Temporal variations in black carbon recorded on Rishiri Island, northern Japan

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Equivalent black carbon (BC) in surface air was measured using an aethalometer on Rishiri Island, northern Japan (45°07' N, 141°12' E), to examine temporal variations in BC between May 15, 2012 and May 8, 2013. Based on the negative relationship observed between BC and 222Rn during the diurnal cycle, the dry deposition velocity of BC was estimated to be between 0.23 and 0.42 cm s⁻¹. High BC events, lasting for hours, occurred from late October to April, and were caused by the long-range transport of air masses that had moved over, or near, high BC emission areas in China. In contrast, air masses associated with low BC events originated near the Sea of Okhotsk and the Bering Sea. The observed slope of the linear regression line between BC and CO (ΔCBC/ΔCO) during high BC events was between 3.6 and 6.8 ng m⁻³/ppb, except for an event on April 23, 2013 when the value of ΔCBC/ΔCO decreased by 6.4 ng m⁻³/ppb (i.e., from 12.0 ± 0.6 ng m⁻³/ppb to 5.6 ± 0.5 ng m⁻³/ppb). It is considered that the dry and wet deposition of BC during transport most likely contributed to the large decrease in values of ΔCBC/ΔCO.

Keywords: black carbon, long-range transport, dry deposition, wet deposition, China

INTRODUCTION

Black carbon (BC) has an important role in the climate system (Bond et al., 2013). It is reported as being the second-largest atmospheric component contributing to current global warming due to the direct effect of its interception and absorption of sunlight (Ramanathan and Carmichael, 2008). In the lower troposphere, BC has the effect of decreasing cloud albedo by mixing with cloud condensation nuclei, and consequently causing variations in the hydrological cycle on regional and global scales (Forster et al., 2007; Ramanathan and Carmichael, 2008). The deposition of BC on snow or ice surfaces reduces surface albedo, resulting in the acceleration of melting over the Himalayan glaciers and Arctic ice (Forster et al., 2007; Ming et al., 2008). However, in addition to the impact on climate system, BC exposure adversely affects human health (Highwood and Kinnersley, 2006).

Although it is known that BC is emitted to the atmosphere by the incomplete combustion of fossil fuels and biomass burning, its impact on the climate system is not yet fully understood due to insufficient data concerning its sources and temporal-spatial variation (Kondo et al., 2011a; Wang et al., 2011). However, approximately one quarter of global BC emissions are estimated from China (Bond et al., 2004; Wang et al., 2011) where the combustion of coal and biofuel is the major source of BC (Wang et al., 2011), and as such the country is considered to be the largest emitter of BC in the world. According to Zhang et al. (2009), BC emissions in China were estimated at 1.8 Tg in 2006.

Japan is located in the atmospheric outflow region of Eurasia. Excluding megacities, studies focusing on the long-range transport of BC from China have been conducted extensively in southern (Koga et al., 2008; Kondo et al., 2011a; Verma et al., 2011) and central areas of Japan (Kaneyasu et al., 2007; Liu et al., 2013). However, only a few studies have reported variations in BC in the remote northern area. Using elemental carbon (EC) measurements on Rishiri and Sado Islands from March 1 to May 31, 2001, Matsumoto et al. (2003) reported that transport patterns of polluted air masses from the East Asian continent to the northern region of the northwestern Pacific often differ from those of the southern regions. It is therefore considered important to examine how polluted air masses migrate throughout an entire year (thereby encompassing all the seasons), and how the air quality changes both temporally and spatially.

Since May 2012, we have measured equivalent BC (hereafter BC, Petzold et al., 2013) using an aethalometer (AE31, Magee Scientific, California, USA) on Rishiri Island, which is located on the northern tip of Hokkaido, Japan, to examine the long-range transport of BC emitted in China. During this study period, a cavity ring-down spectroscopy (CRDS) analyzer (G2401, Picarro), which

enables measurements of atmospheric CO, CH₄, and CO₂, was installed on December 12, 2012. This paper reports the temporal variations in BC and discusses the processes affecting mass concentrations of BC in northern Japan.

**OBSERVATIONS**

**Site description**

Recording of measurements of BC began on May 15, 2012 at Rishiri Observatory (RIO; 45°07' N, 141°12' E, 40 m above sea level (asl)) on Rishiri Island (182 km²) at the northern end of Hokkaido (77,984 km²), Japan (Fig. 1). The RIO is located on a foothill of Mt. Rishiri (1,721 m), which is a Quaternary stratovolcano facing the southwestern coast of Rishiri Island (approximately 800 m from the shore). Rebun Island (80 km²) is located 10 km northwest of Rishiri Island (29 km from north to south and 8 km from east to west). Rishiri Island has 5500 inhabitants, and of these 750 live near a coastal area located 2 km from the RIO. Rebun Island has 2900 inhabitants. There are no major industries on either island. The vegetation consists of deciduous and coniferous trees as well as ground vegetation (evergreen Sasa bamboo) that grows around the RIO.

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Fig. 1. Location of the Rishiri Island Observatory (RIO) on Rishiri Island, where BC, ²²²Rn, and CO concentrations were measured. The color indicates the anthropogenic emission of BC for the year 2006, which was originally reported with a spatial resolution of 0.5° by 0.5° by Zhang et al. (2009).
**BC measurements**

The AE31 aethalometer uses seven wavelengths (370, 470, 520, 590, 660, 880, and 950 nm) to measure light attenuation. BC is the predominant absorber of light in the 880 nm wavelength, and as such this is considered to be the standard channel used for BC measurements (Aethalometer book, 2005.07.03.pdf, available at the Magee Scientific website). BC concentrations are estimated by measuring the amount of light attenuated when it is transmitted through a sample collected on a quartz fiber filter, and where the amount of light attenuated is proportional to the amount of the BC mass deposited on the filter (Hansen et al., 1982, 1984). From the measurement of light attenuation at a wavelength \( \lambda \), the mass concentration of BC is calculated for a specific attenuation cross section \( \sigma(\lambda) \) (\( m^2 \cdot g^{-1} \)). The light attenuation \( (\text{ATN}) \) of the aerosol deposited on the filter is measured by detecting the intensity of the light transmitted through a spot on the filter \((I)\) relative to an unexposed part of the filter \((I_0)\):

\[
\text{ATN} = -100 \times \log_e \left( \frac{I}{I_0} \right)
\]

The change in light attenuation during a time interval set by the operator is used to calculate the mass concentration of BC \((C_{BC})\):

\[
C_{BC}(\lambda) = \frac{d\text{ATN}}{dt} \times \frac{A}{V \times \sigma(\lambda)}
\]

where \( A \) is the spot size (0.5 cm\(^2\)) and \( V \) is the volume of air passed through the filter. In this study, we assumed 16.6 \( m^2 \cdot g^{-1} \) as the value of \( \sigma(880) \) because this amount was recommended by the manufacturer. The following were then employed: the AE31 was operated at a flow rate of 4 L min\(^{-1}\), the time interval was set to 5 min, the air intake was installed close to the inlet to measure atmospheric trace gases at a height of 5 m above ground, and the BC was measured with no aerosol size cut-off.

Aethalometer BC measurements are known to contain a filter loading artifact (Weingartner et al., 2003; Collaud Coen et al., 2010) whereby an amplified underestimation of the measured aethalometer signal (black carbon mass concentration) occurs as the filter load increases. In this study, we adopted the approach presented by Weingartner et al. (2003) for removal of the loading artifact (see Supplementary Materials).

**\(^{222}\text{Rn} \text{ and CO measurements}\)**

\(^{222}\text{Rn}\) is a radioactive noble gas emitted ubiquitously by soils and removed from the atmosphere by radioactive decay (Nazaroff, 1992). Atmospheric \(^{222}\text{Rn}\) concentrations vary widely depending on contact with the terrestrials surface, and as such the use of \(^{222}\text{Rn}\) can be used as a tracer for air mass transport and vertical mixing (Williams et al., 2011 and references cited therein).

Wada et al. (2010) developed a system for measuring atmospheric \(^{222}\text{Rn}\) based on the electrostatic method. The method detects alpha particles from \(^{218}\text{Po}\) and \(^{214}\text{Po}\), which are progeny of \(^{222}\text{Rn}\), in a hemispheric air sample chamber. In this respect, from December 2009 we used a system similar to that of Wada et al. (2010) to continuously monitor atmospheric \(^{222}\text{Rn}\) (Zhu et al., 2012).

The air used as for sampling was continuously pumped at a rate of 10 L min\(^{-1}\) through a 6.35 mm Teflon tube (which was part of the Pyrex glass manifold connected to the inlet) to measure trace gases. An aliquot of sample air (2 L min\(^{-1}\)) obtained from the manifold was then passed through an electric dehumidifier (Model T200, JANS Co., Ltd., Fuchu, Japan) which employs the Peltier effect and Nafion tubing (MD-110-72P, Perma Pure LLC, New Jersey, USA). To supply the Nafion tube dry air at 2 L min\(^{-1}\), a heatless dryer (CKD HD-0.5, CKD Co., Ltd., Komaki, Japan) was used. After the removal of aerosol particles (>0.2 \( \mu \)m) and water vapor, the air sample was introduced into the 32 L hemispheric air sample chamber. Energy measuring 6 to 10 MeV was integrated digitally in 1024 bins at 10-min intervals. The detection limit for \(^{222}\text{Rn}\) in a 60-min measurement was estimated to be between 0.16 and 0.20 Bq m\(^{-3}\) (Wada et al., 2010).

On December 12, 2012, the CRDS analyzer (G2401, Picarro, Inc., California, USA) was installed to enable measurements of atmospheric CO, \(\text{CH}_4\), and \(\text{CO}_2\). A diaphragm pump was used to draw air through a 6.35 mm Teflon tube at a rate of 10 L min\(^{-1}\) from the glass manifold, which was largely vented to the room (8 L min\(^{-1}\)). Following Nara et al. (2012), water vapor was removed using an electric dehumidifier (T200, JANS Co., Ltd.) and a dehydration system consisting of two free-piston Stirling coolers (SC-UE15, JANS Co., Ltd.). Air (2 L min\(^{-1}\)) passed through the electric dehumidifier at a slightly higher pressure (20 kPa) than that of ambient air. After passing through the electric dehumidifier, the air was introduced into the water traps of the Stirling coolers (2 L min\(^{-1}\) each), and the remaining air was vented off from the drain of the electric dehumidifier (1.6 L min\(^{-1}\)). The Stirling coolers were operated alternately at 6-hr intervals. During the first four hours, one Stirling water trap was gradually lowered from 40 to –50 °C. Over the following two hours, the temperature of the second water trap was maintained at –50 °C and the other at 40 °C. The CRDS analyzer was calibrated once a day by successively introducing three calibrated working gases (56, 209, and 412 ppb for CO) into the CRDS analyzer for 10 minutes each.
The concentrations of CO were determined with gravimetric standard gases that were referenced to the “primary” scale at the National Institute for Environmental Studies, Japan (Machida et al., 2009, 2011). Based on replicated measurements of a sample gas in the cylinder, the precision of the analysis (±1σ) was estimated to be 1.1 ppb for CO.

**Meteorological data**

Meteorological data recorded between May 2012 and April 2013 in Kutsukata on Rishiri Island from May 2012 to April 2013 in Kutsukata, and by the northward transport of air that had passed over Hokkaido (which has 5.6 million inhabitants). Yoshikawa-Inoue and Zhu (2013) used a 222Rn exhalation rate of 3.0 mBq m$^{-2}$ s$^{-1}$, which is based on the SiO$_2$ content of the geological constituents on Rishiri Island. The BC mass flux to the surface is conventionally expressed by the product of the BC mass concentration and dry deposition velocity $V_{BC}$. Therefore, $V_{BC}$ is calculated as:

$$V_{BC} = \frac{j_{BC}}{C_{BC}}$$

**Results and Discussion**

Figure 2 illustrates hourly BC data recorded at the RIO from May 15, 2012 to May 8, 2013, where it can be seen that the BC mass concentration increased intermittently to above 1000 ng m$^{-3}$. High BC events occurred either in relation to local sources or to the long-range transport of air mass with a high BC mass concentration. High BC events that decreased rapidly were considered likely to be related to sources in Japan (Tanimoto et al., 2008), whereas those lasting hours were attributed to long-range transport. In the top panel of Fig. 2, the solid circles indicate high BC events in which the BC mass concentration decreased by at least 67% within two hours after the peak. It is considered that these high BC mass concentrations were caused both by local sources, such as vehicles idling near the RIO or driving along the road located to the west of the RIO, and by the northward transport of air that had passed over Hokkaido (which has 5.6 million inhabitants). Examples of these “local” events occurred on June 30 and July 3, 2012. The remaining events are those for which the BC mass concentration remained high for longer than four hours.

**Diurnal variations in BC**

We examined the diurnal variation of BC mass concentration, 222Rn concentration, and 222Rn exhalation rate from the soil surface on Rishiri Island, and Eq. (3) (Zhu et al., 2012):

$$j_{BC} = j_{Ra} \times \frac{\Delta C_{BC}}{\Delta C_{Ra}} \times \left(1 - \frac{1}{\lambda} \frac{\Delta C_{Ra}}{\Delta t}ight) = j_{Ra} \times \frac{\Delta C_{BC}}{\Delta C_{Ra}}$$

where subscript BC is black carbon, subscript Rn is 222Rn, $j$ is the constant flux, $\Delta C$ and $\Delta t$ indicate changes in concentration (relative to maritime air) and time, respectively, and $\lambda$ is the radioactive decay constant of 222Rn. The BC mass flux is calculated from the 222Rn exhalation rate and the change in BC concentration relative to a unit change in the 222Rn concentration, with a correction for radioactive decay (the term within parentheses in Eq. (3)). It is of note that in this work, the correction term for radioactive decay was omitted because there was a decrease of less than 2% in 222Rn activity during the few hours required for an air parcel to move across Rishiri Island. Yoshikawa-Inoue and Zhu (2013) used a 222Rn exhalation rate of 3.0 mBq m$^{-2}$ s$^{-1}$, which is based on the SiO$_2$ content of the geological constituents on Rishiri Island.
concentrations to elucidate the effects of the sources and/or sinks on Rishiri Island (Fig. 3). In this study, winter was defined as December, January, and February; each successive season then comprised three months. It was discovered that the median of BC mass concentrations at each local time (LT) exhibited a distinct diurnal variation during the summer and autumn (Fig. 3), where low BC mass concentrations occurred during the nighttime and high concentrations occurred during the daytime. It is known that in urban areas, high BC mass concentrations often occur in the morning and evening, and this is attributed to vehicular traffic combined with meteorological conditions (Wang et al., 2011; Kondo et al., 2012; Bapna et al., 2013; Tiwari et al., 2013). For example, in New York City the weekday diurnal variation exhibits a morning peak followed by an afternoon minimum; a secondary peak occurs in the late evening. However, although it has been shown that there are no morning peaks in BC diurnal variations on Sundays (Rattigan et al., 2013), there were no marked differences between weekdays and Sundays on Rishiri Island (data not shown). The results therefore indicate that human activity on Rishiri Island minimally affects variations in BC, except for in relation to episodes impacted by emissions from nearby traffic.

The following phenomena were noted during summer and autumn. BC mass concentrations negatively correlated with atmospheric $^{222}$Rn in terms of the diurnal cycle (Fig. 4), showing a high concentration during the night and a low concentration during the day. $^{222}$Rn emitted from the soil surface was mixed with a relatively small volume of air from the shallower nocturnal boundary layer.

Fig. 2. Hourly mean of BC, $^{222}$Rn, and CO concentrations on Rishiri Island from May 2012 to May 2013. In the upper panel, the solid circles represent data greater than 1000 ng m$^{-3}$ that decreased by at least 67% within two hours.

Fig. 3. Diurnal variation in the median value of BC concentrations observed on Rishiri Island. Data are represented as: plus symbols with a dotted line (December–February), triangles with a dotted line (March–May), solid circles with a solid line (June–August), and open circles with a solid line (September–November). The smoothed curve was calculated using KaleidaGraph V4.0.

Fig. 4. Relationship between $^{222}$Rn and BC concentrations during the diurnal variations observed on Rishiri Island. Data are represented as: plus symbols (December–February), triangles (March–May), solid circles with a solid line (June–August) and open circles with a dashed line (September–November). The BC mass concentration ($C_{BC}$) was negatively related to the $^{222}$Rn concentration ($C_{Rn}$): $C_{BC} = (278 \pm 17) - (1 17 \pm 15)C_{Rn}$ ($r = -0.853, p < 0.001$) in summer, and $C_{BC} = (366 \pm 31) - (146 \pm 17)C_{Rn}$ ($r = -0.876, p < 0.001$) in autumn.
compared with that from the deeper boundary layer during the day. In addition, wind speeds were also found to be lower than in the other two seasons (Table 1), delivering a condition conducive for diurnal variation. Furthermore, the presence of Mt. Rishiri leads to a diurnal variation in $^{222}\text{Rn}$ in relation to upslope winds in the daytime and downslope winds in the nighttime (Zhu et al., 2012). Therefore, the atmospheric sinking process on Rishiri Island is observed by low BC mass concentrations during the night in relation to dry deposition in the nocturnal boundary layer.

To estimate the dry deposition velocity, we applied Eq. (3) to hourly BC and $^{222}\text{Rn}$ data (Fig. 4), thereby producing a BC mass flux of 0.35 ng m$^{-2}$ s$^{-1}$ in summer and 0.44 ng m$^{-2}$ s$^{-1}$ in autumn. By using the median value of the BC mass concentration in the summer (150 ng m$^{-3}$) and autumn (105 ng m$^{-3}$), the dry deposition velocity was calculated as 0.23 cm s$^{-1}$ in summer and 0.42 cm s$^{-1}$ in autumn (Eq. (4)). These values agree well with those of the empirical resistance method (i.e., between 0.15 and 0.6 cm s$^{-1}$) (Liu et al., 2011). Liu et al. (2011) reported that a lack of direct measurements for the BC deposition velocity makes it difficult to evaluate the importance of dry deposition on the BC budget. In this work, we applied atmospheric $^{222}\text{Rn}$ to evaluate the dry deposition velocity of BC, which assists in clarifying the temporal and spatial variations therein.

**Synoptic scale variation**

High BC mass concentrations remaining for up to several hours are indicative of an air mass transported from source regions outside of Rishiri Island. To characterize the long-range transport of an air mass with a high or low BC mass concentration, we defined high and low BC events on the basis of the 95th percentile (508 ng m$^{-3}$) and the 5th percentile (51 ng m$^{-3}$) values, respectively, of daily mean data over a one-year period. Based on the diurnal variation in BC mass concentrations (Subsection “Diurnal variations in BC”), we decided to use a daytime sampling window of between 09:00 and 17:00 LT in the summer and autumn to obtain the daily mean BC mass concentration, and to increase the sample size we used data from all hours of the day for the remaining seasons. The beginning (ending) of a high BC event in LT is defined as when increasing (decreasing) BC mass concentrations cross the 67th percentile value for each season before (after) the peak (Table 2). Low BC events were defined as those with a daily mean BC value smaller than the 5th percentile of all data. High BC events, except for episodes impacted by emissions from nearby traffic, were observed from late October 2012 to April 2013. Low BC events occurred in the months of April to July, September, and November–January. Furthermore, we used back trajectories to examine the origins of air masses with high and low BC mass concentrations. Using the HYSPLIT model (Draxler and Rolph, 2010), we thus obtained 120-hour backward trajectories starting at 1500 m above ground level.

The trajectory analysis shows that all air masses with high BC mass concentrations passed between 40°N and 50°N along the eastern edge of Eurasia (Fig. 5). Trajectories could be divided into two groups: the transport of an air mass from latitudes equal to (or lower than) that of Rishiri Island, and transport from a direction west-northwest towards Rishiri Island. It is known that air masses moving over northern China are vulnerable to the relatively high BC emissions of the region (Fig. 1, Zhang et al., 2009).

### Table 2. Seasonal variations in BC mass concentration (ng m$^{-3}$) on Rishiri Island

<table>
<thead>
<tr>
<th>Season</th>
<th>LT</th>
<th>25th percentile</th>
<th>Median</th>
<th>67th percentile</th>
<th>75th percentile</th>
<th>n*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>0:00–24:00</td>
<td>92</td>
<td>218</td>
<td>314</td>
<td>364</td>
<td>2037</td>
</tr>
<tr>
<td></td>
<td>9:00–17:00</td>
<td>95</td>
<td>219</td>
<td>318</td>
<td>378</td>
<td>762</td>
</tr>
<tr>
<td>Summer</td>
<td>0:00–24:00</td>
<td>75</td>
<td>150</td>
<td>213</td>
<td>243</td>
<td>2063</td>
</tr>
<tr>
<td></td>
<td>9:00–17:00</td>
<td>105</td>
<td>183</td>
<td>238</td>
<td>269</td>
<td>769</td>
</tr>
<tr>
<td>Autumn</td>
<td>0:00–24:00</td>
<td>48</td>
<td>105</td>
<td>177</td>
<td>220</td>
<td>2180</td>
</tr>
<tr>
<td></td>
<td>9:00–17:00</td>
<td>64</td>
<td>134</td>
<td>198</td>
<td>235</td>
<td>815</td>
</tr>
<tr>
<td>Winter</td>
<td>0:00–24:00</td>
<td>84</td>
<td>169</td>
<td>246</td>
<td>292</td>
<td>2160</td>
</tr>
<tr>
<td></td>
<td>9:00–17:00</td>
<td>85</td>
<td>170</td>
<td>252</td>
<td>312</td>
<td>810</td>
</tr>
<tr>
<td>Annual</td>
<td>0:00–24:00</td>
<td>70</td>
<td>155</td>
<td>233</td>
<td>278</td>
<td>8440</td>
</tr>
<tr>
<td></td>
<td>(85)**</td>
<td>(178)**</td>
<td>(258)**</td>
<td>(296)**</td>
<td>(5781)**</td>
<td></td>
</tr>
</tbody>
</table>

*Number of data points.  
**Values in parentheses: daytime data are used in summer and autumn.
Air masses with low BC concentrations clearly originated from the Sea of Okhotsk and the Bering Sea (Fig. 5), which are the fetch regions of low $^{222}$Rn concentrations (Zhu et al., 2012). Low BC events were usually accompanied by low $^{222}$Rn concentrations (<1 Bq m$^{-3}$), which suggests removal of BC to the ocean’s surface after leaving the continental source region.

Seasonal variation
The median values of BC concentrations on Rishiri Island exhibited a maximum in spring and a minimum in autumn (Table 2). However, in summer and autumn the diurnal variation was superimposed on the seasonal variation, making the median BC during the daytime (09:00–17:00 LT) high compared with the median using all hours of the day. As discussed previously, high BC events sometimes occurred in winter, but the median BC was relatively low during this period. It is evident that due to the various BC measurement techniques employed, BC values from Rishiri Island need to be carefully compared with values from other sites. However, a comparison of the patterns obtained within the BC season variations is considered feasible.

Kondo et al. (2011a) measured BC mass concentrations using a filter-based absorption photometer (Miyazaki et al., 2008; Kondo et al., 2009) at Cape Hedo (26°52′ N, 128°15′ E, 60 m asl) on Okinawa Island in southern Japan, and reported a maximum median BC in spring (360 ng m$^{-3}$ in 2008, 290 ng m$^{-3}$ in 2009) and a constant median BC during the remaining seasons (210–230 ng m$^{-3}$ in 2008/09). At a remote mountain site in central Japan (Happo, 36°41′ N, 137°48′ E, 1830 m asl), Liu et al. (2013) also reported a maximum BC mass concentration in the spring; the BC mass concentration that originated in Northern China showed minimum values from late autumn to early spring in relation to the suppressed upward transport over China.

Relationship between BC and CO during high BC events
To further investigate the source/sink of BC outside...
Rishiri Island, we analyzed the relationship between BC and CO during high BC events between December 12, 2012 and May 8, 2013. As an example of a high BC event, Fig. 6 shows variations in the hourly BC, CO, 222Rn, and meteorological data from December 14 to 17, 2012. Starting with the low BC mass concentration on the night of December 14, 2012, which is considered to be close to that of the marine background level, the BC mass concentration then increased to 1900 ng m⁻³ along with the CO concentration (Table 3). The correlation coefficient between BC and CO was 0.97, indicating that the two concentrations were related to a similar source. In addition, the BC mass concentration was higher than 1000 ng m⁻³ when the wind speed was lower than 2 m s⁻¹ (Fig. 6 and Supplementary Materials), which is indicative of a stationary air mass with pollutants over Rishiri Island. The back trajectory beginning at 12:00 LT on December 15, 2012, indicates that the air mass originated from the high BC emission region in China. During this event, variations in BC and CO produced a ratio (∆BC/∆CO) of 3.7 ± 0.1 ng m⁻³/ppb (Table 3), where ∆BC represents the concentration increase from a minimum BC value among six successive data values prior to, or after, the high BC event.

In the case of high BC events from December 31, 2012 to March 17, 2013, the correlation coefficient between BC and CO was generally larger than 0.9, and ∆BC/∆CO was within the range of 3.6 to 6.8 ng m⁻³/ppb. High BC events occurred even when the wind speed was high (Supplementary Materials Table S1). It is known that a few factors affect ∆BC/∆CO: the ratio of ∆BC/∆CO emitted from the source, wet deposition, dry deposition, chemical reactions, and dilution (e.g., Kondo et al., 2011a). Because of the relatively long lifetime of two months for the reaction of CO with the OH radical (Jacob, 1999), ∆BC/∆CO was not significantly affected by a chemical reaction. However, a relatively minor dilution effect relating to ∆BC/∆CO has been reported during the air mass transport from China to central Japan (Liu et al., 2013). Wang et al. (2011) estimated that the annual mean BC/CO emission ratios in the three largest cities in China (Beijing, Shanghai, and Guangzhou) are in the range of 8.3 to 10.2 ng m⁻³/ppb, whereas the observed ∆BC/∆CO in these cities varied widely from 3.3 to 11.5 ng m⁻³/ppb. Baumgardner et al. (2002) reported that ∆BC/∆CO ratios at five urban sites in Germany were approximately twice the values found at two sites in Mexico City, and this is likely to be caused by the ratio of diesel to gasoline usage and the combustion efficiency. In Germany, diesel consumption was almost 30% of the total fuel consumption, while in Mexico City it was only 12%.

Kondo et al. (2011a, b) discussed the effect of precipitation on ∆BC/∆CO during air mass transport. Pan et al. (2011) reported a large effect on ∆BC/∆CO from rain washout and/or environmental relative humidity during long-range transport. During high BC events occurring between December and March, the weather at Wakkanai (45°25′N, 141°41′E, 2.8 m asl) was often reported to be snow/rain and cloudy, which suggests that wet deposition produced the fairly low ∆BC/∆CO values on Rishiri Island (Table 3).

We observed a high BC event from April 22 to 24, 2013 (Fig. 7) in which the ∆BC/∆CO decreased by 6.4 ng m⁻³/ppb (i.e., from 12.0 ± 0.6 ng m⁻³/ppb to 5.6 ± 0.5 ng m⁻³/ppb at 19:00 LT on April 23) (Fig. 8). The value of 5.6 ± 0.5 ng m⁻³/ppb was similar to the values of ∆BC/∆CO observed from December 2012 to March 2013.

The back trajectory beginning at 06:00 LT on April 23, 2013, indicates that the air mass migrated from the north (62°N, 126°E) to east-southeast (49°N, 128°E) (Fig.

Table 3: High BC events recorded at the RIO from December 14, 2012 to April 24, 2013

<table>
<thead>
<tr>
<th>Event</th>
<th>Year</th>
<th>Date</th>
<th>∆BC/∆CO (ng m⁻³/ppb)</th>
<th>r</th>
<th>n</th>
<th>Weather at Wakkanai (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2012</td>
<td>December 14–16</td>
<td>3.7 ± 0.1</td>
<td>0.976</td>
<td>43</td>
<td>Snow</td>
</tr>
<tr>
<td>2</td>
<td>2012</td>
<td>December 31–January 3</td>
<td>6.4 ± 0.2</td>
<td>0.958</td>
<td>71</td>
<td>Rain</td>
</tr>
<tr>
<td>3</td>
<td>2013</td>
<td>January 5–7</td>
<td>5.2 ± 0.5</td>
<td>0.896</td>
<td>31</td>
<td>Snow</td>
</tr>
<tr>
<td>4</td>
<td>2013</td>
<td>January 12–13</td>
<td>3.6 ± 0.3</td>
<td>0.915</td>
<td>23</td>
<td>Rain</td>
</tr>
<tr>
<td>5</td>
<td>2013</td>
<td>January 31–February 2</td>
<td>4.1 ± 0.2</td>
<td>0.963</td>
<td>48</td>
<td>Cloudy</td>
</tr>
<tr>
<td>6</td>
<td>2013</td>
<td>February 15–16</td>
<td>6.8 ± 0.3</td>
<td>0.954</td>
<td>42</td>
<td>Rain</td>
</tr>
<tr>
<td>7</td>
<td>2013</td>
<td>March 5–7</td>
<td>5.0 ± 0.3</td>
<td>0.932</td>
<td>51</td>
<td>Rain</td>
</tr>
<tr>
<td>8</td>
<td>2013</td>
<td>March 11–14</td>
<td>4.0 ± 0.2</td>
<td>0.923</td>
<td>52</td>
<td>Rain</td>
</tr>
<tr>
<td>9</td>
<td>2013</td>
<td>April 22–23</td>
<td>12.0 ± 0.6</td>
<td>0.961</td>
<td>40</td>
<td>Snow</td>
</tr>
<tr>
<td>10</td>
<td>2013</td>
<td>April 23–25</td>
<td>5.6 ± 0.5</td>
<td>0.919</td>
<td>30</td>
<td>Snow</td>
</tr>
</tbody>
</table>

*p < 0.001.

Weather reported every 3 hours except at 00:00 LT.

Intermittent snowfall or rainfall during the 3-h interval.
Fig. 8. Relationship between BC and CO observed on Rishiri Island from 00:00 LT April 22 to 18:00 LT April 23 (solid line) and from 19:00 LT April 23 to 23:00 LT April 24, 2013 (dotted line).

Fig. 7. Same as Fig. 6 except the period is from April 22 to April 24, 2013. The arrows mark 19:00 LT on April 23, 2013. The slope of the linear regression between BC and CO was 12.0 ± 0.6 ng m$^{-3}$/ppb ($r = 0.961$) prior to 19:00 LT on April 23 and 5.6 ± 0.5 ng m$^{-3}$/ppb ($r = 0.919$) after 19:00 LT on April 23.

\[ \Delta C_{BC}/\Delta C_{CO} \] values affected by large forest fires in Siberia were caused by a minimal wet removal processes (Kaneyasu et al., 2007), and it is therefore considered likely that the sources in northeastern China/Siberia could lead to high \( \Delta C_{BC}/\Delta C_{CO} \) values.

The trajectory analysis beginning at 06:00 LT on April 23, 2013, shows that the air mass took seven hours to reach Rishiri Island from the eastern coast of Eurasia, whereas the air mass at 03:00 LT on April 24 took 36 hours (Fig. 5). If we assume the BC flux was the same as that on Rishiri Island (0.35 to 0.44 ng m$^{-2}$ s$^{-1}$) and that the air column was 1500 m, then BC decreased by 24 to 31 ng m$^{-3}$ over the Sea of Japan. This simple estimation suggests that dry deposition over the sea contributes to changes in \( \Delta C_{BC}/\Delta C_{CO} \) before, and after, 19:00 LT on April 23, 2013.

On April 22, 2013, the weather was reported as being fair. Clouds and rain occurred late on April 23, and rain occurred on the morning of April 24. These weather conditions support the rapid decrease in \( \Delta C_{BC}/\Delta C_{CO} \) from wet deposition. The significant decrease in \( \Delta C_{BC}/\Delta C_{CO} \) is considered likely to be related to the wet deposition of BC during long-range transport (Kondo et al., 2011a, b; Cristofanelli et al., 2013). To better understand the processes affecting the BC mass concentration in northern Japan, it is therefore considered necessary to accumulate further BC data along with data of co-emitted substances, and then to make a comparison of such values with those from source regions.

**SUMMARY**

To examine temporal variations in black carbon (BC) in northern Japan, BC in the surface air was measured using an aethalometer on Rishiri Island from May 15, 2012 to May 8, 2013. High BC events that exhibited rapid
decreases after reaching peak concentrations were determined to be caused by local sources (vehicles) on Rishiri Island and the northward transport of air masses passing over the source area on Hokkaido. In addition, it was determined that events lasting hours were caused by the long-range transport of BC-polluted air masses from China. Excluding data from high BC events, BC mass concentrations exhibited diurnal variations in the summer (June to August) and autumn (September to November). The median value of hourly BC mass concentrations was high in the daytime and low in the nighttime, which was opposite to the trend of atmospheric $^{222}\text{Rn}$. During diurnal variations in the summer and autumn, the high concentration of $^{222}\text{Rn}$ emitted from the soil surface was caused by mixing with air in the shallow nocturnal boundary layer. However, low BC mass concentrations were caused by dry deposition. Based on the negative relationship between the BC mass concentration, $^{222}\text{Rn}$ concentration and $^{222}\text{Rn}$ exhalation rate from the soil surface on Rishiri Island (3.0 mBq m$^{-2}$ s$^{-1}$), the deposition velocity of BC was estimated to be between 0.23 and 0.42 cm s$^{-1}$.

We selected data from high and low BC events to examine the long-range transport of air masses from China. All of the air masses with high BC mass concentrations passed between 40°N and 50°N of coastal Eurasia. The trajectories were divided into two groups: the transport of air masses from latitudes equal to (or lower than) the latitude of Rishiri Island, and the transport from west-northwest towards Rishiri Island. The former group contains the area in China that delivers large BC emissions, and air masses moving over northern China are considered to be vulnerable to the relatively high BC emissions of the region. Low BC events were associated with low $^{222}\text{Rn}$ concentrations, and air masses with low BC were determined to have originated from the Sea of Okhotsk and the Bering Sea.

From December to March, the $\Delta C_{\text{BC}}/\Delta C_{\text{CO}}$ of high BC events was between 3.6 and 6.8 ng m$^{-2}$ ppb (Table 3). In addition, the weather at Wakkanai was often reported as snow/rain and cloud, which suggests that wet deposition influenced the BC values. From April 22 to 24, 2013, the $\Delta C_{\text{BC}}/\Delta C_{\text{CO}}$ decreased by 6.4 ng m$^{-2}$ ppb, and this low value was similar to the trend observed from December 2012 to March 2013. Anthropogenic sources in northeastern China emit BC and CO with relatively high BC/CO ratios (Zhang et al., 2009), and this is considered likely to be caused by the fuel types used and their combustion efficiency. The lack of wet deposition of BC, and the relatively small amounts of dry deposition are considered likely to contribute to the high $\Delta C_{\text{BC}}/\Delta C_{\text{CO}}$ values. Because data indicating high $\Delta C_{\text{BC}}/\Delta C_{\text{CO}}$ values are insufficient for fully analyzing BC variations, it will therefore be necessary to collect BC data during high BC events at the RIO, along with data related to co-emitted substances to fully understand the factors controlling BC.

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**SUPPLEMENTARY MATERIALS**

URL (http://www.terrapub.co.jp/journals/GJ/archives/data/49/MS356.pdf)
Figure S1
Table S1