

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

K. Jaars et al.

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We thank Referee #2 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 #2.

Anonymous Referee #2 Received and published: 15 April 2014

This work by Jaars et al. presents a years' worth of aromatic hydrocarbon measurements at a rural site in South Africa and an analysis of the sources of the observed hydrocarbons at the site. The authors use back trajectory analyses, dividing the source region into three distinct sectors, use hydrocarbon ratios and correlation coefficients

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to explore hydrocarbon source types, and estimate ozone formation potential from the aromatic hydrocarbons observed. The authors also argue for NAAQS to include more than just benzene in the air quality standards, as toluene is clearly a more significant air pollutant in the region.

General Comments: The authors did a very thorough job of introducing the topic of BTEX measurements and laying the ground-work for why this work should be published, i.e., that there is a knowledge gap in the literature for BTEX measurements in southern Africa, particularly in South Africa. The back trajectory analysis is a good method for investigating the lack of seasonal cycles in the observations, and for creating a framework for the overall analysis of the data collected at the site. Overall, this paper provides information that is useful and relevant, and should be published, following a number of changes outlined below.

Specific: 1) Page 4190, lines 5-6 - Measurements of (what?) were conducted? Be specific.

We agree with this recommendation and have modified the text in the abstract to read: "Measurements of aromatic hydrocarbons were conducted at the Welgegund measurement station (South Africa)"

2) Page 4190, line 29 and page 4191, line 4 – Anthropocentrically is not the correct word to use here. It means "1. Regarding humans as the central element of the universe. 2. Interpreting reality exclusively in terms of human values and experience." Even if it is true that the region is anthropocentric, which is applying a very specific term to a rather broad region, this is not a sociology paper, and the word anthropogenically is a more appropriate word.

Thanks for pointing this out. The text now reads: page 4190, line 29 "... in general significantly higher in air masses that passed over anthropogenically ..." and page 4191, line 4 "...formation potential was also observed in plumes passing over anthropogenically impacted ..." 3) Page 4191, line 6 – "Atmospheric measurements" of what? Be more specific. Gasphase chemicals? Air quality indicators? Particles? Air temperatures and weather patterns?

We agree and have modified the text to read: "Atmospheric measurements, which include but are not limited to, speciated volatile organic compounds and other trace gasses, as well as size resolved aerosols are well established in developed countries. However, less emphasis is placed on such environmental issues in developing countries, since resources are mostly utilised for economic growth."

4) Page 4193, lines 2-3 – to avoid confusion, add "in this region" or something similar after "conducted a study".

We agree and have edited the text to read: "Lourens et al. (2011) conducted a study in this region on BTEX concentrations ..."

5) Page 4198, lines 3-4 "...since toluene levels are usually two to four times higher than benzene concentrations." – although this statement backed up with three references, the claim is too broad and requires more qualifiers. There are MANY situations globally where benzene concentrations are higher than toluene, so please specify where and/or under what circumstances toluene is higher than benzene.

We agree with Referee #2 that this statement is not well defined. However, there are very limited peer reviewed public domain papers on aromatic hydrocarbons for South Africa. The only other paper for this region (Lourens et al., 2011) also found ambient toluene to be higher than benzene in the interior of South Africa. We therefore prefer to delete the references to the papers from dissimilar environments and have simplified the text of lines 3-9 to read: "Lourens et al. (2011) also reported ambient toluene concentrations to be substantially higher than that of benzene over the interior of South Africa. Considering that toluene also has negative effects on human health, as well as that it is a precursor for O3 and secondary organic aerosol formation, it should be considered to be included in future South African air quality legislation."

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6) Page 4203, line 29 – I have serious issues with this statement. One publication from almost 20 years ago from one city (Rome) does not constitute an absolute. I see that there is a second reference to the T/B ratio in Table 2, but again, this is from 20 years ago, and is also from Europe. To say that a value of 2.7 for the ratio of toluene to benzene is "usually an indication of fresh emissions from traffic" says nothing about the fleet of vehicles in question or the relative make-up of the gasoline/diesel mixture in the studied region. If the authors want to say something about the typical toluene/benzene ratio in the emissions of the vehicles in the region in question, they should cite something from that region, otherwise, they need to present a survey of the typical T/B ratios from regions with vehicular emissions that are expected to be similar to South African vehicles, and explain why.

We agree with Referee #2 that one old (20 years) publication does not constitute an absolute. Unfortunately the T/B ratio for the unique South African vehicle fleet (containing a substantial fraction of older vehicles) has not been determined. It is also difficult to get information regarding the composition of the South African fleet and the T/B ratio can therefore not be compared to another country with a similar fleet. The text related to this matter was edited and now reads: "Globally a T/B ratio below 3 was found to be characteristic of fresh emissions originating from traffic, while a T/B ratio > 4.3 is typical for solvent sources (Lan et al., 2013 and references therein)."

7) Page 4205, lines 2-6. There seems to be a gap in the analysis here, specifically considering the varying lifetimes associated with aromatic hydrocarbons. It is entirely possible that the seasonal cycle that is attributed to solvent evaporation is simply due to differences in different aromatic hydrocarbon lifetimes between summer and winter. The authors should provide some simple modeling to show, given a constant emission of aromatic hydrocarbons, what the temporal TEX/total aromatics would look like for each region, and only \*then\* can they say that "it is clear" that solvent evaporation is contributing significantly to their observations. Otherwise, this entire paragraph is very hand-wavy and is not at all backed up, as pointed out in the last sentence of the

paragraph "the magnitude of the contribution was not determined from this data."

We agree with Referee #2 that it is possible that the seasonal cycle that is attributed to solvent evaporation could simply due to differences in aromatic hydrocarbon lifetimes between the seasons. However, if Referee #2 permits, we would prefer to keep Fig. 8 in the paper, since Referee #1 specifically asked that a temperature trace be added to this figure. Although we are currently not in a position to model the temporal TEX/total aromatic ratio, we have altered the text to make it clear to the readers that the observed temporal variation can be due to aspects other than solvent evaporation rates. The text now reads: "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 indicate a similar pattern than the TEX concentration ratios. This further supports the hypothesis that TEX concentrations are strongly influenced by the effect of temperature on evaporation rates. Although not tested in this paper, it is however also possible that the differences in aromatic hydrocarbon lifetimes between the different seasons could result in the aforementioned temporal pattern."

Additionally, we have deleted the text in line 2-5, page 4205 of the ACPD paper "It is therefore clear that aromatic hydrocarbons originating from solvents make a contribution to aromatic hydrocarbons in air masses that had passed over all three source regions, including the Regional Background. However, the magnitude of this contribution was not determined from this data."

Technical Corrections: 1) Page 4192, line 4 – Since it is technically o-xylene, m-xylene and p-xylene, it is more appropriate to write "o-, m-, and p-xylene" here.

Thanks for pointing this out. The text now reads: "... toluene, ethylbenzene o-, m-, and p-xylene (BTEX) are the most commonly ..."

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2) Page 4192, lines 8-9 – "producing peroxyl radicals (RO2)" should be "producing peroxy radicals (RO2)".

We agree and have modified the text to read: "... are oxidised by the hydroxyl radical (âĂćOH) in the troposphere, producing peroxy radicals (RO2âĂć) and hydroperoxy radicals (HO2âĂć) that then oxidise ..."

3) Page 4193, line 19 – this should read "100 km west of Johannesburg".

Thanks for picking this up. We have replaced "from" with "of" in the text.

4) Page 4194, line 18 – remove "in order".

Thanks for pointing this out. The text now reads: "The VOC measurement campaign was conducted for one year (9 February 2011 to 4 February 2012) to observe seasonal variability."

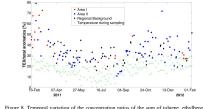
5) Page 4201, line 6 – aforementioned is one word, not hyphenated.

We have edited the text to read: "The aforementioned postulation is strengthened"

6) Page 4205, line 13 - remove "on" from Tropospheric O3 impacts on air quality. . ."

We agree and have edited the text to read: "Tropospheric O3 impacts air quality, food security"

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



2 Figure 8. Temporal variation of the concentration ratios of the sum of toluene, ethylbenzer 3 and xylenes (TEX) to total aromatics from air masses arriving at Welgegund after passing

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**Fig. 1.** 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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