

First Referee Response

Guidelines of the author:

1. Bold lines: referee comments of last manuscript submitted
2. Italics lines: answers to referee comments (the pages and lines are referred to the modified manuscript)
3. Red lines in the modified manuscript: changed or integrated sentences, sections etc.

Page 7128 Lines 20/21: It is not clear to me what “weight average values” means in this case.

The weight average values of the Oxalic, Succinic, Adipic and Azelaic acids have been obtained from the enthalpy results listed in Tab. 3 of the article at each couple of $[T_1, T_2]$. The weight average has been obtained with the weight function $\omega_i = (1/\sigma_i^2)$ where the i index expresses the number of data. The final results (ΔH_{sub}) can be written as: $\Delta H_{sub} = \sum_i \omega_i \times \Delta H_i / \sum_i \omega_i$. The error associated to ΔH_{sub} is: $[\sum_i (1/\omega_i)]^{1/2}$.

Explained at Page 10 line 7-9 and at Page 15, line 7-8.

Page 7129 Line 4: Please define the “fine” word in quantitative terms.

Lower than 1-2 μm . This has been detailed at (Pag.2, line 1-2).

Page 7138 Line 6/7: In the text the authors say that for Succinic and Oxalic acids there was a narrower temperature range. However from Table 3 the following temperature ranges are retrieved: Oxalic: 24.772 \rightarrow 54.952 $^{\circ}\text{C}$; DT = 30.18 $^{\circ}\text{C}$ Succinic: 34.85 \rightarrow 54.64 $^{\circ}\text{C}$; DT = 19.79 $^{\circ}\text{C}$ Adipic: 39.84 \rightarrow 75.30 $^{\circ}\text{C}$; DT = 35.46 $^{\circ}\text{C}$ Azelaic: 34.95 \rightarrow 60.04 $^{\circ}\text{C}$; DT = 25.09 $^{\circ}\text{C}$ Therefore DT for Oxalic acid is broader than Azelaic and the sentence seems to be incorrect. Maybe the authors are referring to lower maximum temperatures used. But also in this case the maximum temperature is sensibly different only for Adipic acid, since there are less than 6 $^{\circ}\text{C}$ of difference among Succinic (54.64 $^{\circ}\text{C}$) and Azelaic (60.04 $^{\circ}\text{C}$) cases. The sentence must be better constrained.

We agree with the comment issued by the reviewer, the meaning of the sentence is not clear. The sentence was related to the sublimation rates of Oxalic and Succinic acids. We would to highlight that the sublimation rates of Oxalic and Succinic acids (at 30-35 $^{\circ}\text{C}$) are two and one order of magnitude respectively higher than those calculated for Adipic and Azelaic acids. The sentence has been changed as:

"At 30 $^{\circ}\text{C}$ with the PCM at -72 $^{\circ}\text{C}$, the Succinic and Oxalic acids already show higher sublimation rates than Adipic and Azelaic acids. Thus, the enthalpy of sublimation has been calculated considering a maximum temperature of 55 $^{\circ}\text{C}$ for Oxalic and Succinic, lower than those used for Adipic acid, i.e. 70 $^{\circ}\text{C}$, and Azelaic, i.e. 60 $^{\circ}\text{C}$ (see Table 3)".

Changed at Page 9, line 14-17.

Line 14/15: Here the authors link the frequency decrease only to larger VOC deposition. But it is also stated that a temperature variation is measured: does this imply some change in frequency? For example in Zinzi et al. (2011) it is clear shown that changing the temperature the frequency of the PCM varies in a non-linear form (Fig. 4 of that paper) as theorized by Salt et al. (1987).

In this experiment there isn't a frequency variation due to the temperature contribution. The deposition process starts only when the PCM is stable at -72°C. The effusion cell temperature does not influence the PCM's temperature (and frequency), which has been shielded by an aluminum case able to thermalized the system.

Explained in the article at Page 8, line 23-24.

Line 16/17: Did the authors perform a parallel check on the mass loss by measuring it also by means of “classic” balances (e.g., before and after the process)? Or they only relied on the PCM sensitivity? In this case how much is this value reliable? What is its error? And is there any reference to be added?

A parallel check has been performed with a "classic" balance measuring the effusion mass loss before and after the heating process. In Table below are summarized the initials and finals mass measured whereas in Table 2 of the article are reported the initial mass and sublimated mass (λ_{Start} and $\lambda_{\text{Sublimated}}$).

Acid	Initial mass (mg)	Sublimated mass (mg)
Oxalic	20.0±0.5	17.0±0.5
Succinic	13.0±1.5	12.0±0.5
Adipic	15.0±2.0	11.0±1.2
Azelaic	19.0±0.5	16.0±0.5

Explained at Page 22, line 3-4-5.

Pages 7139-7141: Sections 5.1-5.4 During all these sections the data are very difficult to understand. In particular Table 3, that is also referred as the reference for the measurements made by the authors, does not reflect what is both viewed in Figs. 4-5, where results are graphically displayed, and described in the text. In the table the temperature ranges are (in °C and rounded here for the sake of simplicity) [25, 55], [35, 55], [40, 75], [35, 60] for Oxalic, Succinic, Adipic and Azelaic acids respectively. On the contrary Figs. 4-5 show, for the same compounds: [25, 65], [30, 75], [30, 75], [35, 80]. Moreover in Table 4 the following ranges are reported for this work: Oxalic [25, 60], Succinic [30, 75], Adipic [30, 75], Azelaic [25, 80]. Again different from both Table 3 and Figs. 4-5. What are the temperature ranges used? Furthermore, what is the “weighted average mean” used? What are the weights used?

The temperature range where the sublimation processes have been monitored are those showed in Figure 5-6 of the paper whereas the weigh average values have been obtained from the results in the temperature range listed in Table 3. The temperature range reported in Table 4 has been

changed accordingly with the temperature range of Table 3 of the paper where Van't Hoff relation has been applied.

Thus, the temperatures where the enthalpies have been calculated are: [25, 55], [30, 55], [40, 70], [35, 60] for Oxalic, Succinic, Adipic and Azelaic, respectively. In particular, for the enthalpy measurement the entire temperature range has not been used due to the unsatisfactory flows of molecules at lower temperatures (i.e. 25-35°C for Adipic acid) and to the sublimation flow instability at high temperatures (75-80°C) (due to the temperature oscillations, i.e. Adipic, Azelaic and Succinic acid).

The weight average values have been calculated using the weight function as ($\omega_i=1/\sigma_i^2$) where σ_i are the errors of each enthalpy come from a couple of $[T_1, T_2]$, i.e. ΔH_i .

Modified in Table 4, at Page 24. Explained in Sec. 5.1-5.2-5.3-5.4, at Page 10-11-12.

Explained at Page 10 line 7-9.

Section 5.1: “choosing T1 quite lower than T2 value a best agreement is obtained, whereas when T1 approaches T2 the agreement is worse”. This sentence seems not to be supported by data presented in Table 3. By looking at the following table with data rearranged from Table 3 it seems that the “central” (out of the set of 3 – highlighted in red) measurement is always the best. : T2-T1 (rounded to first decimal) [°C] Measure – Literature [%] 20.2 -11.30% 15.1 - 5.92% 10.0 -16.89% 25.2 -7.68% 20.1 -2.56% 15.0 -8.77% 30.2 -10.73% 25.1 -7.25% 20.0 - 13.27%.

Considering a more careful data analysis for Oxalic acid the sentence in Sec. 5.1 can be written as:

"Moreover, a best agreement is obtained when the difference between T1 and T2 is between 15°C and 25°C (within 9 % compared with the literature value, Tab. 3)".

Changed at Page 10, line 18-20.

Section 5.3: The final sentence, regarding the last two measurements in Table 3 relative to Adipic acid, seems to be incorrect, as the values of enthalpies shown (133.28 and 128.05 kJ/mol) are only 3 and 7% lower than the 137.2 kJ/mol shown in Table 2 as reference. Furthermore, the large error bars make them completely in agreement with the reference value.

The Adipic acid results in Table 3 for $T_2=75^\circ\text{C}$ have been removed due to the highest temperature oscillations, i.e. larger than $\pm 2^\circ\text{C}$. These values have not been considered for the analysis. The final result of the enthalpy of sublimation has been also replaced in Table 4.

The sentence has been modified at Page 12, line 1-4.

Technical corrections

Page 7128 Lines 10/12: It could preferable to reword the sentence as follows: “Acids of both biogenic and anthropogenic origin with low molecular weight are among the components of organic fraction of particulate matter in the atmosphere.”

The sentences have been rearranged following the second referee indications in the Section 1 (Pages 1-2-3).

Line 22: Results are summarized for Adipic, Succinic and Oxalic acid, but not for Azelaic.

The sentence has been rewritten including the Azelaic acid results (Pag.1, line 20-23).

Line 25: Substitute “therefore” with “so that”.

Changed accordingly (Pag.1, line 26).

Page 7129 Line 7: The groups are carboxyl and hydroxyl, not carboxylic and hydroxides.

Changed accordingly (Pag.2, line 4).

Line 16: In the parenthesis please add “these latter” before subclass, as I guess that only dicarboxylic acids are subclass of carboxylic acids.

Changed accordingly (Pag.2, line 11-12).

Line 17: Change “acid” with “acids”.

Changed accordingly (Pag.2, line 12).

Line 21: Change “with various” with “in various”.

Changed accordingly (Pag.2, line 16).

Line 25: Since you already stated that these acids are present in urban environments change “In addition” with “In particular”.

Changed accordingly (Pag.2, line 19-20).

Line 29: acid → acids (after “Succinic and Malonic”)

Changed accordingly (Pag.2, line 25).

Page 7130 Line 1/2: Put the Hatakeyama reference inside the parenthesis of “reaction of O₃ with cyclohexene”.

Changed accordingly (Pag.2, line 27).

Line 15: Delete “that is” before “commonly”.

Changed accordingly (Pag.3, line 15).

Line 23/24: Please insert some reference to characterization by means of enthalpy.

Changed accordingly (Pag.3, line 22).

Page 7131 Line 1: Reword the sentence as: “The TG-Lab facility, located in IAPS-INAF, is dedicated to. . .”

Changed accordingly (Pag.3, line 28).

Line 22: “prediction of 20%” → “prediction by 20%”.

The sentence has been rewritten (Pag.4, line 15).

Page 7132 Line 10: “acid sublimation, due to the their high volatility”. Change acid → acids or their → its

Changed accordingly (Pag.6, line 30).

Page 7133 Line 1: Please provide a reference for the sentence.

The sentence has been removed according to second referee report (Page 7).

Line 9: Substitute “for” with “by” and it could be of interest to specify the constant physical mean.

Changed accordingly (Pag.7, line 19).

The constant C is the term $(2\pi R/aMi)^{1/2}$ obtained by replacing the Langmuir equation in Clausius-Clapeyron equation. The constant C, remains constant during all the measurement.

Explained (Pag.7, line 21).

Line 14: “temperature” → “temperatures”.

Changed accordingly (Pag.7, line 23).

Line 21: Please reword the last sentence as “temperature is directly proportional to rate constant”.

Changed accordingly (Pag.8, line 4-5).

Page 7134 Line 7: “central area” → “central part”

Changed accordingly (Pag.4, line 28).

Line 8: “proximity electronic” → “proximity electronics”

Changed accordingly (Pag.4, line 29).

Line 26: “PCM temperature” → “PCM temperatures”

Changed accordingly (Pag.5, line 13).

Page 7135 Line 1: “molecule flow” → “flow of molecules”.

Changed accordingly (Pag.5, line 14).

Line 9: “wide 6 mm and deep 10 mm” → “6 mm wide and 10 mm deep”.

Changed accordingly (Pag.5, line 26).

Page 7136 Line 8: “frequencies” → “frequencies”

Changed accordingly (Pag.6, line 21).

Page 7142 Line 10: add “and” between “method” and “shows”

Section 5.5 has been rearranged according to second referee report (Page 12-13-14-15).

Second Referee Response

Some major comments Abstract: The abstract should describe the method and the results. It is in my opinion not relevant to discuss characteristics of the laboratory where the experiments are performed in the abstract (line 5-6). Also the discussion on the dicarboxylic acids belong in the introduction and not the abstract (line 10-14).

The abstract has been rewritten by following these indications (Page 1, Line 9-23).

Introduction: The description of dicarboxylic acids and why they are important is repeated in different versions in abstract, introduction, theoretical approach, and experimental sections. These sections should be merged and presented in the introduction only.

In the new version of the paper the description of dicarboxylic acid is reported only in Section 1 (Introduction; Page 2, line: 14-15, 18-34 and Pages 3, line:1-4).

Theoretical approach: “The enthalpy of sublimation can be seen as . . .— is this not the definition of enthalpy – why is it written in this way?”

The sentence has been changed (Page 6, line 27-29).

“constituting condensation nuclei for clouds formation. Therefore, xxx “? It is possible to determine vapor pressure by thermogravimetry – but this is not related to cloud formation.

The sentence has been removed (Page 7).

m is mass loss rate per unit area — unit area of what? M is molecular weight of the studied molecule. Maybe it would be useful to add an indices i for the molecule.

In our experiment the area used is the electrode's area of the Piezoelectric Crystal Microbalance where the material was collected during the measurement.

The sentence has been changed (Page 7, line:15-16).

Equation (4): explain what C is.

The constant C is the term $(2\pi R/\alpha Mi)^{1/2}$ obtained by replacing the Langmuir equation in Clausius-Clapeyron equation. This term, remains constant during all the measurement.

The sentence has been changed (Page 7, line:21).

Equation 5: explain what k_1 and k_2 are. “i.e. temperature increase is related to rate constant increase” – this should be explained and expanded upon.

The rates constant: k_1 and k_2 are the deposition rates on the PCM at two different temperatures T_1 and T_2 . (Explained at Page 7, line 24).

The sentence has been integrated at Page 8, line 4-6 as:

"i.e. temperature is directly proportional to rate constant. Indeed, the increasing temperature corresponds to an increasing of the deposition rate which should be constant for a fixed temperature set-point."

It would help I think, if the experimental setup was presented before the theory section.

Changed accordingly (Page 4-5-6).

Setup operation and composition: “preliminary calibrations” – this should be explained – which molecule was used for calibration?

The compound used for the preliminary calibration was the Adipic acid. The calibration has been performed at $T_{PCM} = -72^\circ\text{C}$ and at 10^{-6} mbar. The effusion cell has been heated from 30°C to 75°C . The calibration procedure has been explained and modified at Page 5, line:15-20.

Experimental activity What does it mean that samples were provided by e.g. University of Rome – was it a commercial sample or was it synthesized there?’

They were commercial samples.

Measurement procedure: It is not clear what the different temperatures, steps, T_1 and T_2 etc. are – where they are in the system, when they are measured etc.

The temperature range where the sublimation processes have been monitored is: $25-80^\circ\text{C}$. At each temperature set point (chosen every 5°C from 25 to 80°C) the deposition rate has been measured considering 30-20 minutes of stabilization. The couples of temperatures (Table 3 of the article): $[T_1, T_2]$ have been chosen to calculate the enthalpy of sublimation by applying the Van't Hoff relation (Eq.5). Considering the related deposition rates k_1 and k_2 , measured at two different temperatures (T_1, T_2) in Hz s^{-1} , ΔH_{sub} has been inferred.

The sentence has been integrated at Page 9, line 1-4.

The parameters in Table 2 should be clearly explained.

The description of parameters in Table 2 has been detailed (Page 22, line: 3-10).

“an uncertainty of 10“ on the retrieved enthalpy of sublimation could be sufficient to provide a good accuracy for our measurements” – how is the uncertainty of 10 % obtained, is it based only on the temperature stability? What is meant by could be sufficient”

The sentence has been modified. Using a similar setup of Albyn (2001), the expected uncertainty on the enthalpy of sublimation should be 7 percent considering a temperature stabilization on effusion cell of $\pm 0.5^{\circ}\text{C}$. This uncertainty is based on the instabilities of the sample heating and on the efficiency of the deposition process as explained by Albyn (2001).

Changed at Page 9, line:8-13.

Data analysis and results I am wondering: is it not possible also to infer vapor pressures at 298 K from the experimental data? This would be useful for comparison with other studies. The authors have chosen to test the method by studying the vapor pressure of dicarboxylic acids and compare with values in the literature. The authors have chosen to compare with some, but not all of the available literature data. This might be justified, but if so, it is not clear from the text why.

Yes, but it is not straightforward: the Langmuir equation and extrapolation of our data at 298K should be applied. This will be the topic of another paper in preparation.

The selection of the previous works used for the comparison was driven by the following criteria:

- works using a similar effusion method and theoretical approach (i.e. Albyn 2001, Booth et al., 2009 and R. da Silva et al., 2001)*
- works analyzing the same Dicarboxylic acids used in our study (Chattopadhyay et al. 2007, Bilde et al. 2003)*

Changed at Page 10, line 3-6.

As the authors point out, literature values differ by orders of magnitude. As mentioned above I would like to point the attention of the authors to a recent review article in Chemical Reviews summarizing state of the art knowledge on vapor pressures and heat of vaporization of dicarboxylic acids that might be useful in the discussion. The authors should check carefully the references they cite: e.g. line 16 p. 7142 “is due to the presence of unevaporated water within the aerosol particles”. This statement is not quite correct as written here. The error reported in that study is based on a sensitivity analysis. It is true however that a potential effect of remaining water in dried aerosols (as used in TDMA systems) has been suggested as an explanation for differences between different studies. Again I refer to the review paper.

The sentence has been modified at Page 13, line 19-22.

The discussion Section (5.5) has been rearranged and reinforced according to the referee comments and the article of Chemical Review suggested. Pages 12-13-14-15.

Another example: Table 1: The article by Prenni et al is focused on cloud droplet formation and it seems strange to use it as a reference for vapor pressures. It should be cited in the motivation part of the introduction instead.

Changed accordingly at Page 21, line:28-29 and at Page 2, line 34.

Regarding succinic acid I miss a reference for the statement that succinic acid will lose a water molecules above 60°C.

The reference has been added (Page 11, line 20-21).

There are inconsistencies between notation and numbers (e.g. temperatures) given in the text, different tables and figures. Table 2: It is not clear what the different parameters in the table are. In the text M is used for molecular weight but in the tables it is a mass?

The symbol of the mass has been changed. The parameters have been modified and better explained at Page 22, line 3-10.

The temperatures range have been corrected in the text (Section 5 and 6), in Table 2 (Page 22) and in Table 4 (Page 24).

Other Author's comments:

- The reference: Palomba et al. (2013) has been changed with a refereed paper of VISTA instrument.

Reference: Palomba E., Longobardo A., Dirri F., Zampetti E., Biondi D., Saggin B., Bearzotti A., Macagnano A., VISTA: a μ -Thermogravimeter for investigation of volatile compounds in planetary environments, Origin of Life and Evolution of Biospheres, accepted at July, 2015.

Changed at Page 3, line 32-33.

- New $\Delta H_{\text{sublimation}}$ literature values (R. da Silva 1999 and Albyn 2001) have been added in Table 4. Consequently, the average value for $\Delta H_{\text{literature}}$ has been changed in Table 2 for Adipic and Succinic acids. $\Delta H_{\text{literature}}$ for the Oxalic acid comes from the dehydrate values reported in Tab.4.

Changed at Page 22 (Table 2) and at Page 24 (Table 4).

- The discussion Section (5.5) has been rearranged and reinforced according to the second referee comments.

Changed at Pages 12-13-14-15.

- The conclusion section (6) has been reinforced based on the discussion section (5.5).

Modified at Page 16, line 8-20 and 23-25.