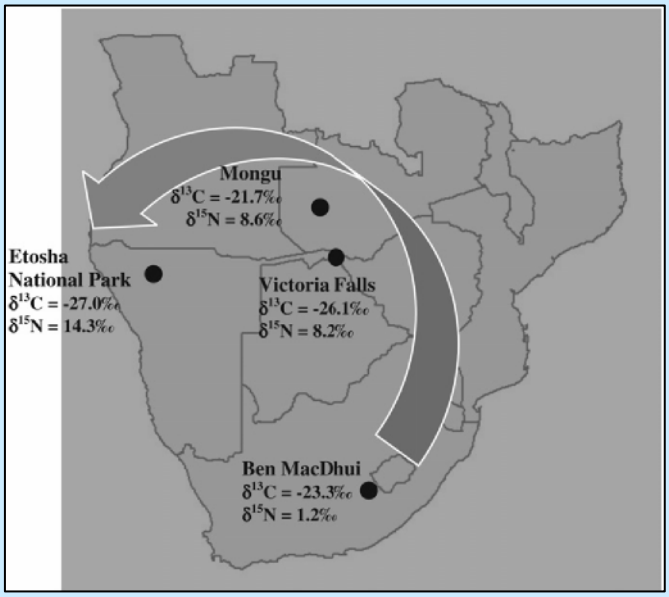
SAFARI 2000 Aerosol Fatty Acid and Stable Isotope Data, Mongu, Dry Season 2000

Abstract

The Southern African Regional Science Initiative (SAFARI 2000) was conducted in part to investigate the impacts of the large-scale transport and deposition of increasingly anthropogenic emissions on southern African biogeochemical cycling. Aerosol samples from the Mongu site in eastern Zambia were collected and analyzed to identify chemical biomarkers during the SAFARI 2000 dry season field campaign. Total suspended aerosol samples were collected diurnally for a period of two weeks during August and September of 2000.



Average ~13C and ~15N values obtained from aerosol samples collected during the August/September SAFARI 2000 field campaign in Mongu, Zambia, and from previous studies (revised from Swap et al.(1996) and Piketh et al.(1999)) in southern Africa.

These data include bulk organic carbon, nitrogen and sulfur stable isotopic measurements of total suspended aerosols and gas chromatography/mass spectrometry (GC/MS) analysis of fatty acids extracted from collected aerosols. These data were used to chemically describe temporal variability in aerosol compositions.

Background Information

Investigators:

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Project: SAFARI 2000

Data Set Title: SAFARI 2000 Aerosol Fatty Acid and Stable Isotope Data, Mongu, Dry Season 2000

Site: Southern Africa

Westernmost Longitude: 23.1553
Easternmost Longitude: 23.1553
Northernmost Latitude: -15.2535
Southernmost Latitude: -15.2535

Data Set Citation:

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Data File Information

Two source characterizing techniques, bulk stable isotope analysis and gas chromatography/mass spectrometry (GC/MS) were used to characterize aerosols collected in Mongu, Zambia as a part of the SAFARI 2000 dry season field campaign. Twelve hour, diurnal total suspended aerosol samples were collected at the Mongu Meteorological Station using a high volume aerosol sampler equipped with a glass fiber filter. A portion of each filter was used for bulk organic carbon, nitrogen and sulfur stable isotope analyses. Fatty acids were extracted from remaining portions for GC/MS analysis.

GC/MS Results:

- The GC/MS fatty acid results are given as percentage abundance relative to

C16:0 (palmitic acid).

- The data files contain ASCII numerical and character fields of varying length separated by commas.
- Blank cells indicate less than detection limit concentrations.
- **Detection limit concentrations were not reported and should be requested from Investigator, Steve Macko.**
- **The measured concentrations of C16:0 (palmitic acid) and other compounds were not reported and should be requested from Investigator, Steve Macko.**

Description of the file **Mongu_GCMS.csv**

Column Name	Column Description	Units/Format
Start Date	Start date of sample collection	mm/dd/yy
Day/Night	Day (D) or night (N) measurement period indicator	D/N
C14:0	Relative abundance of tetradecanoic acid to C16:0 (hexadecanoic acid)	%
C15:0	Relative abundance of pentadecanoic acidto C16:0	%
C17:0	Relative abundance of heptadecanoic acid to C16:0	%
C18:0	Relative abundance of octadecanoic acid to C16:0	%
C18:1	Relative abundance of octadecenoic acid acid to C16:0	%
C18:2	Relative abundance of octadecadienoic acid to C16:0	%
C18:3	Relative abundance of octadecatrienoic acid to C16:0	%
C19:0	Relative abundance of nonadecanoic acid to C16:0	%
C20:0	Relative abundance of eicosanoic acid to C16:0	%
C20:1	Relative abundance of eicosenoic acid to C16:0	%
C21:0	Relative abundance of heneicosanoic acid to C16:0	%
C22:0	Relative abundance of docosanoic acid to C16:0	%
C22:1	Relative abundance of docosenoic acid to C16:0	%
C23:0	Relative abundance of tricosanoic acid to C16:0	%
C24:0	Relative abundance of tetracosanoic acid to C16:0	%

Bulk stable Isotope Results:

- Stable isotope ratios are expressed in the delta notation in units of per mil (‰, which means "per thousand", as percent means "per hundred").

- Blank cells indicate that data are unavailable either due to instrument failure or insufficient sample detection.
- **The standard materials used for carbon and nitrogen isotope analyses were the Chicago PeeDee Belemnite (PDB) and atmospheric air, respectively.**
- **Descriptions of the preparation and analytical methods for sulfur were not provided and should be requested from Investigator, Steve Macko.**
- **The standard material used for sulfur stable isotope analysis was not reported and should be requested from Investigator, Steve Macko.**

Description of the file **Mongu_bulk_stable_isotope.csv**

Columns	Column Description	Units/Format
Start Date	Start date of sample collection	mm/dd/yy
Day/Night	Day (D) or night (N) measurement period indicator	D/N
delta_13C	bulk organic carbon stable isotope composition ($\delta^{13}C$)	per mil (‰)
delta_15N	total nitrogen stable isotope composition ($\delta^{15}N$)	per mil (‰)
delta_34S	total sulfur stable isotope composition ($\delta^{34}S$)	per mil (‰)

Study Site

Mongu is bordered by the Zambezi River on the west and Miombo woodland savanna in all other directions. It also lies at the northern extent of the Kalahari Desert. This region is characterized by high biomass burning emissions of river floodplain grasses and woodland savanna (Miombo woodland) during the dry season. Samples were collected diurnally for a period of two weeks during August and September of 2000. Total suspended aerosols were collected at the Mongu meteorological station. The meteorological station was located approximately 1 km east of the Zambezi floodplain, 0.5 km west of a small regional and military airport and 0.5 km north of the village of Mongu. There is a lightly used paved road directly in front of the main entrance to the meteorological station.

Methods

The approach of this study was to collect aerosol samples in the field for subsequent

laboratory analysis of fatty acids. These data were then compared to synoptic-scale transport patterns and air parcel transports to evaluate existing relationships.

Aerosol Sampling

Aerosol samples were collected during the SAFARI 2000 Dry Season Aircraft Campaign in August and September of 2000. Samples were collected in Mongu, Zambia, where dry season biomass burning fire occurrences within the Miombo woodland community are high. Total suspended aerosols were collected at the Mongu meteorological station using a high-volume sampling pump(approximately 1 m3 min^{-1}) equipped with precombusted (at 5 50°C for 2 hours) 20.3 by 25.4 cm glass fiber filters (Pall Gelman Type A/E). In order to evaluate diurnal fluctuations in atmospheric transport and the influence of secondary diurnal processes, such as solar radiation and fire temperatures on aerosol load and composition, 12-hour daytime and nighttime samples were collected over a period of 18 days.

After collection, the filter holders were removed from the sampling pump, covered and brought to the clean bench inside the meteorological station. The filters were placed inside individual pouches made of precombusted aluminum foil (at 550°C for 2 hours) and then placed in polyethylene bags and frozen. At the conclusion of the field campaign, the frozen samples were shipped to the University of Virginia (UVA) in coolers. Samples remained frozen until extraction.

Gas Chromatography/Mass Spectrometry (GC/MS)

Prior to GC/MS analyses, a portion of each of the glass fiber filters was refluxed with distilled dichloromethane (DCM) to obtain the organic compounds for purification and later analysis. To do this, the filter aliquot was cut into strips and placed in a glass thimble and refluxed using a Soxhlet apparatus for 16 hours. The extract was then concentrated to dryness using a rotoevaporator. The sample was then saponified with 10 ml of 1N ethanolic KOH heated under reflux for 3 hours. The nonsaponifiable lipids were extracted from the sample with distilled hexane using a separatory funnel. The saponified fraction was neutralized with 1N HCl and the fatty acids were extracted with distilled hexane. The fatty acids were then concentrated to near dryness for derivatization. The samples were derivatized with 1M BF_3CH_2OH and washed with KCl. Finally, the samples were dried over Na_2SO_4 and the fatty acid methyl esters (FAMES) were concentrated to 1-2 ml for injection into the gas chromatograph. The individual FAMES were separated and characterized with a Hewlett Packard 5890 Series II gas chromatograph mass selective detector equipped with a 30 m 0.25 mm i.d. 0.25 m film thickness DB-FAPP column (J & W Scientific: Folsom, CA). The GC/MS program consisted of an initial temperature of 100°C holding for a time of 5 min. The temperature was then ramped at a rate of 5°C/min to a final temperature of 220°C and held for 40 min.

Bulk stable isotope analysis.

A portion of all glass-fibre filters was used to determine bulk organic carbon and total nitrogen isotopic compositions. These analyses were performed with a continuous flow system that consisted of a Fisons NA 1500-R Series 2 elemental analyser equipped with an autosampler and VG-Isochrom diluter coupled to a VG Optima isotope ratio mass spectrometer (EA/IRMS). Data for isotopic analyses are reported in the 'delta' notation (δ) in units of 'per mil' (‰). The following equation is used in reporting isotopic compositions:

$R = {}^{m}E/{}^{n}E$; ämE = (Rsample/Rreference – 1) × 1000,

where E is the element in question, m is the heavy stable isotopic form of that element, n is its light stable isotopic form, and R is the molar ratio of the heavy to the light isotope for the sample and for a standard (reference). The resulting ä value represents an enrichment or depletion of the natural abundance of the heavy isotope of the sample compared to the standard. For this study, the stable isotopes of carbon (^{13}C and ^{12}C) and nitrogen (^{15}N and ^{14}N) were of interest. **The standard materials used for carbon and nitrogen isotope analyses were the Chicago PeeDee Belemnite (PDB) and atmospheric air, respectively.** Prior to ^{13}C analysis, portions of aerosol filter samples (~5 cm^2) were acidified with HCl in the vapour phase for 48 h in a desiccator to remove inorganic carbon.

Results

Stable isotope analysis was chosen both to characterize aerosols on a bulk elemental level and to help describe the role of specific chemical species within the organic aerosol fraction. Characterization of the organic fraction allows for more precise measurements of the anthropogenic contribution to aerosols in the haze layer. By focusing on organic materials, uncertainties in bulk characterizations as a result of admixture of natural aerosols from marine sources and chemically variable aeolian dust are minimized. Additionally, future studies will be able to use methods outlined in this paper to assess nutrient deposition and uptake of anthropogenically produced aerosols in the region and throughout the world.

GC/MS results. Aerosols collected in regions with enhanced emissions from biomass burning contain fatty acids in quantities that can be extracted and measured using GC/MS technology (Billmark et al. 2005). Longer-chain unsaturated fatty acids (>C20) are most representative of those lipids that originate from vascular plants15–17 and, as such, are good tracers of biomass representing higher plants within the aerosols collected.

The abundance of extracted fatty acids varied diurnally and over the sampling period (t-tests, P ~ 0.05 for fatty acids C20:0, C20:1, C22:0, C24:0). These results indicate the expansion and contraction of the potential area of origin for the majority of aerosols collected, otherwise referred to as the source 'footprint'. There is a strong atmospheric

inversion that often forms over the southern African region at night during the dry season. Solar warming of the atmosphere weakens this inversion and produces greater vertical mixing. The aerosol footprint, therefore, or the area from which collected aerosols are transported is larger during the day than at night, which allows more distant sources to contribute to the aerosols sampled. Mongu is located in the Miombo woodland savanna on Kalahari sands. However, the extensive grass-dominated Zambezi floodplain lies directly west of the village. Combustion products from a mixture of woodland and grassland species that surround Mongu are therefore likely to dominate the daytime distributions and relative abundance of fatty acids. Nocturnal samples, however, represent woodland combustion, possibly associated with cooking fires in local villages.

Bulk isotopic results. Previous analyses have shown that carbon signatures of southern African aerosols exhibit relative uniformity with values that suggest a predominance of C3 vegetation throughout the region. Owing to different enzymatic and physical processes, typical carbon isotope values of C3 plants are approximately –26‰, whereas C4 plants, such as the grasses prevalent throughout the region, typically exhibit corresponding values of approximately –14‰. Previous studies have also shown that nitrogen values become enriched as one moves from relatively moist to more arid regions within the recirculative synoptic area. Bulk carbon and nitrogen isotope results from this study at the Mongu site fit these general trends, although carbon isotope values for Mongu indicate a slightly stronger C4 grass signal than previous sampling sites. This carbon signal is influenced by sampling season, different fire fuel loads owing to annual variations in moisture levels (in wet years, relatively more grasses burn than trees), and the influence of grass burning on the Zambezi River floodplain due west of Mongu. The wet season prior to aerosol sampling saw extensive flooding. This may have led to a greater production and burning of ^{13}C-enriched grasses than at the other sites, which represent the locations of previous studies during relatively dry sampling years. In addition to these average carbon and nitrogen isotope trends, the results indicate a shift in values from daytime to night-time samples, owing to changes in combustion sources, burning efficiency and/or meteorological changes, which may influence sample characteristics. Carbon values of nocturnal aerosol samples were significantly more depleted in ^{13}C than daytime samples (paired t-test, $P < 0.05$). Observational data at the time of sample collection strongly suggest that night-time samples were heavily influenced by emissions from local cooking fires. An increase in the relative proportion of trees burned versus grasses would contribute to more depleted night-time ^{13}C values, owing to the differing photosynthetic pathways, C3 versus C4, respectively. Other factors may have influenced sample characteristics. For instance, greater wind speeds at night potentially entrain larger, heavier wood smoke particulates, thus better enabling capture by the high-volume sampler. Also, changes in the state of local fires favoring the predominance of smoldering conditions would further result in an isotopic shift towards depleted night-time ^{13}C values. This evidence for diurnal changes in smoke particulate matter has implications for the understanding of contributions from biomass combustion to atmospheric chemistry and global climate. Although these data describe general trends, isotopic evidence is clearly a useful tool for detecting subtle changes in combustion sources.

Acknowledgments

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References

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