

Interactive comment on “The impact of monoaromatic hydrocarbons on OH reactivity in the North Sea boundary layer and free troposphere” by R. T. Lidster et al.

Anonymous Referee #1

Received and published: 21 January 2014

This is an interesting paper which presents airborne and ground based measurements of monoaromatic hydrocarbons using two systems a GC-FID and a GCxGC ToF. The authors show that a suite of normally unmeasured aromatic species could be quantified from canister samples at very low detection limits using the GCxGC ToF. Furthermore the authors suggest that these oft neglected species can contribute significantly to the atmospheric total OH reactivity. It is well written and structured, and certainly suitable for ACP provided the points below are addressed.

1) For the assessment of the OH reactivity or toluene equivalence for that matter it is critical to apply the correct rate coefficients. The reaction of toluene with OH has

C11295

a weak negative T-dependence, i.e. the colder the temperature, the faster the reaction. For lower pressures, though, the amount of redissociation would go up a bit. The authors should specify exactly what rates have been used and state whether the reactivities calculated for the aircraft measurements have accounted for the pressure and temperature at the point of sampling i.e. low temp and pressure). Whether these compounds become more important to reactivity at higher tropospheric altitudes, would be an interesting discussion point to add. Perhaps a table can be added to give the coefficients used with references?

2) Canister sampling of VOC is prone to artifacts, particularly for the larger semi-volatile species which are the focus of this study. Alkenes have been observed to increase over time in canisters while other species decrease. It would be good to include this point in the experimental section adding whatever longevity tests have been performed. This is a potential source of error for reactivity arguments that come later and should be mentioned. Have blanks been performed, i.e. canisters pumped up with scrubbed air and sampled? Or perhaps the two systems have been used to measure ambient air directly while taking canisters in parallel for later analysis?

3) The authors claim that the normally unmeasured suite of monoaromatic species represent a significant fraction of the missing reactivity determined in the TORCH campaigns. In order to assess this claim we need to take into account the total uncertainty of both the OH reactivity measurement itself and that of the summed individual measurement at these rather low levels. Error bars on Figure 9 would already help in this regard but better would be a bar chart breakdown of the contributions to reactivity (in s⁻¹) with error bars as this would show the relative importance of the “new” monoaromatic species to the other main species measurements from the campaign. On page 32434, the authors suggest that the ratio of toluene to the heavier monoaromatic VOC loading reported here could be used by others (who have perhaps measured only toluene) to extrapolate an estimate of the monoaromatic loading which they claim it is a significant fraction of the free tropospheric reactivity. Although this is discussed later I think it

C11296

would be prudent to insert the caveat immediately “assuming the ratios measured off the UK coast are globally applicable” or “assuming similar emission ratios to those in the UK/European region”

It seems to me unfortunate that the authors have chosen J to denote the equivalent mixing ratio of toluene (Jtol) as it could in future studies become confused with photolysis rates. Perhaps Toleq or another alternative could be used? Page 32436, line 22. Surely it depends on the time since emission rather than the distance which works assuming a wind to be present. How about “with air mass age”?

Secondary points Abstract - comma after “however”, line 2

Introduction first sentence, a reference would be appropriate here, perhaps the review article of Heard and Pilling ? Likewise general references for ozone and SOA production can be added in the second line.

Introduction, p32424 – Line 25, here there is no need to shorten OH concentration to [OH] within the text.

Introduction, p 32425, line 25, it would be good to insert “always” between not and fully. To indicate that although many studies show evidence for unaccounted for reactivity, there are also other that show total reactivity matching the sum of the individual reactivities within experimental error.

Experimental - The canisters used have been coated with a layer of silico steel. Were the lines leading to the canisters also silico steel or only stainless steel as line 18, page 32428 implies. Please specify, text presently unclear.

Page 32428, line 2. Typo –“radicals” should be “radical”

Page 32430 for both instrument descriptions it would be informative to give how long each sample takes to analyze on each system. Likewise although detailed LOD information is given later in Table 1, it would be good to include overall accuracy and precision information for both systems in the experimental section so that the reader

C11297

can already appreciate the general comparative differences.

40 psi is not an SI unit please either replace or give alternative.

Page 32429 line 16. Need to add SI units to 1/16” (ID or OD?)

Page 32430, line 5. Comma after the however. Also page 32432 line 25

Page 32435 last line, comma after the however.

Page 32433, line 4 replace “improved” with better

Page 32433 perhaps replace manifest with appear?

Page 32435 line 24, an “in” is missing before Fig 7.

Page 32440 line 7, “bring” should be “bringing”

Page 32438, line 11 The error on the OH reactivity measurement of Ingham et al. should be given here i.e. $1.9 \pm ?$ so the reader may assess how much reactivity really remains open.

Figure 9 needs error bars.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 32423, 2013.

C11298