Significant Influence of Carbonates on Determining Organic Carbon and Black Carbon: A Case Study in Tajikistan, Central Asia

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ABSTRACT: Carbonates cause large uncertainties in determining the concentrations of organic carbon (OC) and elemental carbon (EC), as well as EC's light absorption characteristics, in arid locations, such as Central Asia. To investigate this influence, a comparison between acid (HCl)-treated and original total suspended particle (TSP) samples was conducted in Dushanbe, Tajikistan. According to the results, the OC and EC concentrations were overestimated by approximately 22.8 ± 33.8 and 32.5 ± 33.5%, with the actual values being 11.9 ± 3.0 and 5.13 ± 2.24 $\mu g\ m^{-3}$, respectively. It was found that carbonates had a larger influence from May to October than during the other months, which was significantly correlated with the amount of TSPs on the filter. Furthermore, the mass absorption cross-section of EC (MAC_{EC}) increased from 4.52 ± 1.32 to 6.02 ± 1.49 $m^2\ g^{-1}$; this indicated that carbonates can significantly decrease MAC_{EC}, thus causing an underestimation of approximately 23.9 ± 16.7%. This is the first study that quantifies the influence of carbonates on the light-absorbing abilities of EC.
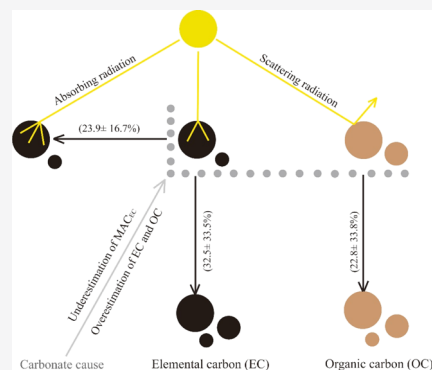
1. INTRODUCTION

Carbonaceous aerosols (CAs), mainly composed of organic carbon (OC) and elemental carbon (EC; also called black carbon), affect the global radiative balance by absorbing and scattering radiation, thus causing large uncertainties in the climate system.[1−4] For solar radiation absorption, EC primarily absorbs visible and infrared wavelengths, whereas part of OC has a positive direct effect on absorption in the blue to the ultraviolet spectral range.[5−8] In general, the mass absorption cross-section (MAC), a parameter calculated based on component concentrations and absorptions, is used to evaluate the radiative forcing of OC and EC.[9−12] Thus far, OC and EC concentrations, as well as their MAC values, have been extensively reported worldwide by studies attempting to understand CAs' effect on climate change.[4,5,13−18] However, the detailed chemical data for ambient CAs in Central Asia have rarely been reported. Only two studies (conducted in Bishkek and Teploklyuchenka in Kyrgyzstan) have reported the chemical characteristics and sources of particulate matter (PM).[19,20] However, neither of them has considered the influence of carbonates on OC and EC measurements.

Carbonates constitute a type of particle component found in mineral dust.[21−23] During OC and EC measurements using the thermal-optical method, carbonates emit CO_2 as the temperature increases, thus causing an overestimation of OC and EC concentrations.[24−27] This overestimation is negligible for fine-mode OC and EC concentrations because the contribution of carbonates to $PM_{2.5}$ is generally very low.[28,29] However, it is significant for PM_{10} or coarse particles under specific

meteorological conditions or in certain areas,[5,25] such as Central Asia, where soil dust outbreaks significantly increase the ambient PM levels.[30,31]

Central Asia is located in the center of a global dust belt, where strong wind speeds, low vegetation coverage, and frequent drought conditions, especially in the context of global warming, contribute excessively to the expansion of arid land and an increase in the frequency of dust storms.[32−34] The Kyzylkum, Karakum, Aralkum, and Balkhash regions in Central Asia have been confirmed to be the major dust source regions.[35−37] Thus, carbonates may account for a larger portion of the particles in Central Asia compared with those in other regions. In addition, recent studies have suggested that Central Asia is an important source region for the long-range transportation of particles to other regions, such as the Tibetan Plateau.[37,38] It is, therefore, essential to comprehensively analyze the chemical characteristics of CAs and the effect of carbonates on CAs in Central Asia. Additionally, because carbonates have a lower influence on light absorption than EC has in the atmosphere, if carbonates are treated as EC, then EC-derived climate forcing will be overestimated.[38−40]

Table 1. Monthly Average Values of Temperature (°C) and Precipitation (mm); Concentrations (μg m^{-3}) of TSP, OC$_A$, and EC$_A$; and MAC$_A$ (m^2 g^{-1}) during the Sampling Period

monthly/year	temperature	precipitation	TSP	OC$_A$	EC$_A$	MAC$_A$
Sep 2018	22.6	2.31	321	11.7	5.22	5.49
Oct 2018	13.9	27.5	567	8.12	4.74	6.84
Nov 2018	8.87	49.1	191	17.3	7.70	4.96
Dec 2018	6.37	64.2	232	27.7	9.40	4.07
Jan 2019	4.64	70.3	133	14.8	6.73	5.51
Feb 2019	5.12	79.3	127	12.0	6.03	5.88
Mar 2019	11.8	118.2	135	7.43	3.68	7.79
Apr 2019	16.7	108.7	117	5.81	2.97	7.62
May 2019	20.7	74.0	135	5.31	2.95	7.20
Jun 2019	23.8	12.6	199	6.43	2.70	7.50
Jul 2019	30.6	1.96	319	12.0	5.28	5.51
Aug 2019	27.3	1.38	436	14.9	4.90	5.33

However, the effects of carbonates on the light absorption characteristics of EC have not been investigated yet.

Therefore, the contributions of carbonates to both CA concentrations and MAC values in Central Asia must be quantitatively evaluated to reduce the uncertainties in evaluating regional air quality and climate change. Tajikistan is a country in Central Asia with a dry continental climate; it is frequently affected by severe dust events and is a net accumulator of dust.[35,41] In this study, total suspended particles (TSPs) were collected in Dushanbe, the capital city of Tajikistan, from September 2018 to August 2019. Both original and HCl-treated samples of OC and EC were measured to evaluate the contributions of carbonates to both components. Additionally, the MAC values of EC (MAC$_{EC}$) for the two types of samples were compared to assess the influence of carbonates on the light absorption characteristics of EC. The present study is an extension of our previous study that was based on the Atmospheric Pollution and Cryospheric Change monitoring and research network.[5,13] This study's findings can ground future research on the effect of carbonates on OC and EC measurement in Central Asia.

2. MATERIALS AND METHODS

2.1. Study Area and Sample Collection. Tajikistan is located in southeastern Central Asia (36°–41°N and 67°–75°E), with Dushanbe as its capital. The total area of the country is approximately 143,100 km^2, with a total population of approximately 9.3 million. The country has a dry continental climate and has a high freshwater availability from glacier regions.[41] The average monthly temperatures range from 4.64 to 30.6 °C, and temperatures averaging over 20 °C are observed from May to September (annual average: 16.0 °C, Table 1). During the sampling period (between September 2018 and August 2019), the annual rainfall of Dushanbe was recorded to be approximately 600 mm, with more than 80% of precipitation occurring between December 2018 and May 2019.

The sample collection was performed at the Physical Technical Institute of the Academy of Sciences of Tajikistan (Figure 1), which is located in an urban environment on a hill in the eastern part of Dushanbe. A sampler was installed on a platform in front of a laboratory and an office building (38°33′34″N, 68°51′22″E, 864 m above sea level).

We collected 62 TSP samples on precombusted quartz fiber filters (90 mm in diameter, Whatman) using a medium-volume sampler at a flow rate of 100 L/min (T2034, Qingdao Laoying,
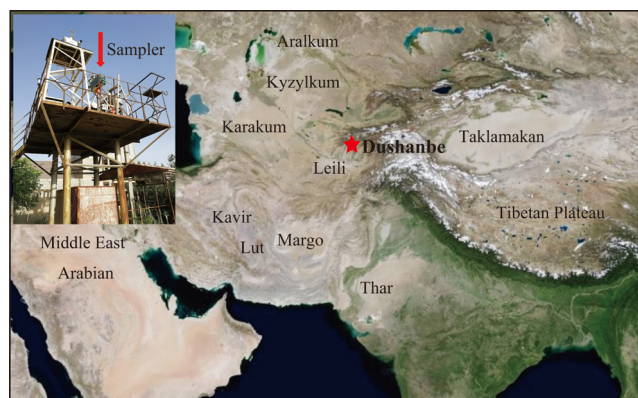

Figure 1. Sampling site in Dushanbe, Tajikistan; sampling tower (photograph), sampler (red arrow), and desert regions (black text).

China). We collected one sample every 6 days to avoid weekend effects, with each round of sampling lasting 24 h. The treatment of the filters, per the methods in previous studies, is detailed in the Supporting Information section (Text S1).[5,13] We collected 12 field blank filters to obtain the background data related to the experiment processes.

2.2. Analytical Procedures and Quality Assurance/Quality Control. Two equal-sized pieces (1.0 cm^2) were cut from each TSP sample, one of which was designated as the original sample. The carbonates were removed from the other piece by fumigation process, which involved exposing the samples to 37% HCl vapor for 24 h. Subsequently, the treated samples were held at 60 °C for over 1 h to remove any acid remaining on the filter (defined as the acid-pretreated sample), by following the method used in the literature.[5,23] In addition, the cut filters were weighted before and after the acid treatment. The acid-treated filters were found to be slightly heavier, with an average filter$_{acid-treated}$/filter$_{original}$ ratio of 1.03. Correspondingly, the TSP loaded on the filter changed with an average TSP$_{acid-treated}$/TSP$_{original}$ ratio of approximately 1.03 probably because of the production of calcium chloride. In addition, a clear seasonal variation in this ratio was observed over the sampling period, with relatively lower values occurring from November to March than in the other months.

Finally, the OC and EC concentrations of both sample types were measured using a thermal/optical carbon analyzer (DRI model 2015, Desert Research Institute, USA) under the IMPROVE-A thermal/optical reflectance protocol, according to which the samples were sequentially heated in an inert (i.e.,

He) and an oxidizing (i.e., He/O_2) atmosphere.[12,26] The samples were heated at temperatures of 140 °C (OC1), 280 °C (OC2), 480 °C (OC3), and 580 °C (OC4) in a pure He atmosphere, and then at 580 °C (EC1), 740 °C (EC2), and 840 °C (EC3) in an oxidizing atmosphere of 2% O_2 and 98% He. OC and EC were split based on the filter transmittance signal (I) at 632 nm.[42]

Thus far, various methods have been proposed to determine the carbonate content and its effect on OC and EC concentrations. The most commonly used method involves pretreatment of the aerosol samples with HCl fumes, followed by direct determination of the concentration of CO_2 evolved during acid treatment or by an estimation of the carbonate content in terms of the difference in the total carbonate concentration between the acidified and untreated samples.[43] Another approach is thermal treatment, in which the filter discs are placed in an O_2 atmosphere at 460 °C for 60 min to remove OC and EC; thereafter, the carbonate concentration is determined using a total carbon instrument.[44] In addition, various temperature protocols (e.g., modified NIOSH protocol) have been tested to identify and quantify atmospheric carbonate.[22] However, these protocols produce results that vary between conditions (e.g., being limited by carbonate content and measurement type). Although high recovery rates of carbonates can be achieved using these protocols, a high level of uncertainty exists due to the manual integration and residual contribution of OC. Previous studies have demonstrated that fumigation treatment almost entirely removes carbonates (by approximately 99% depending on the initial quantity added) from the standard carbonate sample.[22] The present study aimed to assess the effect of carbonates on the measurement of OC and EC concentrations by comparing the original and acid-treated samples. Therefore, we did not calculate the carbonate content and its quantitative efficiency.

The optical attenuation (ATN) of each sample was determined in terms of $\ln(I_{final}/I_{initial})$, where I_{final} and $I_{initial}$ are the I values obtained after and before the thermal/optical analysis, respectively. The ATN value retrieved from the carbon analyzer can be used to determine the absorption coefficient (b_{abs}) of the aerosol on the filter

$$b_{abs} \, (Mm^{-1}) = ATN \times \frac{A}{V} \tag{1}$$

where A is the filter area with particle loading (mm^2) and V is the volume of the air sample (m^3). Thereafter, the MAC of EC can be calculated as

$$MAC_{EC} = \frac{b_{abs}}{EC} = \frac{ATN \times A}{EC \times V} = \frac{ATN}{EC_s} \times 10^2 \tag{2}$$

where EC_s ($\mu g \, cm^{-2}$) is the filter loading of the EC. Per suggestions in previous studies, an empirical factor of 3.6 was used to correct the MAC[11,42]

$$MAC_{correct} = \frac{ATN}{EC_s} \times 10^2 \times \frac{1}{3.6} \tag{3}$$

All analytical procedures were monitored using strict quality assurance/quality control (QA/QC) measures. Procedural and field blanks were analyzed in the same manner as the samples. The measurement accuracy was ±10%, and the detection limits for OC, EC, and the sum of OC and EC (SC) were 0.43, 0.12, and 0.49 $\mu g \, C/cm^2$, respectively.[5] The OC concentration of the field blank filters was 0.48 ± 0.13 $\mu g \, C \, cm^{-2}$, and no EC

was detected. In addition, all reported values were field blank–corrected.

3. RESULTS AND DISCUSSION

3.1. Contribution of Carbonates to CA Concentrations.
The SC concentrations of the original and acid-treated samples (denoted as SC_O and SC_A, respectively) were obtained in this study. The SC_O concentrations ranged from 12.3 to 192.5 $\mu g \, cm^{-2}$, with an average of 49.9 ± 29.2 $\mu g \, cm^{-2}$, whereas SC_A concentrations were lower than SC_O concentrations, with values ranging from 11.9 to 128.1 $\mu g \, cm^{-2}$ (average: 39.8 ± 22.1 $\mu g \, cm^{-2}$). The average SC_A/SC_O value was 0.82 ± 0.14, with all values lower than 1 (Figure 2); this
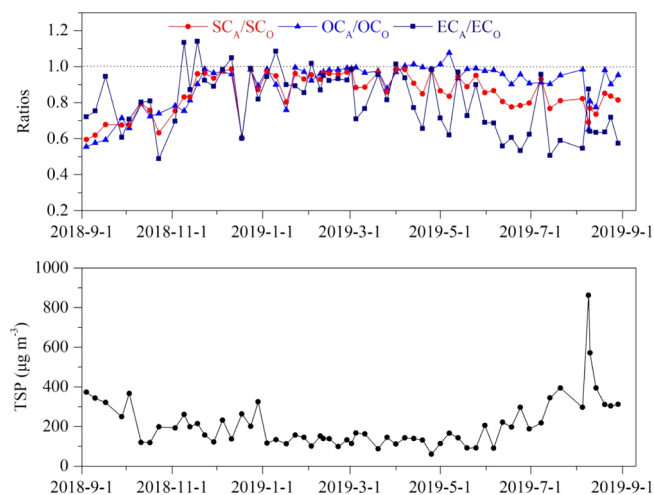
Figure 2. Seasonal variations in the TSP concentrations and SC_A/SC_O, OC_A/OC_O, and EC_A/EC_O values of the samples collected at Dushanbe.

indicated that when measured without acid treatment, SC was overestimated in Dushanbe by approximately 25.8 ± 26.9% (exclude one sample collected on October 7, 2018, Text S2). In addition, a clear seasonal variation was observed in SC_A/SC_O values, with the lowest value occurring at approximately mid-August, which slowly increased to approximately 1 in December 2018 and remained constant until May 2019 before decreasing to the minimum again. The TSP concentration on the filters exhibited an inverse variation, with higher values obtained during June to October than during the other months (Figure 2). The variation observed between TSP concentration and SC_A/SC_O indicated that more carbonates was present during high-particle-concentration days and that its effect became more pronounced because more carbonates was loaded on the filters (Figure S1).

The OC and EC concentrations of the original (OC_O and EC_O) and acid-treated (OC_A and EC_A) samples were analyzed to evaluate the influence of carbonates on OC and EC concentrations. According to the results, OC_O ranged from 7.18 to 144.6 $\mu g \, cm^{-2}$, with an average of 34.7 ± 23.6 $\mu g \, cm^{-2}$, whereas slightly lower OC_A concentrations were observed, with values ranging from 7.07 to 101.9 $\mu g \, cm^{-2}$ (average: 27.8 ± 17.0 $\mu g \, cm^{-2}$). Correspondingly, EC_O and EC_A ranged from 2.92 to 47.9 $\mu g \, cm^{-2}$ (average: 15.2 ± 6.55 $\mu g \, cm^{-2}$) and from 3.67 to 28.8 $\mu g \, cm^{-2}$ (average: 11.9 ± 5.49 $\mu g \, cm^{-2}$), respectively (Figure S2). The OC and EC concentrations demonstrated similar seasonal variations over the sampling period, with higher concentrations observed during August to

February of the following year than during the other months (Table 1 and Figure S2). The average OC_A/OC_O and EC_A/EC_O values were 0.86 ± 0.17 and 0.81 ± 0.28, respectively, suggesting that carbonates contributed to EC more considerably than they did to OC because carbonates are more prone to decomposition at higher temperatures along with EC during analysis.[29] This is explicable under the IMPROVE-A protocol, with the maximum temperature reaching 580 °C in an inert atmosphere but not under other widely used protocols (e.g., EUSAAR2 and NIOSH) because higher temperatures during the inert atmosphere phase facilitate the decomposition of most carbonates before the oxidizing phase.[22] Four and seven samples, respectively, had OC_A/OC_O and EC_A/EC_O values that were slightly greater than 1 (Figure 2). After carefully comparing the measured data of both sample types, the split time of all acid-treated samples was found to move somewhat ahead, which caused an increase in the EC concentration and a corresponding decrease in the OC concentration. In addition, the pyrolysis carbon values of most acid-treated samples were found to increase. Therefore, if the increase in the pyrolysis carbon values was greater than the total reduction in OC caused by the loss of volatile organic acids and being ahead of the split time, higher OC_A values could be obtained. In addition, if the increase in EC caused by the variation in the split time and carbonate decomposition is greater than that in the pyrolysis carbon, higher EC_A values can be obtained.[44] Thus, carbonates have a highly complex influence on the measurement of OC and EC concentrations. However, HCl was removed prior to the measurement by heating the filters at 60 °C for 1 h. Therefore, we believe that first, it is the presence of carbonates and not HCl that caused such uncertainty in the variation of split time and pyrolysis carbon concentration and second, that the data for the acid-treated samples better approximate the actual values. The acid-treatment method has been extensively used to eliminate the influence of carbonate.[18,23,45−47] Therefore, we suggest using the acid-treatment method to obtain more accurate OC and EC data, particularly for TSP samples in an arid region.

A comparison between the acid-treated and original samples showed that the OC and EC concentrations of the acid-treated samples were lower than those of the original TSP samples, indicating that carbonates influence both OC and EC concentrations; this is because they can decompose at relatively low temperatures during the measurement.[22] In summary, we clearly showed how the OC and EC concentrations in TSP samples in Dushanbe were overestimated by approximately 22.8 ± 33.8% and 32.5 ± 33.5%, respectively. These overestimates exceed the corresponding 10% value determined for coarse particles in the central Mediterranean region of Europe[48] and are close to those determined in two remote stations on the Tibetan Plateau.[23] This suggests that acid pretreatment should be conducted for samples obtained from the sites in Central Asia to determine the actual OC and EC concentrations. However, fumigation with HCl can cause the loss of volatile organic acids in the treated samples,[49] thus causing a slight underestimation of OC. In addition, more thermally stable substances, which do not evolve during the inert atmosphere phase, are quantified as EC.[44]

3.2. OC and EC Concentrations in the Atmosphere.
The daily OC and EC concentrations obtained using the acid-treatment method ranged from 3.0 to 41.2 and 1.60 to 12.0 μg m^{-3}, respectively. Both components exhibited the highest and lowest concentrations in December and May, respectively (Table 1 and Figure 3). This differed from the TSP pattern,
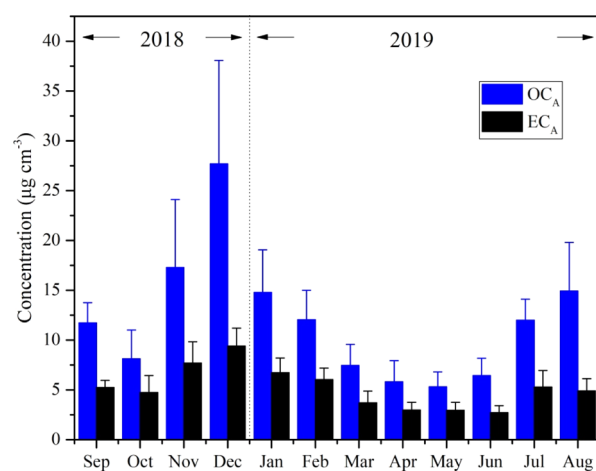

Figure 3. Seasonal variations in the OC_A and EC_A concentrations of samples collected at Dushanbe.

which ranged from 60.1 to 862.2 μg m^{-3}, with maximum values occurring at approximately August and September (Figure 3). TSP exhibited a similar variation with aerosol optical depth in Dushanbe.[41,50] The higher OC and EC concentrations observed during November to December are attributable to the increased activity of emission sources due to lower temperatures and a stable atmospheric boundary layer, which encourages pollutant accumulation. By contrast, the washout from March to May is responsible for lower OC and EC concentrations.[50]

The concentrations of OC (11.9 ± 3.0 μg m^{-3}) and EC (5.13 ± 2.24 μg m^{-3}) were lower than those recorded in other urban areas, such as Kathmandu (Nepal),[10] Karachi (Pakistan),[12] and 14 Chinese cities during winter.[15] However, they were significantly higher than those recorded in remote regions, such as QOMS on the northern side of the Himalayas (Cong et al., 2015), Nam Co (inland of the Tibetan Plateau),[5] and other regions in the Arctic and Antarctic.[51,52]

3.3. Influence of Carbonates on MAC$_{EC}$.
Carbonates also affect the light absorption characteristics of EC. This can be observed when comparing the ATN (at 632 nm) and EC loading (EC_S) between the original and acid-treated samples. Previous studies conducted in Beijing and Lhasa have reported that ATN and EC_S were strongly correlated when EC_S was below 7 μg cm^{-2},[9,11] whereas some studies conducted in South Asia found that this correlation disappeared when the EC_S value exceeded 15 μg cm^{-2}.[10,12,53] In this study, a strong correlation ($R^2 = 0.72$) was observed between these two components for acid-treated samples, whereas a much lower correlation ($R^2 = 0.26$) was observed for the original samples (Figure 4). The deviations between the two sample types indicated a noticeable influence of carbonates on the light absorption characteristics of EC. On one hand, most ATN values of the acid-treated samples increased, suggesting the direct effect of carbonates on the transmittance signal. On the other hand, the high carbonate content of the original samples caused an overestimation of EC, which eliminated the high correlation between EC_S and ATN. In addition, ATN was significantly correlated to EC_S (including EC_S values > 15 μg cm^{-2}) for acid-treated samples. This differed from the findings
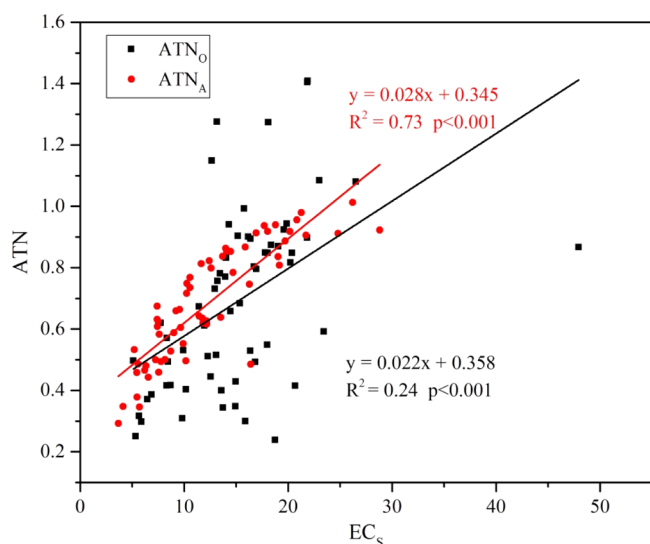
Figure 4. Relationship between ATN and EC_S of original and acid-treated samples.

of previous studies, which indicates that the results of those studies were also affected by the presence of carbonates.

Subsequently, the MAC_{EC} values of the original and acid-treated samples (denoted as MAC_O and MAC_A, respectively) were obtained. The MAC_O values ranged from 1.81 to 9.72 m^2 g^{-1}, with an average of 4.52 ± 1.32 m^2 g^{-1}, and the MAC_A values ranged from 2.96 to 10.2 m^2 g^{-1} (average: 6.02 ± 1.49 m^2 g^{-1}; Table 1 and Figure 5). Most MAC_A values were higher
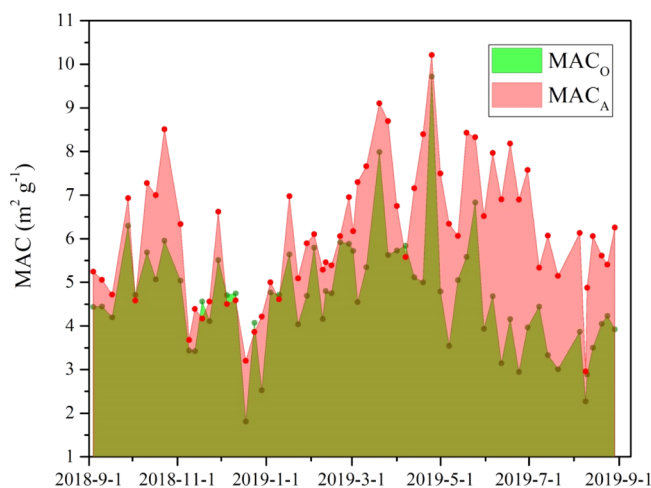

Figure 5. Seasonal variations in MAC_{EC} values of original and acid-treated samples (denoted as MAC_O and MAC_A, respectively).

than the MAC_O values, with the average MAC_A/MAC_O value being 1.38 ± 0.33, indicating that carbonates caused considerable underestimation ($23.9 \pm 16.8\%$) of the actual MAC_{EC} values for no acid treatment. In addition, a clear seasonal variation in MAC_A/MAC_O values was observed, with the highest value occurring at approximately August and then slowly decreasing to approximately 1 and remaining constant from December 2018 to March 2019. A similar variation between TSP concentrations and MAC_A/MAC_O values indicated, first, that the TSP loaded on the filters can influence the MAC_{EC} values and, second, that the effect becomes more pronounced with an increase in the amount of TSP. TSP

includes several soil components, some of which are self-absorbing, such as iron;[54] however, the presence of carbonates also affects the measurement of EC and, by consequence, the calculated MAC values. Therefore, this effect is attributable to the chemical composition of TSP.

3.4. Implications. Most studies on carbon components have generally measured the original samples, and only a few studies have used HCl-pretreated samples. The findings of these studies suggest that carbonate contributions of less than 5% exist in regions are not influenced by mineral dust; therefore, the interference of carbonates in OC and EC measurement is not significant.[27,55] However, related studies conducted in arid regions (e.g., Europe and the Tibetan Plateau) have reported that the interference of carbonates is significantly correlated with dust content.[5,21,23] This phenomenon is obvious, and the contributions of carbonates to OC and EC are likely to be more pronounced in Central Asia because dust storms are more prevalent there than in other arid regions, particularly from July to December.[37,38] The present study determined the extent of overestimation of OC and EC concentrations due to carbonates to be 22.8 ± 33.8 and $32.5 \pm 33.5\%$, respectively. These values are significantly higher than those determined in other studies, indicating the severe effect of mineral dust particles on CA measurement in Dushanbe. Nevertheless, very few studies on CA characteristics have been conducted in Central Asia, and none of them have considered the influence of carbonates.[19,20] Therefore, the influence of carbonates in aerosols must be quantitatively evaluated to determine actual OC and EC concentrations.

Furthermore, we provide evidence regarding the influence of carbonates on MAC_{EC} in Central Asia, and we are the first to quantify this parameter. In our results, carbonates resulted in an underestimation of approximately $23.9 \pm 16.8\%$ for MAC_{EC}. The estimates for the direct radiative forcing of EC span a large range.[2,56] This large uncertainty is attributable to a lack of understanding of MAC_{EC}. We must, therefore, determine the actual MAC_{EC} value for a given region and perform acid treatment in Central Asia in future evaluations. Furthermore, Central Asia contributes significantly to global dust emission and has thus been identified as a potential source region, more so than its neighboring regions. For instance, the westerly atmospheric circulation can transport the air mass from Central and West Asia to the Tibetan Plateau, influencing both the environment and climate.[57,58] Therefore, related studies on other issues, such as atmospheric transport models, based on in situ CA concentrations, must adjust their measurements accordingly.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c05876.

> Methodological details of pretreatment of the filters and OC and EC detection; discussions on the sample significantly affected by dust storm; influence of particles on different ratios; and OC and EC concentrations of two types of samples (PDF)

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Notes

The authors declare no competing financial interest.

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