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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Enhancements of Airborne Particulate Arsenic over the Subtropical Free Troposphere in the Springtime: Impact by South Asian Biomass Burning" *by* Yu-Chi Lin et al.

Anonymous Referee #2

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This paper presents one year of daily TSP samples at Mount Hehuan, Taiwan. The samples were analysed for inorganic ions and trace metals and the analysis is supplemented by CO concentration measurements and air mass history analysis.

The manuscript concentrates on the observation of elevated As concentration in biomass burning (BB) plumes. As is found to correlate strongly with Pb, and based on As/Pb ratio of approx. 0.2 the authors suggest that the elevated As concentrations in BB plumes may originate in the usage of lead arsenate pesticide.

While the observation of elevated As in BB plumes is interesting, the concentrations are well below air quality limits at Mount Hehuan. Also the estimated As emission of

0.17 tons per year in South Asian BB is very small (approx. 0.5%) compared to the annual global emissions of 31 tons. Therefore, the results are of only limited interest.

In my opinion this data set requires a more thorough statistical analysis to merit publication in ACP. Please apply principal component analysis (PCA), or a similar factorisation technique, to the data to see if other sources than biomass burning can be identified. Please provide also average concentrations of trace metals and inorganic ions for the different air mass origins you defined. I believe this would provide a valuable reference point for East Asian free troposphere.

Minor comments

L30-35 "Finally, the net influence of BB activities on airborne As concentrations has been simply estimated by comparing the differences of As concentrations between BB and non-BB days. The result showed, on average, the contribution of BB activities over S Asia to airborne As was approximately 1.0 ng m-3, which accounted 63% for total airborne As concentrations in the springtime."

Do you mean that As concentration was on average 1.0 ng m-3 higher during BB days than non-BB days in the springtime? This is quite a different conclusion than "the contribution of BB activities over S Asia to airborne As was approximately 1.0 ng m-3". Please define springtime and state the BB contribution to As on annual level.

L36-38 "Using this value, arsenic emissions from S Asian BB activities were estimated to be 0.17 tons yr-1, causing extremely high airborne As concentrations over the subtropical free troposphere, and impacted As cycles on a regional scale."

I wouldn't call the concentration "extremely high" as it is below most (if not all) air quality limits. It is high for free troposphere, but much higher average values have been reported from continental boundary layer. Also, 0.17 tons yr-1 is approx. 0.5% of the global annual emissions, so not a huge amount. However, As in BB smoke may pose a serious health risk close to the fire, where the smoke is not yet diluted.

L60-63 “However, whether BB-derived As can be traveled to long distance and influenced As cycles at its downstream regions is still an open question.”

Wai et al. (2016) show that As in general can travel long distances globally. Also it is well known that BB smoke can travel long distances. So it is not a surprise that As released in BB can travel long distances.

L64-65 “volatile organic carbon (VOC) and particulate matters (PM))” Do you mean “volatile organic compounds (VOCs) and particulate matter (PM)” ?

L69 Do you mean “Kondo et al., 2004”? Please check all occurrences of this reference.

L75-77 Most BB smoke is emitted within boundary layer (e.g. Val Martin et al., 2010), though some is of course lifted into free troposphere.

L176 Please explain shortly how the clustering was done. Did you take into account the height of the trajectory?

L209 Please explain which parameters/fields from WRF-Chem did you use in this study. Did you obtain emission sensitivity from the model? Did you take deposition (dry and/or wet) into account?

L231 Are concentrations presented under prevailing conditions or in STP or NTP?

L246-247 “Increased As concentrations coincided with CO peaks on some days, showing some highly anthropogenic As plumes passed over this site.” Please explain what you mean with “highly anthropogenic As plumes”.

L279-286 Please define the enrichment factor in section 2, it belongs to methods.

L287 and Fig. 5. I don’t see much difference between the different seasons in Fig. 5. I think that this is one place where principal component analysis (or similar) would be very useful to differentiate between crustal origins and other sources. See e.g. the analysis by Venter et al. (2017) on trace metal concentrations.

L309-313 “As mentioned above, BB activities may be an important regionally source for high As concentrations over the subtropical free troposphere, especially during the spring period; consequently, in this section, we prove the hypothesis using backward trajectory analyses and MODIS fires observations together with WRF-Chem model simulated results.”

This is quite a strong statement. Given the uncertainties in trajectory calculations, I think the correlation with K+ is a stronger indicator of BB origin of As. Please consider re-phrasing.

L313 Please state (with appropriate references) which MODIS product you mean by “fire spots”. It would be good to include a sub-section in section 2 detailing which methods are used to characterise BB plumes.

L323-326 “For convenience, prior to further analysis we arbitrarily chose a K+ concentration of 109 ng m-3 (the 25th percentile value of potassium ion) as a criterion value for identifying the suspected BB event. A second criterion (CO concentration up to 160 ppb) was also added for selection of the BB plume.”

Do you mean that your site is within a BB plume 75% of time? Using 25th percentile value of K+ as threshold sounds unrealistic to me. At the same time using CO threshold of <160ppb sounds very strange. Please explain.

L332-334 Please plot back-trajectories for high-As BB-plumes and low-As BB-plumes on a map separately (e.g. with different colours). Is there a difference in the footprint area? The back-trajectory clusters have substantial overlap.

Here it would be better to define high and low As plumes based on As/CO or As/K ratio. The absolute As concentration in a plume depends strongly on dilution, whereas the above ratios should remain rather constant independent of dilution. Better still to use excess (delta) As, CO and K+ to calculate the ratios.

It would be interesting to see if principal component analysis finds a factor with high As

and Pb contributions. Inspecting the air mass history of such a factor should make it very clear where the As plumes originate.

L373-378 What is the As/Pb ratio in the ground water in this region? Is it significantly different from the ratio of 0.22 for lead arsenate?

L428-429 Is the difference calculated correct here? Also, this difference depends mostly on BB plume dilution.

L433-436 Please try to find BB-plume As factor with PCA. That will give you a more reliable estimate of the BB-contribution to As load at Mount Hehuan.

L438 How do you define delta? Is this excess concentration in the plume? This should be introduced already in section 2.

L438-442 Please indicate the unit of delta As / delta K+ and delta As / delta CO.

L444-445 For an order of magnitude estimate a 15-year old emission inventory is probably ok, but you may wish to use a newer inventory. At least GFED4 (van der Werf et al., 2017) differentiates between agricultural residue burning and other kind of fires.

L457-458 “Backward trajectory and WRF-Chem model proved that the high As plumes originated mainly from S Asia.”

The high As plumes may have originated from S Asia, but in my opinion this has not been proved. Especially Fig. 8, which is the only place where WRF-Chem is utilised, is misleading and poorly documented. Please see comments on Fig. 8 below.

L461-463 “Furthermore, we roughly estimated that approximately 1.0 ng m-3 of As was contributed by biomass burning activities over the South Asian continent, accounting 63% of total airborne As in the springtime.”

Here “1.0 ng m-3 of As” sounds strange considering that you present only annual mean (0.5 ng m-3) before. Please clarify and state the BB contribution to As on annual level and define “springtime”.

Fig. 6 Please explain how the colour coding (As bins) is done. Now it seems to me that “<5th" refers to highest 5 % of values, though usually 5th percentile would include the lowest 5 % of data points.

Fig.8 Caption: “Figure 8 MODIS fires and WRF-Chem modeled results of BB plumes on (a) April 3 and (b) March 25.” Please check if panel (b) presents March 25 or March 15. The “fire spot” legend in the plot suggests March 15 to me.

Please indicate what the blue arrows and the shaded areas represent.

My main concern with this figure is that for panel (a) all fire observations outside India are left out. This gives a very misleading picture of the potential sources of the BB plumes for April 3 observations at Mount Hehuan, as during March 25 – April 3 there are much more fires between India and Taiwan than in India (see attached screenshot from FIRMS).

Also Fig. 8b the “fire spots” are drawn only for a small sub-region of the map.

Finally, there are still quite a few language issues, which should be carefully checked. Please also consider splitting some very long paragraphs into shorter ones (e.g. L166-207 is all just one paragraph).

From the supplement: Please provide proper caption for all figures. Please indicate also here the proper details of MODIS “fire spots”.

References

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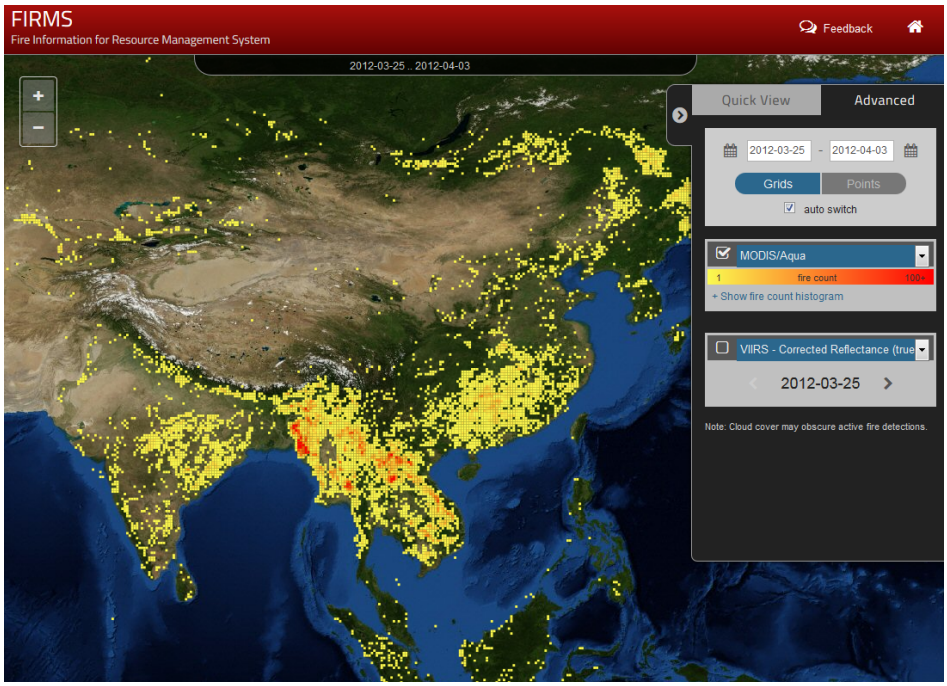

Fig. 1.