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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Carbonyl compounds in boreal coniferous forest air in Hyytiälä, Southern Finland" *by* H. Hellén et al.

Anonymous Referee #1

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General Comments: This paper reports original data on carbonyl compound concentrations at a boreal forest site en northern Europe. Twenty two compounds, ranging from C1 to C12, are reported. This is in itself of interest. However, the data are presented summarily, as average individual concentrations or total carbonyl concentrations. Sources and sinks are only discussed in a general sense, little information is given as to the sources of these compounds and the variability in their concentrations at this particular site. Also, no comparisons are made to similar studies reported in the literature. The few tentative conclusions made about sources and sinks cannot be derived from the results. More effort should be made to understand the results and place them in a scientific perspective.

Specific Comments: Abstract: line 8-9: It is stated that: –reactivity with the hydroxyl radical significantly increased the contribution of larger–. It is not clear what is meant

by contribution. Contribution to what?

line 16-17: It is stated that: –the main sinks for–. This has not been shown in the paper. It is also stated (line 20) that: –Due to the relatively short lifetimes of aldehydes and ketones, –. This is a weak statement which is not supported by the text of the paper. Local anthropogenic sources have not been ruled out.

2.2 Sampling and analysis: p.2995, line 4-5: –Detection limits of the compounds varied from 1 ng/m3 to 135 ng/m3.– Please give more information about how these DLs were determined. How many blanks? Average blank values? DL = 3 times stdev? What were the DLs for the most common carbonyls? Also, what is the efficiency of DNPH cartridges for carbonyl sampling? There has been some discussion in the literature specifically about sampling efficiency for formaldehyde.

3.1 Ambient concentrations: p.2995, line 9: It is stated: –contributing to 75% of all measured carbonyls–. I assume you mean 75% by mass.

p.2995, line 10: –Average 24-h concentrations–. These results should be compared to other results reported in the literature. Do the concentrations appear to be on the level of pollution, aged pollution, background concentrations? What is already known and how do these results fit into what we already know? Also, the data should be presented and discussed in more detail in an effort to understand the concentrations and their variations.

p. 2995, line 22, 24 and thereafter: In discussing equivalent concentrations, it is unclear what you mean and what the significance of the exercise is. At one point you use –carbonyl reactivity– and at another –OH-reactivity–. How are they different and do either of them express what you really mean? It is stated that: –Although the concentrations of heavier C5-C12 aldehydes were lower than the light aldehydes, their contribution to local photochemistry is important due to faster reactions with the hydroxy radical.– The concentrations are then scaled by equation (1) and the statement made –The contribution—-to the total carbonyl reactivity was 34%.– Equation (1) only takes

ACPD

4, S938–S942, 2004

into consideration the reaction with OH. Neither photolysis nor reactons with ozone or the nitrate radical are included. These you discuss in section 3.3, and some of these pathways are important for some of the compounds. Therefore, Ceqv does not give a full measure of their contribution to local photochemistry, or more accurately, local carbonyl photochemistry, or total carbonyl reactivity. Ceqv is an equivalent concentration with respect to OH-reactions, and that is all. Even HCHO is photolysed faster than it reacts with OH. What does that do to the interpretation of Ceqv.? Also, what do you really mean by –total carbonyl reactivity–? What you show is that the heavier aldehydes, while contributing only 10% to the total carbonyl mass concentration, account for 29% of the carbonyl reactions with OH (Numbers come from Fig 1. I cannot find how you got 34%). In the next sentence MHO is stated to comprise –12% of the total OH-reactivity–. I assume you mean the same thing as when referring to carbonyl reactivity. That is, that MHO accounts for 12% of carbonyl reactions with OH? This is not total OH-reactivity since OH reacts with other compounds as well. Finally, one wonders, what is the purpose of this exercise? What useful information do we get from it? It would be of some interest to include aromatic hydrocarbons, monoterpenes, and carbon monoxide in this comparison. That is, with what do most of the OH-radicals react at this site? One more thing. I assume that the calculated Ceqv varies over time as the ratio between individual carbonyl compounds and HCHO varies. It would be of interest to know the variability of Ceqv for the individual carbonyls. How solid are your conclusions? It should also be made clear in Figure 1, that the numbers are average contributions to the average total concentration and total average equivalent concentration.

p. 2996, eq.(1): Define the terms in the equation and make clear how the averaging procedure was done when calculating percent contributions.

p. 2996, l.6-7: Figure 3 is presented, showing daily variations of concentrations and temperatures. The figure needs to be commented on. Why is temperature interesting? Is it interesting? Can temperature explain any of the variations in carbonyl concentra-

ACPD

4, S938–S942, 2004

tions? What else might explain them? How about a wind rose? or trajectory analysis? or comment on cloudiness/sunshine, precipitation, boundary layer stability? You discuss photochemistry a good deal. Do absolute or relative (ratios) concentrations vary with meteorological conditions?

p.2997, l.21-25: It is stated that –The uncertainty in estimating quantum yields is demonstrated– and –For acetaldehyde quantum yields varied—-at wavelengths 290-330 nm–. I am confused. The uncertainty found in the literature, was this different quantum yield values for different wavelengths, or different values for the same wavelength? Obviously, quantum yields vary with wavelength and you need information about that variation as well as the variation in absorption cross section, and actinic flux for each relevant wavelength interval over the course of the day. This is something I assume you use in equation (2). Yes? Please explain more clearly what you have done.

3.3 Lifetimes: p. 2998, line1-2: It is stated that: –For most of the compounds, the main sinks—-are expected to be reactions–. Why? Later in the discussion you mention wet scavenging and deposition as well as dry deposition as being important sinks. So, if there are no measurements or calculations for these loss processes, how do you know that these sink processes are less important than photochemistry, especially at a northern site and in early spring when sunlight is relatively scarce?

3.4 Sources: Most of this section is a general discussion of sources with a few references to correlations between individual carbonyls in the data set. There is very little support for statements of the kind –The main source of these light carbonyls in Hyytiala is probably the oxidation of higher hydrocarbons– (p.2999, line 15-16). A more thorough analysis of possible sources at this particular site would be of interest. What are the anthropogenic sources in the different wind sectors? What was the meteorology, especially wind and air mass trajectories? No conclusions can be made from the present discussion.

ACPD

4, S938–S942, 2004

4. Conclusions: p. 3002, line 3: It is stated that: –contribution from higher molecular weight aldehydes and ketones increased–. As discussed above: contribution to what is not clear. p. 3002, line 12-14: –Main sinks for most–. As discussed above, there is not evidence in this paper to warrant such a conclusion.

p.3002, line 15-19: –Because of the relatively short lifetimes—-secondary production—-are expected to dominate–. There is no real evidence in the discussion to warrant even this rather weak statement. That –some small local anthropogenic sources—-may also exist– compromises the attempt at a tentative conclusion in the preceding sentence. More effort should be made to identify and quantify the anthropogenic sources.

Technical Corrections: I would add some commas here and there, and there are a few questionable choices of words and grammar, but nothing really terribly serious.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 2991, 2004.