Clim. Past Discuss.,
https://doi.org/10.5194/cp-2018-19-AC5, 2018

Climate of the Past
Discussions
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Interactive comment on "Fire, vegetation and Holocene climate in the south-eastern Tibetan Plateau: a multi-biomarker reconstruction from Paru Co" *by* Alice Callegaro et al.

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Received and published: 9 July 2018

J. L. Toney (Referee) The manuscript "Fire, vegetation and Holocene climate in the south-eastern Tibetan Plateau: a multi-biomarker reconstruction from Paru Co" uses a suite of biomarkers to assess vegetation and fire change during the Holocene from a sedimentary record of a small lake on the Tibetan Plateau. This study presents original data with potentially interesting new results on fire history that has not been widely studied on the Tibetan Plateau. The manuscript is well written and methodologies are robust. Given that this is a relatively new field of research, mainly the application of fire-related biomarkers to paleoclimate records, there are additional aspects that the

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authors should consider.

A: We are grateful to Dr. Toney for the useful review and the kind suggestions. We improved the paper according to the suggestions and we incorporated most of the indicated references. We reply to the specific comments below.

PAHs: For instance, although they suggest that there are only a few studies of PAHs as tracers of biomass burning and only cite two (Page 3, Line 12), there are others out there that may help with their interpretations, for instance: Page et al. 1999, Marine Pollution Bulletin; Yunker et al. 2002, Organic Geochemistry; Denis et al. 2012, Organic Geochemistry; Yan et al. 2014, Environmental Toxicity and Chemistry; Yunker et al. 2015, Organic Geochemistry; and Denis et al. 2017, Organic Geochemistry. In particular, not all PAHs result from biomass burning, so using the sum of PAHs, for example, may not be as useful as targeting the pyrogenic PAHs (examples in Page et al. - fluoranthene, phenanthrene, benzo(e)pyrene). Denis et al. 2012 suggest that there are differences in high molecular weight PAHs representing the intensity of the fire (also see McGrath et al. 2003, Journal of Analytical and Applied Pyrolysis), whereas, the low molecular weight PAHs more consistently record local fire events. These considerations may or may not be applicable, but could be tested without acquiring more data. This analysis may help to resolve differences in between the MAs and the PAHs.

A: Thanks for the useful guideline. We incorporated your changes in the sentence (page 3 lines 5-10 of the new version) as following: “PAHs are semi-volatile, persistent, and ubiquitous in the environment with multiple possible sources, and therefore commonly detected in soil, air, and water (Abdel-shafy and Mansour, 2016; Johnsen et al., 2005). The investigation on PAHs as tracers of biomass burning in past climate archives such as sediments (Jiang et al., 1998) and ice (Gabrieli et al., 2010) increased in the last decades (Yan et al., 2014; Page et al., 1999)”. Following also the indication from referee#3, we reanalysed all the PAHs fractions, obtaining new interesting results which also include the application of some diagnostic ratios: Ant/(Ant+Phe), IP/(IP+Bghi) and FluA/(FluA+Pyr). We also looked at the signal from different group of PAHs according to their molecular weight. The paper went, therefore, through a deep revision in sections 4 and 5 (Results and Discussion). For example, a new paragraph describing PAHs results sounds as: "The lowest PAH value is 0.2 ng g-1 of benzo[b]fluoranthene (BbFl) while the highest PAH concentration is 310.3 ng g-1, of naphthalene (Naph). Phenanthrene (Phe), benzo[e]pyrene (BePyr) and Naph respectively represent 20.9%, 18.9% and 17.5% of the total PAH signal in Paru Co. The total sum of PAHs () shows higher valuesin the middle Holocene, with major peaks at 6.3, 5.8, 5.2, 4.8, 3.9 and 3.5-3.3 cal ky BP. The general trend shows increases from 2.2 to 1.3 cal ky BP. The molecular weight and/ or number of aromatic rings of PAHs allows investigating the influence of different PAH types through time. The group of 3ring-PAHs includes Phe, anthracene (Ant) and fluoranthene (FluA), demonstrating a similar pattern to the . The group of 4ring-PAHs encompasses pyrene (Pyr), benzo[a]anthracene (BaAnt), chrysene (Chr), retene (Ret), benzo[b]fluoranthene (BbFl) and benzo[k]fluoranthene (Bkfl), which also has higher values during the middle Holocene and then an increasing trend towards 1.3 cal ky BP. The group of 5-6ring-PAHs is composed by benzo[a]pyrene (BaPyr), BePyr, benzo[ghi]perylene (Bghi), Indeno[1,2,3,-c,d]pyrene (IP) and dibenzo[a,h]anthracene (DBahAnt), with a more noisy trend and dissimilar behaviour from the rest of the groups. 5-6ring-PAHs are high in the early Holocene, peaking at 10.3-9.9 cal ky BP, and then have separate high concentrations at 9.3, 8.6, 7.2, 5.2, 3.9, 3.5, 2 and 1.3 cal ky BP". Another paragraph in which we discuss the PAHs ratios sounds as: "The diagnostic ratios and associated error propagation (Figure 2g, 2h, 2i) do not allow quantitatively assigning PAH sources. IP/(IP+Bghi) contains values above the 0.5 threshold for combustion of wood, wood soot and/or grasses, creosote, as well as almost all wood and coal combustion aerosols and bush fire (Yunker et al., 2002b). The FluA/(FluA+Pyr) ratio, with values above 0.5 for the majority of the samples, indicates the combustion of grass, wood or coal, although this threshold is not definitive (Yunker et al., 2002b). The Ant/(Ant+Phe) ratio with values > 0.10 is generally related to pyrogenic PAH sources, but overlapping values between petroleum and combustion sources are reported (Yunker et al., 2002b).

In Paru Co, when including the error propagation, the majority of samples show values of Ant/(Ant+Phe) > 0.10. Due to the improbability that petroleum sources were burned near Paru Co during the geological time period covered by the analysed core, the obtained values for the ratio Ant/(Ant+Phe) must be related to vegetation combustion. In general, Ant undergoes more rapid photochemical reaction in the atmosphere than Phe. In contrast, FluA/Pyr and IP/Bghi isomer pairs degrade at comparable rates and the original composition information is preserved during atmospheric transport (Yunker et al., 2002b) suggesting that their ratios may be more reliable compared to the Ant/(Ant+Phe) ratio. Given these considerations, we confirm that diagnostic ratios are important tools for the source assignment but cannot be completely trusted due to overlapping values and error propagation that may hinder the correct allocation of the signal origin. However, PAHs in Paru Co can function as pyrogenic markers as we did not find any evidence of other sources (e.g. volcanic eruptions, anthropogenic emissions)".

Finally, with respect to the PAHs (Page 13, Line 28), if there is a change in the biogenic/ diagenic signal of the PAHs, then it would likely manifest specifically in the PAHs like perylene - it would be worth having a look at how the individual PAH profiles change when this signal becomes prominent. Degradation, if it is of the overall organic material should also manifest in changes in the carbon preference index (CPI) values, but these data are not plotted. If a low CPI is seen during times of highly charred material, this index could help support the argument made on Page 16, Line 3.

A: As we answered to the previous point, we looked at the at the signal from different group of PAHs according to their molecular weight. Due to the fact that the new interpretation addressed PAHs as pyrogenic derived, we no more discussed the biogenic/diagenic sources. Regarding CPI, we calculated the ratio in range of chain length of 21-33 and we compared it to the fire signals, in the new figure 3. Our interpretation of these results in the new discussion section 5.2 "combustion sources" sounds as: "In order to obtain more information from the burning conditions, we compared CPI values to L/M and PAHs. Considering that PAHs and n-alkanes are both local indicators, variations in CPI corresponding to spikes in local fire markers may link combustion and vegetation types demonstrated by n-alkane abundances. While no correlation exists between PAHs and CPI, the CPI and L/M have a slight positive correlation (r = 0.31, p-value = 0.03). Medeiros and Simoneit (2008) found that the n-alkanes in green vegetation smoke contained distributions ranging from C23 to C35, with strong odd-to-even carbon number predominance evidenced by CPI ranging from 9 to 58. MAs are better at recording smouldering fires than are PAHs, which may in part explain the similarity between MA and CPI variability through time. The Paru Co CPI values peak around 10 cal ky BP, in the period between 7.8 and 3.5 cal ky BP, and at 2.3 cal ky BP, with values up to 41.2, similar to the peak distributions of L/M. Another argument for relationship between CPI and MAs fire is the fact that lower temperature fires (MAs) essentially steam-distil the vascular plant lipids into the smoke, while high-temperature fires (PAHs) can result in decrease of the CPI (Schefuss et al., 2003 and references therein). In addition, the distance from the vegetation to the sediments may influence the CPI record as plants that are in or near the water pools contain shorter carbon chains, whereas more distant plants have higher CPI values (García-Alix et al., 2017). From these considerations can be assumed that, when CPI parallels L/M, fire from the surrounding areas, and not only near the lake catchment, could have been recorded".

n-Alkanes: It is worth applying some caution in the use of the Paq from Ficken et al. 2000, which was derived in from Mt. Kenya in Africa. The organic geochemistry community is finding that a site-specific approach may be needed and while the assertions about long-chain and short-chain n-alkanes generally hold true, in some environments the relationship is slightly more complex. For example, in Garcia-Alix et al. 2018, Scientific Reports, the supplemental information shows how this index and the ACL vary with distance from water source. Because grasses are prominent during more humid conditions in the arid Sierra Nevada region, the C31 shows aquatic rather than terrestrial-type vegetation changes. This may apply to similar high-elevation sites on the Tibetan Plateau and should be discussed. It is not a fault of the authors, just a really recent paper that might change the interpretations made here. This could help explain why the n-alkanes are showing a different pattern of change than the MAs and the grass/wood prevalence of pollen data (Page 16, Line 27). Overall, this is a very interesting and well thought out study, but further analysis given the above comments could help with discussion.

A: Thanks for your comments. We checked both Garcia-Alix et al. 2017, Scientific Reports and Garcia-Alix et al. 2018, Scientific Data, finding your useful consideration, as well as other papers. We focused our discussion on Paq and ACL in relation to lake level changes (in the new figure 4) and we found increasing ACL (and diminished Paq) when lake levels are lower and vice versa. Part of the new paper in which we explain this fact sounds as: "Fluctuations in lake levels (Fig. 4d) can be associated with fluctuations in Paq, suggesting a general relationship between higher lake levels and the prevalence of submerged plants between 10 and 5 cal ky BP. The opposite situation occurs between 5 and 1.3 cal ky BP, when a decreasing trend in lake level corresponds to diminishing Paq values. ACL confirms this trend with where the majority of values near 25 occur during higher lake levels (10-5 cal ky BP) and majority of values around 27 occur from 5 to 1.3 cal ky BP. The se high lake levels are consistent with wet conditions from a more intense ISM prevailing until $\sim$ 6 cal ky BP, as evidenced by dD wax and pollen records (Figures 3 and 4)." Thanks again for your comments that really improved the quality of our paper.

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