Specific Absorption Cross-section and Elemental Carbon Content of Urban Aerosols


Abstract

To investigate the light absorption efficiency of aerosols, samples of fine particulate matter (PM2.5) were collected during a field experiment in Taipei, Taiwan. Mass concentration and the elemental carbon (EC) content of the PM2.5 samples were measured, and in addition, the light absorption cross-section of the EC in PM2.5 was derived. On average, elemental carbon contributed 8.6±3.5% to the PM2.5 mass. The aerosol light absorption coefficient was linearly proportional to the ambient EC concentration. Consequently, an average specific absorption cross-section of 10.8±2.6m²/g was obtained for EC in the aerosols. Analyses of the variations in the absorption cross-section revealed that the cross-section converged towards the average level as the ambient EC concentration increased. The scattering in the low EC regime is proposed to be due to differences in the mixing state: internal mixing enhanced the cross-section, whereas external mixing resulted in a decreasing trend.

Introduction

Radiative forcing by anthropogenic aerosols has been identified as a critical component in the planetary radiation budget. In addition to scattering the solar radiation, aerosols are also known to be a major short-wave absorber in the atmosphere, due to the light-absorbing constituents like elemental carbon (EC) and iron oxides. The absorption of solar radiation can lead to a warming effect similar to that from greenhouse gases, and it might also affect the regional atmospheric stability and result in changes in the hydrologic cycle.

The specific absorption cross-section of the EC in atmospheric aerosols ($\sigma_{EC}$) is a key parameter in the calculation of the radiation field for an EC-containing particle. Rosen et al. [1] identified the graphitic structure in the light-absorbing aerosols. However, the values of $\sigma_{EC}$ reported in the literature vary over an order of magnitude [2], and most are larger than that of pure graphite particles. Theoretical calculations have shown that coating the graphite particles with a transparent shell can significantly enhance $\sigma_{EC}$.
This theoretical prediction got support from a recent chamber study [4]. In spite of the theoretical results, there is still a large discrepancy in the $\sigma_{EC}$ values obtained in respective field experiments. Even in the same campaign of SCAR-B, which was conducted in Brazil to characterize the aerosols from specific sources (i.e. biomass burning), the $\sigma_{EC}$ values were scattered by nearly a factor of four [5]. Thus, to date, an accurate estimation of the forcing due to aerosol absorption cannot be achieved.

**Experimental**

Samples of PM2.5 (particulate matter with an aerodynamic diameter less than 2.5 $\mu m$) were collected in Taipei, Taiwan (25.0 °N, 121.5 °E) during the last week of each month in 2003. Two aerosol samples were collected on PTFE and quartz fiber filters, respectively, using a multi-channel sampler operated at a channel flow rate of 10 liter per minute. The sampling period for each sample was 12 hours: Daytime samples were collected between 08:00-20:00 LST; nighttime sampling was carried out between 20:00 LST to 08:00 LST the next day. Mass concentrations of PM2.5 were determined from the gravimetric measurements of the PTFE filters, whereas the quartz filter samples were used for the analyses of carbonaceous composition and light absorption coefficient. The organic carbon (OC) and elemental carbon (EC) contents in the aerosol samples were analyzed using a DRI-2001 Carbon Analyzer, which was designed and operated as per the IMPROVE/TOR protocol. Because the operational definition of EC in the TOR protocol is based on the reflectance of the 632.8 nm laser beam from the particle-laden filter samples, the measured EC is essentially the light-absorbing carbonaceous component (i.e. BC) in aerosols. The absorption coefficients ($b_{abs}$) of the aerosol samples on quartz fiber filters were measured using the laser transmission method [6]. Specific absorption cross-section of particulate matter is given by the ratio of $b_{abs}$ and mass concentration of PM2.5 ($C_{PM2.5}$). Assuming that EC is the sole light-absorbing component in PM2.5 the $\sigma_{EC}$ can be calculated by taking the ratio of $b_{abs}$ to the mass concentration of EC in the aerosol samples. This assumption may result in an overestimated $\sigma_{EC}$ because there are some other light-absorbing constituents, particularly minerals like iron oxides, in ambient aerosols. However, considering that the mineral content is quite limited in

<table>
<thead>
<tr>
<th>2003</th>
<th>Sample Number</th>
<th>EC ($\mu g/m^3$)</th>
<th>PM2.5 ($\mu g/m^3$)</th>
<th>EC/PM2.5 (%)</th>
<th>$b_{abs}$ (Mm$^{-1}$)</th>
<th>$\sigma_{EC}$ (m$^2/g$)</th>
<th>$\sigma_{PM2.5}$ (m$^2/g$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan.</td>
<td>10</td>
<td>4.3(1.7)</td>
<td>49.8(14.7)</td>
<td>8.7(2.3)</td>
<td>46.2(12.7)</td>
<td>11.3(2.6)</td>
<td>0.9(0.2)</td>
</tr>
<tr>
<td>Feb.</td>
<td>20</td>
<td>2.8(1.0)</td>
<td>45.6(14.7)</td>
<td>6.5(2.0)</td>
<td>31.5(14.1)</td>
<td>10.9(1.9)</td>
<td>0.7(0.3)</td>
</tr>
<tr>
<td>Mar.</td>
<td>24</td>
<td>3.3(1.2)</td>
<td>39.4(20.1)</td>
<td>9.4(3.5)</td>
<td>31.2(16.8)</td>
<td>9.2(2.1)</td>
<td>0.8(0.3)</td>
</tr>
<tr>
<td>Apr.</td>
<td>11</td>
<td>2.6(0.9)</td>
<td>39.3(15.3)</td>
<td>7.3(2.6)</td>
<td>29.0(11.3)</td>
<td>11.1(2.6)</td>
<td>0.8(0.2)</td>
</tr>
<tr>
<td>May</td>
<td>13</td>
<td>3.2(1.4)</td>
<td>41.3(24.3)</td>
<td>9.3(3.8)</td>
<td>32.5(15.7)</td>
<td>9.8(1.9)</td>
<td>0.9(0.4)</td>
</tr>
<tr>
<td>Jun.</td>
<td>14</td>
<td>2.8(0.6)</td>
<td>35.6(9.5)</td>
<td>8.5(3.4)</td>
<td>32.5(8.5)</td>
<td>11.6(1.8)</td>
<td>1.0(0.3)</td>
</tr>
<tr>
<td>Jul.</td>
<td>13</td>
<td>2.7(1.0)</td>
<td>38.8(20.9)</td>
<td>8.5(3.4)</td>
<td>28.1(12.4)</td>
<td>10.0(2.8)</td>
<td>0.8(0.2)</td>
</tr>
<tr>
<td>Aug.</td>
<td>6</td>
<td>2.5(0.8)</td>
<td>35.6(12.6)</td>
<td>7.3(1.3)</td>
<td>28.4(12.7)</td>
<td>10.9(2.4)</td>
<td>0.8(0.1)</td>
</tr>
<tr>
<td>Sep.</td>
<td>9</td>
<td>1.9(1.0)</td>
<td>35.0(13.3)</td>
<td>5.5(2.7)</td>
<td>17.0(3.7)</td>
<td>11.0(5.1)</td>
<td>0.5(0.2)</td>
</tr>
<tr>
<td>Oct.</td>
<td>13</td>
<td>3.8(1.7)</td>
<td>38.8(24.0)</td>
<td>11.1(4.2)</td>
<td>39.7(19.3)</td>
<td>11.0(2.8)</td>
<td>1.1(0.3)</td>
</tr>
<tr>
<td>Nov.</td>
<td>10</td>
<td>2.6(0.8)</td>
<td>31.8(15.7)</td>
<td>9.5(3.8)</td>
<td>30.7(11.5)</td>
<td>11.8(2.2)</td>
<td>1.1(0.5)</td>
</tr>
<tr>
<td>Dec.</td>
<td>9</td>
<td>3.6(2.1)</td>
<td>35.6(23.7)</td>
<td>11.2(3.2)</td>
<td>44.6(26.4)</td>
<td>12.7(2.9)</td>
<td>1.4(0.6)</td>
</tr>
<tr>
<td>Annual</td>
<td>152</td>
<td>3.0(1.3)</td>
<td>39.5(18.2)</td>
<td>8.6(3.5)</td>
<td>32.6(15.8)</td>
<td>10.8(2.6)</td>
<td>0.9(0.4)</td>
</tr>
</tbody>
</table>
urban aerosols and that the mineral particles exist mostly in the coarse mode of aerosol size spectra, the aforementioned positive bias should be limited to a certain extent in the measurement of PM2.5 samples.

**Results and Discussion**

Table 1 summarizes the monthly averages of aerosol measurements in 2003. In general, the ambient concentration of EC varied coincidently with that of PM2.5. This characteristic is attributed to the consistent composition of air pollutants in the urban environment and implies that the ambient concentrations of the aerosol species were dominated by meteorological conditions, particularly the dynamics of the boundary layer. Consequently, the EC content in the PM2.5 remained at a relatively stable level.

Figure 1 shows a robust linear regression between $\alpha_{\text{abs}}$ and the ambient concentration of EC. The tiny intercept shows that the light absorption capability of the urban aerosols is primarily due to the EC. Actually, the intercept is statistically insignificant ($p=0.7155$) and should therefore be regarded as zero. Thus, Figure 1 well justifies the aforementioned assumption that EC is the sole light-absorbing component in urban PM2.5, and it facilitates the following analysis on the optical properties of EC-containing aerosols. It is noteworthy that the light absorption coefficient of aerosols is linearly proportional to the ambient EC concentration. The robust linear correlation allows us to deduce an average $\sigma_{\text{EC}}$ of 10.8 m$^2$/g for the EC in urban PM2.5.

Due to its important implications for radiative forcing, the values of $\sigma_{\text{EC}}$ have attracted a lot of attention in recent years. The average $\sigma_{\text{EC}}$ obtained here is consistent with that deduced from the aircraft measurements over East Asia during the ACE-Asia Campaign, which reported an average $\sigma_{\text{EC}}$ of 11.0 [7], whereas the values of $\sigma_{\text{EC}}$ from the other earlier studies are scattered over an order of magnitude. The variability of $\sigma_{\text{EC}}$ is usually attributed to size distribution and the mixing state of the EC in the aerosol particles. However, this argument is still subject to debate. Petzold et al. [8] suggested that ambient EC was mostly mixed externally with the other aerosol species and that it had an absorption cross-section of about 4 m$^2$/g, as the value derived from pure graphite particles. Fuller et al. [1999] calculated the values of $\sigma_{\text{EC}}$ for a variety of scenarios and concluded that the aggregation of tiny particles can enhance the light absorption capability of EC by about 30%, but the values of $\sigma_{\text{EC}}$ should rarely exceed 10 m$^2$/g. On the contrary Posfai et al. [9] showed that EC was mostly internally mixed with sulfate in the North Atlantic aerosols. Martins et al. [5] reported $\sigma_{\text{EC}}$ values of 12.1±4.0 m$^2$/g for biomass burning aerosols measured in Brazil during the SCAR-B experiment.

In contrast to the highly linear correlation between the absorption coefficient and the ambient EC concentration shown in Figure 1, Figure 2 illustrates the diversity in $\sigma_{\text{EC}}$ along EC levels. In the case of the EC being less than 2 μg/m$^3$, the values of $\sigma_{\text{EC}}$ varied by a factor of four, ranging from 4.8 to 19.4 m$^2$/g. As the EC concentration increased, the values of $\sigma_{\text{EC}}$ converged towards the average level (10.8 m$^2$/g). The reasons for the variations in $\sigma_{\text{EC}}$ were not clear. Martins et al. [5] reported $\sigma_{\text{EC}}$ ranging from 5.2 to 19.3 m$^2$/g for the SCAR-B samples.
almost identical with the range obtained in this work. The results of ACE-Asia were even more scattered, ranging between 5 and 40 m²/g \[7\]. However, considering the lower EC levels (< 2 µg/m³) during ACE-Asia, the higher variability is in agreement with the trend shown in Figure 2. Thus, coupling the ACE-Asia data with those from the current study further substantiates the diverging trend in the low EC regime. The uncertainties in the thermo-optical measurement of EC should account, at least in part, for the increasing variability in the $\sigma_{EC}$ of lower EC levels. However, our results showed that this factor could merely result in a variation in $\sigma_{EC}$ of about 30%, even in case of an EC level of 1 µg/m³. The $\sigma_{EC}$ of aerosol samples collected during the INDOEX were also calculated from the published data set of $b_{abs}$ and EC (BC) concentration \[10\]. Apparently the $\sigma_{EC}$ of the INDOEX is lower than that of the ACE-Asia and that of the present study. However, it should be noted that, in the INDOEX, the EC was analyzed using the EGA method, which is known to overestimate the EC in aerosol samples for the positive bias from the pyrolysis of organic matter. Figure 2 illustrates that calibrating the $\sigma_{EC}$ of INDOEX by a factor of 1.5 will bring the results of INDOEX into good agreement with those of ACE-Asia and the present study.

In this study we propose that the variability of $\sigma_{EC}$ was mostly due to the non-homogeneous mixing state of EC in aerosols. We divided the data points with \( EC < 2 \ \mu g/m^3 \) into two subsets (shown in Figure 2). Regime-I has $\sigma_{EC}$ larger than the average level, whereas regime-II contains the data points of lower $\sigma_{EC}$. It was found that the samples in regime-I have an average EC content (EC/PM2.5) of 6.9±3.4%, which is significantly lower (p<0.05) than the whole average by a factor of 20%. Previous theoretical studies [e.g., Fuller et al, 1999] have shown that the light absorption efficiency of an internally-mixed particle can be enhanced significantly by reducing the mass fraction of EC in the particle. Our field experiment results agree with the theoretical prediction in this context. In contrast, the samples in regime-II had an average EC/PM2.5 ratio of about 9%, consistent with the whole average. Hence the low $\sigma_{EC}$ cannot be as a result from a higher EC mass fraction in an internal mixture. Recalling the proportion of EC to PM2.5, the low EC levels corresponded to low PM2.5 concentrations, implying a relatively clean air mass with quite a low number density of aerosol particles. Thus, the collision probability might decrease and, consequently, inhibit the coagulation between EC particles and other particles.

![Figure 2. Variations of the absorption cross-section of elemental carbon (\( \sigma_{EC} \)) along the ambient EC level. The blue solid line exhibits the annual average level from this work. The bold dotted lines divide the data points with EC<2 µg/m³ into two subsets in regimes I and II, respectively. The INDOEX data was adjusted by a factor of 1.5 for the positive bias in EC concentration.](image)
non-light-absorbing particles. As a result, some of the primary EC particles can exist in their original state, i.e. external mixture, and reduce the average $\sigma_{EC}$ of the aerosols.

The data points in Figure 2 construct a clear picture of $\sigma_{EC}$. The attributes of graphite setup the fixed lower limit for ambient aerosols of externally-mixed constituents. This limit is the so-called “external-mixing limit” here. In contrast, it is apparent that the data are also limited by a concave upper boundary. Previous investigators showed that the $\sigma_{EC}$ of an internally-mixed aerosol depends upon the micro-physical properties (e.g., size distribution, mixing ratio, etc.). Thus the “internal-mixing limit” can only be showed conceptually in Figure 2. Note that all the field samples possessed a $\sigma_{EC}$ higher than the external-mixing limit, implying that the EC tended to be internally mixed in the atmosphere. Although the coagulation might be inhibited in the condition of low aerosol concentration, secondary aerosols, particularly the condensable organic matter, could coat the primary EC particles and result in an internal mixture.

Conclusions

A field experiment was conducted in Taipei, Taiwan to analyze the carbonaceous composition and corresponding light absorption characteristics of urban aerosols. The average EC content in PM2.5 is 8.6±3.5% without significant seasonal variation. This stable EC content allows us to draw meaningful conclusions from the optical features of the urban aerosols. It was found that the aerosol absorption coefficient was linearly proportional to the ambient level of EC. The robust linear correlation led to two important conclusions: 1. The aerosol absorption capability can be attributed almost entirely to the EC contained in the particles; and 2. The light absorption efficiency of the EC in aerosols can be characterized by an average specific absorption cross section ($\sigma_{EC}$) of 10.8±2.6m$^2$/g.

Analysis on the variation in $\sigma_{EC}$ revealed that the value of $\sigma_{EC}$ converged towards the average level as the ambient EC concentration increased, and diverged in a low EC regime. The high $\sigma_{EC}$ was suggested to be as a result of the low EC content in an internal mixture, whereas the low $\sigma_{EC}$ was proposed to be due to the existence of externally-mixed EC particles. The results of this study were compared to those from the regional campaigns ACE-Asia, INDOEX, and SCAR-B. The consistency among the results from the independent studies suggests that the discrepancy in the $\sigma_{EC}$ is diminished.

The original paper was published in Geophysical Research Letters 32 (2005): L21808.

References: