Atmospheric Concentrations of Polycyclic Aromatic Hydrocarbons in the Watershed of Lake Victoria, East Africa

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Supporting Information

ABSTRACT: In the first study of its kind in Africa, PAHs were measured in high volume (24 h) air samples collected from two sampling stations, at Kakira and Entebbe (KAK and EBB, respectively) within the Lake Victoria watershed in Uganda, to assess source contributions and generate a baseline reference data set for future studies in the East African region. Sampling was conducted over two periods [2000–2004 (KAK and EBB1) and 2008–2010 (EBB2)]. The samples were extracted by accelerated solvent extraction and analyzed for 30 PAHs by GC−MS. The mean total PAH concentrations (ng/m³) were found to be 74.3 (range; 19.3−311, N = 39) for KAK, 56.8 (range; 13.3−126, N = 22) for EBB1 and 33.1 (range; 4.9−108, N = 56) for EBB2. The 3-ringed PAHs were the most predominant group with mean concentrations of 35.9 ng/m³(EBB1), 30.5 ng/m³(KAK) and 23.2 ng/m³(EBB2). Naphthalene had an exceptionally high mean concentration (21.9 ng/m³) for KAK compared to 0.44 and 0.39 ng/m³ in EBB1 and EBB2 respectively, likely due to intensive agricultural operations nearby KAK. Principal component and diagnostic ratio analyses showed that the measured levels of PAHs were associated with mixed sources, combustion of petroleum, and biomass being the major sources.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous, persistent in the environment, and potentially harmful to human health.1−3 Many studies have been done to investigate release of PAHs from various sources, including combustion of biomass, petroleum, coal, and natural sources.4 Consequently, some PAH-source patterns have been recognized, and a number of PAHs have been suggested as source markers. These marker PAHs have been used in explorative and source apportionment studies, which have involved application of PAH diagnostic ratios and principle component analysis.1,4−7 In the Lake Victoria basin, probable sources of PAHs in the atmosphere, in addition to atmospheric transfer from elsewhere, are automobiles, thermo power generators, fossil fuel drilling, biomass burning, and biogenic sources. In East Africa, the largest source of domestic energy is biomass burning in the form of wood fuel and charcoal. Domestic use of biomass fuel is common in both rural and urban homes in the watershed of Lake Victoria (Table S1 of the Supporting Information, SI). Wood burning is also largely used in firing bricks, a method that is widely employed in the Ugandan construction industry.8 A large fraction of the East African population lives in the Lake Victoria basin, which is home to over 30 million people. The Ugandan watershed of the lake is dominated by agricultural, industrial, and various urban activities that are likely to release PAHs into the atmosphere. From the 2002 census, the central and eastern regions of Uganda, which are in the heart of the lake’s watershed, had over 80% of their communities engaged in crop farming.9 Previous studies support the fact that land clearing and tilling activities are likely to contribute to the atmospheric levels of biogenic and anthropogenic lightweight PAHs following biomass burning10 and volatilization from soil.11 The same census established that the central region of the country had the highest proportion of the households owning at least a motor vehicle or a motorcycle with almost a half (for motor vehicles) and more than a half (for motor cycles) of households in this region being in Kampala alone.9 This does not include the heavy trucks and commuter vehicles. The high density of automobiles and industries in the urban centers on the shoreline of the lake (Figure S1 of the SI) accounts for a potentially important source of pollutants, including petrogenic PAHs, in the watershed. An important source of petrogenic PAHs in the watershed is thermo power
diesel and gasoline generators which are used to supplement the insufficient and often irregular hydroelectric power. They are also largely used by homes and businesses in areas that are not on the general hydro power grid. The consumption of oil in Uganda in 2008 was estimated to be between 13,000−15,000 barrels of oil per day, diesel being the major component largely due to use in the transport sector and in generators.12 In spite of the importance of biomass and petroleum combustion, there are very few cases of PAH measurement in atmospheric environmental samples in the East African region, or indeed in sub-Saharan Africa. Klanova et al. (2009) measured the 16 EPA priority PAHs in passive air samples collected every 28 days over a six month period from 15 African countries, including Kenya.13 Total PAHs were found to be in the range of about 0.72 ng/m3 (at Kenya Mt. Kenya) to 115 ng/m3 (at the site in Cairo, Egypt). Generally, the industrial sampling sites had higher concentrations than urban background and remote sites. Another study measured selected PAHs in indoor smoke from selected household kitchens in southern Tanzania.14

The purpose of this study was to generate a baseline reference data set for future local and regional studies related to ambient levels of PAHs in the East African region. In order to assess the contribution of various sources to ambient PAH levels in the Lake Victoria watershed, we analyzed high volume air samples, collected at two sites in the Ugandan part of Lake Victoria watershed, for 30 PAHs. We hypothesized that given the high use of wood and charcoal in the region, we would see a predominantly biomass combustion source pattern. As far as we are aware, this is the first study to measure spatial and long-term temporal trends of PAHs in Africa using high volume sampling.

METHODOLOGY

**Study Area.** Sampling stations were set up at Kakira sugar cane plantation in Jinja (KAK, 0°30′40.53″ N, 33°16′48.97″ E) and at the Directorate of Water Resources Management (DWRM) at Entebbe (EBB, 0°02′55.38″ N, 32°28′19.50″ E) (Figures 1, S2, and S-3 of the SI). Both locations are in the Ugandan part of Lake Victoria watershed and had meteorological stations on site. Kakira sugar plantation, located close to the shores of Lake Victoria in Jinja, also has a sugar factory and workers homes on site. Motor vehicles and other motorized machinery are used on the plantation. The DWRM at Entebbe is on the northwestern shore of Lake Victoria directly overlooking the lake. Lake Victoria (1°0′S 33°0′E) is traversed by the equator and has a surface area of about 68,800 km2 and watershed area of 284,000 km2.15

**Sampling.** Samples were collected at KAK from January 2000 to August 2004 (39 samples). Samples from EBB were collected in two campaigns. The first campaign (EBB1) took place from March 2003 to July 2004 (22 samples) and the second one (EBB2), was from October 2008 to July 2010 (56 samples). The air samples were collected with a TE-1000 PUF high volume air sampler (Tisch Environmental Inc., OH, USA) (Figure S4 of the SI). For every sample collected, about 280 m3 of air was drawn continuously through a precleaned polyurethane foam plug (PUF) (Φ2.5 in. × 3 in. length) over a 24 h cycle. A glass microfiber filter (Whatman GF/F, 10 cm diameter) was placed before the PUF to trap particulates. Sampling was done weekly, rotating the sampling week days to minimize bias in the data. In addition to the date and sample code, minimum and maximum temperatures, and wind direction were also recorded during sampling. After sampling, the samples were stored at subzero temperatures at Makerere University, before shipping them to Canada for extraction and analysis. The samples were analyzed for PAHs at AirZoneOne Laboratories, Mississauga, Ontario.

**Sample Preparation and Analysis.** The particulate filter and PUF were combined and spiked with Phenanthrene-d10 (0.025 ng/μL) and Chrysene-d12 (0.025 ng/μL) as internal standards. The sample was then extracted by accelerated solvent extraction (ASE 200, Dionex, U.S.) with Hexane/
Acetone 70:30. The extract was then concentrated to 0.5 mL. Fluoranthene-d10 and Pyrene-d10 were added to the final extracts as performance internal standard prior to transfer to a vial ready for GC analysis. The samples were analyzed for 30 individual PAHs (Tables S-2 of the SI) by GC−MS (Agilent 5890 Series II GC and 5971 MSD, transfer line at 260 °C) in splitless mode. A DB-5MS 12 m × 0.25 mm × 0.25 μm column (J&W 122−5532) and Helium carrier gas were used. Each sample run was temperature-programmed as follows: Initial temperature at 90 °C for 1 min, 90−180 °C at 20 °C/min, 180−240 °C at 10 °C/min, 240−310 °C at 24 °C/min for 3.08 min, giving a total run time of 18.5 min.

Quality Control. The high volume air samplers were regularly calibrated following the manufacturer’s manual. Field PUF blanks were also analyzed as well as laboratory procedure blanks. Multilevel calibration for the target analytes (R² ≥ 0.99) was used. The method detection limits (MDLs) for the analytes were calculated as average blank concentration (n = 7) plus 3.28 times the standard deviation.16 The MDLs (Table S2 of the SI) were determined as 0.005−0.009 ng/m³ for individual compounds. For compounds not detected in the blanks, one-half of the instrument detection limit (IDL) was applied. The IDL was determined as the concentration of the target analyte giving rise to a signal/noise ratio in the range of 2.5−5.16 All solvents used were GC grade.

Data Analysis. Principal component analysis (PCA), using SIRIUS 8.1 (Pattern Recognition Systems AS, Bergen, Norway) software, was done on the transformed data to explore relationships within the data. The raw data was 1/3 root transformed in order to remove heteroscedasticity.17 PCA was used in conjunction with source marker and Diagnostic Ratio (DR) approaches to further understand the PAH concentrations in relation to their potential sources in the environment. Threshold values from literature6,18 were used for the following ratios: a 178 mass PAH ratio, anthracene/(anthracene+phenanthrene) ratio (or ANT/Σ178); a 202 mass PAH ratio, fluoranthene/(fluoranthene+pyrene) or (FTH/FTH + PYR); a 228 mass PAH ratio, benz(a)-anthracene/(benz(a)anthracene+chrysene) or (BaA/Σ228); a 276 mass PAH ratio, indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene+benzo[ghi]perylene) ratio or (IPY/IPY + BghiP). Pearson correlation of the raw data with reference data for PAHs from the literature was performed using SYSTAT 13 (Systat Software Inc., Chicago, Illinois). Bonferroni adjusted probabilities and the Pearson correlation were also computed using the same software. Back trajectory analysis was done.
using NOAA HYSPLIT Model\textsuperscript{19,20} with REANALYSIS and GDAS meteorological data archives.

\section*{RESULTS AND DISCUSSION}

The average concentrations of total (Σ) PAHs and 2-ring to 6-ring groups are summarized in Table 1. Descriptive statistics for 30 individual PAHs measured at the two stations are shown in Table S3. The KAK samples had the highest mean total concentration of all PAHs (74.3 ng/m\textsuperscript{3}, range; 19.3–311 ng/m\textsuperscript{3}) compared to samples from EBB1 (56.8 ng/m\textsuperscript{3}, range: 13.3 - 126 ng/m\textsuperscript{3}) and those from EBB2 (33.1 ng/m\textsuperscript{3}, range: 4.91 - 108 ng/m\textsuperscript{3}). The large difference is partly due to the predominantly high concentration of naphthalene in the KAK samples. The range of naphthalene in KAK samples was 0.16–140 ng/m\textsuperscript{3} as opposed to ranges in EBB1 (6.00 \times 10^{-3} – 1.59 ng/m\textsuperscript{3}) and EBB2 (6.00 \times 10^{-3} - 2.45 ng/m\textsuperscript{3}) for the same PAH. The mean concentrations (ng/m\textsuperscript{3}) for KAK, EBB1, and EBB2 were 74.3, 56.8, and 33.1 respectively. With the exception of naphthalene in KAK samples, the three sets of data exhibited similar trends of proportions of total individual PAHs from each site, with phenanthrene being the most abundant followed by fluoranthene and pyrene (Figure S5 of the SI).

Acenaphthylene, fluorene, and anthracene had slightly elevated proportions in the ΣPAH profile of EBB2 (3%, 5% and 8% respectively) compared to those in EBB1 (1%, 3%, and 5% respectively), while a reduction in the proportion of retene was observed in the EBB2 samples (2% down from 6% in the EBB1 samples). The 3-ringed PAHs were the highest group (by ring number) in the three sets of samples (Table 1, Figures 2 and S7 of the SI) with their fractions in KAK, EBB1, and EBB2 samples being 41%, 63%, and 70%, respectively. The substituted PAHs (including heterocyclic PAHs) constituted 6%, 13% and 10% in KAK, EBB1, and EBB2 samples respectively.

The temporal profile of ΣPAHs in the three sets of data is shown in Figures 2 and S6 of the SI. The KAK samples show more than a 2-fold increase in ΣPAH concentrations from the year 2001 to 2002 before falling to a generally lower and stable level in 2003 and 2004. The PAH profiles by ring number (Figures 2 and S7 of the SI) show that the elevated levels of ΣPAHs in 2001 and 2002 KAK samples were due to high levels of 2-ring PAHs, most especially, naphthalene (Table S3 of the SI). The ΣPAH levels in EBB1 samples were generally higher in 2003 samples than in 2004 samples (Figure S6 of the SI). For EBB2 data, the ΣPAH levels in 2008 were considerably lower than the levels previously measured in EBB1 samples. However, the ΣPAH levels in EBB2 samples gradually increased in 2009. There was a slight decline in early 2010 samples before increasing further with some samples exceeding the 2009 peak levels. Ring-number profiles show that the 3-ring PAHs had consistently the highest totals (13.1–160 ng/m\textsuperscript{3} for KAK, 9.03–77.7 ng/m\textsuperscript{3} for EBB1 and 4.27–80.1 ng/m\textsuperscript{3} for EBB2), followed by the 4-ring PAHs (3.23–130 ng/m\textsuperscript{3} for KAK, 3.53–40.8 ng/m\textsuperscript{3} for EBB1 and 0.38–25.7 ng/m\textsuperscript{3} for EBB2) in all of the three sets of data. The increase in ΣPAHs from 2009, in EBB2 samples, coincides with a significant increase in 4-ring PAH levels, as a result of elevated pyrene levels. The profile of coronene (7-ring PAH) was very similar to the one for 4-ring PAHs (especially pyrene). In all of the data sets, the 3-ring and 4-ring PAH profiles were very similar and were largely influenced by phenanthrene and pyrene profiles, respectively.

The variations of ΣPAHs with daily rainfall (range 0–44 mm) and daily average temperature (range 21.5–25.6 °C), for the dates of sampling, were studied using EBB2 data set and are shown in Figure S8 of the SI. The lowest and highest temperatures recorded on a sampling day, for the EBB2 data set, were 16.5 and 31.2 °C, respectively. This is a very narrow range of temperature variation when compared to the ranges observed between the summer and winter seasons of temperate regions. There was no relationship between the profiles of ΣPAH and rainfall or temperature (Figure S8 of the SI).

A wind rose based on wind direction recorded at the sampling site for days of sampling (Figure S9 of the SI) shows predominance of northerly and easterly winds. Therefore, the directional properties of the wind at the sampling site suggest that local emissions from Entebbe and the Kampala area, to the north of the site, are more likely to influence the PAH levels observed in the EBB2 samples. In order to assess the longer term (72 h) air mass movements associated with the samples, backward air trajectories of selected data points that corresponded to high and low proportion of ΣPAHs were generated using the NOAA HYSPLIT model\textsuperscript{19,20} Four samples (9 January 2009, 13 July 2004, 27 July 2004, and 17 May 2010) with elevated ΣPAHs and four samples (5 July 2004, 31 May 2004, 17 January 2009, and 15 Mar 2009) with very low levels of ΣPAHs were used to compute reference 72 h backward trajectories at 1000, 600, and 300 m above ground level. The calculated trajectories (Figures S10 and S11 of the SI) show that the samples at KAK were associated with slow moving local in-country air masses while the samples at EBB1 and EBB2 were mainly associated with relatively fast moving westerly and northwesterly air masses from neighboring Tanzania and Kenya sweeping in over the Ssesse Islands (Figure 1) of Lake Victoria and the watershed .

PCA was performed on the data, following 1/3 root standard transformation of the data, to extract three significant components. The EBB1 and EBB2 data sets were combined for PCA while KAK data was treated separately. The loading matrices are combined in Table S4 of the SI. The PCA scores and loadings plots are shown in Figures S12 and S13 of the SI. The three factors explained 89% and 76% of the variance in KAK and the combined EBB data sets, respectively. Generally, all of the PAHs showed medium to low loadings on all components for the two sets of data, with the exception of naphthalene (0.902) in KAK samples.

For the EBB data, phenanthrene, fluoranthene, and pyrene had the highest loadings on component 1. Studies have indicated that high loadings of these three PAHs are associated with diesel combustion.\textsuperscript{1,21,22} Retene also had a high loading on component 1, indicating wood combustion sources.\textsuperscript{23,24} Benzo(b,j)fluoranthene and benzo(k)fluoranthene also exhibited high loadings on this component. Some studies have suggested that the presence of fluoranthene and pyrene with high loadings of benzo(b)- and benzo(k)fluoranthene indicates diesel-powered vehicle emissions.\textsuperscript{4} In addition, this component showed medium loadings (0.150–0.200) of indeno(1,2,3-cd)pyrene, benzo(g,h,i)pyrene, and benzo(g,h,i)pyrene, which are key products of gasoline combustion.\textsuperscript{25} On this component, chrysene and benzo(a)anthracene had medium loadings (0.180 and 0.186, respectively). High emission factors of these two PAHs have been found in particulate matter associated with diesel fuel combustion.\textsuperscript{26} Therefore, component 1 was designated a “mixed source” representing combustion of diesel, gasoline, and woody biomass.

The highest loadings on component 2 of EBB were for naphthalene, 1-methylnaphthalene, fluorene, acenaphthylene,
and 7,12-dimethylbenz(a)anthracene. High loadings of the former four PAHs are associated with both biomass combustion and fossil fuel, both burned and unburned.\textsuperscript{1,10,26,27}

Petroleum and emissions from low temperature combustion sources are key sources of alkylated PAHs. Therefore, the high loading of 7,12-dimethylbenz(a)anthracene could reflect these sources. Therefore, component 2 was designated “Multiple Sources”.

Of all the PAHs in EBB data, retene had the overall highest loading factor of 0.575 which was on component 3. Other high loading factors were due to, naphthalene, 1-methylnaphthalene, acenaphthylene, and fluorene. This profile is characteristic of biomass combustion emissions and retene being a molecular marker for wood combustion,\textsuperscript{23,24} component 3 was assigned a “biomass combustion” source representation.

Multiple linear regression (MLR) of the elements in the factor score matrix against the ΣPAH concentrations was done on the EBB data to estimate the contribution of each source to the ΣPAH concentration per sample. The regression coefficients ($R^2 = 0.903, N = 78$) were significant at 95% confidence level. The regression results based on the 3 factor scores showed that component 2 ($p = 0.313$) did not significantly influence the ΣPAH value and the regression was reduced to two factors. The MLR equation for was found to be as follows:

\[
\Sigma PAH = 19.61*SC1 + 8.86*SC3 + 39.79
\]

where SC1 and SC3 are factor scores of the samples on component 1 (mixed sources representing diesel, gasoline and wood combustion) and component 3 (biomass combustion), respectively. This model accounted for 90% of the variation in the ΣPAH data for EBB. The correlations of measured and estimated values of ΣPAH for either component are shown in Figure S14 of the SI. There was a strong correlation ($R = 0.930, p < 0.001$) between the measured and estimated ΣPAH for the EBB data.

The data from KAK showed exceptionally high loading of naphthalene on component 1. Although it is not easy to associate this loading with a particular source, it is worth noting that this sampling station was located in the midst of a sugar cane plantation and in close proximity to a sugar factory. The several activities, employing petroleum and biomass based fuel, that went on at this vast plantation could have contributed to the high loadings of naphthalene. Therefore, component 1 was tagged “mixed sources”. Component 2 of KAK data was rich in pyrene, fluoranthen, phenanthrene, and anthracene. As already mentioned, this pattern strongly correlated with diesel combustion sources and component 2 was designated as such. The highest loadings on component 3 were from Indeno[1,2,3-cd]pyrene, benzo(g,h,i)pyrene and coronene. This suggested “gasoline combustion” sources and this was the designation conferred upon component 3. The source contribution to the ΣPAH concentrations in the samples was further analyzed through MLR ($R^2 = 0.934, p < 0.001$) and the resulting equation was as follows:

\[
\Sigma PAH = 21.19*SC1 + 40.42*SC2 - 37.58*SC3 + 74.33
\]

where SC1, SC2, and SC3 are factor scores of samples on component 1 (mixed sources), component 2 (diesel combustion) and component 3 (gasoline combustion) respectively. The agreement between ΣPAH measured vs estimated ΣPAH was strong ($R = 0.966, p < 0.001$). The correlation plots of measured versus estimated ΣPAH values for individual components are shown in Figure S15 of the SI.

To further evaluate possible sources, levels of 18 PAHs measured in studies of emissions from biomass,\textsuperscript{10,27} and petrogenic sources\textsuperscript{27} were compared with those of the same PAHs measured in KAK, EBB1 and EBB2 samples using PCA. The scores and loading plots based on three major extracted components are shown in Figures S16 and S17 of the SI. The KAK data showed the closest correlation with the reference data sets for petrogenic sources (DP1, DP2 and GAS). A sizable fraction of the KAK samples (KK) were influenced by naphthalene. The samples whose scores were mostly correlated with the wood combustion score (WD) were from KAK data set. The EBB1 sample scores (BB; in orange color) and a sizable fraction of EBB2 sample scores were similar to the scores of Pine and Walnut wood.

The distribution, by ring size, of the percentage of PAHs to the total mass of 20 PAHs from a reference source\textsuperscript{1} and in the standard reference materials for diesel particulate matter (SRM 1650b) and urban dust (NIST SRM 1649a)\textsuperscript{22} was compared with the ring-size distribution of the percentage of PAHs to the total mass of 30 PAHs in samples from KAK, EBB1 and EBB2 (Figure 3). EBB1 and EBB2 had a predominance of 3-ring PAHs as was the case with diesel engines and wood combustion. The distribution in KAK mildly resembled the petrol engines and coke oven sources due to relatively high naphthalene proportions. The Pearson correlation coefficients (Table S7a of the SI) and normalized Euclidean distances ($D$) were computed (Table S7b of the SI). The distributions in EBB1 and EBB2 had good correlations with those from diesel engines ($r = 0.909, 0.936$ with $D = 0.217, 0.208$, respectively) and wood combustion ($r = 0.905, 0.945$ with $D = 0.237, 0.183$, respectively) but showed very weak correlation with petrol engines and the NIST SRMs (Table S7 of the SI). The Euclidean distances were used to generate a dendrogram (Figure S18 of the SI) for graphical cluster comparison of these data sets. The ring-size distributions in EBB1 and EBB2 were found to be very close, forming their own cluster. The distributions in the latter two sets of data were closest to those in wood combustion and diesel engine emissions. The ring-size distribution in KAK data was equally close to the distributions

![Figure 3. Comparison of current results with similar results reported in literature, for source distribution, by ring size, of the percentage of PAHs to the total mass of PAHs. All are gas phase + particle profiles.](dx.doi.org/10.1021/es302238w)
in diesel and petrol engine emissions. These observations are consistent with the estimations projected from PCA results discussed before. The KAK profile did not show significant Pearson correlation with any specific source profile, but it showed modest correlation (r = 0.51 - 0.72) with all the referenced data sets except the NIST SRMs.

Further analysis of the PAH-source qualitative analysis of the three sets of data was done using selected diagnostic PAH ratios (Table 2). A threshold value of 0.10 for the An/Σ178 ratio has been used to distinguish between unburned petroleum sources and petroleum combustion sources, with a ratio <0.10 indicating unburned petroleum sources while a value >0.10 indicates petroleum combustion sources.6,18 The mean An/Σ178 ratio in all three data sets was greater than 0.1 indicating more combustion sources. The combustion source character was most pronounced in the EBB2 samples. The case of combustion as the major source was further reinforced by the FTH/FTTH + PYR ratios, which were found to be above 0.50 in three sets of data. FTH/FTTH + PYR ratios above 0.5 have been reported to suggest combustion of grass, wood, coal,18 and kerosene.6 Values exceeding 0.5 for the same ratio have also been reported in savanna fire particulate matter and NIST SRMs 1648 and 1649a for urban air. The BaA/Σ228 ratios measured the three sets of data were above 0.35. Values above 0.35 for the BaA/Σ228 ratio have been reported to suggest combustion of wood, grass, kerosene, and vehicular emissions.18 The BaA/Σ228 ratio for the EBB2 (0.57) was highest and has been previously reported in samples from a tunnel that was used by heavy diesel trucks and gasoline vehicles.6 The IPY/IPY + BghiP ratio measured for EBB2 samples was 0.53, suggesting combustion of wood, grass, and coal.18 The values for the same PAH measured in KAK and EBB1 samples were between 0.2 and 0.5, a range that is reported to suggest petroleum combustion and savanna fire sources.6 With the exception of the BaA/Σ228 ratio, all of the PAH ratios reported here for the three data sets from Uganda were in agreement with values for the same ratios in the NIST SRM 1650b for diesel particulates and 1649a for urban air. The BaA/Σ228 ratio for SRM 1650b did not show agreement (Table 2).

Selected data from EBB2 and PAH data reported by Klanova et al.22 in passive air samplers for other African sites15 were compared (Figure 4). Our study is the only one to have measured atmospheric PAH levels in the East African region using "active" sampling. We selected time periods from 2008 and 2009 in EBB2 data to correspond to either the same year or the same months (for 2009) of the year sampled with passive samplers in 2008 by Klanova et al. Nine samples collected from October to December 2008 (EBB2a), nine samples from January to March 2009 (EBB2b) and five samples from June to July 2009 (EBB2c) were selected for use in this comparison. The sites in Kenya were of the more interest since air trajectory analysis (e.g., in Figure 5a of the SI) has shown potential occasional influence from as far as the Kenyan coast through long-range air mass movement at the Uganda sampling sites in this study. It is important to note that the passive samplers are designed to quantitatively measure gas phase and not particle phase PAHs, but are able to sample fine aerosols.29,30 Thus they may give lower concentrations of ΣPAHs than the filter-plus-PUF method we used with the high volume active samplers, especially for high molecular mass organic compounds which are usually bound to coarse particulates.13,29,30 The average PAH levels observed in EBB2a, EBB2b and EBB2c were within the range reported in 2009 by Klanova et al. The PAH levels observed in the EBB data were exceeded by values from the industrial sites of Kenya (Kenya Industrial and Kenya Dandora) but relatively higher than the non industrial sites of Kenya. Generally, levels at urban industrial sites in Africa, with the exception of the Ethiopian site, were higher than the ones observed in EBB2 samples. Conversely, EBB2 levels were generally higher than those observed in samples from urban background sites or sites moved far from industrial activity.

In general, the mean concentrations measured in this study were higher than those from most semirural areas in North America and western Europe. For example, mean concentrations of selected PAHs in this study were higher than those measured at Sandy Hook, New Brunswick in New Jersey and some other semirural sites from the coastal and North American Great Lakes area.31,32 However, some urban sites in the great lakes area have been found to have much higher levels of PAHs than those seen at the Uganda sites.30 The PAH levels in this study also exceeded levels observed at semirural sites in the St. Lawrence River basin.31 The mean levels of PAHs from the Uganda sites were comparable to the pre-2005 levels measured at some sites in the United Kingdom34 with some 5-6 ring PAHs (e.g., Benzo(a)pyrene) in EBB1 and EBB2 being lower than those from some of the U.K. sites. The

### Table 2. Diagnostic PAH Ratios (mean ± SD) for Samples from the Three Data Sets

<table>
<thead>
<tr>
<th>data set</th>
<th>An/Σ178</th>
<th>FTH/FTTH + PYR</th>
<th>BaA/Σ228</th>
<th>IPY/IPY + BghiP</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBB2</td>
<td>0.15 ± 0.04</td>
<td>0.57 ± 0.14</td>
<td>0.57 ± 0.08</td>
<td>0.53 ± 0.14</td>
</tr>
<tr>
<td>KAK</td>
<td>0.11 ± 0.02</td>
<td>0.52 ± 0.03</td>
<td>0.54 ± 0.12</td>
<td>0.35 ± 0.22</td>
</tr>
<tr>
<td>EBB1</td>
<td>0.11 ± 0.09</td>
<td>0.55 ± 0.02</td>
<td>0.49 ± 0.06</td>
<td>0.47 ± 0.07</td>
</tr>
<tr>
<td>NIST SRM 1650b</td>
<td>0.10</td>
<td>0.52</td>
<td>0.81</td>
<td>0.43</td>
</tr>
<tr>
<td>NIST SRM 1649a</td>
<td>0.09</td>
<td>0.55</td>
<td>0.50</td>
<td>0.44</td>
</tr>
</tbody>
</table>

*Anthracene/(anthracene+phenanthrene). Fluoranthene/(fluoran-
thene+pyrene). Benz(a)anthracene/(benz(a)anthracene+chrysene. Indeno[1,2,3-cd]-pyrene/(indeno[1,2,3-cd]pyrene+benzo[g,h,i]-pyrene). Fluorene/(fluorene+pyrene). Benzo(a)Pyrene/(Benzo-
(a)Pyrene+chrysene). Mean ratios only.*
results reported here were compared with measurements reported in 2007 from a study done in the Atlantic Ocean atmosphere, from an oceanographic cruise off the West African coast15 (Table S8 of the SI). The concentration ranges reported in their study were below those reported here save for dibenzothiophene which had higher concentrations for the gas phase. Profiles of PAHs in KAK and EBB sites were generally highly correlated to the gas phase concentrations observed off the West African coast (Table S9a of the SI), especially, the low molecular mass PAH profiles (Table S9b of the SI). As expected, the higher mass PAHs were more likely to be associated with the aerosol phase, but not significantly (Table S-9b of the SI).

The PAH data sets in this study have established a time series on which future changes in PAH trends and sources can be assessed. Contrary to our initial hypothesis, the major contributor of atmospheric PAHs in the northern Lake Victoria region was found to be combustion of both petroleum and biomass. Biogenic sources have been suggested for net volatilization of light PAHs from soils along a positive temperature gradient.11 This is consistent with the phenanthrene levels observed in this study and suggest possible contribution of volatilization of the low molecular mass PAHs following biogenic production in the soil. Back trajectory analysis suggested the sources were mainly from within the region, with elevated and reduced ΣPAHs associated with slow moving and fast moving air masses, respectively. This study has also revealed that due to the narrow range of temperature variation in the tropics, especially in proximity to the equator, temporal variation of atmospheric levels of PAHs does not exhibit temperature-dependent seasonality. The ambient levels are more likely to be influenced by the air mass movement and PAH emission characteristics of the area than temperature at the sampling location. The Kakira site (KAK) was found to be heavily associated with diesel as well as non-woody biomass combustion sources and this was consistent with the physical characteristics of the site; it is located at sugar cane plantation, close to a sugar factory. The pattern of decreasing predominance of the most abundant US EPA priority PAHs close to a sugar factory. The pattern of decreasing predominance of the most abundant US EPA priority PAHs in the KAK data set (i.e., naphthalene > phenanthrene > fluoranthene > pyrene > anthracene) is the same as the one observed in air samples from the United Kingdom (UK) in 1990, 34 a time when, industrial processes and agricultural burning were said to be the major sources of PAH emissions.34 This profile is consistent with the characteristics of the KAK site. This may be typical of other agricultural estates in the region. The results of source apportionment of PAHs in air samples by way of molecular diagnostic ratios have been shown to be suspect due to influence of environmental conditions. Interpretation should be done with caution, especially when PAHs are measured away from known sources.35 It is also worth noting that the diagnostic ratios here have been computed for total PAHs in gas + particulate phases (due to combined extraction of the two phases). Because environmental conditions such as temperature, wind, and suspended particulate matter affect the partitioning of PAHs in the atmosphere, molecular diagnostic ratios based on total PAHs in gas + particulate phases have been recommended.18 The two data sets from the Entebbe site (EBB) had reduced local interfering sources and therefore gave a better indication of the atmospheric PAH pattern in the immediate watershed of Lake Victoria.

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