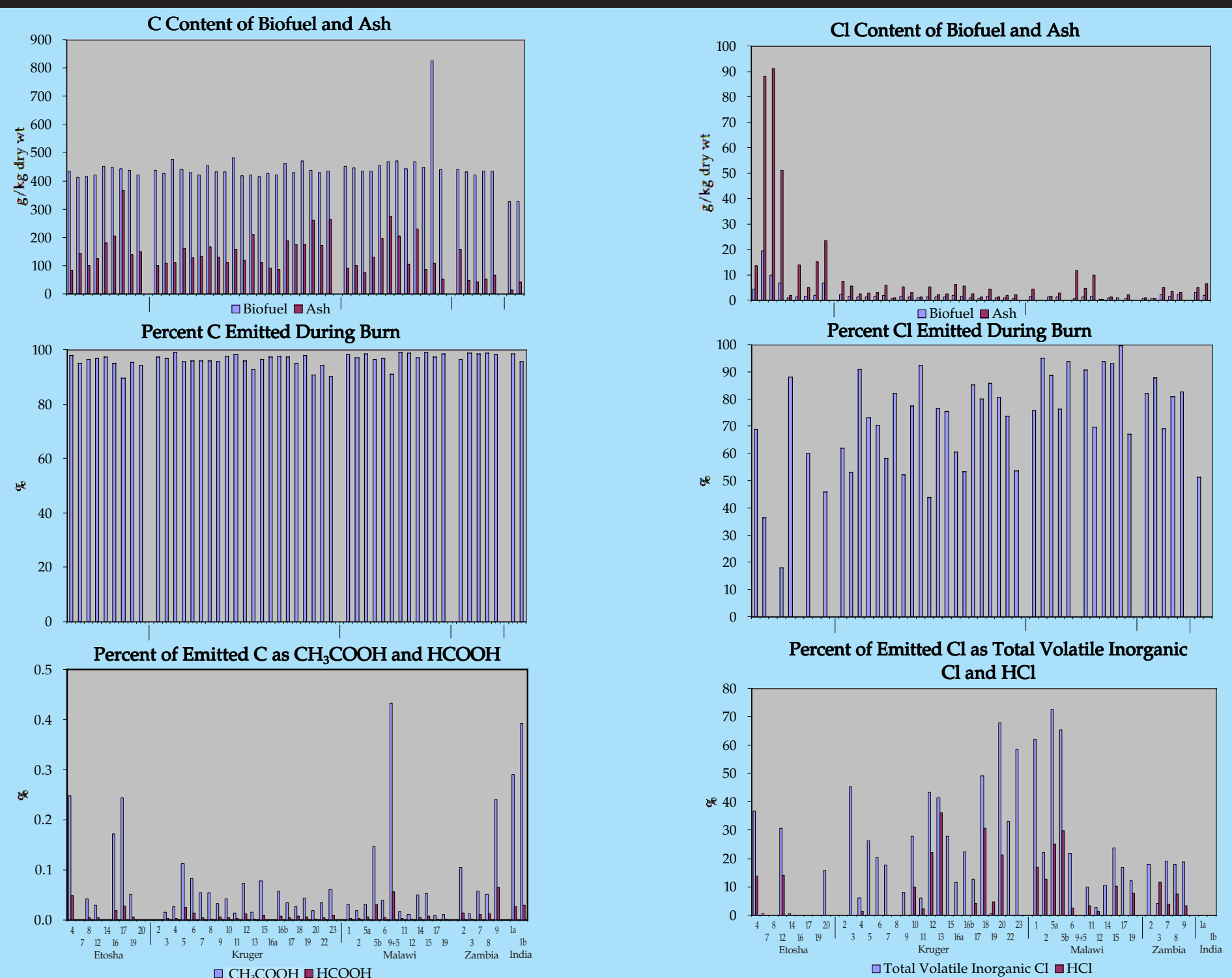


Figure 4. C contents of fuel and ash and emissions of total C, CH₃COOH, and HCOOH.

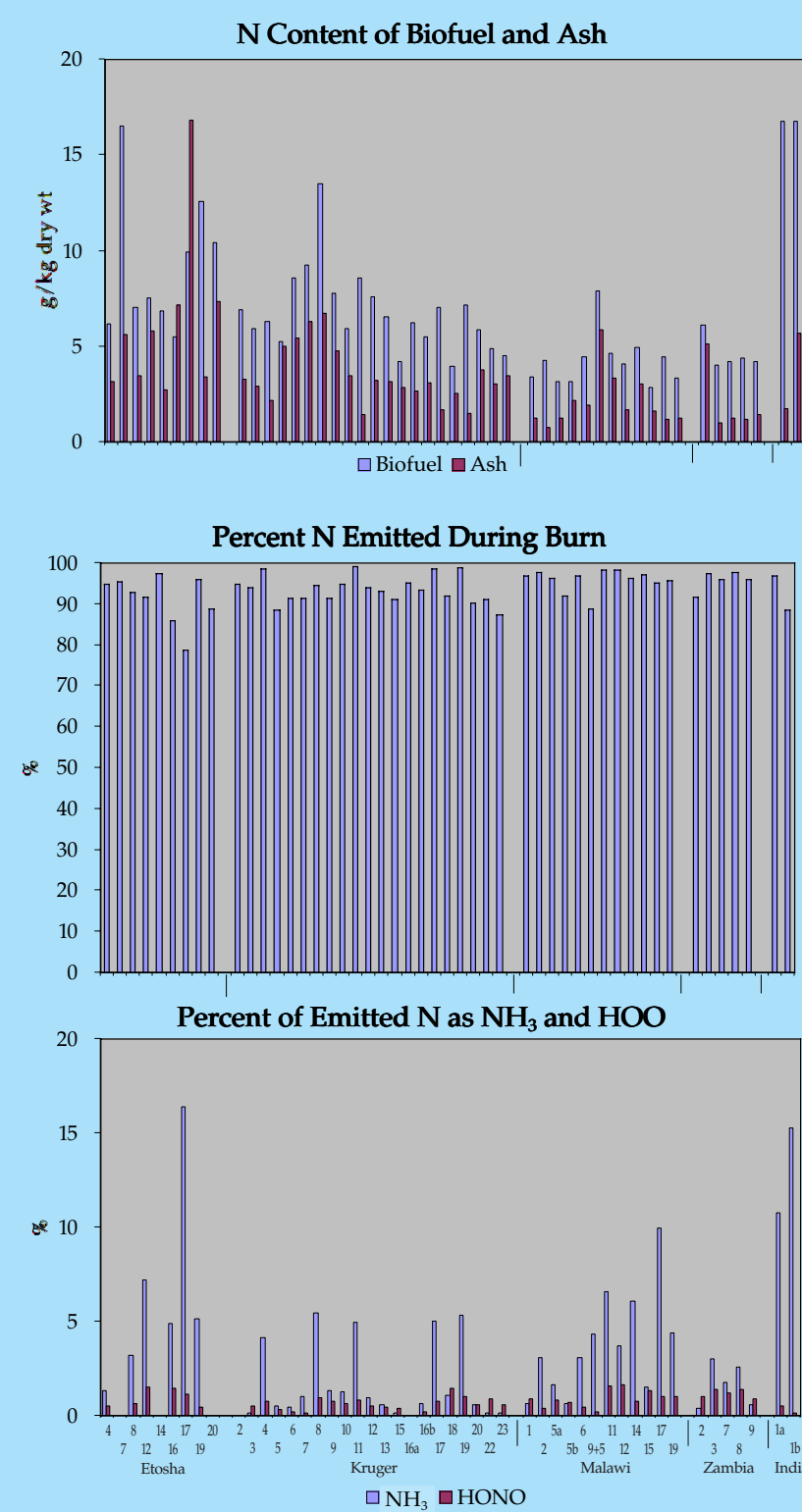


Figure 5. N contents of fuel and ash and emissions of total N, NH₃, and HONO.

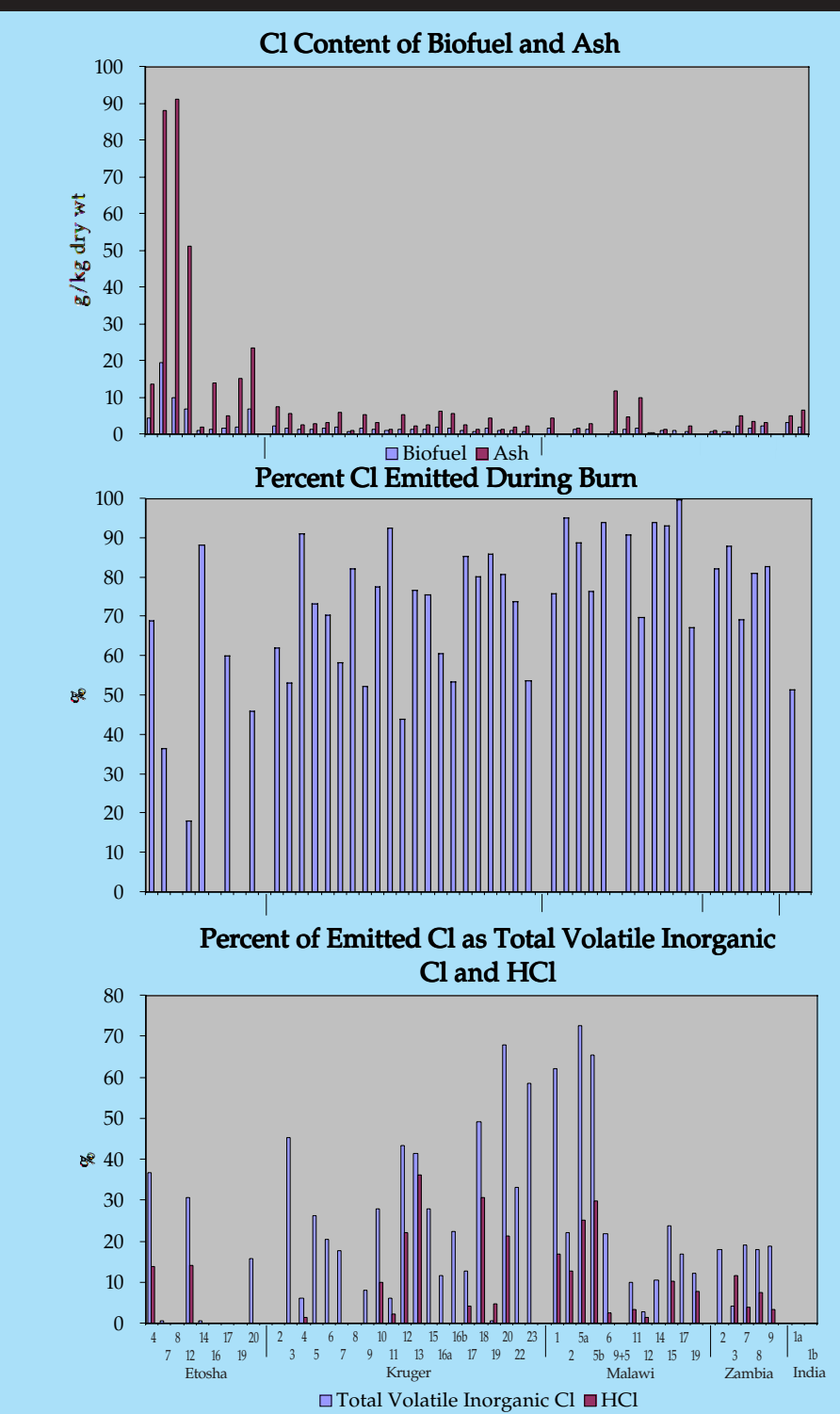


Figure 6. Cl contents of fuel and ash and emissions of total Cl, volatile inorganic Cl, and HCl.

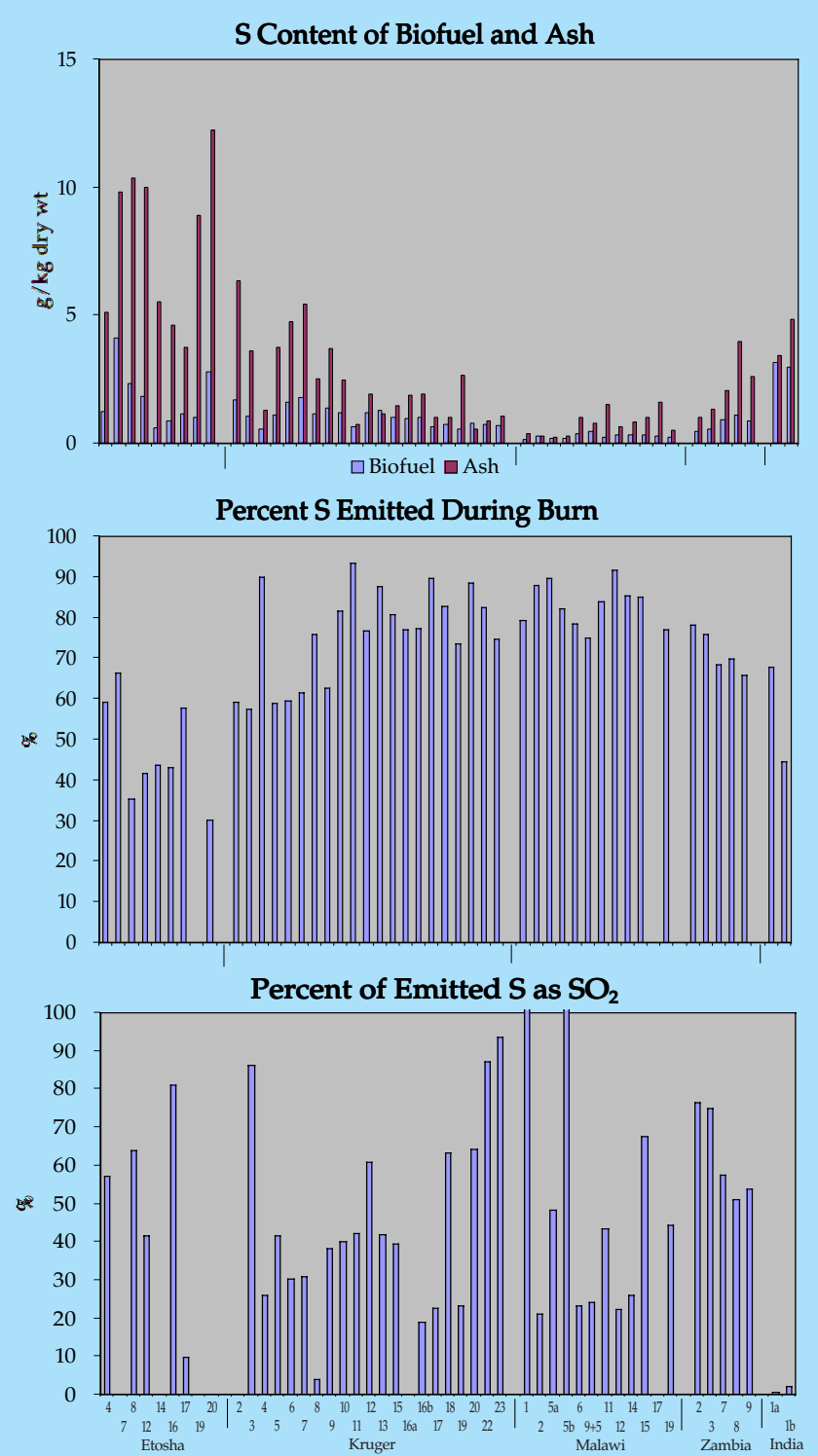


Figure 7. S contents of fuel and ash and emissions of total S and SO₂.

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