

RC2: ['Comment on egusphere-2024-3656'](#), Anonymous Referee #2, 22 Mar 2025 [reply](#)

The manuscript “Carbonate content and stable isotopic composition of aerosol carbon in the Canadian High Arctic” by Vodička et al., utilizes measurements from the arctic to quantify the contribution of carbonate to total suspended particle mass. The manuscript is clearly written and of interest to the community. My comments are included below

We thank the reviewer for his insightful comments. We have tried to deal with them as best as possible. As part of addressing the comments, we have also performed additional analyses for some standards, as noted in the comments below. Original comments are in black, our answers are in blue.

- The authors mention some of the interferences for carbonate quantification, such as oxalates. Is it possible to provide a bound on the uncertainty arising from this. For example, in the text the authors state that oxalates peaks likely appear in the OC4, while CaCO<sub>3</sub> appears in EC2. The mass lost in the EC2 fraction may provide a lower bound for the carbonate fraction.

Determining a bound on the uncertainty in the CC measurement is difficult in this case. The resolution of oxalate in OC4 and CaCO<sub>3</sub>, follows from both our observations and the literature. However, as can be seen, for example, from Fig. 2a, other types of carbonate may be released in OC4 that are not as common but are counted in the CC. Other compounds in the sample may then also have an effect on the carbonate release temperature (Karanasiou et al., 2011). Some literature mentions possible removal of salts of volatile organic acids together with carbonates by HCl fuming (Chow et al., 1993) which may interfere with CC determination. However, we could not find specific examples with CaCO<sub>3</sub> compared to oxalate, before and after HCl fuming. Therefore, we performed additional analyses, whose results are newly included in **Fig. S2b** in supplement. In the case of CaCO<sub>3</sub> it appears that after 2h its removal was similar to that after 20h. In the case of potassium oxalate monohydrate, which was released as a representative of the less volatile organics in the OC4 step, there was a surprising increase in the concentration of this peak after HCl fuming. It follows that HCl did not directly lead to the removal of this organic material, but had an effect on its modification, which was reflected in the thermogram. This may also be the case for other organics and their charring during EC/OC analysis as e.g. mentioned by Jankowski et al. (2008). In both cases (CaCO<sub>3</sub> and oxalate), artefacts appear in the thermogram, which make an exact quantitative analysis difficult.

We have added the following text in the manuscript regarding this comment (red is newly added): “Nevertheless, it cannot be excluded that some of the prominent CC peaks in the OC4 region are also from oxalates **as confirmed also by additional analyses of CaCO<sub>3</sub> and potassium oxalate monohydrate standards before and after HCl fumigation (Fig. S2b).**”

- Line 140: The authors state that for some samples the largest material loss in EC2, while for others it is in EC1 or OC4. Is the presence of the CaCO<sub>3</sub> peak in EC2 repeatable, or is there a situation where it is shifted to lower temperatures, like EC1. Asked another way, is the loss of material at these lower temperatures suggestive that compounds other than CaCO<sub>3</sub> dominates the material lost during HCl fumigation.

The presence of CaCO<sub>3</sub> in the EC2 region is repeatable assuming a stable temperature profile in the analyzer and the same CaCO<sub>3</sub> sample. Hypothetically, minor temperature changes can occur, e.g. when changing hardware (heating filaments, glass oven or temperature sensor in the analyzer), which can lead to minor changes in the real temperature profile even when using the

same temperature protocol. Another factor is the sample itself. Carbonate is part of the dust mix where it usually does not contribute more than 50%. Depending on the carbonate fraction in the sample and interference with other substances, CaCO<sub>3</sub> can be released at lower temperatures as mentioned by Chow et al. (2001). Nevertheless, even if carbonate peaks may shift in the thermogram, removal of carbonate by HCl fumes should be considered as a determining factor in their analysis. From this point of view, the shift of the peak in the thermogram (e.g. between EC1 and EC2) is not essential. From this perspective, it is also not possible to distinguish that the material lost after HCl fumigation is a form of CaCO<sub>3</sub>, other carbonates (e.g. dolomite) or possibly other material.

- Were any tests of HCl fumigation performed on the carbonate standards or are there references for this procedure to ensure there is quantitative removal of carbonate.

In some works, quantitative methods are focused on carbonate standards analysis but are not tested on aerosol samples (Baudin et al., 2023). In literature on aerosol analyses by EC/OC analyzer, experiments with carbonate standards are mentioned (Cavalli et al., 2010; Karanasiou et al., 2011). Karanasiou et al. (2011) reported carbonate recovery from samples containing 25-250 ugCC/sample at around 90%. It can be assumed that at least similar recovery rates can be achieved with lower amounts of CC corresponding to our sample concentrations. However, as reported elsewhere (Jankowski and Chow 1993), other compounds (e.g., salts of carboxylic acids) may also be transformed during HCl fumigation, which introduces an uncertainty into the quantification of carbonates.

Regarding to this comment, we have added following new sentence to the subsection 2.3.: “ This procedure is probably not able to analyze all carbonates (Baudin et al., 2023) but quantitatively, this method leads to the analysis of at least 90% of the carbonates in samples (Karanasiou et al., 2011).”

- One of the important concluding points in section 4 is that the mis-identification of CC as either EC or OC will result in incorrect estimates of aerosol effects on radiative forcing. Are there any previous reports on the optical properties of carbonate aerosol to help expand on this point?

A study by Raman et al. (2011) reported a positive radiative effect of carbonate rich dust, although this effect is lower than that of particles from transport, which are assumed to contain more BC. However, this study was conducted in India, where the composition, and therefore the color, of the dust may be different, potentially leading to a different radiation effect. Similarly, Chen et al. (2021), shows the effect of carbonates and BC on the calculation of the radiative forcing of dust in Tajikistan. However, these are studies where CC is part of dust, which may have regionally different compositions and thus a different influence on the radiative effect. In general, however, determining the effect of Arctic CC and/or dust on radiative forcing is beyond the scope of this study. It would be a broad topic for a future study.

Regarding this comment, we have added following new sentence to introduction: “It is reported that carbonate rich dust also has a slightly positive effect on radiative forcing, although lower than BC (Chen et al., 2021; Raman et al., 2011).”

In conclusions, we have also changed word “opposite” to “lower” as follows: “This could, for example, affect modelling of the effect of carbonaceous aerosols on the Arctic climate, as EC

(or black carbon) has a warming effect on the atmosphere, while CC has a lower warming effect.”

- Figure 3: I find this figure hard to interpret, and I recommend simplifying it, or splitting into different panels. There are a number of items on it that are not discussed. For example, the laser intensity. Also, the textboxes “PC”, “HCl” and “EC” and the short dashed lines around 600 seconds are not defined. There are also a few periods (OC3 and OC4) where the HCl treated is higher than the untreated. Is there an explanation for this?

Fig. 3 has been simplified. It is true that some data, such as laser intensity, are not relevant in this case to show material loss by HCl fumigation. For this reason, we have removed them and thus we made this graph more readable.

The higher periods in OC3 and OC4 after HCl treatment are probably due to the transformation of some organic substances by HCl fumigation into less volatile ones (e.g. polymers and other substances), which are released at higher temperatures. In our case, however, it is still OC. This phenomenon is documented, e.g., by Jankowski et al. (2008). Regarding to this we added following new text to the subsection 2.3: “Exposing samples to HCl can also affect the transformation of organic matter, which is then released at higher temperatures. Therefore, the thermogram after fumigation may not reflect only the expected CC loss (Jankowski et al., 2008).”

Figure 7: Are the outliers for the calculated  $\delta^{13}\text{C}_{\text{CC}}$  that are  $>100\%$  simply due to the low abundance of carbonates during those periods? If so, it may be worthwhile to filter out those points as they are misleading.

Yes, it is likely that the  $\delta^{13}\text{C}_{\text{CC}}$  calculation is affected at low CC concentrations. This is also evident, e.g., from Fig. S5 in the supplementary material, and we mention this possibility at the end of subsection 2.4.

You are right that it is not necessary to show the outliers calculated in this way (probably Fig. S5 is sufficient). For this reason, we have adjusted the y-axis range in Fig. 7 for  $\delta^{13}\text{C}_{\text{CC}}$  to range from -40 to +20. This should make Fig. 7 more straightforward to the relevant values of  $\delta^{13}\text{C}_{\text{CC}}$ .

Typographical:

Line 57: This is not a complete sentence

We have expanded the sentence (see the red text below) to make it complete.

“Arctic regions are affected by long range transport of dust and also contributed by dust locally”

Line 280: should this be particles?

Corrected. Thank you.

## References:

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