Evidence for a gas-flaring source of alkanes leading to elevated ozone in air above West Africa

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As part of the African Monsoon Multidisciplinary Analysis (AMMA) project, the FAAM BAe-146 research aircraft sampled the lower and mid-troposphere around the West Africa sub-region. Back trajectory analysis of the air parcels sampled on-board during the entire duration of the flights showed the history and fate of the air parcels. Data from flights B228 and B231 showed strongly enhanced carbon monoxide (CO) and ozone levels attributable to emissions of anthropogenic origin from the city of Lagos and gas flaring activities in the Nigeria oil fields. The elevated levels of ozone and CO observed at about 6 km above the sea-level on flight B231 were attributed to long-range transport of biomass burning plume from the East, around Sudan. The strongly enhanced mixing ratios of short-chained alkanes and CO (> 400 ppbv) observed from measurements on flights B228 and B231 are indicative of natural gas/combustion sources. Flight B222 sampled air parcels strongly impacted by emissions from Lagos but not from the Nigeria oil field and measured relatively lower mixing ratios of ozone, CO and short-chained alkanes species. Results from this study strongly suggests gas flaring emissions in the Niger Delta area to be a prominent contributor to the enhanced levels of short-chained alkane species observed in Lagos metropolis, especially during the West Africa Monsoon (WAM) months and, hence, a significant source of atmospheric aerosol in the sub-region.

Key words: African Monsoon Multidisciplinary Analysis (AMMA), gas flaring, West Africa Monsoon, alkanes, ozone, Niger Delta.

INTRODUCTION

African Monsoon Multidisciplinary Analysis (AMMA), an internationally funded program, was undertaken to enhance our understanding of the West African Monsoon (WAM) and the impact of its variability on the environment, atmospheric chemistry and socio-economy of the sub-region (Redelsperger et al., 2006). The program was designed to run between 2001 and 2009. During the Enhanced Observing Period (EOP) between 2005 and 2007, there was the implementation of specific land-based and sea-based measurements while 2006
was the year of Special Observing Period (SOP) (Lebel et al., 2010). During the SOP, there were intensive surface and air (research aircraft and balloons) measurements.

The FAAM BAE-146 research aircraft was based in Niamey, Niger (Reeves et al., 2010), and made about 19 scientific flights (labelled B215 - B235) during SOP2 between July 17 and August, 17, 2006. Of particular interest in this study are BAE-146 flights that are suggested, by back-trajectories analysis, to have been significantly impacted by gas flaring emissions from the intense flaring activities in the Nigeria oil field, south of the country. Specifically, air parcels sampled on three of the flights (B222, B228 and B231) were suggested to have been impacted by anthropogenic emissions from the south of Nigeria, which compared to the North, is more industrialised and has higher population density.

The Niger Delta, the region of intense gas flaring in southern Nigeria, contains over 300 active flare sites (Elvidge et al., 2015) scattered around local communities and farm sites on a land mass of about 70,000 km² (Osuji and Onojake, 2004) (Figure 1a). In 2012, of the 325 active flare sites identified in the Nigeria oil field, 97 (~30%) ranked among the top 1000 largest flares identified globally. The heart of the Niger Delta is less than 300 and 400 km from Lagos (Nigeria) and Cotonou (Benin), respectively. With an average wind speed of 6 m s⁻¹, a common occurrence in the region, emissions from the region of intense gas flaring in the Niger Delta take about 13 and 18 h to be transported to Lagos and Cotonou, respectively. It should be noted that August marks the peak of the WAM when the Intertropical Convergence Zone (ITCZ) and Intertropical Front (ITF) are northernmost (Sultan and Janicot, 2003). Hence, significant inland transport of emissions from the region of intense flaring is highly favoured. Pollutants from gas flaring are highly buoyant when exiting the stack due to the exit temperature which could be >1900 K in a typical gas flare in the oil and gas industry. Nigeria, Africa’s leading oil exporting country, still flares about a quarter of her annual natural gas production (Ite and Ibok, 2013). In 2006, as a result of an increase in Nigeria’s daily oil production quota by the Organization of Oil Producing Countries (OPEC) (OPEC, 2015), there was an increase in the estimated amount of gas flared compared to the preceding years (Anejionu et al., 2015a; Fawole et al., 2016). The years 2005 and 2006 were years of intensive oil prospecting and production in Nigeria as a result of the increased quota of production by OPEC, with the achievement of the all-time high daily production in November, 2005. In 2006, the level of air pollution from gas flaring from the Niger Delta was more intense than preceding years due to the level of oil exploration and exploitation (Anejionu et al., 2015b). Despite the significant contributions of gas flaring to atmospheric aerosol loading (Johnson and Coderre, 2012; Weyant et al., 2016), emission factors for pollutants exiting the stacks are very scarce and the few in the literature are significantly inadequate. For instance, black carbon, a chief climate forser and a prominent pollutant from gas flaring (USEPA, 2012), is very poorly estimated. To adequately understand the contributions of gas flaring to atmospheric aerosol level and quantify their impact on the atmosphere on both region and global scales, there is the need to research into and establish emission factors that are representative of the huge level of emissions from typical gas flares.

Significantly enhanced CO and alkanes mixing ratios are indicative of fossil fuel combustion (De Gouw et al., 2004). Short-chain alkanes (C3-C6) have been used as indicators of fossil fuel combustion as they are less common from biomass burning sources (Seila et al., 1989). Volatile organic compounds such as cyclopentane and cyclohexane in ambient air have been strongly linked to gas flares, oil refineries, and natural gas sources (Gilman et al., 2013; Liu et al., 2008; Sanchez et al., 2008). The ability of an air mass to form ozone is strongly dependent on the ratio of NOx to non-methane hydrocarbon (NMHC) it contains (Seinfeld and Pandis, 2016).

**METHODOLOGY**

**Meteorological conditions over the West Africa region**

The WAM is characterised by two prominent seasons, the dry (November-February) and the rainy (March-October) seasons. Desert dust and biomass burning aerosols are predominant during the dry season while the onset of the WAM brings in the moist south-westerly wind which is associated with rainfall. The meteorological condition over West Africa is significantly influenced by the ITCZ which is the zone of convergence of the trade winds of the two hemispheres. The movement of the ITCZ shifts the belt of planetary winds and pressure systems both northwards and southwards depending on the period of the year. In Coastal area of West Africa, the rainy season is generally observed between April and July, and a second but shorter spell of rainy season in September and October (WMO, 2015). In West Africa, the Sahel and Coastal areas have annual rainfall range of 450 - 1050 and 1400 - 2700 mm, respectively.

In the West Africa sub-region, the shifts of the ITCZ and ITF, to a large extend, control the circulation in the lower troposphere. During the peak of the (WAM) between July and September, the ITCZ and ITF can shift as far as 12 and 20°N, respectively. At this period of the year, there is the formation of mesoscale convective systems (MCS) as a result of the position of the ITCZ and presence of elevated terrains to the east (Mari et al., 2011). Large organised MCS develop on a regular basis during the peak of the WAM enabling the rapid vertical uplift of gases and aerosols to the upper troposphere. Compared to preceding years, during the peak of the WAM in 2006, convective activity resulting from MCS was slightly enhanced (Janicot et al., 2008).

**Back trajectory calculations**

In this study, to understand the history of air masses sampled on
the selected AMMA flights, trajectory ensembles associated with different measurement periods on selected AMMA flights were identified and assessed. A 7-day back trajectory along every second of the entire flight periods for flights B222, B228 and B231 was initiated. As a result of the large volume of time for each flight, each flight time was split into two almost equal parts (a and b) before the trajectory calculations. For example, the 24012 seconds on flight B321 was split into 12000 and 12012 s, and herein referred to as B321a and B321b, respectively. An analysis of every second of the flight duration rather than the 10 s time steps often used in similar studies in the literature were done because of the highly varying nature of plumes encountered on these flights as indicated by the broad range of the concentration of emissions measured on these flights.

Using the flight data (flight time, longitude, latitude and atmospheric pressure), 7-day back trajectories were calculated using the UK Universities Global Atmosphere Modelling Programme (UGAMP) offline trajectory model (Methven, 1997). This model is driven by six-hourly ERA-Interim (European Centre for Medium-Range Weather Forecasts Interim Re-Analysis) wind analyses data. Three dimensional meteorological data are interpolated to the trajectory locations. For each integration time, values of meteorological fields (temperature, potential temperature and pressure) are assigned as attributes to the particle in the trajectory. A detailed technical description of the UGAMP trajectory model can be found in Methven (1997) and Methven et al. (2001).

The trajectories were plotted using the National Center of Atmospheric Research (NCAR) Graphics/NCL trajectory plotting package, kmapline (Noone and Simmonds, 1999). Output of the trajectories calculation from UGAMP is imported in Openair as CSV files. Openair is an R package primarily developed for the analysis of air pollution measurement data (Carslaw and Ropkins, 2012). The trajectory density plot was done using the trajLevel option in the back trajectory function of the Openair package written in the R software (Carslaw and Ropkins, 2012). The trajLevel option in Openair considers the number of trajectories (that is, trajectory frequency) in a particular grid square (Carslaw, 2015).

### RESULTS AND DISCUSSION

From the trajectory-density plots of flights B228b and B231b trajectories, more than 25% of the air parcels sampled on-board both flights had been impacted by anthropogenic emissions from Lagos (green boxes in Figure 2) and the oil fields in the Niger Delta area (black boxes in Figure 2). The trajectory-density plot of B222 shows that more than 25% of the air parcel sampled on this flight had been impacted by anthropogenic urban emissions from Lagos while less than 1% had been impacted by emissions from the oil fields in the Niger Delta. Figure 2 shows the trajectory-density plots for the (b) portions of the three flights considered in this study. The (b) portions of the flights have been considered because those were the portions of the flights that came within proximity of emissions from either Lagos or the Niger Delta region.

Using the trajectory density plots, the extent of the contributions of different regions to aerosol loadings in air parcels sampled can be quantified. The (b) portions of the selected flights were chosen because at some time during the flight air parcels sampled during these
Figure 1. Flight track for (a) B228 (b) B231 (c) B222 and (d) active flare sites in the Niger Delta.

stretches of the flight were suggested by trajectory analysis to have been impacted by emissions from the oil fields in Niger Delta and urban emissions from Lagos. Elevated concentrations of carbon monoxide, ozone and alkane were observed during these portions of the flights. Plots of the 7-day back trajectory of entire air parcels sampled on the three selected AMMA flights are shown in Figure 3.

Case study I: Flight B228

Flight B228 took place on August 8, 2006 during the SOP 2 phase of the AMMA campaign in West Africa. The flight was from Niamey (Niger) to Cotonou (Benin), and then to Lagos to map emissions around the city. Figure 4 presents the plots of the mixing ratio of alkanes, carbon monoxide (CO), ozone, NOX against flight time, and 7-day back trajectory at flight times with elevated measurements of these pollutants.

Here attempts are made to demonstrate that strongly elevated levels of NOX, CO and O3 (> 90 ppbv) were observed simultaneously in air parcels that have been impacted by both gas flaring emissions and urban aerosols in Lagos. For multiyear (1997-2003) analysis from the MOZAIC programme, the range of ozone observed within the planetary boundary layer (PBL) during August around Lagos is in the range of 30 to 70 ppbv (Sauvage et al., 2005).

Figure 4(b) shows the back trajectory plot for flight time between 43600 to 44700 s, a period of elevated ozone, NOx and CO measurements shown in Figure 4a. As shown in Figure 4c, higher mixing ratios of NMHCs were also measured during this portion of the flight. These elevated measurements of ozone, CO and NOx were observed around an altitude of 1.5 to 3 km (Figure 5a), which corresponds to the 700 to 800 hPa shown in the colour-coded pressure in the back trajectory plot in Figure 4b.

Of all BAe-146 flights during the AMMA flight campaign, concentration of ozone in excess of 90 ppbv was measured on B228 and B231 only. These are the only flights that measured air parcels that were suggested to have been significantly impacted by gas flaring emission from the Nigeria oil field, as shown in the trajectory density plot in Figure 2. With combustion
temperature often >1900 K and fuel-rich combustion conditions, gas flaring is a significant source of atmospheric NO\textsubscript{X} by both thermal NO\textsubscript{X} and prompt NO\textsubscript{X} processes (Fawole et al., 2016). Carbon monoxide (CO) and NMHCs are also common emissions from gas flaring, and their emission rates increase steadily with decreasing completeness of combustion process of the fuel gas. It should, however, be noted that while CO, O\textsubscript{3} and NO\textsubscript{X} are measured every second, NMHCs measurements are averaged between 30 and 90 s.

During flight times between 43600 and 44700 s, there was significant enhancement of CO to up to 300 ppbv in the layer between 2 and 3 km; with accompanying enhanced NMHC measurements. The green vertical lines in Figures 4a and 4c shows the range of times within which elevated measurements of ozone, CO and NO\textsubscript{X} were observed and the corresponding time-step for alkane species measurements on flight B228. Figure 4c
shows the time series plot of ethane, butanes, pentanes, and cycloalkanes with mixing ratio of over 250, 300 - 10000, 2000 and 300 - 2000 pptV, respectively. Such high mixing ratio of alkane species are indicative of natural gas sources, particularly from the oil and gas sector (Hopkins et al., 2009; Minga et al., 2010). These enhanced levels of CO and alkane together with elevated NOX mixing ratio (> 2 ppbv) are suggested to be responsible for the elevated ozone level (120 ppbv) rather than long-range transport. Long-range transport of pollutants is not evident in the 7-day back trajectory plot shown in Figure 4b. Table 2 shows a summary of the statistics of the carbon monoxide (CO), ozone (O₃) and alkane species measured on-board flight B228.

Case study II: Flight B231

Flight B231 flew from Niamey to Cotonou and over the ocean around the Gulf of Guinea on August 13, 2006.
Figure 4. For flight B228b: (a) mixing ratio of CO, NO\textsubscript{X} and O\textsubscript{3} against flight time; (b) back trajectory plot of time with elevated CO and O\textsubscript{3} in time step of 10 s; (c) mixing ratio of alkane species against flight time.

Table 2. Statistics of alkane species measured on flight B228.

<table>
<thead>
<tr>
<th>Alkane species</th>
<th>Mean</th>
<th>Min</th>
<th>Max</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO (ppbv)</td>
<td>127.2</td>
<td>0.043*</td>
<td>1999.9</td>
<td>98.4</td>
</tr>
<tr>
<td>Ozone (ppbv)</td>
<td>44.1</td>
<td>9.5</td>
<td>117.8</td>
<td>43.8</td>
</tr>
<tr>
<td>ethane (pptv)</td>
<td>1068.3</td>
<td>553.1</td>
<td>2817.5</td>
<td>865.8</td>
</tr>
<tr>
<td>i-butane (pptv)</td>
<td>120.3</td>
<td>54.3</td>
<td>338.9</td>
<td>94.8</td>
</tr>
<tr>
<td>n-butane (pptv)</td>
<td>1757.0</td>
<td>429.9</td>
<td>11143.6</td>
<td>813.6</td>
</tr>
<tr>
<td>i-pentane (pptv)</td>
<td>226.5</td>
<td>26.0</td>
<td>2252.1</td>
<td>42.6</td>
</tr>
<tr>
<td>cyclopentane (pptv)</td>
<td>1152.5</td>
<td>556.1</td>
<td>2123.1</td>
<td>1093.9</td>
</tr>
<tr>
<td>cyclohexane (pptv)</td>
<td>135</td>
<td>47.8</td>
<td>429.4</td>
<td>104.5</td>
</tr>
</tbody>
</table>

*Very low value might be due to equipment failure.

The 'b' portion of the flight (B231b) came within proximity of Nigeria and the air parcel sampled on-board was suggested to have been impacted by emissions from the gas flaring region in the Niger Delta and Lagos, Nigeria (Figure 2b). The back trajectory plots in Figures 7a and b are for flight times 31000 - 32000 and 34500 - 36000 s, respectively. These times correspond to the periods of elevated CO and ozone measurements; there was also a corresponding increase in NO\textsubscript{X} measurements at these periods. Although, fewer and 20 to 30 s averages,
Figure 5. Variation of flight height with flight time for (a) B228b, and (b) B231b; vertical green lines show region of flight when elevated VOCs were sampled.

Figure 6. For flight B231b: (a) back trajectory plot of flight time 31000 to 32000 in time step of 10 s, and (b) back trajectory plot of flight time 34500 to 36000 in time step of 10 s.

NMHCs measurements shows significantly similar trends at these periods of elevated CO, ozone and NOx measurements (Figure 6b). Heights at which air plumes from the intense gas flaring region were encountered during flight times 31000-32000 and 34500-36000 s are between 3-3.5 and 2-3 km, respectively. These heights correspond to that shown in the colour coded atmospheric pressures, in Figures 6a and b, 650-800 and 750-850 hPa, respectively. These times, that is, 31000 - 32000 and 34500 - 36000 s, were on the to - and
The periods of strong enhancement of CO and NO\textsubscript{x} occurred during flights times 31000-32000 and 34500-36000 s. During these enhancement periods of mixing ratios, CO mixing ratio was up to 480 and 440 ppbv, respectively while ozone was up to \sim 128 and 118 ppbv, respectively. These periods equally exhibited elevated NO\textsubscript{x} mixing ratio up to \sim 2.5 ppbv. As shown in Figure 7b, mixing ratio for alkanes - ethane, propane, butanes and
pentanes were also enhanced during these periods. The green vertical lines in Figures 7a and b shows the range of times within which elevated measurements of ozone, CO and NOx were observed and the corresponding time-step for alkane species measurements on flight B231. Minga et al. (2010) suggested, from their simulation, that the only way to reach excessively high ozone concentration within few hours in their model was to increase amount of reactive VOCs to levels recorded around petrochemical facility. In their study to estimate emissions from Lagos (Hopkins et al., 2009) concluded that the substantial downwind enhancement of ethane is attributable to fugitive natural gas leakage. The enhanced CO measured simultaneously is indicative of a combustion source rather than a leak, which in this study, has been suggested to be gas flaring sources in the Niger Delta. Owing to the unique and significantly varying nature of gas flaring emissions, ratios of emissions often used as tracers for fossil fuel combustion could not be directly applied to emissions analysed in this study. Hence, a case is made for further studies to adequately characterise emissions from gas flares in the oil and gas sector, especially for VOCs.

Slight enhancement of ozone to up to 75 ppbv was measured around flight time between 38570 and 38700 seconds at a height of ~5 - 6 km. This was accompanied by a similar enhancement of CO up to ~220 ppbv, but there was no substantial enhancement in the levels of alkanes measured. This could be attributed to long range transport of biomass burning plume from the East, around Sudan (Figure 3d). Table 3 presents the statistics summary of CO, O3 and alkane measured on flight B231.

Table 3. Statistics of alkane species measured on flight B231.

<table>
<thead>
<tr>
<th>Alkane species</th>
<th>Mean</th>
<th>Min</th>
<th>Max</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO (ppbv)</td>
<td>163.6</td>
<td>0.043</td>
<td>535.1</td>
<td>123.1</td>
</tr>
<tr>
<td>Ozone (ppbv)</td>
<td>44.0</td>
<td>0.0</td>
<td>128.9</td>
<td>31.7</td>
</tr>
<tr>
<td>Ethane (pptv)</td>
<td>961.2</td>
<td>467.2</td>
<td>2758.1</td>
<td>859.3</td>
</tr>
<tr>
<td>Propane (pptv)</td>
<td>94.2</td>
<td>22.0</td>
<td>248.2</td>
<td>81.1</td>
</tr>
<tr>
<td>i-Butane (pptv)</td>
<td>33.3</td>
<td>0.0</td>
<td>92.8</td>
<td>18.3</td>
</tr>
<tr>
<td>n-Butane (pptv)</td>
<td>45.2</td>
<td>2.6</td>
<td>200.2</td>
<td>27.7</td>
</tr>
<tr>
<td>i-Pentane (pptv)</td>
<td>40.5</td>
<td>859.3</td>
<td>12.2</td>
<td></td>
</tr>
<tr>
<td>n-Pentane (pptv)</td>
<td>22.7</td>
<td>264.3</td>
<td>9.6</td>
<td></td>
</tr>
</tbody>
</table>

*Value might be due to equipment failure.

Case study III: Flight B222

AMMA flight B222 flew around Benin on July 30, 2006 carrying out the mapping of biogenic emissions. As shown in the trajectory density plot in Figure 2c and Figure 3c, < 1 % of the air mass sampled on the flight is suggested to have been impacted by gas flaring emissions while >25% were impacted by anthropogenic emissions from Lagos. There is no significant enhancement in the mixing ratio of CO which was around 200 ppbv throughout the duration of the flight except for very few spikes (Figure 8a). Mixing ratios of ozone and NMHCs are also relatively low (Figure 8b and Table 4) in contrast to the other two flights that sampled air parcels...
that were suggested to have been impacted by emissions from both the region of intense gas flaring and Lagos, Nigeria. Table 4 presents the statistics summary of CO, O$_3$ and alkane species measured on flight B222.

Conclusion

During AMMA SOP 2, on 30 July, 8 and 13 August 2006, FAAM BAe-146 carried out three scientific flights that sampled air parcels around Benin and the ocean around the Gulf of Guinea during sections of the flights durations. Portions of the air parcel sampled were suggested to have been significantly impacted by anthropogenic emissions from the gas flaring activities in the Niger Delta region and the city of Lagos. These flights sampled air parcels within the lower and mid-troposphere. On flights B228 and B231, there were portions of the flight with strongly enhanced mixing ratios of carbon monoxide (CO) and ozone. These enhancements were attributed to emissions from the region of intense gas flaring in the Niger Delta and Lagos, Nigeria because of the highly enhanced levels of short-chained alkane species and histories of air parcel sampled which is obtained from the back trajectory analysis. At a height of about 6 km, slight enhanced mixing ratios of CO and ozone observed is attributable to long-range transport of pollutants. Air parcels sampled on flight B222 was suggested to be strongly impacted by emissions from Lagos but almost insignificantly by emissions from the Niger Delta, hence, the relatively low mixing ratios of CO, ozone and short-chained alkanes. Analysis of short-chained alkanes species and cycloalkanes are limited by the number and cycles of NMHCs measurements on these flights. With our understanding of the extent of contributions of gas flaring in this region to levels of ambient pollutants coupled with limited and insufficient data to characterise emission from this source (gas flaring), we make a strong case for the need for further in-depth studies to understand the emissions, atmospheric transport and behaviour of emissions from this unique stationary source of aerosol pollutant under the impact of the peculiar climatic conditions of the West Africa region.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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