Seasonal source variability of carbonaceous aerosols at the Rwanda climate Observatory

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Abstract

Sub-Saharan Africa (SSA) is a global hotspot for aerosol emissions, affecting the regional climate and air quality. In this paper we use ground-based observations to address the currently large uncertainties in source-resolved emission estimation of carbonaceous aerosols. Ambient fine fraction aerosol were collected on filters at the high altitude (2590 m.a.s.l.) Rwanda Climate Observatory (RCO), a SSA background site, during dry and wet seasons in 2014 and 2015. The concentrations of both carbonaceous and inorganic ion components show a strong seasonal cycle, with highly elevated concentrations during the dry season. Source marker ratios, including carbon isotopes, show that the wet and dry seasons have distinct aerosol compositions. The dry season is characterized by elevated amounts of biomass burning products, approaching ~ 95% for carbonaceous aerosols. An isotopic mass-balance estimate show that the amount of the carbonaceous aerosols stemming from savanna fires may increase from 0.2 µg/m³ in the wet season up to 10µg/m³ during the dry season. Taken together, we here quantitatively show that savanna fire is the key modulator of the seasonal aerosol composition variability at the RCO.
Sub-Saharan Africa (SSA) currently faces major challenges for sustainable development, including industrial development, agriculture, fresh water supply, climate change, energy resources and air pollution (IPCC 2014; UNDP, 2018). Either directly, or indirectly, these challenges are linked to aerosol emissions. Aerosols offset the ongoing regional climate warming in SSA, shift monsoon and precipitation patterns, and are detrimental for air quality (IPCC 2013; WHO 2016). Ambient air pollution in SSA is estimated to cause 563,000 premature deaths annually, making it one of the main causes for mortality in the region (Bauer et al., 2019). However, the level of scientific understanding of the overall health- and climate impact is still low, owing to the complex aerosol lifecycle, where emissions, transformations and sinks are associated with large uncertainties, in particular given their vast physical and chemical complexity. A major limiting factor for improving our understanding of these effects in SSA are the limited number of in situ observations (Williams, 2007; Cais et al., 2011; Kulmala, 2018; López-Ballesteros et al., 2018).

A major source of aerosol emissions in SSA are dry season regional fires, clearly visible from space (Fig. 1). These are occasionally ignited naturally by lightning strikes, but are mainly lit by humans. There is evidence that slash-and-burn agriculture in SSA has been a common practice for thousands of years (Bird and Cali, 1998; Archibald et al., 2012). This long-term anthropogenic perturbation is a significant modulator of current ecosystem structure. A number of studies have specifically focused on characterizing emissions of aerosols and gases from African fires, e.g., the Southern African Regional Science Initiative Project (SAFARI 2000), conducted between 1999 to 2001 (Swap et al., 2003). Ground- and airborne chemical characterization from this and other campaigns suggest a rather distinct aerosol chemical composition, including elevated BC, K\(^+\) and NO\(_3^-\) concentrations (Table 1).

Carbonaceous aerosols, often quantified as total carbon (TC), are generally divided into two main components: black carbon (BC; here we use elemental carbon (EC) to quantify the amounts of BC) and organic carbon (OC). Although overlapping to some extent, these two pools generally have distinct atmospheric lifecycles and environmental effects. Formed from incomplete combustion, sunlight-absorbing BC contributes to regional warming and is a particularly health detrimental component in air pollution (WHO 2012; WMO/UNEP 2011; IPCC 2013; Bond et al.,
BC is chemically inert to atmospheric reactions, and thus the lifetime is mainly determined by deposition. OC is also emitted from incomplete combustion (however, with different emission factors) but is also of non-combustion origins and is formed in the air through secondary processes. OC is thought to have an overall cooling effect on the climate (IPCC, 2013). Being more chemically reactive, the OC pool to some extent has a more complex atmospheric lifecycle, with continuous heterogenous chemistry, rendering the lifetime dependent on both precipitation and chemical transformations. Emissions from SSA fires are expected to contribute to a significant part of the global TC atmospheric burden (Lioussse et al., 2015).

In general, the actual environmental impact of TC on SSA is poorly constrained. Bottom-up emission projections suggests that the TC emissions from SSA are expected to increase rapidly during the coming decades, perhaps reaching 50% of the global burden by 2030 (Lioussse et al., 2014). To quantify and evaluate such model predictions, as well as to characterize the overall aerosol composition, it is valuable to conduct measurements at regional background sites. Dual carbon isotope characterization ($\Delta^{14}C$ and $\delta^{13}C$) of TC at background sites in South and East Asia and the Arctic has been shown to be a valuable tool for quantitatively constraining the emissions from different sources (Gustafsson et al., 2009; Andersson et al., 2015; Sheesley et al., 2012; Kirillova et al., 2014; Winiger et al., 2019).

In this paper we present dual carbon isotope constraints of TC, along with chemical characterization of inorganic ions and different carbonaceous pools, from a study conducted at the Rwanda Climate Observatory (RCO), during October 2014 to September 2015. A key objective of the study was to estimate the relative contributions from major TC source categories at this regionally representative site in the SSA. In particular, we investigate the source variability associated with the seasonal variations between prevailing wet and dry monsoon seasons in the region and the contributions from savanna fires.

### 2. Methods and Materials

#### 2.1 Field site and regional meteorology

The sampling site, the Rwanda Climate Observatory (RCO), is located on the top of Mt. Mugogo, in mountainous western Rwanda. (1.586° S, 29.566° E, 2590 m above sea level, 5 m.a.g.l.). The
station was established as a collaboration between the Massachusetts Institute of Technology (MIT, USA) and the Rwandan Government in 2013. The station is described in more detail by DeWitt et al. (2019). The station is an Advanced Global Atmospheric Gases Experiment (AGAGE) network site (for full list of instruments see http://agage.mit.edu).

The meteorology of Rwanda is governed by the East African monsoon, with peak rainfalls in in April and November. There are thus two dry seasons, December-January-February (DJF) and the main dry season June-July-August (JJA). The dry seasons in SSA are characterized by extensive biomass burning. During JJA the fires mainly occur to the south of Rwanda (Fig. 1). Savannas are the main biomes in SSA, covering ~ 65% of the landmass, and are the main source of fire emissions (Cahoon et al., 1992). Located in a highly elevated region, Rwanda is, broadly speaking, surrounded by savanna regions, except to the west, where the tropical rainforests of Africa are located.

2.2 Filter sampling

Quartz filter samples (Millpore, 150 mm diameter) were collected with a high-volume sampler operating at 30 m$^3$h$^{-1}$ using a PM$_{2.5}$ inlet (DH-77, Digitel Inc. Switzerland). Night-time only (1AM to 6AM) was conducted to minimize the effects of local emissions and day-time local atmospheric chemistry and to increase likelihood to capture the regional, free troposphere, signals. This strategy is supported by high temporal resolution investigations of the diurnal cycle of, e.g., BC (DeWitt et al., 2019). Each sample was collected over a period of 7 days. The samples were pre-combusted together with aluminum foil envelopes (400°C for 5h), and were treated with special attention to minimize contamination. The samples were subsequently shipped to Stockholm University for chemical analysis and isolation for carbon isotope analysis. The samples were stored in freezers both on site and at Stockholm University. Field blanks were collected on a monthly basis. The present campaign covers the period October 2014 to September 2015. However, the period December 2014 to April 2015 is missing due to a lightning strike which damaged the instrument. Thus, this study presents results from analysis of filter samples (in total 25) collected for the periods that cover the beginning of the 2014 fall rainy season (Oct-Nov), the end of the spring 2015 rainy season (April – May) and the dry 2015 summer season (June – September). We jointly refer the October-November 2014 and the April-May 2015 periods as the wet seasons.
2.3 Concentrations analysis

The concentrations of elemental carbon (EC – mass-based tracer for black carbon) and organic carbon (OC) were determined using a Sunset Inc. (Tigard, Oregon, USA) thermal-optical instrument using the NIOSH 4050 protocol (Birch and Cary, 1996; Table S1). Pre-treatment using acid fumigation with 1M HCl ensured efficient removal of carbonates. A glucose solution was used to calibrate the FID-response of the instrument, and the long-term performance of the instrument was checked through running of National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM) standards. All the concentrations were blank corrected and the field blank input was on average 2% for OC and 0% for EC. The average relative standard deviation of the triplicate analysis was 5% for OC, 7% for EC.

Water-soluble organic carbon (WSOC) was extracted from filter sub-samples in ultra-pure Milli-Q water by shaking for 1.5 hours. The extracts were filtered using 0.45 µm cutoff PTFE syringe filters (Minisart-SRP 10, Sartorius Stedim biotech, Germany). The concentration of WSOC was quantified in the filtered solutions as the difference between total water-soluble carbon and water-soluble inorganic carbon using a high temperature catalytic oxidation instrument TOC-5000A (Shimadzu, Japan). The samples were neither acidified nor purged, to avoid the loss of volatile organic compounds. The accuracy of the measurement ranges from 7% (70 µg L\(^{-1}\)) for 1 mg L\(^{-1}\) of carbon solution to 3% for concentrations higher than 2 mg L\(^{-1}\) of carbon (corresponding to 60 µg L\(^{-1}\)). All the measurements were blank corrected. WSOC field blanks corresponded to an average 0.5%. The average relative standard deviation of the triplicate analysis was 10%.

The concentrations of water-soluble inorganic anions were determined by ion chromatography using a Dionex ICS-2000 system. Anions were separated using an IonPac AG11 2x50 mm Dionex guard column, IonPac AS11 2x250 mm Dionex separation column and ASRS 300 self-regenerating suppressor. A solution of KOH was used as eluent. Cations were separated using an IonPac CG16 3x50 mm Dionex guard column, IonPac CS11 3x250 mm Dionex separation column and CSRS 300 self-regenerating suppressor. The analysis of cations was performed using 30 mM solution of MSA as eluent. Field blanks constituted on average 3% of NO\(^3^-\), 2% of SO\(^4^{2-}\) and 1% of NH\(^4^+\) and K\(^+\) ion concentrations. The triplicate analysis showed the average relative standard deviation of 2% for NO\(^3^-\) and K\(^+\), 5% for SO\(^4^{2-}\) and 6% for NH\(^4^+\).
2.4 Isotope analysis

Approximately every second sample (n = 12) were selected for carbon isotope (Δ^{14}C and δ^{13}C) analysis of total carbon (TC = OC + EC; Table S1). The filter samples were combusted using the Sunset analyzer (total carbon protocol) and the evolved CO\(_2\) was collected in glass vials using a liquid nitrogen cryo-trap (Andersson et al., 2015). The vials were subsequently shipped to the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at the Woods Hole Oceanographic Institute (Falmouth, Massachusetts, USA) for analysis of the dual carbon isotope signatures. The Δ^{14}C-signature was measured using accelerator mass spectrometry (AMS), while the δ^{13}C-signature was measured using an Isotope Ratio Mass Spectrometer (IRMS).

2.5 Source Apportionment

The Δ^{14}C-signature allows the differentiation between the relative contributions of biogenic/biomass burning and fossil sources. The fraction biogenic/biomass burning (f\(_{\text{bio}}\)) may be calculated using isotopic mass-balance (f\(_{\text{fossil}} = 1 - f_{\text{bio}}\)):

\[
f_{\text{bio}} = \frac{\Delta^{14}C_{\text{sample}} - \Delta^{14}C_{\text{fossil}}}{\Delta^{14}C_{\text{bio}} - \Delta^{14}C_{\text{fossil}}}\]  \hspace{1cm} (1)

The fossil endmember is -1000‰, as it is completely depleted in \(^{14}C\). The biomass endmember is more complex. For annual plants it is fairly straight-forward: the biomass Δ^{14}C-signature equals the Δ^{14}C value of CO\(_2\) for that year (~ +20‰ for 2014/15, Graven, 2015; Turnbull et al., 2017). For more long-lived species (e.g., trees) the Δ^{14}C-signature is the average of the atmospheric CO\(_2\) values (weighted by yearly carbon accumulation) over the plants’ lifetime. Bottom-up estimation of Δ^{14}C\(_{\text{bio}}\) therefore requires information regarding the plant distribution in the area of interest, and the annual bioaccumulation of carbon for the different plants. As an alternative we here use the combined Δ^{14}C-signature of dissolved organic carbon (DOC) in three of the regions’ major rivers, Congo, Zambezi and Tana, to obtain a regional Δ^{14}C\(_{\text{bio}}\) = +57 ± 52 ‰, which is well in the expected range of a mixture of annual and multi-year plants (Marwick et al., 2015; Wild et al., 2019, Winiger et al., 2019).
The vegetation in SSA may be divided into two main photosynthetic classes: C$_3$-plants and C$_4$-plants, see discussion in Section 3.5. These two groups have distinct $\delta^{13}$C-signatures, allowing isotope-based separation. We may then resolve three source classes by combining $\Delta^{14}$C and $\delta^{13}$C: C$_3$-plants, C$_4$-plants and fossil, through isotopic mass-balance (Andersson et al., 2015):

\[
\begin{pmatrix}
\Delta^{14}C(i) \\
\delta^{13}C(i)
\end{pmatrix} =
\begin{pmatrix}
\Delta^{14}C_{\text{C}_3} & \Delta^{14}C_{\text{fossil}} & \Delta^{14}C_{\text{C}_4} \\
\delta^{13}C_{\text{C}_3} & \delta^{13}C_{\text{fossil}} & \delta^{13}C_{\text{C}_4}
\end{pmatrix} \begin{pmatrix}
f_{\text{C}_3}(i) \\
f_{\text{fossil}}(i) \\
f_{\text{C}_4}(i)
\end{pmatrix}
\] (2)

Endmember variability may significantly influence the calculated source fractional contributions (Andersson, 2011). For a discussion on the specific endmember ranges used here, see Section 3.5.

In Eq. (2) the isotopic data is treated as independent. However, here we find that there is a dependence between the isotope ratios and the TC concentrations, such that $\Delta^{14}$C(i) ~ A/TC(i) + B, where A and B are constants, and i is the sample index (Fig. 5). This is known as a Keeling relation, and is discussed in more detail in Section 3.4. The relation holds for both $\Delta^{14}$C ($R^2=0.85, p<0.01$) and $\delta^{13}$C, while the correlation is weaker for $\delta^{13}$C ($R^2=0.55, p<0.1$). A method for using correlations within the framework Bayesian source apportionment has recently been developed (Martens et al., 2019). The rationale is based on both statistical concepts and the averaging expected from atmospheric mixing. The endmember ranges used in the calculations are from isolated sources, but during long-range transport the variability within a given source, e.g., savanna fires, will be reduced. Using correlations between data points, a means for accounting for the mixing is obtained, and more realistic source fraction estimates are obtained. When using the estimated source fractions to back-calculate the isotope signatures, the agreement is good compared with direct fits (Fig. 5 and Fig. S2). A sensitivity analysis is discussed in section 3.5 (Fig. S3)

To account for the correlations in the data-set we therefore add a second constraint in the source apportionment calculations, based on the relation to the TC concentrations:

\[
\begin{pmatrix}
f_{\text{C}_3}(i) \\
f_{\text{fossil}}(i) \\
f_{\text{C}_4}(i)
\end{pmatrix} = \frac{1}{[\text{TC}(i)]} \begin{pmatrix}
f_{\text{C}_3,\text{slope}} \\
f_{\text{fossil,\text{slope}}} \\
f_{\text{C}_4,\text{slope}}
\end{pmatrix} + \begin{pmatrix}
f_{\text{C}_3,\text{intercept}} \\
f_{\text{fossil,\text{intercept}}} \\
f_{\text{C}_4,\text{intercept}}
\end{pmatrix}
\] (3)
Where we, instead of fitting a source vector \((f_{C3}, f_{\text{fossil}}, f_{C4})\) for each individual data pair, fit two vectors: a slope and an intercept of the line, to all data points. This clearly holds the advantage of having fewer fitting parameters. We emphasize that the strength of the correlation of the isotope signatures relative to \(1/TC\) is naturally incorporated into this relation, such that lower correlation of \(\delta^{13}C\) w.r.t \(1/TC\) impose weaker constraints on the calculated source fractions, compared to \(\Delta^{14}C\).

The source fractions were computed using numerical Markov chain Monte Carlo simulations, implemented in Matlab, ver. 2015b, using 1000.000 iterations with a burn-in (initial search phase) of 10.000 and a data thinning of 10 (removing step-wise correlations). The stochastic perturbation parameter was adjusted as to obtain an acceptance ratio of 0.23, which has been suggested to be optimal for Metropolis-Hastings algorithms (Roberts et al., 1997). For this set-up, the variability in the numerically estimated parameters, e.g., the standard deviation of the relative source fraction, is lower than 1\% of the mean value, suggesting good convergence (Winiger et al., 2017).

2.6 Air Mass Back trajectories and Remote Sensing

10-days air mass back-trajectories (arrival height 2690 m.a.s.l. (100 m.a.g.l.) and 3090 m.a.s.l. (500 m.a.g.l.) were calculated using the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) (Figs. 1 and S1). Remote sensing fire-spot detections were retrieved from the NASA Fire Information for Resource Management Services (FIRMS) database, based on retrievals from the Moderate Resolution Imaging Spectroradiometer (MODIS) satellite product.

3 Results and Discussion

3.1 Back-trajectory analysis

Air mass back-trajectory analysis show that the air masses arriving at the Rwanda Climate Observatory (RCO) during the filter collection periods are overall easterly/southeasterly (Figs. 1 and S1). There is some overlap between the wet and boreal summer dry seasons, but overall there is a seasonal switch, where the wet seasons air masses are more of directly eastern origins (e.g., Uganda and Kenya and Tanzania), whereas the dry are more directly southeastern (e.g., Burundi, Tanzania and Democratic Republic of Congo). During the dry season there are extensive fires to
the south of RCO, mainly to the south-west (DR of Congo and Angola). However, the air masses also pass over regions with comparably high fire activities in the southeast, mainly in Tanzania. Nevertheless, we emphasize that back-trajectory analysis is challenging in mountainous regions (e.g., Winiger et al., 2019), and the actual geographical footprints are expected to be broader, e.g., due to the propagating effects of turbulence. Here we interpret the back-trajectories qualitatively to visualize overall air mass transport patterns.

3.2 Concentrations of fine aerosol components

During the present campaign, the PM$_{2.5}$ carbonaceous and inorganic ion components show a strong seasonal variability, with elevated levels during the dry JJA season (Fig. 2, Table S1). The dry/wet season ratios for TC, EC, WSOC, NO$_3^-$, SO$_4^{2-}$, NH$_4^+$ and K$^+$, were 4.2, 7.0, 4.1, 12.6, 3.0, 3.2 and 8.8, respectively (Table 1). This variability suggests differences in the aerosol sources and atmospheric processing, in addition to seasonality in meteorology, e.g., varying boundary layer heights or precipitation. The sea-salt contributions to the ions are overall estimated to be less than 1%, using corrections with sodium ions (Blanchard and Woodcock, 1980). We here report the actual concentrations to facilitate direct comparisons with previous studies (Table 1). Overall, these differences reflect differences in aerosol atmospheric lifetime, air mass transport pathways and emissions seasonality (e.g., fires). Elevated ratios of EC and K$^+$ suggests an increased influence from biomass burning during the dry season. NO$_3^-$, which displays the largest seasonal shift, is often associated with oxidized NO$_x$ from traffic emissions or lightning strikes. However, it is also typically elevated in emissions from savanna fires (Table 1; e.g., Gao et al., 2003; Formenti et al., 2003).

The dry season concentrations of carbonaceous aerosols components and inorganic ions reported here are overall in good agreement with the concentrations observed dry season rural and aged savanna fire air masses (Table 1). The BC values are in the same range as has previously been observed at Mt. Kenya (0.72 ± 0.06 μgC m$^{-3}$, Gatari et al., 2003). During atmospheric aging of a biomass plume, the values of OC, EC and K$^+$ decrease by a factor of 2-3, whereas other components are relatively unaffected (Table 1). However, the effects appear variable, as compared with savanna fires in South Africa (Gao et al., 2003).
RCO is situated not far away from the Nyiarogongo and Nyamuragira Volcanoes in eastern Democratic Republic of Congo. High spatial resolution (13x24km$^2$) satellite-monitoring of the SO$_2$ levels show a near-constant emissions from these volcanoes over the time period covering the present campaign, likely affecting the observed sulfate levels (Barrière et al., 2017). Here we observe a spike in sulfate levels (~ 5μg m$^{-3}$) during the week starting of the 13th of June 2015 (Fig. 2), but with no clear linkage to an increase in volcanic SO$_2$ emissions.

3.3 Source marker ratios and correlations

Overall, the ratios of different aerosol components provide insights into sources or atmospheric processes. Here, the EC/TC shows a distinct seasonality (Fig. 3 and Table S1). More commonly analyzed, though, is the OC/EC ratio (= (TC-EC)/EC), with elevated levels during the wet season (11±3) compared to the dry season (7±3; Table S1). The OC/EC-ratio is sometimes used as a marker for biomass burning, but is highly influenced by burning conditions such as flaming or smoldering fires. In addition, it is highly influenced by atmospheric processes such as secondary organic aerosol (SOA) formation or photo-chemical aging (e.g., Dasari et al., 2019). The dry season values observed here are similar to what has been observed in background air at other dry season Sub-Saharan African sites (Table 1).

Similarly, the NH$_4^+$/TC and SO$_4^{2-}$/TC are also elevated during the wet seasons (Fig. 3), while decreasing during the dry seasons, suggesting a different source profile compared to EC, K$^+$ and NO$_3^-$, including potential volcanic input of SO$_2$. In contrast, the WSOC/OC-ratio shows no clear seasonality, indicating small differences in sources and atmospheric processing of water-soluble and water-insoluble organic components over the year. TC correlates with K$^+$ ($R^2 = 0.95$, p<0.01) and NO$_3^-$ ($R^2 = 0.95$, p<0.01), suggesting that the incomplete combustion regime during the present campaign is governed by biomass emissions, e.g., savanna burning. Taken together, these ratios qualitatively suggest that the aerosol regime at RCO is strongly influenced by occasional input of biomass burning products during the boreal dry season.

3.4 Carbon isotopes
Radiocarbon ($\Delta^{14}C$) and stable-carbon ($\delta^{13}C$) provides detailed information regarding the sources and atmospheric processing of carbonaceous aerosols. Here, we investigated the signatures of TC for roughly every second sample during the campaign. The $\Delta^{14}C$-marker is not influenced by atmospheric processing, and may be used to directly compute the relative contributions of fossil vs biomass/biogenic sources with high precision, Eq. (1). The $\Delta^{14}C$-signature show an oscillation over the seasons, ranging between -84‰ (November, 2014) and +30‰ (July, 2015) (Fig. 4 and Table S1). Thus, during the JJA season, the $\Delta^{14}C$-signature exceed the signature for atmospheric CO$_2$ (+20‰, Graven, 2015; Turnbull, 2017).

Using Equation (1), the percentage biomass/biogenic TC for the $\Delta^{14}C = +30‰$ sample is 97%. During the wet season, the percentage derived from fossil reaches 13%, possibly of a more local derivation. $\Delta^{14}C$ correlates with 1/TC ($R^2 = 0.85$, $p<0.01$), which suggests that the variability in concentrations can be explained as a two-component mixture: a stable background and a temporally fluctuating source (Keeling, 1958) (Fig. 5A). This inverse relation gives $\Delta^{14}C = +37 \pm 6‰$ as TC approaches infinity, showing that the non-background component is of biogenic/biomass burning origins. The $\Delta^{14}C$ signatures for TC reported here are overall higher than for monitoring sites in South and East Asia (Sheesley et al., 2012; Kirillova et al., 2014; Bikkina et al., 2016).

In contrast to $\Delta^{14}C$, the $\delta^{13}C$-value is influenced by both atmospheric processes (i.e., kinetic isotope effects, KIE) and source signatures. Here, the $\delta^{13}C$-value shows a similar pattern relative to the $\Delta^{14}C$-value, depleted in $^{13}C$ (min $\delta^{13}C = -27‰$) during wet seasons, and higher during the dry season (max $\delta^{13}C = -21 ‰$) (Fig. 4B). The correlation w.r.t. 1/TC ($R^2=0.55$, $p<0.1$) is weaker compared to $\Delta^{14}C$ (Fig. 5B). The direct fossil vs biomass source correlation from the $\Delta^{14}C$ Keeling curve is also driving the $\delta^{13}C$-signatures, but the higher variability is explained by larger endmember variability and potential influence of KIE, see Section 3.5. An overall enrichment in $^{13}C$ has been found in aged air masses in South Asia, especially for WSOC (Kirillova et al., 2013; Dasari et al., 2019), but less so for TC. In fact, the enrichment of $^{13}C$ in WSOC often appears to be counter-acted by a decrease in water-insoluble OC (e.g., Yan et al., 2017; Fang et al., 2017).

The TC $\delta^{13}C$ values, and their seasonal trend, are similar to what has previously observed in fine aerosols at a rural site in Tanzania (May – August, 2011, Mkoma, et al., 2014). However, the
temporal trend appears shifted in the RCO samples from values around -25 ‰ to around 22 ‰ in mid-May. At the Tanzanian site, a similar shift occurs in mid-June. In addition to the complications of comparing measurements conducted at different sites during different years, there is a good agreement in the $\delta^{13}C$-values, and the temporal offset may be explained by inter-tropical convergence zone position variability. Similarly, the $\delta^{13}C$-value for TC at a savanna woodland site in Zambia, observed during August-September 2000, was -21.8±0.8 ‰ (Billmark et al., 2003), while values between -19.3 and -23.6 ‰ were observed at sites in the Ivory Coast (Cachier et al., 1985).

3.5. Carbon isotope-based source apportionment

By combining the $\Delta^{14}C$ and the $\delta^{13}C$-values we can by isotopic mass balance resolve three major sources of TC at the RCO, Eq. (2). However, there are some important considerations to this approach: First, the $\delta^{13}C$-value is not an exclusive source marker, but is also affected by atmospheric processing (e.g., photo-chemical oxidation and secondary formation). Second, the main source categories must be defined and distinguishable using carbon isotopes. Third, the source-values of the isotope-signatures, the endmembers, and their natural variability need to be established.

As mentioned, the $\delta^{13}C$-value of bulk TC appears to be considerably less affected by atmospheric processing compared to sub-components, such as WSOC. Here, the temporal variation of the $\delta^{13}C$-value is qualitatively similar to that of $\Delta^{14}C$-value (Fig. 4). Since $\Delta^{14}C$ is not affected by atmospheric reactions, this suggests that source variability is a key driver of the $\delta^{13}C$ variability. Furthermore, the WSOC/OC is virtually constant throughout the year (Fig. 3); the WSOC/OC has been found to be highly affected by atmospheric processing and related to shifting $\delta^{13}C$ (Kirillova et al., 2013; Yan et al., 2017; Fang et al., 2018; Dasari, 2019). Here, we therefore assume that the $\delta^{13}C$-ratio of TC is not strongly perturbed by atmospheric processing during long-range transport, and may thus be used as a source marker. Nevertheless, we explore the potential influence on KIE, as well as endmember variability, on the source apportionment results in a sensitivity analysis.

Turning to potential sources, there is a multitude of potential source categories for TC in SSA. However, many of these fall in broad categories, with similar carbon isotope signatures. Around the world, the applications of dual carbon isotope source apportionment techniques in ambient TC
mainly identified/considered 6 broad source categories: C$_3$ plants, C$_4$ plants, liquid fossil fuels (e.g., traffic), coal combustion (solid fossil), gas flaring (gaseous fossil) and marine emissions (Winiger et al., 2019; Andersson et al., 2015; Kirillova et al., 2013). Overall, the practice of coal combustion in SSA is expected to be much less frequent than in, for example, South and East Asia, and we therefore do not consider this source further. In addition, marine emissions are not expected to have a large influence at RCO, supported by the low estimates of marine contributions to the inorganic ions (<1%). For gas flaring, there are potential distant sources around the Arabian Peninsula and off the west coast of Africa, in the Gulf of Guinea. However, given the distances to the RCO station and the prevailing wind directions, emissions from flaring are not expected to affect the site, while the $\delta^{13}$C-signatures for gas-flaring are strongly depleted in $^{13}$C ($\delta^{13}$C<-38‰; Winiger et al., 2017) and even a small contribution would shift the observed values significantly.

The remaining three main source categories are the two biomass sources of C$_3$ (e.g., trees) and C$_4$ plants (e.g., sugarcane and certain grasses) and liquid fossil fuels (Fig. 6). Aerosols from liquid fossil fuel sources have a $\Delta^{14}$C$_{fossil} = -1000$‰ (completely depleted in $^{14}$C) and a $\delta^{13}$C$_{fossil} = -25.5\pm1.3$‰ (Widory, 2006; Andersson et al., 2015). The $\Delta^{14}$C of biomass was established in Section 2.4 as $\Delta^{14}$C$_{C3} = \Delta^{14}$C$_{C4} = +57 \pm 52$‰. The $\delta^{13}$C of C$_3$-plants in general is -27.1±2‰ (Bender, 1971; O’Leary, 1988). However, for aerosols generated from C$_3$-plants this value may be either enriched (e.g., ~ 0.5‰ biomass burning) or depleted (e.g., ~ 0 to 4‰ during SOA formation) (Turekian, 1998; Das et al. 2010, Mkoma et al., 2014; Aguilera and Whigham, 2018). In any case, the numerical spread in the $\delta^{13}$C-value of these different sources are largely overlapping with that of the raw materials, and we therefore use this value here. The $\delta^{13}$C of C$_4$-plant materials is -13.1±1.2‰ (Bender, 1971; O’Leary, 1988; Turekian 1998). However, during incomplete combustion, the $\delta^{13}$C$_{C4}$ may be reduced by a factor ranging from 0 to 7‰, largely dependent on burning conditions and species (Martinelli, 2002; Das et al., 2010; Aguilera and Whigham, 2018). Accounting for such effects in source apportionment is a challenge, especially since the reported values are ranges and not mean and variability, and thus are highly influenced by potential outliers. We here use a method discussed in Andersson et al. (2015) to address the issue of statistical analysis of ranges by assuming that the total range corresponds to the 95% confidence intervals of a normal distribution. This corresponds to the range of 4 times the standard deviation, yielding $\sigma = 7/4$‰, while the mean is -7/2‰. Combining this with the variability of the of pure C$_4$-plants we
obtain: $\delta^{13}\text{C}_4$: -16.6 ± 2.2‰, where $\sigma^2 = 1.2^2 + (7/4)^2$ ‰². These values are also what is obtained by numerical estimation of the convolution of a normal distribution ($\mu = -16.6$, $\sigma = 1.2$‰) with a uniform distribution ([-7, 0] ‰), adding to the strength of statistical representation.

The fractional source contributions of fossil fuel, C³ and C⁴ to TC are computed with Eqs. (2) and (3) (Fig. 7). It is well-established that accurate estimation of the fractional source contributions requires explicit incorporation of the endmember variability, and we here use a Bayesian framework driven by Markov chain Monte Carlo simulations for this purpose (Andersson, 2011; Andersson et al., 2015). To estimate the influence of the intra-endmember mixing during atmospheric transport we use the correlations of the isotopes with TC within the Bayesian framework, see section 2.5, to account for the endmember averaging during atmospheric transport (Martens et al., 2019) (Fig. 5). The resulting fractional contributions display a large variability when comparing wet and dry conditions (Fig. 7A and Table S2). The dry season is characterized by relatively higher C⁴-plant contributions, whereas the relative contributions of fossil fuels and C³-plants increase during the wet seasons. Back-calculating the isotope signatures from the computed source fractions from the MCMC-simulations essentially reproduce the Keeling relations relative to 1/TC (Figs. 5 and S2). To check influence of the number of data points used in the Keeling-based MCMC, we computed comparative scenarios where every third data point was used (starting at data point 1, 2 and 3 respectively) (Fig S3). The standard deviations for the calculated fC³ are on average doubled when only every third point are used (5% vs 10%), showing how correlations between multiple data points aids in constraining the sources.

Since the $\delta^{13}$C endmembers for, in particularly C⁴-plants, are not well-constrained, we also employed a sensitivity analysis w.r.t. endmembers and the potential influence of KIE (Tables S2 – S5 and Figs. S4 – S6). In addition to the above discussed best estimate scenario, we tested two $\delta^{13}$C⁴ scenarios: a ‘minimum KIE scenario’ with zero KIE ($\delta^{13}$C⁴ -13.1±1.2‰) and a ‘maximum KIE scenario’, with a depletion by 5.9‰ ($\delta^{13}$C⁴ -19.0±2.2‰). The maximum KIE scenario was established such as the fC⁴/(fC⁴+fC³)-ratio would be 62% as TC approach infinity, and thus 100% savanna contributions, see Eq. (4). As expected, these scenarios significantly shift the estimated relative C⁴ contributions, resulting in a total range of the sample period averages of 24% (min-KIE; min 6% max 32%) to 42% (max-KIE; min 10%, max 58%), thus providing lower and upper bounds (Figs. S4 and S5 and Tables S3 and S4). The corresponding value for our best estimate is
32% (max 44%, min 8%). In addition, we investigated a scenario with a 3‰ depletion of the fossil endmember ($\delta^{13}C_{\text{fossil}} - 28.5 \pm 1.3‰$). Since the fossil contribution is overall low as determined by $\Delta^{14}C$, and since $\Delta^{14}C$ constrains the fossil contribution independently of the $\delta^{13}C$ data, this shift has no significant influence on the computed source fractions 6% (max 11%, min 3%) (Fig. S6 and Table S5). Overall, we stress that these three sensitivity test scenarios represent extreme limits, and the a priori least biased scenario is the initially outlined best scenario.

By combining the estimated fractional source contributions with the TC concentrations, we can estimate the concentrations from the different sources (Fig. 7B), revealing a more accentuated source variability. The average dry-to-wet ratios of the TC to C$_3$-plants, C$_4$-plants and fossil fuels are 3, 5 and 2, respectively.

Savannas are the main biome supporting C$_4$-plants in SSA. For East African savannas, $\delta^{13}C$ data suggests that ~62% ($f_{\text{C4,NPP}}$) of the net primary production (NPP) is from C$_4$-plants (the rest mainly C$_3$-plants, Lloyd et al., 2008). Thus, one may assume that the source characteristics of TC emitted from savanna burning should represent this plant-signature distribution. However, the aerosol emissions modulate the NPP activity through emission factors (EF). The uncertainties of EFs from different biomass burning activities are generally large and overlapping (Andreae, 2019). As a first approximation, we here use $f_{\text{C4,NPP}}$ to estimate the fractional contribution of savanna emissions to TC ($f_{\text{savanna}}$) as (i = sample index):

$$f_{\text{savanna}}(i) = \frac{f_{\text{C4}}(i)}{f_{\text{C4,NPP}}}$$

This analysis shows that the dry season carbonaceous aerosol regime is dominated by savanna fire emissions reaching up to 71% (Fig. 7 and Table S2). These results agree with the elevated levels of EC, K$^+$ and NO$_3^-$ during the dry season (Table S1).

5. Outlook

In this paper we find that the aerosol composition of the emissions affecting the Rwanda Climate Observatory (RCO) may be described as a two-state source mixture: a regional/local background signal modulated by savanna fire emissions. Multiple studies have shown that savanna fires strongly influence the aerosol regime in SSA. Here, we estimate the savanna fire contributions for
carbonaceous aerosols to range from 13% (wet season; \(T_{C^{savanna}} = 0.2 \ \mu g \ m^{-3}\)) to 71% (dry season; \(T_{C^{savanna}} = 9.7 \ \mu g \ m^{-3}\)) at RCO (Fig. 7). The savanna fires are believed to be mainly lit by humans, and although these activities have been ongoing perhaps throughout the Holocene, these anthropogenic activities strongly perturb the regional ecosystems, climate and air quality (e.g., Bird and Cali, 1998; Archibald et al., 1998). The annual SSA savanna carbon budget represents a net \(CO_2\) source to the atmosphere (Williams, 2007; Cais et al., 2011; Valentini et al., 2014; Palmer et al., 2019). Finding more sustainable alternatives to the slash-and-burn practices in SSA could therefore possibly turn the region into a carbon sink. For instance, implementation of early dry season burning may be a possible strategy (Lipset-Moore et al., 2018). Savanna fire mitigation would also improve the regional air quality and stabilize precipitation patterns (Hodnebrog et al., 2015; Heft-Neal et al., 2018; Bauer et al., 2019).

Nevertheless, the current level of scientific understanding of the impact of savanna burning on the environmental system is poor, as are the couplings/responses to climate change, population growth, urbanization and other key socio-economic and environmental challenges for sustainable development in SSA (e.g., IPCC, 2014; Lioussse et al., 2015; Brandt et al., 2017; UNDP, 2018). Savanna burning mitigation, or shifts in in fire regime due to climate change, may change the present steady-state in unpredictable ways (e.g., Abreu et al., 2017). To better constrain the multiple environmental impacts of savanna burning in SSA, the comparably few ongoing ground-based in situ observations should be expanded and solidified (Williams, 2007; Cais et al., 2011; Kulmala, 2018; López-Ballesteros et a., 2018). For instance, observations of source-segregated aerosol concentrations provides multiple opportunities for advancing our knowledge of environmental processes relevant to SSA, including providing means for testing chemical-transport models; examining the relative importance of cooling vs warming (e.g., BC) aerosols; ground-truthing remote sensing products and detailed monitoring of the expected rapid change over the coming decades, including the effects of climate warming, population growth and urbanization.

_Data availability:_ The chemical and isotopic data, as well as the MCMC-derived relative source contributions of \(C_3\)-plants, \(C_4\)-plants and fossil, and the corresponding source-segregated TC concentrations is provided in the supplementary information.
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Author contributions: AA wrote the manuscript, set-up the PM$_{2.5}$ high-volume sampler at RCO, and analyzed the data. ENK and SD conducted the carbonaceous aerosol quantifications and isolations for isotopes, and IC analysis. JG worked with the instruments, including helping or leading installation, and provided feedback on data analysis. KEP was instrumental in setting up the RCO and did most of the initial instrument installation. HLD served as the RCO station chief scientist for three years. JN and JdDN worked as technical coordinators of the project at different times and facilitated the operations of the station as well as providing feedback on analysis. BS was our University of Rwanda liaison as the head of the Master’s program in atmospheric and climate science. RGP is the head of the AGAGE network and is the MIT liaison to the RCO, and was essential in the setup of the observatory and scientific analysis. All authors commented on the manuscript.

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Table 1. Concentrations of carbonaceous aerosol (μgC m⁻³) and inorganic ions (μg m⁻³) in fine aerosols from ground-based and airborne measurements over Sub-Saharan Africa (bkg = background).

| Sampling site | TC    | OC    | BC/EC | WSOC | NO₃⁻ | SO₄²⁻ | NH₄⁺ | K⁺ |
|---------------|-------|-------|-------|------|-------|-------|------|----|
| RCO, dryᵃ     | 9.5±3.7 | 8.2±3.2 | 1.3±0.6 | 5.7±2.1 | 1.2±0.7 | 2.1±1.0 | 0.8±0.3 | 0.7±0.3 |
| RCO, wetᵇ     | 2.4±1.2 | 2.2±1.1 | 0.20±0.1 | 1.5±0.7 | 0.1±0.1 | 0.7±0.3 | 0.3±0.1 | 0.08±0.05 |
| Rural Tanzania, dryᵇ | 7±2 | 6±2 | 1.0±0.3 | 4±1 | 0.18±0.06 | 0.2±0.1 | 0.9±0.7 | 1.5±0.7 |
| Rural Tanzania, wetᵇ | 4±1 | 4±1 | 0.5±1.3 | 3±1 | 0.06±0.03 | 0.1±0.1 | 0.2±0.1 | 0.4±0.2 |
| Aircraft, Southern Africa, smokeᶜ | N/A | N/A | N/A | N/A | 4.84±0.02 | 10.4±0.6 | N/A | 13.1±0.1 |
| Aircraft, Southern Africa, bgkᶜ | N/A | N/A | N/A | N/A | 0.48±0.00 | 2.2±0.1 | N/A | 0.31±0.02 |
| Aircraft, Southern Africa freshᵈ | N/A | 20±18 | 2±1 | N/A | 1.4±1.8 | 1.9±1.4 | 1.6±2.4 | 4.5±8.1 |
| Aircraft, Southern Africa agedᵈ | N/A | 6±3 | 1.03±0.04 | N/A | 1.0±0.8 | 2.0±1.5 | 0.9±0.8 | 0.6±0.4 |
| Aircraft, Southern Africa, plumeᵉ | 106±86 | 91±74 | 15±12 | N/A | N/A | N/A | N/A | N/A |
| Aircraft, Southern Africa hazeᵉ | 10.5±8.2 | 9.5±6.8 | 2.3±1.8 | N/A | N/A | N/A | N/A | N/A |
| Aircraft, Southern Africaᶠ | 8.5±4.8 | N/A | 2.3±1.9 | N/A | 0.8±0.3 | 4.5±3.6 | N/A | 0.4±0.1 |
| National Park, South Africaᵍ | N/A | N/A | 1.2 - 2.2 | N/A | N/A | N/A | N/A | 0.22 - 0.34 |
| Savanna, South Africaʰ | 9.1 | N/A | 0.61 | N/A | 0.4 | 11.08 | 2.85 | 0.28 |
| Aircraft, W. Africa, bgkʰ | N/A | N/A | 0.33 – 0.35 | N/A | 0.11 – 0.12 | 1.64 – 1.70 | 0.63 – 0.68 | N/A |
| Aircraft, W. Africa, urban plumeʰ | N/A | N/A | 0.64 – 0.72 | N/A | 0.49 – 0.53 | 2.70 – 3.03 | 1.20 – 1.38 | N/A |
| Grassland, South Africa, dryʰ | N/A | N/A | 0.6 | N/A | 0.3 | 1.4 | 0.2 | N/A |
| Grassland, South Africa, wetʰ | N/A | N/A | 0.3 | N/A | 0.2 | 0.4 | 0.3 | N/A |
| Savanna, South Africa, springʰ | N/A | N/A | 0.40 | N/A | 0.05 | 2.48 | 0.05 | 0.17 |
| Savanna, South Africa, summerʰ | N/A | N/A | 0.16 | N/A | 0.01 | 5.65 | 0.01 | 0.2 |

a. Present study
b. Mkoma et al., 2014
c. Gao et al., 2003
d. Formenti et al., 2003
e. Kirchstetter et al, 2003
f. Sinha et al., 2003
g. Maenhaut et al., 1996
h. Puxbaum et al., 2000
i. Brito et al., 2018
j. Tiitta et al., 2014
k. Aurela et al., 2016
Figure 1 Fire counts and air mass back trajectories for the October 2014 to September 2015 campaign at the Rwanda Climate Observatory (RCO, black and white circle). The fire counts are from the Fire Information for Resource Management System (FIRMS) derived from the NASA Moderate Resolution Imaging Spectroradiometer (MODIS) satellite product for June-July-August (JJA), 2015. The thin lines represent (4AM, C.A.T.) 5-day air mass back-trajectories arriving at RCO 100 m.a.g.l. (2690 m.a.s.l.). The blue lines correspond to what we here refer to as the ‘wet’ seasons (October-November 2014 and April-May 2015), whereas the green lines represent the dry JJA season.
Figure 2. Concentrations of carbonaceous aerosols (TC = total carbon; EC = elemental carbon; OC = organic carbon; WSOC = water-soluble organic carbon) and inorganic ions in PM$_{2.5}$ during October 2014 to September 2015 at the Rwanda Climate Observatory. Instruments were hit by lightning resulting in a data gap November 2014 to April 2015. The concentrations of EC were multiplied by 5 and K$^+$ by 2 for visual clarity.
Figure 3. Ratios of carbonaceous aerosols (EC = elemental carbon; OC = organic carbon; WSOC = water-soluble organic carbon) and inorganic ions relative to total carbon (TC) in PM$_{2.5}$ during October 2014 to September 2015 at the Rwanda Climate Observatory. Instruments were hit by lightning resulting in a data gap November 2014 to April 2015. The concentrations of K$^+$/TC and NH$_4^+$/TC ratios were multiplied by 2 for visual clarity.
Figure 4: Dual carbon isotope data for TC vs time. Panel A. $\Delta^{14}$C and Panel B. $\delta^{13}$C. The uncertainties for $\Delta^{14}$C are below 50‰ and ~ 0.2‰ for $\delta^{13}$C. Instruments were hit by lightning resulting in a data gap November 2014 to April 2015.
Figure 5. Interrelations of carbon isotope signatures and TC (blue circles). Panel A. $\Delta^{14}C$ vs TC, Panel B. $\delta^{13}C$ vs TC. The black line is the mean fit of the equation $\Delta^{14}C, \delta^{13}C = A/[TC]+B$, using Markov chain Monte Carlo simulations, where A and B are fitting parameters. For $\Delta^{14}C$, $A = -135 \pm 16 \%_o \ \mu g \ m^{-3}$; $B = 37 \pm 6 \%_o$. For $\delta^{13}C$, $A = -5.8 \pm 1.5 \%_o$; $B = -21.8 \pm 0.6 \%_o \ \mu g \ m^{-3}$. The grey shaded area display the 1σ spread of the fit.
Figure 6: Dual carbon ($\Delta^{14}C$ vs $\delta^{13}C$) isotope plot of TC. Blue circles represent Oct-Nov 2014 (wet), yellow circles Apr-May 2015 (wet), and red circles Jun-Sep 2015 (dry). The boxes represent the endmember ranges (mean ± stdev; see Section 3.5 for details) of the three main sources: C3-plants (green), C4-plants (orange), and fossil (black).
**Figure 7:** Carbon isotope source-segregated fractions and concentrations of TC vs time computed with the ‘best endmember scenario’. Panel A. Relative source contributions (%) of C₃-plants (green circles), C₄-plants (orange diamonds) and fossil (black triangles). Estimated savanna contributions are shown as blue squares. Panel B. Source segregated concentrations of TC of C₃-plants (green circles), C₄-plants (orange diamonds) and fossil (black triangles). The error bars (standard deviations) were calculated using Markov chain Monte Carlo simulations.