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Comment on acp-2022-86

Anonymous Referee #2

Referee comment on "Reversible and irreversible gas–particle partitioning of dicarbonyl compounds observed in the real atmosphere" by Jingcheng Hu et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-86-RC2, 2022

Jingcheng Hu and co-authors have measured the gas-particle partitioning of dicarbonyl compounds, especially glycol and methylglyoxal, at field sites in China. This is a highly relevant topic for the readership of ACP. As far as I can tell (being a computational chemist, not an experimentalist), the study is well carried out, and the manuscript is well written. I can thus recommend publication subject to some fairly minor revisions.

Detailed issues

-The authors spend a lot of time pointing out that the measured partitioning is much higher than what they call the “theoretical” values - the latter seem to correspond to values obtained for the partitioning coefficient (or Henry’s law constant) of pure molecular glyoxal and methylglyoxal. However, as evident from their own introduction section, it is already very well known that the partitioning of these compounds is driven mainly by various reactions. For example, hydration alone is well-known to increase the Henry’s law coefficient of glyoxal by about five orders of magnitude (as discussed e.g. in Ip et al 2009, https://doi.org/10.1029/2008GL036212, or Kampf et al 2013 cited in the manuscript). The authors contribution to separating reversible and irreversible pathways is substantial and valuable - but just reporting that partitioning is much stronger than the “theoretical” values is not really novel (or even that interesting), and this aspect of the abstract and discussion should be toned down. For example, the speculation about “misidentification” or “discrepancies” around lines 175-180 is not really warranted: we already know mechanisms which can easily explain at least most of the observed deviations from the “theoretical” pure-compound values.

-Concerning the saturation vapour pressures discussed around line 190: are there any estimates of the relative saturation vapour pressures of the reversible vs irreversible products? Both are of course much lower than the saturation vapour pressures of the parent dicarbonyls (this is quite well-known and obvious), but how do the two product sets compare with each other? This would be a very interesting parameter to know in

terms of evaluating the atmospheric impact of the "reversible vs irreversible" competition.

-Line 208: “strong and positive dependence on particle acidity (pH)”. Please be clear here: did the concentration increase with acidity (i.e. with decreasing pH), or did it increase with pH? These are opposite things.