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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ambient aromatic hydrocarbon measurements at Welgegund, South Africa" *by* K. Jaars et al.

K. Jaars et al.

pieter.vanzyl@nwu.ac.za

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We thank Referee #1 for a detailed review of our manuscript. The comments and remarks have been processed in the manuscript, which we believe has gained in clarity and scientific soundness. Below is a point-by-point reply to the comments of Referee #1.

Anonymous Referee #1 Received and published: 21 April 2014

The paper by Jaars et al. presents extremely valuable results from ambient aromatic VOC measurements in South Africa. Such papers are particularly needed since VOC data for Africa, in particular on the atmospheric abundance of aromatic compounds, are essentially unavailable. Furthermore, the measurements of aromatic VOCs seem par-

ticularly relevant for many African regions which suffer from significant pollution, where no national thresholds for aromatic hazardous VOCs exist with a single exception for benzene.

Not only do the authors report long-term measurements of gas-phase aromatic compounds but they also further analyze polluted air masses in terms of their source origin by using HYSPLIT back-trajectories. They also examine the correlations and ratios between different aromatics in an attempt to recognize the source characteristics (e.g. the use of solvents) and age of air masses. Three distinct source-area categories were constructed based on the back-trajectories which seemed to work well for providing interesting insights into different regional anthropogenic influences and the characteristics of a more diluted regional background. Finally the authors also look at the effect of these aromatic compounds on ozone formation potential.

The methodology and data analyses seem appropriate. Overall, it is an interesting paper relevant for publication in ACP, if the following comments/suggestions are addressed.

General: 1) The samples were taken twice a week, always on the same days of the week (Tuesday and Saturday) and the same hours of day. Despite certain limitations of such a sampling schedule, it is still impressive to have all years' worth of data for aromatic VOCs from South Africa. However, these limitations at least should be mentioned in the text.

We agree with Referee #1 that the sampling schedule was prone to some bias. Obviously, rotating sampling days and hours of the day would have been better. However, logistically it was not possible; hence the selected schedule at least enabled the collection of a full year of data. In order to make sure the readers take note and understand the limitations, the text on page 4194, lines 18-20, under the method section of the published ACPD paper was modified as follows: "Obviously this repetitive sampling schedule, i.e. same days of each week and hours of the day, were prone to some bias.

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Large point sources, i.e. industrial stack emissions, in South Africa are regulated on an availability basis. This implies that off-gas cleaning equipment must be operational a certain percentage of the overall operating time (typically 97-99%) and not on a specific time basis, e.g. specific days or hours that emissions are allowed. It was therefore not possible to set a sampling schedule to capture possible large releases of VOCs by these point sources. Traffic emissions, which can be considered as a point or regional source, depending on the distance between emissions and the measurement site, are another example of a potential time-bound VOC source that had to be considered. At the Welgegund site only a small gravel road, used by a few farmers, are nearby. Local traffic emissions are therefore almost negligible. Large traffic volumes in especially the Johannesburg-Pretoria megacity could be a significant regional source of VOCs at Welgegund. However, since Welgegund is $\sim$100 km west of Johannesburg, it was difficult to set a sampling schedule to capture time-bound emissions that are transported at different rates and days with different meteorological conditions. Considering the remote nature of the sampling site and logistical limitations during the sampling campaign, the applied sampling schedule was the most feasible option that enabled the collection of data for a complete year."

a) Could there be a strong source that occurred regularly outside the sampling periods (e.g. a potential fugitive emission that is released by an industrial facility regularly on Thursdays)? It might be useful to add just a short clarification about data interpretation and the possibility of missed emissions.

We agree with Referee #1 that it is necessary to clarify whether strong sources (be it point or area sources) could have been missed due to the sampling schedule. This concern was already addressed in the reply above to the General comment number 1.

b) Would there be expected any consequences from sampling outside of the traffic rush hours? I am also curious if there were any differences between the Tuesday data and Saturday data?

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We agree with Referee #1 that it is necessary to clarify whether traffic emissions were missed due to the sampling schedule. This concern was already partially addressed in the reply above to the General comment number 1. Additionally, the text in lines 18-23 under the "Results and discussion" Section 3.2, page 4198, of the published ACPD paper was modified to read: "Although samples were collected during daytime and night-time in order to identify possible diurnal influences, results indicated no statistically significant differences in the concentrations of aromatic hydrocarbons measured during daytime and night-time. Also, no statistically significant differences were observed between Tuesdays and Saturdays. This indicates that there are no major local sources such as traffic that would result in a distinct diurnal pattern. Therefore, no distinction in the results was made in subsequent sections based on daytime and night-time, or day of the week."

c) It could be interesting to see the diurnal variations if such data even for the short period are available or this could be an idea for future measurements.

Unfortunately no additional data was gathered outside the specified sampling periods and we can therefore not present a tentative diurnal cycle. We do, however, recognise the importance of such data, considering the lack of data for this region as pointed out by Referee #1. In order to bring this matter to the attention of the readers, the text in lines 20-23 under the "Conclusions", page 4206, of the published ACPD paper was modified to read: "No statistically significant differences in the concentrations of aromatic hydrocarbons measured during daytime and night-time, or during Tuesdays and Saturdays, were found. This indicated the lack of local sources. However, it should be regarded as an important future perspective to set sampling schedules that would eliminate all possible time-bound biases. This could be achieved with continuous online analysis, which would also enable proper assessment of diurnal cycles and specific case studies."

2) There seems to be a small inconsistency in using mean and median in the manuscript. For example, the annual NAAQS standard for benzene is expressed as

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average but it is compared to the measured median value. If the pollution events are episodic it might be that the mean is much larger than the median. However, I like the box plots in Fig. 2 which contain both, and I find particularly interesting very high monthly mean values of benzene concentration in May and November which could be worth discussing further (e.g. for specific pollution episodes). Generally, the mean and maximum values are mostly not discussed but might serve additional interesting information potentially worth discussion.

We thank Referee #1 for pointing out this inconsistent use of mean and median. It is true that mean values should be compared to the NAAQS, but median values also have statistical value. To address the inconsistent use of median/mean in the context of the NAAQS comparison, we have added the mean values in the text under Section 3.1, but have kept the median values in brackets. An example of how the text has been modified, specifically in lines 11-13, page 4198 of the published ACPD paper is: "The Welgegund annual mean (median) benzene concentration was 0.29 (0.13) ppb, which is well below the SA standard." The text was similarly modified for all the other compounds discussed in Section 3.1, where previously only median values were given.

As pointed out by Referee #1, we specifically used box and whisker plots in our figures to indicate proper statistical representation of the data, instead of just giving mean and/or median values. This statistical spread of data will hopefully make the data more useful for the scientific community, especially considering the current lack of data for this region. However, in most of our discussions were referred to median values, since we believe it to be representative, ignoring possible outliers. As correctly pointed out by Referee #1, it would be possible to consider specific case studies where there were large differences between the median and mean values, e.g. "benzene concentration in May and November". As stated earlier by Referee #1 "VOC data for Africa, in particular on the atmospheric abundance of aromatic compounds, are essentially unavailable". Specifically for this reason, we attempted in this paper to present an overall statistical perspective of the data, possible source(s) and source regions and O3 formation po-

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tentials, but did not consider specific case studies. If Referee #1 permits, we would prefer not to extent the scope to include such possible case studies.

3) Conclusions seem to have a potential for improvement. The current version contains some unnecessary repeated material that perhaps does not need to be highlighted, while the most interesting points and take-home messages could probably be stronger emphasized. See also comment #18 for some example specific changes that could be considered.

We have critically considered the "Conclusion" and agree with Referee #1 that it is in general too long with unnecessary repetition of results and that it does not make recommendations for future measurements. To address this, we have shortened the conclusion from 532 words in six paragraphs to 406 words in four paragraphs, which also includes two well defined recommendations, i.e. i) the inclusion of more aromatic hydrocarbon in the national air quality legislation, as well as ii) more such measurements in higher resolution to also elucidate diurnal cycles and make case studies possible.

Specific: 4) Page 4190, Line 21: Consider providing the range also for mean values (e.g. in parentheses).

We agree that also providing mean values/ranges (in parentheses) in addition to the median values/ranges in the Abstract would improve the paper. This was done everywhere in the Abstract, i.e. lines 21 and 23 on page 4190 of the published ACPD paper.

5) P4190 L22 Insert the value of the local air quality standard and over what time range it corresponds to.

We agree with this recommendation and have modified the text to read: "Benzene levels did not exceed the local air quality standard limit, i.e. annual mean of 1.6 ppb."

6) P4190 L23 Consider adding also annual mean concentration value (e.g. in parentheses).

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We agree. This was done, as indicated in our response to “Specific” comment number 4.

7) P4190 L25 “proved” should probably be “indicated”

We agree and have replaced “proved” with “indicated” in the text.

8) P4192 L3 “consist” should be “consists”

Thanks for picking this up. We have replaced “consist” with “consists” in the text.

9) P4191 L16 Replace “pollutant species” with “pollutants”. In general the use of the word “species” seems excessive and sometimes can be confused with biological species. Consider replacing some of them with “compound”, “chemical”, etc.

Thanks for highlighting the excessive use of the word “species”. We also agree that it can be confused with biological species. We have totally eliminated the use of the word “species” by i) replacing it with the words compound(s) or hydrocarbon(s) or ii) deleting it completely, e.g. replacing “pollutant species” with “pollutants”.

10) P4194 L21-24 How was the metal part of the inlet joined with the Teflon inlet part? What was the temperature of the Teflon section?

The Teflon section was joined to the stainless steel section with a stainless steel male-to-female Swagelok connection. The last bit of the stainless steel section and the entire Teflon section of the inlet was not heated. The text related to this matter, on page 4194, lines 21-24, was modified to read: “The first 1.2 m of the stainless steel section of the inlet was heated to 120°C using heating cables and thermostats (Thermonic) to remove O3 that could possibly lead to sample degradation (Hellén et al., 2012). The last 0.05 m of the stainless steel section and the entire Teflon section was housed within the measurement container, wherein the temperature was regulated at 24°C.”

11) P4196 L19 Spell out the acronym HYSPLIT.

The text was modified to first spell out the acronym and now reads as follows: “In-

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dividual hourly back trajectories were calculated with the Hybrid Single-Particle Lagrangian Intergrated Trajectory (HYSPLIT) version 4.8 model, developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (Draxler & Hess, 2004)."

12) P4199 L5 you probably meant aromatic hydrocarbons, not "aromatic carbons".

Thanks for pointing this out. The text now reads: "The reason for these higher levels of aromatic hydrocarbons observed during these two months will be explored in Section 3.3."

13) P4201 L22 consider replacing "will" with "can"

We agree that "can" will be more appropriate than "will" in this context. The text now reads: "This longer travelling time can result in the increased oxidation of the aromatic hydrocarbons."

14) P4201 L25 "Aromatic hydrocarbons measured in air masses from the Regional Background... may also be associated with natural emissions (e.g. Heiden et al., 1999)." These emissions would be very interesting and novel, in particular that you do see smaller number of aromatics intercorrelated over the regional background while there toluene seems anticorrelated with CO and NOx (Fig. 7c). Although it might probably be still difficult to separate those from anthropogenic influences, I wonder, if you can see correlations or coincidences with elevated temperatures? Would it be possible to add the temperature trace to Fig 8?

Heiden et al. (1999) proved that some plant species release toluene. Of the species evaluated by Heiden et al. (1999), only sunflower is relevant to the situation at Welgegund – sunflower is the second most common crop species in the area. It would therefore indeed be novel/interesting to prove/disprove that natural emissions (construed as being represented by sunflowers, which is not a natural species) of toluene are significant/not significant. Heiden et al. (1999) stated that significant diurnal varia-

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tion of toluene emissions from sunflowers occur, with daytime emissions being a factor of 2 higher than night-time emissions. According to Heiden et al. (1999) the difference between daytime and night-time emissions can be due to differences in PAR and/or T. Since source regions I and II are strongly anthropogenically influence, it would be most appropriate to test the possible natural contribution to toluene concentrations in the Regional Background. Therefore, Figs. 7a-c were augmented by added T also to the correlations. Text after line 15, page 4203 was added, which reads: "Additionally, the natural emissions of aromatic hydrocarbons were also explored. Heiden et al. (1999) proved that certain plant species release toluene. Of the species evaluated by Heiden et al. (1999), only sunflower is relevant at Welgegund, since sunflowers is the second most common crop species in the area. Heiden et al. (1999) stated that significant diurnal variation of toluene emissions from sunflowers occurred, with daytime emissions being a factor of two higher than night-time emissions. This was attributed to either differences in PAR and/or T between daytime and night-time. As is evident from the Fig. 7c toluene did not correlate or anti-correlate with T for the Regional Background. Therefore, although it is not impossible that vegetation contribute to toluene concentrations measured, it does not seem to be the major source."

Additionally, as requested by Referee #1, the average temperatures during the sampling periods were added to Fig. 8. However, we do not consider the addition of this temperature trace as adding significantly to the above-mentioned discussion on the possible contribution of vegetation to aromatic hydrocarbon concentrations. The addition of the temperature trace to Fig. 8 does however support the statements that TEX concentration varied seasonally due to evaporation rates being influenced by temperature. Therefore, the text in line 28, page 4204 to line 2, page 4205 of the published ACPD paper was amended to read: "The ratios show a seasonal pattern with the maximum values in summer and minimum in winter. This is similar to the observation made by Rappenglück and Fabian (1999) who reported that the evaporation of solvents makes a greater contribution to atmospheric VOCs during summer. The average temperatures measured during the sampling periods, as presented in Fig. 8, also in-

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dicate a similar pattern than the TEX concentration ratios. This further supports the hypothesis that TEX concentrations are strongly influence by the effect of temperature on evaporation rates."

15) P4202 L2 "each other" should be "one another"

We agree that "one another" will be more appropriate than "each other" in this context. The text now reads: "... to correlate the concentrations of the different aromatic hydrocarbons measured to one another, as well as to trace gas concentrations ..."

16) P4202 L28 Please revise this sentence as to what was related and what unrelated "Therefore, it seems that the sources of benzene and toluene were related, while the sources of the other aromatic hydrocarbons were related."

We agree that this sentence could be confusing and have modified it to read: "Therefore, it seems that benzene and toluene had a similar source(s), while the other aromatic hydrocarbons had a different source(s)."

17) P4204 Sect. 3.5 a) Regarding the inter-compound ratios, it should be stated in the text whether the medians or means were used to derive them.

The text (line 19-21, page 4203) was modified, as to clearly indicate that average values were used: "The inter-compound ratios of the average atmospheric concentrations of aromatic hydrocarbons with benzene are presented in Table 1."

b) The ratios between different aromatics (e.g. shown in Table 1) are the annual ratios. Was there any variation in those ratios on the weekly, monthly basis? If so this might be very interesting to show, for instance, on a graph for each source region, as this could provide an indication of how the specific source contributions varied within each source region.

We agree with Referee #1 that it would be nice to indicate the variation of the aromatic ratios as a function of time, e.g. weekly or monthly. However, as is evident from Fig. 5, which indicates the fractional distribution of air mass back trajectories passing over the

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defined source regions (Area I, Area II, Regional Background and Mixed), air masses did not pass over all source regions every month. As an example in May, April, Oct and Nov'11 no air masses passed over Area I. We therefore believe that the dataset is too small to present meaningful temporal variations of the aforementioned ratios.

18) P4206-4207 The conclusions could be expanded to encourage more such measurements, and perhaps could suggest incorporation of national thresholds for toluene and other hazardous pollutants which showed the highest concentrations in the region. On the other hand, there are potentially redundant sentences which might not be necessary and could be removed for achieving more coherent message. One example of an unclear sentence which may be distracting is "For air masses that had passed over the Regional Background, benzene and toluene were again linked, but the sources of the other aromatic hydrocarbon species were not necessarily linked." It is unclear what you mean by "linked benzene and toluene". As correlation does not imply causation, it might be better to refer just to the correlations. In any case, there is no need to summarize the entire paper, but it would definitely be worth including the most interesting key findings and take-home messages. Finally it would be nice to see some recommendations for the future studies.

We indicated under the general comment number 3 how this was addressed.

19) Fonts in some figures could be enlarged, in particular, I could hardly read Fig 6.

We agree with Referee #1 that the text sizes of the legends/captions/scales in most figures were too small after the page setting of the ACPD paper was done. Since the figures will be a similar size in the ACP paper, we have enlarged the text sizes to be clearly legible in all figures.

20) Figure 7a-c. These are nice figures! If possible enlarging the numbers on the color scale could be helpful.

As indicated in the previous comment, we have enlarged all legends/captions/scales

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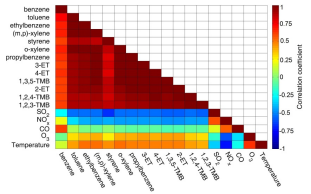
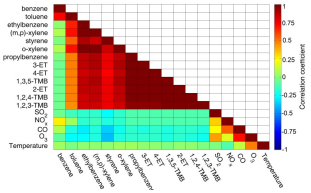
text sizes.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 4189, 2014.



(a)



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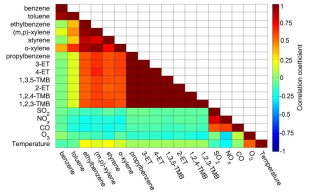

(c)

Fig. 1. Figure 7. Correlation analysis for aromatic hydrocarbons with one another and with inorganic trace gases, in samples that were collected when back trajectory sets had passed over Area I (a), Area II (

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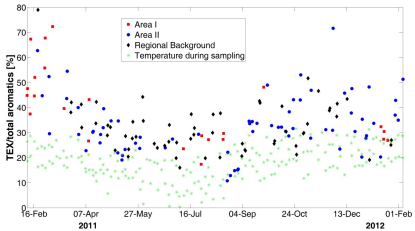

Figure 8. Temporal variation of the concentration ratios of the sum of toluene, ethylbenzene and xylenes (TEX) to total aromatics from air masses arriving at Welgegund after passing

Fig. 2. Figure 8. Temporal variation of the concentration ratios of the sum of toluene, ethylbenzene and xylenes (TEX) to total aromatics from air masses arriving at Welgegund after passing

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