Interactive comment on "Personal exposure to PM<sub>2.5</sub> emitted from typical anthropogenic sources in Southern West Africa (SWA): Chemical characteristics and associated health risks" by Hongmei Xu et al.

### **Anonymous Referee #1**

Received and published: 11 November 2018

We would like to thank the reviewer for both comments and suggestions on our manuscript. We have addressed and responded to each comment below.

Comments and suggestions for improvement:

- I understand that the authors are not native speakers but in some parts of the manuscript, the clumsy phrasing hinders comprehension. This point should be taken care of.

Response: The manuscript has been proofread by a native speaker.

- In the chemical analysis, I am surprised by the choice of Fe as a tracer of the crustal component of the aerosol. It is well known that at least a part of its concentration is contributed by anthropogenic activities. Wouldn't Al or Ca be a better choice? By the way, why were these elements not quantified by the XRF analysis?

Response: This is a good point. In order to analyze the carbonaceous aerosol, the authors selected quartz fiber filters to collect personal exposure PM<sub>2.5</sub> samples in this study. Due to the limitations of personal exposure sampling, it is difficult to collect both quartz and Teflon filter samples simultaneously.

Moreover, the analytical uncertainties by using ED-XRF for small molecular weight crustal elements in quartz fiber filter (due to high background for Na, Al, Ca and Mg), such as Al, Si and Ca, are high. So, Al, Si and Ca are not suitable to be used as a tracer for the crustal component of the aerosol in this study. Meanwhile, the high accuracy of Fe analysis with ED-XRF has been demonstrated in our previous publication (Xu et al., 2016b), and it has been often used as a tracer for crustal component in PM<sub>2.5</sub> (e.g., Cao et al., 2005b; Hao et al., 2007; Sun et al., 2014; Wu et al., 2012; Xu et al., 2016b).

Furthermore, based on the previous references (Gelado-Caballero et al., 2012; Zhuang et al., 2001), the enrichment factors of Fe in dust storm period and non-dust storm were both 1-2, always < 10, proving that Fe in aerosol was still mainly derived from the crustal source. Therefore, taking into account the above points, the authors finally picked Fe as a tracer of the crustal component in this study.

Reference:

- Cao, J. J., Rong, B., Lee, S. C., Chow, J. C., Ho, K. F., Liu, S. X., and Zhu, C. S.: Composition of indoor aerosols at emperor Qin's terra-cotta museum, Xi'an, China, during summer, China Part., 3(3), 170-175, 2005b.
- Gelado-Caballero, M. D., López-García, P., Prieto, S., Patey, M. D., Collado, C., and Hérnández-Brito, J. J.: Long-term aerosol measurements in Gran Canaria, Canary Islands: Particle concentration, sources and elemental composition, J. Geophy. Res.-Atmos., 117, D03304, doi:10.1029/2011JD016646, 2012.
- Hao, Y. C., Guo, Z. G., Yang, Z. S., Fang, M., and Feng, J. L.: Seasonal variations and sources of various elements in the atmospheric aerosols in Qingdao, China, Atmos. Res., 85, 27-37, 2007.
- Sun, Y. Y., Hu, X., Wu, J. C., Lian, H. Z., and Chen, Y. J.: Fractionation and health risks of atmospheric particle-bound As and heavy metals in summer and winter, Sci. Total Environ., 493, 487-494, 2014.
- Wu, F., Zhang, D. Z., Cao, J. J., Xu, H. M., and An, Z.S: Soil-derived sulfate in atmospheric dust particles at Taklimakan desert, Geophy. Res. Lett., 39, L24803, doi:10.1029/2012GL054406, 2012.
- Xu, H.M., Cao, J. J., Chow, J. C., Huang, R.-J., Shen, Z. X., Chen, L. W. A., Ho, K. F., and Watson, J. G..: Inter-annual variability of wintertime PM<sub>2.5</sub> chemical composition in Xi'an, China: Evidences of changing source emissions, Sci. Total Environ. 545-546, 546-555, 2016b.
- Zhuang, G. S., Guo, J. H., Yuan, H., and Zhao, C. Y.: The compositions, sources, and size distribution of the dust storm from China in spring of 2000 and its impact on the global environment, Chinese Sci. Bull., 46(11), 895-900, 2001.

- In the health risk assessment, it would be useful to detail the type of risk quantified. The categories 'cancer risk' and 'non-cancer risk' are very broad. Also, is the risk a long-term or a short-term one? Why did you assess only the risks resulting from exposure to Mn, Ni, Zn, Pb, the PAHs and the PAEs? There is also a risk due to exposure to PM<sub>2.5</sub> and given the large concentrations reported in your work, I expect this one might be very important.

Response: We do agree and understand the reviewer's concern. The details of these categories have been clarified and revised in the manuscript:

"The heavy metals non-carcinogenic risks and toxic organics carcinogenic risks of  $PM_{2.5}$  via inhalation were calculated according to the U.S. EPA health risk assessment model (USEPA, 2004, 2011)."

U.S. EPA health risk assessment model is the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environmental media, now or in the future. The reason for choosing Mn, Ni, Zn, Pb, PAHs and PAEs to assess the health risks in personal exposure PM<sub>2.5</sub> samples is because these chemicals (among all the chemicals we analyzed in this study) are included in this model and they are assessed to be hazardous to human health in the previous studies (e.g., Hu et al., 2018; Kong et al., 2015; Sun et al., 2014; Xu et al.,

2018a).

Moreover, indeed, as the reviewer said "There is also a risk due to exposure to  $PM_{2.5}$ ", but  $PM_{2.5}$  is a complex mixture containing a lot of chemicals. There is no clear and better way to assess its whole health risks for now based on  $PM_{2.5}$  chemical concentrations (except for the model simulation and medical animal exposure experiments). So, at this moment, we calculated the risks of the certain toxic chemicals in  $PM_{2.5}$  to estimate  $PM_{2.5}$  health risks.

### Reference:

- Hu, Y. J., Bao, L. J., Huang, C. L., Li, S. M., Li, Liu, P., and Zeng, E. Y.: Assessment of airborne polycyclic aromatic hydrocarbons in a megacity of South China: Spatiotemporal variability, indoor-outdoor interplay and potential human health risk, Environ. Pollut., 238, 431-439, 2018.
- Kong, S. F., Li, L., Li, X. X., Yin, Y., Chen, K., Liu, D. T., Yuan, L., Zhang, Y. J., Shan, Y. P., and Ji, Y. Q.: The impacts of firework burning at the Chinese Spring Festival on air quality: insights of tracers, source evolution and aging processes, Atmos. Chem. Phys., 15, 2167-2184, 2015.
- Sun, Y. Y., Hu, X., Wu, J. C., Lian, H. Z., and Chen, Y. J.: Fractionation and health risks of atmospheric particle-bound As and heavy metals in summer and winter, Sci. Total Environ., 493, 487-494, 2014.
- Xu, H. M., Guinot, B., Cao, J. J., Li, Y. Q., Niu, X. Y., Ho, K. F., Shen, Z. X., Liu, S. X., Zhang, T., Lei, Y. L., Zhang, Q., Sun, J., and Gao, J. J.: Source, health risk and composition impact of outdoor very fine particles (VFPs) to school indoor environment in Xi'an, Northwestern China, Sci. Total Environ., 612, 238-246, 2018a.

- In the results section (line 328-330), you cannot extrapolate to the whole SWA region your results collected during two weeks at three very specific locations.

Response: Thank you for pointing out. The authors have revised this statement to:

"The average PE PM<sub>2.5</sub> mass concentrations were  $331.7\pm190.7$ ,  $356.9\pm71.9$  and  $242.8\pm67.6 \ \mu g \ m^{-3}$  for women at Domestic Fires (DF), students at Waste Burning (WB) and drivers at Motorcycle Traffic (MT), respectively, in this study."

Moreover, the authors have checked related issue and made corresponding changes throughout the revised manuscript.

- Line 400: you say that total carbon was the most important chemical species in PE  $PM_{2.5}$  but it contributes only about 20% to the mass concentration. Isn't this contradictory? What about mineral dust?

Response: We are sorry for the confusion. In section "3.1.2. PE  $PM_{2.5}$  chemical compositions", the authors were talking about the PE  $PM_{2.5}$  chemical compositions,

which include carbon fractions (OC and EC), water-soluble inorganic ions and heavy metals. Total carbon (TC=OC+EC) was the most important chemical species in PE  $PM_{2.5}$ , which means TC was the most important chemical species among these three kinds of major components of  $PM_{2.5}$ .

Strictly speaking, the mineral dust in  $PM_{2.5}$  is not directly analyzed by the instrument. It is estimated by empirical formula based on the concentration of some chemical components (mineral elements). Therefore, mineral dust cannot be regarded as the chemical composition of  $PM_{2.5}$ . It should be considered as the source of  $PM_{2.5}$ . On this issue, the authors will standardize the terms used in the text to avoid ambiguity. Thank you for your suggestion!

-Paragraph 705-724: First, you say that there is no non-carcinogenic risk linked with the exposure to Mn, Pb, Ni, and Zn (line 709), then you discuss the fact that the risk is much higher in the dry season (line 718). What is the point of discussing the magnitude of this risk, especially before repeating (line 723-724) that it is negligible?

Response: Although our results show that the average non-carcinogenic risk linked to heavy metals in this study was below the international thresholds, we have noticed that it has a seasonal behavior, especially for the driver group. We now first present the risk and then highlight this latter point by giving the dry/wet season ratios.

#### Anonymous Referee #2

Received and published: 27 November 2018

We would like to thank the reviewer for all the suggestions and comments. Below we have responded to each comment in point to point format.

Megacities in Africa are pollution hotspots, for which very little data have been published. Personal exposure in such environments have also received virtually no research attention. Therefore, the authors are commended for this work.

General comments: I regard the language in this paper as poor. In many instances, this transfer to reader proper knowledge the and prevents can cause misunderstanding/interpretation of the text. Additionally, it makes the paper difficult/cumbersome to read. It is not the job of the reviewer/editor to do language and/or text editing. In my opinion, this paper should not have been published in ACPD before the language and text was acceptable. Therefore, I recommend that final review of this paper should only be considered once the language/text is improved. In the current form, too many uncertainties exist in the paper, because of the poor language.

Response: The manuscript has been revised by a native speaker before re-submission.

I am also not 100% convinced that the content of this paper fits into the scope of ACP. According to the journal, ACP "... is an international scientific journal dedicated to the publication and public discussion of high-quality studies investigating the Earth's atmosphere and the underlying chemical and physical processes." My uncertainty arises from the fact that this paper focused more on personal exposure and not on "... underlying chemical and physical processes." Would the paper not fit better into a journal specifically considering atmospheric exposure and/or health impacts? I leave the decision to the editor. This comment should not be considered as negative in any way and it is also not a reflection of the science presented.

Response: We understood the reviewer's concern and respected the decision from the editor. We would like to explain that our work is absolutely related to the  $PM_{2.5}$  chemical composition, emission sources and variability. This topic should be within the scope of ACP. Moreover, there are some related works on air quality conducted in sWA (same work package on Air pollution and Health) published in the ACP/AMT DACCIWA special issue, forming a coherent whole.

Specific comments: The authors must please not use the name "South West Africa" as they did in line 105, but rather keep to the term "southern West Africa", as it the rest of the paper. "South West Africa" was the name for modern-day Namibia from 1915 to

1990. I would even go so far as to recommend that the term "southern West Africa" that is abbreviated at "sWA" ("southern" in lower case) be consistently used, instead of "Southern West Africa" that is abbreviated at "SWA" ("Southern" in upper case), to ensure that the reader does not confuse the area investigated with "South West Africa" that was abbreviated at "SWA".

Response: We totally agreed. The abbreviation for southern West Africa (sWA) has been revised throughout the document.

The authors refer to "... garbage spontaneous combustion..." a couple of times. Is the garbage really combusting spontaneously, or are garbage dumps being set alight to reduce the volume of waste, to reduce pests (rats and mice) and prevent disease?

Response: Akouédo dump in Abidjan is a vast and old landfill. We used the term of "spontaneous combustion" as we observed several smoke plumes in the middle of the dump, far from the working area. Spontaneous combustion is a well-known phenomenon in such outdated landfill, but there was difficulty in counting its frequency of occurrence compared to control ignition. Landfill workers often burn waste when they collect trashes and recycle some of useful items. The "controlled burnt" occurs in the active part of the dump. Both processes have a high occurrence during daytime and in the dry and hot season. Here we referred waste burning in a more general manner rather than specifying spontaneous combustion.

The quality of the Google Earth images presented in Figure 1 and the photos presented in Figure 2 are not good and might deteriorate further in page setting during publication (e.g. if the images are printed even smaller). I encourage the authors to ensure the best possible quality for these images.

Response: We definitely payed more attention to the pixel issues on the figures in the revised manuscript.

In its current form, the paper is long. If the authors and editor agree, I would suggest that Appendixes A, B, C and D, which present the questionnaires, rather be included as supplementary material, instead of appendixes. Appendixes are published as part of the paper, while supplementary material are published separately. Readers who want to assess the content of the questionnaires can download the supplementary material, instead of the paper becoming excessively long.

Response: We agreed with the reviewer's comment. We have moved the current Appendix A-D to the supplementary material as supporting information (SI A-D).

I agree with Referee #1 that the authors cannot interpolate their results obtained from

individuals with specific occupations and at specific locations to the wider southern West African region. All such statements should be revised.

Response: Thank you for this point. We have made the necessary changes within the text.

In general, there is little comparison of the results presented in this paper to results obtained elsewhere. I appreciate that very little, if any, personal exposure data have been presented for African cities. However, even if the results presented are compared to ambient/indoor air quality results obtained in the rest of Africa (or Asia, or some other developing settings, if African reference cannot be found), the reader will be able to easier contextualize the exposure concentrations reported here. For instance, indoor air quality in semi- and informal settlements (low-income households) in South Africa (Kapwata et al., Atmosphere 2018, 9(4), 124; https://doi.org/10.3390/atmos9040124) could be compared to "Night" personal exposure of individual in this study. Also, characterization of the plume of fire grilling of meat in an African context (Venter et al., S. Afr. J. Chem., 2015, 68, 181-194; DOI: http://dx.doi.org/10.17159/0379-4350/2015/v68a25) could possibly be compared to the exposure of woman by Domestic Fires (DF) ("grilling meat or roasting peanuts") in this study. Such comparisons will help the reader to contextualize the results presented - currently only comparing the different groups with one another does not enable the reader to contextualize the results. There might be many more references, such as the afore-mentioned, these two are just examples that I found with a quick online search.

Response: We understood this point of view. The citations on our work are related to either ambient concentrations or source characterization. The suggested references should not be applicable. Venter et al. (2015) presented a study on charcoal combustion with a specific type of barbecue, totally different from the conditions at DF (wood in barrel). Kapwata et al. (2018) showed the work on PM<sub>4</sub> (dissimilar with our PM<sub>2.5</sub>) and no chemical composition was provided.

In lines 370 and 384 of our original manuscript, we firstly compared the average PE  $PM_{2.5}$  levels to the weekly ambient  $PM_{2.5}$  concentrations obtained in the same area and similar sampling period, and also compared the daytime PE  $PM_{2.5}$  mass concentrations with the daytime ambient  $PM_{2.5}$  in the same area and exactly the same sampling dates (Djossou et al., 2018). We also used the results of the PAHs exposure measured in Cotonou in a previous study (Fanou et al., 2006). We provide additional references of previous works on personal exposure to  $PM_{2.5}$  in household in Tanzania (Titcombe and Simcik, 2011) and for students in Ghana (Arku et al., 2014). And we compared the results with our data in this study as follows:

"The 5-h PM<sub>2.5</sub> average personal exposure concentration was 1574  $\mu$ g m<sup>-3</sup> (±287, n = 3) for open wood fires in households in the Njombe district of Tanzania (Titcombe and Simcik, 2011), and was comparable to the highest 12-h exposure level to PM<sub>2.5</sub> for women at DF site in this study (1164.7  $\mu$ g m<sup>-3</sup>, daytime in wet

season, July 5<sup>th</sup>), and was 4.7 times of the daily average PE PM<sub>2.5</sub> concentration in dry and wet seasons  $(331.7\pm190.7 \ \mu g \ m^{-3})$ ."

"In the study of Titcombe and Simcik (2011), the authors found that the 5-h average total PAH personal exposure concentration was 5040 ng m<sup>-3</sup> (±909, n = 3) for open wood fires in households in the Njombe district of Tanzania, which was much higher (~65 times) than the women exposure PAHs at DF site in the current research. The highest 12-h exposure PAHs for women at DF site in this study was 469.7 ng m<sup>-3</sup> (daytime in wet season, July 6<sup>th</sup>), approximately one-tenth of the PAHs concentration from open wood fires in Tanzania mentioned above. The large PE PAH concentrations difference between these two studies may be influenced by many factors such as wood type, combustion state, stove structure and sampling time."

"Student (10-17 years old)  $PM_{2.5}$  exposures ranged from less than 10 µg m<sup>-3</sup> to more than 150 µg m<sup>-3</sup> (mean 56 µg m<sup>-3</sup>) in four neighborhoods in Accra, Ghana (Arku et al., 2014), much lower than that for students at WB site (356.9±71.9 µg m<sup>-3</sup>). It can be seen that the high exposure of students in this study is likely to be related to the waste burning emissions, while there was no obvious strong  $PM_{2.5}$ emission source in the study of Arku et al. (2014)."

We have also added the comparisons as mentioned above in the revised manuscript.

#### *Reference:*

- Arku, R. E., Dionisio, K. L., Hughes, A. F., Vallarino, J., Spengler, J. D., Castro, M. C., Agyei-Mensah, S., and Ezzati, M.: Personal particulate matter exposures and locations of students in four neighborhoods in Accra, Ghana. J. Expo. Sci. Environ. Epidemiol., 1–10, 2014.
- Titcombe, M. E., and Simcik, M.: Personal and indoor exposure to PM<sub>2.5</sub> and polycyclic aromatic hydrocarbons in the southern highlands of Tanzania: a pilot-scale study. Environ. Monit. Assess., 180, 461–476, 2011.

Line 415. The author state that "The previous studies (Cao et al., 2008; Li et al., 2009; Tian et al., 2017) suggested that average OC/EC characterizes 1.1 as motor vehicle exhaust, 2.7 as coal combustion and 9.0 as biomass burning. The OC/EC in the present study points out that biomass burning emission was the main contributor to carbonaceous aerosols for women at DF, and the mixed emissions from biomass and coal burning, even or/and motor vehicle exhaust dominated the carbonaceous aerosol sources for students at WB and drivers at MT." However, the authors should clarify these statements, since OC/EC ratio will change in a plume with aging, with the formation of secondary OC and deposition of EC. Therefore, if the above OC/EC ratios are used to characterize fresh emissions/plumes, it should be stated as such and not left to the reader to interpret.

Response: The statements have been revised as follows:

"Previous studies (Cachier et al., 1989; Cao et al., 2005a; Cao et al., 2008; Li et al., 2009; Tian et al., 2017; Watson et al., 2001) summarized that average OC/EC characterizes 1.1 as motor vehicle exhaust, 2.7 as coal combustion and 9.0 as biomass burning from their source samples (i.e., fresh emissions/plumes)."

The reason why we could compare the OC/EC results of the personal exposure data in this study with the above source samples is because that the participants were close or around to the typical anthropogenic sources in this study. In addition,  $PM_{2.5}$  emitted from the pollution sources still maintained a relatively fresh state (less aging) without long-distance transport, and then was inhaled into human body. Therefore, the OC/EC ratio comparison results in this study could yield reliable conclusions as described in the texts (originally lines 418-421).

### Reference:

- Cachier, H., Bremond, M. P., and Buat-Menard, P.: Carbonaceous aerosols from different tropical biomass burning sources. Nature, 340, 371–373, 1989.
- Cao, J. J., Wu, F., Chow, J. C., Lee, S. C., Li, Y., Chen, S. W., An, Z. S., Fung, K. K., Watson, J. G., Zhu, C. S., and Liu, S. X.: Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China. Atmos. Chem. Phys., 5, 3127–3137, 2005a.
- Watson, J. G., Chow, J. C., and Houck, J. E.: PM<sub>2.5</sub> chemical source profiles for vehicle exhaust, vegetative burning, geological material, and coal burning in northwestern Colorado during 1995. Chemosphere, 43, 1141–1151, 2001.

Line 247. Fe and the heave metals reported (V, Cr, Mn, Co, Ni, Cu, Zn, Sb, Ba and Pb) were analyzed with ED-XRF. How sure are the authors that some of the heavy metals were not part of the GM and are therefore partially double accounted for in the mass balance (Figure 5, line 493 onwards), i.e. accounted as heavy metal mass and also contributing to the mass of the GM?

Response: The abundance of Fe in the earth's crust is about 4% (discussed in next comment detailly), and the abundances of the other nine elements (i.e., V, Cr, Mn, Co, Ni, Cu, Zn, Sb, Ba and Pb) in the earth's crust ranged from  $0.2 \times 10^{-6}$  (Sb) to  $660 \times 10^{-6}$  (Mn), which are 2-5 orders of magnitude lower than Fe (Taylor and McLennan, 1985). From the above crustal content comparison, the authors had reason to believe that the overlap contributions to PM<sub>2.5</sub> from the other nine elements and the estimated crustal material content (by using Fe) can be neglected.

Line 511. Although the authors give a citation (i.e. "Taylor and McLennan, 1985") to support the use of Fe as a tracer for geological material (GM), how accurate is this method? The authors state "Fe constitutes about 4.0% of the Earth's crust in dust of the earth's crust (Cao et al., 2005)". Are there any indications of Fe contents of local soils (and the variation on Fe contents) and how it differs from the global average value of 4%, which was used? Basically, I am asking how accurate the method is. Can the

authors give any indication of accuracy? This is important, since ". . . it is found that GM contributed  $35.8\%\pm2.1\%$ ,  $46.0\%\pm3.7\%$  and  $42.4\%\pm4.7\%$  of PE PM<sub>2.5</sub> mass concentrations for women at DF, students at WB and drivers at MT, respectively."

Response: Fe is the most important metal and one of the major constituents of the lithosphere. Its average content of the Earth's crust is about 5%. The global abundance of Fe is around 4.5% (Kabata-Pendias and Mukherjee, 2007). The typical range of Fe contents in soils is between 0.1 and 10% and its distribution in soil is variable, which is controlled by several soil parameters (Kabata-Pendias and Mukherjee, 2007). The authoritative study from Taylor and McLennan (1985) of elemental content in soils showed that the global abundance of Fe is around 3.5%.

Because of the lack of elemental composition obtained in topsoil of Africa, the authors used 4.0% (global mean Fe content from the mentioned literatures) as a percentage of Fe in the topsoil of African study area for geological material estimation in this study. The value was widely used in other literatures (Cao et al., 2005b; Hao et al., 2007; Sun et al., 2014; Wu et al., 2012; Xu et al., 2016b). In our opinion, this method can roughly indicate the contribution of the geological material to atmospheric particle matters to a certain extent. Moreover, since the geological material of three sampling sites in this study were estimated using a consistent method, the relative results were comparable.

#### *Reference:*

- Hao, Y. C., Guo, Z. G., Yang, Z. S., Fang, M., and Feng, J. L.: Seasonal variations and sources of various elements in the atmospheric aerosols in Qingdao, China, Atmos. Res., 85, 27-37, 2007.
- Kabata-Pendias, A., and Mukherjee, A. B.: Trace Elements from Soil to Human. Springer-Verlag, Berlin Heidelberg, Germany, pp. 381-393, 2007.
- Sun, Y. Y., Hu, X., Wu, J. C., Lian, H. Z., and Chen, Y. J.: Fractionation and health risks of atmospheric particle-bound As and heavy metals in summer and winter, Sci. Total Environ., 493, 487-494, 2014.
- Wu, F., Zhang, D. Z., Cao, J. J., Xu, H. M., and An, Z. S.: Soil-derived sulfate in atmospheric dust particles at Taklimakan desert, Geophy. Res. Lett., 39, L24803, doi:10.1029/2012GL054406, 2012.

Line 529 "From Figure 5, evident diurnal distinguishes are observed in two major chemical compositions (OM and GM) in this study. We can see that GM exhibits the lower proportion at night (35.3%) than daytime (47.5%), indicating its close relationship with human activities." However, does meteorology not also play a role? In Line 483 the authors imply that precipitation is higher during night-time, i.e. ". . . spontaneous combustion of waste occurs frequently during the day, because of less precipitation and higher air temperature at daytime. . ."

Response: As our best knowledge, the main source of the geological material in  $PM_{2.5}$  is from crust dust. In addition to the effects of crust erosion by water and wind, it is largely related to the physical activities of human, such as resuspension from individual

activities, construction activities and etc. The second reason (meteorological factor) shown in original line 483 explained the day-night ratio of heavy metals in PM<sub>2.5</sub>, that is, the absolute concentrations of heavy metals; while the content in original line 529 discussed the proportion of geological material in PM<sub>2.5</sub>. The meteorological factors, including precipitation, indeed cause scouring action on particulate matters (i.e., wet deposition), but they have little effect on altering the proportion of geological material in PM<sub>2.5</sub>. Therefore, lower geological material proportion in PM<sub>2.5</sub> at night in this study was mainly due to the resuspension of the geological material from the less individual activities.

Line 539 "... due to the influence from the damp wood burning at the working time." I could not find any place where the wood moisture content was reported. Therefore, this statement and previous, as well as subsequent deductions, based on this statement, are not fact based. However, I do agree with later statements (line 566) that the wood will be damper in the wet season, i.e. "... increase in humidity (moisture content) of the wood used for grilling meat in wet season...".

Response: In this study, we did not measure the moisture of the wood used for barbecue in women's work. Since the grilling fuel (wood) was placed in the open area (no shield or roof), the abundant rainfall in wet season inevitably led to moisture increase in the wood. With on-field observation, it frequently took a long time to ignite the wood, which emitted more plume from damp fuels in the wet season during the sampling period. In previous studies (Chen et al., 2010; Grandesso et al., 2011; Keita et al., 2018; Shen et al., 2012, 2013), the results showed that biomass fuel with high moisture often required additional energy to vaporize the water and hence resulted in low combustion efficiency and high pollutant emissions. The emission factor (EF) of OC increase with the fuel moisture content (Chen et al., 2010).

The authors have modified the original statement in lines 538-541 as follows:

"An exception is that OM proportion of women PE  $PM_{2.5}$  at daytime (50.8%) was much higher than nighttime (38.2%) in wet season, due to the influences from the damp wood burning at the working time. Burning biomass fuel with high moisture often results in low combustion efficiency, long smoldering period and high air pollutant emissions (Grandesso et al., 2011; Shen et al., 2012, 2013). The emission factor of OC usually increases with the fuel moisture content (Chen et al., 2010; Keita et al., 2018). Therefore, burning the damp wood led to higher OC emission than dry wood, in-line with the observation for women PE results in this study."

### Reference:

- Chen, L.-W. A., Verburg, P., Shackelford, A., Zhu, D., Susfalk, R., Chow, J. C., and Watson J. G.: Moisture effects on carbon and nitrogen emission from burning of wildland biomass. Atmos. Chem. Phys., 10, 6617–6625, 2010.
- Grandesso, E., Gullett, B., Touati, A., and Tabor, D.: Effect of moisture, charge size, and chlorine concentration on PCDD/F emissions from simulated open

burning of forest biomass. Environ. Sci. Technol., 45, 3887–3894, 2011.
Shen, G., Wei, S., Wei, W., Zhang, Y., Min, Y., Wang, B., Wang, R., Li, W., Shen, H., Huang, Y., Yang, Y., Wang, W., Wang, X., Wang, X., and Tao, S.: Emission factors, size distributions, and emission inventories of carbonaceous particulate matter from residential wood combustion in rural China. Environ. Sci. Technol., 46, 4207–4214, 2012.

Line 584. "Students at WB: nighttime PE PAHs were higher in dry season and lower in wet season compared with daytime levels, with the average D/N ratios of 0.7 and 1.8, respectively. The higher concentrations of combustion markers-BbF and BeP were observed during the day, while the higher concentrations of gasoline vehicle emission markers-DahA and BghiP were found at night (Baek et al., 1991; Wang et al., 2006), which was related to the garbage truck for waste transportation from city to the landfill during night." I am not sure that the latter explanation can be so simple, i.e. only due to "garbage truck".

Response: We apologized for the misleading. Referring to the middle panel of Figure 6A, it shows that the distributions of PAHs in students'  $PM_{2.5}$  personal exposure samples in the dry and wet seasons were basically the same, with the higher concentrations in the dry season. The authors discussed the diurnal variation of PAHs concentration in different seasons and the dominant PAH species in daytime and nighttime. Both PAH profiles had a similar feature of high combustion markers of BbF and BeP, and gasoline emission markers of DahA and BghiP. Besides, with the large error bars (standard deviations) of PAH concentrations shown in this Figure, we believe that the previous statements about the dominant PAHs species in the daytime and nighttime are not so supportive, and thus the statements have been deleted from the revised manuscript.

In addition, the statements in lines 586-591 have been revised as following:

"Both the PAH profiles were featured with high combustion markers of BbF and benzo[e]pyrene (BeP), and high gasoline vehicle emission markers of dibenzo[a,h]anthracene (DahA) and BghiP (Baek et al., 1991; Wang et al., 2006)."

Line 706. Can the authors please explain the selection of species included in the "Noncancer risks", wherein only "four heavy metals (Mn, Ni, Zn and Pb)" were considered?

Response: The non-carcinogenic risks of heavy metals in  $PM_{2.5}$  via inhalation were calculated according to the U.S. EPA health risk assessment model (USEPA, 2004, 2011). U.S. EPA health risk assessment model is the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environmental media, now or in the future. The reason we only chose Mn, Ni, Zn and Pb to assess the health risks in personal exposure  $PM_{2.5}$  samples is because

these four metals (among all the chemicals we analyzed in this study) are included in this U.S. EPA health risk assessment model and they are assessed to be hazardous to human health in the previous studies (e.g., Hu et al., 2018; Kong et al., 2015; Sun et al., 2014; Xu et al., 2018a).

1	Personal exposure to PM <sub>2.5</sub> emitted from typical anthropogenic sources in
2	Southern southern West Africa (SWAsWA): Chemical characteristics and
3	associated health risks
4	
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28	

### 29 Abstract

30 Urbanization is an strongly emerging issue strongly emerging in in Southern southern 31 West African (SWAsWA)-region. There is a general-lack of full understanding about-on chemical compositions and the personal exposure (PE) levels to fine particulate matter 32 (PM<sub>2.5</sub>), -its chemical components and its health risks related to the various anthropogenic 33 sources in this region. In the current this study, personal exposure to PM<sub>2.5</sub> (PE PM<sub>2.5</sub>) 34 sampling was for the first time carried outstudied in dry season (January) and wet (July) 35 seasons (July) of 2016 to characterize PE PM<sub>2.5</sub>the contributions -offrom Domestic Fires (DF) 36 for to women and Waste Burning (WB) for to students in Abidjan, Côte d'Ivoire, and 37 Motorcycle Traffic (MT) for to drivers in Cotonou, Benin. 38

The average PE PM<sub>2.5</sub> mass concentrations were 331.7±190.7, 356.9±71.9 and 39  $242.8\pm67.6 \ \mu g \ m^{-3}$  at DF, WB and MT for the women, students and drivers, which were 2.4, 40 10.3 and 6.4 times of the ambient PM<sub>2.5</sub> concentrations, respectively. Elevated Mean 41 concentrations of PE PM<sub>2.5</sub> levels in dry season were found at at-DF (358.8±100.5 µg m<sup>-3</sup>), 42 WB (494.3 $\pm$ 15.8 µg m<sup>-3</sup>) and MT (335.1 $\pm$ 72.1 µg m<sup>-3</sup>)-were much elevated in dry season, on 43 average 15% higher than that at DF and 55% higher at both WB and MT in coldwet season. 44 The changes in PE PM<sub>2.5</sub>seasonal variations can be were attributed to the source emission 45 46 sources, meteorological factors and personal activities. In addition, T the results also show that geological material (35.8%, 46.0% and 42.4%) and organic matter (34.1%, 23.3% and 47 24.9%) were always the major components in of PE PM<sub>2.5</sub> at DF, WB and MT sites. It is 48 worth noting that the contribution to of PE PM<sub>2.5</sub> from heavy metals was higher at WB (1.0%) 49 50 than at DF (0.7%) and MT (0.4%), which was strongly influenced by the waste burning emission strongly. This results in , leading to the highest heavy metal non-cancer risks on 51 52 heavy metal -for students, which are (5.1 and 4.8 times the values of for women and drivers, respectively' non-cancer risks). 53

54 By In-conducting organic species speciation of PE PM<sub>2.5</sub>, some fingerprints werecan be used to quantify access the exposure concentrations and identify trace the source 55 contributions from local typical local anthropogenic sources to different samples. The 56 We women exposure concentration to particulate polycyclic aromatic hydrocarbons (PAHs) in 57  $PM_{2.5}$ -at DF (77.4±47.9 ng m<sup>-3</sup>) was 1.6 and 2.1 times, respectively, of that for students at 58 WB (49.9 $\pm$ 30.7 ng m<sup>-3</sup>) and <del>2.1 times for</del> for drivers at MT (37.0 $\pm$ 7.4 ng m<sup>-3</sup>). This can be 59 associated with the higher contributions from , which is related to the solid fuels burning and 60 meat grilling meat activities to women, resulting in 5 times higher exceed of the cancer risk 61 safety threshold  $(1 \times 10^{-6})$ -to women. Phthalate esters (PAEs), commonly used as plasticizers 62

in many-products, were observed toin-be extremely high levels in the student exposure PM<sub>2.5</sub>
samples (1380.4±335.2 ng m<sup>-3</sup>)\_-at WB site,owing to owing to the obvious waste burning
activities emission nearbyobviously. The Ddrivers' exposures to fossil fuel emission
combustions (especially traffic) markers of -hopanes in PE PM<sub>2.5</sub> at MT (50.9±7.9 ng m<sup>-3</sup>)
was <u>32.0-32.3</u> times higher thanof those for women at DF (17.1±6.4 ng m<sup>-3</sup>) and students at
WB (15.6±6.1 ng m<sup>-3</sup>), correlating with the elevated exposure to traffic emissions for drivers.

69 Overall, the current study shows that wood combustion, waste burning, fugitive dust and 70 motor vehicle emissions were the dominated sources dominated for the PE PM<sub>2.5</sub> mass and mainly contributed to its toxicities mainly. The exposure to heavy metals of Pb and Mn had 71 high non-cancer risks to students at WB, while severe cancer risk of PAHs was found for 72 women at DF via inhalation Heavy metals and organics chemicals in PE PM<sub>2.5</sub> in SWA 73 brought about Pb and Mn non-cancer health risks for students at WB site and serious PAHs 74 cancer risks for women at DF site via inhalation pathway. The result of thisis study provides 75 basic original data, and initial perspective of  $PM_{2.5}$  personal exposure, and health risk 76 assessment in the underdevelopinged areas. The information -to-encourages the governments 77 to improve the air quality and living standard of residents in this region. 78

79

*Keywords:* personal exposure to PM<sub>2.5</sub>; domestic fires; waste burning; motorcycle traffic;
 <u>southern</u> West Africa

82

### 83 **1. Introduction**

The southern West Africa (SWAsWA) region has is experiencingexperienced an 84 economic upturn. and increasingly s-ignificant aAnthropogenic air pollutant emissions of air 85 pollutants haves been increasing since during the last last few years, leading to- poor air 86 qualityand causes serious air pollution to the areas (IMF, 2017; Norman et al., 2007). Fine 87 particulate matter (PM<sub>2.5</sub> with equivalent aerodynamic diameters  $\leq 2.5 \mu m$ ) is one of the 88 89 major concerns of from international organizations and publics because of its high the health effects impacts by personal associated with exposure levels, health of individuals and 90 91 pollutant emission sources exposures (Bruce et al., 2000; Chen et al., 2013; Owili et al., 2017). Owili et al. (2017) found that the four types of ambient PM<sub>2.5</sub>, including mineral dust, 92 anthropogenic pollutant, biomass burning and mixture aerosols are significantly associated 93 with under-five and maternal mortality in Africa. However, studies on PM<sub>2.5</sub>, especially 94 direct personal exposure (PE) tests to PM<sub>2.5</sub> (non-t-stationary sampling) and its health 95 assessment, effects - are still very limited in these low gross domestic product (income-GDP) 96 97 countries in this region.

Since the 1990s, several international campaigns have been performed in Africa. Some 98 99 of them were mainly focused on the particles or aerosols, for examplesuch as DECAFE 100 (Lacaux et al., 1995), EXPRESSO (Delmas et al. 1999; Ruellan et al., 1999), SAFARI-1992 101 (Lindesay et al., 1996), SAFARI-2000 (Swap et al., 2002), AMMA (Léon et al., 2009; 102 Liousse et al., 2010; Marticorena et al., 2010) and INDAAF (Ouafo-Leumbe et al., 2017). As 103 we known, tIn fact, he Africa has is the largest production of source of mineral dust particles 104 from the Sahara Desert and unpaved road surfaces (Laurent et al., 2008; Marticorena et al., 105 2010; Reeves et al., 2010), and carbonaceous aerosols originated from wild fires (mainly 106 savannah fires) as well (Capes et al., 2008; Gaudichet et al., 1995) among the world. 107 Therefore, these campaigns were more biased towards the natural sources of aerosols in 108 Africa. Liousse et al. (2014) have showed thatn the increase of the relative importance of particulate emissions from domestic fires and fossil fuel combustions in Africa. In previous 109 110 literature, the major contributions to the aerosol chemistry in the dry season in northern Benin in the dry season were dust (26%-59%), primary organic matters (POC, 30%-59%), 111 112 elemental carbon (EC, 5%-9%) and water soluble inorganic ions (3%-5%) (Ouafo-Leumbe et 113 al., 2017). Liousse et al. (2014) showed that the increase of relative importance of particulate 114 emissions from domestic fires and fossil fuel combustions in Africa. Uncertainty has been raised by the residents who live in urban areas as they do concern on the health impact from 115 air quality. This poses serious health questions for people who frequent the city on a daily 116

basis. However, the there is still limited literature works on the health effects of personal exposure PE to  $PM_{2.5}$  emitted from the typical anthropogenic sources in the emerging cities in Africa are still scarce.

- 120 The main anthropogenic emission sources of PM<sub>2.5</sub> in SWAsWA include domestic wood 121 burning, fossil fuel combustion, unregulated traffic and industries, waste burning and road 122 dust-associated to human activities. An ongoing project in Africa-DACCIWA (Dynamics-123 Aerosol-Chemistry-Cloud Interactions in West Africa) (Africa-DACCIWA) aims at-to quantifyquantifying the influences of anthropogenic and natural emissions on the atmospheric 124 125 pollutant composition over South-southern West Africa and to assessing their impacts on 126 human health, ecosystem health and agricultural productivity. The information which will be gathered and discussed -communicated to-with policy-makers, scientists, operational 127 128 centrers, students and general publics. The current work involved in the framework of the Work Package 2 "Air Pollution and Health" of DACCIWA is tryingtends to link emission 129 sources, air pollution and health impacts over representative differentiated urban sources: 130 131 domestic fires and waste burning in Abidjan (Ivory Coast) and two-wheel vehicle traffic 132 emission in Cotonou (Benin) for different target groups of populations.
- 133 Smoking meat (e.g., fish and pork) by biomass fuels (mainly woods) is an important diet 134 pattern for residents of coastal countries in SWAsWA area. Many female workers\_without 135 any personal health protection are engaged in roasting activities without any personal health 136 protectiony. They are directly exposed to extremely the high PM<sub>2.5</sub> emissions pollution from wood burning and smoking meat, causing which could cause very serious health 137 138 problemsissues. Besides, Uurbanization leads to explosive population growth and rural depopulation in SWAsWA, generating a huge amount resulting in a large amount of urban 139 140 domestic wastes. The biggest landfill in Abidjan focused-involved in this study receivesd 141 more than 1,000,000 t waste per year (Adjiri et al., 2015). W-A mass of garbage ithout lacks 142 any processing capacity and reasonable appropriate treatment method, resulting in a large amount of air pollutants was thus emitted during from the combustion and stacking of waste, 143 Such which phenomenon damages the living environment and harm the residents' health 144 145 (especially for children) condition of the populations in Abidjan, especially for children 146 (UNEP, 2015). Moreover, in many-most low-GDPincome countries, motorbike taxis areis a major mode of local transportation (Assamoi and Liousse, 2010). In Benin, motorbike taxi 147 148 drivers (mainly male) represented almost ~2.5% of the total population of Benin in 2002 149 (Lawin et al., 2016). As-Due to they spend many-long working hours dailyin the middle of traffic every day, these drivers are highly exposed to traffic-related PM<sub>2.5</sub> pollution emissions 150

151 over years.

152 Major chemical components in PM<sub>2.5</sub>, likelike OC, EC, and ions and EC mentioned 153 above, not only have strong impact on PM<sub>2.5</sub> physicochemical characteristics, but also 154 causeaffect its health risks. Typical trace toxic chemicals, such as heavy metals and 155 polycyclic aromatic hydrocarbons (PAHs), in can be attached on PM<sub>2.5</sub>, have which would cause various health damages to problems for humans (Cao et al., 2012; WHO, 1998; Xu et 156 157 al., 2015). For instance, example, Pb is a neuro-developmental metal which, affectsing children health and mental development-seriously (USEPA, 2006; Xu et al., 2017). Several 158 159 Few\_PAHs can beare teratogenic and carcinogenic for humans strongly (Tang et al., 2008). Up to now, only few studies have investigated PM<sub>2.5</sub>-chemical compositions of the personal 160 161 exposure PE PM<sub>2.5</sub> samples, and little is known regarding the sources and health risks of 162 personal exposure PM<sub>2.5</sub>-in SWAsWA region. This poses a challenge to-on formulation of strategies aimed atto mitigateing PM<sub>2.5</sub> pollution and its health effects in this area. 163

164 Therefore, our study relies on the portative device sampling PM<sub>2.5</sub> personal exposure <u>PE</u> 165 samples in SWAsWA area in 2016. OurStudy objectives include <u>for the purpose of 1</u>) to characterizeing the the personal exposure PE to  $PM_{2.5}$  as variation of from different typical 166 167 local typical anthropogenic PM2.5-sources by the chemical component analysis and PM2.5 mass balance analysis; 2) to identifying potential pollution sources to different exposed 168 populations by from fingerprint of organic markers; and 3) to evaluate the ing PE the 169 170 personal exposure to PM<sub>2.5</sub> health risks by the United States Environmental Protection Agency (U.S. -EPA) health risk assessment model. This information will provideoffers 171 172 scientific understanding of the personal exposure PE to PM<sub>2.5</sub> in SWA<sub>SWA</sub> and try to arouses 173 the government's attention to protect residents' health <u>there</u> from various anthropogenic 174 sources.

175

## 176 **2. Materials and methods**

# 177 2.1. Site description and participants selection

Personal exposure<u>PE</u> to PM<sub>2.5</sub> (hereafter defined as PE PM<sub>2.5</sub>) filter samples were collected using portative devices in the polluted atmosphere of different<u>unique</u> source<u>dominated</u>-environments for different target groups of humanss, including Domestic Fires (DF) for women<u>and</u>, Waste Burning (WB) for students both in Abidjan, Côte d'Ivoire, and Motorcycle Traffic (MT) for drivers in Cotonou, Benin (Figure 1). Abidjan (5°20' N, 4°1' W) is the economic capital of Côte d'Ivoire with 6.5 million inhabitants in 2016. It is characterized by a high level of industrializsation and urbanization in <u>SWAsWA</u> area. Cotonou (6°21' N, 2°26' W) is the largest city and economic center of Benin, with about 1.5 million inhabitants in 2016. Both <u>the</u> cities experience a tropical wet and dry <u>mixed</u> climate, with relatively constant <u>ambientair</u> temperatures (<u>in a range of 24-30–°</u>C) and <u>an average of</u> relative humidity (RH) <u>>above-80%</u> throughout thea year.

189 DF site in Abidjan is located in the market of Yopougon-Lubafrique (5°19.7' N, 4°6.4' 190 W) where in-is a large courtyard with about 25 fireplaces (Figure 2). The major fuels used 191 isare essentially heve wood-, which is a (one-kind of local rubber trees) locally. Several adult 192 female adult workers were employed to-for grilling meat and/or roasting peanuts from 06:00 193 to 15:00 UTC (working time) in the working day. In this study, we selected two healthy, non-194 smoking female workers (an average age of 32.5 years old) to investigate conduct personal 195 exposure to PM<sub>2.5</sub> from domestic fire and related sources, such as grilling (Figure 2). WB site in Abidjan is near the public landfill of Akouédo (5°21.2' N, 3°56.3' W), which has received 196 197 all the wastes collected produced from Abidjan for the last past 50 years (Figure 2). We 198 selected two healthy, and non-smoking primary school students (an average age of 11 years 199 old) who live and study next to WB site (within 100 m straight-line distance) to determine the 200 personal exposure features to PM2.5 from waste burning (spontaneous combustion at high air 201 ambient temperatures condition and irregular combustion by the landfill workers-sometimes) 202 emissions at landfill and other daily sources. Lastly, MT site in Cotonou is located in the 203 Dantokpa area (6°22.1′ N, 2°25.9′ E), one of the biggest markets in western Africa (Figure 2). 204 It is largely dominated by a mass of emissions from motorcycle traffic (two-wheel vehicles 205 powered by petrol, also named zemidjan in local language) and a small quantity of other 206 motor vehicles emissions. We chose two healthy, and non-smoking male motorcycle drivers 207 (an average age of 50 years old) to survey PM<sub>2.5</sub> personal exposure from motorcycle emission 208 and related sources (such as road dust).

209 Two women (woman A and B) involved in this study at DF are-were both in charge of 210 cooking at home by charcoal and butane gas as fuel, (Figure S1abc) and daily household 211 cleaning house in daily life (Figure S1abc). One of the student participators (student A, boy, 8 212 years old) at WB didoesn't not involve in cooking activities -at home by himself [(energy 213 sources for cooking energy isare charcoal and liquefied petroleum gas (LPG)]) (Figure S1ac), 214 but the another student (student B, girl, 14 years old) is usually responsible for household 215 cooking at home with burning by burning solid fuels (, i.e., wood) (Figure S1d). Two 216 motorcycle drivers (driver A and B) focused in this study aat MT are both working for a local 217 motorcycle operation company, whose working time is usually from 06:30 to 10:30, 12:00 to 17:00 and 18:30 to 21:00 UTC. They are droive ing on road almost all the working time and 218

219 <u>go backreturned</u> home for meals. They did not participate <u>on't cookany cooking</u> -at home by
 220 <u>themselves</u> (energy source for cooking is charcoal) (Figure S1a).

221

222

## 2.2. Personal exposure to $PM_{2.5}$ samples collection and QA/QC

223 12Twelve-hour time integrated (daytime: 07:30 to 19:30 UTC; nighttime: 19:30 to 07:30 224 on the next day UTC) PE PM<sub>2.5</sub> samples were collected in two major southwestern African cities (Figure 1) during the dry season (from January 6<sup>th</sup> to 11<sup>th</sup>) and wet season (from July 5<sup>th</sup> 225 to 10<sup>th</sup>) in, 2016 in two major southwestern African cities mentioned above (Figure 1). PE 226 227 PM<sub>2.5</sub> sampling was conducted during for three consecutive days with the same type participants synchronously, using the PEM (Personal Environmental Monitor) sampling 228 devices with SKC pump (SKC Inc., USA) at a flow rate of 10 liter per minute (lpm). The 229 230 PEM PM<sub>2.5</sub> sampling head worn in the breathing zone of participants in this study. PM<sub>2.5</sub> Samples-were collected on 37 mm pre-baked quartz filters (800-°C, 3 hours, QM/A®, 231 232 Whatman Inc., UK). A total of 72 personal exposurePE samples, including 24 samples (12 233 pairs of diurnal samples, the same as thereafter daytime + 12 nighttime samples) for women 234 at DF, 24 (12 + 12 pairs) for students at WB and 24 (12+12 pairs) for drivers at MT, were collected in this study. Moreover, 12 PE PM<sub>2.5</sub> field blanks (one field blank for each 235 236 participant in one season, collected on the second day of the three consecutive sampling days) 237 were sampled obtained in this study as well.

238 In order to verify the comparability of personal exposure PE samples and data caused by not identical sampling devices, 10 pairs of PM<sub>2.5</sub> samples were synchronously collected by 239 240 two sets of actual PEMs with SKC pumps. The comparison results led showto- a significant correlation between the PM<sub>2.5</sub> mass concentrations obtained from two sampling devices 241 (y=0.986x+0.189,  $R^2$ =0.974, P<0.0001). Identical membrane type (quartz fiber) and 242 243 analytical treatments were used applied in this study. After sampling, the filter samples were 244 placed in Petri dishes, sealed with parafilm and stored in a freezer at -20-°C freezer to prevent loss of mass through volatilization prior to analysis. Blank values from blank filter samples 245 were used to account for any artifacts caused by gas absorption and subtract the background 246 PM<sub>2.5</sub> and chemical compositions concentrations in this area. 247

We report t<u>T</u>he meteorological observations during the dry (December 2015 to March 249 2016) and wet (April to July 2016) seasons at the sampling <u>placessites were shown</u> in Table 1. 250 <u>The Meme</u>teorological data <u>are-were</u> retrieved from the NOAA Global Surface Summary of 251 the Day I (GSOD) at the airports of each cities, namely Felix Houphouet Boigny Airport 252 (Abidjan) and Cardinal Bernadin Gantin International Airport (Benin). <u>We give tT</u>he daily average air temperature, wind speed and rainfall accumulation <u>are summarized</u> in Table 1 <u>as</u>
well.

255

# 256 2.3. *PM*<sub>2.5</sub> gravimetric and chemical analysis

257 PE PM<sub>2.5</sub> filter samples were analyzed gravimetrically for mass concentrations with a 258 high-precision electronic microbalance (Sartorius MC21S, Germany) at Laboratoire 259 d'Aérologie (Toulouse, France) before and after sampling in the weighing room after 260 equilibration at 20-23-°C and the RH of 35%-45% for <u>at least</u> 24\_-hour. The absolute errors 261 between replicate weights were less than 0.015 mg for blank filters and 0.020 mg for sampled 262 filters.

Total carbon (TC) was determined on 0.5 cm<sup>2</sup> punch-out of the filters by a carbon 263 analyzer (Ströhlein Coulomat 702C, Germany) at the Observatoire Midi-Pyrenees (OMP, 264 Toulouse, France). The quartz filter samples were subjected to a thermal pretreatment step 265 266 (kept at 60°C for 20 mins) in order to remove the volatile organic compounds (VOCs) and 267 eliminate water vapor. Subsequently, the filters were combusted at 1200°C under O<sub>2</sub> and detected as CO<sub>2</sub> in the carbon analyzer. Elemental carbon (EC) was obtained using a two-step 268 269 thermal method: step 1 consisted in a pre-combustion at 340-°C under O<sub>2</sub> for 2 h in order to 270 remove organic carbon (OC); step 2 consisted in the oxidation of the remaining EC at 1200 °C under O<sub>2</sub>. The difference (TC-EC) yielded OC concentration (Benchrif et al., 2018; 271 272 Cachier et al., 2005).

273 To extract the water-soluble inorganic ions from the quartz filters, a quarter  $\frac{1}{4}$  of the 274 filter was placed in a separate 15 mL vials containing 10 mL distilled-deionized water (18.2  $M\Omega$  resistivity). The vials were placed in an ultrasonic water bath and shaken with a 275 276 mechanical shaker for 45 min (15 min  $\times$  3 times) to extract the ions. The extracts were filtered through 0.45 µm pore size microporous membranes. After that, three anions (Cl<sup>-</sup>, 277  $NO_3^-$  and  $SO_4^{2-}$ ) and five cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) in aqueous extracts of the 278 filters were determined by an ion chromatograph (IC) analyzer (Dionex-600, Dionex, 279 280 Sunnyvale, CA, USA), which was is equipped with an AS11-HC anion column and a CS12 281 cation column for separation. Details of the IC measurement method are-are described in 282 Bahino et al. (2018) and Cachier et al. (2005).

283 One element<u>: of</u> Fe (representing earth's crust emission) and ten heavy metals (i.e., :-V, 284 Cr, Mn, Co, Ni, Cu, Zn, Sb, Ba and Pb) in PE PM<sub>2.5</sub> samples were determined by Energy 285 Dispersive X-Ray Fluorescence (ED-XRF) spectrometry (the PANalytical Epsilon 5 ED-XRF 286 analyzer, the Netherlands) on-with <u>1/4a quarter</u> of filters in this study as well. The relative errors for all measured elements were < 6% between the NIST Standard Reference Material</li>
(SRM) 2783 and our ED-XRF results, which is well within the required range of error,
demonstrating the accuracy of ED-XRFmethod. Replicate analysis of one quartz-fiber filter
sample (five times) yielded an analytical precision between 5.2%-13.9%. Details of the ED-XRF measurements are are showndescribed in Brouwer (2003) and Xu et al. (2012).

 $0.1-1.0 \text{ cm}^2$  punch-outs a Aliquot punches (0.1-1.0 cm<sup>2</sup>)s from the quartz filters were 292 293 used to quantify the organic compounds, including polycyclic aromatic hydrocarbons (PAHs), 294 phthalate esters (PAEs) and hopanes (see the specific details of target organic species and their 295 abbreviations measured in this study shown in Table 5) by an in-injection port thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) method. The approach has 296 the advantages of shorter sample preparation time (< 1 min), minimizing of contaminations 297 from solvent impurities, and higher sensitivity, compared with the traditional solvent 298 extraction-GC/MS method. The detail analytical procedures have been reported in previous 299 300 publications (Ho and Yu, 2004; Ho et al., 2008, 2011; Xu et al., 2013, 2016a). The results of 301 the blank analyses showed only trace contamination levels (<-5.0%) of PE PM<sub>2.5</sub> samples 302 concentrations.

303

# 304 *2.4. Health risk assessment model*

305 <u>A number of As we known, hh</u>eavy metals and toxic organic species are associated 306 with negative personal exposure PE health effects (Škrbic et al., 2016; Val et al., 2013; Wang 307 et al., 2017a; Xu et al., 2018a). In this study, four heavy metals (Mn, Ni, Zn and Pb) and all 308 measured PAHs and PAEs species in PE PM<sub>2.5</sub> were selected to determine the personal 309 exposurePE inhalation health risks (Xu et al., 2018a). The heavy metals non-carcinogenic 310 risks and toxic organics carcinogenic and non-carcinogenic health risks of PM<sub>2.5</sub> via 311 inhalation chemical species were calculated according to the U.S. EPA health risk assessment model (USEPA, 2004, 2011). The average daily exposure dose (D) via inhalation was 312 estimated to assess the risk by the equations (1) as follows: 313

$$\mathbf{D} = (\mathbf{C} \times \mathbf{R} \times \mathbf{EF} \times \mathbf{ED} \times cf) / (\mathbf{BW} \times \mathbf{AT})$$
(1)

the definitions and recommended values of parameters are shown in Table 2.

A hazard quotient (HQ) for non-cancer risk of heavy metals in PE PM<sub>2.5</sub> samples can be
 obtained from equation (2):

318

$$HQ = D_{/RfD}$$
(2)

the threshold value of RfD indicates whether there is an adverse health effect during a certain
 period. Hazard index (HI) can be obtained by summing up the individual HQ to estimate the

total non-cancer risks. If the HI < 1, then non-carcinogenic effect is impossible; HI  $\geq$  1, adverse health effect might likely appear (Hu et al., 2012).

The incremental lifetime cancer risk (ILCR) of PAHs and PAEs in <u>personal exposurePE</u> PM<sub>2.5</sub> samples can be calculated by multiplying the cancer slope factor (CSF) of PAHs and PAEs with D as equation (3):

ILCR =  $D_{-} \times CSF$ 

(3)

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for cancer risk, the value of  $1 \times 10^{-6}$  is an internationally accepted as the precautionary or threshold value above which the risk is unacceptable (Jedrychowski et al., 2015).

It is worth noting that, among the nineteen PAHs, BaP has been used as an indicator of PAHs carcinogenicity (Wang et al., 2006). The carcinogenic health risk of PAH species can be assessed by [BaP]<sub>eq</sub> instead (Yassaa et al., 2001) by equation (4):

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### $\Sigma[BaP]_{eq} = \Sigma (C_i \times TEF_i)$ (4)

<u>Additionally, Besides</u>, the carcinogenic risk for PAEs was assessed by DEHP, which is identified as a possible carcinogen to humans by the International Agency for Research on Cancer (IARC) (IARC, 1982; Li et al., 2016). The definitions and recommended values of the parameters in equations (2-4) are also shown in Table 2 and Table 3.

# 338 2.5. *Questionnaire and time-activity diary*

339 Questionnaire (Supporting information (SI)Appendix A-C) and time-activity diary 340 (SIAppendix D) were collected from each participant during the sampling period, respectively, to fully grasp the basic information, potential personal exposurepotential 341 342 exposure PE sources and activities of participants. In the questionnaire, personal information, family status, dermatological, asthma symptoms, medical history, current health status and so 343 344 on were first asked from each participant. Besides, the questions for women include: (1) living habits and environment (past and current living conditions, general living habits, 345 cooking habits and domestic fuel type/usage); (2) work environment and travel habits 346 (workplace, work nature, working hourtime and daily travel mode/time); and (3) affected by 347 348 the burning of domestic solid fuels and roasting meat. The questions for students include: (1) living habits and environment (past and current living conditions, general living habits, 349 350 participation in household duties, the family cooking habits and domestic fuel type/usage; distance from home to WB site); (2) school environment and travel habits (school location 351 352 and related environment and daily travel mode/time); and (3) affected by the burning of waste and household air pollution sources. The questions for drivers include: (1) living habits and 353 environment (past and current living environments, general living habits, participation in 354

household duties, the family cooking habits and domestic fuel type/usage); (2) working environment and travel habits (motorcycle power type, driving conditions, working time <u>hours</u> and daily travel mode/time); and (3) affected by the motorcycle emission and household air pollution sources.

The time-activity diaries requested the participants to mark on half an hour basis (sleeping time excluded) to assess each microenvironment time spending and detailed activities.

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### 363 **3. Results and discussion**

364 *3.1. Personal exposure to PM*<sub>2.5</sub> and its chemical compositions

365 *3.1.1. PE PM*<sub>2.5</sub> mass concentration

The average personal exposure PE to  $PM_{2.5}$  (PE  $PM_{2.5}$ ) mass concentrations were 366  $331.7\pm190.7$ ,  $356.9\pm71.9$  and  $242.8\pm67.6 \ \mu g \ m^{-3}$  for women at Domestic Fires (DF), students 367 at Waste Burning (WB) and drivers at Motorcycle Traffic (MT), respectively, in this study in 368 2016 in Southern West Africa (SWAsWA) in this study. Among these three types of subjects, 369 the average concentrations of PE  $PM_{2.5}$  for women and students were quite similar, ~40% 370 371 higher than that of the drivers. PE PM<sub>2.5</sub> ranged from 106.2  $\mu$ g m<sup>-3</sup> (nighttime in dry season, January 7<sup>th</sup>) to 1164.7 µg m<sup>-3</sup> (daytime in wet season, July 5<sup>th</sup>) for women at DF; from 37.8 µg 372 m<sup>-3</sup> (nighttime in wet season, July 8<sup>th</sup>) to 1137.0 µg m<sup>-3</sup> (daytime in dry season, January 11<sup>th</sup>) 373 for students at WB; and from 65.0 µg m<sup>-3</sup> (nighttime in wet season, July 11<sup>th</sup>) to 648.5 µg m<sup>-3</sup> 374 (daytime in dry season, January 15<sup>th</sup>) for drivers at MT. The ranges and standard deviations 375 376 of PE PM<sub>2.5</sub> concentrations were extremely large, especially for women, because there are the direct combustion sources were close to around the participants women workers in this study. 377 378 Moreover, tThe variations of personal physical s-activities and intensities of air pollution 379 sources potentially intensities lead to a drastic fluctuation for PE PM<sub>2.5</sub>.

The average mass concentrations of PE PM<sub>2.5</sub> were 358.8±100.5, 494.3±15.8 and 380 335.1±72.1 µg m<sup>-3</sup> in dry season (January), and 304.6±284.5, 219.5±71.3 and 150.6±10.4 µg 381 m<sup>-3</sup> in wet season (July) for women at DF, students at WB and drivers at MT, respectively 382 (Table 4). Compared to dry season, the reduction rate of PE PM<sub>2.5</sub> for women at DF in wet 383 384 season was approximately 15%, while the sharp reductions by more than 50% were observed for students and drivers at a similar level by more than 50%. PE PM<sub>2.5</sub> concentrations 385 reducing could be attributed to the occurrence of increased levels of rainfall in wet season in 386 387 SWAsWA (Table 1), which causes the large reduction of road dust exposed to drivers and limits the garbage spontaneous combustion significantly around students. Moreover, large 388

389 scale transport of mineral dust and combustion aerosols emitted by savannah wild fires 390 contribute significantly to the aerosol load during the dry season (Djossou et al., 2018), which 391 is more important at WB and MT than at DF (women worked in the crowded community 392 environment).

393 The PE PM<sub>2.5</sub> mass concentrations in the daytime were much higher than those at nightnighttime, no matter in both dry or wet seasons (Table 4 and Figure 3). The 12-hour 394 395 averaged PE PM<sub>2.5</sub> concentrations showed day/night (D/N) ratios of 3.4 (3.8 in dry season 396 and 3.1 in wet season, the same sequence thereafter), 2.7 (2.8 and 2.5) and 2.4 (1.5 and 3.3) 397 for women at DF, students at WB and drivers at MT, respectively. Intensive human activities 398 during the daytime, such as solid fuel combustion, waste combustion or motor vehicle 399 emission around influenced the different group subjects, enhancelevating e-the exposure levels-of\_of\_PM<sub>2.5</sub>-exposure in the daytime. For exampleIn the same case, lower PE\_PM<sub>2.5</sub> 400 personal exposure level for students at night at WB in the nighttime can be explained also by 401 402 the fact that the participants in this study usually spentd most of their time indoors at night 403 with limited physical activity, leading them to be able to stay away a distance and/or shelter 404 from obvious emission sources (e.g., waste combustion) outdoors. Besides, Moreover, big 405 large fluctuations of D/N ratios for drivers were observed, with lower valueaverage in dry 406 season and but higher in wet season. Relatively lower D/N ratio probably attributes to nighttime driving (18:30 to 21:00 UTC) after dinner, which enhances their PM<sub>2.5</sub> exposed 407 408 levels from vehicle emission and road dust. Much Wet season higher D/N ratios in wet season 409 attribute to the increase in precipitation in wet season in Cotonou (Table 1), especially 410 duringat nightime (Sealy et al., 2003)., This leadsing to the lower PE PM<sub>2.5</sub> exposure for drivers at night after aerosol scavenging. and the lessShorter driving time in wet season is 411 another explanation for the phenomenon, because of the unfavorable weather occasionally 412 413 (e.g., rain and storm).

The 5-h PM<sub>2.5</sub> average personal exposure concentration was 1574  $\mu$ g m<sup>-3</sup> (±287, n = 3) for 414 open wood fires in households in the Njombe district of Tanzania (Titcombe and Simcik, 415 416 2011), and was comparable to the highest 12-h exposure level to PM<sub>2.5</sub> for women at DF site in this study (1164.7  $\mu$ g m<sup>-3</sup>, daytime in wet season, July 5<sup>th</sup>), and was 4.7 times of the daily 417 average PE PM<sub>2.5</sub> concentration in dry and wet seasons (331.7±190.7 µg m<sup>-3</sup>). Besides, the 418 419 lower D/N ratio probably attributes to the nighttime driving (18:30 to 21:00 UTC), when the drivers still exposed to vehicle emission and road dust. Student (10-17 years old) PM2.5 420 exposures ranged from less than 10  $\mu$ g m<sup>-3</sup> to more than 150  $\mu$ g m<sup>-3</sup> (mean 56  $\mu$ g m<sup>-3</sup>) in four 421 422 neighborhoods in Accra, Ghana (Arku et al., 2014), much lower than that for students at WB

423 site  $(356.9\pm71.9 \ \mu g \ m^{-3})$ . It can be seen that the high exposure of students in this study is 424 likely to be related to the waste burning emissions, while there was no obvious strong PM<sub>2.5</sub> 425 emission source in the study of Arku et al. (2014).

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427 T—The average PE  $PM_{2.5}$  levels are compared to the weekly ambient  $PM_{2.5}$ 428 concentrations (Djossou et al., 2018) obtained in the same area during and similar sampling 429 period. The average PE PM<sub>2.5</sub> were 3.0 and 2.0 times of the ambient values found at DF, and 430 6.1 and 8.8 times at MT in dry and wet seasons, respectively. The highest PE PM<sub>2.5</sub> to 431 ambient (A) (PE/A) ratios were found at WB, i.e., 10.3 in dry and 10.5 in wet seasons. Such 432 large PE/A ratios are probably due to the impact of waste combustion affected on the respiratory exposure of residents in this area, especially on children; on the other hand, high 433 434 PE/A ratios can be attributed to the fact that WB site is located in the lowest living quality 435 poorest-region of Abidjan, where the extremely-simplest\_stove and non-qualified wood as 436 fuel used in house at home (Figure S1d). These, leading to an extremely very high personal 437 PE PM<sub>2.5</sub> exposure level indoors during the cooking time in this area (especially for student B 438 who was in charge of cooking, at home sometimes recorded in the activity logging and 439 questionnaire). Meanwhile, the ambient PM2.5 sampling equipment at WB was neither fixed very close to (blue marker in Figure 1C) nor in located at the downwind direction of the 440 441 landfill (Djossou et al., 2018), that which cause direct suggests the huge differences between 442 the ambient and personal exposurePE PM<sub>2.5</sub> concentrations.

443 Moreover, we also compare the daytime PE and ambient PM2.5 mass concentrations with 444 theon daytime ambient PM2.5, which collected in the same area and exactly the same 445 sampling dates dates as the personal exposure sampling period were also compared. The average women daytime women-PE PM<sub>2.5</sub> for women were 3.7 and 1.2 times of the ambient 446 447 PM<sub>2.5</sub> at DF in dry and wet seasons, respectively, consistent , which was similar as with -the finding from the weekly comparatison with the weekly PM2.5-mentioned above. But However, 448 449 for the students at WB and drivers at MT, the PE/A ratios were both much lower smaller than those compared with the weekly ambient PM2.5, with averages of 5.1 and 7.0 for the students 450 451 at WB and, 1.9 and 3.3 for the drivers at MT in dry and wet seasons, respectively. The PE/A 452 ratios for students were also showedhad the highest values, which is consistent with the 453 results found earlier.- In addition, tThe PE/A ratios observed all above 1.0 and the greatlarge 454 variability of PM<sub>2.5</sub> mass concentrations between personal exposurePE and ambient 455 concentrations samples imply that fix-point sampling is likely to underestimate the PE PM<sub>2.5</sub> 456 personal exposure PE and consequent human health hazards, The results and further

457 <u>ceonfirm the importance of portative PE PM<sub>2.5</sub> sampling for to PM<sub>2.5</sub>-health risk assessment 458 again.</u>

459  $3.1.2. PE PM_{2.5}$  chemical compositions

460 Table 4 summarizes the average concentrations of PE PM<sub>2.5</sub> chemical compositions, 461 including carbon fractions (OC and EC), water-soluble inorganic ions and several-target heavy metals. Total carbon (TC) hadwas the highest composition was the most important 462 chemical species in PE PM<sub>2.5</sub>, accounting for 24.4%±4.5%, 16.6%±2.0% and 17.8%±4.9% of 463 464 PE PM<sub>2.5</sub>-mass forof women, students and drivers, respectively. High level of OC values 465 proves suggest the strong contribution of combustion sources to PE PM<sub>2.5</sub> in SWAsWA in this study (Djossou et al., 2018; Ouafo-Leumbe et al., 2017). The OC and EC concentrations 466 varied significantly, ranging from 28.3 to 460.0, 8.0 to 189.9 and 14.7 to 65.1 µg m<sup>-3</sup> for OC 467 and 1.5 to 31.1, 0.8 to 35.1 and 1.9 to 18.2 µg m<sup>-3</sup> for EC for the women, students and drivers, 468 reseparatelypectively. The average OC concentration (83.2  $\mu$ g m<sup>-3</sup>) and percentage 469 composition (24.4%) in women PE PM<sub>2.5</sub> samples were the highest among the three types of 470 471 exposed PE participants, due to their close-direct contact with the ignition, and the direct close 472 to burning of the solid fuels (wood in this study) burning and meat roasting meat at the 473 workplace, and alsoeven their own residential unitscooking at home, etc. However, the EC 474 concentrations (8.4-10.5  $\mu$ g m<sup>-3</sup>) and proportions compositions (3.0-3.5%) were very elose betweensimilar among for these three different PE groupstargets were similar (8.4-10.5 µg m<sup>-</sup> 475 <sup>3</sup>-and 3.0% 3.5%), representing meaning that EC is was less affected by human activities 476 477 related to combustion sources in this study.

478 The OC and to EC ratio (OC/EC) has been used to determine emission and 479 transformation characteristics of carbonaceous aerosols (Cao et al., 2008). The OC/EC 480 averaged 9.9±5.3 for women at DF, 6.1±0.7 for students at WB, and 5.8±2.7 for drivers at MT. 481 The pPrevious studies (Cachier et al., 1989; Cao et al., 2005a; Cao et al., 2008; Li et al., 2009; Tian et al., 2017; Watson et al., 2001) suggestedsummarized that average OC/EC 482 characterizes 1.1 as motor vehicle exhaust, 2.7 as coal combustion and 9.0 as biomass 483 484 burning forrom their source samples (i.e., fresh emissions/plumes) The previous studies (Cao et al., 2008; Li et al., 2009; Tian et al., 2017) suggested that average OC/EC characterizes 1.1 485 as motor vehicle exhaust, 2.7 as coal combustion and 9.0 as biomass burning. In present study, 486 The OC/EC in the present study points suggests out that biomass burning emission was was 487 488 the main contributor to PE carbonaceous aerosols for women at DF, while and the mixed 489 emissions from of biomass and coal burning, even or/and motor vehicle exhaust were 490 dominant ted the carbonaceous aerosol sources for students at WB and drivers at MT. The

491 OC/EC was almost always mostly higher duringin wet season than dry season, which 492 mayascribed to be related to the fact that the fact that the higher RHrelative humidity in wet 493 season favors the formation of secondary organic carbon (SOC) (Huang et al., 2014). 494 Drivers' The daytime OC/EC for drivers' PE samples shows were relatively low (an average: 495 of 3.7) and constant stable ratios inbetween wet and dry seasons, indicating promising that motor vehicle exhaust was the most important dominant and stable pollution source to drivers' 496 497 OC and EC in the daytime in, consistent with their working environment of motorcycle drivers in this study. PEersonal exposure of women displays the higher (an average of: 13.9) 498 499 and more scattered OC/EC than those collected from students and drivers in wet season 500 (Figure 4). This was induced by , resulting from the particularly high and dramatic changes in 501 individual exposure to obvious carbonaceous aerosol sources (e.g., wood burning and grilling). 502

503 In With the data shown in <u>a previous study of Djossou et al.</u> (2018), the <u>about OC/EC at</u> ambient (A) environment, PE OC/EC for the participants in personal exposure samples were 504 505 about ~1.2 and 2.5 times of the ambient valuesOC/EC in dry and wet seasons for women at 506 DF, 1.7 and 2.8 times for students at WB, and 1.1 and 2.0 times for drivers at MT. Therefore, theSuch higher OC/EC values in personal exposurePE samples can be resulted from some 507 508 specific individual's activities and potentially contamination ated microenvironments (Crist et 509 al., 2008; Meng et al., 2009). In addition, From the results we can also see that the influences 510 of precipitation and other meteorological factors on OC/EC in ambient samples OC/EC of the 511 ambient samples wereare less than those on PE personal exposure samples (i.e., Ddry season 512 OC/EC was more comparable between the ambient and PEpersonal exposure samples in this 513 study).

The average concentrations of total measured-quantified water-soluble inorganic ions 514 were 23.6 $\pm$ 12.8, 35.5 $\pm$ 18.3 and 22.7 $\pm$ 5.0 µg m<sup>-3</sup> for women at DF, students at WB and drivers 515 at MT, accounting for  $8.5\%\pm1.0\%$ ,  $12.1\%\pm2.7\%$  and  $11.9\%\pm0.4\%$  of PE PM<sub>2.5</sub> masses, 516 respectively. Unlike Dissimilar with of the ion compositions in heavy polluted cities inof 517 518 China  $(SO_4^{2-}, NO_3^{-} \text{ and } NH_4^{+} \text{ were the most abundant ions in ambient } O_2^{-}PM_{2.5}$ 519 accounting for 50%-90% of quantified measured ions and ~30% of PM<sub>2.5</sub> masses) (Xu et al., 2016b, 2018b; Zhang et al., 2013), Ca<sup>2+</sup>, a marker of fugitive dust, was the most abundant ion, 520 accounting for ~28% (in a range from from 25.3% to 29.3%) of total quantified ions in this 521 study, following by Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and K<sup>+</sup> for women at DF, Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> for students at WB, 522 and  $SO_4^{2-}$ ,  $Na^+$  and  $NO_3^-$  for drivers at MT. The profiles It can thus indicate be seen that the 523 particle resuspension by personal activities is-was the main contributor to the PE PM<sub>2.5</sub> in 524

525 SWAsWA (Chen et al., 2017; Xu et al., 2015). The day and nightdiurnal -variations of on  $Ca^{2+}$  contribution composition of  $Ca^{2+}$  to total ions (i.e., daytime=30.6% and 526 nighttime=22.8%) also illustrate this conclusion (i.e., daytime=30.6% and nighttime=22.8%). 527 Moreover, SO<sub>4</sub><sup>2-</sup> forms primarily through atmospheric oxidation of SO<sub>2</sub> emitted mainly from 528 coal and diesel combustions (Seinfeld and Pandis, 2006;, Xu et al., 2016b). As the second 529 most enriched ion, the average proportion of  $SO_4^{2-}$  was 17.7%, which implies that 530 purification of raw coal and diesel (Wang et al., 2013) canshould be applied inin this area 531 532 forto lead to lowering sulfur emissions and therefore decreasing decrease the PEpersonal exposure to  $SO_4^{2-}$  in PM<sub>2.5</sub>. The Drivers'  $SO_4^{2-}$  exposure levels for the drivers were 33% and 533 40% higher than the women and students respectively, indirect which may indirectly 534 indicatinge that the emission of SO<sub>2</sub>  $SO_4^2$ -precursor  $SO_2$ -might beis higher in Cotonou or 535 targeted drivers the participants -affected by vehicle emissions are exposed to higher SO<sub>2</sub> or 536  $SO_4^{2^-}$ , especially from the diesel vehicle emissionss. 537

Generally, Na<sup>+</sup> and Cl<sup>-</sup> ranked the were the third and fourth ranked abundant ions in the 538 PE samples. The sampling sites in SWAsWA cities in this study are all close to the sea and 539 540 are-were affected by sea salt particles-strongly. It's is also worth noting that biomass burning 541 marker- $K^+$  (Kang et al., 2004; Zhang et al., 2014b) displayeds a high absolute average concentration of (3.4 µg m<sup>-3</sup>) and composition percentage (of 14.5%) in women' PE PM<sub>2.5</sub> 542 samples, confirming their distinct exposure from biomass burning during the roasting at the 543 544 workplace. As we know To the best knowledge,  $NO_3^-$  derives from  $NO_x$  emitted mainly from motor vehicle exhaust (especially gasoline vehicle), industry and power plants (Seinfeld and 545 Pandis, 2006; Xu et al., 2016b). Additional consideration here: includes that the industry is not 546 547 well-developed in this area (i.e., much less industry in Cotonou than Abidjan) and thus is not 548 the main contributor to source of PM<sub>2.5</sub> (Ouafo-Leumbe et al., 2017). In comparison with the 549 findings for from the other two sites, It suggests that motor vehicle emission obviously contributed to drivers' exposure PE concentrationsobviously in this study, comparing with 550 women at DF and students at WB, consistent with the conclusion for<del>about</del> SO<sub>4</sub><sup>2-</sup> as discussed 551 above. 552

The concentrations of 10 targeted heavy metals, including V, Cr, Mn, Co, Ni, Cu, Zn, Sb, Ba and Pb, <u>can be foundare also shown</u> in Table 4. The total concentrations of these 10 elements were  $1.4\pm0.3$ ,  $3.9\pm6.5$  and  $0.8\pm0.2 \ \mu g \ m^{-3}$  for women at DF, students at WB and drivers at MT-during the sampling period, accounting for  $0.7\%\pm0.4\%$ ,  $1.0\%\pm1.2\%$  and  $0.4\%\pm0.1\%$  of <u>the PE PM<sub>2.515</sub> respectively</u>correspondingly. The <u>PE</u> heavy metal for the exposed concentration of students was 1.8 and 3.9 times higher than of -those for the women 559 and drivers, resulting mainly due to from the emissions from garbage combustion at landfill 560 which emit extremely high level of heavy metals as we known (Wang et al., 2017b). The D/N 561 ratios ranged from 0.8 to 2.1 for women and drivers, but averaged 4.0 in dry season and 7.0 562 in dry and wet seasons respectively -for students. There is can be explained by the are two 563 reasons:- for this phenomenon: tThe first is that reason could be related with there were intense physical activities from the students and strong disturbances from landfill workers in 564 565 the daytime at landfill; Another the second reason is that spontaneous combustion of waste 566 occurring s-frequently during the day due to , because of less precipitation and higher 567 ambientair temperature in the at-daytime. Ba, Zn and Mn were found to be the dominant heavy metals, <u>accounting of</u> ~73% of <u>total quantified</u> elemental concentration in all samples. 568 569 It is worth mentioning that Ba tooookk up a decisive advantage over other elements, accounting having a contribution of >50% for for more than half of all the elements for 570 571 students. Because Balt is usually added to in rubber and plastic products to improve acid and 572 alkali resistance. SHowever, , at the same time thesesuch products wereare main fractions are 573 the main components of the garbage at landfill in this area (Feng et al., 2006). Zn and Mn 574 ranked the first and second **PEpersonal exposure elements** places for drivers at MT, which are mainly derived from the motor oil additive, tyre wear and brake pads worn (Zhao and Hopke, 575 576 2006).

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## 3.2. Mass balance of personal exposure to PM<sub>2.5</sub>

579 Calculation of mass balance for of the PE PM<sub>2.5</sub> is an effective method to figure out the 580 principal components in PM<sub>2.5</sub> and for itsdistinguish the -pollution sources discrimination 581 (Gokhale et al., 2008). PE PM<sub>2.5</sub> mass in this study can be classified into six parts: organic matter (OM), EC, water-soluble inorganic ions, geological material (GM), heavy metals and 582 583 unknown-unresolved partfraction (Figure 5). The first five main resolved partsfractions can 584 explain 78.3%% to 90.6% of total PE PM<sub>2.5</sub> mass concentrations in this study. Unresolved fraction Unknown part may include water and other undetected substances in PE PM2.5. For 585 OM, since there is no the full chemical organic composition -profiles composition of the 586 587 aerosol organic fraction for the PE PM<sub>2.5</sub> is largely unknown, a conversion factor 1.4 (1.4 588 corrects the organic carbon mass for other constituent associated with the organic carbon 589 molecule) is generally used (Turpin and Lim, 2001) to shift-quantify OC to-OM by the equation (5): 590

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$$OM = 1.4 \times OC \tag{5}$$

592 based on the equation (5), OM accounted for  $34.1\% \pm 6.3\%$ ,  $23.3\% \pm 2.8\%$  and  $24.9\% \pm 6.9\%$  of

the PE PM<sub>2.5</sub> mass for women at DF, students at WB and drivers at MT, respectively. The
 results show , indicating that there are distinct sources to for PE PM<sub>2.5</sub>-OC for women at DF.
 According to the information gathering from the questionnaires, the combustion sources,
 such as roasting meat/peanuts and burning wood, should beare the major contributors \_ the
 sources toto PE -OC for for women personalwomen in this study exposure samples, \_ which
 consistent with the results mentioned above.

In addition, Fe has been widely used to estimate the upper limit of GM in previous studies (Taylor and McLennan, 1985). Fe constitutes about ~4.0% of the Earth's crust in dust of the earth's crust (Cao et al., 2005Cao et al., 2005b; Hao et al., 2007; Kabata-Pendias and Mukherjee, 2007; Sun et al., 2014; Wu et al., 2012; Xu et al., 2016b). The amount of GM is calculated by equation (6):

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# $GM = (1/4.0\%) \times Fe$ (6)

605 based on this equation, iIt is found that GM contributed 35.8%±2.1%, 46.0%±3.7% and 42.4%±4.7% of PE PM<sub>2.5</sub> mass concentrations for women at DF, students at WB and drivers 606 607 at MT, respectively. Fugitive dusts, including road dust resuspension from disturbance of 608 motor vehicles and human activitiess, construction dust from uncovered construction sites, 609 and the dusts generated related to-from burning activities, could be the domination-inant 610 sources to PE PM<sub>2.5</sub> in this study. OM and GM showed the almost identical similar proportions (34.1% and 35.8%, respectively) of PE PM<sub>2.5</sub> mass for women at DF. The 611 612 fractions of GM in PE samples percentages for students and drivers were approximately 10% and 7% higher than that for women. Therefore, Therefore, ttThe fugitive dust related 613 614 contributions wasis are the most important sources for PE PM<sub>2.5</sub> in this less developed area, shown by meaning that there are nearly half 50% PE PM<sub>2.5</sub>-contribution sources offor 615 616 students and drivers, attributable to human physical activities and a large amount of covered 617 land. As mentioned above, iIt is surprising to note that the secondary formed ions (i.e.,  $SO_4^{2^-}$ ,  $NO_3^-$  and  $NH_4^+)_7$  and the -even-total measured-quantified water-soluble inorganic ions show 618 wereare the in exceedingly low proportions in to PE PM<sub>2.5</sub> for all subjects groups. This 619 reconfirms the limited contribution to PE PM2.5 from secondary ionic formation again ionic 620 621 sources.

From-In Figure 5, evident diurnal distinguishes are can be observed in on the two major chemical compositions of (OM and GM) in this study. We can see that GM exhibiteds the lower proportion at nightime (35.3%) than daytime (47.5%), indicating suggesting its close relationship with human activities. For different seasons, we find the hHigher GM was found for bothall each type of groupsparticipant in dry season, because of the harmattan haze 627 introducedbringing mineral dusts and the lakcke of precipitation increasing road dust resuspension. Moreover, OM showeds the equal or lower proportions in PE PM<sub>2.5</sub>in 628 629 thebetween -at daytime (25.0%) that nighttime (30.0%), relative to which is mainly related 630 with the meteorological parameters (i.e., factor they affected the formation of secondary 631 organic carbonaceous aerosol) and diurnal changes of combustion sources around subjects variations between day and night. There is aAn exception is found that in the last case, i.e., 632 OM proportion at daytime of women PE  $PM_{2.5}$  at daytime (50.8%) was much higher (50.8%) 633 than nighttime (38.2%) in wet season, due to the influences from the damp wood burning at 634 635 the working time. As we know, bBurning biomass fuel with high moisture often results in lower combustion efficiency, longer smoldering period and high air pollutant emissions 636 (Grandesso et al., 2011; Shen et al., 2012, 2013). The emission factor of OC usually increases 637 with the fuel moisture content (Chen et al., 2010; Keita et al., 2018). Therefore, burning the 638 damp wood led to morehigher OC emission than dry wood, in-line with the observation for 639 to-women PE results in this study There is an exception in the last case, i.e., OM-proportion at 640 daytime women PE PM<sub>2.5</sub> was much higher (50.8%) than nighttime (38.2%) in wet season, 641 due to the influence from the damp wood burning at the working time. As we know, the damp 642 643 wood burning emits more smoke (PM) than dry wood (Shen et al., 2013) or change in 644 emission factors (Keita et al., 2018).

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## 4. Fingerprint oOrganic species fingerprint in of personal exposure to PM<sub>2.5</sub>

OIn this section, we use organic fingerprint markers can be used to that indicate specific 647 648 emission sources and to further characterize investigate the sources and detailed characteristics of PE PM2.5-pollutions impacted on for different populations. Unlike PE PM2.5 649 650 mass concentration variations (students > women > drivers), organic fingerprint measured in 651 this study, such as PAHs, PAEs and hopanes (Table 5), show different concentration orders in 652 this study. The average PE concentrations of PM<sub>2.5</sub>-bound PAHs, PAEs and hopanes PE mass concentrations were 54.8±20.3, 986.8±82.2 and 27.9±1.0 ng m<sup>-3</sup>-in this study, respectively, 653 representing showing a high very serious PM<sub>2.5</sub>-organic pollutions in SWAsWA region 654 (Table 5). Dissimilar with the trend on  $PM_{2.5}$  masses (students > women > drivers), the PE to 655 target organic compounds for different groups were varied, -Thewith a descending following 656 657 orders of were-women > students > drivers for PAHs, students > women > drivers for PAEs, and drivers > women > students for hopanes (Table 5 and Figure 6). 658

659 *4.1. PAHs* 

660 The total quantified PAHs concentration (SPAHs) accounted for 0.12%-0.21%% of PE PM<sub>2.5</sub> mass concentration. Benzo[b]fluoranthene (BbF) was the most abundant PAH for 661 662 women at DF, followed by benzo[a]pyrene (BaP) and indeno[1,2,3-cd]pyrene (IcdP). The average **BbF**-concentration of **BbF** (athe maker of low temperature combustion, such as wood 663 burning) was 11.6 $\pm$ 19.2 ng m<sup>-3</sup>, accounting for up to approximately 15.0% of the  $\Sigma$ PAHs for 664 women <u>PE samples (Table 5)</u> (Wang et al., 2006) (Table 5). While tThe most abundant PAH 665 species for students at WB and drivers at MT were IcdP ( $6.4\pm4.5$  ng m<sup>-3</sup>) and 666 benzo[ghi]perylene (BghiP) (6.4±0.5 ng m<sup>-3</sup>), respectively, which indicatinge the 667 contributions from the waste incineration and/or high temperature fuel-combustion of fuel 668 (e.g., gasoline vehicle emission) (Baek et al., 1991; Wang et al., 2006). The average ΣPAHs 669 average concentrations in wet season increased 326% and 52% forof women at DF 670  $(125.4\pm54.8 \text{ ng m}^{-3})$  and drivers at MT  $(44.6\pm10.8 \text{ ng m}^{-3})$  in wet season were 326% and 52% 671 higher than those in dry season (29.4 $\pm$ 5.6 and 29.4 $\pm$ 4.4 ng m<sup>-3</sup> respectively), while the 672  $\Sigma$ PAHs decreased 42%-in wet season (36.8±15.7 ng m<sup>-3</sup>) was reversibly 42% lower than that 673 dry season (62.9±45.0 ng m<sup>-3</sup>) <del>compared with dry season (62.9±45.0 ng m<sup>-3</sup>)</del> for students at 674 WB. The dramatic increase in women's-PEexposure to PAHs for women is mainly due to 675 raise the increase inof humidity (moisture content) of in the wood used for grilling meat in 676 677 wet season, promoting more resulting in PAHs formationemission from emissions sharp raising from wood combustion processes (Shen et al., 2013). The restraint of waste 678 679 combustion in wet season is the main factor in the for the decrease-lower of students' exposurePE to PM<sub>2.5</sub>-bound PAHs at landfill, in accordance with seasonal pattern on PE 680 PM<sub>2.5</sub> mass seasonal change pattern. Fanou et al. (2006) measured the PE PAHs 681 concentrations were measured in Cotonou in the previous study (Fanou et al., 2006), the resu 682 and found lt showed that the PAHs level of total PAHs associated with particles ranged from 683 76.21 to 103.23 ng m<sup>-3</sup> for 35 taxi-moto drivers in March 2001. Our values The PAH levels 684 determined in this study for drivers at MT site was 50%-64% lower than their values in 685 Fanou et al. (2006) study, suggesting that the exposure toon PAHs for the motorbike driver 686 exposure to PAHs in this region has been improved has improved. 687

strongly impacted the PE PAHsduring working hours. The average D/N ratios were 1.7 in dry 694 season with the 12-hour average  $\Sigma$ PAHs of 37.4±25.1 ng m<sup>-3</sup> for daytime and 21.4±17.2 ng 695 m<sup>-3</sup> for nighttime and 3.5 in wet season with 195.6±121.9 ng m<sup>-3</sup> for daytime and 55.3±44.3 696 ng m<sup>-3</sup>-for nighttime; 2)-For the sStudents at WB, : nighttime-PE PAHs at night\_time\_were 697 higher in dry season but and lower in wet season compared with daytime levels, with the 698 average D/N ratios of 0.7 and 1.8, respectively. Both of the PAH profiles in the day and night 699 700 were with the featureds with of higher combustion markers of -BbF and benzo[e]pyrene 701 (BeP), and high gasoline vehicle emission markers of dibenzo[a,h]anthracene (-DahA) and BghiP (Baek et al., 1991; Wang et al., 2006). For ; The higher concentrations of combustion 702 markers-BbF and BeP were observed during the day, while the higher concentrations of 703 704 gasoline vehicle emission markers DahA and BghiP were found at night (Baek- et al., 1991; Wang et al., 2006), which was related to the garbage truck for waste transportation from city 705 to the landfill during night. Moreover, we should also note that the impact of garbage truck 706 emission was offset by PM<sub>2.5</sub> wet deposition during the wet season; 3) Dthe drivers at MT, + 707 708 we are surprised to see that the average dry season D/N ratio in dry and wet seasons wereas 0.8 and with the  $\Sigma$ PAHs of 26.3 $\pm$ 7.6 ng m<sup>-3</sup> for daytime and 32.5 $\pm$ 13.8 ng m<sup>-3</sup> for nighttime, 709 710 and the average wet season D/N ratio was 0.3, with 21.9±8.4 ng m<sup>-3</sup> for daytime and  $67.3\pm23.7$  ng m<sup>-3</sup> for nighttime, respectively. The higher PE nighttime  $\Sigma$ PAHs concentrations 711 at nighttime and lower D/N ratios for drivers in this study may be explained by the possibility 712 that there are potential combustion sources (Pfor PAAHs sources) aroundclose to the 713 participants-drivers (e.g., especially sources nearby around the drivers' homes-at-night) in 714 715 Cotonou, Benin at night rather than the motor vehicle exhaust, especially in wet season. This 716 can be deduced by the -(combustion-emission marker of BaP which was the highest PAH 717 species at night in wet season), even though although the drivers exposed to the traffic emissions during the night working time (18:30 to 21:00 UTC). Further studies are thus 718 719 required to confirm the findings and figure out the reasons.

In the study of Titcombe and Simcik (2011), the authors found that the 5-h average total PAH personal exposure concentration was 5040 ng m<sup>-3</sup> ( $\pm$ 909, n = 3) for open wood fires in households in the Njombe district of Tanzania, which was much higher (~65 times) than the women exposure PAHs at DF site in the current research. The highest 12-h exposure PAHs for women at DF site in this study was 469.7 ng m<sup>-3</sup> (daytime in wet season, July 6<sup>th</sup>), approximately one-tenth of the PAHs concentration from open wood fires in Tanzania mentioned above. The large PE PAH concentrations difference between these two studies 727 728 may be influenced by many factors such as wood type, combustion state, stove structure and

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729 Diagnostic ratios of PAHs with similar molecular weights have been widely used in 730 source identification (Tobiszewski and Namiesnik, 2012; Yunker et al., 2002). In our study, 731 the average values of BeP/(BeP+BaP) and IcdP/(IcdP+BghiP) were 0.47 and 0.52 for women 732 at DF, 0.51 and 0.52 for students at WB, and 0.64 and 0.34 for drivers at MT, respectively 733 (Figure 7), showing indicating that the unique impacts on the PE PM<sub>2.5</sub> from of different 734 atmospheric pollution sources on the different type participants are very significant, and that 735 the diagnostic ratios of PAHs can be applied to identify the source of PAHs in PE PM<sub>2.5</sub> 736 effectively. The average BeP/(BeP+BaP) ratios ranged from 0.47 to 0.64, comparable with 737 those reported in Chinese megacities of Guangzhou (0.41-0.72) and Xi'an (0.59-0.73) of China (Li et al., 2005; Xu et al., 2018cb), and but lower than the value measured at reported 738 in Shanghai (all samples >-0.70), China (Feng et al., 2006). This, implies ying the low 739 740 oxidability of the PAHs in the less-developed cities in SWAsWA cities (less developed than 741 Chinese cities). PAHs in drivers' PE samples wereare more prone to aging (i.e., the average 742 ratio was 1.3-1.4 times of those for women and students) because of their -re-suspension 743 ofonto road dusts where PAHs are attached to (i.e., longer residence lifetime) and longer 744 outdoor activity time (i.e., exposure to more sunlight).; and mFore fine and ultra-fine particles-bound PAHs are emitted infrom high-temperature combustion in-from motor 745 746 vehicular engine, which are more easily photochemically oxidized oxidation in the 747 atmosphereir (Baek et al., 1991; Lima et al., 2005). The differences of BeP/(BeP+BaP) ratios 748 in-between dry and wet seasons is arewere not obvious, and without general patternno fixed 749 rule. However, thise ratio exhibiteds a significant day-night changevariation, with the 750 values an average -of 0.59 and a0.49t in theat daytime and 0.49 at nighttime, respectively. It This represents means that more favorable more beneficial meteorological conditions at 751 752 daytime (suchi.e., as more sunlighthigher light intensity) and stronger more individual 753 physical activities y (i.e., time extending for increasing the time of particulate re-suspension) 754 at daytime are more conducive to the aging of PM2.5 and its bounded PAHs. Moreover, IcdP/(BghiP+IcdP) of < 0.2, 0.2-0.5 and > 0.5 were used to identify represent-petrogenic, 755 petroleum combustion and a mix of grass, wood, and coal combustions, respectively (Yunker 756 757 et al., 2002). The quite-relatively low ratios for drivers at MT (0.34) demonstrates indicates that the PAHs in those samples were mainly produced from motor vehicles emissions 758 759 (petroleum combustion), while grass, wood and coal combustions were more dominant for women at DF (0.52) and 760 students at WB (0.52) (Figure 7). However, lcdP/(lcdP+BghiP) ratio dide not in all samples from our study show snot significant seasonal 761 variation.

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### 763 *4.2. Phthalate esters (PAEs)*

764 Phthalate esters are widely used as plasticizers in plastic-materials and can be released 765 into the air from the matrix evaporation and plastics combustion (Gu et al., 2010; Wang et al., 2017a). The personal exposure PE levels of PAEs could be mainly attributed to the usage of 766 767 the household products, painting material-at-home, plastic waste incineration and municipal 768 sewage release (Zhang et al., 2014a). The total concentrations of six phthalate esters (the first six species of PAEs in Table 5i.e., DMP, DEP, DBP, BBP, DEHP and DNOP) and one 769 plasticizer (bis(2-ethylhexyl)adipate, DEHA) (abbreviated as named **SPAEs** for the total all 770 771 these seven species) were 882.0 $\pm$ 193.3, 1380.4 $\pm$ 335.2 and 698.1 $\pm$ 192.4 ng m<sup>-3</sup>, respectively, for women at DF, students at WB and drivers at MT (Table 5). Bis(2-ethylhexyl)phthalate 772 (DEHP) was the most dominant PAE species, followed by di-n-butyl phthalate (DBP) in this 773 study for all the three groups kinds of participants. DEHP is mainly used as a plasticizer for 774 775 manufacture of polyvinyl chloride (PVC); and . And together with DBP, they are the most widely used phthalate estersPAEs globally (Meng et al., 2014). The average DEHP and DBP 776 concentrations were 543.6 and 304.6 ng m<sup>-3</sup>, accounting for up to approximately 55.1% and 777 30.9% of the  $\Sigma$ PAEs, respectively (Figure 6B). The elevated  $\Sigma$ PAEs for students-at WB in 778 this study are mostly result from can be ascribed to the combustion of the plastic products at 779 780 landfill nearby. The Our results in this study are similar to as the previous studies conducted carried out in Xi'an and, Tianjin, -of-China (Kong et al., 2013; Wang et al., 2017a). The 781  $\Sigma$ PAEs ranged from 376.6 to 1074 ng m<sup>-3</sup> in-outdoors, and from 469.2 to 1537 ng m<sup>-3</sup> in 782 student classrooms in Xi'an (Wang et al., 2017a), wherein which DEHP and DBP were also 783 the most abundant PAEs dominant species, with a sum of composition of totally accounting 784 for 68% and 73% of the  $\Sigma$ PAEs in outdoor and indoor environments, respectively. 785

786 The average concentrations of the  $\Sigma$ PAEs for women at DF, students at WB and drivers 787 at MT were comparable in dry season. ButHowever, the average concentrations were 927.2±154.9, 1929.8±340.4 and 594.6±16.6 ng m<sup>-3</sup> in wet season in this study, 1.1, 2.3 and 788 0.7 times of the  $\Sigma$ PAEs values in dry season (Figure 6B). A significant increase in students 789 790 PE ΣPAEs for student at WB in wet season can be attributed to the enhanced PAEs emission in the daytime with high RH (3173.6±1028.3 ng m<sup>-3</sup>), consistent with the findings on PE 791 PM<sub>2.5</sub>-above. Dry and wet seasons led to almosthad similar PAEs profiles with different 792 793 diurnal day and night variations (Figure 6B). The average D/N ratios of the  $\Sigma$ PAEs in dry season 794 demonstrate constant concentrationsshow limited changes, with an average of the values of 1.0, 1.0 and 1.3, respectively, for women, students and drivers, while <u>a much larger variations of 1.1, 4.6 and 0.7 were found</u>
for in-wet season. Noticeably different <u>diurnal</u>-D/N ratios between two seasons observed in
this study for students at WB is interrelated with the human activities (specially related to the
emissions from plastic materials <u>emissions</u>) and the subdued waste <u>spontaneous</u> combustion
resulting led by from diurnal variations of meteorological <u>conditionsparameters</u> (i.e., more
precipitation at night in wet season), which had been mentioned in Section 3.1.1.

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### 802 *4.3. Hopanes*

803 Hopanes have been used as are markers for fossil fuels (e.g., petroleum) combustion, 804 especially for petroleum combustion (Simoneit, 1999; Wang et al., 2009). The average PE to concentration of drivers who exposed to the sum of eight quantified hopanes ( $\Sigma$ hopanes) in 805 this study for the drivers was  $50.9\pm7.9$  ng m<sup>-3</sup>, 2.0 and 2.3 times higher than for the women at 806 DF (17.1 $\pm$ 6.4 ng m<sup>-3</sup>) and students at WB (15.6 $\pm$ 6.1 ng m<sup>-3</sup>) (Table 5), respectively (Table 5), 807 The results -which pindicateroves thean extremely high driver personal respiratory exposure 808 809 contribution from the motor vehicle emissions (e.g., gasoline combustion) for the driversin 810 this study. Then, iIt is important to note that numbers of automobiles areis rapidly increasing 811 in SWAsWA cities, which further exacerbating es-the air pollution and consequencerelated 812 health issuesproblems there. The Shopanes showed the unobvious seasonal variations for three kinds types of PEexposure participants. The ,-i.e., 0.9, 1.8 and 0.7 times Shopane 813 concentrations were observed in dry season were 0.9, 1.8 and 0.7 times of those in wet season. 814 815 Even though Although the  $\Sigma$ hopane concentrations were changeable in this study varied 816 among three sites, their profiles distribution of ion individual species of species hopanes 817 were similar for each participant.  $17\alpha(H)-21\beta(H), 30$ -norhopane ( $\alpha\beta$ -NH) and  $17\alpha(H)-21\beta(H)$ hopane ( $\alpha\beta$ -HH) were two most dominant-abundant hopanes in all PE PM<sub>2.5</sub> samples, with 818 the the average concentrations of 6.0 and 6.5 ng m<sup>-3</sup> and the percentages compositions of 21.4% 819 and 23.3% of the  $\Sigma$ hopanes, respectively (Table 5 and Figure 6C). 820

821 Compared with D/N ratios of the  $\Sigma$ PAHs and  $\Sigma$ PAEs,  $\Sigma$ hopanes exhibited a more stable 822 diurnal trend in this study, which namely, the daytime concentrations were higher in the 823 daytime always greater than nighttime due to, owing to the obvious heavier -traffic emissions 824 during the day. For women at DF, D/N ratio was both 2.0 in dry and wet seasons, with the Σhopanes of 24.0±11.1 and 12.2±5.0 ng m<sup>-3</sup> for daytime and nighttime in dry season, and 825 826 21.4 $\pm$ 17.5 and 10.9 $\pm$ 3.6 ng m<sup>-3</sup> in wet season. Emphasize that The D/N ratio of the  $\Sigma$ hopane for drivers at MT pesentshalthehighestvalue of (115) for all the detected domical species in this study, with the concentrations of 780±19.1 and 44.9±164 ngm<sup>3</sup> for day in early 827 nighttime in dry season, and  $74.2\pm16.3$  and  $6.5\pm1.7$  ng m<sup>-3</sup> in wet season. It is notable We notice that the 828

daytime concentrations <u>for drivers</u> were comparable <u>for drivers</u> between <u>the</u> two seasons, while the nighttime hopanes in wet season were <u>mostly</u> washed away by rainfall<u>mostly</u>, resulting in a very large <u>drop-decline</u> in <u>its</u> concentration<u>s levels</u>.

- Therefore, althoughEven though these organic groupsPAHs, PAEs and hopanes are not 832 833 major fractionsabundant components in PE PM<sub>2.5</sub>, theirse fingerprints organics can more 834 accurately illustrate trace the contributions of air pollution sources to PM2.5. PAHs, PAEs and 835 hopanes The PAHs, PAEs and hopanes are source markers for representing the emissions 836 from combustion activitiessources, plastics emissions and fossil fuel combustion emissions 837 (e.g., from gasoline vehicles), -respectively, are very well matchinged to the potential air 838 pollution sources impacted on around these three PE PM<sub>2.5</sub> for type-participants in this study. 839 The Our results not only indicate that the PM<sub>2.5</sub> respiratory exposure was can be strongly contributed from the environmental pollution sources and individual activities, but also prove 840 841 reliable -the successful application of organic tracers inon characterization of human personal 842 exposure study.
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## 5. Health risk assessment of personal exposure to PM<sub>2.5</sub>

845 Non-cancer risks of four heavy metals (i.e., Mn, Ni, Zn and Pb) and cancer risks of 846 PAHs and PAEs via inhalation exposure way for women at DF, students at WB and drivers at MT are shown in Table 6. In general, the non-carcinogenic risks of Mn and Pb were relatively 847 848 higher than those of Ni and Zn, but still well below behind the international threshold value 849 of (1.0). Among those four metals, Hazard Quotient (HQ) of Pb in wet season for students at WB was the highest  $(2.95 - x \times -10^{-2} E - 0^{-2})$ , which suggests that Pb non-carcinogenic risk to 850 children is more obvioussevere -in that area compared with other participants and metals. 851 852 Except that Ni shows the stable wet season greater non-carcinogenic risk than dry season for 853 all three kinds targets, tThere was no stable consistent changedifference on the risks between 854 in dry and /wet seasons risks of other components, except Ni which showeds much greater value in wet than dry season for both participants. Counting Summing up these four me total 855 of four toxic heavy metalstals, Hazard Index (HI) values for women at DF, students at WB 856 and drivers at MT in dry and wet seasonsparticipants were also are also represented shown in 857 Table 6. The Ddry/wet season ratios of HI were 0.9, 0.5 and 2.3 for women, students and 858 drivers, respectively, -suggesting that the non-cancer risk of personal PEexposure to metals in PM25 for drivers 859 indry season was much significantly higher in dry than that in wet seasons for drivers, owing to a mass of fugitive dust on the road 860 at low RHin dry season. Moreover, the yearly average HI levels were  $8.06 \times 10^{EG}$ ,  $4.13 \times 10^{EG}$  and  $8.68 \times 10^{EG}$  for the 861 862 women at DF, students at WB and drivers at MT, respectively. , showing tThe highest noncancer health risks from of the heavy metals in <u>PE</u>PM<sub>2.5</sub> for students arewere, 5.1 and 4.8
times of those for women and drivers. Overall, Mn, Zn, Ni, Pb and HI were all within below
the safety limit for the all-populations involved in this study, pointing outrepresenting the
negligible non-cancer health risks of heavy metals in <u>PE</u> PM<sub>2.5</sub> in <u>SWAsWA</u> region.

867 InAs shown in Table 6, the ILCRs of PAHs were all beyond exceed the international acceptable level of -1×10<sup>-6</sup> (international acceptable level), suggesting non-negligible cancer 868 risks of PAHs for women at DF, students at WB and drivers at MT whenever either in dry or 869 870 wet season. Meanwhile, the ILCRs of PAEs were all below  $1 \times 10^{-6}$ , well within the safety limit of cancer risk. For all types of target participants, higher cancer risks of PE PM<sub>2.5</sub>-871 872 bound PAHs and PAEs were shownfound in wet season were more likely to cause cancer 873 risks than dry season. ; thus, tThe seasonal changes variations such as increase of , mainly due 874 to increased humidityRH could lead, result in raise of PE an increased personal exposure cancer risks to toxic organics-species in PM2.5. In dry season, the average ILCR values of 875 876 PAHs for women and drivers were comparable for women and drivers, both ~50% lower than 877 those for students, implying the high toxicity originated from the waste burning sources and 878 high sensitivity to juveniles. In wet season, PAHs exhibited the highest ILCR for women at 879 DF, 2.5 and 2.7 times of those for students and drivers, respectively. It can be seen that tThe 880 domestic wood burning and meat grilling meat can trigger nearly ten times the safety limit for 881 <u>PAHs</u> of cancer risks to target women in this study. The cancer risks of PAEs showed the 882 similar pattern-trend in dry and wet seasons (Yang et al., 2011), with the descending order of 883 students at WB-> women at DF-> drivers at MT (Yang et al., 2011). The carcinogenic risks of 884 PAEs for the drivers in traffic environment was the lowest, much lower (45% and 76% lower for in-dry and wet seasons) than those PAEs for students who livedare close to the source of 885 waste incineration. In a word, the ILCRs of PAHs exceeded the threshold value of  $1 \times 10^{-6}$  for 886 887 all the participants, indicating that the carcinogenic PAHs are a threat to the individual's 888 health and subsequently alerting a need of effective emission control in SWAsWA. However, Even though PAEs had show limited low carcinogenic risks in this study, but the 889 effects from of waste burning source to students is needed to should not be ignored pay more 890 891 attention and proper reasonable control measures s-for both PM2.5-bound heavy metals and 892 toxic organic must be established compounds.

In addition, it should be noted that <u>the-both</u> non-cancer and cancer risks could be potentially underestimated since many toxic chemical components <u>could not be detectedwere</u> <u>not involved</u> in this study. <u>It is concluded bB</u> ased on the <u>current</u>, there are <u>data thaa variety</u> <u>oft -emission sources impacted on the different</u> different degrees of impacts on the population groups in sWA region targets present different levels of risks from different chemical species
 in PE PM<sub>2.5</sub> from various air pollution sources. We must pay a<u>A</u>ttention should be paid on to
 heavy metal non-cancer health risks for chemicals via inhalation way, especially Pb and Mn
 for students at WB site as well as PAHs cancer risks for women at DF site in wet season in
 SWAsWA region.

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## 903 **6. Conclusions**

904 We explore the chemical characteristics and health risks of personal exposure to PM<sub>2.5</sub> (PE PM2.5) from different typical anthropogenic air pollution sources in sSouthern West 905 Africa. Our study finds that organic matter and geological material are the almost identical 906 proportions (34.1% and 35.8%) for women at domestic fire site. Nearly half contribution to 907 PE PM<sub>2.5</sub> for students at waste burning site and drivers at motorcycle traffic site comes from 908 fugitive dust. Therefore, the primary source (mainly dust) is the most important source for PE 909 PM<sub>2.5</sub> in these undeveloped regions. The contribution to PE PM<sub>2.5</sub> from heavy metals was 910 higher for students (1.0%), owing to the waste burning emissions strongly, leading to the 911 912 highest non-cancer risk among these three kinds of participants, as well as the extremely high PAEs concentrations (indicator of plastic emissions). PE PM<sub>2.5</sub>-bound PAHs concentration for 913 women at domestic fire site was 1.6 times for students and 2.1 times for drivers, which is 914 mainly attributed to the wood burning and grilling meat activities, resulting in approximately 915 five times higher of international cancer risk safe limit (nearly ten time of threshold value in 916 wet season). Drivers' exposure to hopanes in PE PM<sub>2.5</sub> was 2.0-2.3 times higher than women 917 918 and students, correlating with the elevated traffic emissions on road environment well.

919 This work can be regarded as the first attempt for health assessment in underdeveloped 920 country of Africa at the current condition, even though, although there are some few drawbacks, such as relatively short sampling period and a limited number of participants. 921 More investigations on personal exposurePE and related potential health effects by cohort 922 study method will be considered in the futurefurther. The policy implication of our findings is 923 that developing and implementing appropriate preventive and control measures on\_ different 924 PM<sub>2.5</sub> anthropogenic pollution sources in different regions are appropriate, such as using dry 925 wood for barbecues for the female workers and improving waste treatment equipment at 926 landfill as soon as possible to reduce waste inorganized waste stack and open combustion. 927

<u>This work can be regarded as a first attempt for the assessment of personal exposure to</u>
 <u>particulate matter originating from main sources of combustion aerosols in representative</u>
 <u>cities of southern West Africa. We targeted in this study different groups of people exposed</u>

931 to domestic fires, traffic and waste burning. Even though there are few drawbacks such as 932 relatively short sampling period and limited number of participants, our findings provide a 933 new insight on the health risk due to PM<sub>2.5</sub> exposure in areas with scarce observations. 934 Developing countries of southern West Africa are facing a great challenge regarding air 935 pollution mitigation strategy and more investigations on personal exposure and related potential health effects by cohort method will be considered in the future. In the short terms, 936 937 developing and implementing appropriate preventive and control measures on anthropogenic 938 combustion sources downtown such improving waste treatment equipment at landfill or 939 efficient smoking equipment for domestic use, are appropriate.

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# 953 Author Contributions

H.X. and C.L. conceived and designed the study. H.X., J.-F.L., C.L. and B.G.
contributed to the literature search, data analysis/interpretation and manuscript writing. J.-F.L.,
C.L., B.G., V.Y., A.A., K.H., S.H., Z.S. and J.C. contributed to manuscript revision. H.X., J.F.L., E.G., J.A and L.L. <u>carried outconducteed</u> the particulate samples collection and
chemical experiments, analyzed the experimental data.

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### 960 Additional Information

Fig. S1 <u>and SI A-D</u> accompany this manuscript can be found in Supplementary
Information.

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## 964 **Competing financial interests**

The authors declare no competing financial interests.

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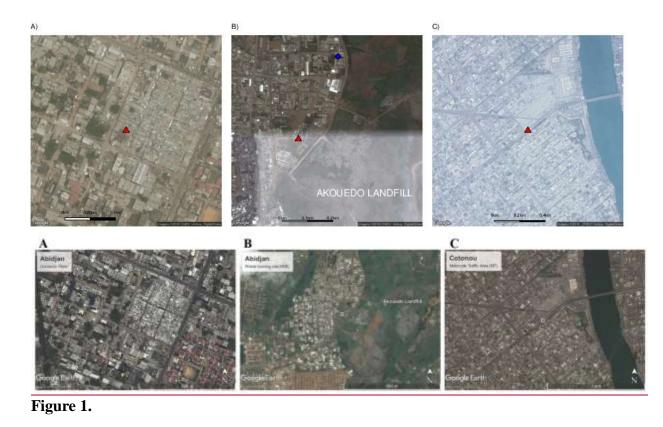
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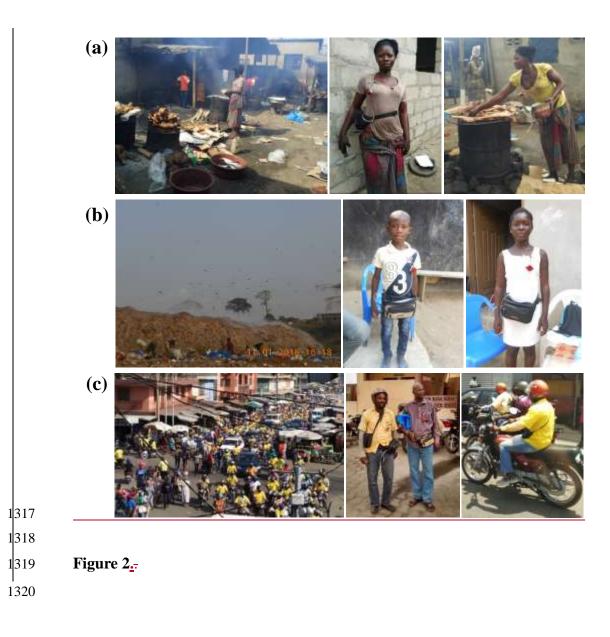
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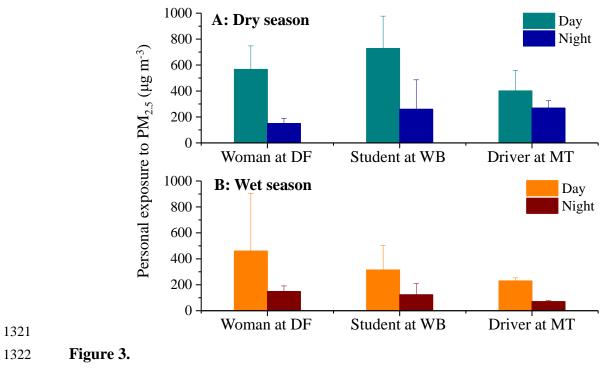
# 1294 **Figure Caption:**

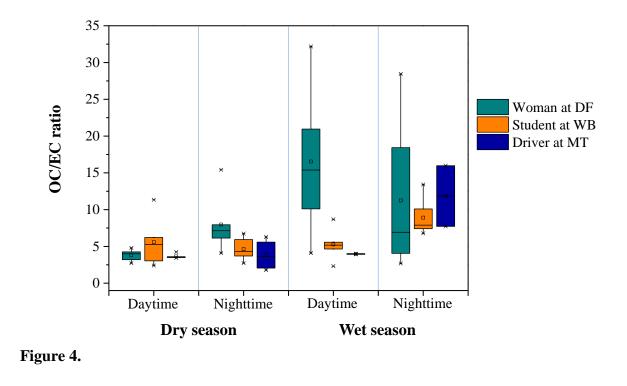
- **Figure 1.** Locations of the sampling sites <u>(white square)</u> within the cities. A: Domestic Fires (DF) site at the Yopougon-Lubafrique market in Abidjan; B: Waste Burning (WB) site at the landfill of Akeoudo in Abidjan<del>, the location of the long-term sampling site is given by the</del> blue marker; and C: Motorcycle Traffic (MT) site at Dantokpa area in Cotonou.
- **Figure 2**. Pictures showing the sampling sites and corresponding participants: (a) women at DF; (b) students at WB; (c) drivers at MT.
- **Figure 3.** Personal exposure to PM<sub>2.5</sub> mass concentrations of woman at DF, student at WB and driver at MT in dry season (January) and wet season (July) of 2016 in SWAsWA area.
- **Figure 4**. Variations of OC/EC ratios in personal exposure to PM<sub>2.5</sub> samples for women at
- 1304 DF, students at WB and drivers at MT (The box plots indicate the average concentration and 1305 the min,  $1^{\text{st}}$ ,  $25^{\text{th}}$ ,  $50^{\text{th}}$ ,  $75^{\text{th}}$ ,  $99^{\text{th}}$  and max percentiles).
- **Figure 5.** Personal exposure to PM<sub>2.5</sub> mass concentration closures for women at DF, students
- 1307 at WB and drivers at MT in different sampling seasons.
- Figure 6. Distributions of A: PAHs; B: PAEs; and C: hopanes in  $PM_{2.5}$  personal exposure samples for women at DF, students at WB and drivers at MT in dry and wet seasons of 2016.
- **Figure 7.** Correlations between PAHs diagnostic ratios (average ratio points of each type
- 1311 participant indicate day and night value respectively).

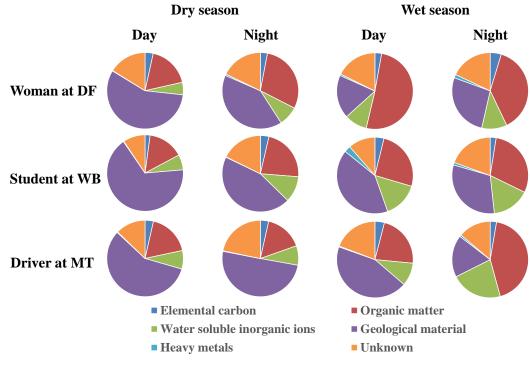




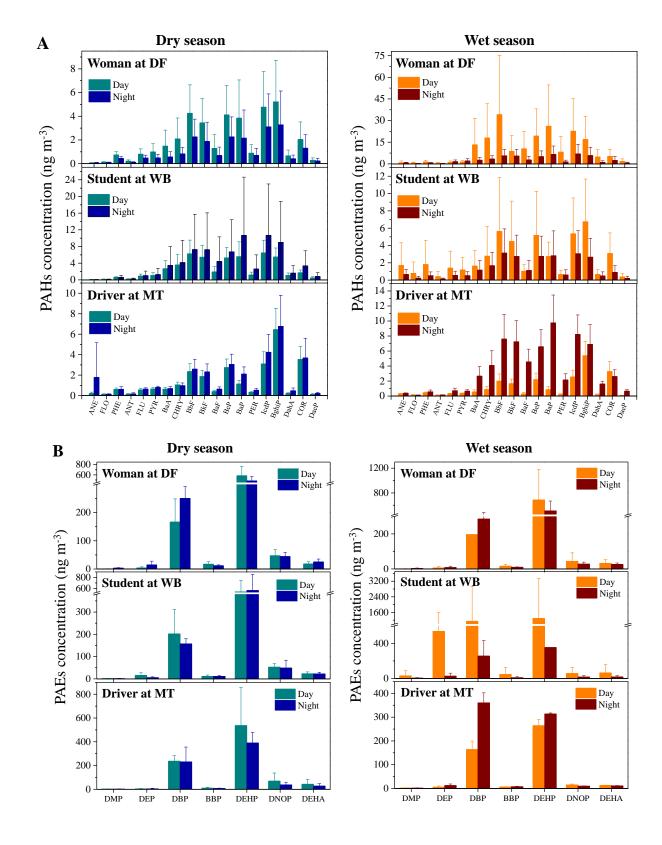


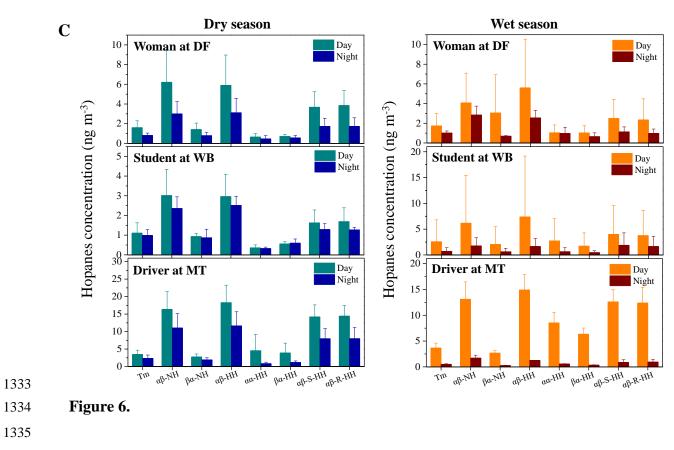


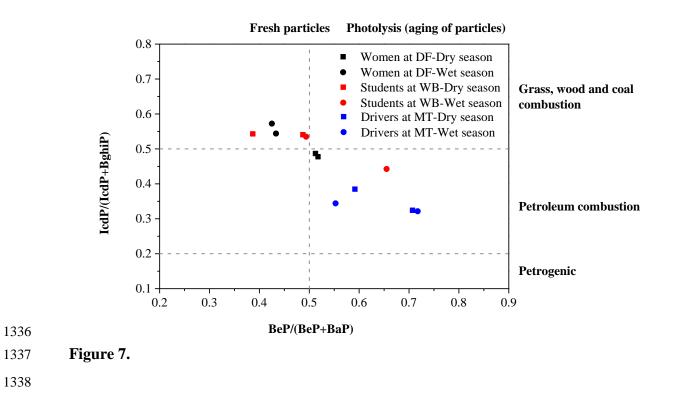












**Table 1** Meteorological parameters of the studied two cities during the dry (December 2015
to March 2016) and wet (April to July 2016) seasons.

	Season	Abidjan	Cotonou
Moon doily on tomporature (°C)	Dry	28.0	28.3
Mean daily air temperature (°C)	Dry         26.0           Wet         27.5           Dry         268	27.5	27.7
Total minfall (mm)	Dry	268	92
Total rainfall (mm)	Wet	626	558
Moon wind snood (m s <sup>-1</sup> )	Dry	3.0	3.0
Mean wind speed (m $s^{-1}$ )	Wet	3.4	4.3

Parameter	Definition (unit)	Value used in this study (reference)
D	average daily exposure dose (mg kg <sup>-1</sup> day <sup>-1</sup> )	/
С	heavy metals concentrations in equations (ng $m^{-3}$ )	/
R	inhalation rate, air volume a child inhaled each day $(m^3 day^{-1})$	16.0 for women and drivers; 15.2 for students (USEPA, 2011)
EF	exposure frequency (day year <sup>-1</sup> )	130 for women and drivers (half working days); 182 for students (half year)
ED	exposure duration (year)	30 for women and drivers (working years); 15 for students (before going to high school)
BW	body weight (kg)	62.5 for women <sup>a</sup> ; 37.5 for students <sup>a</sup> ; 85.0 for drivers <sup>a</sup>
AT	averaging time (day)	30 or $15 \times 365$ (non-cancer); 70 × 365 (cancer)
cf	conversion factor (kg mg <sup>-1</sup> )	10 <sup>-6</sup>
ĤQ	hazard quotient	/
RfD	reference dose, estimated as the maximum permissible risk on human by daily exposure (mg kg <sup>-1</sup> day <sup>-1</sup> )	Table 3
HI	hazard index	/
ILCR	incremental lifetime cancer risk (ILCR)	/
CSF	cancer slope factor (mg kg <sup>-1</sup> day <sup>-1</sup> ) <sup>-1</sup>	Table 3
[BaP] <sub>eq</sub>	equivalent BaP toxicity concentration (ng m <sup>-3</sup> )	/
Ci	individual PAH species concentration (ng m <sup>-3</sup> ) (i means target PAH species)	/
TEFi	toxicity equivalency factor of each target PAH compound (i means target PAH species)	(Nisbet and Lagoy, 1992)

**Table 2** Definitions and recommended values of the parameters in equations (1-4) in thisstudy.

a: Measured in this study.

**Table 3** Reference dose (RfD) (mg kg<sup>-1</sup> day<sup>-1</sup>) and cancer slope factor (CSF) (mg kg<sup>-1</sup> day<sup>-1</sup>)<sup>-1</sup>1347via inhalation exposure way used in this study.

RfD	CSF	Reference
1.8×10 <sup>-3</sup>	/	Liu et al., 2015
5.4×10 <sup>-3</sup>	/	Zhou et al., 2014; Liu et al., 2015
3.0×10 <sup>-1</sup>	/	Zhou et al., 2014
3.5×10 <sup>-3</sup>	/	Zhou et al., 2014; Hu et al., 2012
/	3.140	USEPA, 2011
/	0.014	USEPA, 1997; Wang et al., 2017a
	1.8×10 <sup>-3</sup>	$\begin{array}{cccccc} 1.8 \times 10^{-3} & / \\ 5.4 \times 10^{-3} & / \\ 3.0 \times 10^{-1} & / \\ 3.5 \times 10^{-3} & / \\ / & 3.140 \end{array}$

**Table 4** Statistical analysis (arithmetic mean±standard deviation) of personal exposure to  $PM_{2.5}$  mass concentrations and the chemical1/349compositions (units:  $\mu g m^{-3}$ ) during the sampling period in  $\frac{SWAsWA}{region}$  region.

	Dry season							Wet season					
	Women at D	F	Students at V	VB	Drivers at M	Т	Women at DF		Students at WB		Drivers at N	/IT	
	Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime	
PE PM <sub>2.5</sub>	567.0±180.6	150.6±38.5	728.5±248.5	260±226.1	401.3±158.0	269.0±56.1	460.5±445.2	148.6±42.9	315.2±186.9	123.7±86.1	230.4±22.8	70.7±8.1	
OC	72.4±24.6	31±5.0	85.0±57.4	40.9±34.4	49.5±12.5	31.8±14.2	189.3±197.8	40.1±9.3	$65.2 \pm 65.2$	$28.5 \pm 26.8$	37.0±3.5	22.2±10.6	
EC	19.5±7.3	$4.7 \pm 2.2$	$15.0 \pm 4.7$	8.6±5.7	13.6±3.6	9.0±2.3	$11.5 \pm 10.8$	6.3±3.7	$12.3 \pm 11.4$	$3.6 \pm 3.6$	9.3±0.8	$1.9\pm0.0$	
Total carbon	91.9±31.1	35.7±6.8	100.0±60.1	49.5±39.5	63.1±16.0	40.8±13.6	200.8±207.1	46.3±7.2	77.4±76.2	32.1±30.3	46.3±4.2	24.1±10.6	
Cl	4.4±1.3	$1.6\pm0.6$	$6.5 \pm 3.6$	$6.4 \pm 9.4$	$2.4\pm0.8$	2.2±0.6	$8.6 \pm 8.4$	$1.9{\pm}1.0$	$4.6 \pm 5.4$	$1.9\pm0.7$	3.1±0.2	2.3±0.2	
NO <sub>3</sub> -	$2.7\pm0.7$	$2.2 \pm 1.4$	5.5±1.3	3.0±0.7	3.7±1.3	$2.7 \pm 0.5$	$2.2\pm0.8$	$1.6\pm0.7$	$5.0\pm6.0$	$1.8 \pm 1.3$	$1.6\pm0.2$	1.2±0.1	
$SO_4^{2-}$	$4.0{\pm}1.1$	$1.8\pm0.6$	$7.5 \pm 2.5$	3.6±0.9	$7.5 \pm 2.5$	5.3±0.6	$6.8 \pm 5.2$	2.3±0.8	$6.4 \pm 5.9$	2.3±0.4	5.2±0.3	$3.2\pm0.5$	
Na <sup>+</sup>	2.9±0.4	1.6±0.3	4.1±1.1	$1.9{\pm}0.8$	3.3±1.1	2.4±0.3	$4.2 \pm 2.2$	$4.4{\pm}1.7$	$16.2 \pm 17.3$	3.3±3.1	3.6±0.2	2.6±0.1	
$NH_4^+$	$0.6\pm0.2$	$0.4\pm0.5$	$1.4\pm0.4$	3.0±4.1	1.1±0.2	$0.9\pm0.2$	$0.6\pm0.5$	$0.1\pm0.0$	$0.6\pm0.2$	$0.4\pm0.3$	$0.7\pm0.0$	$0.1\pm0.0$	
<b>K</b> <sup>+</sup>	3.2±0.6	$1.7\pm0.6$	$5.8 \pm 4.0$	$2.2 \pm 0.8$	$1.9\pm0.4$	2.1±0.9	$7.6 \pm 8.0$	1.3±0.8	3.3±4.4	1.3±0.6	$1.1\pm0.0$	3.6±1.5	
$Mg^{2+}$	$0.6\pm0.2$	$0.2\pm0.1$	0.8±0.3	0.3±0.2	$0.4\pm0.2$	$0.3\pm0.1$	$1.1 \pm 1.2$	0.3±0.1	$1.0\pm0.9$	$0.3\pm0.2$	$0.3\pm0.0$	$0.2\pm0.0$	
Ca <sup>2+</sup>	11.0±3.2	3.1±0.9	$14.9 \pm 4.5$	4.9±3.2	$10.6 \pm 5.5$	$6.0{\pm}1.2$	6.6±4.3	3.2±0.8	17.3±13.9	$4.5 \pm 3.8$	6.8±0.3	2.3±0.1	
Total ions	29.3±6.6	12.5±3.7	46.6±15.4	25.2±18.8	30.9±11.9	21.9±3.2	37.6±29.5	15.1±2.2	54.4±50.0	15.8±8.8	22.3±1.0	15.5±1.9	
Fe	14.61±5.25	$2.64 \pm 0.36$	21.17±4.64	$4.85 \pm 3.30$	$10.99 \pm 6.50$	$5.90 \pm 0.37$	3.37±3.34	$1.87 \pm 0.96$	$5.07 \pm 1.74$	$1.76 \pm 1.24$	4.56±0.64	$0.57 \pm 0.05$	
V	$0.04 \pm 0.02$	$0.00 \pm 0.00$	$0.07 \pm 0.02$	$0.02 \pm 0.01$	$0.03 \pm 0.02$	$0.01 \pm 0.01$	$0.01 \pm 0.01$	$0.00 \pm 0.00$	$0.03 \pm 0.03$	$0.01 \pm 0.01$	$0.01 \pm 0.00$	$0.01 \pm 0.00$	
Cr	$0.04 \pm 0.02$	$0.01 \pm 0.00$	$0.06 \pm 0.02$	$0.01 \pm 0.01$	$0.03 \pm 0.03$	$0.01 \pm 0.01$	$0.05 \pm 0.02$	$0.06 \pm 0.03$	0.31±0.35	$0.04 \pm 0.05$	$0.03 \pm 0.00$	0.03±0.00	
Mn	$0.18 \pm 0.06$	$0.04 \pm 0.03$	$0.29 \pm 0.08$	$0.07 \pm 0.04$	0.35±0.12	$0.21 \pm 0.11$	$0.14 \pm 0.16$	$0.04 \pm 0.00$	$0.37 \pm 0.36$	$0.06 \pm 0.06$	$0.17 \pm 0.02$	$0.04\pm0.00$	
Со	$0.05 \pm 0.02$	$0.01 \pm 0.01$	$0.09 \pm 0.02$	$0.01 \pm 0.01$	$0.05 \pm 0.03$	$0.02\pm0.02$	$0.02 \pm 0.02$	$0.02 \pm 0.02$	$0.04 \pm 0.05$	$0.02 \pm 0.02$	$0.02 \pm 0.01$	$0.01 \pm 0.00$	
Ni	$0.02 \pm 0.01$	$0.00 \pm 0.00$	$0.02 \pm 0.01$	$0.01 \pm 0.01$	$0.02 \pm 0.01$	$0.01 \pm 0.01$	$0.02 \pm 0.02$	$0.03 \pm 0.02$	$0.12\pm0.14$	$0.02 \pm 0.03$	$0.02 \pm 0.00$	$0.01 \pm 0.00$	
Cu	$0.04 \pm 0.01$	$0.02 \pm 0.01$	$0.14 \pm 0.03$	$0.02 \pm 0.01$	$0.05 \pm 0.03$	$0.03 \pm 0.01$	$0.13 \pm 0.07$	$0.13 \pm 0.07$	$0.67 \pm 0.81$	$0.10 \pm 0.09$	$0.07 \pm 0.02$	$0.06 \pm 0.02$	
Zn	$0.40 \pm 0.22$	$0.55 \pm 0.73$	0.49±0.19	$0.15 \pm 0.12$	0.33±0.16	$0.19 \pm 0.07$	0.51±0.32	$0.32 \pm 0.17$	1.41±1.55	$0.26 \pm 0.27$	$0.29 \pm 0.04$	$0.12 \pm 0.00$	

Sb	0.02±0.01	0.05±0.02	0.02±0.02	0.00±0.00	0.02±0.04	0.01±0.01	0.12±0.08	0.21±0.18	1.16±1.38	0.22±0.29	0.07±0.04	0.08±0.09
Ba	$0.19 \pm 0.09$	$0.16 \pm 0.12$	$0.25 \pm 0.11$	$0.07 \pm 0.09$	$0.22 \pm 0.18$	$0.05 \pm 0.07$	$0.47 \pm 0.39$	$1.02 \pm 0.60$	$6.80 \pm 8.30$	$0.84{\pm}1.41$	$0.18 \pm 0.18$	$0.14 \pm 0.01$
Pb	$0.07 \pm 0.03$	$0.07 \pm 0.07$	$0.17 \pm 0.07$	$0.04 \pm 0.03$	$0.07 \pm 0.05$	$0.02 \pm 0.03$	$0.14 \pm 0.02$	$0.09 \pm 0.03$	$0.92{\pm}1.01$	0.13±0.18	$0.05 \pm 0.02$	$0.03 \pm 0.01$
Heavy metals	1.05±0.28	0.91±0.80	1.59±0.51	0.40±0.31	1.16±0.66	0.56±0.28	1.62±0.65	1.93±1.10	11.80±13.91	1.69±2.38	0.90±0.26	0.53±0.09

<b>G</b> • <b>(P</b> • <b>(11</b> • <b>(</b> • ))	Women a	t DF	Students	at WB	Drivers a	t MT
Specific species (abbreviation)	Average	Stdev*	Average	Stdev*	Average	Stdev*
acenaphthene (ACE)	0.4	0.5	0.6	1.2	0.7	1.7
fluorene (FLO)	0.3	0.3	0.3	0.6	0.1	0.0
phenanthrene (PHE)	0.8	0.4	0.9	1.2	0.6	0.1
anthracene (ANT)	0.3	0.2	0.2	0.2	0.2	0.0
fluoranthene (FLU)	1.0	0.4	1.0	0.7	0.6	0.1
pyrene (PYR)	1.2	0.5	1.0	0.5	0.6	0.1
benzo[a]anthracene (BaA)	4.5	8.5	2.2	1.5	1.1	0.5
chrysene (CHR)	6.1	11.2	3.0	1.6	1.8	0.8
benzo[b]fluoranthene (BbF)	11.6	19.2	5.6	2.7	3.6	1.2
benzo[k]fluoranthene (BkF)	4.9	4.2	5.0	2.9	3.3	1.1
benzo[a]fluoranthene (BaF)	3.8	5.3	2.1	2.4	1.5	0.8
benzo[e]pyrene (BeP)	7.7	8.1	5.0	2.5	3.6	0.7
benzo[a]pyrene (BaP)	9.7	12.5	5.5	5.7	3.5	1.6
perylene (PER)	2.8	5.0	1.3	1.4	0.8	0.4
indeno[1,2,3-cd]pyrene (IcdP)	9.4	9.3	6.4	4.5	4.5	0.7
benzo[ghi]perylene (BghiP)	7.8	6.1	6.0	3.6	6.4	0.5
dibenzo[a,h]anthracene (DahA)	1.8	2.2	1.0	0.6	0.6	0.1
coronene (COR)	2.8	1.6	2.3	1.4	3.3	0.4
dibenzo[a,e]pyrene (DaeP)	0.7	0.7	0.5	0.3	0.3	0.1
ΣΡΑΗs	77.4	47.9	49.9	30.7	37.0	7.4
dimethyl phthalate (DMP)	2.2	1.0	9.6	27.9	1.9	0.5
diethyl phthalate (DEP)	8.3	4.1	146.5	517.0	6.8	1.4
di-n-butyl phthalate (DBP)	224.8	90.6	440.7	848.4	248.2	42.1
benzyl butyl phthalate (BBP)	13.8	4.3	19.7	37.3	8.1	2.9
bis(2-ethylhexyl)phthalate (DEHP)	566.4	181.4	688.0	899.1	376.3	144.5
di-n-octyl phthalate (DNOP)	40.9	16.9	43.8	26.2	33.0	31.0
bis(2-ethylhexyl)adipate (DEHA)	25.6	6.0	32.0	41.8	23.8	19.0
ΣPAEs	882.0	193.3	1380.4	335.2	698.1	192.4
17α(H)-22,29,30-trisnorhopane (Tm)	1.3	0.5	1.3	1.9	2.5	0.5
$17\alpha(H)-21\beta(H),30$ -norhopane ( $\alpha\beta$ -NH)	4.0	1.2	3.3	4.1	10.6	1.9
$17\beta(H)-21\alpha(H),30$ -norhopane ( $\beta\alpha$ -NH)	1.5	1.8	1.1	1.5	1.9	0.3
$17\alpha(H)-21\beta(H)$ -hopane ( $\alpha\beta$ - HH)	4.3	1.9	3.6	5.4	11.5	2.2
17α(H)-21α(H)-hopane (αα-HH)	0.8	0.2	1.0	2.0	3.6	2.1
17β(H)-21α(H)-hopane (βα-HH)	0.7	0.2	0.8	1.2	2.9	1.2
$17\alpha(H)-21\beta(H),(22S)$ -homohopane ( $\alpha\beta$ -S-HH)	2.3	0.7	2.2	2.4	8.9	1.3
$17\alpha(H)-21\beta(H),(22R)$ -homohopane ( $\alpha\beta$ -R-HH)	2.2	0.8	2.1	2.1	8.9	1.3
Σhopanes	17.1	6.4	15.6	6.1	50.9	7.9

**Table 5** Mass concentrations of PE  $PM_{2.5}$ -bound PAHs, PAEs and hopanes species for women at DF, students at WB and drivers at MT (ng m<sup>-3</sup>).

\*: standard deviation

**Table 6** Non-cancer risks of heavy metals and cancer risks of PAHs and PAEs via inhalation exposure way in PE  $PM_{2.5}$  of women at DF, students at WB and drivers at MT in dry and wet seasons.

		Dry seaso	n		Wet season					
	Women	Students	Drivers	Women	Students	Drivers				
Non-cancer risk										
Mn	5.71E-03	2.02E-02	1.09E-02	4.83E-03	2.31E-02	4.26E-03				
Ni	1.44E-04	5.60E-04	1.77E-04	4.49E-04	2.59E-03	2.00E-04				
Zn	1.45E-04	2.15E-04	6.16E-05	1.24E-04	5.45E-04	5.05E-05				
Pb	1.75E-03	5.98E-03	9.33E-04	2.97E-03	2.95E-02	7.75E-04				
HI	7.74E-03	2.70E-02	1.21E-02	8.37E-03	5.57E-02	5.29E-03				
Cancer risk (ILCR)										
PAHs ([BaP] <sub>eq</sub> )	3.13E-06	6.43E-06	3.22E-06	9.33E-06	3.68E-06	3.42E-06				
PAEs (DEHP)	2.92E-07	3.36E-07	1.86E-07	3.15E-07	4.86E-07	1.16E-07				