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Particulate and water-soluble carbon measured in recent snow at Summit, Greenland

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[1] Water-soluble organic carbon (WSOC), water-insoluble particulate organic carbon (WIOC), and particulate elemental carbon (EC) were measured simultaneously for the first time on the Greenland Ice Sheet in surface snow and in a 3-meter snow pit. Snow pit concentrations reveal that, on average, WSOC makes up the majority (89%) of carbonaceous species, followed by WIOC (10%) and EC (1%). The enhancement of OC relative to EC (ratio 99:1) in Greenland snow suggests that, along with atmospheric particulate matter, gaseous organics contribute to snow-phase OC. Comparison of summer surface snow concentrations in 2006 with past summer snow pit layers (2002–2005) found a significant depletion in WSOC (20–82%) and WIOC (46–65%) relative to EC for 3 of the 4 years. The apparent substantial loss of WSOC and WIOC in aged snow suggests that post-depositional processes, such as photochemical reactions, need to be considered in linking ice core records of organics to atmospheric concentrations. Citation: Hagler, G. S. W., M. H. Bergin, E. A. Smith, J. E. Dibb, C. Anderson, and E. J. Steig (2007), Particulate and water-soluble carbon measured in recent snow at Summit, Greenland, Geophys. Res. Lett., 34, L16505, doi:10.1029/2007GL030110.

1. Introduction

[2] Organic (OC) and elemental carbon (EC) in snow and ice on the Greenland Ice Sheet are of interest for their potential usefulness as chemical signatures of anthropogenic and biogenic pollution in ice cores. Meteorological modeling indicates that anthropogenic emissions in distant regions (e.g., south Asia) can be major contributors to carbonaceous species in the Greenland atmosphere [Koch and Hansen, 2005]. Natural sources, such as biomass burning, have also been observed to significantly impact particulate carbonaceous concentrations in the air above the Greenland Ice Sheet [Jaffrezo et al., 1998; Stohl et al., 2006]. Measurements of black carbon (i.e., light-absorbing particulate matter), carboxylic acids, polycyclic aromatic hydrocarbons (PAHs), and isotoopes of carbon in Greenland ice and snow have been used to interpret the recent and long-term history of combustion emissions [Cachier and Pertuisot, 1994; Chylek et al., 1995; Legrand and de Angelis, 1995; Legrand and de Angelis, 1996; Masclet et al., 2000; Slater et al., 2002].

[3] While elemental carbon (closely linked to black carbon) is believed to be inert, the accurate interpretation of organic compounds measured in snow and ice may be hindered by post-depositional processes. Several researchers found elevated levels of gaseous organics in the interstitial air of surface snow and firn at Summit, Greenland [Dibb and Arsenault, 2002; Jacobi et al., 2004; Swanson et al., 2002]. Also, enhanced levels of the highly-reactive hydroxyl radical were observed in the air above the snowpack at Summit, Greenland [Stostedt et al., 2007], which has been suggested to be mostly formed by the photolysis of hydrogen peroxide in snow [Chu and Anastasio, 2005]. In addition, photo-oxidation of snow-phase organic matter has been observed in laboratory and field experiments [Dolinova et al., 2006; Grannas et al., 2004; Klun et al., 2003]. Based on previous research, it is hypothesized that snow-phase organic species undergo photo-degradation during sunlit periods on the Greenland Ice Sheet.

[4] This paper presents measurements of the major carbon classes in the snow and firn at Summit, Greenland, including water-soluble organic carbon (WSOC), water-insoluble particulate organic carbon (WIOC), and particulate elemental carbon (EC). To provide an estimate of possible degradation of OC and EC in the snow, a series of surface samples collected in Summer 2006 are compared with past buried summer layers in a 3-meter snow pit.

2. Methods

[5] Organic and elemental carbon were measured in the snow and firn at the highest point of the Greenland Ice Sheet (Summit, Greenland, 72°N, 38°W, elevation 3200 m) during the summer of 2006. All snow sampling was performed near a small satellite camp site located in the clean air sector about 1 km from base camp. A 3-meter snow pit, located near 100 m from the satellite camp, was dug and sampled at 5–10 cm increments for WSOC, WIOC, EC, major ions, and deuterium/hydrogen ratio (δ2H). To avoid contamination, the snow pit was sampled within approximately 12 hours and each layer of snow was scraped back at 10 cm prior to obtaining a snow sample. Duplicates of WIOC, EC, ions, and δ2H were collected each 50 cm, while WSOC had duplicates at every layer. Surface snow samples (top 1–3 cm of snow) for WSOC, WIOC, and EC were collected from 30 May to 20 July 2006. WIOC and EC samples (10 L of snow) were collected daily at 17:00 (local
time), with duplicates collected every 3rd day. WSOC samples (250 mL of snow) were collected at varying intervals (every 6 hours from 30 May to 1 June, 24 hours from 2–11 June, and 4–6 hours from 12 June–20 July), with duplicates or triplicates collected at each sampling event. Great care was taken to detect and prevent contamination during sampling and analysis. The sample collection was conducted facing into the wind and successive samples were collected progressively further upward. All carbon samples were collected using a glass scraper and stored in glass sample jars with Teflon-lined caps, with all glassware undergoing intensive cleaning (rinsing in ultrapure water and baking to 550°C for 12 hours) prior to use in the field. Due to the high volume of carbon samples, sample jars were often recycled after in-field analysis by rinsing in ultrapure deionized water in-field and drying face-down in a clean hood. Laboratory tests found negligible carbon addition by the sample bottles. Snow pit ion samples were collected in pre-cleaned HDPE bottles and $\delta^2$H sample volumes (20 mL) were aliquotted from WIOC/EC samples.

[s] Collection of particulate WIOC and EC was performed by melting and weighing 10 L of snow, followed by vacuum-filtration through quartz fiber filters (Pall Corp: #2500 QAT-UP, 25 mm) and drying under a clean hood in Petri dishes lined with pre-fired aluminum foil. After drying, all filter samples were kept sealed at below-freezing temperatures until later analysis at the Georgia Institute of Technology. WIOC and EC were quantified using a Sunset Laboratory carbon analyzer following the NIOSH protocol of thermal evolution and combustion [Birch and Cary, 1996]. WSOC samples were melted and measured in the field using a Sievers 900 UV-oxidation-based carbon analyzer with an in-line quartz fiber filter as the operationally-defined split between WSOC and WIOC. Although the quartz fiber filters are rated at a nominal pore size of 700 nm, past studies report that smaller particles (<100 nm) are efficiently captured (95% or higher), likely due to the tortuous pathway through the filter media [Ducret and Cachier, 1992; Lavanchy et al., 1999]. Therefore, although the operational size cut of the quartz fiber filters is not precisely known, it is expected that WIOC and EC represent particles with diameters >100 nm and likely even smaller particles. Reliable detection of very low levels of WSOC (<40 $\mu$g kg$^{-1}$) was achieved by pre-acidifying samples using phosphoric acid (85 %, ACS grade, 40 $\mu$L per ~50 mL melted snow sample) to suppress the potentially interfering signal of inorganic carbon. Laboratory tests were performed prior to analysis to determine no additional background WSOC was added by the pre-acidification step. Major ions were measured at the University of New Hampshire using ion chromatography [e.g., Dibb et al., 2007] and $\delta^2$H was measured at the University of Washington by mass spectrometry with Cr reduction of H$_2$O.

3. Results and Discussion

[7] Concentrations of particulate and water-soluble carbonaceous species in the 3-meter snow pit are shown in Figure 1, with $\delta^2$H, calcium (Ca$^{2+}$), potassium (K$^+$), and sulfate (SO$_4^{2-}$) also provided for reference. Past summer layers are shaded in Figure 1 and were estimated by the seasonal temperature-dependent fluctuations in $\delta^2$H (Figure 1d) and using Ca$^{2+}$ (Figure 1e) as a known springtime marker [Dibb et al., 2007]. However, isolating the 2005 summer period was challenging due to a noisier $\delta^2$H signal. An additional calculation of a secondary summer marker, the ratio of Cl$^-$/Na$^+$, was performed (not shown) and, using all three data sets, the layer 50–70 cm was isolated as the most reasonable selection for Summer 2005.

[s] Particulate elemental (EC) and organic carbon (WIOC) were detectable at all levels of the 3-meter snow pit as shown in Figures 1a and 1b. Duplicates at 50, 100, 150, 200, and 250 cm had an average difference of 2.1 $\mu$g kg$^{-1}$ for WIOC and 0.20 $\mu$g kg$^{-1}$ for EC. Numerous field blanks (quartz fiber filters placed in the filtration apparatus, rinsed with 100 mL of ultrapure water, and allowed to dry alongside the sample filters) were found to have detectable WIOC (1.1 ± 0.5 $\mu$g cm$^{-2}$ filter area) but no measurable EC. All snow samples were thus only blank-corrected for WIOC. The variability in the WIOC blanks is small compared to the typical WIOC filter mass (e.g. snow pit 5–300 cm average = 6.7 $\mu$g cm$^{-2}$, ranging 3.2–12.9 $\mu$g cm$^{-2}$) although it adds greater uncertainty at low WIOC concentrations. From 5–300 cm in depth, approximate 4-year average WIOC and EC concentrations were 4.6 $\mu$g kg$^{-1}$ snow (range 1.7–10.2 $\mu$g kg$^{-1}$) and 0.4 $\mu$g kg$^{-1}$ (range 0.1–1.4 $\mu$g kg$^{-1}$), respectively. To our knowledge, no previous measurements of EC and WIOC on the Greenland Ice Sheet have been made using the same analytical procedure, which prevents direct comparison. A rough comparison with past optical measurements of black carbon (BC) in recent snow on the Greenland Ice Sheet puts our measured EC concentrations on the lower end of previously measured BC of 1–4 $\mu$g kg$^{-1}$ in 1988–1989 snow [Cachier and Pertuisot, 1994] and 1.4–2.7 $\mu$g kg$^{-1}$ in 1989–1990 snow [Chylek et al., 1995]. Comparison with previously measured EC by an alternative thermal method finds our levels well below reported values of 4.2–30.1 $\mu$g kg$^{-1}$ in 1994–1996 snow, although the authors mention that possible artifacts in their analysis may have induced the higher observed concentrations [Slater et al., 2002]. Very limited measurements are available for comparison with WIOC, including a solitary measurement of 78 $\mu$g kg$^{-1}$ for surface snow at Summit in 2001 [Grannas et al., 2004] and total particulate carbon (including BC) measured by coulometric analysis of 18–35 $\mu$g kg$^{-1}$ in 1988–1989 snow [Cachier and Pertuisot, 1994]. Our WIOC sample range (1.7–10.2 $\mu$g kg$^{-1}$) is significantly lower, although direct comparison is again difficult due to different analytical techniques.

[s] Water-soluble organic carbon in the 3-meter snow pit is shown in Figure 1c. Prior analysis of spatial variability in snow concentrations, taking 4 sets of 5 co-located samples, determined a relatively constant standard deviation of 24 $\mu$g kg$^{-1}$ for sample sets averaging 88–112 $\mu$g kg$^{-1}$. The variability in side-by-side measurements is expected to be lower for snow pit replicates in comparison to surface snow, given the higher likelihood of human error in collecting homogenous surface snow layers. Based upon this, two layers (180–190 cm, 230–240 cm) of the 3-meter pit were flagged for contamination concerns and removed from analysis due to duplicate differences exceeding 2$\sigma$ (48 $\mu$g kg$^{-1}$). Excluding these two layers, the 5–300 cm
Figure 1. 3-meter snow pit profiles of (a) elemental carbon, (b) water-insoluble organic carbon, (c) water-soluble organic carbon, (d) deuterium ratio, (e) calcium ion, (f) potassium ion, and (g) sulfate ion. Estimated summer periods are shaded.
average WSOC concentration was found to be 40.5 μg kg⁻¹ (ranging 18.3–84.9 μg kg⁻¹) and duplicates at approximately every layer had an average difference of 7.9 μg kg⁻¹. This WSOC observed range is on the lower end of 30–320 μg kg⁻¹ reported using a similar analytical process for a 2.3 m snow pit in 1984 near Dye 3, Greenland [Twickler et al., 1986], the difference in location and time likely playing a major role in the dissimilarity of measured WSOC. A much higher level of WSOC (~480 μg kg⁻¹) was quantified in a Summit surface sample in 2001, although a difference in analytical methods and the lack of multiple measurements limits comparison [Grannas et al., 2004].

[10] As seen in Figure 1, all carbonaceous species show a seasonal trend, with higher levels observed in the spring or summer. Sulfate and potassium (Figures 1f and 1g) also have spring/summer maxima, which may be due to a combination of meteorology and source types (biomass burning and fossil fuel combustion) related to the carbonaceous species. An observed prominent summer maximum in EC in 2004 is likely linked to emissions from major forest fires in Alaska and Canada [Stohl et al., 2006]. Potassium, a common indicator of biomass burning, is also seen to have maximum snow pit concentrations during this period.

[11] Averaging over the buried snow pit layers (5–300 cm, with layers 180 cm and 230 cm excluded), it appears WSOC makes up the vast majority (89%) of carbonaceous species in Greenland Snow, with substantially lower fractions in WIOC (10%) and EC (1%). The particulate-phase ratio of WIOC/EC (10:1) is similar to atmospheric particulate OC/EC ratios at background sites in the Northern Hemisphere [Carrico et al., 2003; Lee et al., 2001; Tanner et al., 2004]. However, adding the WSOC fraction leads to an extremely high ratio of total OC/EC (99:1) compared with typical atmospheric carbonaceous particulate matter. These results suggest either the oxidation of EC (which is usually considered inert) or, more likely, that gaseous organics are a source of OC in Greenland snow.

[12] In order to determine whether buried snow pit layers are representative of surface deposition, previous summer layers (50–70 cm, 140–160 cm, 190–210 cm, and 270–290 cm) were selected for approximate comparison with surface snow collected daily throughout the summer campaign. In ratio to Summer 2006 surface concentrations, 3 of the 4 years (2002, 2004, and 2005) have lower ratios-to-surface of organic species (WSOC and WIOC) relative to EC (Table 1). For example, while EC concentrations in 2004 more than double the 2006 surface snow, levels of WSOC and WIOC are substantially lower than their respective 2006 surface snow concentration. Assuming biomass-burning emissions in the summer of 2004 were the major source of the buried EC [Stohl et al., 2006], one would expect similarly high OC levels in the 2004 snow; thus, it appears there was a substantial loss in the particulate and water-soluble OC record. Years 2002 and 2005 also have lower WSOC and WIOC ratios-to-surface in comparison to EC, although the difference is smaller. Assuming EC is conserved after deposition and acts as a tracer for the original levels WSOC and WIOC, the estimated loss of WSOC and WIOC relative to EC for years 2002, 2004, and 2005 is 20–82% and 46–65%, respectively. Year 2003 stands out as an exception with all three species within similar ratio range. Given that 2003 also has the lowest EC concentrations (all other years are over a factor of 2 higher) and an extremely high OC/EC ratio (280:1), this observation may be explained by a different combination of sources impacting carbonaceous particulate matter reaching the Greenland Ice Sheet in 2003. For example, air masses reaching Summit may have contained carbonaceous particulate matter mainly from high OC/low EC sources, such as the gas-to-particle conversion of biogenic plant emissions.

[13] With higher frequency (every 4–6 hours) surface snow sampling for WSOC that took place from 12 June to 20 July 2006, it is possible to compare average daily maximum concentrations with buried summer layers. Given that concentration spikes in WSOC were associated with precipitation events (fog, snowfall) [G. S. W. Hagler et al., unpublished results, 2007], the daily maximum can be considered to be freshly deposited concentrations prior to degradation. Using the average daily maximum value (129.8 μg kg⁻¹), the estimated loss of WSOC (years 2002, 2004, 2005) relative to EC elevates to 32–84%. As precipitation events most often occurred in the late-evening/early-morning, our daily sampling for WIOC (and EC) at 17:00 may have missed capturing the “fresh” WIOC concentrations and thus the comparison of surface snow to buried snow layers possibly underestimates the actual loss of WIOC from the snowpack.

Table 1. Comparison of Surface Snow With Buried Summer Snow Layers

<table>
<thead>
<tr>
<th>Time Period</th>
<th>C_μg kg⁻¹</th>
<th>Ratio to Surface</th>
<th>C_μg kg⁻¹</th>
<th>Ratio to Surface</th>
<th>C_μg kg⁻¹</th>
<th>Ratio to Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface (5/30–7/20/06)</td>
<td>111.1</td>
<td>1.00</td>
<td>11.9</td>
<td>1.00</td>
<td>0.60</td>
<td>1.00</td>
</tr>
<tr>
<td>Summer 2005</td>
<td>56.9</td>
<td>0.51</td>
<td>3.1</td>
<td>0.26</td>
<td>0.39</td>
<td>0.64</td>
</tr>
<tr>
<td>Summer 2004</td>
<td>41.6</td>
<td>0.37</td>
<td>8.4</td>
<td>0.71</td>
<td>1.21</td>
<td>2.02</td>
</tr>
<tr>
<td>Summer 2003</td>
<td>40.3</td>
<td>0.36</td>
<td>3.5</td>
<td>0.29</td>
<td>0.16</td>
<td>0.26</td>
</tr>
<tr>
<td>Summer 2002</td>
<td>56.4</td>
<td>0.51</td>
<td>4.4</td>
<td>0.37</td>
<td>0.41</td>
<td>0.69</td>
</tr>
</tbody>
</table>

4. Conclusion

[14] Snow-phase particulate and water-soluble carbon compounds are of interest as unique tracers of natural and anthropogenic emissions trapped in the Greenland snow and ice. However, the post-depositional chemical stability of the organic fraction is in question. To better understand the nature and fate of carbon compounds on the Greenland Ice Sheet, particulate (WIOC, EC) and water-soluble (WSOC) carbonaceous species were measured at Summit, Greenland in the surface snow from 30 May to 20 July 2006 and in a 3-meter snow pit representing approximately four years of snowfall. Snow pit samples revealed very high OC
(WSOC + WIOC) relative to EC (99:1 ratio), suggesting that gas-phase organics are a major source of snow-phase OC.

Isolating the past summer layers (2002–2005) in the snow pit and comparing with surface snow samples collected throughout the summer of 2006, a loss in the organic carbon record from the snowpack is evident. Using EC as a tracer for the original magnitude of deposited organic species, it is seen that 3 of the 4 past summers had significant loss in WSOC (20–82%) and WIOC (46–65%) relative to EC. When averaging only the daily maximum WSOC surface concentrations, likely more representative of fresh deposition, the loss in the WSOC fraction for years 2002, 2004, and 2005 elevates to 32–84%. The one year (2003) with no substantial loss observed for the organic fraction also had extremely low EC concentrations and a very high OC/EC ratio. Thus, it appears low-EC/high-OC sources (such as biogenic emissions from plants) were a more significant source that year and that EC may not be an accurate tracer for OC loss from the snowpack in 2003. While significant depletion of organic carbon within the snowpack is apparent for 3 of the 4 buried summer layers, the fact that the loss is less than 100% suggests that inert organic compounds may be in existence and useful for ice core research. However, the degree of loss observed for WSOC and WIOC indicates that post-depositional processing needs to be considered in the interpretation of specific organic species entrapped in snow and ice on the Greenland Ice Sheet.

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