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Interactive comment on “EVAPORATION: a new vapor pressure estimation method for organic molecules including non-additivity and intramolecular interactions” by S. Compernelle et al.

Anonymous Referee #1

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S. Compernelle, K. Ceulemans, and J.-F. Müller present a new vapour pressure estimation method, EVAPORATION, that can be used to predict pure compound (sub-cooled) liquid vapour pressures of organic compounds. Their new method includes intramolecular and non-additivity effects to better predict vapour pressures of multifunctional organic compounds, important with regard to the partitioning of semivolatile organic aerosols. The EVAPORATION method includes a large number of atmospherically relevant functional groups and covers a wide temperature range. The authors have compiled and assessed a large database of experimental vapour pressure data

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from the literature to fit their model parameters and they critically discuss the problem of disagreement between different measurements in the case of dicarboxylic acids. They also mention the compound classes, for which the available literature data is insufficient, e.g., for hydroperoxides and PANs.

Although the calculation of vapour pressures with EVAPORATION requires more molecular information as input than necessary for simpler group-additive methods, the authors show that a significantly better representation of vapour pressures of multifunctional compounds can be achieved with EVAPORATION. This is especially of interest in the light of new experimental data (e.g., Booth et al., 2010), which suggest that sometimes highly functionalised (oxygenated) compounds have a higher vapour pressure than similar, but less functionalised structures. The authors employ statistical tests to justify the use of second order descriptors in the model when significant improvement can be achieved. They also do a good job in describing possible physicochemical reasons for different structure-related effects.

Since accurate vapour pressure estimation methods are essential for gas-particle partitioning calculations of atmospheric aerosols, this new method is of great interest for the atmospheric chemistry and physics community. The article is well structured, but could be improved at some points regarding the general readability and the graphical quality of the figures. I therefore recommend publication in ACP after consideration of the general and specific comments and corrections listed below.

General Points

1. Two modelling methods for the calculation of (subcooled) liquid vapour pressures are introduced. First, a group-additive method with some additional second order descriptors applicable to non-functionalized hydrocarbons and to monofunctional

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compounds. Second, a method termed “full method” that is improved for the description of multifunctional compounds. It is not clear to the reader, which method is used as the “EVAPORATION” method. Do the authors apply both methods under this name depending on the compound type? Which method has been used for the comparison of monofunctional compounds with experimental data and other vapour pressure estimation methods in Section 5 and corresponding figures (e.g., Fig. 6)? I might have missed it, but it is also not clear to me, whether the authors used the full database including monofunctional compounds for the parameter fitting of the full method. A few sentences concerning these points would help the reader understand what has been done.

2. Related to the point above. If hydrocarbons and monofunctional compounds were also used to fit the parameters of the full method, how do the predictions of the two methods compare for monofunctional groups?
3. While the mathematical expressions for the calculation of vapour pressures with the proposed method are relatively simple, the correct assignment of the different descriptors to a given compound is likely the more complicated step. It might therefore be helpful if the authors present a few calculation examples illustrating the assignments of the descriptors to different compounds, perhaps in an appendix.
4. According to the ACP guidelines, SI units should be used wherever possible. The authors use three different units for pressure in the text and figures (atm, Torr, kPa). I consider this a minor issue, but worth mentioning. While Torr is an often encountered unit for vapour pressure data, there is no reason not to use units of Pa (or kPa).
5. Given the applicability and predictability of the EVAPORATION method for a large variety of organic compounds, this method has the potential to become widely

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used in the community. Do the authors intend to make EVAPORATION available to the wider community, for example via a web-interface?

Specific Points

- Abstract: “a method to predict vapour pressure p^0 ”. At least at this point it would be more correct to write “a method to predict pure compound (subcooled) vapour pressure p^0 ”, as to clearly distinguish it from the vapour pressure of compounds in mixtures or the vapour pressure of a solid. The same distinction should be made at the first occurrence of “vapour pressure” in the Introduction.
- p. 13231, l. 16-19: The sentence at these lines could be understood as if there is no positive aspect of using boiling points with vapour pressure estimation methods. It should also be mentioned why some methods benefit from boiling point data as input.
- p. 13232, l. 18: a pressure-temperature ($p^0(T)$) correlation,” are these correlations e.g. in the form of Antoine Equation parameters? If so, it might be worth mentioning.
- p. 13233, l. 12: “Following groups of compounds can be distinguished:” Here either the rest of the sentence is missing or the whole sentence should be written differently to introduce the different compound classes discussed in the following Sections.
- p. 13235, Eq. (1): No citation for the source of this equation is given in the text. It should also be mentioned that in Eq. (1) the melting point temperature (T_{fus}) is used instead of the (theoretically correct) temperature at the triple point.
- p. 13240, l. 1: “sublimation data of Soonsin et al. (2010) was selected, partly because their data on saturated solutions should be more reliable than data on

solid particles themselves,” This formulation is confusing and needs editing. If the saturated solutions data is more reliable than the sublimation data of solid particles, why would one use the sublimation data (of solid particles) and not the data from the saturated solutions. Of course, the sublimation vapour pressure of the solid particles and the vapour pressures of the saturated solutions should be equal, but that is not what the sentence is saying. What data of Soonsin et al. (2010) have been used, sublimation data of solids or saturated solution data?

- p. 13241, l. 4: With Section 3, there is a somewhat sudden change in topic. It is not clear from the first sentence in this section, why there should be statistical evaluators discussed / introduced at this point. A sentence or two, introducing the idea and use of statistical evaluators later in the model description, would likely enhance the readability of and justification for this section.
- p. 13243, l. 1: “Note that setting $K = 1$ returns the basic Clausius-Clapeyron equation under assumption of a temperature-independent enthalpy of vaporisation, valid only in a small temperature interval.” It might be worth mentioning that with $K = 1$, Eq. (13) is also known as the August Equation.
- p. 13243, l. 7: It should be noted that “term A is directly related to the entropy of boiling” at 1 atm total pressure.
- p. 13244, l. 5: At this point in the text, it is unclear for a reader what the authors mean by “first-order group contribution” and “second-order corrections”. Please explain.
- p. 13244, l. 6: “and c_k are descriptor values of the molecule. A descriptor is a property of the molecule that is readily obtained or calculated, e.g. the number of times a certain functional group occurs.” These two statements can lead to some confusion concerning the meaning and use of the terms “descriptor” and “descriptor values” as later in the manuscript it seems that the descriptors are

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actually the accountable molecule properties listed in Tables 2 and 4, indexed by k (attributed with specific a_k and b_k values). See also the statement on line 2 of page 13245. Could the set of c_k be described as a molecule-specific list (vector) with entries that relate to the number of times a certain “descriptor k ” has to be accounted for, i.e., by evaluating column 1 of Tables 2 and 4?

- p. 13245, l. 22 (Eq. 24): While I agree with the authors’ conclusion that the “#observables” in the definition of degree of freedom, df , should be related to the “(number of species where descriptor occurs)”, I wonder why in a similar sense “#parameters” is not also replaced by #(parameters influencing species where descriptor occurs) in Eq. (24) instead of ignoring it.
- p. 13248, l. 17: Related to my general comments, in case the “Full method” is not recommended / used for the calculation of vapour pressures of monofunctional compounds, then this Section would probably be better named “Method for multifunctional compounds”.
- p. 13251, l. 15: “A molecule with two vicinal carbonyl groups will have a higher vapour pressure, because”, higher vapour pressure than what?
- p. 13253, l. 14: replace “generally” by “typically” in the Section title.
- p. 13254, l. 14: “had to be below the MG”, abbreviation MG is not defined.
- p. 13255, l. 12: “the predictions of EVAPORATION”, maybe better: “the predicted MAD of EVAPORATION”
- p. 13255, l. 19: why “ad-hoc modification”? delete “ad-hoc”. Same thing on the following page.
- p. 13265, Table 2: Related to the point about the term “descriptor”, would it be correct to add “Descriptor, c_k ” as header of column 1? At the entry “Zero point”

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one could add “Zero point ($c_1 = 1$). It should also be noted that the symbol “#” in column 1 stands for “number of”. Functional groups: instead of “-OH (alcohol)” writing “-OH (hydroxyl)” would be better, as I believe this descriptor is also used for OH-groups in non-alcohols (e.g. citric acid), or not?

- p. 13267, Table 4: Column “Type”: mentioning in a footnote again what the abbreviations lin, CL, and HB stand for would be helpful to read the table.
- p. 13270, Table 7: Naming of molecule classes. Could “Carbonyls” be replaced by “Aldehydes + Ketones”, as carbonyl is a rather general group name that includes carboxylic acids. “Oxo-acids”, are these keto-acids only? Monocarboxylic acids and diacids are also oxo-acids in the general sense.
- p. 13273, Fig. 1: Are the data points of Ribeiro (1999, 2001)(s) really sublimation vapor pressures? This figure could be improved by using more different symbols and more emphasis on the symbol visibility (bolder) than on the lines (which are only intended to relate the different data points of the same reference).
- p. 13274, Fig. 2: This figure should be improved concerning the horizontal positioning of the y-axis and the thickness of the frame borders. Last sentence in caption: “converted to subcooled liquid if necessary”, better “converted to the subcooled liquid state, if necessary”.
- p. 13275, Fig. 3: It is not mentioned in the figure caption nor the key, what the black line represents (presumably the 1:1 line). Also, it should be mentioned for clarity what the abbreviations stand for; better: “Left: modeled (est) vs. experimental (exp) $\log_{10} p^0$ for...”. I would also recommend the authors to mention in the figure caption that these plots represent the poor performance of the additive group-contribution model when applied to compounds >monofunctional, i.e. to compounds it was not optimized for. In this context, it would also be illustrative to

show the improvement when the full method is used instead. Same issues apply to Fig. 4.

- p. 13277, Fig. 5: Since the dark blue and black symbols are hard to distinguish, different symbols would be helpful.
- p. 13278, Fig. 6: Caption: “with data points selected between”, better: “with experimental data points selected between”

Technical Corrections

- Title: “vapor pressure” is written using American English, while throughout the text the British English spelling “vapour pressure” is used.
- p. 13230, l. 16: “regulating its distribution”, better: “influencing its distribution”
- p. 13230, l. 25: “volatile organic compounds”
- p. 13231, l. 4: “formation Model Capouet et al., 2008;”, spelling: “by Capouet et al. (2008)” or change to appropriate citation style with ().
- p. 13231, l. 4: “, the GECKO-A“, better: “, or the GECKO-A”
- p. 13231, l. 5: spelling: “Kinefics”, same line correct citation style for (Aumont et al., 2005)
- p. 13231, l. 6: “leading to the oxygenated” delete “the”
- p. 13231, l. 7: “To simulate SOA formation, the chemical mechanism”, to what is “the” referring to?

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- p. 13231, l. 9: “partition to the SOA according to their vapour pressure” better: “partition to the condensed phase as a function of their vapour pressure” (to make clear that gas-particle partitioning is not governed by vapour pressure only).
- p. 13231, l. 10: “where the SOA is considered”, better: “where the (organic) aerosol is considered” (whether the organic aerosol is secondary or primary is not of importance here).
- p. 13231, l. 11: check year of Cappa and Wilson citation
- p. 13231, l. 28: “assume additivity in $\ln p^0$ ”, define here or above in the Introduction text the meaning of symbol p^0 .
- p. 13231, l. 29: “for all functional groups”, maybe better: “with respect to contributions from different functional groups”.
- p. 13232, l. 4: “group-group combinations”, maybe better: “group-group interactions”
- p. 13232, l. 8: “very recently”, delete “very”
- p. 13232, l. 12: “For these reasons, the need of a new estimation method addressing the above issues is clear.”, better “For these reasons, a new estimation method addressing the issues mentioned above is desirable.”
- p. 13233, l. 2: “KDB” this abbreviation is not defined at this point.
- p. 13233, l. 6: “the fusion temperature and enthalpy”, maybe better: “the melting point temperature and enthalpy of fusion (see Section 2.2)”
- p. 13234, l. 26: “or or”, spelling
- p. 13236, l. 1: no new paragraph

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- p. 13239, l. 10: “this also applies to Ribeiro da Silva et al.”, better: “this also applies to the data of Ribeiro da Silva et al.”
- p. 13243, l. 18: delete “into”
- p. 13246, l. 27: “as they are counted already for $k = 2$.” better: “as they are already accounted for by descriptor $k = 2$.”
- p. 13247, l. 11: “have lower vapour pressures than secondary alcohols”, maybe write “corresponding secondary alcohols”
- p. 13253, l. 25: replace “hitherto by us” by “in our previous SOA modelling studies”

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 13229, 2011.

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