Measured solid state and sub-cooled liquid vapour pressures of nitroaromatics using Knudsen effusion mass spectrometry

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Abstract. Knudsen Effusion Mass Spectrometry (KEMS) was used to measure the solid state saturation vapour pressure (P_S^{sat}) of a range of atmospherically relevant nitroaromatic compounds over the temperature range from 298 to 328 K. The selection of species analysed contained a range of geometric isomers and differing functionalities, allowing for the impacts of these factors on saturation vapour pressure (P^{sat}) to be probed. Three subsets of nitroaromatics were investigated, nitrophenols, nitrobenzaldehydes and nitrobenzoic acids. The P_S^{sat} were converted to sub-cooled liquid saturation vapour pressures (P_L^{sat}) using experimental enthalpy of fusion and melting point values measured using differential scanning calorimetry (DSC). The P_L^{sat} were compared to those estimated by predictive techniques and, with a few exceptions, were found to be up to 7 orders of magnitude lower. The large differences between the estimated P_L^{sat} and the experimental can be attributed to the predictive techniques not containing parameters to adequately account for functional group positioning around an aromatic ring, or the interactions between said groups. When comparing the experimental P_S^{sat} of the measured compounds the ability to hydrogen bond (H-Bond), and the strength of a H-bond formed appear to have the strongest influence on the magnitude of the P^{sat} with steric effects and molecular weight also being major factors. Comparisons were made between the KEMS system and data from diffusion-controlled evaporation rates of single particles in an electrodynamic balance (EDB). The KEMS and the EDB showed good agreement with each other for the compounds investigated.

1 Introduction

Organic aerosols (OA) are an important component of the atmosphere with regards to resolving the impact aerosols have on both climate and air quality (Kroll and Seinfeld, 2008). To predict how OA will behave requires knowledge of their physiochemical properties. OA consist of primary organic aerosols (POA) and secondary organic aerosols (SOA). POA are emitted directly into the atmosphere as solid or liquid particulates and make up about 20% of OA mass globally (Ervens et al., 2011), but the exact percentage of POA varies by a significant amount from region to region. SOA are not emitted into the atmosphere directly as aerosols, but instead form through atmospheric processes such as gas phase photochemical reactions ~~(Ervens et al., 2011) or~~followed by gas-to-particle ~~conversion~~ partitioning in the atmosphere (Pöschl, 2005). A key property for predicting the partitioning of compounds between the gaseous and aerosol phase is the pure component equilibrium vapour pressure, also known as the saturation vapour pressure (P^{sat}) (Bilde et al., 2015). It has been estimated that the number of organic compounds in the atmosphere is in excess of 100,000 (Hallquist et al., 2009); therefore it is not feasible to measure the P^{sat} of each experimentally. Instead, P^{sat} are often estimated using group contribution methods (GCMs) that are designed to capture the functional dependencies on predicting absolute values. GCMs start with a base molecule with known properties, typically the carbon skeleton. A functional group is then added to the base molecule. This addition will change the P^{sat} and the difference between the base molecule and the functionalised molecule is the contribution from that particular functional group. If this concept is true then the contribution from the functional group should not be affected by the base molecule to which it is added (Bilde et al., 2015). Whilst this is true in many cases, there are numerous exceptions. These exceptions normally occur when proximity effects occur, such as neighbouring group interactions or other mesomeric effects. In this work there will be a focus on the Nannoolal et al. method (Nannoolal et al., 2008), the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) and~~,~~ SIMPOL (Pankow and Asher, 2008)~~ (Pankow and Asher, 2008) and EVAPORATION (Compernolle et al., 2011)~~. Detailed assessments of such methods have been made by Barley and McFiggans (~~Barley and McFiggans,~~ 2010) and O'Meara et al. (~~O 'meara et al.,~~ 2014) often showing predicted values differ significantly from experimental data. The limitations and uncertainties of GCMs come from a range of factors including underrepresentation of long chain hydrocarbons (>C_{18}), underrepresentation of certain functional groups, such as nitro or nitrate groups, a lack of data for the impact of intramolecular bonding, and the temperature dependence due to the need for extrapolation over large temperature ranges to reach ambient conditions (Bilde et al., 2015). This has important implications for partitioning modelling, in a mechanistic sense, such as an over or underestimation of the fraction partitioning to the particulate state. Different GCMs have different levels of reliability for different classes of compound and perform much more reliably if the compound of interest resembles those used in the parametrisation data set of the GCM (Kurtén et al., 2016). For example, in the assessment by O'Meara et al. (~~O'Meara et al., ~~2014), for the compounds to which it is applicable, EVAPORATION (Compernolle et al., 2011) was found to give the minimum mean absolute error, the highest accuracy for SOA loading estimates and the highest accuracy for SOA composition. Despite this ~~it has been recommend that the ~~EVAPORATION ~~method ~~should not be used for aromatic compounds, as there are no aromatic compounds in the parametrisation dataset (Compernolle et al., 2011). ~~However, even the m~~Methods developed with OA in mind, such as ~~the ~~EVAPORATION~~-~~ (Compernolle et al., 2011)~~method~~, are not without their limitations due to the lack of experimental data available for highly functionalised, low volatility organic compounds (Bannan et al., 2017). As the degree of functionality increases so does the difficulty in predicting the P^{sat} as more intramolecular forces, steric effects, and shielding effects must be considered. The majority of GCMs designed for estimating P^{sat} of organic compounds were developed for the chemical industry with a focus on monofunctional compounds with P^{sat} on the order of $10^3 – 10^5$ Pa (Bilde et al., 2015). SOA, in contrast, are typically multifunctional compounds with P^{sat} often many orders of magnitude below 10^{-1} Pa (Barley and McFiggans, 2010). GCM development, with a focus on the P^{sat} of SOA has to deal with a lack of robust experimental data and, historically, large differences in measurement data depending on the technique and instrument used to acquire the data. To address this problem Krieger et al. (~~Krieger et al., ~~2018) identified a reference data set for validating P^{sat} measurements using the polyethylene glycol (PEG) series. To improve the performance of GCMs when applied to highly functionalised compounds, more data is required that probes both the effect of relative functional group positioning and the effects of interaction between functional groups on P^{sat}, such as in the work by Booth et al. (~~Booth et al., ~~2012) and Dang et al. (~~Dang et al., ~~2019). In this study the solid state saturation vapour pressure (P_S^{sat}) and sub-cooled liquid saturation vapour pressures (P_L^{sat}) of three families of nitroaromatic compounds are determined using KEMS, building on the work done by Dang et al. (~~Dang et al., ~~2019) and Bannan et al. (~~Bannan et al., ~~2017). These include substituted nitrophenols, substituted nitrobenzoic acids and nitrobenzaldehydes. Nitroaromatics are useful tracers for anthropogenic emissions (Grosjean, 1992), and many nitroaromatic compounds are noted to be highly toxic (Kovacic and Somanathan, 2014).

Studies quantifying the overall role of nitrogen containing organics on aerosol formation would also benefit from more refined P^{sat} (Duporté et al., 2016; Smith et al., 2008). Even if mechanistic models perform poorly predicting aerosol mass due to missing process phenomena, resolving the partitioning is still important. Several studies have reported the observation of methyl nitrophenols (Chow et al., 2016; Kitanovski et al., 2012; Schummer et al., 2009) and nitrobenzoic acids (van Pinxteren and Herrmann, 2007). Nitrobenzaldehydes can form from the photo-oxidation of toluene in a high NO_x environment (Bouya et al., 2017). Both nitrophenols and nitrobenzoic acids were identified in the review paper by Bilde et al. (~~Bilde et al., ~~2015) as compounds of interest and recommendations for further study. Aldehyde groups tend to have little impact on P^{sat} by themselves but the =O of the aldehyde group can act as a hydrogen bond acceptor.

There is a general lack of literature vapour pressure data for nitroaromatic compounds, and despite recent work on nitrophenols by Bannan et al. (~~Bannan et al., ~~2017), there is still a lack of data on such compounds in the literature. This is reflected, in part, in the effectiveness of the GCMs to predict the VP of such compounds.

Here we present P_S^{sat} and P_L^{sat} data for 20 nitroaromatic compounds. The P_S^{sat} data was collected using Knudsen effusion mass spectrometry (KEMS) with a sub-cooled correction performed with thermodynamic data from a differential scanning calorimeter (DSC). The trends in the P_S^{sat} data are considered and chemical explanations are given to explain the observed differences.

As identified by Bilde et al. (~~Bilde et al., ~~2015), experimental P^{sat} can differ by several orders of magnitude among techniques. One way of mitigating this is to collect data for a compound using multiple techniques, whilst running reference compounds to assess consistency among the employed methods. We therefore use supporting data from the electro dynamic balance (EDB) at ETH Zurich for three of the nitroaromatic compounds.

The P_L^{sat} data is then compared with the predicted P_L^{sat} of the GCMs, highlighting where they perform well and where they perform poorly. Finally, these measurements using the new PEG reference standards are compared to past KEMS measurements using an old reference standard due to differences in experimental P^{sat} between this work and previous KEMS work.

2 Experimental

Compound Selection

A total of 10 nitrophenol compounds were selected for this study including 9 monosubstituted, 4 nitrobenzaldehydes including 1 monosubstituted, and 6 nitrobenzoic acids including 5 monosubstituted. The nitrophenols are shown in Table 1, the nitrobenzaldehydes are shown in Table 2, and the nitrobenzoic acids are shown in Table 3. All compounds selected for this study were purchased at a purity of 99% and were used without further preparation. All compounds are solid at room temperature.

2.1 Knudsen effusion mass spectrometry system (KEMS)

The KEMS system is the same system that has been used in previous studies (Bannan et al., 2017; Booth et al., 2009, 2010) and a summary of the measurement procedure will be given here. For a more detailed overview see Booth et al. (~~Booth et al.,~~ 2009). To calibrate the KEMS, a reference compound of known P^{sat} is used. In this study the polyethylene glycol series (PEG series), PEG-3 ($P_{298} = 6.68\text{x}10^{-2}$ Pa) and PEG-4 ($P_{298} = 1.69\times10^{-2}$ Pa) (Krieger et al., 2018), were used. The KEMS has been shown to accurately measure the - P^{sat} of PEG-4 in the study by Krieger et al. (~~Krieger et al.,~~ 2018) but the KEMS did not measure the P^{sat} of PEG-3. In this study when using PEG-4 as a reference compound for PEG-3 the measured P^{sat} of PEG-3 had an error of 30 % compared to the experimental values from Krieger et al. (~~Krieger et al.,~~ 2018), well within the quoted 40 % error margin of the KEMS (Booth et al., 2009). When using PEG-3 as the reference compound for PEG-4 the measured P^{sat} of PEG-4 had an error of 20 %.

~~The PEG series is a homologous series that covers 5 orders of magnitude from 10^{-2} to 10^{-7} Pa and includes PEG-3 through PEG-8. The P^{sat} of the PEG series were determined using multiple different techniques including multiple electrodynamic balances (EDBs), a flow tube tandem differential mobility analyser system (FT-TDMA), and a Knudsen effusion mass spectrometry system (KEMS) (Krieger et al., 2018). By using multiple different techniques it was possible to identify the lower limits of detection as these were typically where the deviations between measured values occurred. By corroborating expected trends and absolute values with other methods, it was found that the KEMS was able to determine P^{sat} of PEG-4 to PEG-7, through good agreement with the other techniques, yet did not capture the expected value of PEG-8. For PEG-8 the P^{sat} was~~

~~determined to be 9.2E-08 Pa at 298 K using the EDB and the KEMS system. The KEMS system showed almost no temperature dependence, which may indicate that the lower limit of detection has been reached at these P^{sat} (Krieger et al., 2018)~~.

~~The PEG series has now been employed by new techniques such as, those in Booth et al. (Booth et al., 2017) and Bannan et al. (Bannan et al., 2019).~~

The reference compound is placed in a temperature controlled Knudsen cell. The cell has a chamfered orifice through which the sample effuses creating a molecular beam. The size of the orifice is ≤1/10 the mean free path of the gas molecules in the cell. This ensures that the particles effusing through the orifice do not disturb the thermodynamic equilibrium of the cell. The molecular beam is then ionised using a standard 70 eV electron impact ionisation, and analysed using a quadrupole mass spectrometer.

After correcting for the ionisation cross section (Booth et al., 2009) the signal generated is proportional to the P^{sat}. Once the calibration process is completed it is possible to measure a sample of unknown P^{sat}. When the sample is changed it is necessary to isolate the sample chamber from the measurement chamber using a gate valve so that the sample chamber can be vented, whilst the ioniser filament and the secondary electron multiplier (SEM) detector can remain on and allow for direct comparisons with the reference compound. The P^{sat} of the sample can be determined from the intensity of the mass spectrum, if the ionisation cross section at 70 eV, and the temperature at which the mass spectrum was taken are known. The samples of unknown P^{sat} are typically solid so it is the P_S^{sat} that is determined. After the P_S^{sat} (Pa), has been determined for multiple temperatures, the Clausius-Clapeyron equation (Eq. 1) can be used to determine the enthalpy and entropy of sublimation as shown in Booth et al. (~~Booth et al.,~~ 2009).

$$\ln(P^{sat}) = \frac{\Delta H_{sub}}{RT} + \frac{\Delta S_{sub}}{R} \qquad (1)$$

where T is the temperature (K), R is the ideal gas constant (J mol^{-1} K^{-1}), ΔH_{sub} is the enthalpy of sublimation (J mol^{-1}) and ΔS_{sub} is the entropy of sublimation (J mol^{-1} K^{-1}). P^{sat} was obtained over a range of 30 K in this work starting at 298 K and rising to 328 K. The reported solid state vapour pressures are calculated from a linear fit of $\ln(P^{sat})$ vs 1/T using the Clausius-Clapeyron equation.

2.2 Differential scanning calorimetry (DSC)

According to the reference state used in atmospheric models, and as predicted by GCMs, P_L^{sat} is required. Therefore it is necessary to convert the P_S^{sat} determined by the KEMS system into a P_L^{sat}. As with previous KEMS studies (Bannan et al., 2017; Booth et al., 2010, 2017) the melting point (T_m) and the enthalpy of fusion (ΔH_{fus}) are required for the conversion. These values were measured with a TA Instruments DSC 2500 Differential Scanning Calorimeter (DSC). Within the DSC, heat flow and temperature were calibrated using an indium reference, and heat capacity using a sapphire reference. A heating rate of 10 K min^{-1} was used. 5-10 mg of sample was measured using a microbalance and then pressed into a hermetically sealed aluminium DSC pan. A purge gas of N_2 was used with a flow rate of 30 mL min^{-1}. Data processing was performed using the 'Trios' software supplied with the instrument. $\Delta c_{p,sl}$ was estimated using $\Delta c_{p,sl} = \Delta S_{fus}$ (Grant et al., 1984; Mauger et al., 1972).

2.3 Electrodynamic balance (EDB)

The recently published paper by Dang et al. (2019) measured the P^{sat} of several of the same compounds that are studied in this paper using the same KEMS system, however in this study the newly defined best practice reference sample was used (Krieger et al., 2018), whereas Dang et al. (2019) used malonic acid. The difference in reference compound led to a discrepancy in the experimental P^{sat}. Supporting measurements for the compounds were performed using the EDB from ETH Zurich in order to rule out instrumental problem with the KEMS. The EDB from ETH Zurich has been used to investigate P^{sat} of low volatility compounds in the past (Huisman et al., 2013; Zardini et al., 2006; Zardini and Krieger, 2009) and a brief overview will be given here. For full details see Zardini et al. (~~Zardini et al.,~~ 2006) and Zardini and Krieger (~~Zardini and Krieger,~~ 2009). The EDB can be applied to both liquid particles and non-spherical solid particles (Bilde et al., 2015). The EDB uses a double ring configuration (Davis et al., 1990) to levitate a charged particle in a cell with a gas flow free from the evaporating species under investigation. There is precise control of both temperature and relative humidity within the cell. Diffusion-controlled evaporation rates of the levitated particle are measured at a fixed temperature and relative humidity by precision sizing using optical resonance spectroscopy in backscattering geometry with a broadband LED source and Mie theory for the analysis (Krieger et al., 2018). P^{sat} is calculated at multiple temperatures and the Clausius-Clapeyron equation can be used to calculate P^{sat} at a given temperature (Eq. 1).

As single particles injected from a dilute solution may either stay in a supersaturated, liquid state or crystallize, it is important to identify its physical state.

For 4-methyl-3-nitrophenol a 3 % solution dissolved in isopropanol was injected into the EDB. After the injection and fast evaporation of the isopropanol, all particles were non-spherical, but with only small deviations from a sphere, meaning that it was unclear whether the phase was amorphous or crystalline. To determine the phase of this first experiment, a second experiment was performed, where a solid particle was injected directly into the EDB. Mass loss with time was measured by following the DC voltage necessary to compensate the gravitational force acting on the particle to keep the particle levitating. When comparing the P^{sat} from both of these experiments it is clear that the initial measurement of 4-methyl-3-nitrophenol was in the crystalline phase.

3-methyl-4-nitrophenol was only injected as a solution but the particle crystallized and was clearly in the solid state.

4-methyl-2-nitrophenol was injected as both a 3 % and 10 % solution. Despite being able to trap a particle, the particle would completely evaporate within about 30 seconds. This evaporation time scale is too small to allow the EDB to collect any quantitative data. Using the equation for large particles neglecting evaporative cooling (Hinds, 1999) (Eq. 2) it is possible to estimate P_L^{sat}

$$t = \frac{R\rho \cdot {d_p}^2}{8DM\frac{Psat}{T}} \qquad (2)$$

where t is the time that the particle was trapped within the cell of the EDB, R is the ideal gas constant, ρ is the density of the particle, d_p is the diameter of the particle, D is the diffusion coefficient, M is the molecular mass, T is the temperature, and P^{sat} is the saturation vapour pressure. Eq. 2 gives approximately 4.3E-03 Pa for P_L^{sat} at 290 K.

3 Theory

3.1 Sub-cooled correction

The conversion between P_S^{sat} and P_L^{sat} is done using the Prausnitz equation (Prausnitz et al., 1998) (Eq. ~~2~~3)

$$\ln\left(\frac{P_L^{sat}}{P_S^{sat}}\right) = \frac{\Delta H_{fus}}{RT_m}\left(\frac{T_m}{T} - 1\right) - \frac{\Delta c_{p,sl}}{R}\left(\frac{T_m}{T} - 1\right) + \frac{\Delta c_{p,sl}}{R} ln\left(\frac{T_m}{T}\right)$$

(~~2~~3)

where P_L^{sat}/P_S^{sat} is the ratio between P_L^{sat} and P_S^{sat}, ΔH_{fus} is the enthalpy of fusion (J mol^{-1}), $\Delta c_{p,sl}$ is the change in heat capacity between the solid and liquid states (J mol^{-1} K^{-1}),T is the temperature (K) and T_m is the melting point (K).

3.2 Vapour pressure predictive techniques

The most common P^{sat} prediction techniques are GCMs. Several different GCMs have been developed (Moller et al., 2008; Myrdal and Yalkowsky, 1997; Nannoolal et al., 2008; Pankow and Asher, 2008) with some being more general and others, such as the EVAPORATION method (Compernolle et al., 2011), having been developed with OA as the target compounds. The Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997), the Nannoolal et al. method (Nannoolal et al., 2008), and the Moller et al. method (Moller et al., 2008) are combined methods requiring a boiling point, T_b, as an input. If the T_b of a compound is known experimentally it is an advantage, but most atmospherically relevant compounds have an unknown T_b so the T_b that is used as an input is calculated using a GCM. The combined methods use a T_b calculated using a GCM for many of the same reasons that GCMs are used to calculate P^{sat}, i.e. the difficulty in acquiring experimental data for highly reactive compounds or compounds with short lifetimes. The Nannoolal et al. method (Nannoolal et al., 2004), Stein and Brown method (Stein and Brown, 1994), and Joback and Reid method (Joback et al., 1987) are most commonly used. The Joback and Reid method is not considered in this paper due to its known biases (Barley and McFiggans, 2010) and the Stein and Brown method being an improved version of Joback and Reid. The T_b used in the combined methods is, however, another source of potential error and for methods that extrapolate P^{sat} from T_b, the size of this error increases with increasing difference between T_b and the temperature to which it is being extrapolated (O'Meara et al., 2014). EVAPORATION (Compernolle et al., 2011) and SIMPOL (Pankow and Asher, 2008) do not require a boiling point, only requiring a structure and a temperature of interest. The main limitation for many GCMs, aside from the data required to create and refine them, is not accounting for intramolecular interactions, such as hydrogen bonding, or steric effects. The Nannoolal et al. method (Nannoolal et al., 2008), Moller et al. method (Moller et al., 2008), and EVAPORATION (Compernolle et al., 2011) attempt to address this by having secondary interaction terms. In the Nannoolal et al. method (Nannoolal et al., 2008), there are terms to account for -ortho, -meta, -para isomerism of aromatic compounds, however there are no terms for dealing with tri- or greater substituted aromatics, and in these instances all isomers give the same prediction. A common misuse of GCMs occurs when a GCM is applied to a compound containing functionality not included in the training set, e.g. using EVAPORATION (Compernolle et al., 2011) with aromatic compounds or using SIMPOL (Pankow and Asher, 2008) with compounds containing halogens. As the GCM does not have the tools to deal with this functionality it will either misattribute a contribution, in the EVAPORATION (Compernolle et al., 2011)~~(2011)~~ example the aromatic structure would be treated as a cyclical aliphatic structure, or simply ignore the functionality, as is the case when SIMPOL (Pankow and Asher, 2008)~~(2008)~~ is used for halogen containing compounds. When selecting a GCM to model P^{sat} it is essential to investigate whether the method is applicable to the compounds of interest. Of the popular P^{sat} GCMs, the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) contains only three nitroaromatic compounds, the Nannoolal et al. method (Nannoolal et al., 2008) contains thirteen, the Moller et al. (Moller et al., 2008) contains no more than fourteen, SIMPOL (Pankow and Asher, 2008) contains twenty five, and EVAPORATION (Compernolle et al., 2011) contains zero. The specific nitroaromatics used by the Nannoolal et al. method and the Moller et al. method are not stated (to the author's knowledge) as the data was taken directly from the Dortmund Data Bank. Despite the SIMPOL (2008) method containing twenty five nitroaromatic compounds, eleven of these are taken from a gas chromatography method using a single data point from a single data set (Schwarzenbach et al., 1988).

3.3 Inductive and resonance effects

All functional groups around an aromatic ring either withdraw or donate electron density. This is a result of two major effects, the inductive effect and the resonance effect, or a combination of the two (Ouellette et al., 2015a). The inductive effect is the unequal sharing of the bonding electron through a chain of atoms within a molecule. A methyl group donates electron density, relative to a hydrogen atom, so is therefore considered an electron donating group, whereas a chloro group withdraws electron density and is therefore considered an electron withdrawing group. The resonance effect occurs when a compound can have multiple resonance forms. In a nitro group, as the oxygen atoms are more electronegative than the nitrogen atom, a pair of electrons from the nitrogen-oxygen double bond can be moved onto the oxygen atom followed by a pair of electrons being moved out of the ring to form a carbon-nitrogen double bond and leaving the ring with a positive charge. This leads to the nitro group acting as an electron withdrawing group. In an amino group, on the other hand, the hydrogens are not more electro negative than the nitrogen; instead the lone pair on the nitrogen can be donated into the ring, causing the ring to have a negative charge, and the amino group to act as an electron donating group. Examples of the inductive effect and the resonance effect are given in Fig. ~~1~~1 (Ouellette et al., 2015a).

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Some functional groups, such as an aromatic OH group, can both donate and withdraw electron density at the same time. In phenol the OH group withdraws electron density via the inductive effect, but it also donates electron density via the resonance effect. This is shown in Fig. 2~~2~~. As the resonance effect is typically much stronger than the inductive effect, OH has a net donation of electron density in phenol (see Fig.~~ ~~2~~2~~).

The positioning of the functional groups around the aromatic ring determine to what extent the inductive and resonance effects occur. The changes in electron density due to the inductive effect and the resonance effect also change the partial charges on the atoms within the aromatic ring. These changes impact the strength of any potential H-bonds that may form.

4 Results and discussion

4.1 Solid state vapour pressure

P_S^{sat} measured directly by the KEMS are given in Tables 4~~5~~, 5~~6~~ and 6~~7~~ for the nitrophenols, nitrobenzaldehydes and nitrobenzoic acids respectively. Measurements were made at increments of 5 K from 298 to 328 K ~~(~~with the exception of the following compounds that melted during the temperature ramp~~)~~. 2-nitrophenol was measured between 298 K and 318 K, 3-methyl-4-nitrophenol was measured between 298 K and 313K, 4-methyl-2-nitrophenol was measured between 298 K and 303 K, 5-fluoro-2-nitrophenol was measured between 298 K and 308 K, and 2-nitrobenzaldehyde was measured between 298 K and 313 K. The Clausius-Clapeyron equation (Eq. 1) was used to calculate the enthalpies and entropies of sublimation. The melting points of compounds studied are given in ~~Tables 8, 9 and 10 for the nitrophenols, nitrobenzaldehydes and nitrobenzoic acids respectively~~7. ~~2-nitrophenol was measured between 298 K and 318 K, 3-methyl-4-nitrophenol was measured between 298 K and 313K, 4-methyl-2-nitrophenol was measured between 298 K and 303 K, 5-fluoro-2-nitrophenol was measured between 298 K and 308 K, and 2-nitrobenzaldehyde was measured between 298 K and 313 K.~~ Generally speaking, considering the different groups of compounds as a whole, the nitrobenzaldehydes studied exhibit higher P_S^{sat} (order of magnitude) than the nitrophenols and nitrobenzoic acids studied. This is most likely due to the fact that none of the nitrobenzaldehydes studied herein are capable of undergoing hydrogen bonding (H-bonding) whilst all of the nitrophenols and nitrobenzoic acids, to varying extents, are capable of hydrogen bonding. The nitrophenols and nitrobenzoic acids studied exhibit a range of overlapping P_S^{sat} so nothing can be inferred when considering these two types of compounds together as groups; therefore the differences *within* each of the groups must be considered.

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~~Some functional groups, such as an aromatic OH group, can both donate and withdraw electron density at the same time. In phenol the OH group withdraws electron density via the inductive effect, but it also donates electron density via the resonance effect. This is shown in Fig. 2. As the resonance effect is typically much stronger than the inductive effect, OH has a net donation of electron density in phenol (see Fig. 2).~~

~~The positioning of the functional groups around the aromatic ring determine to what extent the inductive and resonance effects occur. The changes in electron density due to the inductive effect and the resonance effect also change the partial charges on the atoms within the aromatic ring. These changes impact the strength of any potential H-bonds that may form. For instance, in the case of a functionalised phenol, the partial charge of the phenolic carbon is a major factor in the overall strength of the H-bond (see Fig. 3). The more positive the partial charge of the phenolic carbon the stronger the H-bond formed (Remko and Polcin, 1977). In the work by Remko and Polcin (Remko and Polcin, 1977) the effect on the H-bonding ability of phenol and its ortho, meta and para methoxy substituted derivatives were investigated. Remko and Polcin found that the ortho and para~~

~~substituted phenol had weaker intermolecular H-bonds relative to the unsubstituted phenol. The meta substituted derivative, however, possessed stronger intermolecular hydrogen bonds than the unsubstituted phenol. This trend is supported by the experimental work by Stymne et al. (Stymne et al., 1973) which also showed the meta substituted derivative having a higher H-bond energy relative to the unsubstituted phenol and the para isomer having a lower H-bond energy. The work by Remko and Polcin (Remko and Polcin, 1977) investigated the H-bonding potential to formamide and the work by Stymne et al. (Stymne et al., 1973) investigated the H-bonding potential to dimethylacetamide. The H-bond energies and the partial charge of the phenolic OH are shown in Table 4 and the chemical structures of the methoxyphenols are shown in Fig. 3.~~

~~The increase or decrease of the H-bond energy relative to the unsubstituted phenol matches an increase or decrease in the partial charge of the phenolic carbon. There is a slight discrepancy between 2-methoxyphenol and the 4-methoxyphenol where 2-methoxyphenol has a higher H-bond energy, but a lower partial charge of the phenolic carbon than 4-methoxyphenol. This is likely due to 2-methoxyphenol being capable of forming an intramolecular H-bond, which whilst being weak and the intermolecular H-bond dominating (Remko and Polcin, 1977), will still impact the calculated partial charge.~~

Considering first the nitrophenols, Table 4~~5~~, the highest P_S^{sat} compound is 2-fluoro-4-nitrophenol (2.75E-02 Pa). There are two potential H-bonding explanations for why this compound has such a high P_S^{sat} relative to the other nitrophenols and fluoro nitrophenols. First, in this isomer the presence of the F atom on the C adjacent to the OH group gives rise to intramolecular H-bonding (Fig. 3~~4~~ left) which reduces the extent of intermolecular interaction possible and increases P_S^{sat}. This effect can clearly be seen from the fact that in 3-fluoro-4-nitrophenol, where the F atom is positioned further away from the OH group, the P_S^{sat} is significantly lower (4.55E-03) due to the fact that intermolecular H-bonding can occur (Fig. 3~~4~~ right).However, in the work by Shugrue et al. (~~Shugrue et al.,~~ 2016) it is stated that neutral organic fluoro and nitro groups form very weak hydrogen bonds, which whilst they do exist, can be difficult to even detect by many conventional methods.

The second explanation depends on the inductive effect mentioned previously. By using MOPAC2016 (Stewart, 2016), a semi empirical quantum chemistry program based on the neglect of diatomic differential overlap (NDDO) approximation (Dewar and Thiel, 1977), the partial charges of the phenolic carbon can be calculated. The partial charge of the phenolic carbon can be dependent on the orientation of the OH if the molecule doesn't have a plane of symmetry, so in this work the partial charge used is an average of the two extreme orientations of the OH, as shown in Fig. 4~~5~~. A plot of P_S^{sat} vs the partial charge of the phenolic carbon for the nitrophenols can be found in Fig. 5.

The partial charge of the phenolic carbon in 2-fluoro-4-nitrophenol is 0.275 with a P_S^{sat} of 2.75E-02 Pa, whereas for 3-fluoro-4-nitrophenol it is 0.379 with a P_S^{sat} of 4.55E-03 Pa. The more positive the partial charge of the phenolic carbon the better it is able to stabilise the increased negative charge which will develop on the O atom as a result of H-bond formation. As a result stronger intermolecular H-bonds are formed, therefore giving rise to a lower P_S^{sat}. Moving the nitro group from being para to the OH in 3-fluoro-4-nitrophenol to meta to the OH in 5-fluoro-2-nitrophenol further reduces the P_S^{sat} to 4.25E-03 Pa. This reduction in P_S^{sat} can also be explained via the combination of the inductive effect and the resonance effect as the partial charge of the phenolic carbon rises from 0.379 to 0.396, again implying stronger intermolecular H-bonds and, therefore, a lower P_S^{sat}. For the fluoro nitrophenols, as shown in Fig. 5, as the partial charge of the phenolic carbon increases the P_S^{sat} increases.

A s~~S~~imilar trend~~s~~ occurs in the methyl nitrophenols as in the fluoro nitrophenols with a larger partial charge of the phenolic carbon corresponding to a lower P_S^{sat}, as shown in Fig 5. 3-methyl-2-nitrophenol is an exception to this and is discussed shortly.~~.~~ 3-methyl-4-nitrophenol has the most positive partial charge with 0.362 and the lowest P_S^{sat} of 1.78E-03 Pa, 4-methyl-2-nitrophenol has the next most positive partial charge of 0.343 and the next lowest P_S^{sat} of 3.11E-03, and 4-methyl-3-nitrophenol has the least positive partial charge of 0.249 and the highest P_S^{sat} of 1.08E-02. 3-methyl-2-nitrophenol does not follow this trend, however, with it having a partial charge of 0.378 and a P_S^{sat} of 9.90E-03. As shown in Fig. 5 3-methyl-2-nitrophenol would be expected to have a much lower P_S^{sat} than is observed due to the high partial charge on the phenolic carbon. A possible explanation as to why 3-methyl-2-nitrophenol does not follow this same trend is the positioning of its functional groups. As shown in Fig. 6~~6~~ (left), all of the functional groups are clustered together and the proximity of the functional groups sterically hinders the formation of H-bonds, thus increasing the P_S^{sat}. Conversely as shown in Fig. ~~6~~ 6 (right) the fact that the methyl group is further away in 4-methyl-2-nitrophenol leads to less steric hindrance of H-bond formation.

Whilst 3-methyl-2-nitrophenol has a higher P_S^{sat} than is expected given the partial charge on the phenolic carbon, 4-amino-2-nitrophenol has a much lower P_S^{sat} (Fig. 5). This is likely due to 4-amino-2-nitrophenol being capable of forming more than one hydrogen bond, whereas all the other compounds investigated were only capable of forming one H-bond. However, despite 4-amino-2-nitrophenol being capable of forming more than 1 H-bond, r~~R~~eplacing the methyl group on 4-methyl-2-nitrophenol with an amino group to form 4-amino-2-nitrophenol surprisingly increases the P_S^{sat} from 3.11E-03 Pa to 3.36E-03 Pa.~~ This is unexpected, as unlike 4-methyl-2-nitrophenol, 4-amino-2-nitrophenol contains two H-bond donors and so would be expected to have a lower P_S^{sat}.~~ The higher P_S^{sat} can be explained via the combination of the inductive effect and the resonance effect. Whilst the partial charge of the phenolic carbon in 4-methyl-2-nitrophenol is 0.343, the partial charge of the phenolic carbon in 4-amino-2-nitrophenol is only 0.264 and the partial charge of the carbon bonded to the amine group is only 0.211. So whilst 4-amino-2-nitrophenol is capable of forming two intermolecular H-bonds compared to 4-methyl-2-nitrophenol's one, they will be much weaker. 4-amino-2-nitrophenol is a good example of a compound with multiple competing factors affecting P_S^{sat} leading to higher P_S^{sat} than would be expected due to one factor and lower P_S^{sat} than expected from another.

Similar to 4-amino-2-nitrophenol, 4-chloro-3-nitrophenol also has a lower P_S^{sat} than expected according to the partial charge of the phenolic carbon. This can be seen in Fig. 5. Unlike 4-amino-2-nitrophenol the explanation for 4-chloro-3-nitrophenol is simpler. Replacing the methyl group on 4-methyl-3-nitrophenol with a chloro group to form 4-chloro-3-nitrophenol reduces the P_S^{sat} from 1.08E-02 Pa to 2.26E-03 Pa. This reduction in P_S^{sat} can be explained by the increase in partial charge of the phenolic carbon from 0.249 to 0.266, as well as a 13% increase in molecular weight.

Replacing the F atom in 3-fluoro-4-nitrophenol with a methyl group to form 3-methyl-4-nitrophenol further reduces the P_S^{sat} (1.78E-03) although exactly why is unclear. The methyl group cannot engage in intermolecular H-bonding, it will sterically hinder any H-bonding that the NO_2 group undergoes and it reduces the ~~net dipole moment~~partial charge of the phenolic carbon of the molecule (from ~~6.36 D~~0.379 to ~~5.41 D~~0.362) (Stewart, 2016) which would reduce the ~~extent of dipole-dipole type~~strength of H-bonding interactions between the molecules.~~ The net dipole moments were calculated using MOPAC2016 (Stewart, 2016), and similarly to the partial charges, are an average taken from the extreme orientations of the OH group, aldehyde groups, or carboxylic acid group~~. It is possible that the crystallographic packing density of 3-methyl-4-nitrophenol is higher although no data is available to support this, although when looking at P_L^{sat} data (Section 4.2) 3-methyl-4-nitrophenol exhibits a higher P_L^{sat} than 3-fluoro-4-nitrophenol which is what would be expected given the respective partial charges of the phenolic carbons.

Removing the methyl group~~s~~ from ~~both 3-methyl-2-nitrophenol and~~ 4-methyl-2-nitrophenol to give 2-nitrophenol causes the P_S^{sat} to drop from ~~9.90E-03 Pa and~~ 3.11E-03 Pa~~, respectively,~~ to 8.94E-04 Pa. This reduction in P_S^{sat} matches an increase in the positive partial charge of the phenolic carbon, from ~~0.378 and~~ 0.343 to 0.383, implying an increase in the strength of the intermolecular H-bonds and therefore a reduction in P_S^{sat}.

Now considering the nitrobenzaldehydes (Table 5~~6~~) the highest P_S^{sat} compound is 2-nitrobenzaldehyde (3.32E-01). Comparing this to 2-nitrophenol (8.94E-04) shows how significant the ability to form H-bonds is to the P_S^{sat} of a compound, with replacing a hydroxyl group (capable of H-bonding) with an aldehyde group (incapable of H-bonding) raising the P_S^{sat} of the compound by more than two orders of magnitude. The decrease in P_S^{sat} observed by moving the nitro group from being ortho to the aldehyde group in 2-nitrobenzaldehyde, to being meta in 3-nitrobenzaldehyde (1.21E-01) and para in 4-nitrobenzaldehyde (3.40E-02) can be explained using the different crystallographic packing densities of the three isomers as shown i~~f~~n Fig. 7. Crystallographic packing density is a measure of how densely packed the molecules of a given compound are when they crystallise, the more closely packed molecules are the greater the overall extent of interaction between them and the lower the P_S^{sat}. The order of the P_S^{sat} observed here for the three isomers of nitrobenzaldehyde matches that of their crystallographic packing densities (Coppens and Schmidt, 1964; Engwerda et al., 2018; King Jnr and Bryant Jnr, 1996), with the lowest P_S^{sat} correlating with the highest packing density and vice versa.

The addition of a Cl atom to 3-nitrobenzaldehyde is also observed to decrease the compounds P_S^{sat}. This can be simply rationalised due to the greater than 25% increase this causes to the molecular weight. The higher a compounds molecular weight the greater the overall extent of interaction between its molecules and the lower its P_S^{sat}.

~~The trend of the nitrobenzaldehyde P_S^{sat} matches the measured melting point trend shown in Table 9, where 2-nitrobenzaldehyde has the highest P_S^{sat} (3.54E-01 Pa) and the lowest melting point (44.51 °C) and 4-nitrobenzaldehyde has the lowest P_S^{sat} (3.40E-02 Pa) and the highest melting point (107.25 °C).~~

Finally considering the nitrobenzoic acids (Table 6~~7~~), the highest P_S^{sat} compound is 4-methyl-3-nitrobenzoic acid (4.67E-03). Its isomer 3-methyl-4-nitrobenzoic acid possesses a slightly lower P_S^{sat} (3.97E-03) ~~which could be attributed to the slight increase in~~as well as a slightly lower ~~the~~ partial charge of the carboxylic carbon ~~within the carboxylic acid group~~ (~~from 0.628 to~~ 0.644 vs 0.628) although the difference in P_S^{sat} is not significant. ~~4-methyl-3-nitrobenzoic acid and 3-methyl-4-nitrobenzoic acid both exhibit lower P_S^{sat}s than their corresponding nitrophenols (4-methyl-3-nitrophenol and 3-methyl-4-nitrophenol respectively) which demonstrates the increased suppressive effect on P_S^{sat} that carboxylic acid groups have compared to~~

~~hydroxyl groups. This is due to the fact that carboxylic acid groups allow for a molecule to H-bond to three neighbouring molecules (Fig. 7 left), whilst a hydroxyl group allows for only two H-bonds (Fig. 7 right), and this increased extent of intermolecular interaction leads to a reduction in P_S^{sat}.~~

Removing the methyl group from 4-methyl-3-nitrobenzoic acid to give 3-nitrobenzoic acid (1.10E-03) reduces the observed P_S^{sat} most likely due to the reduction in steric hindrance around the nitro group which would allow for more effective H-bonding. In addition 3-nitrobenzoic acid possesses a lower P_S^{sat} than the corresponding 3-nitrobenzaldehyde due to its ability to form H-bonds. Adding a hydroxyl group or a Cl atom to 3-nitrobenzoic acid to give 2-hydroxy-5-nitrobenzoic acid (1.79E-03) or 2-chloro-3-nitrobenzoic acid (1.97E-03) respectively increases the observed P_S^{sat} as the addition of the extra functional group leads to increased intramolecular H-bonding occurring. Additionally, comparing 2-hydroxy-5-nitrobenzoic acid with 2-fluoro-4-nitrophenol demonstrates how the increased ability of carboxylic acid to partake in H-bonding compared to a F atom leads to a suppression of P_S^{sat}. 5-Chloro-2-nitrobenzoic acid has a higher P_S^{sat} (2.98E-03 Pa) than 2-chloro-3-nitrobenzoic acid (1.97E-03 Pa), its structural isomer. The increase in P_S^{sat} can be attributed to the increase partial charge of the carbon within the carboxylic acid group (0.627 increasing to 0.640).

When comparing nitrobenzoic acids as a whole with nitrophenols, nitrobenzoic acids have a much higher P_S^{sat} than would be expected based solely on the partial charges of the carboxylic carbon. As can be seen in Fig. 8, there is overlap in the range of P_S^{sat} for the nitrobenzoic acids and many of the nitrophenols, however there is no overlap in terms of partial charges of the carboxylic and phenolic carbons, with all of the nitrobenzoic acids having partial charges of the carboxylic carbon greater than 0.6, whilst the nitrophenols had much lower partial charges of the phenolic carbon between 0.2 and 0.4. It is widely known that the H-bonds of carboxylic acids are stronger than the H-bonds of alcohols (Ouellette et al., 2015b) so therefore it would be expected that the carboxylic acids would have a lower P_S^{sat}. A likely reason as to why the P_S^{sat} of the nitrobenzoic acids is higher than would be expected, compared to the nitrophenols, based only on the partial charge of the carboxylic carbon is the propensity for carboxylic acids to dimerise (see Fig. ~~10~~9). Nitrophenols are unable to dimerise, instead being able to form H-bonds with up to 2 other molecules as shown in Fig. 9. By dimerising the nitrobenzoic acids, despite having much stronger H-bonds than the nitrophenols, will not have a proportionally lower P_S^{sat}.

In summary the ability to form H-bonds appears to be the most significant factor affecting the P_S^{sat} of a compound, where molecules that are able to form these strong intermolecular interactions generally always exhibit lower P_S^{sat} than those that cannot. Additionally different functional groups are able to form different numbers of H-bonds; with those that are able to form more H-bonds generally supressing P_S^{sat} to a greater extent than those that form less. The relative positioning of those functional groups responsible for the H-bonding is also important as when positioned too close together intramolecular H-bonding can occur, which competes with intermolecular H-bonding and generally raises P_S^{sat}. The positioning of non H-bonding functional groups within the molecule can also have an impact upon the extent of H-bonding, with bulky substituents positioned close to H-bonding groups causing steric hindrance which reduces the extent of H-bonding and generally raises P_S^{sat}. The positioning of all the functional groups around the aromatic ring effect the partial charges of the atoms, via a combination of the inductive effect and the resonance effect. The inductive effect and the partial charges appear to be most important when comparing isomers, and less important when one functional group has been swapped for another. In addition ~~higher molecular dipole moments,~~ greater molecular weight, and increased crystallographic packing density also negatively correlate with P_S^{sat} as they both ~~all~~ lead to increased overall intermolecular interactions. However in many cases these different factors compete with each other, making it difficult to predict the expected P_S^{sat} and currently it is not possible to determine which factor will dominate in any given case. Dipole moments were also investigated but overall showed very little impact on P_S^{sat}.

4.2 Sub-cooled liquid vapour pressure

The P_L^{sat} were obtained from the P_S^{sat} using thermochemical data obtained through use of a DSC and Eq. 3~~2~~. The results are detailed in Table~~s~~ 7~~8, 9 and 10 for the nitrophenols, nitrobenzaldehydes and nitrobenzoic acids respectively~~.

Comparing the P_L^{sat} of the nitrophenols with the solid state values there are a few changes in the overall ordering but they mostly have little effect upon the preceding discussion. A few previously significant increases/decreases in P^{sat} become insignificant and a few that were insignificant are now significant. One point of note however, is that 3-methyl-4-nitrophenol (5.86E-02) now exhibits a higher P^{sat} than 3-fluoro-4-nitrophenol (3.32E-02). This trend is what would be expected based on the reduction in steric hindrance, increased potential for H-bonding and increase in ~~molecular dipole moment~~the partial charge of the phenolic carbon that the F atom provides in comparison to the methyl group.

For the nitrobenzaldehydes one change in the overall ordering of the P^{sat}s is observed after converting to P_L^{sat} but this has no effect on the preceding discussion.

Finally for the nitrobenzoic acids whilst some previously insignificant differences in P_S^{sat} have now become significant, the only change that impacts upon the discussion is that the P^{sat} of 3-methyl-4-nitrobenzoic acid (3.04E-01) is now higher than that of 4-methyl-3-nitrobenzoic acid (5.76E-02). This change could be explained as a result of the higher ~~molecular dipole moment~~partial charge of the carboxylic carbon of 4-methyl-3-nitrobenzoic acid (~~4.306 D~~0.646 vs 0.628~~3.555 D~~) (Stewart, 2016) playing a more important role in the subcooled liquid state than in the solid state.

4.3 Comparison with estimations from GCMs

In Fig. 10~~8~~ the experimentally determined P_L^{sat} of the nitroaromatics are compared to the predicted values of several GCMs. The average difference between the experimental P_L^{sat} and the predicted P_L^{sat} for each class of compound and overall is shown in Table 8. These GCMs are SIMPOL (Pankow and Asher, 2008), ~~EVAPORATION (Compernolle et al., 2011),~~ the Nannoolal et al. method (Nannoolal et al., 2008), and the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997). The Nannoolal et al. method (Nannoolal et al., 2008) and the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) are both combined methods which require a boiling point to function. As for many compounds where the experimental boiling point is unknown boiling point group contribution methods are required. The Nannoolal et al. method (Nannoolal et al., 2004) and the Stein and Brown method (Stein and Brown, 1994) are used.

The Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) shows poor agreement with the experimental data for almost all compounds, but is not particularly surprising given that it only contains 3 nitroaromatic compounds in this method's fitting data set, with none of these compounds containing both a nitro group and another oxygen containing group. The Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) is the oldest method examined in this study, and much of the atmospherically relevant P^{sat} data has been collected after the end of the development of this model. The Myrdal and Yalkowsky method's (Myrdal and Yalkowsky, 1997) reliance on a predicted boiling point may also be a major source of error in the P^{sat} predictions of the nitroaromatics.

On average the SIMPOL method (Pankow and Asher, 2008) predicts values closest to the experimental data, on average predicting P_L^{sat} 1.3 orders of magnitude higher than the experimental values, despite absolute differences of up to 4.4 orders of magnitude.

~~EVAPORATION (Compernolle et al., 2011) has the worst agreement with the experimental data, on average predicting $\mathbf{P_L^{sat}}$ 3.9 orders of magnitude higher than the experimental values and absolute differences of up to 7.0 orders of magnitude. This outcome is not unexpected because, whilst EVAPORATION (Compernolle et al., 2011) was designed with SOAs in mind, it does not contain any aromatic parameters and is therefore unsuitable for any aromatic compounds. It has been used to demonstrate the effects of using GCMs that do not contain the functionality of the compounds of interest and the large errors in estimation that this can cause.~~

The Nannoolal et al. method (Nannoolal et al., 2004) is persistently worse than the Stein and Brown method (Stein and Brown, 1994) for the nitroaromatic compounds involved in this study as shown in Table 8. When discussing the Nannoolal et al. method (Nannoolal et al., 2008) and the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) from this point onwards it is used with the Stein and Brown method (Stein and Brown, 1994) unless stated otherwise.

The Nannoolal et al. method (Nannoolal et al., 2008) has slightly better agreement with the experimental data when compared to the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) on average predicting P_L^{sat} 2.52 orders of magnitude higher than the experimental values, whereas the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) on average predicts P_L^{sat} 2.65 orders of magnitude higher than the experimental values. The Nannoolal et al. method (Nannoolal et al., 2008), unlike the others, contains parameters for ortho, meta, para isomerism and even demonstrates the same trend as the experimental data for 2-nitrobenzaldehyde, 3-nitrobenzaldehyde and 4-nitrobenzaldehyde, although 3 orders of magnitude higher. Despite the ortho, meta, para parameters, as soon as a third functional group is present around the aromatic ring the Nannoolal et al. method (Nannoolal et al., 2008) no longer accounts for relative positioning of the functional groups.

Figure 10~~8~~a shows the comparison between the experimental and predicted $\mathbf{P_L^{sat}}$ for the nitrophenols. Both SIMPOL (Pankow and Asher, 2008) and the Nannoolal et al. method (Nannoolal et al., 2008) contain nitrophenol data from Schwarzenbach et al. (Schwarzenbach et al., 1988). This data of Schwarzenbach et al. (Schwarzenbach et al., 1988), however, is questionable in reliability due to being taken from a single data point from a single data set. The values given are also 3-4 orders of magnitude greater than those measured in this work as well as those measured by Bannan et al. (Bannan et al., 2017) and those measured by Dang et al. (Dang et al., 2019). The use of the Schwarzenbach et al. (Schwarzenbach et al., 1988) nitrophenol $\mathbf{P^{sat}}$ data, which makes up 11 of the 12 nitrophenol data points within the fitting data set of the SIMPOL method (Pankow and Asher, 2008), is a likely cause of the SIMPOL method (Pankow and Asher, 2008) overestimating the $\mathbf{P^{sat}}$ of nitrophenols by 3 to 4 orders of magnitude. The one nitrophenol used in the SIMPOL method(Pankow and Asher, 2008) not from Schwarzenbach et al. (Schwarzenbach et al., 1988), 3-nitrophenol from Ribeiro da Silva et al. (Ribeiro da Silva et al., 1992), has a much lower $\mathbf{P^{sat}}$ than those of Schwarzenbach et al. and is only one order of magnitude higher than that from Bannan et al. (Bannan et al., 2017). Additionally, Whilst the Nannoolal et al. (Nannoolal et al., 2008) method performs slightly better than the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) overall for this study, when taking the nitrophenol data in isolation this performance is flipped with the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) showing better performance (overestimating on average by 3.4 to 3.5 orders of magnitude).

Figure 10~~8~~b shows the comparison between the experimental and predicted P_L^{sat} for the nitrobenzaldehydes. There are no nitrobenzaldehydes present in any fitting data set of the GCMs considered in this study. Despite this, whilst not capturing the effects of ortho, meta, para isomerism, SIMPOL (Pankow and Asher, 2008) predicts the P^{sat} of the nitrobenzaldehydes to, on average, 0.29 orders of magnitude. As polar groups such as aldehydes have been shown to have little impact on volatility in the pure component, and by extension P^{sat} (Bilde et al., 2015), this implies that SIMPOL (Pankow and Asher, 2008) captures the contribution of the nitro group very well. Similar to the nitrophenols the performance of the Nannoolal et al. method (Nannoolal et al., 2008) and the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) has switched for the nitrobenzaldehydes compared to the entire data set. The Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) overestimates by 2.4 orders of magnitude compared to the Nannoolal et al. method (Nannoolal et al., 2008) which overestimates by 2.5 orders of magnitude.

Figure 10~~8~~c shows the comparison between the experimental and predicted P_L^{sat} for the nitrobenzoic acids. SIMPOL (Pankow and Asher, 2008) contains, though in limited amounts, nitrobenzoic acid data in its fitting parameters. Although there are no lists of the data used to form the Nannoolal et al. method (Nannoolal et al., 2008) available (to the authors knowledge), it is stated that the values come from the Dortmund Data Bank and from searches on this database there is nitrobenzoic acid P^{sat}

data available. Having even this limited data available for the nitrobenzoic acids allows for SIMPOL (Pankow and Asher, 2008) to predict the P_L^{sat}s of 5-chloro-2-nitrobenzoic acid, 3-nitrobenzoic acid, 2-chloro-3-nitrobenzoic acid and 2-hydroxy-5-nitrobenzoic acid to within one order of magnitude of the experimental values. On average the SIMPOL (Pankow and Asher, 2008) method underestimates P_L^{sat} by 0.8 orders of magnitude. The nitrobenzoic acids that had large discrepancies with SIMPOL (Pankow and Asher, 2008), 4-methyl-3-nitrobenzoic acid and 3-methyl-4-nitrobenzoic acid, as well as 2-hydroxy-5-nitrobenzoic acid agreed to within one order of magnitude of the Nannoolal et al. method (Nannoolal et al., 2008). On average the Nannoolal et al. method (Nannoolal et al., 2008) overestimates P_L^{sat} by 0.9 orders of magnitude.

Overall SIMPOL (Pankow and Asher, 2008) performs relatively well for the nitrobenzaldehydes and the nitrobenzoic acids, and the Nannoolal et al. method (Nannoolal et al., 2008) performs moderately well for the nitrobenzoic acids when compared to the experimental values found in this study. All of the methods perform poorly when compared to the experimental nitrophenol values. These observations are not particularly surprising when taking into account how the methods were fitted and what data is present in the fitting set.

One surprising observation comes when looking at the halogenated nitroaromatics. SIMPOL (Pankow and Asher, 2008) has the smallest order of magnitude difference between experimental and predicted P_L^{sat} for all of the halogenated nitroaromatics in this study. This is particularly surprising as SIMPOL (Pankow and Asher, 2008) contains no halogenated compounds in its fitting data set, whereas the other GCMs do. This implies that accurately predicting the impact on P_L^{sat} of carbon skeleton and other functional groups such as, nitro, hydroxy, aldehyde and carboxylic acid are more important than the impact of a chloro or fluoro group.

When looking at nitroaromatics as a whole SIMPOL (Pankow and Asher, 2008) shows the smallest difference between experimental and predicted P_L^{sat} (as shown in Table 8) and would therefore be the most appropriate method to use when predicting P_L^{sat} for this group of compounds. In the case of nitrophenols, despite SIMPOL (Pankow and Asher, 2008) showing the best performance the absolute differences are still close to 3 orders of magnitude, so any work using these predictions should be aware of the very larger errors that these predictions could introduce. For nitrobenzaldehydes SIMPOL (Pankow and Asher, 2008) shows very good agreement and is the clear choice to be used when predicting P_L^{sat}. For nitrobenzoic acids the preferred method for predicting P_L^{sat} is not quite as clear. Both the Nannoolal et al. method (Nannoolal et al., 2008) and

SIMPOL (Pankow and Asher, 2008) predict P_L^{sat} within an order of magnitude, with Nannoolal et al. (Nannoolal et al., 2008) generally overestimating and SIMPOL (Pankow and Asher, 2008) underestimating.

4.4 Comparison with existing experimental data

For the compounds in this study that had previous literature data there are differences from the values determined experimentally in this work. The differences between the values from this work and those of Dang et al. (~~Dang et al.,~~ 2019) are discussed in sect. 4.5 but can be attributed to the use of a different reference compound.

For the nitrophenols, shown in Fig. 10~~8~~a, the differences between the experimental values and the literature values from Schwarzenbach et al. (~~Schwarzenbach et al.,~~ 1988) range from 3 to 4 orders of magnitude. The relationship between the P_L^{sat} and temperature from Schwarzenbach et al. (~~Schwarzenbach et al.,~~ 1988) was derived from gas chromatographic (GC) retention data. This GC method requires a reference compound of known P^{sat}, and for the reference compound and the compound of interest to have very similar interactions with the stationary phase of the GC. Schwarzenbach et al. (~~Schwarzenbach et al.,~~ 1988) used 2-nitrophenol as the reference compound for all of the other nitrophenol data they collected. In this work the P_L^{sat} at 298 K was 1.38E-03 Pa whereas Schwarzenbach et al. (~~Schwarzenbach et al.,~~ 1988) reported it as 2.69E+01 Pa. As the difference between the P^{sat} of 2-nitrophenol in this work and Schwarzenbach et al. (~~Schwarzenbach et al.,~~ 1988) differs by approximately 4 orders of magnitude this could explain why the other nitrophenol measurements also differ by 3-4 orders of magnitude.

For the nitrobenzaldehydes, shown in Fig. 10~~8~~b, the literature data from Perry et al. (~~Perry et al.,~~ 1984) and the experimental data from this work agree within one order of magnitude with 2-nitrobenzaldehyde especially agreeing very closely (2.39E+00 Pa vs 2.15E+00 Pa).

The nitrobenzoic acids are shown in Fig. 10~~8~~c. The value for 3-nitrobenzoic acid from this work is 1.90E-03 Pa compared to 5.05E-03 from Ribeiro da Silva et al. (~~Ribeiro Da Silva et al.,~~ 1999) Whilst not matching perfectly, the P^{sat} of 3-nitrobenzoic acid is on this order of magnitude. The disagreements between the values of this work and the values from Monte et al. (~~Monte et al.,~~ 2001) for 4-methyl-3-nitrobenzoic acid and 3-methyl-4-nitrobenzoic acid are quite large. 4-methyl-3-nitrobenzoic acid differs by over one order of magnitude and 3-methyl-4-nitrobenzoic acid is closer to two orders of magnitude. Monte et al. (~~Monte et al.,~~ 2001) where collected using a Knudsen mass loss method. Knudsen mass loss is similar to KEMS in that it also utilises a Knudsen cell which effuses the compound of interest. However for an amount of mass to be lost such that it can be detected the experiments need to be performed at higher temperatures than the KEMS. This means that the data must be extrapolated further to reach ambient temperatures. This is a potential source of error and could explain the difference. Measurement by a third or even fourth technique would be required to confirm this.

4.5 Sensitivity of vapour pressure measurement techniques to reference standards

The recently published paper by Dang et al. (2019) measured the P^{sat} of several of the same compounds that are studied in this paper using the same KEMS system, however in this study the newly defined best practice reference sample was used (Krieger et al., 2018), whereas Dang et al. (2019) used malonic acid. These compounds were 4-methyl-3-nitrophenol, 3-methyl-4-nitrophenol and 4-methyl-2-nitrophenol. The difference in reference compound led to a discrepancy in the experimental P^{sat} (shown in Table 9~~4~~). Due to these differences additional measurements were made using malonic acid as the reference material. Additionally, supporting measurements for the compounds were performed using the EDB from ETH Zurich in order to rule out instrumental problem with the KEMS. ~~As single particles injected from a dilute solution may either stay in a supersaturated, liquid state or crystallize, it is important to identify its physical state.~~ Comparisons between P^{sat} at 298 K from the KEMS using a PEG reference, the KEMS using a malonic acid reference, Dang et al. (2019) and the EDB are shown in Table 9~~4~~. Following this P_L^{sat}, extrapolated down to 290 K, from KEMS using a PEG reference and the KEMS using a malonic acid reference are compared to the estimated P_L^{sat} based on the findings from the EDB using Eq. 2~~3~~.

Whilst the absolute values of the nitrophenols shown in Table 9~~4~~ changed, the P^{sat} trends did not. The values from Dang et al. (2019) are between 4.39 and 7.81 times lower than those in this work using the PEGs as the reference compound, which is now deemed as best practice in the community. To ensure that the difference in reference compound was the cause of the difference in P^{sat} 4-methyl-2-nitrophenol, 4-methyl-3-nitrophenol and 3-methyl-4-nitrophenol were also measured using malonic acid as a reference again. The differences between the P^{sat} determined by Dang et al. (2019) and those in this work using malonic acid as a reference compound were between 2 % and 27 %, well within the quoted 40 % error margin of the KEMS, (Booth et al., 2009) therefore showing that the instrument is behaving reproducibly but with now improved reference standards being used, as is discussed below.

Starting with 4-methyl-3-nitrophenol the EDB has much better agreement with the KEMS when the PEGs are used as the reference compound than when malonic acid is used as the reference compound. When the quoted errors of both the EDB (shown in Table 94) and the KEMS (± 40% for $\mathrm{P_S^{sat}}$ and ± 75% for $\mathrm{P_L^{sat}}$ (Booth et al., 2009)) are taken into account the lower limit of the EDB (1.57E-02 Pa) and the upper limit of the KEMS using the PEG references (1.51E-02 Pa) almost overlap whereas the EDB data is almost 1 order of magnitude larger than the KEMS when the malonic acid reference is used (shown in Fig. 11).

For 3-methyl-4-nitrophenol a comparison can be made for both $\mathrm{P_S^{sat}}$ and $\mathrm{P_L^{sat}}$. Looking first at the $\mathrm{P_S^{sat}}$ the EDB appears to be somewhere in between the KEMS depending on what the KEMS is using as a reference, with its absolute value being closer to that of the Malonic acid reference. However when the quoted errors are taken into account (shown in Table 94) the EDB actually has better agreement with the KEMS when the PEG references are used. This can be seen more clearly in Fig. 11. For $\mathrm{P_L^{sat}}$ the EDB and the KEMS when using the PEG references appears to agree very well with a large overlap when the quoted errors are taken into account. This can also be seen in Fig. 11.

The confidence with which the comparison between the EDB and the KEMS can be made for 4-methyl-2-nitrophenol is lower than with the other compounds looked at due to how quickly 4-methyl-2-nitrophenol evaporated in the EDB. To make this comparison the $\mathrm{P_L^{sat}}$ from the KEMS measurements has been extrapolated down to 290 K to match that of the EDB estimation. The predicted EDB value (shown in Fig. 11) is higher than the KEMS for both references but has a very large error margin (approximately a factor of 5). When this error is considered the KEMS using the PEG reference is within this range, whereas there is close to an order of magnitude difference between the lower limit of this estimate and the upper limit of the KEMS when malonic acid is used as the reference.

In all cases the EDB showed better agreement with the KEMS using the PEGs as the reference material compared to when malonic acid was used as the reference material. For 4-methyl-3-nitrophenol the agreement was very close between the EDB and the KEMS using the PEGs as the reference compounds, and for 3-methyl-4-nitrophenol the measurements for the EDB and the KEMS agreed with each other within the quoted errors. For 4-methyl-2-nitrophenol the KEMS with PEG as a reference also showed the best agreement with the EDB, but as this was an estimate with a large error range this comparison is the least certain.

5 Conclusions

Experimental values for the P_S^{sat} and P_L^{sat} have been obtained using KEMS and DSC for nitrophenols, nitrobenzaldehydes, and nitrobenzoic acids.

The predictive models have been shown to overestimate P_L^{sat} in almost every instance by several orders of magnitude. As the P^{sat} from these predictive techniques are often used in mechanistic partitioning models (Lee-Taylor et al., 2011; Shiraiwa et al., 2013), the overestimation of the P^{sat} can lead to an overestimation of the fraction in gaseous state. The experimental values from this study can be used in conjunction with other measurements to improve the accuracy of GCMs, and give an insight into the impact of functional group positioning which is missing, or only available in a limited capacity, for the currently available GCMs.

The differences in trends of the experimental P^{sat} have been explained chemically, with the potential and strength of H-bonding appearing to be the most significant factor, where present, in determining the P^{sat}. With the stronger the hydrogen bond and the increasing number of possible hydrogen bonds decreasing the P^{sat}. Whilst H-bonding is typically the most important factor, it isn't the only factor. Steric effects by functional groups can also have significant effects on the P^{sat}~~, and in systems without the potential to form H-bonds the dipole moment of a compound can become important~~. In the solid state crystallographic packing density can also be an important factor. To further investigate the impacts of H-bonding, inductive and resonance effects, and steric effects on P^{sat} more compounds need to be investigated, with select compounds being chosen to probe these effects.

The predictive models consistently overestimate the P_L^{sat}s by up to 6 orders of magnitude with the nitrophenols performing especially poorly. This demonstrates a need for more experimental data to be used in the fitting data sets of the GCMs to reduce the errors and give more accurate results for nitroaromatic compounds.

Deviations between the measurements in Dang et al. (~~Dang et al., ~~2019) and this work can be explained by the difference of the reference material used which demonstrates the necessity of a consistent, widely used reference compound. The PEG series, looked at by Krieger et al. (~~Krieger et al.~~, 2018), is currently the preferred reference/calibration series.

Comparisons between the KEMS and the EDB from ETH were made for several nitrophenols. The EDB showed close agreement with the KEMS when the PEG series was used as the reference compounds.

Compounds such as the nitrobenzaldehydes, which are capable of being H-bond acceptors but not H-bond donors, are likely to deviate negatively from Raoult's law in mixtures with compounds that can act as H-bond donors, due to the adhesive forces present. This could call into question the validity of pure component vapour pressure measurements for looking at atmospheric systems due to the atmosphere not being made up of the pure component. This would be an interesting avenue of research and the natural progression from pure component measurements to investigate their usefulness.

Data Availability

All data in this paper is available from http://doi.org/10.5281/zenodo.3613581 (Shelley et al., 2020b).

Supplementary Material

The supplementary material is available from https://doi.org/10.5281/zenodo.3625641 (Shelley et al., 2020a)

Author Contributions

Petroc D. Shelley carried out the experiments on the KEMS and DSC. Ulrich K. Krieger carried out the experiments on the EDB. Formal analysis of the data was carried out by Petroc D. Shelley, Stephen D. Worrall and Ulrich K. Krieger. Project supervision was undertaken by David Topping, M. Rami Alfarra and Thomas J. Bannan. KEMS training was performed by Thomas J. Bannan. Access to and training on the DSC was undertaken by Arthur Garforth. Verification on the reliability of the KEMS was carried out by Ulrich K. Krieger, with the EDB measurements being used to validate the KEMS measurements. The original draft manuscript was written by Petroc D. Shelley, Stephen D. Worrall and Carl J. Percival. Internal review and editing was performed by Thomas J. Bannan, David Topping, M. Rami Alfarra, Stephen D. Worrall and Ulrich K. Krieger.

Competing Interests

The Authors declare that they have no conflict of interest.

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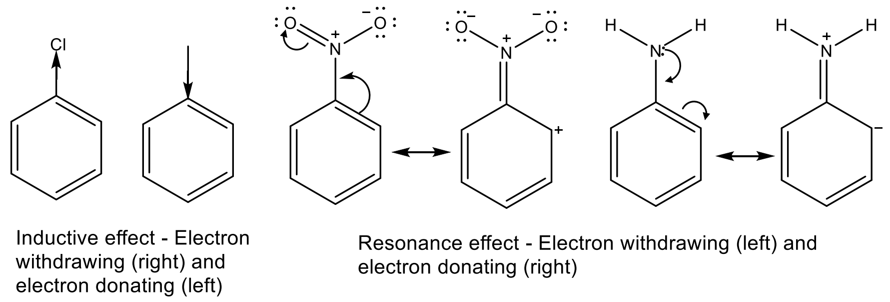


Figure 1: The inductive effect and the resonance effect

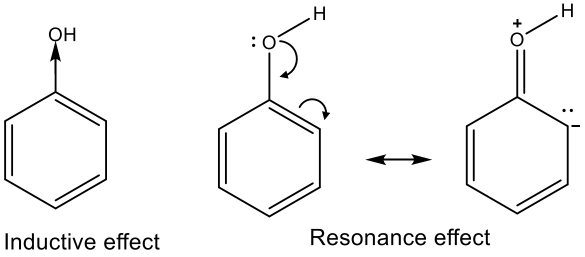
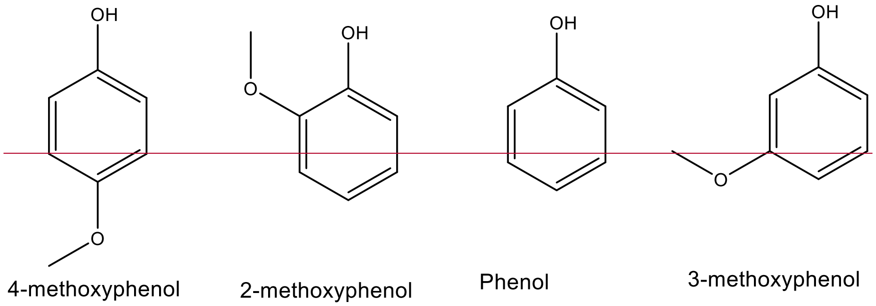
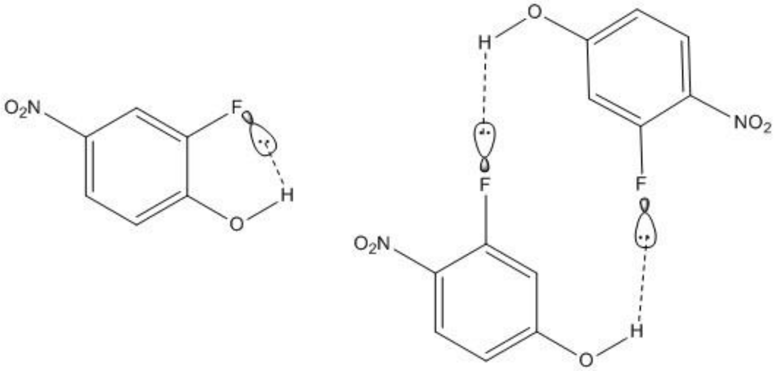


Figure 2: Phenol can withdraw electron density via the inductive effect (left) and donate electron density via the resonance effect



~~**Figure 3: structures of phenol and the methoxyphenol isomers**~~



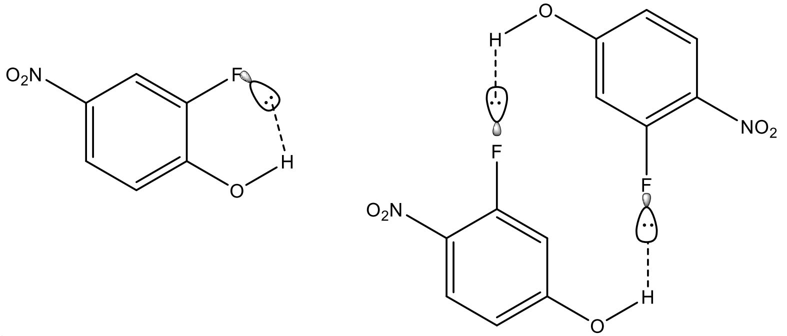


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Figure 3~~4~~: Intramolecular hydrogen bonding in 2-fluoro-4-nitrophenol (left) in comparison to intermolecular hydrogen bonding in 3-fluoro-4-nitrophenol

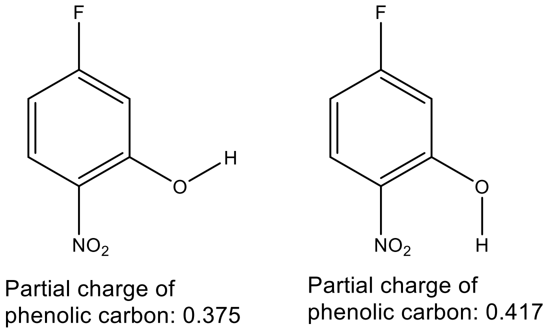

Figure 4~~5~~: The orientation of the OH group can impact the partial charge of the phenolic carbon

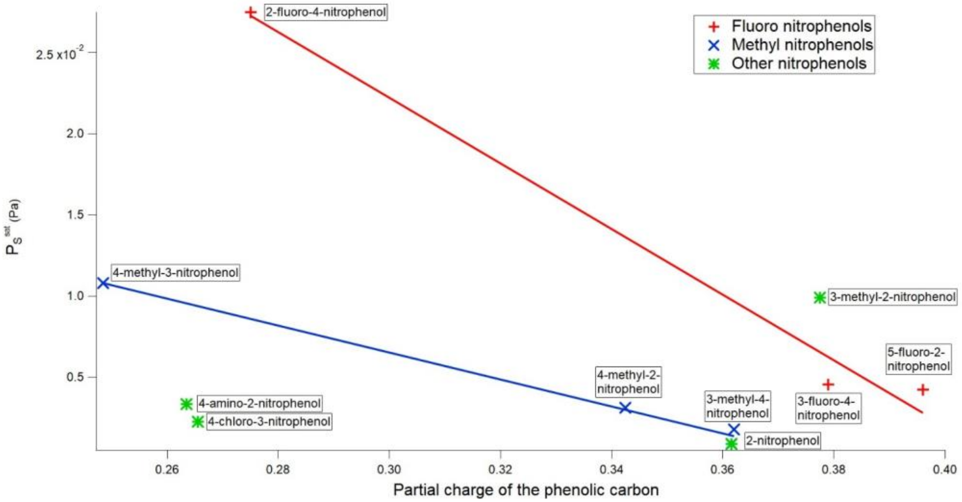

Figure 5: P_S^{sat} vs partial charge of the phenolic carbon of the nitrophenols.

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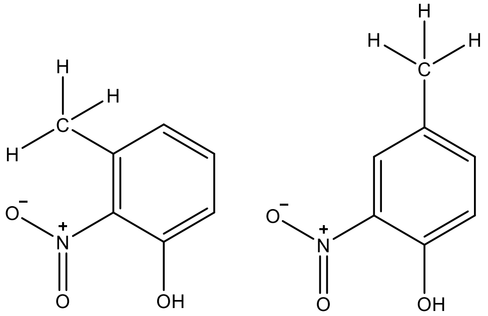

Figure 6: Diagram emphasising how the proximity of the bulky methyl group sterically hinders intermolecular interactions with the nitro group in 3-methyl-2-nitrophenol (left) but not in 4-methyl-2-nitrophenol (right).

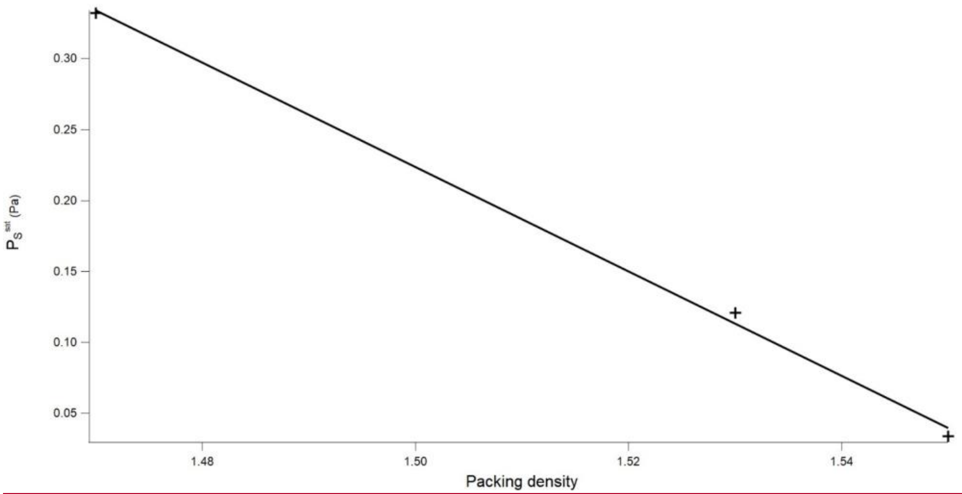

Figure 7: P_S^{sat} vs Packing density of the nitrobenzaldehydes

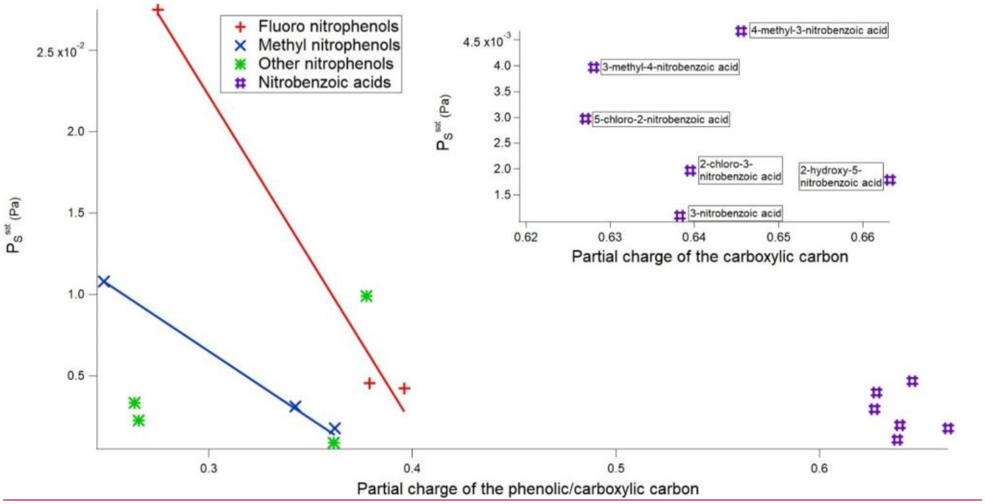

Figure 8: P_S^{sat} vs partial charge of the phenolic/carboxylic carbon of the nitrophenols and nitrobenzoic acids.

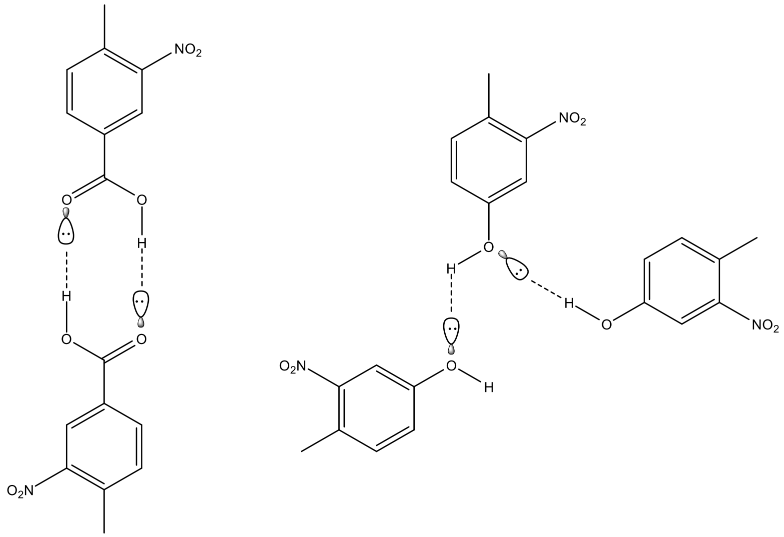

Figure ~~7~~9: Diagram demonstrating how ~~the~~ a carboxylic acid functionality allows a molecule to dimerise using ~~hydrogen b~~H-bonds ~~to three other molecules~~ in 4-methyl-3-nitrobenzoic acid (left) whilst a hydroxyl group only allows for hydrogen bonding to two other molecules with no opportunity to dimerise in 4-methyl-3-nitrophenol (right).

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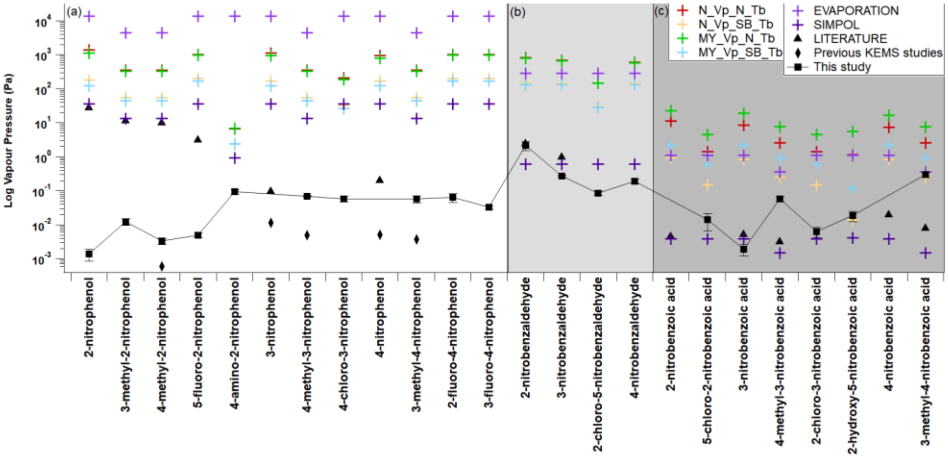

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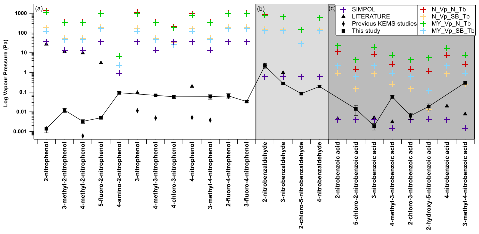


Figure 10~~8~~: Comparison of estimated and measured sub-cooled saturation vapour pressures. N_Vp (Nannoolal vapour pressure), MY_Vp (Myrdal and Yalkowsky vapour pressure), ~~EVAPORATION (EVAPORATION vapour pressure),~~ SIMPOL (SIMPOL vapour pressure), N_Tb (Nannoolal boiling point), SB_Tb (Stein and Brown boiling point), LITERATURE - black triangle (2-nitrophenol, 3-methyl-2-nitrophenol, 4-methyl-2-nitrophenol, 5-fluoro-2-nitrophenol, 4-nitrophenol from (Schwarzenbach et al., 1988)**, 3-nitrophenol from** (Ribeiro da Silva et al., 1992) **2-nitrobenzaldehyde, 3-nitrobenzaldehyde from** (Perry et al., 1984)**, 2-nitrobenzoic acid, 3-nitrobenzoic acid, 4-nitrobenzoic acid from** (Ribeiro Da Silva et al., 1999)**, 4-methyl-3-nitrobenzoic acid, 3-methyl-4-nitrobenzoic acid from** (Monte et al., 2001)**) - black diamond for literature data for previous KEMS work (3-nitrophenol,**

4-nitrophenol from (Bannan et al., 2017)**, 4-methyl-2-nitrophenol, 4-methyl-3-nitrophenol, 3-methyl-4-nitrophenol from** (Dang et al., 2019)**) Error bars on the Experimental data points are +/- 1 standard deviation. Section (a) contains nitrophenols, Section (b) contains nitrobenzaldehydes, and Section (c) contains nitrobenzoic acids.**

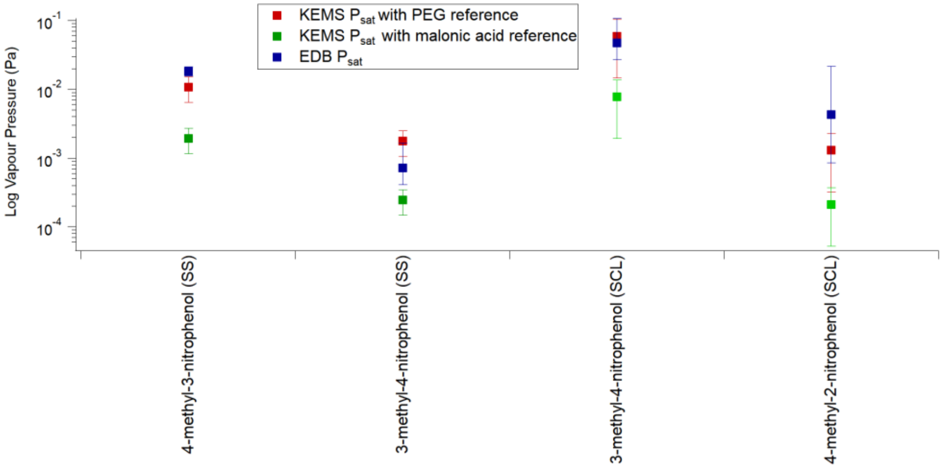
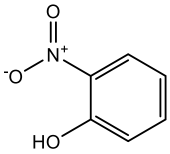
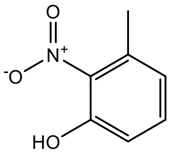
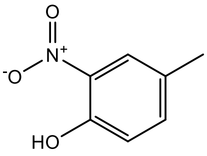
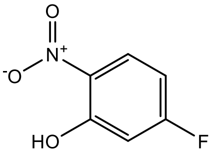
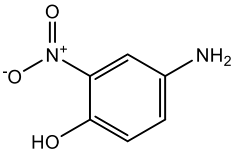
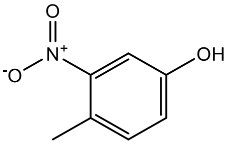
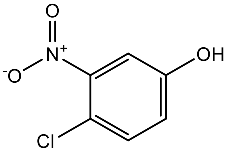
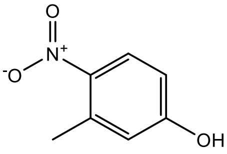


Figure 11~~9~~: Comparison of P^{sat} between the EDB and the KEMS using both PEGs and Malonic acid as the reference compound (SS – solid state, SCL – sub-cooled liquid)

Table 1: Nitrophenols measured with the KEMS

Compound	Structure	CAS	Supplier
2-nitrophenol		88-75-5	Acros Organics
3-methyl-2-nitrophenol		4920-77-8	Sigma Aldrich

4-methyl-2-nitrophenol		119-33-5	Acros Organics
5-fluoro-2-nitrophenol		446-36-6	Fluorochem
4-amino-2-nitrophenol		119-34-6	Acros Organics
4-methyl-3-nitrophenol		2042-14-0	Sigma Aldrich
4-chloro-3-nitrophenol		610-78-6	Alfa Aesar
3-methyl-4-nitrophenol		2581-34-2	Fluorochem

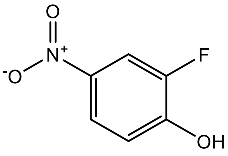
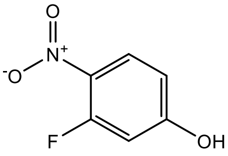
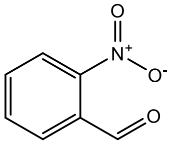
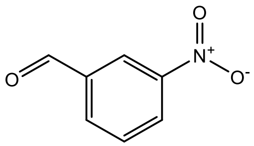
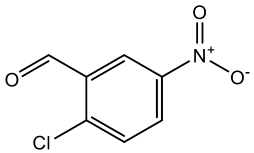
2-fluoro-4-nitrophenol		403-19-0	Fluorochem
3-fluoro-4-nitrophenol		394-41-2	Acros Organics

Table 2: Nitrobenzaldehydes measured with the KEMS

Compound	**Structure**	**CAS**	**Supplier**
2-nitrobenzaldehyde		552-89-6	Sigma Aldrich
3-nitrobenzaldehyde		99-61-6	Sigma Aldrich
2-chloro-5-nitrobenzaldehyde		6361-21-3	Acros Organics

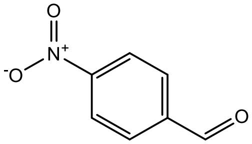
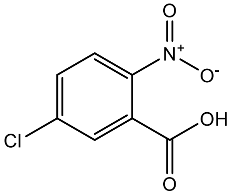
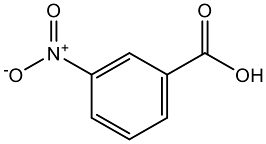
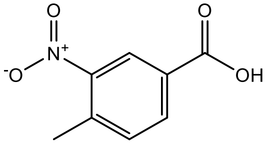
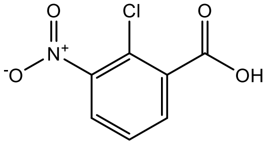
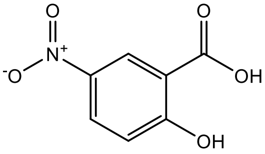
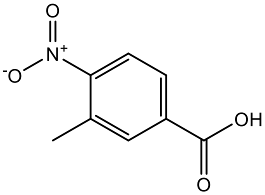
4-nitrobenzaldehyde		555-16-8	Sigma Aldrich

Table 3: Nitrobenzoic acids measured with the KEMS

Compound	**Structure**	**CAS**	**Supplier**
5-chloro-2-nitrobenzoic acid		2516-95-2	Sigma Aldrich
3-nitrobenzoic acid		121-92-6	Sigma Aldrich
4-methyl-3-nitrobenzoic acid		96-98-0	Sigma Aldrich
2-chloro-3-nitrobenzoic acid		3970-35-2	Sigma Aldrich

2-hydroxy-5-nitrobenzoic acid		96-97-9	Sigma Aldrich
3-methyl-4-nitrobenzoic acid		3113-71-1	Sigma Aldrich

~~**Table 4: partial charge of phenolic carbon compared to the H-bond energy (E$_{HB}$)**~~

~~**Compound**~~	~~**Partial charge of the phenolic carbon**~~	~~**Remko and Polcin** (Remko and Polcin, 1977) **E$_{HB}$ (kJ mol^{-1})**~~	~~**Stymne et al.** (Stymne et al., 1973) **E$_{HB}$ (kJ mol^{-1})**~~
~~4-methoxyphenol~~	~~0.222~~	~~43.5~~	~~23.8~~
~~2-methoxyphenol~~	~~0.199~~	~~44.1~~	
~~Phenol~~	~~0.294~~	~~44.7~~	~~24.3~~
~~3-methoxyphenol~~	~~0.354~~	~~45.6~~	~~26.4~~

Table 4~~5~~: P_S^{sat} at 298 K, ~~and~~ enthalpies and entropies of sublimation, and partial charge of the phenolic carbon of nitrophenols determined using KEMS

Compound	**P$_{298}$ (Pa)**	**ΔH$_{sub}$ (kJ mol^{-1})**	**ΔS$_{sub}$ (J mol^{-1} K^{-1})**	**Partial charge of the phenolic carbon**
2-nitrophenol	8.94E-04	79.32	206.78	0.362
3-methyl-2-nitrophenol	9.90E-03	94.79	279.50	0.378
4-methyl-2-nitrophenol	3.11E-03	95.26	271.45	0.343
5-fluoro-2-nitrophenol	4.25E-03	95.84	276.14	0.396

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4-amino-2-nitrophenol	3.36E-03	111.24	325.81	0.264
4-methyl-3-nitrophenol	1.08E-02	96.14	284.98	0.249
4-chloro-3-nitrophenol	2.26E-03	104.49	299.83	0.266
3-methyl-4-nitrophenol	1.78E-03	90.85	251.97	0.362
2-fluoro-4-nitrophenol	2.75E-02	103.76	317.90	0.275
3-fluoro-4-nitrophenol	4.55E-03	108.61	319.55	0.379

Table 5~~6~~: P_S^{sat} at 298 K,~~ and~~ enthalpies and entropies of sublimation, and crystallographic packing densities of nitrobenzaldehydes determined using KEMS

Compound	**P_{298} (Pa)**	**ΔH_{sub} (kJ mol^{-1})**	**ΔS_{sub} (J mol^{-1} K^{-1})**	**Crystallographic packing density**
2-nitrobenzaldehyde	3.32E-01	73.81	238.13	1.473
3-nitrobenzaldehyde	1.21E-01	83.51	262.67	1.528
2-chloro-5-nitrobenzaldehyde	4.21E-02	101.26	313.39	
4-nitrobenzaldehyde	3.40E-02	103.80	320.10	1.546

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Table 6~~7~~: P_S^{sat} at 298 K,~~ and~~ enthalpies and entropies of sublimation, and partial charge of the carboxylic carbon of nitrobenzoic acids determined using KEMS

Compound	**P_{298} (Pa)**	**ΔH_{sub} (kJ mol^{-1})**	**ΔS_{sub} (J mol^{-1} K^{-1})**	**Partial charge of the carboxylic carbon**
5-chloro-2-nitrobenzoic acid	2.98E-03	80.66	221.09	0.627
3-nitrobenzoic acid	1.10E-03	87.82	237.49	0.638
4-methyl-3-nitrobenzoic acid	4.67E-03	74.66	205.82	0.646
2-chloro-3-nitrobenzoic acid	1.97E-03	73.54	194.48	0.640
2-hydroxy-5-nitrobenzoic acid	1.79E-03	78.20	209.30	0.663

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3-methyl-4-nitrobenzoic acid	3.97E-03	65.95	175.21	0.628

Table 7~~8~~: P_L^{sat}, melting point, and the enthalpy and entropy of fusion of the nitrophenols.

Compound	P_{298} (Pa)	T_m (K)	ΔH_{fus} (kJ mol^{-1})	ΔS_{fus} (J mol^{-1} K^{-1})
2-nitrophenol	1.38E-03	319.77	18.55	58.02
3-methyl-2-nitrophenol	1.22E-02	313.47	10.73	34.23
4-methyl-2-nitrophenol	3.29E-03	306.67	2.43	7.92
5-fluoro-2-nitrophenol	5.01E-03	309.16	11.63	37.62
4-amino-2-nitrophenol	9.29E-03	401.89	37.15	92.44
4-methyl-3-nitrophenol	6.85E-02	351.59	32.74	93.13
4-chloro-3-nitrophenol	5.80E-02	400.32	36.15	90.31
3-methyl-4-nitrophenol	5.86E-02	401.27	38.87	96.86
2-fluoro-4-nitrophenol	6.42E-02	394.17	9.95	25.24
3-fluoro-4-nitrophenol	3.32E-02	366.46	29.36	80.12
2-nitrobenzaldehyde	2.15E+00	317.66	77.98	245.49
3-nitrobenzaldehyde	2.75E-01	332.71	20.66	62.09
2-chloro-5-nitrobenzaldehyde	8.41E-02	353.38	12.30	34.82
4-nitrobenzaldehyde	1.93E-01	380.40	22.51	59.16
5-chloro-2-nitrobenzoic acid	1.40E-02	458.17	13.75	30.00
3-nitrobenzoic acid	1.90E-03	418.03	5.57	13.33
4-methyl-3-nitrobenzoic acid	5.76E-02	464.70	21.87	47.06
2-chloro-3-nitrobenzoic acid	6.29E-03	458.17	10.28	22.43
2-hydroxy-5-nitrobenzoic acid	1.87E-02	505.55	18.68	36.95

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3-methyl-4-nitrobenzoic acid	3.04E-01	492.43	35.39	71.86

Table 8: Average difference between the experimental P_L^{sat} and the predicted P_L^{sat}. N_VP is the Nannoolal et al. method (Nannoolal et al., 2008), MY_VP is the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997), N_Tb is the Nannoolal et al. method (Nannoolal et al., 2004), SB_Tb is the Stein and Brown method (Stein and Brown, 1994).

Average difference (orders of magnitude)	**N_VP_N_Tb**	**N_VP_SB_Tb**	**MY_VP_N_Tb**	**MY_VP_SB_Tb**	**SIMPOL**
nitrophenols	4.24	3.49	4.21	3.40	2.92
nitrobenzaldehydes	3.18	2.50	3.17	2.46	0.29
nitrobenzoic acids	2.06	0.91	2.56	1.52	-0.83
all compounds	3.38	2.52	3.50	2.65	1.26

~~**Table 9: P_L^{sat}, melting point, and the enthalpy and entropy of fusion of the nitrobenzaldehydes.**~~

~~**Compound**~~	~~**P_{298} (Pa)**~~	~~**T_m (K)**~~	~~**ΔH_{fus} (kJ mol^{-1})**~~	~~**ΔS_{fus} (J mol^{-1} K^{-1})**~~
~~2-nitrobenzaldehyde~~	~~2.15E+00~~	~~317.66~~	~~77.98~~	~~245.49~~
~~3-nitrobenzaldehyde~~	~~2.75E-01~~	~~332.71~~	~~20.66~~	~~62.09~~
~~2-chloro-5-nitrobenzaldehyde~~	~~8.41E-02~~	~~353.38~~	~~12.30~~	~~34.82~~
~~4-nitrobenzaldehyde~~	~~1.93E-01~~	~~380.40~~	~~22.51~~	~~59.16~~

~~**Table 10: P_L^{sat}, melting point, and the enthalpy and entropy of fusion of the nitrobenzoic acids.**~~

~~**Compound**~~	~~**P_{298} (Pa)**~~	~~**T_m (K)**~~	~~**ΔH_{fus} (kJ mol^{-1})**~~	~~**ΔS_{fus} (J mol^{-1} K^{-1})**~~
~~5-chloro-2-nitrobenzoic acid~~	~~1.40E-02~~	~~458.17~~	~~13.75~~	~~30.00~~
~~3-nitrobenzoic acid~~	~~1.90E-03~~	~~418.03~~	~~5.57~~	~~13.33~~
~~4-methyl-3-nitrobenzoic acid~~	~~5.76E-02~~	~~464.70~~	~~21.87~~	~~47.06~~
~~2-chloro-3-nitrobenzoic acid~~	~~6.29E-03~~	~~458.17~~	~~10.28~~	~~22.43~~
~~2-hydroxy-5-nitrobenzoic acid~~	~~1.87E-02~~	~~505.55~~	~~18.68~~	~~36.95~~
~~3-methyl-4-nitrobenzoic acid~~	~~3.04E-01~~	~~492.43~~	~~35.39~~	~~71.86~~

Table 9~~11~~: Comparison between nitrophenols measured in this paper and by Dang et al. (2019)

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Compound	**Solid State P_{298} (Pa)**	**Sub-Cooled P_{298} (Pa)**	
4-methyl-3-nitrophenol	1.08 ± 0.43E-02	6.85 ± 5.14E-02	This work - PEG reference
	1.94 ± 0.78E-03	1.23 ± 0.92E-02	This work - malonic acid reference
	2.46 ± 0.98E-03	4.85 ± 3.64E-03	Dang et al. (Dang et al., 2019)
	$1.84^{+0.30}_{-0.27}$E-02		EDB
3-methyl-4-nitrophenol	1.78 ± 0.71E-03	5.86 ± 4.40E-02	This work - PEG reference
	2.45 ± 0.98E-04	7.80 ± 5.85E-03	This work - malonic acid reference
	2.28 ± 0.91E-04	3.78 ± 2.84E-03	Dang et al. (Dang et al., 2019)
	$7.20^{+9.30}_{-3.10}$E-04	$4.70^{+6.00}_{-2.00}$E-02	EDB
4-methyl-2-nitrophenol	3.11 ± 1.24E-03	3.29 ± 2.47E-03	This work - PEG reference
	5.61 ± 2.24E-04	5.76 ± 4.32E-04	This work - malonic acid reference
	5.72 ± 2.29E-04	5.97 ± 4.48E-04	Dang et al. (Dang et al., 2019)

~~Table 12: Comparison between the P^{sat} for 4-methyl-2-nitrophenol measured with the KEMS and estimated based on behaviour within the EDB~~

	~~P_L^{sat} (Pa)~~	
~~4-methyl-2-nitrophenol~~	~~1.30 ± 0.98E-03~~	~~KEMS with PEG reference~~
	~~2.10 ± 1.57E-04~~	~~KEMS with malonic acid reference~~
	~~$4.30^{+17.20}_{-3.44}$E-03~~	~~EDB estimation based on Eq. 3~~

Response to comments on:

Measured solid state and sub-cooled liquid vapour pressures of nitroaromatics using Knudsen effusion mass spectrometry

We thank the reviewers and editor for their time evaluating this manuscript and their comments relating to this work. The corrections and additions made as a result of these comments have greatly improved the focus of this work.

The response to each of the referees' points, which are repeated in black, is provided in blue text with the new additions to the text in the paper in red. References to the original text are made in orange.

Anonymous Referee #1:

Major comment 1

Why do you consider the comparison to GCM EVAPORATION at all, if it should not be used for aromatic compounds? I suggest to leave out the parts regarding EVAPORATION.

The authors agree with this comment. EVAPORATION is a commonly used GCM and it is important to show where it is not appropriate to use it. Additional text had been added to the introduction discussing the strengths of EVAPORATION, before explaining why it is not suited to aromatic compounds and its omission from the comparisons made in this study.

(Line 59 – 62 All Markup updated manuscript):

For example, in the assessment by O'Meara et al. (2014), for the compounds to which it is applicable, EVAPORATION (Compernolle et al., 2011) was found to give the minimum mean absolute error, the highest accuracy for SOA loading estimates and the highest accuracy for SOA composition. Despite this EVAPORATION should not be used for aromatic compounds, as there are no aromatic compounds in the parametrisation dataset (Compernolle et al., 2011).

Mention of EVAPORATION has been removed from the results and discussion section, and the EVAPORATION data points have been removed from Figure 10 in the revised manuscript (Figure 8 in the original manuscript).

Major comment 2

The Results section contains results and discussions. Either results and discussions must be separated into two independent section. Or the type of section should be indicated by "Result and Discussion".

Agreed, as a result we have changed the name of the section to "Results and Discussion" as suggested.

Major comment 3

Line 243-260: Why do you put so much emphasize on the methoxy phenols? This has not much to do with your work and the concepts of inductive, mesomeric and H-bond effects are so general that you don't have to introduce it by this specific example. In any case, it is not your result and therefore misplaced in a Result section. Moreover, I don't understand what is supposed to be learned from Figure 3, it is not showing the overall importance of the H-bond (line 244). The methoxy phenols could help the discussion of your findings, though, if you could relate their vapor pressures to their H-bond abilities.
I suggest to omitting whole part with the methoxy phenols and Figure 3 and Table 4 should be skipped (In Table 4, something happened to the table header). That would make some space for my next suggestion to put more illustrations to section 4.1.

Discussion of methoxyphenols has been removed along with Figure 3 and Table 4 as suggested. The more general resonance and inductive effect theory has been moved the theory section in subsection 3.3 titled Inductive and resonance effects.

Major comment 4

line 261-312: Here you present and discuss your findings for the nitro phenols. It is very difficult to follow your description and interpretations based only on the text and on the tables, because you present many numbers in combination with similar looking compound names. I understand that the authors have access to MOPAC2016 and were able to calculate by themselves the partial charges on the carbon which carries the phenol group and estimate H bond strength as well as calculate dipole moments. I suggest to present all used helping quantities, i.e. (relative) strength of I- and M-effect, partial charge on phenolic C, dipole moments, in an extra table or add it to the Table 5. The authors then should try to plot the vapor pressures as function of (some of) these quantities in addition to table(s) and text. I know, it may be challenging to clearly arrange that information in a graphical way. However, it would help the readability of the manuscript a lot. E.g. “outliers” could be used as start for your discussion of secondary effects like steric effects, or intramolecular H-bonding (as presented in the current text).

The partial charges of the phenolic carbons have been added to table 4, along with a new figure (Figure 5 in the updated manuscript) as requested. Figure 5 shows a plot of P_S^{sat} vs partial charge of the phenolic carbon with the methyl nitrophenols plotted in blue, fluoro nitrophenols plotted in red, and the other/outlier nitrophenols plotted in green with each compound labelled. This together with explicit references to the Figure 5 in the text when directly comparing the P_S^{sat} of two compounds should help the readability of the section significantly. By referencing figure 5 additional discussion of the compounds marked in green has been added to explain why they deviate from what would be expected given one factor or another.

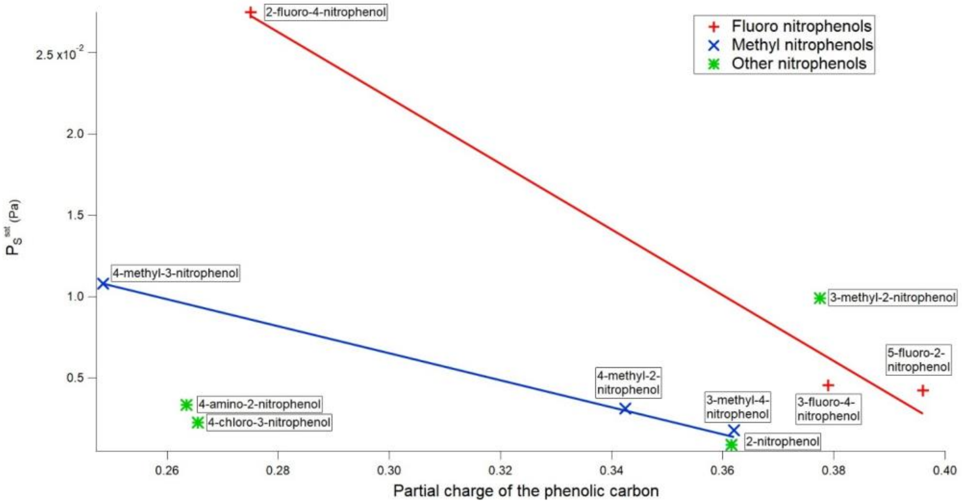


Figure 5: P_S^{sat} vs partial charge of the phenolic carbon of the nitrophenols.

(Line 320 – 321 All Markup updated manuscript):

A plot of P_S^{sat} vs the partial charge of the phenolic carbon for the nitrophenols can be found in Fig. 5.

(Line 329 All Markup updated manuscript):

For the fluoro nitrophenols, as shown in Fig. 5, as the partial charge of the phenolic carbon increases the P_S^{sat} increases.

(Line 330 – 332 All Markup updated manuscript):

A similar trend occurs in the methyl nitrophenols as in the fluoro nitrophenols with a larger partial charge of the phenolic carbon corresponding to a lower P_S^{sat}, as shown in Fig 5. 3-methyl-2-nitrophenol is an exception to this and is discussed shortly.

(Line 335 – 337 All Markup updated manuscript):

As shown in Fig. 5 3-methyl-2-nitrophenol would be expected to have a much lower P_S^{sat} than is observed due to the high partial charge on the phenolic carbon.

(Line 341 – 345 All Markup updated manuscript):

Whilst 3-methyl-2-nitrophenol has a higher P_S^{sat} than is expected given the partial charge on the phenolic carbon, 4-amino-2-nitrophenol has a much lower P_S^{sat} (Fig. 5). This is likely due to 4-amino-2-nitrophenol being capable of forming more than one hydrogen bond, whereas all the other compounds investigated were only capable of forming one H-bond. However, despite 4-amino-2-nitrophenol being capable of forming more than 1 H-bond, replacing the methyl group on 4-methyl-2-nitrophenol with an amino group to form 4-amino-2-nitrophenol surprisingly increases the P_S^{sat} from 3.11E-03 Pa to 3.36E-03 Pa.

(Line 351 – 355 All Markup updated manuscript):

4-amino-2-nitrophenol is a good example of a compound with multiple competing factors affecting P_S^{sat} leading to higher P_S^{sat} than would be expected due to one factor and lower P_S^{sat} than expected from another.
Similar to 4-amino-2-nitrophenol, 4-chloro-3-nitrophenol also has a lower P_S^{sat} than expected according to the partial charge of the phenolic carbon. This can be seen in Fig. 5. Unlike 4-amino-2-nitrophenol the explanation for 4-chloro-3-nitrophenol is simpler.

(Line 364 – 367 All Markup updated manuscript):

It is possible that the crystallographic packing density of 3-methyl-4-nitrophenol is higher although no data is available to support this, although when looking at P_L^{sat} data (Section 4.2) 3-methyl-4-nitrophenol exhibits a higher P_L^{sat} than 3-fluoro-4-nitrophenol which is what would be expected given the respective partial charges of the phenolic carbons.

Replaced mention of dipole moment between line 358 and 361 with partial charge as on looking at the data, as a whole dipole moments have very poor correlation with vapour pressure, and for H-bonding compounds partial charge and strength of H-bonds will be much more important.

(Line 359 – 362 All Markup updated manuscript):

The methyl group cannot engage in intermolecular H-bonding, it will sterically hinder any H-bonding that the NO_2 group undergoes and it reduces the partial charge of the phenolic carbon of the molecule (from 0.379 to 0.362) (Stewart, 2016) which would reduce the strength of H-bonding interactions between the molecules.

Removed mention of 3-methyl-2-nitrophenol between line 368 and 370 as it is clearly an outlier.

Major comment 5

line 313-326: In the same sense as before: do you have dipole moments of the nitrobenzaldhydes? Could you add this information to Table 6, make a graphics and discuss the results in similar terms as the phenols?

We agree that this is a useful addition. We have therefore added column to Table 5 containing the crystallographic packing density of the nitrobenzaldehydes and added a new figure (Figure 7) showing a plot of P_S^{sat} vs Packing density. Figure 7 shows a very strong correlation between P_S^{sat} vs Packing density for the nitrobenzaldehydes.

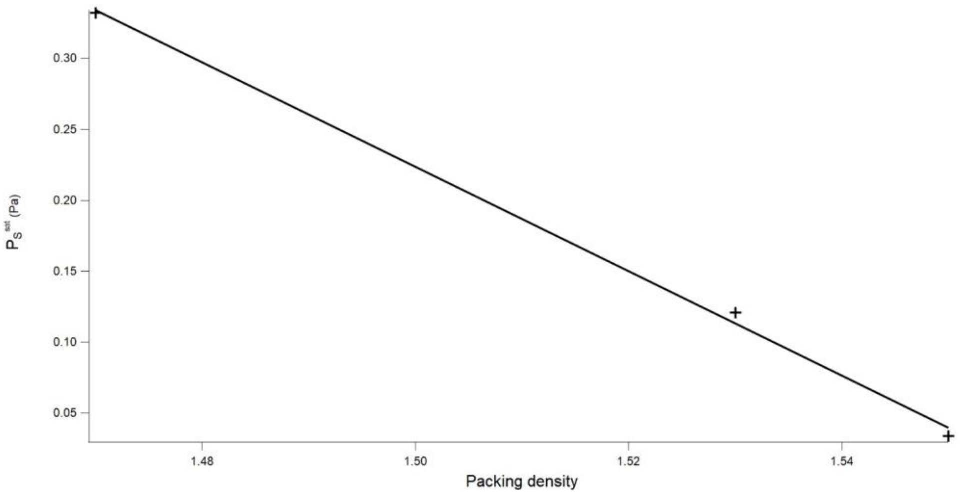


Figure 7: P_S^{sat} vs Packing density of the nitrobenzaldehydes

Major comment 6

line 327-329: Why don’t you show that relation in a plot

This has been removed as it is more of an observation than anything else and does not add very much to the discussion.

Major comment 7

line 330-348: In the similar sense as commented above: try to find a good graphical presentation of your findings. Using partial charge on the carboxylic C, would that enable comparison of the acids to the phenols, in terms of H-bond donor strength?

The partial charge of the carboxylic carbon has been added to Table 7, and a new figure has been made (Figure 8). Figure 8 contains both the nitrophenols and nitrobenzoic acids, with a zoomed in section of the nitrobenzoic acids. Figure 8 plots P_S^{sat} vs partial charge of the phenolic/carboxylic carbon. Each individual carboxylic acid is labelled. In this section originally there were some errors that have been corrected. A more detailed comparison of the nitrophenols and nitrobenzoic acids has been added. Figure 9 (originally Figure 7) has been adjusted.

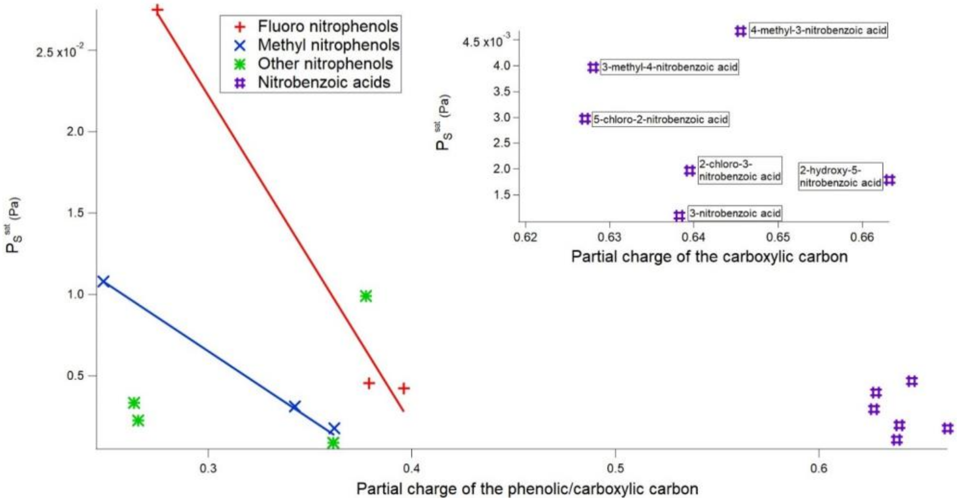
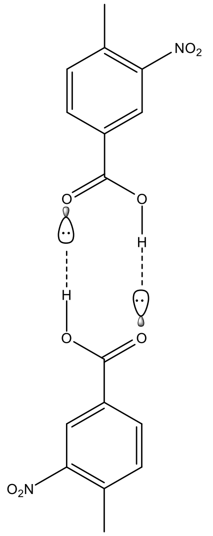


Figure 8: P_S^{sat} vs partial charge of the phenolic/carboxylic carbon of the nitrophenols and nitrobenzoic acids.



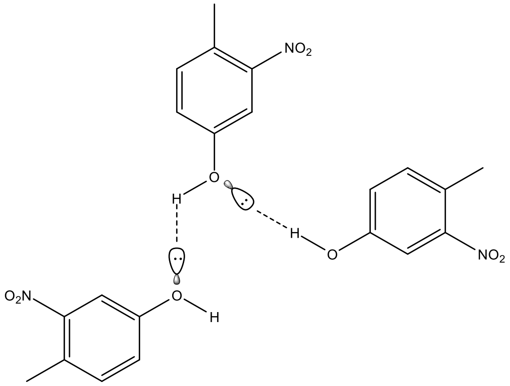


Figure 9: Diagram demonstrating how a carboxylic acid functionality allows a molecule to dimerise using H-bonds in 4-methyl-3-nitrobenzoic acid (left) whilst a hydroxyl group only allows for hydrogen bonding to two other molecules with no opportunity to dimerise in 4-methyl-3-nitrophenol (right).

Corrected error between lines 390 and 392.

(Line 390 – 392 All Markup updated manuscript):

Its isomer 3-methyl-4-nitrobenzoic acid possesses a slightly lower P_S^{sat} (3.97E-03) as well as a slightly lower partial charge of the carboxylic carbon (0.644 vs 0.628) although the difference in P_S^{sat} is not significant.

Removed incorrect comparison between 3-methyl-4-nitrophenol, 4-methyl-3-nitrophenol, 3-methyl-4-nitrobenzoic acid and 4-methyl-3-nitrobenzoic acid between lines 391 and 396.

Added more detailed comparison between nitrophenols and nitrobenzoic acids as a whole between lines 408 to 418.

(Line 408 – 418 All Markup updated manuscript):

When comparing nitrobenzoic acids as a whole with nitrophenols, nitrobenzoic acids have a much higher P_S^{sat} than would be expected based solely on the partial charges of the carboxylic carbon. As can be seen in Fig. 8, there is overlap in the range of P_S^{sat} for the nitrobenzoic acids and many of the nitrophenols, however there is no overlap in terms of partial charges of the carboxylic and phenolic carbons, with all of the nitrobenzoic acids having partial charges of the carboxylic carbon greater than 0.6, whilst the nitrophenols had much lower partial charges of the phenolic carbon between 0.2 and 0.4. It is widely known that the H-bonds of carboxylic acids are stronger than the H-bonds of alcohols (Ouellette et al., 2015b) so therefore it would be expected that the carboxylic acids would have a lower P_S^{sat}. A likely reason as to why the P_S^{sat} of the nitrobenzoic acids is higher than would be expected, compared to the nitrophenols, based only on the partial charge of the carboxylic carbon is the propensity for carboxylic acids to dimerise (see Fig. 9). Nitrophenols are unable to dimerise, instead being able to form H-bonds with up to 2 other molecules as shown in Fig. 9. By dimerising the nitrobenzoic acids, despite having much stronger H-bonds than the nitrophenols, will not have a proportionally lower P_S^{sat}.

Major comment 8

line 349-362: Summary, yes, it this very informative. I argue again, it would be great to have the proposed diagrams in the previous sections, which show the trends and the exceptions, highlighting the statements in this summary

New figures have been added to the previous sections to more clearly show the properties that have a large impact on P_S^{sat}. Mention of dipole moments have been removed from this section with a sentence added at the end stating that dipole moments showed little impact on P_S^{sat}, with dipole moments showing positive correlation, negative correlation and no correlation with P_S^{sat}.

(Line 433 All Markup updated manuscript):

Dipole moments were also investigated but overall showed very little impact on P_S^{sat}.

Minor comment 1

line 114 – line 118: I understand that you only used PEG-3 and PEG-4 to calibrate your KEMS? I feel, the discussion of the PEG series is distracting and confusing (me) here. It is covered by the Krieger et al. (2018) reference. If you feel the need to discuss PEG in such detail, I suggest to move it to the supplement.

The authors agree that this is unnecessary detail covered by the Krieger et al. (2018) study and this additional discussion has therefore been removed.

Minor comment 2

line 118f: You mentioned the PEG-4 is a suited standard, but you obviously used also PEG-3. What is the quality of the KEMS for PEG-3 measurements?

The KEMS wasn’t used to measure PEG-3 in Krieger et al. (2018), but it is a suitable reference standard and over the multiple measurements taken during data collection PEG-3 agreed within 20 – 30 % of the experimental P_S^{sat} measurements from Krieger et al. (2018). Information about the quality of PEG-3 measurements using the KEMS has been added.

(Line 115-120 All Markup updated manuscript):

The KEMS has been shown to accurately measure the P^{sat} of PEG-4 in the study by Krieger et al. (2018) but the KEMS did not measure the P^{sat} of PEG-3. In this study when using PEG-4 as a reference compound for PEG-3 the measured P^{sat} of PEG-3 had an error of 30 % compared to the experimental values from Krieger et al. (2018), well within the quoted 40 % error margin of the KEMS (Booth et al., 2009). When using PEG-3 as the reference compound for PEG-4 the measured P^{sat} of PEG-4 had an error of 20 %.

Minor comment 3

line 268f: I suggest to take the sentence to the previous paragraph and make the new paragraph after the sentence.

This has been done as suggested.

Minor comment 4

Section 4.5: I suggest to move some details of the EDB measurements to the EDB section 2.3 and to focus here on the comparison itself.

This has been done. The following has been moved from section 4.5 to 2.3.

(Line 161 – 165 All Markup updated manuscript):

The recently published paper by Dang et al. (2019) measured the P^{sat} of several of the same compounds that are studied in this paper using the same KEMS system, however in this study the newly defined best practice reference sample was used (Krieger et al., 2018), whereas Dang et al. (2019) used malonic acid. The difference in reference compound led to a discrepancy in the experimental P^{sat}. Supporting measurements for the compounds were performed using the EDB from ETH Zurich in order to rule out instrumental problem with the KEMS.

(Line 175 – 192 All Markup updated manuscript):

As single particles injected from a dilute solution may either stay in a supersaturated, liquid state or crystallize, it is important to identify its physical state.
For 4-methyl-3-nitrophenol a 3 % solution dissolved in isopropanol was injected into the EDB. After the injection and fast evaporation of the isopropanol, all particles were non-spherical, but with only small deviations from a sphere, meaning that it was unclear whether the phase was amorphous or crystalline. To determine the phase of this first experiment, a second experiment was performed, where a solid particle was injected directly into the EDB. Mass loss with time was measured by following the DC voltage necessary to compensate the gravitational force acting on the particle to keep the particle levitating.

When comparing the P^{sat} from both of these experiments it is clear that the initial measurement of 4-methyl-3-nitrophenol was in the crystalline phase.

3-methyl-4-nitrophenol was only injected as a solution but the particle crystallized and was clearly in the solid state.

4-methyl-2-nitrophenol was injected as both a 3 % and 10 % solution. Despite being able to trap a particle, the particle would completely evaporate within about 30 seconds. This evaporation time scale is too small to allow the EDB to collect any quantitative data. Using the equation for large particles neglecting evaporative cooling (Hinds, 1999) (Eq. 2) it is possible to estimate P_L^{sat}

$$t = \frac{R\rho \cdot {d_p}^2}{8DM\frac{P^{sat}}{T}} \qquad (2)$$

where t is the time that the particle was trapped within the cell of the EDB, R is the ideal gas constant, ρ is the density of the particle, d_p is the diameter of the particle, D is the diffusion coefficient, M is the molecular mass, T is the temperature, and P^{sat} is the saturation vapour pressure. Eq. 2 gives approximately 4.3E-03 Pa for P_L^{sat} at 290 K.

Minor comment 5

line 560: I would suggest to slightly reformulate. “in non-protic systems the dipole moment. . .”

This part of the sentence has now been removed as dipole moments are no longer being considered an important factor for P_S^{sat}.

Minor comment 6

Figure 9: I think there is space to show all data discussed and given in Tables 11 and 12, also some are less complete.

The data not included in Figure 9 (now Figure 11) is a second set of measurements using malonic acid as a reference compound. As malonic acid is already represented in the figure including the second set isn’t necessary.

Table 12 has been removed at the suggestion of another reviewer.

Minor comment 7

In general: check your literature input: e.g. McFiggans, O’Meara

This has been done.

Anonymous referee #2:

Major comment 1

Line 224- 260 First of all, the authors spend a lot of effort in introducing some general information about inductive, resonance, and H-bond effects. I don’t think it is appropriate to put all of this background information in the Results section. This information could be moved to the Theory section or even supporting information. Second, methoxy-phenols are not compounds of interest measured by this study. This study already included a lot of chemical compounds. I believe the authors can use the studied species to illustrate the relationship between H-bond energy and partial charge of the phenolic carbon. Moreover, figure 3 does not contain much useful information, and table 4 should be changed accordingly.

The more general Inductive and resonance theory has been moved to a new sub section of the theory section (section 3.3 Inductive and resonance theory). Discussion of methoxy phenols, as well as figure 3 and table 4 have been removed.

Major Comment 2

Line 270-348: Here, the authors present a lot of results to illustrate how the H-bond effect, steric effects, dipole moments, and crystallographic packing densities affect the Psat. It is challenging to follow the description and interpretations based only on the text. I think a summary table including key parameters involved (e.g. partial charge on phenolic C, dipole moments, crystallographic packing densities) will be beneficial. Additionally, some correlation figures (e.g. partial charge vs Psat, dipole moment vs Psat, crystallographic packing vs Psat) or visual images could be useful for the discussion and for readers to follow.

Many of the comments here were also raised by reviewer 1. We have therefore made the changes recommended as a priority. The partial charge of the phenolic carbon has been added to Table 4 (originally Table 5), crystallographic packing density has been added to Table 5 (originally Table 6) and partial charge of the carboxylic carbon has been added to Table 6 (originally Table 7). In line with the comments from reviewer 1, Figure 5 has been added showing P_S^{sat} vs partial charge, Figure 7 has been added showing a plot of P_S^{sat} vs Packing density and Figure 8 has been added illustrating P_S^{sat} vs partial charge of the phenolic/carboxylic carbon. Detailed discussions of each figure has now also been added to aid the interpretation of the results presented here. Full details of the changes made between lines 271-349 in the original manuscript are given in the response Anonymous Referee #1 between Major comment 4 to Major comment 7 earlier in this document.

Major comment 3

The author evaluated the Psat data predicted by the GCM comprehensively. Could the authors make a summary table to show the features of each GCM method, the performance of the prediction (the difference as compared to measurements), and short explanation of why the predictions differ from measurements. Furthermore, could the authors make a summary to say which prediction method may provide best result for a type of compound? This will help the researchers to get a more reasonable result when use GCMs doe predicting Psat for new compounds.

We agree that a summary table is of use for ease of interpretation. We have therefore added a summary table (Table 8) containing the average order of magnitude difference between the predicted and measured Psat for nitrophenols, nitrobenzaldehydes, nitrobenzoic acids and all three combined.

Table 8: Average difference between the experimental P_L^{sat} and the predicted P_L^{sat}. N_VP is the Nannoolal et al. method (Nannoolal et al., 2008), MY_VP is the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997), N_Tb is the Nannoolal et al. method (Nannoolal et al., 2004), SB_Tb is the Stein and Brown method (Stein and Brown, 1994)

Average difference (orders of magnitude)	**N_VP_N_Tb**	**N_VP_SB_Tb**	**MY_VP_N_Tb**	**MY_VP_SB_Tb**	**SIMPOL**
nitrophenols	4.24	3.49	4.21	3.40	2.92
nitrobenzaldehydes	3.18	2.50	3.17	2.46	0.29
nitrobenzoic acids	2.06	0.91	2.56	1.52	-0.83
all compounds	3.38	2.52	3.50	2.65	1.26

The suggestion of adding a discussion of the most appropriate GCM for a particular compound is an important one. We have therefore added paragraph describing which GCMs performed best for each group of compound and which GCM would be best to use.

(Line 535 – 543 All Markup updated manuscript):
When looking at nitroaromatics as a whole SIMPOL (Pankow and Asher, 2008) shows the smallest difference between experimental and predicted P_L^{sat} (as shown in Table 8) and would therefore be the most appropriate method to use when predicting P_L^{sat} for this group of compounds. In the case of nitrophenols, despite SIMPOL (Pankow and Asher, 2008) showing

the best performance the absolute differences are still close to 3 orders of magnitude, so any work using these predictions should be aware of the very larger errors that these predictions could introduce. For nitrobenzaldehydes SIMPOL (Pankow and Asher, 2008) shows very good agreement and is the clear choice to be used when predicting P_L^{sat}. For nitrobenzoic acids the preferred method for predicting P_L^{sat} is not quite as clear. Both the Nannoolal et al. method (Nannoolal et al., 2008) and SIMPOL (Pankow and Asher, 2008) predict P_L^{sat} within an order of magnitude, with Nannoolal et al. (Nannoolal et al., 2008) generally overestimating and SIMPOL (Pankow and Asher, 2008) underestimating.

We agree that an explanation of why the predictions differ from the measurements is important, however this is already discussed, with respect to Myrdal and Yalkowsky in lines 460-466,

(Line 460 – 466 All Markup updated manuscript):
The Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) shows poor agreement with the experimental data for almost all compounds, but is not particularly surprising given that it only contains 3 nitroaromatic compounds in this method's fitting data set, with none of these compounds containing both a nitro group and another oxygen containing group. The Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997) is the oldest method examined in this study, and much of the atmospherically relevant P^{sat} data has been collected after the end of the development of this model. The Myrdal and Yalkowsky method's (Myrdal and Yalkowsky, 1997) reliance on a predicted boiling point may also be a major source of error in the P^{sat} predictions of the nitroaromatics.

With respect to Nannoolal between in lines 483 – 487,

(Line 483 – 487 All Markup updated manuscript):
The Nannoolal et al. method (Nannoolal et al., 2008), unlike the others, contains parameters for ortho, meta, para isomerism and even demonstrates the same trend as the experimental data for 2-nitrobenzaldehyde, 3-nitrobenzaldehyde and 4-nitrobenzaldehyde, although 3 orders of magnitude higher. Despite the ortho, meta, para parameters, as soon as a third functional group is present around the aromatic ring the Nannoolal et al. method (Nannoolal et al., 2008) no longer accounts for relative positioning of the functional groups.

And with respect to the very poor performance of nitrophenols between lines 488 – 499

(Line 488 – 499 All Markup updated manuscript):
Both SIMPOL (Pankow and Asher, 2008) and the Nannoolal et al. method (Nannoolal et al., 2008) contain nitrophenol data from Schwarzenbach et al. (Schwarzenbach et al., 1988). This data of Schwarzenbach et al. (Schwarzenbach et al., 1988), however, is questionable in reliability due to being taken from a single data point from a single data set. The values given are also 3-4 orders of magnitude greater than those measured in this work as well as those measured by Bannan et al. (Bannan et al., 2017) and those measured by Dang et al. (Dang et al., 2019). The use of the Schwarzenbach et al. (Schwarzenbach et al., 1988) nitrophenol P^{sat} data, which makes up 11 of the 12 nitrophenol data points within the fitting data set of the SIMPOL method (Pankow and Asher, 2008), is a likely cause of the SIMPOL method (Pankow and Asher, 2008) overestimating the P^{sat} of nitrophenols by 3 to 4 orders of magnitude. The one nitrophenol used in the SIMPOL method(Pankow and Asher, 2008) not from Schwarzenbach et al. (Schwarzenbach et al., 1988), 3-nitrophenol from Ribeiro da Silva et al. (Ribeiro da Silva et al., 1992), has a much lower P^{sat} than those of Schwarzenbach et al. and is only one order of magnitude higher than that from Bannan et al. (Bannan et al., 2017).
Specific comment 1

Line 37-38. The sentence regarding SOA formation mechanism is not rigorous. Gas phase photochemical reactions do not produce SOA directly. Another step of gas-to-particle conversion is needed.

Sentence has been adjusted.

(Line 37-38 All Markup updated manuscript):

SOA are not emitted into the atmosphere directly as aerosols, but instead form through atmospheric processes such as gas phase photochemical reactions followed by gas-to-particle partitioning in the atmosphere (Pöschl, 2005).

Specific comment 2

Line 112-123: The discussion on the PEG has been presented by Krieger et al. (2018) already. It is not necessary to show it here again. Moreover, the author stated that "KEMS was able to determine Psat of PEG-4 to PEG-7, through good agreement with the other techniques". Why the author used PEG3 here for calibration if only measurements for PEG-4 to PEG-7 have good agreement?

This point was also raised by reviewer 1. The more general PEG discussion has been removed and a comment on using PEG 3 as a reference compound has been added. The full changes that have been made are shown in response to Anonymous Referee #1 minor comment 1 and minor comment 2.

Specific comment 3

Line 124-125 This sentence seems to be redundant.

Sentence has been removed.

Specific comment 4

Line 214-217 Why the measurement temperature range needs to be listed here and why only listed for 5 compounds?

The 5 compounds with temperature range listed were those that melted during the temperature ramp up to 328 K. Moved the sentences around to make this clearer.

(Line 259 – 262 All Markup updated manuscript):

Measurements were made at increments of 5 K from 298 to 328 K with the exception of the following compounds that melted during the temperature ramp. 2-nitrophenol was measured between 298 K and 318 K, 3-methyl-4-nitrophenol was measured between 298 K and 313K, 4-methyl-2-nitrophenol was measured between 298 K and 303 K, 5-fluoro-2-nitrophenol was measured between 298 K and 308 K, and 2-nitrobenzaldehyde was measured between 298 K and 313 K

Specific comment 5

Line 268-269: I suggest to take the first sentence to the previous paragraph.

Done as suggested.

Specific comment 6

Line 381-382. Why the authors still used EVAPORATION to estimate the Psat of studied compounds and used SIMPLO for fluoro-aromatics? It is stated clearly that "A common misuse of GCMs occurs when a GCM is applied to a compound containing functionality not included in the training set, e.g. using EVAPORATION (Compernolle et al., 2011) with aromatic compounds or using SIMPOL (Pankow and Asher, 2008) with compounds containing halogens." (lines 194-196)

The use of EVAPORATION was also raised by reviewer 1. EVAPORATION is still discussed in the introduction as it is a commonly used GCM, but has ben omitted from the results and discussion section. EVAPORATION has also been removed from Figure 10 (originally Figure 8). Full details of the changes regarding EVAPOTATION are given in response to Anonymous Referee #1 Major comment 1.
When using SIMPOL for halogenated species, despite on paper not being a suitable GCM, SIMPOL performed the best for all of the halogenated species. For this reason, it has been left in. An additional paragraph has been added to draw attention to this.

(Line 529 – 534 All Markup updated manuscript):
One surprising observation comes when looking at the halogenated nitroaromatics. SIMPOL (Pankow and Asher, 2008) has the smallest order of magnitude difference between experimental and predicted P_L^{sat} for all of the halogenated nitroaromatics in this study. This is particularly surprising as SIMPOL (Pankow and Asher, 2008) contains no halogenated compounds in its fitting data set, whereas the other GCMs do. This implies that accurately predicting the impact on P_L^{sat} of carbon skeleton and other functional groups such as, nitro, hydroxy, aldehyde and carboxylic acid are more important than the impact of a chloro or fluoro group.

Specific comment 7

Line 422, A full stop is needed after "by Dang et al. (2019)"

Full stop added

Specific comment 8

Section 4.5: Details of EDB measurements regarding physical state determination and Psat estimation should be moved to section 2.3

This point was also raised by reviewer 1. The details of details of the physical state determination and Psat estimation have been moved to section 2.3 as suggested. Full details of the changes made can be found in response to Anonymous Referee #1 minor comment 4.

Specific comment 9

section title "Result" should be replaced by "Result and Discussion".

This has been changed as suggested

Specific comment 10

The reference style should be checked throughout. For example, Line 51-52 "Barley and McFiggans (Barley and McFiggans, 2010) and O'Meara et al. (O 'meara et al., 2014)" should be changed to "Barley and McFiggans (2010) and O'Meara et al. (2014)".

This has been done.

Specific comment 11

There is not much information in table 12. These numbers are listed in the text and displayed in Figure 9 already

Table 12 has been removed

Specific comment 12

PL sat sometimes are in Bold in the text (e.g. on Page 17).

Bold removed where present for PL sat

Specific comment 13

I think table 5,6,7 can be merged into 1 table, also table 8,9,10. These two sets of tables show similar information.

Additional data has been added to tables 5, 6 and 7 (now tables 4, 5, 6) now containing different information. Also, as the data of each is mostly discussed separately, I think separate tables are appropriate. Tables 8, 9 and 10 have been merged.

Specific comment 14

The quality of Figure 4 is poor.

Figure has been remade at a higher quality