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Interactive comment on "Sources and sinks of acetone, methanol, and acetaldehyde in North Atlantic air" *by* A. C. Lewis et al.

Anonymous Referee #2

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The paper, 'Sources and sinks of acetone, methanol, and acetaldehyde in North Atlantic Air', by Lewis et al, is a clearly written paper presenting measurements of the three oxygenated VOCs made at Mace Head Ireland during the NAMBLEX campaign.

Reviewer 1 has already highlighted several excellent points, the most notable of which concern the measurements of acetaldehyde and their validity. Therefore this review will focus predominantly on the model study and its conclusions.

It is not entirely clear from the text, but it is assumed that the model study consists of initializing a box model with concentrations of a range of VOCs typical of a polluted source and allowing this model to evolve with time. One also assumes that the model

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study consists of one model run performed at a nominal temperature and surface pressure at a time of year commensurate with the NAMBLEX study period.

1. What was the temperature and pressure of the box model integration? The authors will know that alkoxy radicals formed by the degradation of the precursor compounds identified will in many cases have competing loss mechanisms, e.g. isomerisation, reaction with O2 and bond scission. Integrating the model under different temperature and pressure regimes, whilst still being consistent with air masses largely confined to the marine boundary layer, may yield some subtle but interesting variations in the production rates for these OVOCs. Indeed, model studies integrated using different water vapour levels would also be of considerable value, since water vapour levels experienced by air masses arriving from clean air sectors to Mace Head will vary enormously. Is it possible that under some combinations of pressure, temperature and water vapour, methanol, acetone or acetaldehyde production is maximized? As an aside is there any differences in the ratio of acetone to acetaldehyde as a function of the different sectors sampled? Is there any evidence that this ratio is lower the higher the likely humidity of the air mass?

2. It is clear that the model study has not considered halogen chemistry, but what would be the impact of a chlorine atom level of say 1 x 10ˆ4 molecule cmˆ-3 on the ratios and absolute levels of the three OVOCs under investigation? Does chlorine atom chemistry bias formation of any of these compounds?

3. It is well known that Mace Head is blessed with high levels of iodocarbons such as alkyl iodides. Although I sincerely doubt that they would play a significant role, what levels of higher alkyl iodides would be required to make a modest 5% impact on acetone (from 2 iodo propane for example) and acetaldehyde (variety of higher alkyl iodides). Just to rule this route out would be a worthwhile exercise.

4. When it is stated that methanol is derived continuously from the degradation of methane, it is assumed that the authors refer to the self and cross reactions of CH3O2

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radicals? The MCM has of course generic rate coefficients for these processes, derived from a rather scant kinetic database. It would be a useful exercise to look at the sensitivity of the methanol production and ultimately its concentration to the error in these peroxy radical rate coefficients and product yields. Presumably such an analysis will also affect to some extent the acetaldehyde production yield too? 5. It is emphasized that the modelling study does not attempt to reproduce the levels of species observed and that there must be background levels of acetone and methanol present. Is it not possible given the wealth of data to determine a background concentration for these compounds, especially since there are hydrocarbon data available as well?

6. If 5 is possible, as I think it is, then you can use ratios of these OVOCs to at least see if the model predictions are sensible.

7. Referee 1 makes a good point regarding acetaldehyde; in that the lifetime of this species means that if air masses are many days old, as judged by benzene and toluene ratios, any acetaldehyde must be made within the last few days of the transit to Mace Head. Since the box model study must produce a maximum amount of acetaldehyde from the species present initially, the high levels of acetaldehyde measured warrant more comment from the authors;

It may well be that no clear cut conclusion can be drawn, it may be that the measurements are anomalously high but I would like to see some further exploration of these measurements given the fact that other workers have indeed noted that acetaldehyde is a highly problematic species to measure. For example, would an injection of NOx (from shipping lanes) make a significant impact to the budget? Would a flux of PAN from aloft make an impact?

I would like the authors to consider and respond to these comments before this paper is published.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 1285, 2005.