Vapour pressures of substituted polycarboxylic acids are much lower than previously reported

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The formation and fate of secondary organic aerosol (SOA) is governed by the partitioning of compounds between the aerosol and gas phase. This gas-particle partitioning of SOA is generally represented by an equilibrium partitioning model. A key physical parameter which governs gas-particle partitioning is the pure component vapour pressure (p^0) over the liquid state, which is difficult to accurately measure at atmospheric temperatures for low- and semi-volatile organic compounds such as polycarboxylic acids. Subcooled liquid state vapour pressures of substituted polycarboxylic acids inferred from measurements made in the solid state differ by many orders of magnitude from the predictions of current vapour pressure estimation methods, leading to large uncertainties in predictions of SOA partitioning. In this study, vapour pressures are inferred from the evaporation rate of single liquid particles levitated in an electrodynamic balance.

We present measurements of the liquid pure component vapour pressure for 2-Methylmalonic (isosuccinic) acid, 2-Hydroxymalonic (tartronic) acid, 2-Methylglutaric acid, 3-Hydroxy-3-Carboxyglutaric (citric) acid and 2,3-Dihydroxysuccinic (tartaric) acid which were measured in the subcooled liquid state (Huisman et al, 2013). Here we report also on measurements for 2-Oxoglutaric acid and compare those with literature data.

While the measurements of isosuccinic and 2-Methylglutaric acids agree with previous measurements, the data for tartaric and citric acid are 6 orders of magnitude lower than those previously reported, see Fig. 1. Also, our data of tartronic acid and 2-Oxoglutaric acid are significantly lower (2-3 orders of magnitude) lower than those inferred from measurements in the solid state by Booth et al. (2010). Please note that the agreement between our data and those of the vapour pressure estimation method by Compernolle et al. (2011) is significantly better when neglecting the empirical correction terms introduced to model the inexplicably high vapour pressures of some of substituted dicarboxylic acids reported by Booth et al. (2010). This holds particularly true for tartaric and citric acid.

We conclude first, that vapour pressure measurements should be performed in the liquid state whenever possible, second, that the empirical correction term introduced within the estimation model by Compernolle et al. (2011) should not be used and third, that more measurements using different techniques are needed to elucidate the reason for the many order of magnitude differences between our measurements and those of Booth et al. (2010).
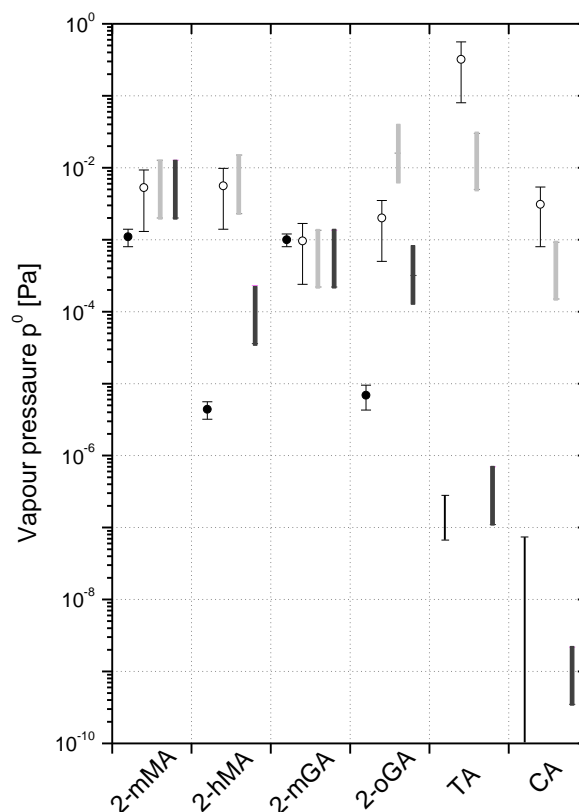

Fig. 1. Vapour pressures (T=298 K) of the liquid for 2-Methylmalonic acid (2-mMA), 2-Hydroxymalonic acid (2-hGA), 2-methlyglutaric acid (2-mGA), 2-oxoglutaric acid (2-oGA), tartaric acid (TA), and citric acid (CA), from this work (solid symbols and bars, when only a data range is reported), Booth et al. (open symbols), model prediction (Compernolle et al.) with correction (light gray) and without empirical correction term (dark gray).

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Compernolle, S., Ceulemans, K., and Müller, J.-F. (2011) *ACP* **11**, 9431-9450.

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