

Dear reviewer,

First, we would like to extend our gratitude to the reviewers, for their time and constructive comments, which allowed us to substantially enhance the quality of our manuscript. Please find below our responses to each of the comments made by the reviewer 1. The text in black represents our response and in red are the questions from reviewer 1.

Best regards,

Emeline Bellet, on behalf of the coauthors

Specific comments

Thank you for your comments. Concerning the analytical methodology, the section has been improved following your comments. Thank you to have highlighted the sentences and the figures that required clarification. We took your comments into consideration for the revised manuscript and improved the conclusion.

Technical corrections

We have preferred to use the terms 'cal a BP' rather than 'cal BP' or 'cal yr BP' following the comment of a reviewer from a previous paper. He said that when reporting a duration of time it is better to use 'yrs', but when reporting a date to use 'cal a BP' and that in "cal BP" and "BP" there is no time unit. He had suggested me to consult the following webpage <https://www.sedgeochem.uni-bremen.de/kiloyears.html>.

Thank you for your comments on grammar, spelling and missing references, we have modified the manuscript accordingly.

Charcoal is limited as a regional wildfire proxy contrary to PAHs because they are heavier and deposited in closer to the sources.

We have also completed the text concerning the origin of the charcoal as follows:

« Finally, from ca. 1000 yr ago, an increase in Cyperaceae and Poaceae supports the development of a peat bog, which currently covers a large part of the lake and indicates increasingly shallow conditions (Teixeira et al., 2021). At the same time, charcoal particles began to occur in the sediment core, indicating an increase in fire activity. However, today, the rainforest surrounding the lake in the Montagne d'Ambre is too humid to burn regularly, whereas fires occur frequently in the drier piedmont areas. Charcoals recorded in the uppermost sediments have thus likely been transported by wind from these surrounding drier areas rather than produced directly within the rainforest surrounding the lake. The same process may have contributed to the occurrence of charcoals in the sediment record during the past 1000 years. This interpretation is further supported by evidence from a second lake in the Montagne d'Ambre, also surrounded by rainforest (Lake Mahasarika; Montade et al., 2024). At this site, shallower conditions were also recorded at around the same time, suggesting that the increase in fire activity and human influence documented in the region may have occurred in association with drier environmental conditions (Montade et al., 2024). »

We did not spike the samples with an internal standard prior to the extraction for PAH. The two possible internal standards are marked either with ^2H or with ^{13}C . Because the fraction F1 was subsequently analysed for alkanes and their isotopy, we didn't use molecules marked with ^2H or ^{13}C , in order not to damage the analytical machine used to determine the alkane isotopy.

Concerning the solution for the elutions. Yes, we really made the solution with the proportion 98/2 v/v. Then

the proportion is 80/20 v/v for the 2mL of Hep/DCM. The F2 is the elution of those two fractions. Initially when our laboratory extracted the PAHs, they realized those two fractions and they kept them separately. But they discovered that some PAHs remain in the elution of the second fraction (Hep/DCM, 80/20, v/v) so they decided to pool the two fractions for the analysis of the PAH. In this project we have extracted not only the PAH but also the alkanes and the GDGT. That is why we realized 3 fractions.

If pigment remained in fraction 1, a second separation by SiO₂ column chromatography was performed. When the pigment remained, a second separation was realised to remake the same separation described just above in the text. Then, we obtained from this F1 three fractions (F1, F2, F3) that we grouped with the corresponding fractions F1, F2 or F3. The sentences have been added in the manuscript to clarify it. We were obliged to do it otherwise the analysis of PAH by HPLC-fluo will be distorted because some pigments absorb and emit at the selected wavelength.

Change has been made between lines 186 and 187 : «The second separation of F1 was performed to repeat the same separation described just above. Then the new three fractions were added to their corresponding fractions. »

Thank you for your comment on the final tasks of the extraction of PAHs. More details have been added. The two fractions, F1 and F2, have been evaporated and analysed separately. We did not combine them. The DMSO cannot be removed before the analyses because it is soluble with methanol. It is just used to change the solvent without passing through a dry step (which generates a loss of PAH). The DMSO did not evaporate and kept its volume. Like this, we can control this final volume to compute the concentration of PAH in the solution and then in the sediment.

Change has been made between lines 189 and 194 : «The fractions 1 and 2 were evaporated separately under a nitrogen flux. Dimethylsulfoxide (DMSO) was used as a keeper and to change the solvent to methanol for the analysis. It is used to change the solvent for the analyses without passing through a dry step, which could generate a loss of PAH. During the evaporation, just under a nitrogen flux, the DMSO keeps its volume and the rest of the solvent evaporates. Then a known volume of methanol was added. The DMSO cannot be removed before the analyses because it is soluble in methanol. Then, the fractions 1 and 2 were analysed separately. »

Concerning the analytical procedure of PAHs more information will be added notably in including a schedule a table listing the wavelengths used for excitation and emission for each PAH analysed.

Changes have been made between lines 201 and 203 : « Briefly, nine phases of excitation and emission detection have been scheduled. The selected wavelengths depend on the PAH sensitivity. Different wavelengths have been selected for the excitation and emission (Table SM 0). »

Thank you for your remark on PAH solubility. As you mention, by nature PAHs are not hydrophilic. We added some sentences to insist upon the fact that PAHs are hydrophobic naturally but separated them into two groups based on their relative hydrophobicity strength, based on the study by Garagnon et al. (2024). We have however preferred using the solubility criteria rather than the coefficient of partitioning water/organic-carbon, because solubility represents better the physical mechanisms triggering the incorporation – or not - of PAHs within the rain droplets. We clarified the hydrophobic nature of PAHs in lines 223 to 226 : « For the rest of the article we will use the terms “hydrophobic group” and “hydrophilic group” to characterise those two groups. However, one must note that all PAHs are hydrophobic. This separation hence separates the most hydrophobic from the least – yet still - hydrophobic PAH congeners.”

For lines 205-206, the sentence was incomplete. Thank you to have note this. There was an equation but the special characters had disappeared : « However, if the value of a PAH concentration in a sample is comprised between the value of the LOD and the the LOQ, then its concentration is estimated equal to $LOQ/\sqrt{2}$ »

For the reference “(Ana Lúcia C. Lima et al., 2005)”, the part ‘Ana Lucia C.’ have been deleted.

For Line 298, the Per is present in the figure SM2 and Pyr, Flu, Fla, Phe in figure SM3. A precision has been added in the text.

Concerning the charcoal data, the plot presents the fraction of particles $>160\mu\text{m}$. The charcoal fraction presented in the figure 4 has been added, in line 326 « We confronted our PAH data with the charcoal record of particles $>160\mu\text{m}$ »

For line 312, the sentence has been modified: « These results effectively demonstrate that charcoal particles $>160\mu\text{m}$ capture a proximal/local fire signal originating from a few km away, i.e., the drier, low-elevation dry forest/savanna zones where wildfires occur nowadays. ». It is unlikely that the evergreen forest of Ambre Mountain is subjected to wildfire, the fire activity surely occurred – as it does nowadays - at the savanna-covered foothill.

Lines 320-321: “Therefore, the northern region of Madagascar cannot be considered as a source of PAHs”

It is the comparison between the PAH and charcoal signals which gives the information that PAH come from a distal source, because the charcoal signal represents local wildfires.

Line 322-323: “but this would reflect more remote sources supplying PAHs.” Supplying all PAHs, or the “hydrophilic” ones?

For all PAHs, because we observe no charcoal but high concentrations of both “hydrophobic” and ‘hydrophilic’ PAH groups.

Lines 341-342: “Therefore, this implies that although distant, the fire source is not excessively far.” What does this mean in terms of distance? Is there any study of the atmospheric transportation distances of PAHs that can be cited here?

Vachula et al. (2022) compared a historical fire calendar with a PAH signal from lake sediments. They concluded that each individual PAH presents its own behaviour. They hence concluded that the heavier congeners (Ace, Flu, Phe) accurately record any fire within a distance of 40 km whereas the lighter ones (BbF, BkF) record fire within a 150 km distance. However, this depends also on the efficiency of the transportation. Halshall et al. (2001), modelled the transportation of PAH over longer distances (~ 3500 km). They show that lighter PAHs travel on longer distances. This depends on deposition and degradation. In our study, as we observed the presence of both heavier and lighter PAH showing similar signals we supposed that the predominant PAHs source is not too far away, like the Australian region, where maybe the partitioning between heavy and light molecules would be more important due to the long transport with the photodegradation and deposition processes which also depend on gaz/particle partitioning. We decided to not add the numerical distance because it depends on a lot of parameters such as the meteorology, the degradation or the climate of the study site (Halshall et al. 2001 conducted their study in high latitudes).

Line 367: Please correct to “In a different site” and clarify which one is it.

This sentence was misleading and has thus been deleted.

Lines 375-376: “PAHs likely originate from regional biomass burning, but the variation was not due to fire activity variation.” Please clarify this information.

Thank you for your remark. The figure 4 now displays new curves of charcoal fluxes in Eastern Africa. We interpret the discrepancy between these signals and our Madagascar curve, between 8000 and 6000 cal a BP, as a change in the efficiency of the atmospheric fallout of PAHs. The modification in the text is between lines 425 and 435:

“The fire activity reconstructed from the Eastern Africa charcoal records (Fig. 4H) exhibits a pattern markedly distinct

from the Lake Maudit PAH record during the mid-Holocene. The charcoal records from Eastern Africa presented high values during the Early Holocene until 8000 cal a BP as did our PAH record. However, between 8000 and 5500 cal a BP our PAH record presented high value of concentration. PAH concentration increased in Lake Maudit sediment from 8000 to 6000 cal a BP, whereas during the same period, the biomass burning in Eastern Africa decreased and presented its lowest values. As a consequence, we note that whereas PAHs likely originate from African biomass burning, their variations in concentration seem decoupled from the gross amount of African biomass burning during the period from 8000 to 5500 cal a BP.”

Thank you for your comment on figure 4. This figure have been improved in taking in consideration your comments.

The conclusion has been reworked taking in consideration your remark on the lack of information as well as comments from reviewer 2:

« Concentration profiles of PAH in sedimentary archives are usually used to infer palaeofires in complementarity with charcoal records. In our record from the North of Madagascar, despite the absence of charcoal prior to 1000 cal a BP, the concentrations in PAH present high values and significant variations over the Holocene. This suggests they represent a remote signal of fire activities from East Africa, thanks to monsoon winds. However, the signal of PAH does not perfectly match the recorded fire activity from Eastern Africa, especially between 8000 and 5500 cal a BP, when PAHs concentrations reach a maximum in Madagascar and an independent precipitation record from Madagascar. To explain this pattern, two hypotheses can be highlighted: 1) PAHs originated from specific region of the Eastern Africa where biomass still burned, or 2) enhanced precipitation led to a more efficient atmospheric PAH fallout. Our preliminary study does not permit to decide between these hypothesis, however, we argue that changes in wet deposition must not be neglected when interpreting pluri-centennial PAH profiles. Under some conditions which remain to be constrained, PAH could hence be a complementary tool in the attempt to reconstruct past hydroclimate fluctuations.»

Thank you for having taken the time to check the bibliography. The references which needed information have been completed. The references' DOIs have been added or changed when necessary.