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Atmospheric Chemistry and Physics
Discussions

# *Interactive comment on* "Historic records of organic aerosols from a high Alpine glacier: implications of biomass burning, anthropogenic emissions, and dust transport" *by* C. Müller-Tautges et al.

**Anonymous Referee #2**

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The paper reports on the concentrations of various organic compounds ($\alpha$-dicarbonyls, carboxylic acids or carboxylates) and calcium analysed along an ice core drilled in the Grenzgletscher (Swiss Alps) and covering the period 1937-1994. Results are discussed in terms of anthropogenic and biogenic emissions as well as burned vegetation area over the last 60 years. Whereas such a large array of organic species is rarely documented in ice cores and from this point of view merits to be published, there are many weaknesses in the paper as it stands. In addition to miss a few previous works and important conclusions (minor criticism), there are several misleading wordings and

the text contains too many uncomfortable abbreviates rendering the understanding of the text sometimes difficult. Furthermore, the discussion of data is not enough argued. Therefore, given the interest of these kinds of organic data in ice, I would recommend to authors to work further their data discussion in view to reach a sufficient level of usefulness to be published in the ACP journal.

Missed previous works and conclusions:

Your statement "For the first time, long-term records of the carboxylic acids and dicarbonyls as well as their source apportionment are reported for Western Europe" is not correct for carboxylic acids since Legrand et al. (2003) already extensively discussed the budget of formic acid in the Alps concluding that vegetation emissions largely dominate anthropogenic emissions (vehicular emissions of alkenes). The trend of C2-C5 dicarboxylic acids was also discussed in terms of anthropogenic versus natural sources over Western Europe (one third and two thirds, respectively) by Legrand et al. (2013). Finally the long-term trend of polyacids (HUmic LIke Substances, HULIS) was discussed by Guilhermet et al. (2013) in the study of an ice core extracted from the Mt Blanc. More generally concerning previous works, I think that the idea of your Table 2 was (and it is legitimate) to summarize organics measured in ice (including those in this work and the previous ones) related to at least aldehydes and acids. If so, you missed species discussed in the following paper that includes HCHO (the dominant aldehyde in ice), short-chain monocarboxylates other than formate (lactate, acetate, glycolate, and glyoxylate), short chain dicarboxylates other than oxalate (malate, malonate, succinate, and glutarate) as well as polyacids (HUmic LIke Substances, HULIS).

Legrand, M., S. Preunkert, B. May, J. Guilhermet, H. Hoffmann, and D. Wagenbach, Major 20th century changes of the content and chemical speciation of organic carbon archived in Alpine ice cores: implications for the long-term change of organic aerosol over Europe, J. Geophys. Res. Atmos., 118, doi :10.1002/jgrd.50202, 2013.

All your discussion in section 3.3.3 missed to introduce a key point related to the effect of pH (not only the effect of calcium) on deposition of formate as already detailed for the case of Alpine ice cores by Legrand et al. (2003).

Misleading wording

The title of the paper is misleading since species like formate (in fact formic acid) is a gaseous atmospheric species not an aerosol species: see the paper from Preunkert et al. 2007 who examined the gas/particulate phase of formic acid nearby the Mt Blanc summit (French Alps) (see also references therehein on previous works done at Sonnblick by Kasper and Puxbaum). The rest of the title is also misleading what means “implications” you mean “influence on their budget” ?

Preunkert, S., M. Legrand, B. Jourdain, and I. Dombrowski-Etchevers, Acidic gases (HCOOH, CH3COOH, HNO3, HCl, and SO2) and related aerosol species at a high mountain Alpine site (4360 m elevation) in Europe, J. Geophys. Res., 112, D23S12, doi:10.1029/2006JD008225, 2007.

The first sentence of the abstract and at other places in the text: Historic records of $\alpha$-dicarbonyls (glyoxal, methylglyoxal), carboxylic acids (C6–C12 dicarboxylic acids, pinic acid, p-hydroxybenzoic acid, phthalic acid, 4-methylphthalic acid), and major ions (oxalate, formate, calcium) were determined. . ..: The wording is confusing since formate (or formic acid) is a carboxylate (or carboxylic acid) and oxalate (or oxalic acid) is a C2 dicarboxylic acid (see also my comment on Table 1). Also for me, calcium, ammonium, nitrate and sulfate are major ions in Alpine ice cores, not oxalate.

The use of abbreviates throughout the text like VAN for vanillic acid or G for glyoxal renders the lecture of the manuscript very difficult. The reader needs to know that G is an aldehyde and that VAN is an acid, please use the chemical name everywhere in the text. The abbreviate used for calcium (CAL) is very confusing and totally un-useful compared to the common notation Âń Ca Âż or Ca2+. When reading a sentence with the abbreviate Âń C6 Âż I think about benzene or cyclohexane etc. So as many chemists are expected to read your paper, please use the normal wording using complete chemical name of compounds.

In Table 1 you separate formate and oxalate from other carboxylate like phthalate etc: I cannot see at all why ?

In Table 3: while I understand that PC4 that includes mainly formate and oxalate merges from the correlation with calcium, I think the wording transport with mineral dust is very misleading. Referring to the paper from Legrand et al. (JGR, 2013) you can say that these two carboxylates mainly originate from vegetation emissions with an effect of the pH of cloud (partly and only partly driven by its calcium level) on their scavenging in snow? See more comments later on your section 3.3.3.

Data Discussion

Your discussion in terms of sources is only based on PCs and leads to strange (conflicting or unexpected) conclusions. This part has to be reworked. I just list below the most critical points that need to be addressed.

Since you stated Âń To obtain annual averages, equal aliquots of the ice sections belonging to a certain year (2 to 9 sections per year) were combined Âż you can therefore report on the seasonality of your organic species. Such information certainly will strengthen the discussions in terms of sources (biogenic and wild fires are restricted to the summer season whereas most of anthropogenic emissions, except domestic wood burning, are similar in winter and summer). Also this will serve to demonstrate that the trends seen in your core are not biased by change of the winter to summer partitioning over the past. That may also permit to address partly the possible post depositional effect. For instance when discussing aldehydes I think you cannot discard the possibility that changes seen with depth for methyl glyoxal is due to destruction of this species in the glacier (aqueous phase oxidation of methyl glyoxal are know to be quite efficient, see Ervens et al., JGR 2004).

The discussion of data using PCs seems to me too strong. Some existing correlations may be driven by something else than the sources.

The correlation with burned area is not obvious at all.

I am surprised that you attributed pinic acid to biomass burning: if so that means that the precursors (pinenes emitted by conifers) have been produced and here I am surprised that vanillic acid is not there ?

In addition to the fact that I don't believe that your signal is restricted to sources located in Switzerland, many organic that you have investigated are also produced during domestic wood burning (a common practice in mountain alpine area) not only wild fires.

Also the presence of azelaic acid suggests me a source emitting precursors like unsaturated fatty acids like oleic acid: so what about cooking in summer during which you emit both wood burning and cooking derived products like fatty acids ?

Methyl glyoxal and glyoxal are produced by oxidation of toluene emitted by cars: any comment in discussing their trends ?

Discussing of formate in section 3.3.3 missed a key point: formate in ice has been incorporated from the gaseous weak acid (formic acid). The dependency of the henry law constant to the pH of cloud has to be considered for past change. Not only the input of calcium from alkaline dust material controls the pH but also the huge acidification of precipitation in Europe after 1940. So at first the decreasing trend of formate is also relative to acidification over the recent decades by growing SO2 and NOx emissions. By the way not that your trend of oxalate is opposite to the ones found at the Mt Blanc glacier ? This oxalate trend is quite unexpected: Are you sure that you have not lost a part of oxalate because of bacterial activity acting during your sampling (many researchers have experienced such a problem).

End of the review

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 13747, 2015.