SECTION A.   PROJECT SUMMARY

Collaborative Research: Biomass Burning Emissions Over Southern Africa

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Biomass burning is a major source for atmospheric pollution over southern Africa as well as globally (e.g. Crutzen et al, 1979; Crutzen and Andreae, 1990). Biomass burning from the African continent currently accounts for about 35% to the global total (Logan and Yevich cited in: Lobert et al, 1999) and substantial absolute and percentage increases are projected for the future based on demographic predictions (Crutzen and Andreae, 1990, Lelieveld et al., 1998). Biomass burning emits a large variety of gaseous and particulate compounds with significant implications to atmospheric and biogeochemical cycles. Consequently, quantification of biomass burning emissions is essential for understanding and predicting associated environmental impacts. However, despite intense scientific study over the past two decades, global and regional emissions of some compounds are still poorly constrained.

We propose a 2-year investigation of biomass burning over southern Africa as part of the SAFARI-2000 campaign based on a coupled analysis of biomass composition, emission measurements, and mass-balance calculations for representative vegetation types. Biofuels will be sampled by collaborating SAFARI-2000 investigators during the dry season of 2000 in three regions of southern Africa that are representative for major ecosystem types: The Etosha National Park in northern Namibia, the Kruger National Park in northeast South Africa and woodland sites in Zambia, Malawi, Tanzania, Zimbabwe and Mozambique (the Miombo Network).

Experimental fires will be conducted at the beginning of 2001 utilizing an existing facility at the Max Planck Institute for Chemistry, Mainz, Germany. This facility had been established by P.J. Crutzen and J.M. Lobert (Lobert 1989, Lobert et al. 1990, 1991) and has been used by many other researchers. It provides a partially controlled burning environment and will be used to measure major exhaust species (CO_2; CO; CH_3Cl, CH_3Br, CH_3I; NO_X; N_2O; CH_4; NH_3; HCl, HNO_3; SO_2, $HCOOH$, CH_3COOH; alkaline-reactive, volatile Cl, Br and I; the ionic composition of particles including Cl^-, Br^-, NO_3^-, SO_4^{2-}, $HCOOH$, CH_3COOH; and the elemental composition of particles including C, N, Cl, Br, I, S) as well as the elemental content of both biofuels and ash-residues. These analyses will provide for a partial or full balance for fuel carbon, nitrogen, sulfur, chlorine, bromine and possibly iodine. Sampling and analytical techniques will include canister samples, mist chambers, filter-pack sampling and continuous online sampling as well as non-dispersive infrared and chemoluminescence detection, gas chromatography / mass spectrometry, ion chromatography and other methods. Emissions will be interpreted based on a mass balance for fuel carbon, nitrogen, sulfur, chlorine, bromine, and possibly iodine.

Results will be integrated with those from other SAFARI-2000 investigators to model regional biomass burning emissions of halogen-, nitrogen-, sulfur-, carbon-containing compounds. This study will provide hitherto unavailable resolution in our ability to predict these fluxes and to assess associated regional and global implications.

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SECTION C. PROJECT DESCRIPTION

C.1. INTRODUCTION

Biomass burning is a major source for atmospheric pollution over southern Africa as well as globally (e.g. Crutzen et al, 1979; Crutzen and Andreae, 1990). Similar amounts of carbon are emitted to the atmosphere from both biomass burning and fossil fuel combustion (Crutzen and Andreae, 1990). Biomass burning from the African continent currently accounts for about 35% to the global total (Logan and Yevich cited in: Lobert et al, 1999) and substantial absolute and percentage increases are projected for the future based on demographic predictions (Crutzen and Andreae, 1990, Lelieveld et al., 1998). Biomass burning emits a large variety of gaseous and particulate compounds with significant implications to atmospheric and bio-geochemical cycles. Consequently, quantification of biomass burning emissions is essential for under-standing and predicting associated environmental impacts. However, despite intense scientific study over the past two decades, global and regional emissions of some compounds are still poorly constraint.

We propose a 2-year investigation of biomass burning over southern Africa as part of the SAFARI-2000 campaign based on a coupled analysis of biomass composition, emission measurements and mass-balance calculations for representative vegetation types. Results will be integrated with those from other SAFARI-

2000 investigators to model regional biomass burning emissions of halogen-, nitrogen-, sulfur- and carbon containing compounds.

C.2. BACKGROUND INFORMATION

The most abundant products from the burning of biomass are water vapor, carbon dioxide (CO_2) and carbon monoxide (CO), but several thousand minor gaseous and particulate compounds have been detected in the smoke from burning plant material (e.g., Johnson, 1959). All emissions from open biomass burning are controlled by a few basic but highly variable factors including fuel moisture, physical size and arrangement of the fuel and wind conditions. All of these factors determine overall burning efficiency (e.g., Lobert and Warnatz, 1993), which is defined as the fraction of emitted CO_2 to the total amount of plant carbon, unity indicating a complete conversion of all carbon to CO_2. However, open burning is never 100% efficient and hence many minor compounds from inefficient burning can be found in significant quantities.

In addition to the above factors, the elemental composition of biofuels exerts and important controlling influence on corresponding emissions of compounds that contain nitrogen (Lobert et al, 1991, Hao et al. 1991), sulfur (Delmas, 1982; Bingemer et al, 1991) and halogens (e.g. Rasmussen et al., 1980; Andreae et al., 1996, Blake et al., 1996). These elemental components of biofuels exist in association with organic constituents (nitrogen and sulfur) and as electrolytes (halogens). They often form reactive, short-lived intermediates during the high temperature conversion of the fuel (Lobert and Warnatz, 1993) and subsequently recombine with carbon-containing fragments or hydrogen atoms into the more stable products that are emitted to the atmosphere.

Compared to carbon emissions, our knowledge of emissions of speciated N-, S-, and especially halogen-containing compounds from different types of biomass burning and different ecosystems is very limited and, consequently, regional and global flux estimates are highly uncertain. Despite these uncertainties, however, available evidence indicates that biomass burning emissions represent major fluxes in regional and/or global budgets (for N, see Lobert et al., 1991; for S, see Bingemer et al., 1991; for Cl, see Lobert et al., 1999; for Br and I see Andreae et al., 1996, Blake et al., 1996, Ferek et al., 1998).

The GEIA / Reactive Chlorine Emissions Inventory (RCEI) was the first comprehensive attempt to estimate global emissions of major chlorinated compounds from biomass burning on a 1° latitude × 1° longitude grid (Keene et al., 1999; Lobert et al., 1999). Results from RCEI clearly demonstrated that (a) integrated, global fluxes of individual compounds from biomass burning varied by a factor of three between various emission scenarios and (b) reported underlying data for different regions, fuels and fire types varied by orders of magnitude between investigated regions, fuels and fire types. Whereas large variations between individual fires are characteristic of the biomass burning system, the very limited availability of coupled data for fuel elemental content and associated emission factors seriously limits our ability to predict emissions from biomass fires and their associated environmental impacts.

The RCEI effort demonstrated this limitation in our understanding of chlorine emissions, which are of special interest with respect to several important processes including stratospheric ozone depletion, but similar constraints are true for emissions of N-, S-, Br- and I-containing compounds as well. To-date, no effort similar to the RCEI project has been published for any of these compound classes. Considering their importance for many Earth systems including climate, a more detailed emissions and mass-balance database is urgently needed. For example, Lobert et al. (1991) and Kuhlbusch et al. (1991) showed that the loss of nitrogen through "pyrodenitrification" could potentially reduce soil fertility in certain ecosystems on the long-term, yet a comprehensive nitrogen balance is lacking for most biomass burning studies carried out during the last decade. The research proposed herein is designed to fill this critical information gap for southern Africa as part of the SAFARI-2000 project.

SAFARI-2000 (Swap and Annegarn, 1999; http://safari.gecp.virginia.edu/) will integrate investigations of ecosystems chemistry, atmospheric chemistry, wet- and dry season dynamics, vegetation and soil systems of southern Africa. The number and breadth of studies during SAFARI-2000 - including onsite biomass burning efforts, satellite observations, and associated ecological, chemical and biological processes- make it an ideal base for the research proposed herein. Logistical support and the variety of measurements will enable a unique opportunity for overlapping science that will extend far beyond a localized effort. The SAFARI-2000 rationale best describes the unique nature of the study region:

> [..] the atmospheric environment, with clearly defined inflow and outflow regions, and the geography of Africa south of the Equator permits a reasonably discrete study region, which in turn permits mass-balance calculations to be performed with acceptable accuracy. This is especially the case during austral winter when anticyclonic circulations and associated clear sky conditions that are favorable for satellite remote sensing dominate the region on as many as four out of every five days [..]. It will be possible to conduct a closed experiment within southern African that is focused on the characterization of biogeochemical and biogeophysical inflow and outflows to the region. The existing regional scientific database, when combined with the sufficient regional scientific and logistic base, provides the framework necessary for the conduction of the SAFARI 2000.

The results of our proposed research effort will be essential in meeting the major SAFARI-2000 objectives.

C.3.   RESEARCH OBJECTIVES

The principal objective of this research effort is to reliably model halogen-, nitrogen-, sulfur- and carbon fluxes to the atmosphere over southern Africa during the dry season. This objective will be met by addressing the following specific research objectives:

1. In collaboration with other SAFARI investigators, we will sample representative biofuels from three regions in southern Africa supporting major ecosystem types including Etosha National Park, Namibia; Kruger National Park, South Africa; and the woodlands of the Miombo Network in Zambia, Malawi, Tanzania, Zimbabwe and Mozambique.

2. We will analyze the elemental composition (C, N, Cl, Br, I, S) of the biomass and of the residual ash after combustion.

3. We will burn the samples under semi-controlled conditions and measure the emissions of major species (CO_2; CO; CH_3Cl, CH_3Br, CH_3I; NO_X; N_2O; CH_4; NH_3; HCl, HNO_3; SO_2, HCOOH, CH_3COOH; alkaline-reactive, volatile Cl, Br and I; the ionic composition of particles including Cl^-, Br^-, NO_3^-, SO_4^{2-}, HCOOH, CH_3COOH; and the elemental composition of particles including C, N, Cl, Br, I, S).

4. We will assess a mass balance for each individual fire and group of experiments and develop predictive algorithms for biomass burning emissions.

5. We will collaborate with SAFARI-2000 investigators in applying algorithms to estimate regional emissions from biomass burning.

C.4.   RESEARCH PLAN AND METHODOLOGY

C.4.1. Sampling Sites and Collaborators; Vegetation Samples

SAFARI-2000 combines many study areas in southern Africa and also overlaps with other science initiatives such as the IGBP Miombo Network (http://miombo.gecp.virginia.edu/), the Kalahari Research (http://kalahari.gecp.virginia.edu/) and research activities in the Kruger National Park (http://www.ecoafrica.com/krugerpark/). The proposed project will utilize biomass samples from three regions that represent major ecosystem types (Figure 1), the Etosha National Park (ENP) in northern

Namibia; the woodlands of the Miombo Network in Zambia, Malawi, Tanzania, Zimbabwe and Mozambique; and the Kruger National Park (KNP) in north-east South Africa. Collaborators for sampling include M. Garstang (U. Virginia) and Conrad Brain at Etosha; P. Desanker (U. Virginia) in the Miombo region and H. Annegarn and L. Marufu at Kruger National Park. See appended letters of intent.

Etosha National Park in north central Namibia, at 22 km^2, is one of the world's largest game preserves. The park includes the Etosha Pan, a shallow depression of land that collects water during the wet season. The area is dominated by the Kalahari ecosystem, which covers a large portion of central Africa extending from the humid equatorial zone to the arid subtropics in the south. Average annual precipitation decreases by an order of magnitude from north to south and associated vegetation varies from evergreen tropical forests through semi-deciduous woodlands and various savannas types to semi-arid Shrubland (Scholes and Parsons, 1997).

The largest area of global, tropical dry forests and woodlands is situated in Africa (5.5 million km^2; Figure 1), about half of which occurs in the Miombo region of central Africa. The Miombo Woodlands system includes all those southern and central African ecosystems which occur under a hot, sub-humid, seasonally-wet climate. The components of this system include woodlands and grasslands (called *dambos*). Miombo woodland is the dominant vegetation type of the central African plateau, extending from Tanzania and the Democratic Republic of Congo (formerly Zaire), through Zambia, Malawi and eastern Angola, to Zimbabwe and Mozambique (Desanker et al., 1997) and it covers about 3 million square km of area. In contrast to the Kalahari's diversity, the Miombo woodlands are relatively uniform over an area covering approximately one half of central and southern Africa (Desanker et al., 1997). The Kalahari and Miombo overlap in western Zambia.

The predominant vegetation types in the remaining part of southern Africa are woodland, semi-arid, and arid savannas. The Kruger National Park is located further south in the low-lying savannas of South Africa and comprises an area of about 19000 km^2. It contains mostly arid savanna with only some moist savanna in the far north and south (locally called *bushveld*; Stocks et al., 1996). KNP is locally managed and the primary goals are the development and maintenance of maximum biotic diversity through minimum interference (Joubert, 1988). Prescribed biomass burning has been a common practice ever since the park's establishment in 1926.

Figure 1: Map of southern Africa showing the main ecological zones and proposed locations for vegetation sampling indicated in white (Etosha National Park, Namibia; Kruger National Park, South Africa; rectangle describes the Miombo Transect region with its five main study sites).

Savannas in southern Africa generally consist of grassy material with some ground litter (partially decomposed bio-material mostly from trees and bushes) and dispersed trees, which compete with grassy material for dominance and can cover between a few and 80% of the area. According to Kelly Kaylor, (University of Virginia, personal communication 1999), woody cover in woodland savannas generally decreases from north to south, with ~80% in northwestern Zambia and ~40% cover in northern Botswana and virtually no trees in arid savanna regions. Grass cover is fairly continuous throughout the region of annual burning. Although much of the biomass found in these ecosystems is burned annually (grasses, small brushes and trees) or used to produce charcoal (wood), the relative amounts of different components that burn vary depending on fuel load, types of woody vegetation, and fire conditions. Juvenile trees may be susceptible to fires and much of the woody litter and all of the grass typically burns annually.

In collaboration with SAFARI investigators within each region, we will identify and sample representative biofuels that are locally consumed by fire during the dry season, i.e. only those parts of plants that actually contribute to biomass burning emissions. This will involve selective sampling of trees, bushes, grasses and ground litter as well as agricultural fuels and charcoal (if applicable). We will collect about 20-30 samples of biofuels per study region and will conduct a total of approximately 60 burning experiments with individual fuels and combinations of fuels. The amount needed for each experiment is about 1 kg (for grassy materials) to 4 kg (for woody material). In collaboration with local researchers, we will identify the

major types of vegetation burned in reach region. we will provide collaborators with detailed procedures for sampling, treating, storing and shipping the biofuels. Samples will be weighed and air dried for a minimum of 24 hours on site before shipment. Where possible, samples will be weighed before and after drying to determine the actual moisture content. Samples may require a conditioning step for the experiments that involves re-moisturization to their original water content.

C.4.2. Sample Shipment, Treatment and Import.

Samples from the collaborating sites will be loosely packed in cardboard boxes, which act as an efficient moisture buffer. Holes in the boxes will enable air circulation and prevent built-up of mold or other rapid alteration of the material. Shipment of samples will be in accordance with local and international customs regulations and, if necessary, will be done in a sealed overpack that allows for internal circulation.

Biofuels will be shipped directly from each sampling site to MPI by airmail or air cargo services. German customs does not have general import restrictions on plant materials. The office for the protection of plant life ("Pflanzenschutzbehörde") of the state of Rheinland Pfalz permits the import of the required amounts of plant materials for scientific purposes. Scientific usage has to be verified with an official letter from MPI and appropriate disposal of the samples after use is required. Burning and shipping out of the country are acceptable methods for disposal as stated by Mr. Eichman of the Pflanzenschutzbehörde in Neustadt a.d. Weinstr. The application for import of plant material has to be submitted before the actual shipment and will be filled out by onsite collaborators and submitted along with the samples from Africa in order to permit German customs to grant the import free of customs duties.
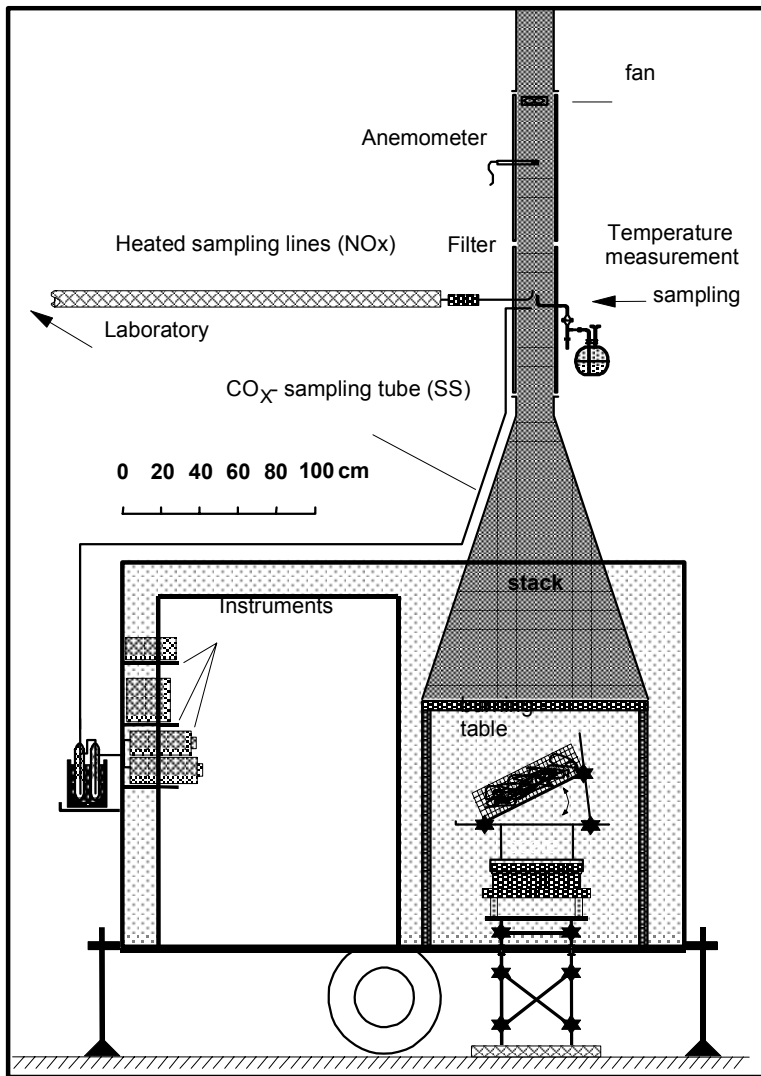
Representative sub-samples of each biofuel and ash will be oven-dried in Germany, sealed in air-tight containers, and shipped to the U. Virginia for elemental analysis. The import of non-sterilized plant material into the United States is generally restricted and requires a permit. In consultation with representatives from the US Department of Agriculture, we are currently preparing a permit application for importing the heat-treated samples. Based on these discussions, we anticipate no problems in obtaining the necessary permit. The normal processing time for permit applications is 3 to 4 months.

C.4.2. Fire experiments

C.4.2.1.   Burning Facility

The burning facility at MPI is shown in Figure 2 and was described and tested in detail by Lobert (1989) and Lobert et al. (1990, 1991), and also previously utilized by Manö and Andreae (1994) and Holzinger et al. (1999) among others. Briefly, the main parts of the apparatus include a hood in the form of an inverted funnel and a burning table of 60×60 cm which is placed on a high (1 g) resolution scale (E1210 & EB60; Mettler), calibrated with standard brass weights (Mettler) with 1 g accuracy. A simple mechanism allows the adjustment of the burning table to an angle up to $60°$ in order to simulate different wind directions, namely heading fires (fire front moving with the wind flow) and backing fires (fire front moving against the wind flow). All major parts are made of stainless or galvanized steel and are mounted in a trailer (Fladafi) which also contains data acquisition modules, CO and CO_2 analysis and other equipment required for carrying out the experiments.

A differential pressure anemometer (Furness Controls Ltd., Bexhill, England) is used to measure the flow rate of stack gases through the inverted funnel. A fan is built into the top of the stack to establish a minimum draft of about 200 l min^{-1} during low temperature combustion and to prevent the exhaust gases from exiting the funnel at the bottom. Temperature sensors (Ni/Cr-Ni, TICON) are used to determine both stack gas and fuel temperatures and can also be mounted at sample inlets. Several heated sampling tubes (stainless steel and Teflon; Heraeus) allow to draw exhaust gases into instruments placed in an adjacent laboratory, e.g. the NO_X analyzer. Other sample ports allow for online sampling with canisters or mist chambers. . All continuous measurements (T, CO, CO_2, NOx, flow, weight etc.) are recorded with a 16 bit

fan

Anemometer

Heated sampling lines (NOx) Filter

Temperature measurement

sampling

Laboratory

CO_X sampling tube (SS)

0 20 40 60 80 100 cm

stack

Instruments

table

data logger (WES) at a frequency of 1 to 0.2 sec^{-1} and stored on a personal computer. Environmental data such as humidity, ambient temperature etc. could also be logged.

Figure 2: Schematic of the burning facility at MPI. The inside main burning table, is shown raised to simulate different wind directions. The outside stack accommodates the attachment ports for continuous and discrete sampling, temperature probes and flow meter.

C.4.2.2. Observations and Fire Behavior

Besides the reduced cost of operation and logistics, the two main advantages of utilizing a burning facility such as the one at MPI are a) the capability to calculate a complete mass balance for each experiment and b) the ability to simulate different fires and, by doing so, to distinguish the two principal stages of open burning. These two stages are flaming combustion, where hot, open flames predominate the process and efficiently convert the biofuels, and smoldering combustion where low-temperature burning predominates and the fuel is converted in a much less efficient way, typically leaving more residue behind and incompletely converting biofuels (Figure 3). Gases that are very stable or highly oxidized are emitted during the flaming stage of a fire (e.g. CO_2, SO_2, NO_X, N_2O, N_2), whereas most emissions are products of incomplete combustion and are formed during the smoldering stage (e.g. all pure, halogenated, oxygenated, nitrogen-containing and other hydrocarbons, as well as compounds like NH_3, HCl, HBr). Only few compounds are produced in similar amounts in both stages (e.g. C_2H_2, NCCN).

The arrangement of the fuel bed to burn at an angle of 30-45° allows to simulate "backing" fires when the fuel bed is ignited at the top and the flame front slowly moves against the wind direction (i.e. the air flow through the hood) and "heading" fires, in which the flame front quickly moves with the wind / air flow. Flames during backing fires tend to be smaller but, due to the slow movement, convert the biofuels more efficiently compared to fast moving flames in heading fires. These simulations allow to investigate the differences in the nature and amounts of combustion products and to improve understanding of involved processes. Natural, open fires are usually a combination of all burning stages, although one usually predominates over the other to a certain extent. When applying appropriate algorithms to the results of the proposed experimental fires, different open fire scenarios can be simulated and emissions can be calculated accordingly.
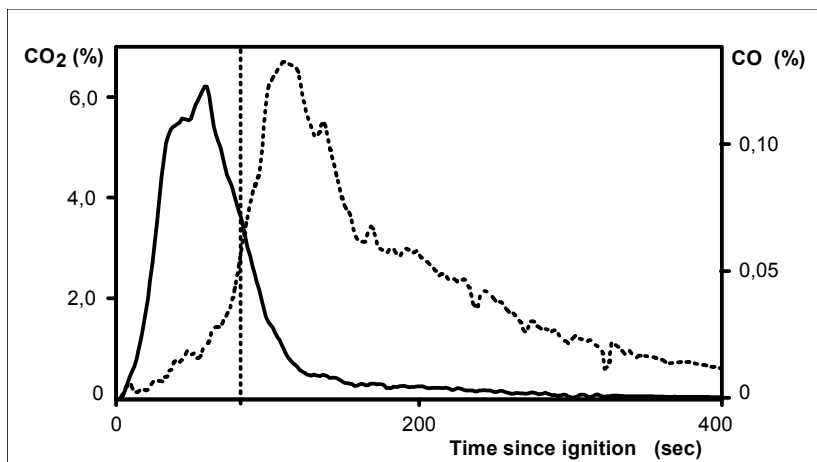
Figure 3: Typical fire of savanna grass in a backing configuration (Lobert et al., 1990). Mixing ratios of CO_2 (solid) and CO (dashed) are shown during the course of the fire and represent the pre-dominant fire emissions during the flaming (CO_2) and smol-dering (CO) stage of the fire. The transition between stages occurs at about the time when the curves cross (dashed, vertical line).

The overall mass balance of each experiment allows for quantitation of fire emissions and fuel conversion in a more accurate fashion than can be done for natural, open fires, mostly due to a lack of accurate fuel amount estimates in open fires and the difficulties in complete sampling of ash residues. However, an inherent limitation of the experimental approach is the lack of variability both in fire behavior and consumed fuels, but this can be minimized by choosing appropriate fuels, fuel arrangements and algorithms when scaling the results to regional emission scenarios. These complexities are inherent features of biomass burning experiments.

C.4.3. Measurements

Table 1: Summary of Proposed Sample and Analytical Loads for a Total of 60 Burning Experiments. Each Entry Corresponds to a Separate Analytical Technique or Measurement (see text).

Individual Measurement	Biofuels	Ash	Fire exhaust	Ambient Air
C, N, S (biomass and particles)	120	120	60[$]	60
Cl, Br, I (biomass and particles)	120	120	60[$]	60
HNO_3, HCOOH, CH_3COOH, HCl, SO_2			60[$]	60
NH_3			60[$]	60
Alkaline-reactive, volatile Cl, Br, I			60[$]	60
Particulate base cations			60[$]	60
Particulate NH_4^+			60[$]	60
Particulate anions			60[$]	60
CO			60[#]	[#]
CO_2			60[#]	[#]
NO_X			60[#]	[#]
CH_3Cl, CH_3Br, CH_3I			$\geq$120*	60
CH_4			$\geq$120*	60
N_2O			$\geq$120*	60

[$] Integrated sampling.
[#] Continuous sampling including ambient air before and after each experiment.
* Between two (integrated) and twelve (discrete) samples per experiment.

C.4.3.1. Elemental Analysis of Biomass and Ash

Biomass samples will be prepared for elemental analysis at MPI following standard procedures. Representative air-dried samples of biofuels and ash will be 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 will then be dried at 72° C for 48 hours (e.g., McKenzie et al., 1996; the minimum temperature of 72° is required for designation as "heat treated" for purposes of import into the USA), cooled in a desiccator, and stored in sealed polyethylene containers prior to analysis. Replicate sub-samples of approximately 100 mg will weighed and analyzed at UVa for C, N, and S using a Fisons EA 1108 Elemental Analyzer. With a detection limit of 10 mg kg^{-1} dry weight (Fisons Instruments, 1992), this technique should provide adequate analytical resolution for reliable quantification of C, N, and S over the range of expected elemental compositions (e.g., Kuhlbusch et al., 1991; Saito et al., 1994; Kauffman et al., 1995). If N or S contents of some biofuels are less than analytical detection limits, they will be reanalyzed using a variation of the Parr oxygen bomb technique described below, which employs an oxidizing (e.g., 1% H_2O_2) rather than reducing absorbent solution (Rubin, 1987). This approach offers analytical resolution one to two orders of magnitude greater than that of the Elemental Analyzer but requires an additional, independent set of extractions and analyses.

At UVa, replicate biofuel and ash sub-samples of approximately 1 g will be weighed, and combusted in a Parr bomb (Parr Company) charged with 40 atmospheres of oxygen. Halogen-containing products will be quantitatively reduced to Cl$^-$, Br$^-$, and I$^-$ and dissolved in 20 ml of 1% hydrazine hydrate and subsequently analyzed by ion chromatography (e.g., Smith et al., 1977; Butler et al., 1979; Rubin, 1987) using a Dionex IonPac AS11 column and 45 mM NaOH eluent. Reported performance characteristics for the analytical technique (Dionex Corp., 1997) would yield detection limits of approximately 0.1 mg Cl kg^{-1} dry weight, 0.2 mg Br kg^{-1}, and 0.4 mg I kg^{-1}, thereby providing sufficient resolution to reliably quantify Cl, Br, and I over the range of reported biofuel compositions (Andreae et al., 1996; McKenzie et al., 1996; Lobert et al., 1999). However, iodine is associated with a lower signal to noise ratio. If the iodine content of samples are a factor of 3 to 4 (or more) lower that those reported by Andreae et al. (1996), they will be undetectable.

C.4.3.2. Emissions of Water Soluble Reactive Trace Gases

During each burn experiment, major soluble nitrogen (HNO_3, NH_3), carbon (HCOOH, CH_3COOH), chlorine (HCl), and sulfur (SO_2) gases in the exhaust will be sampled with a tandem pair of standard mist chambers each containing Type 1 (>18.3 Mohm cm) deionized water and operated at nominal flow rates of 20 standard liters per minute. We will also attempt to quantify HBr and HI but, based on reported biomass compositions (see above), anticipate that these compounds will be undetectable. The mist-chamber design is similar to that described by Keene and Savoie (1998). Sampling rates will be measured with a Hastings Raydist Mass Flow meter calibrated with a bubble flow meter. The housing will be mounted immediately adjacent to the exhaust stack to minimize the length of the stainless steel sample tube (and any associated surface losses). Particles will be removed with a 47 mm quartz filter (Pallflex QAT-UP 2500) mounted in a stainless steel housing immediately downstream of the stack. The connecting tube between the particle filter and the mist chamber nebulizer will be cooled with a water jacket to 100° C. Evaporative losses of mist solutions will be manually replaced during operation to minimize variability in collection efficiencies (e.g., Keene et al., 1993). The dissolved ions in exposed solutions will be measured on site by high performance ion chromatography and gas-phase mixing ratios calculated based on the volume of air sampled.

Performance characteristics of standard mist-chamber samplers for these reactive trace gases have been critically evaluated and results for most are reported in the reviewed literature (e.g., for HNO_3, see Talbot et al., 1990; Lefer et al., 1999; for NH_3 see Lefer et al., 1999; for carboxylic acids see Keene et al., 1989; Talbot et al., 1995; for SO_2 see Stecher et al., 1997; for HCl, see below). Collection efficiencies for all species in ambient air are greater than 95%. To our knowledge, however, collection efficiencies for sampling fresh biomass burning plumes have not been critically evaluated and reported. Consequently, we propose to deploy tandem samplers to independently assess collection efficiencies based on relative recoveries from each chamber. Assuming that a given compound is sampled with equal efficiency on both tandem chambers, the collection efficiency and original mixing ratio in the burn exhaust can be calculated

directly. Precision in ambient air estimated from accumulation of individual uncertainties and/or from paired measurements ranges from +/-10% to +/-25%. Based on a typical 20-minute burn experiment, estimated detection limits for this suite of analytes in burning exhaust will range from about 25 to 90 pptv.

Although volatile inorganic Cl in marine air has been measured using standard mist chambers containing deionized water (Singh et al., 1996), potential artifacts associated with the non-specific nature of the sampling media for HCl complicate interpretation of resulting data (e.g., Graedel and Keene, 1995). Testing at UVa (Keene, W. C. and J. R. Maben, 1999, unpublished data) verify that HCl is collected at virtually 100% efficiency (i.e., with no detectable breakthrough) in deionized mist. However, Cl_2 and HOCl (and perhaps other forms of volatile Cl) also solubilize, albeit at less than 100% efficiency, in this sampling media and produce Cl^-. Consequently, measured Cl^- in exposed deionized mist solutions represents an upper limit for ambient HCl and a lower limit for soluble, reactive Cl. Reactive Cl measured with the standard mist chamber will be compared with total, alkaline-reactive Cl measured with a high-volume filter pack (described below) to assess potential emissions of volatile reactive Cl other than HCl.

C.4.3.3. Emissions of Alkaline-Reactive Halogen Gases

During each burn experiment, alkaline-reactive Cl, Br, and I in exhaust air will be sampled with a filter pack (e.g., Rancher and Kritz, 1980; Li et al., 1994; and references therein) at a nominal rate of 100 l min^{-1} (or less). Air will be drawn into the sampler through a 20 cm long stainless steel inlet positioned with minimal deviation from the exhaust stream and sized to maintain isokinetic flow. Sampling rates will be adjusted based on test burns prior to the actual experiments to maximize volume without significantly attenuating sample flow by overloading particle filters. Flow rates will be measured with a critical orifice flow tube calibrated with a manometer. Particles will be removed from the air stream with an upstream 90 mm quartz fiber filter (Pallflex QAT-UP 2500) mounted in a stainless steel housing and analyzed as described below. Alkaline-reactive, halogen gases will be sampled downstream on 47 mm tandem Rayon filters (Schleicher and Schuell 8S) impregnated with 10% K_2CO_3 -10% glycerol (Bardwell et al., 1990) and mounted in stainless steel housings cooled to 100° C. Although quantitative in ambient air, this technique has not to our knowledge been applied to sample halogens emitted by biomass burning. Consequently, sampling efficiencies for each halogen will be explicitly evaluated based on relative recoveries from the tandem impregnated filters as described above for mist chamber samplers. Filter packs will be loaded and unloaded in a class 100 clean bench; samples will be stored frozen in clean polyethylene tubes and halogen ions will be analyzed at UVa by high performance ion chromatography using matrix-matched standard solutions and procedures similar to those employed for particulate samples (summarized below). Data will be blank corrected based on dynamic exposure blanks. Assuming 20-minute exposures, estimated detection limits for the burn exhaust will be about 4 pptv Cl, 8 pptv Br, and 16 pptv I.

C.4.3.4. Emissions of Particulate Material

Upstream particle filters from the filter pack will be halved on site in a class 100 clean bench and stored frozen in clean polyethylene tubes. Half sections of each sample will be extracted in a clean bench under sonication in 10 ml DIW for 20 minutes. Base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) will be measured by flame spectroscopy, $NH4^+$ by automated colorimetry, and organic and inorganic anions (Br^-, Cl^-, NO_3^-, SO_4^{2-}, $HCOO_t$ ($HCOO^-$ + $HCOOH_{aq}$), CH_3COO_t (CH_3COO^- + CH_3COOH_{aq}) and $(COOH)_2$) by ion chromatography using procedures similar to those reported by Pszenny et al. (1989; 1998) and Galloway et al. (1993, 1996). The other set of half sections will be sub-sampled and analyzed for elemental C, N, S, Cl, Br, and I using procedures similar to those described previously for analysis of biomass samples.

C.4.3.5. Emissions of CO_2, CO and NO_X

For the analysis of CO and CO_2, exhaust gases are continuously pumped through the analyzers using stainless steel tubing (6.3 mm × 5 m) connected to downstream flow controllers and passing three different, upstream filter units including a cold trap (-20° C), a glass fiber filter (Alltech) and a stainless

steel sinter-filter (Valco) in order to remove water vapor, particles and tar, which otherwise could condense on the analyzer's optical parts. Sample gases are dynamically diluted in order to match the concentration ranges of the analyzers. NO_X is continuously sampled by pumping the exhaust gases through a heated, 6.3 mm OD Teflon tube of 8 m length followed by a Teflon filter (0.5 μm, Supelco) and a cold trap at -20° C to remove large particles and water vapor. Data resolution for all continuous measurements is only limited by the data acquisition sampling frequency (typically 1 to 0.2 s^{-1}); instrumental response times for CO and CO_2 are on the order of 5-10 seconds, for NO_X about 50 seconds.

Carbon monoxide and carbon dioxide will be determined by using two non-dispersive infrared analyzers (model BINOS, Heraeus) which operate at two different concentration ranges. The CO instrument contains one measurement cell which is electronically split into ranges of 0-100 ppmv and 0-2000 ppmv whereas the CO_2 instrument contains two separate cells with ranges of 0-1500 ppmv and 0-6 Vol-%, respectively. The detection limits for these instruments are about 5 ppmv (at a noise level of about 1 ppmv). Calibration of the instruments is carried out with commercial standard gas mixtures of CO and CO_2 (Steininger) in the measured concentration ranges.

The sum of the nitrogen oxides NO and NO_2 (referred to as NO_X) is determined by using a chemolumi-nescence NO_X analyzer type 14A equipped with a stainless steel converter (Thermo Electron). The con-verter temperature is maintained at 600° C in order to minimize interference by other nitrogen-containing compounds. At this temperature there is no interference of, e.g., acetonitrile (CH_3CN), while at 800° C about 80% of ambient acetonitrile content is recorded with this detector. According to experiments by Lobert et al. (1991), NO_X in fresh biomass burning emissions consists of about 90% NO and only 10% NO_2. For calibration of the instrument, commercial standards of NO and NO_2 in air or nitrogen are used. The detection limit of this instrument for NO_X is about 5 ppbv in air.

C.4.3.6. Emissions of CH_3Cl, CH_3Br, CH_3I

Methyl halides will be detected from discrete samples. Evacuated stainless steel canisters of 1.2 and 2.4 l volume will be attached to the exhaust stack and opened in appropriate intervals to collect the fire exhaust. Two sampling configurations will be utilized: one with 10-12 spot samples per experiment, spaced such that a descriptive profile of discrete sampling points will be obtained over the course of the experiment. The second approach will utilize integrated sampling by using canisters that are equipped with capillary inlets, effectively restricting the flow into the canister, which provide an integrated exhaust sample over portions of each experiment. This approach will require only 2-3 samples per experiment and will significantly reduce the analytical load without compromising quantitative information. We will use only one of the two approaches for most experiments but will compare both approaches in parallel for a small subset of experiments.

The stainless steel canisters that will be used for this study are electron-beam or Argon-welded and electropolished inside to ensure a smooth surface without diffusion-traps such as scratches and holes. Biomass burning gases are drawn through a glass fiber filter and enter the canister through one of two quick-open, metal bellows valves (Nupro SS 4H). Analysis starts about 20 minutes after taking the first sample and is followed by a flask cleaning procedure that involves evacuation of the used canisters, repeated flushing at about 100° C and storage under reduced pressure until the next sampling cycle.

Methyl halides will be analyzed on a gas chromatograph / mass spectrometer combination (GC/MS; Hewlett Packard) and involves preconcentration of compounds on a Unibeads 1S (Supelco) precolumn at -50° C followed by flash injection at 120° C onto a 60 m × 0.32 mm DB-5 or equivalent capillary column (J&W) and mass-specific detection of individual compounds in single ion mode. Details of the analysis procedure are described in Lobert et al. (1995, 1996). Detection limits for CH_3Cl, CH_3Br and CH_3I are several parts per trillion (ppt, 10^{-12} moles per mole) range in air with expected mixing ratios in the parts per billion (ppb, 10^{-9} moles per mole) to parts per million (ppm, 10^{-6} moles per mole) range during the

fires. Calibration gases will be tied to either the NOAA/CMDL or the SIO calibration scales. Canister storage and stability tests for the described compounds were carried out for ambient, marine samples by Lobert et al. (1995) and other investigators, indicating sufficient stability of all compounds for the period of analysis. To ensure accurate quantification of gases, storage behavior in the significantly more complex matrix of biomass burning exhaust gases needs to be evaluated and frequent stability tests as well as alternate sampling schemes will be carried out onsite.

Due to the high concentrations of sample gases, associated residue build-up and memory effects of tubing and valves and the fact that the existing GC/MS system is normally utilized for low-concentration, ambient air samples, we will need to modify the system's inlet front-end, which will be dedicated to high-concentration measurements. Specifically, we will replace two stream-selection valves (Valco), all inlet tubing, the pre-concentration column and the separation column of the system with new items in such a way that they can be easily replaced with the currently existing system and also be reused for future high-contamination measurements.

C.4.3.7. Emissions of N_2O and CH_4

Methane analysis will be carried out with a gas chromatograph (GC, Shimadzu) equipped with a flame ionization detector (FID) and a stainless steel 3 m × 3.1 mm OD column packed with 60/80 mesh molecular sieve 10 Å and supplied with high purity nitrogen carrier gas at a flow rate of 25 ml min^{-1}, the column temperature is maintained at 110° C isothermally. Gas samples of 2 ml, taken from the above described canisters, will be injected with a gas switching valve allowing a detection limit of about 9 ppb (3 times noise level) of methane (equal to 9 picogram C). For the calibration of methane measurements commercial standard gases of 1.5 to 1000 ppm will be used (Steininger). CH_4 is very stable in biomass burning samples.

Nitrous oxide will be analyzed by taking 2 ml of gas sample from each canister described above with gas-tight syringes and injecting them into a GC equipped with electron capture detector (ECD, Dani, HP, Carlo Erba). Gas samples first pass through a cold trap at -30 °C to remove water, then through a precolumn (20 cm × 6.25 mm OD) packed with NaOH coated asbestos (Supelco) to remove CO_2 followed by a 1.5 m × 3.1 mm OD stainless steel column packed with 60/80 mesh Porapak N (Supelco) for separation. The flow rate of the carrier gas N_2 is maintained at 25 ml min^{-1} with the addition of 3 ml min^{-1} of makeup gas (N_2 / 5% CH_4); oven temperature is held constant at 55° C. For calibration purposes, gas mixtures containing from 310 ppb to 360 ppm are used. Further details of N_2O analysis from biomass burning samples are described in Hao et al. (1991). Even though N_2O is known to increase slowly in samples with enhanced SO_2 and water vapor content (Muzio and Kramlich, 1988), it was shown to be stable within a few percent during the time required for analysis of biomass burning samples if necessary precautions are met (Hao et al., 1991).

C.4.4. Analysis of results

C.4.4.1. Data analysis

The primary results of the proposed measurements will be mixing ratios of all compounds in the exhaust gas of each fire. The mixing ratio of each analyte in ambient air is then subtracted from that measured in the exhaust to calculate the 'above-background' concentration of each compound contributed by biomass combustion. Typically, this background correction is small to negligible in the proposed type of measurements. Emission ratios will be calculated for each experiment to characterize fluxes of each analyte from different types of fuels and burning conditions. Emission ratios are defined as the above-background mixing ratio of the each analyte, divided by the above-background mixing ratio of a reference compound (typically CO or CO_2). The mass flux of each analyte will be quantified over each experiment based on the flow rate through the system, the elapsed time and the measured mixing ratios. Integration of this mass

flux over one of the burning stages or the whole fire results in a total mass emitted during that burning stage or the entire fire, respectively, expressed in g carbon or g nitrogen.

Calculating mass fluxes relative to the elemental content of fuels is an alternate way of expressing emission ratios. This approach is known as the *carbon balance method* described by Radke et al. (1988) for carbon emissions only and a similar balance for nitrogen has been described by Lobert et al. (1991). While Radke et al. used an approximate average percentage for the carbon content of 49.7%, we will be able to use the actual elemental contents of both biomass and ash for each individual experiment, which, in the case of nitrogen and halogens, typically differ widely. The proposed research will attempt to calculate similar mass balances for carbon, nitrogen and sulfur, but also for chlorine, bromine and iodine. To our knowledge, comprehensive mass balance analyses of halogen emissions (including fuel, gaseous, particulate and residue halogen) have not been previously attempted.

Finally, burning efficiencies can be calculated for each fire and are defined as the sum of carbon emissions compared to the emissions of CO_2 (or the total carbon content of the biofuel). The higher the relative amount of CO_2, the higher the burning efficiency is (i.e. the more complete or closer to the theoretical combustion a fire is; Ward et al., 1993). Burning efficiencies can be scaled to regional vegetation and climate maps to derive regional emission scenarios for individual compounds or fire regimes.

C.4.4.2. Data Integration into SAFARI Objectives, Emission Modeling

As a first step for emissions modeling, we plan to implement emission factors for various compounds into a 1° latitude × 1° longitude emissions grid of carbon emissions developed by J.A. Logan and R. Yevich (in preparation, 1999), which was also utilized for the RCEI effort on chlorine emissions from global biomass burning (Lobert et al., 1999). The emission factors determined during this proposed study will substantially improve currently available information about the types and amounts of many biomass burning emissions in southern Africa and, hence will diminish uncertainties in regional estimates of these compounds.

Our results will also be integrated with data for the amounts and areal extent of biomass burning estimated by other SAFARI investigators and applied to model fluxes over space and time. Results will provide hitherto unavailable resolution in our ability to predict these fluxes and to assess associated regional and global implications.

C.4.5. Data analysis workshop and Data Dissemination

Should this project be funded, we plan to organize a two-day data analysis workshop at the University of Virginia. The workshop will be held after preliminary data have been exchanged between participants and during the second year of funding and will be aimed at promoting data integration and interpretation as well as the planning for publication of results. Final, published results will be distributed on the internet at the same time of availability in print. The University of Virginia will provide server space for public access, data may also be distributed on a website permanently dedicated to scientific data dissemination, such as the GEIA archive. If permitted by the chosen journals, electronic versions of the final manuscripts will be made available on these internet sites. Regular reprints and data on CD ROM or other appropriate formats will also be made available for researchers who do not have convenient access to the internet. This approach has proven to be successful, the existing website for the RCEI project at http://groundhog.sprl.umich.edu/geia/rcei/ serves as an example on how this goal can be achieved.

C.4.6. Schedule

Year 1:

* 15. May 2000 - Start date.

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* June to December 2000 - Methods development at UVa.
* August and September 2000 - Sampling and shipment of biofuels
* November/December 2000 - Instrumental development of GC/MS and setup of fire facility.
* January / February 2001 - System setup, processing of samples, and burning experiments at MPI in Germany.
* March to May 2001 - Sample analysis, data reduction and quality assurance at U Va and MPI.

Year 2:

* May to July 2001 - Completion of sample analysis, data reduction and quality assurance.
* August 2001 - Distribution of quality assured data to participants.
* October-2001 - Data analysis workshop in Virginia.
* December 2001 - Presentation of results at scientific meetings.
* Spring 2002 - Manuscript submission to journals.

C.5. SOURCES OF FUNDING

Considerable resources have been committed to this research effort from other agencies and will be available at no cost to this proposal. All costs associated with the involvement of P. Crutzen will be covered by the Max Planck Institute and Scripps Institution of Oceanography. In addition, MPI will provide at no charge the burning facility in Mainz, associated technical support and several analytical instruments (for measurements of CO, CO_2, NO_X, N_2O, CH_4, as well as the GC/MS system). A portion of the costs for J. Lobert's involvement will be covered by C4 at no cost to this proposal. Biofuel samples will be collected at no cost by collaborating SAFARI investigators. Finally, SAFARI-2000 investigators will collaborate with us in integrating results of this analysis into a larger, regional assessment.

C.6. EDUCATION AND OUTREACH

Students working under the direction of the investigators will directly benefit by participating in this research effort. The involvement of technical staff also has the potential to inspire some to pursue careers as higher-level scientists. Several former technicians have returned to school and completed advanced-degree programs. The involvement of researchers from southern Africa will facilitate the transfer of information and technology and thereby enhance infrastructure development in the host countries. Finally, the continuing educational development of the principal investigators has a broad reaching potential for enhancing the infrastructure of science. Through classroom instruction, interaction with graduate students, collaboration with other colleagues, and publications, knowledge gained in this effort will be disseminated to current and future scientists, thereby ensuring continued progress in the field.

C.7. PROJECT MANAGEMENT, RESPONSIBILITIES OF PARTICIPATING SCIENTISTS

P. Crutzen will provide access to the MPI facilities, laboratory and office space in Mainz, technical support for the duration of the experiments and the measurements of N_2O, CH_4, and others. He will advice the project on development of emission models and their incorporation into global models and, in collaboration with J. Lobert, will be responsible for the overall project management.

J. Lobert will be sub-contracted as a collaborating 'other professional' for this effort. He has extensive previous experience with the proposed type of project, including preparation for and refinement of biomass burning experiments and interpretation of resulting data. He has also prepared for and conducted large, international field experiments. He will have primary responsibility for conducting the experiments at the Max Planck facility, measuring trace gases with gas chromatograph / mass spectrometer and online gas monitors and for operating the data acquisition system. He will take the lead on at least one major publication and publish available data online.

W. Keene will be responsible for U. Virginia components of the effort. He will take the lead in arranging shipments of biomass samples and will supervise elemental analyses and measurements of soluble, reactive trace gases and particulate emissions. He will also take the lead on at least one major publication, organize the data analysis workshop and assist in the final publication of online data.

Colleagues affiliated with SAFARI 2000 and/or working in the region will assist in identifying, sampling, preparing, and shipping representative biofuels for this investigation. They will also collaborate with us in interpreting and publishing results. These collaborators include M. Garstang (UVa) and C. Brain (Etosha) for sampling at Etosha; H Annegarn and L. Marufu (U. Witwatersrand) for sampling at KNP; P. Desanker (UVa) for sampling in Miombo (see Letters of Intent in Section I.1.).

C.8. RELATIONSHIP TO OTHER PROJECTS

The proposed research will be tightly integrated into the international SAFARI-2000 project and its many experiments, which are aimed at developing a better understanding of the southern African earth-atmosphere-human system (Swap and Annegarn, 1999). The program will also be directly tied to the International Global Atmospheric Chemistry (IGAC) program's Global Emissions Inventory Activity (GEIA) through the Reactive Chlorine Emissions Inventory (RCEI). Specifically, the proposed study will provide critical information with which to develop a reliable update of chlorine emissions from biomass burning. This work will also generate results relevant to several other IGAC-sponsored activities including the biomass burning experiment (BIBEX) and the deposition of biogeochemically important trace species (DEBITS) among others.

In addition, the SAFARI-2000 study region borders that of the Indian Ocean Experiment (INDOEX), which investigated chemical and physical interactions between continental and marine derived material in the atmosphere over the Indian Ocean (Ramanathan et al., 1996). It can be shown that emissions from southern Africa influence the atmospheric composition in the tropical, northern-hemispheric Indian Ocean (Lobert et al., in preparation, 1999). Consequently, results from SAFARI-2000 and INDOEX are directly interrelated. In addition, P. Crutzen and J. Lobert were actively involved in INDOEX as one of two co-PIs and a project scientist, respectively. To the extend possible, results from the proposed study will be integrated with those from INDOEX to facilitate a larger regional analysis.

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