Fluorescence characteristics, absorption properties, and radiative effects of water-soluble organic carbon in seasonal snow across northeastern China

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Abstract. Although water-soluble organic carbon (WSOC) in the cryosphere can significantly influence the global carbon cycle and radiation budget, WSOC in the snowpack has received little scientific attention to date. This study reports the fluorescence characteristics, absorption properties, and radiative effects of WSOC based on 34 snow samples collected from sites in northeastern China. Sampling sites were divided into five groups, comprising southeastern Inner Mongolia (SEIM), northeastern Inner Mongolia (NEIM), the south of northeastern China (SNC), the north of northeastern China (NNC), and the Changbai Mountain area (CBM). Together, these groups represent a significant degree of regional WSOC variability, with concentrations ranging from 0.5 ± 0.2 to 5.7 ± 3.7 μg g^{-1} (mean = 3.6 ± 3.2 μg g^{-1}). We then identified the three principal fluorescent components of WSOC as (1) a high-oxygen humic-like substance (HULIS-1) of terrestrial origin, (2) a low-oxygen humic-like substance (HULIS-2) of mixed origin, (3) and a protein-like substance (PRLIS) derived from autochthonous microbial activity. In SEIM, a region dominated by desert and exposed soils, the WSOC content exhibits the highest humification index (HIX) but the lowest fluorescence (FI) and biological (BIX) indices; the fluorescence signal is mainly attributed to HULIS-1, and thus implicates soil as the primary source. By contrast, the HIX (FI and BIX) value was the lowest (highest) and PRLIS most intense in the remote grasslands and forested areas of NEIM, suggesting a primarily biological source. For SNC and NNC, both of which are

characterized by intensive agriculture and industrial activity, the fluorescence signal is dominated by HULIS-2 and the HIX, FI, and BIX values are all moderate, indicating mixed origins for WSOC (anthropogenic activity, microbial activity, and soil). We also observed that, throughout northeastern China, the light absorption of WSOC is dominated by HULIS-1, followed by HULIS-2 and PRLIS. The contribution of WSOC to albedo reduction (average concentration 3.6 μg g^{-1}) in the ultraviolet–visible (UV–vis) band is approximately half that of black carbon (BC: average concentration 0.6 μg g^{-1}); radiative forcing is 3.8 (0.8) W m^{-2} in old (fresh) snow, equating to 19 % (17 %) of the radiative forcing of BC. These results indicate that WSOC has a profound impact on snow albedo and the solar radiation balance.

1 Introduction

Seasonal snow plays a significant role in Earth's solar radiation energy budget owing to its high reflectivity (Beniston et al., 2017; Usha et al., 2020; Xie et al., 2018). In recent decades, however, the extent of snow-covered areas has trended downward, partially as a result of the presence of light-absorbing particles (LAPs) in the snowpack (Barnett et al., 2008; Groisman et al., 1994; Dumont et al., 2014). The LAPs in seasonal snow, such as black carbon (BC), organic carbon (OC), mineral dust (MD), and biota (Beres et al., 2020; Di Mauro, 2020; Els et al., 2020; Qian et al., 2015; Wu et al., 2016), can strongly absorb solar radiation, which together serves to lower surface albedo and impose a positive radiative forcing (Cui et al., 2021; Dumont et al., 2014; Hansen and Nazarenko, 2004; Shi et al., 2022b; Warren and Wiscombe, 1980; Zhang et al., 2017). Ultimately, LAPs can accelerate snow melting (Li et al., 2021b) and disturb the global radiative balance, therefore, have important implications for regional and global climate change (Skiles et al., 2018; Shi et al., 2022a).

Snowpack BC and MD have been the focus of considerable research in snow-covered regions worldwide (Li et al., 2021a; Zhang et al., 2018; Antony et al., 2014; Hegg et al., 2010; Doherty et al., 2014; Wang et al., 2014b). As the most important LAP (Bond et al., 2013; Doherty et al., 2010; Wang et al., 2014b; Shi et al., 2020), the radiative efficiency of snowpack BC can be more than three times greater than that of carbon dioxide (Flanner et al., 2007), and MD, another important snowpack LAP, is also known to alter the cryospheric environment owing to its light-absorbing properties (Di Mauro et al., 2015; Painter et al., 2007; Sarangi et al., 2020; Shi et al., 2021). Recently, researchers have also begun evaluating the influence of biomes on global snow albedo (Hotaling et al., 2021). In contrast, however, the role of OC remains poorly understood because of its complex composition and a relative dearth of OC-focused research. Consequently, substantial uncertainty surrounds the origins, optical properties, and radiative effects of snowpack OC.

The recent study has reported that the storage of OC in mountain glaciers and ice caps (~11 % of Earth's land surface) could be as high as 6 petagrams (Pg), the majority of which is water-soluble organic carbon (WSOC) (Hood et al., 2015; Yan et al., 2016). The substantial part of WSOC in glacier is highly bioavailable and can be a source of labile organic matter for downstream ecosystems (Singer et al., 2012). The physical and photochemical processes can occur within various WSOC in snow cover and glaciers, and therefore have a great effect on atmospheric and glacier chemistry (Domine, 2002; Grannas et al., 2007; Antony et al., 2011). Moreover, WSOC has important influences on the energy budget and radiative forcing of snow cover and glaciers (Kirillova et al., 2014; Ram et al., 2010; Yan et al., 2016). As the chief absorber of WSOC, water-soluble brown carbon (WS-BrC) can absorb significant measures of solar radiation in the ultraviolet–visible (UV–vis) wavelengths (Murphy et al., 2008). For instance, in their analysis of 21 Arctic and Antarctic snow samples, Anastasio and Robles (2007) observed that 50 %

of the total light absorption coefficients at wavelengths > 280 nm might be attributed to organic chromophores of WSOC. Beine et al. (2011) reported that WSOC occupies almost the entire absorption spectrum of the photochemically active region (300–450 nm) in surficial snow samples from Barrow, Alaska. And Feng et al. (2016) observed that absorption in cryoconite samples from the central Tibetan Plateau is dominated by WSOC components in the 300–350 nm range. Similarly, Yan et al. (2016) measured WSOC in glacial snow from Laohugou, northern Tibetan Plateau, where they found that the radiative forcing is ~10 % that of BC. Together, these studies indicate that WSOC plays a key role in global snowpack energy absorption (Niu et al., 2018; Zhang et al., 2020). We note that recent researches on cryospheric WSOC mainly focused on alpine glaciers and polar regions (Li et al., 2022; Guo et al., 2022), while the extensive mid-latitude regions impacted by seasonal snowpack remain relatively understudied.

The composition of WSOC is typically complex, and characteristics of fluorescence and absorption can vary widely among the different components. Nonetheless, recent studies have tended to treat WSOC as a single entity and focus on the overall impacts (Barrett and Sheesley, 2017; D'Sa et al., 2014; Niu et al., 2018; Wu et al., 2019), such that the specific roles of individual components are poorly constrained. One commonly used analytical method for distinguishing the components and properties of fluorescence is the fluorescence excitation-emission matrices (EEMs), which has the advantage of high sensitivity and small sample size (Coble, 1996; Kowalczuk et al., 2005). First applied in oceanic contexts (Coble et al., 1990), EEMs have been gradually extended to lakes, fog water, rainwater(Birdwell and Valsaraj, 2010; Huguet et al., 2009; McKnight et al., 2001). At present, the application of EEMs on atmospheric aerosols has entered a mature stage. EEMs have been used to identify fluorescent WSOC components in aerosols from polar regions or urban backgrounds, and it has been found that different structures of WSOC fractions exhibit different oxidation properties, which may provide a clue to understand the chemical formation or loss of organic chromophores in atmospheric aerosols (Chen et al., 2016; Fu et al., 2015). Recently, this method has been gradually extended to the analysis of glacier samples and snow samples (Feng et al., 2018; Guo et al., 2022; Zhou et al., 2019b). Concurrently, parallel factor analysis (PARAFAC) is an effective approach for extracting from complex EEMs the individual fluorescence components and their corresponding fluorescence information, thus making EEM–PARAFAC a direct and viable means for exploring sources of WSOC. For example, Zhou et al., (2019b) used EEM–PARAFAC to identify the multiple sources of WSOC measured in seasonal snow in northwestern China. Accordingly, we have applied EEM–PARAFAC in our analysis of snow samples for this study.

EEM-PARAFAC can only provide plausible information about the component-specific influence of WSOC on fluorescent properties, and the quantitative fractional contributions of specific components to light absorption are still unknown. Recently, Chen et al. (2019a) collected atmospheric aerosol samples in $PM_{2.5}$ over Xi'an, China, and successfully attributed the dithiothreitol (DTT) activity levels to various BrC components by coupling DDT and BrC datasets. A similar attribution method has been applied to various research areas, including climate change, extreme weather, and atmospheric environments (Cao et al., 2015; Pokrovsky, 2019; Xin et al., 2016; Zhao et al., 2019). In this study, we applied a multiple linear regression method comparable to that of Chen et al. (2019a) to derive the fractional contribution of each WSOC component to light absorption. Despite this method having been used elsewhere (Wu et al., 2022; Wu et al., 2021), it remains a highly innovative approach to evaluating the light absorption of snowpack WSOC.

Northeastern China supports an extensive snowpack during winter and spring. As a major industrial and agricultural center, this region is also the principal source of heavy airborne pollutants that are incorporated into seasonal snow via wet and dry deposition (Wang et al., 2017). Coupled with intensive tilling of farmland, the geographical proximity of northeastern China to neighboring desert regions also provides a source of soil organic matter that becomes entrained into the snowpack (Wang et al., 2013b). Compared with research on BC-snow mixing ratios and their radiative impact in northeastern China (Dang et al., 2017; Huang et al., 2011; Pu et al., 2019), studies of WSOC are still in their infancy. To address this deficiency, we make the primary investigation of the fluorescence characteristics, absorption properties, and radiative effects of WSOC in seasonal snow samples in northeastern China. Specifically, we applied EEM–PARAFAC to identify the origins and fluorescence characteristics of snowpack WSOC, after which we derived individual absorption contributions for each WSOC component using fluorescence data, an absorption data series, and an attribution method. Finally, we estimated the reduction of snow albedo and radiative forcing caused by WSOC and BC via the Spectral Albedo Model for Dirty Snow (SAMDS) radiative transfer model.

2 Methods

2.1 Sample collection

During the months of January and December 2020 and January 2021, we collected 34 snow samples from sites across northeastern China, including the eastern part of Inner Mongolia and Heilongjiang and Jilin provinces. Sample numbers were set following previous campaigns (Pu et al., 2017; Wang et al., 2013b, 2017), with the exception that samples from the Changbai Mountain area are numbered individually. The geographical distribution of sampling sites and respective land-cover types are shown in Figure 1a; our sites are characterized by five land-cover types, including forest, grassland, desert, cropland, and frozen lake/river (Fig. 1b–g). On the basis of these geographical and environmental classifications, we divided the sampling sites into five broad regions: southeastern Inner Mongolia (SEIM;

Q494–495, Q497–499), the south of northeast China (SNC; Q470–471, Q473–474, Q477, Q484, Q486–Q489, Q491–Q493, Q501), the north of northeast China (NNC; Q480–483), the Changbai Mountain area (CBM; CM1–CM2, CM5, CM11, CM13–CM14), and northeastern Inner Mongolia (NEIM; Q440, Q443, Q447, Q449, Q454).

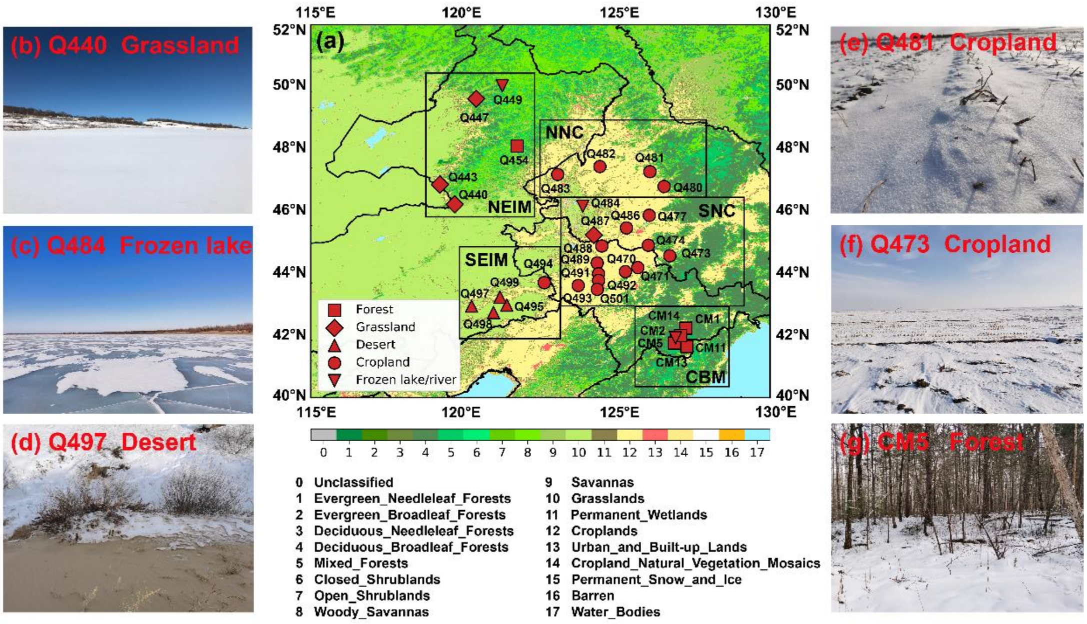

Figure1: (a) Information on sampling site distributions in northeastern China, including the land cover type, site number, and grouping. Land cover types are derived from Collection 5.1 of the MODIS global land cover type dataset (MCD12Q1: https://lpdaac.usgs.gov/products/mcd12q1v006/) and are indicated by specific colors and symbols relative to sampling sites. Sampling sites are divided into the five groups defined by black rectangles. (b–g) Photographs depicting the typical snow and ground-cover conditions of our various sampling sites.

Our sampling sites were chosen at random but had to be located ≥ 20 km from cities and villages and at least a kilometer upwind of roads or railroads to minimize the influence of single-point pollution sources and to ensure the broadest regional representation. Furthermore, we performed sample collection oriented toward the wind to avoid contamination from personnel. At each site, we used a sterile disposable shovel to collect 0–5 cm-thick samples of surface snow, which were subsequently stored in sterile Whirlpak (Nasco, WI, USA) bags. For snow depths < 5 cm, we determined the sampling depth according to the actual conditions to avoid inducting significant soil impurities during sampling. Snow samples were melted at room temperature (25 ℃) and stored in a freezer at −20 °C until analysis in the laboratory. For more operational details, we refer the reader to Wang et al. (2013b).

2.2 Chemical species analysis

All collected snow samples were stored in a freezer at −20 °C until analyzed in the laboratory. In the lab process, the samples were firstly melted at room temperature (25 ℃). Then 30 mL meltwater was taken for each sample with the clean disposable syringe (Jiangnan, Anhui, China) and injected into the pre-baked (4h, 450 ℃) glass bottle passing through 0.45 μm pore-sized polytetrafluoroethylene filters (Jinteng, Tianjin, China). Finally, the concentration of WSOC was measured by the total organic carbon analyzer (Aurora 1030W, OI Analytical, TX, USA), and measurement detection limits and relative standard deviations were 2 μg L^{-1} and 1 %, respectively. Additionally, a blank sample prepared with ultrapure water was measured for blank correction before the sample measurement. The blank concentration of WSOC is 0.35 mg L^{-1} and the blank-corrected WSOC concentrations are provided in Table S1.

We used 0.4 μm pore-sized polycarbonate filter membranes (Whatman, USA) to isolate BC and other insoluble particles, following the protocols outlined by Wang et al. (2020), after which we employed a custom-developed two-sphere integrating-sandwich (TSI) filter-based spectrophotometer to measure particle absorption. Coupled with the mass of filtered meltwater, these optical measurements were then converted to snowpack BC concentrations. To make these calculations, we applied a BC mass-absorption coefficient (MAC) and absorption Ångström exponent (AAE) of 6.3 m^2 g^{-1} (550 nm) and 1.1, respectively, after Pu et al. (2017). We note that TSI provides greater accuracy and smaller overall uncertainties in the quantification of seasonal snow BC than do thermo-optical carbon analysis (Wang et al., 2020), and thus it has been applied widely in this type of research (Shi et al., 2020). For more detailed information, we refer the reader to Wang et al. (2013b).

2.3 Fluorescence and absorption measurement

We obtained absorbance and fluorescence EEMs for filtered meltwater samples via synchronous absorption-3D Fluorescence scanning spectrometry (Aqualog, Horiba Scientific) with the following measurement parameters: fluorescence spectra excitation range = 240–800 nm in 3 nm intervals, emission range = 152.25–929.92 nm in 5.04 nm (8 pixels) intervals, scanning interval = 0.3 seconds. Prior to sample measurement, we analysed aliquots of filtered ultra-pure water (18.2 M ω cm, Milli-q Purification System, Millipore) as analytical blanks. We normalized fluorescence intensity to that of the water Raman unit (RU), which exhibits a peak excitation wavelength of 350 nm, and deducted this Raman signal from all subsequent sample tests (Lawaetz and Stedmon, 2009). The inner filtration effect correction is based on the absorbance-based approach (Kothawala et al., 2013), using the measured absorbance at each pair of excitation and emission wavelengths across the EEMs to convert the observed fluorescence intensity into the corrected fluorescence intensity. Rayleigh scattering peaks were processed by interpolation algorithm in EEMscat MATLAB toolbox (Bahram et al. 2006). As fluorescence spectra with wavelengths greater than 600 nm are primarily noise (Zhou et al., 2019b), they are not considered further in this study. Likewise, any samples with absorption spectra of >600 nm wavelengths were subtracted for the baseline correction (Chen et al., 2019b).

We used version 0.6.3 of the MATLAB drEEM toolbox (http://dreem.openfluor.org/; Murphy et al., 2013) to perform PARAFAC analysis on EEMs. Comprising the consistency index, residuals, and visual inspections, the 3-component model is considered more reliable and representative than are the 2–7-component models (Fig. S1 in the Supplement) and passes the S4C6T3 split scheme (Fig. S2; Murphy et al., 2013). The contributions of these three components to the overall fluorescence signal are expressed as relative percentages of F_{max} in RU, and the total fluorescence volume (TFV; RU nm^2) is calculated from the EEMs (Song et al., 2019). Normalized TFV equates to NFV (RU nm^2 (mg L^{-1})$^{-1}$), TFV c(WSOC)$^{-1}$), where c(WSOC) is the concentration of WSOC in the snow (mg L^{-1})), and represents a sample's fluorescence ability (Chen et al., 2019a).

We calculated three fluorescence-derived indices—the fluorescence index (FI), biological index (BIX), and humification index (HIX)—from the ratio of fluorescence intensity at specific excitation and emission wavelengths. As demonstrated by previous studies (Birdwell and Valsaraj, 2010; Huguet et al., 2009; McKnight et al., 2001), these ratios can help characterize potential sources of WSOC. Specifically, the FI is taken to represent the relative amount of DOM derived from terrestrial and microbial/algae sources (McKnight et al., 2001); high values correspond to terrestrially derived organics, and low values reflect microbial sources. The HIX describes the degree of humification of soluble organic matter (Zsolnay et al., 1999). During humification, the aromaticity of organic matter increases as microbial availability decreases, such that higher HIX values correspond to more strongly humified and/or higher aromaticity organics (principally of terrestrial origin), whereas lower values indicate autochthonous or microbial origins. As a measure of autochthonous productivity (Huguet et al., 2009), elevated BIX values are associated with increased contributions of microbial-derived fluorescent organic matter. The three indices are calculated by the following equations (Ohno, 2002; Huguet et al., 2009; McKnight et al., 2001; Feng et al., 2016):

$$\mathrm{FI}=\frac{\mathrm{I(Ex = 370,\ Em = 470)}}{\mathrm{I(Ex = 370,\ Em = 520)}}, \tag{1}$$

$$\mathrm{BIX}=\frac{\mathrm{I(Ex = 310,\ Em = 380)}}{\mathrm{I(Ex = 310,\ Em = 430)}}, \tag{2}$$

$$\mathrm{HIX}=\frac{\mathrm{I(Ex = 254,\ Em = 435 - 480)}}{\mathrm{I(Ex = 254,\ Em = 300 - 345) + I(Ex = 254,\ Em = 435 - 480)}}, \tag{3}$$

where I is the fluorescence intensity, and Ex and Em represent the excitation and emission wavelengths, respectively. To ensure a direct comparison with prior results, we recalculated published HIX data using the same calculation methods as in our own analyses. According to a previous study, FI values of ≤1.4 correspond to terrestrial sources and values of ≥1.9 denote a primarily microbial origin. The values of 1.4–1.9 suggest a mixed origin (McKnight et al., 2001).

The absorption spectra of WSOC were derived from 240 to 800 nm in 3 nm intervals. The baseline shifts and scattering effects of the measurement for the absorption spectra were corrected by subtracting the average absorbance above 600 nm from the whole spectrum (Chen et al., 2019b). We converted sample absorbance to an absorption coefficient using the following equation:

$$a_{WSOC}(\lambda)=\ln(10)\cdot Abs(\lambda)\cdot L^{-1}, \quad (4)$$

where Abs is absorbance, λ is wavelength, L is the path length of the cuvette (0.01 m), and a_{WSOC} is the absorption coefficient (m^{-1}).

Owing to the absorption characteristics of WSOC, we selected the absorption coefficient at 280 nm ($a_{WSOC}(280)$) to characterize the absorption intensity of WSOC for comparison with other studies (Zhang et al., 2010).

To investigate the wavelength dependence of WSOC absorption, we obtained the Absorption Ångström exponent (AAE) via the following equation (Doherty et al., 2010; Niu et al., 2018; Wang et al., 2013b; Yan et al., 2016):

$$a_{WSOC}(\lambda)=K\cdot\lambda^{-AAE}, \quad (5)$$

where K is a constant related to WSOC concentration.

We calculated the mass absorption coefficient (MAC_λ, $m^2\ g^{-1}$) of our samples using the equation (Chen et al., 2019b; Yan et al., 2016):

$$MAC_{\lambda}=a_{WSOC}(\lambda) / c(WSOC), \tag{6}$$

where a_{WSOC} is the absorption coefficient derived from Equation (4) and c(WSOC) (mg L^{-1}) is the concentration of WSOC.

2.4 Snow albedo modeling and radiative forcing calculations

To establish the radiative effect impact of snowpack WSOC in northeastern China, we used SAMDS to simulate spectral snow albedo. This model is based on asymptotic radiative transfer theory, which has been verified by previous studies (Li et al., 2021b; Wang et al., 2017). As described in detail by Wang et al. (2017), the model involves parameters including solar zenith angle, impurity concentrations, mass absorption coefficient of impurities, and snow grain radius. Measured values include the concentration of BC and absorption coefficients of WSOC. To quantify the influence of pollutants on snow albedo, we assumed a semi-infinite snow layer and uniform snow grain radii of 100 μm for fresh snow and 1000 μm for old snow, consistent with previous studies (Pu et al., 2021). With the solar zenith angle fixed at 60°, consistent with our sampling dates and locations, we calculated the reduction ($\Delta\alpha_i$, i represents BC only, WSOC only, and BC + WSOC, similarly hereinafter.) in spectral snow albedo derived from different types of impurities for the UV–vis (280–400 nm) and ultraviolet–near infrared (UV–NIR; 280–1500 nm) bands. Radiative forcing resulting from either BC or WSOC in snow (RF_i) was then derived by multiplying the albedo reduction value by the incident solar radiation (Painter et al., 2013):

$$RF_i=E\cdot(\alpha_{pure} - \alpha_i)=E\cdot\Delta\alpha_i, \tag{7}$$

where α_{pure} is snow albedo for pure snow and E is the average daily downward shortwave solar radiation flux acquired from NASA's Clouds and the Earth's Radiant Energy System (CERES) product "CERES SYN1deg" (https://ceres.larc.nasa.gov/products. php?product=SYN1deg).

3 Results and discussion

3.1 Characteristics of chemical species

Figure 2a shows the spatial distribution of measured WSOC in seasonal snow across northeastern China. Averaged across our entire study area, the mean WSOC concentration (arithmetic mean ± standard deviation) is 3.6 ±3.2 μg g^{-1}, with a maximum of 18.0 μg g^{-1} and a minimum of 0.3 μg g^{-1}. Among the five regions, WSOC concentrations are highest in SNC (average 5.7 ±3.7 μg g^{-1}), likely reflecting the greater degree of agricultural and industrial activity there compared with other regions (Lu et al., 2011; Wang et al., 2013b). We highlight that both agricultural and industrial sources are considered anthropogenic. In contrast, our second highest measured concentrations (3.4 ± 1.5 μg g^{-1}) are from SEIM, where desertification occurs (Fang et al., 2007) and is therefore considered a natural source of WSOC. For most sites, the underlying surface is desert (Fig. 1a) that was incompletely covered by seasonal snow during the sampling period (Fig. 1d). Consequently, the exposure of natural sandy soils is a potentially significant contributor of WSOC through aeolian erosion and dry deposition. In NNC, where both the population density and agricultural intensity are lower than in SNC (Choi et al., 2020), the contribution of anthropogenic pollution to snowpack is correspondingly lower, resulting in a moderate WSOC concentration of 2.7 ± 0.8 μg g^{-1}. Meanwhile, far from intensive human activity, both CBM and NEIM (Fig. 1a, b, and g) returned low WSOC concentrations (CBM: 2.0 ± 1.3 μg g^{-1}; NEIM: 0.5 ± 0.2 μg g^{-1}). Nonetheless, the higher value for CBM betrays the influence of far-traveled anthropogenic pollutants (Wang et al., 2015; Wu et al., 2020; Zhang et al., 2013).

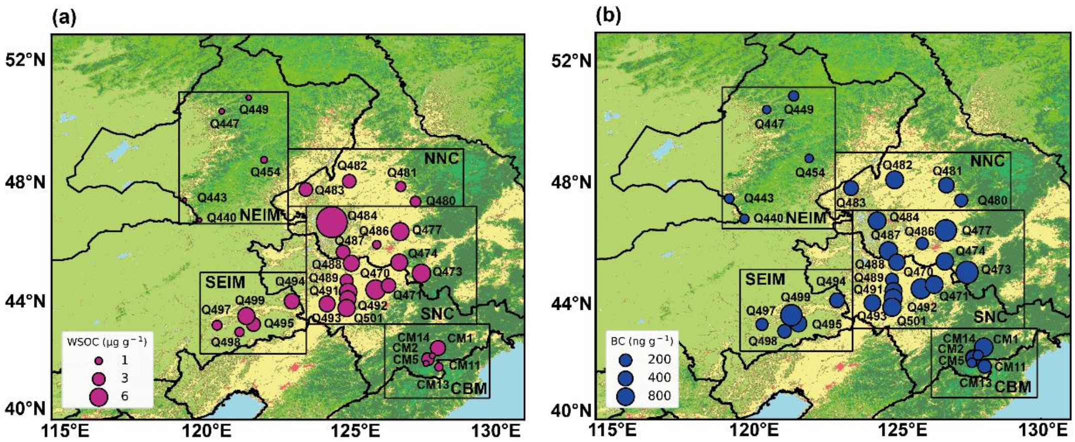

Figure 2: Spatial distributions of concentrations of (a) WSOC and (b) BC in snow samples. Sampling sites are divided into the five groups defined in Figure 1. Bubble sizes are proportional to concentrations of WSOC and BC.

In comparison with previous studies, we observed that, with the exception of NEIM, our measured WSOC concentrations are significantly higher than those reported for snow/ice from the Tibetan Plateau (TGL; ~0.71–1.02 μg g^{-1}; Feng et al., 2016), the Alps (~0.14–0.78 μg g^{-1}; Vione et al., 2021), North America (~0.1–0.3 μg g^{-1}; Fellman et al., 2015), and polar regions (~0.12–0.27 μg g^{-1}; Antony et al., 2014), but comparable to values in Laohugou glacier ice from the Tibetan Plateau (~1.02–2.6 μg g^{-1}; Feng et al., 2018, 2016) and seasonal snowpack in northwestern China (0.48–7.07 μg g^{-1}; Zhou et al., 2021). This finding implies that snowpack WSOC in northeastern China is contributing significantly to regional and global climate change (Domine, 2002).

A similar spatial pattern is exhibited by snowpack BC (Fig. 2b). For example, of all five regions, the regional mean BC concentration is highest for SNC (mean: 923 ±512 ng g^{-1}), followed by SEIM (659 ±582 ng g^{-1}), NNC (494 ±224 ng g^{-1}), and the CBM (391 ±312 ng g^{-1}). BC concentrations are lowest in NEIM (60 ±19 ng g^{-1}), in agreement with the values in remote areas reported by Doherty et al. (2010).

3.2 Fluorescence characteristics of WSOC

Three fluorescent components (C1–C3) were captured by resolving the EEMs spectra; all fluorescence information is summarized in Table S2. C1 exhibits a primary peak at Ex = 240 nm, Em = 448 nm, indicating a high-oxygenated humic-like substance (HULIS) found primarily in aromatic conjugated macromolecules (Chen et al., 2016). The weaker secondary peak occurs at longer excitation wavelengths (Ex / Em = 308 / 448 nm), implying a higher aromatic content and greater molecular weight (Coble et al., 1998). Wen et al. (2021) concluded that C1 is probably derived from natural terrestrial sources, such as dust and soil, as proposed originally by Stedmon et al. (2003) and Osburn et al. (2016). Accordingly, we classified C1 as a terrestrial, humic-like substance, hereafter referred to as HULIS-1.

C2 exhibits a primary (secondary) peak at Ex = 240 (293) nm, Em = 398 nm, suggestive of lower-oxygenated HULIS (Chen et al., 2016). Observed in a variety of sources, Stedmon et al. (2003) reported this component in terrestrial end-member samples. Whereas, both Murphy et al. (2011) and Osburn et al. (2016) have since linked C2 to anthropogenic sources, such as urban runoff and sewage. Microbial activity and the degradation of phytoplankton in natural aquatic systems are also thought to contribute to this component (Yamashita et al., 2008; Zhang et al., 2009). Accordingly, we classified C2 as humic-like substances with complex origins in terrestrial, anthropogenic, and/or microbial sources, hereafter termed HULIS-2. Unlike HULIS-1 and HULIS-2, C3 is recognizable as a UVB-like protein or tyrosine-like fluorescence (hereafter PRLIS) with a primary (secondary) peak at Ex = 240 (293) nm, Em = 398 nm (Osburn et al., 2016; Stedmon and Markager, 2005). PRLIS reflects autochthonously labile DOM produced by biological processes (Stedmon et al., 2003) and has been reported in previous studies of seasonal snow (Zhou et al., 2019b).

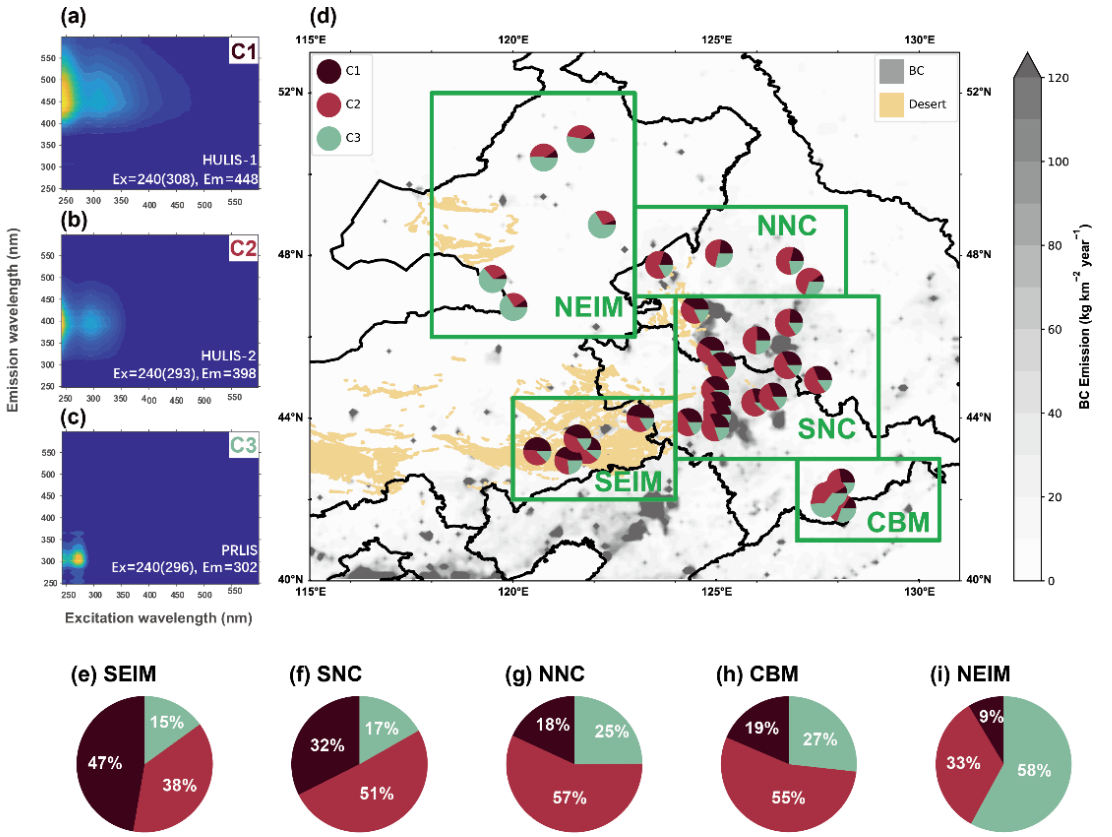

Figure 3: (a–c) Three fluorescent components identified by PARAFAC analysis. (d) Relative contributions of the three components to total fluorescence at each site. HULIS-1, HULIS-2, and PRLIS are represented by the specific colors shown in the legend (top left corner). The distributions of BC emissions and desert areas in our study area are indicated by gray and light yellow, respectively, with darker gray colors indicating higher black carbon concentrations. (e–i) Average contributions of the three components in different groups of samples. BC emission data are derived from the research group at Peking University (http://inventory.pku.edu.cn/ home.html, Wang et al., 2014a); the Chinese desert (sand) distribution dataset is provided by the National Tibetan Plateau Data Center (http://poles.tpdc.ac.cn/zh-hans/data/122c9ac2-53ee-4b9a-ae87-1a980b131c9b/; Wang et al., 2013a).

Figure 3d depicts the spatial distribution of the relative contribution of three components to fluorescence, with the regional averages given in Figure 3e–g. In SEIM, the greatest contribution is that of HULIS-1 (47 %), followed by HULIS-2 (38 %) and PRLIS (15 %), indicating that the signal is dominated by local soil/dust sources, consistent with the local environment (Figs. 2 and 3d). HULIS-2 plays a greater role in SNC, where it accounts for half of the total fluorescence signals; of the remaining half, HULIS-1 is most important. This difference in key components between SEIM and SNC illustrates the change in primary source of fluorescence intensity. Indeed, although HULIS-2 might be derived from any combination of terrestrial, anthropogenic, and microbial sources (Osburn et al., 2016; Stedmon et al., 2003; Yamashita et al., 2008; Zhang et al., 2009), human activity (e.g., agriculture, industrial emissions) is most intensive in SNC. Therefore, our combined analysis suggests that anthropogenic source is the main contributor to seasonal snow in SNC (Figs. 1a and 3d; Guo and Hu, 2022). The conclusion is also in good agreement with previous study (Zhou et al., 2019b). As in SNC, HULIS-2 also represents approximately half of the fluorescence signal in both NNC and CBM. The background environment of NNC is similar to that of SNC, with dense urban cities and population. In the CBM, which is although heavily forested (Fig. 1a; Guo and Hu, 2022), the long-range transport of anthropogenic pollutants is responsible for the dominance of HULIS-2, as discussed in Sect. 3.1. HULIS-1 accounts for less than PRLIS in both NNC and the CBM, which we posit reflects the concealment of bare soil surfaces by deep snow and the importance of biological processes due to the heavy vegetation cover. PRLIS accounts for >50 % of the total fluorescence signal in NEIM, followed by HULIS-2; HULIS-1 contributes relatively little in this region. We attribute this pattern to both the extensive grassland and forest cover, which obscures bare soil surfaces, and the distance from anthropogenic pollution. These together serve to amplify the importance of biological processes (Zhou et al., 2019a). Taken as a whole, the respective contributions of HULIS-1, HULIS-2, and PRLIS to the fluorescence signals in our study area are ~30 %, ~50 %, and ~20 %. We note that these findings correspond well with the background environmental conditions.

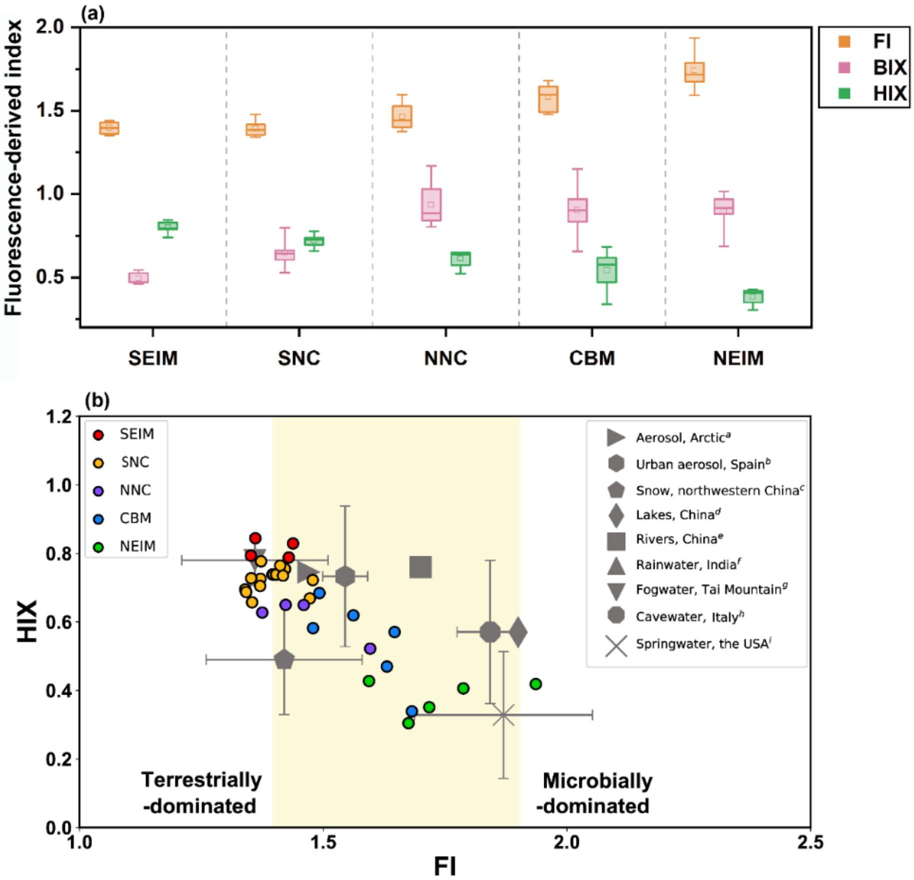

Figure 4: (a) Variations in fluorescence-derived indices among the five groups. Boxes denote the 25^{th} and 75^{th} quantiles, and horizontal lines represent median values. Averages are shown as small boxes, the whiskers denoting maximum and minimum data. (b) Comparison plots of HIX versus FI for the seasonal snow surface samples (colored dots) from northeastern China, together with the average and standard deviation of different types of WSOC (grey markers) adapted from: Arctic aerosols ([a] Fu et al., 2015), Spanish urban aerosols ([b] Mladenov et al., 2011), seasonal snowpack in northwestern China ([c] Zhou et al., 2019b), Chinese lakes and rivers ([d, e] Zhou et al., 2017), rainwater from Rameswaram, India ([f] Salve et al., 2012), fog water from Tai Mountain, China ([g] Birdwell and Valsaraj, 2010), cave water from Frasassi Caves, Italy ([h] Birdwell and Engel, 2010), and spring water in the USA ([i] Birdwell and Engel, 2010). Shaded areas represent mixed WSOC signatures.

The FI, BIX, and HIX indices reveal spatial variability in fluorescence characteristics and thus permit the tracing of potential sources. Regionally averaged FI, BIX, and HIX values are depicted in Figure 4a. Our results show that, in general, FI varies in the range of 1.34–1.94 (mean = 1.49), BIX between 0.46 and 1.17 (mean = 0.74), and HIX between 0.30 and 0.84 (mean = 0.64). By comparison, reported mean FI, BIX, and HIX values for seasonal snow in Xinjiang (northwestern China) are 1.42, 0.76, and 0.55, respectively (Zhou et al., 2019b), suggesting that the impact of humification and WSOC aromaticity are slightly higher in our study area than in Xinjiang. This outcome implies a relatively strong terrigenous signal and correspondingly weaker biogenic signal in the seasonal snowpack of northeastern China. Regionally, SEIM exhibits the lowest FI (mean = 1.40) and BIX (mean = 0.49) values but the largest HIX value (mean = 0.80), further confirming the strong influence of highly aromatic, terrestrially derived WSOC in this region relative to the others. In contrast, NEIM returns the highest FI (mean = 1.74) and BIX (mean = 0.89) values, but the lowest HIX value (mean = 0.38), indicating the dominance of low-aromatic WSOC of microbial origin. Intriguingly, our results reveal that FI and BIX rise generally with decreasing (increasing) fractional contributions of HULIS-1 (PRLIS), whereas HIX exhibits a similar but contrasting pattern. Together, the comprehensive dataset described above verifies the regional variability in the terrestrial contributions to WSOC, in which SEIM > SNC > NNC > CBM > NEIM; this pattern is reversed for microbially sourced WSOC.

Figure 4b illustrates HIX versus FI as a scatterplot, compared with published data for different sample types; the shaded area depicts the region in which the FI value is >1.4 but <1.9. In general, FI exhibits a rising trend with declining HIX across northeastern China. For both SEIM and SNC, FI occupies a narrow range centered on 1.4, indicating either a predominantly terrestrial or mixed origin. We note that these results are comparable to those of fog water from the Tai Mountain, Arctic atmospheric aerosols, and seasonal snow in northwestern China (Birdwell and Valsaraj, 2010; Fu et al., 2015; Zhou et al., 2019b). Further, we highlight that HIX values are marginally higher in SEIM than elsewhere, suggesting a stronger influence from highly humified WSOC that probably reflects the extensive deserts and exposed earth in this region. FI values for NNC and the CBM fall within the range of 1.4–1.7 and thus reflect a mixed origin, in line with previous data from urban aerosols in Spain and Chinese river water samples (Mladenov et al., 2011, Zhou et al., 2017). When combined, FI and HIX values for NNC and

CBM snowpack indicate that WSOC in these regions bears a stronger terrestrial signature than do water samples from Chinese lakes and Italian caves (Birdwell and Engel, 2010; Zhou et al., 2017). Finally, FI values for NEIM fall within a range of 1.6–2.0, comparable to values from spring water in the USA (Birdwell and Engel, 2010), thus implying a predominantly microbial or mixed origin.

3.3 Comparisons of fluorescence and absorption characteristics

Figure 5a describes the spatial distribution of $a_{WSOC}(280)$ as WSOC absorption in the snowpack of northeastern China; Figure 5b depicts TFV as a measure of the spatial distribution of absolute WSOC fluorescence intensity for comparison. In general, TFV and $a_{WSOC}(280)$ both exhibit large spatial variability in the range of 690–18600 RU nm^2 and 0.42–16.98 m^{-1}, respectively. Regional mean values are 7700 ± 2800 RU·nm^2 (TFV) and 6.90 ± 2.39 m^{-1} ($a_{WSOC}(280)$) for SEIM, 12400 ± 4300 RU·nm^2 (TFV) and 11.48 ± 3.96 m^{-1} ($a_{WSOC}(280)$) for SNC, 7800 ± 500 RU·nm^2 (TFV) and 7.02 ± 0.88 m^{-1} ($a_{WSOC}(280)$) for NNC, 3900 ± 2500 RU·nm^2 (TFV) and 3.97 ± 2.46 m^{-1} ($a_{WSOC}(280)$) for the CBM, and 1000 ± 300 RU·nm^2 (TFV) and 0.83 ± 0.23 m^{-1} ($a_{WSOC}(280)$) for NEIM. We note that both distributions are consistent in space (Fig. 5e), with the highest concentrations in SNC and the lowest in NEIM. Moreover, the $a_{WSOC}(280)$ value for SNC is an order of magnitude larger than that for NEIM, implying that the impact of WSOC on snow albedo at UV wavelengths is significant in SNC but less notable in NEIM in general (see Sect. 3.5). Previous work has reported a similarly broad range of snowpack $a_{WSOC}(280)$ (0.15–10.57 m^{-1}) in northwestern China (Zhou et al., 2019b).

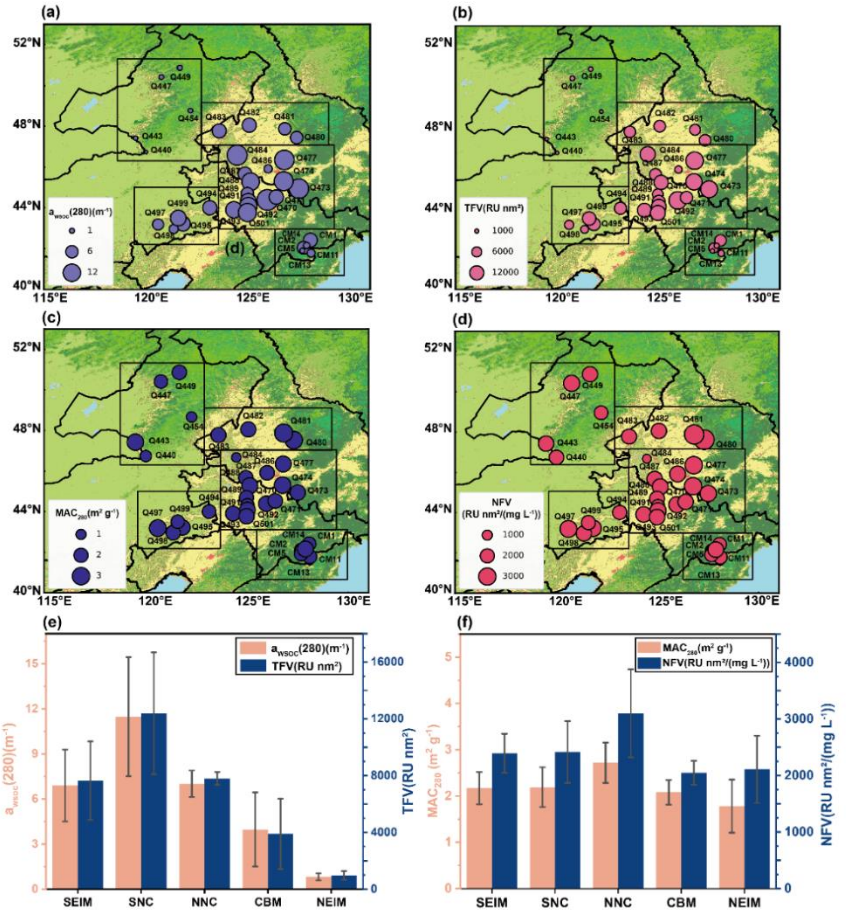

Figure 5: Spatial distribution of (a) $a_{WSOC}(280)$ (m^{-1}), (b) TFV (RU nm^2) , (c) MAC_{280} ($m^2\ g^{-1}$) and (d) NFV (RU nm^2 (mg L^{-1})$^{-1}$). Regional averages for (e) $a_{WSOC}(280)$, TFV, (f) MAC_{280} and NFV for the five groups. Error bars in (e) and (f) represent the standard deviations of $a_{WSOC}(280)$, MAC_{280}, TFV, and NFV for the five groups, respectively.

Two additional fluorescence and absorption capacity indices, identified as NFV and MAC_{280}, are proven tools for revealing WSOC's fluorescence and absorption characteristics and they are related to chemical composition, structure, and source (Chen et al., 2019a). For our study area as a whole, mean NFV and MAC_{280} values are 2412 ± 374RU nm^2 (mg L^{-1})$^{-1}$ and 2.2 ± 0.5 $m^2\ g^{-1}$, respectively. Both indices exhibit a narrow range, with regional means ranging from 2100 ± 600 to 3100 ± 800 RU nm^2 (mg L^{-1})$^{-1}$ and from 1.8 ± 0.6 to 2.7 ± 0.4 $m^2\ g^{-1}$, respectively, in contrast to the broad inter-regional disparities in TFV and $a_{WSOC}(280)$. Moreover, the spatial patterns of NFV and MAC_{280} are similar, with the highest values in NNC. We speculate that this result reflects the comparatively high low-oxygenated HULIS-2 fraction measured in the NNC samples (Fig. 3g), as the lower-oxygenated BrC (e.g., HULIS-2) has a higher absorption capacity (Browne et al., 2019).

Scatterplots for $a_{WSOC}(280)$ with TFV, F_{max}(HULIS-1), F_{max}(HULIS-2), and F_{max}(PRLIS) are provided in Figure S4 to further demonstrate the close relationship between fluorescence and the absorption characteristics of WSOC in our snow samples. As samples Q480, Q484, and Q477 deviate considerably from the respective confidence intervals, we did not include them in our analyses. Surprisingly, we found that TFV is closely correlated to $a_{WSOC}(280)$, with $P < 0.001$ and all datapoints located close to the line of best fit, indicating that the three components (HULIS-1, HULIS-2, PRLIS) contributing to the total fluorescence are also responsible for the majority of absorption. For each component, our data show that F_{max}(HULIS-1) is most closely correlated with $a_{WSOC}(280)$, followed by F_{max}(HULIS-2). The correlation between F_{max}(PRLIS) and $a_{WSOC}(280)$ is the poorest, yet it is still significant ($P < 0.001$). Together, our results imply that HULIS-1 is probably the greatest contributor to light absorption, with PRLIS being the least important.

3.4 Fractional contributions of different WSOC components to light absorption

In this study, we applied a multiple linear regression method comparable to that of Chen et al. (2019a) to derive the fractional contribution of each WSOC component to light absorption. Table S3 lists the statistical results of the fitted light absorption coefficient, based on the F_{max} data for three fluorescent components of EEM analysis. As the fitted results can explain ~94 %–99 % of the variance in measured light absorption within the 280–400 nm range, we conclude that the fusion of multiple fluorescent components is an effective means of describing most of the spatial features of WSOC light absorption throughout northeastern China. Accordingly, the wavelength-dependent fractional contributions of each component of light absorption in this band (280–400 nm) are reported in Figure 6. For our entire study area, light absorption is dominated by high-oxygenated HULIS-1, which accounts for ~56 %–65 % of the contribution across UV wavelengths. Further, we observed that the HULIS-1 contribution rises slightly from 280 to ~340 nm, after which there is a decreasing trend as wavelength increases. In contrast, HULIS-2 exhibits a valley-type pattern in fractional contribution between 280 and 400 nm and is responsible for ~19 %–30 % of all light absorption.

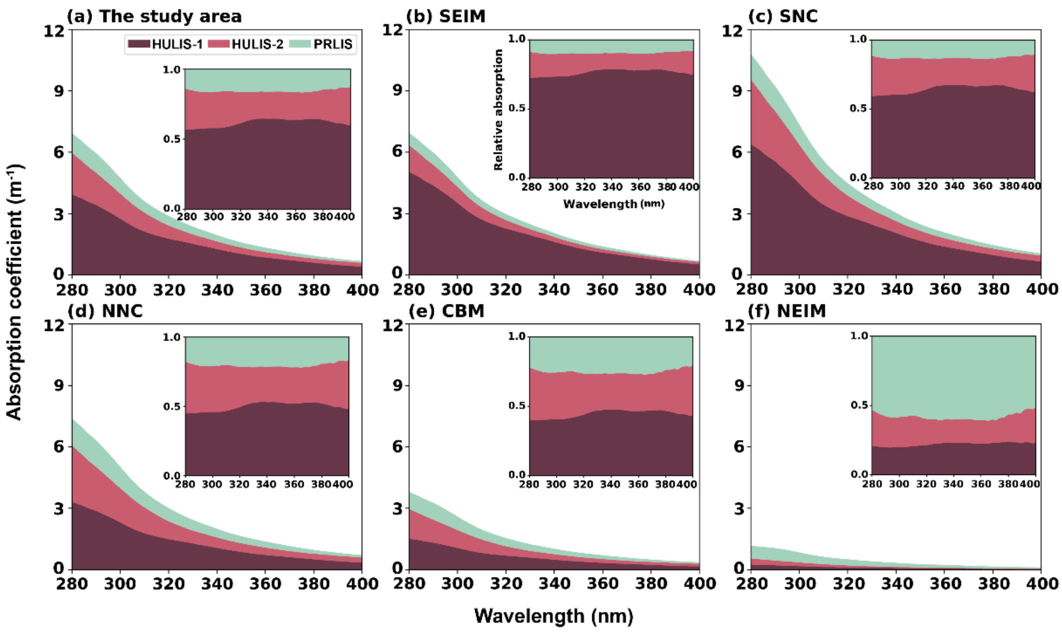

Figure 6: Relative contributions of the three components to the total absorption of samples in (a) the whole study area and (b–f) each of the five groups.

PRLIS contributes the least (~12 %–17 %) to light absorption and exhibits a similar wavelength-dependent pattern to HULIS-1. These results are consistent with the qualitatively comparative analysis described in Sect. 3.3. Previous studies have also highlighted this dominance of high-oxygenated compounds in WSOC light absorption, based on samples impacted by naturally and anthropogenically derived soils (Zhou et al., 2022). Conversely, the total absorption coefficient of WSOC decreases with increasing wavelength between 280 and 400 nm, in accord with previous studies (Andreae and Gelencser, 2006; Chakrabarty et al., 2010; Gustafsson et al., 2009; Wu et al., 2019). The AAE lies primarily between 5.0 and 8.0 (mean = 6.6) in the range of 280–400 nm, which is in agreement with results from snow collected from the Arctic, the northern Tibetan Plateau, and northwestern China (Voisin et al., 2012; Yan et al., 2016; Zhou et al., 2021).

For each component, the wavelength-dependent variability in light absorption is similar among all five regions, although the magnitude of each contribution varies from region to region. Moreover, compared with the spectral results, we found that the solar-radiation-weighted broadband light absorption was a more meaningful parameter for researchers studying climate change and atmospheric radiation. Therefore, the broadband results in Figure 7a for 280–400 nm absorption contributions—HULIS-1 (62 %), HULIS-2 (21 %), and PRLIS (17 %)—are average values for the whole study area. On a regional scale, the HULIS-1 contribution to light absorption (280–400 nm) follows the spatial pattern SEIM > SNC > NNC > CBM > NEIM. We note that HULIS-1 dominates light absorption in SEIM, SNC, and NNC but has a minor impact in NEIM compared with the other two components. In contrast, the impact of HULIS-2 varies only slightly among the five regions, with the greatest contributions in NNC and CMB, and the lowest in NEIM. The contribution of PRLIS is essentially opposite that of HULIS-1, being dominant in NEIM but of relatively minor important elsewhere. As shown in Figure 7b, light absorption contributions at 280 nm are consistent with the broadband results (Fig. 7a) in terms of the regional pattern, although specific values differ because of the different wavelength-dependent properties of light absorption for the three WSOC components.

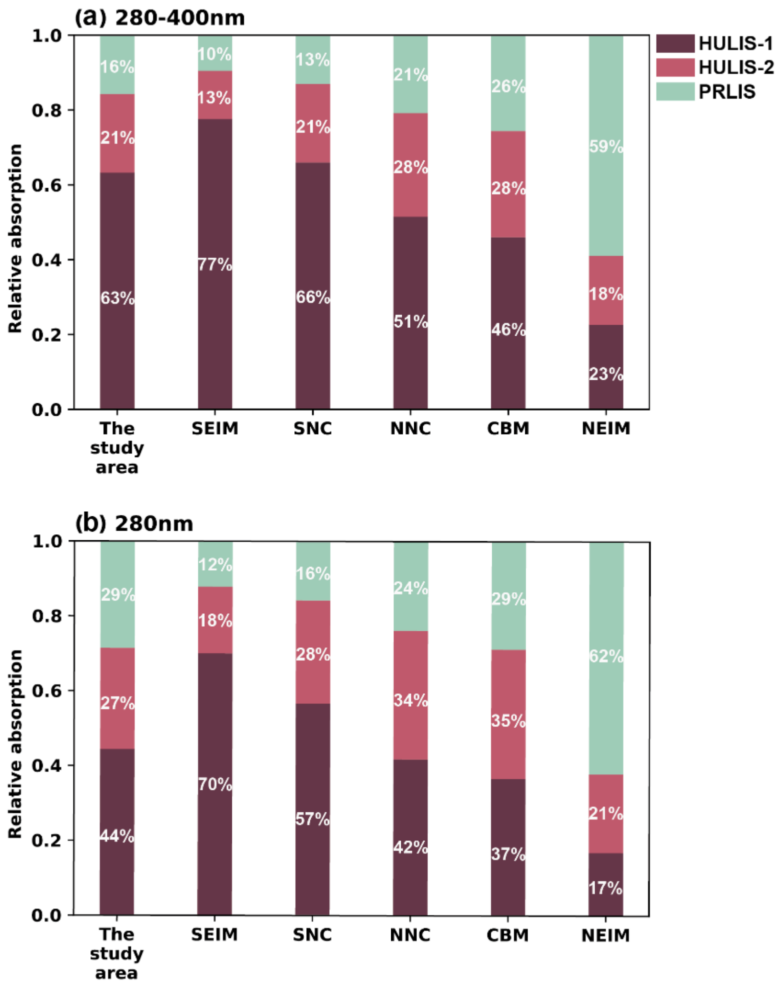

Figure 7: Regional averages for the relative contributions of the three fluorescent components to light absorption at wavelengths of (a) 280–400 nm and (b) 280 nm.

We find it noteworthy that, for each component, the overall regional pattern of its contribution to light absorption aligns with its impact on fluorescence signals, thereby confirming the viability of the attribution analysis employed in our study. Nonetheless, we observed that the magnitude of each component's contribution varies relative to its respective fluorescence signal. For instance, HULIS-1 returns a greater contribution to light absorption than its fluorescence signal, in contrast to HULIS-2. One plausible explanation for this discrepancy is that the fluorescence quantum yields (AQYs), which are essentially the ratio of fluorescence intensity versus absorption intensity, are different for each component. Indeed, in their comprehensive field-based study of BrC fluorescence and absorption properties in northern China, Wen et al. (2021) reported that the AQYs of WSOC decrease with increasing HIX, meaning that components with higher HIX values. Such as HULIS-1, have lower AQYs than does HULIS-2. Thus, the contribution of HULIS-1 to the fluorescence signals will be smaller than its contribution to light absorption, and vice versa for HULIS-2.

3.5 Albedo reduction and radiative forcing attributed to snowpack WSOC

The strong light absorption of WSOC in UV bands has important ramifications for snow albedo and radiative forcing throughout northeastern China. However, owing to the chemical and optical complexity of WSOC components, quantitative estimates for snowpack light absorption remain poorly understood. For example, although prior work in northeastern China has focused on BC (Wang et al., 2013b) and other water-insoluble light-absorbing particles (Wang et al., 2017; Zhao et al., 2014) via field measurements, model simulations, and satellite remote sensing (Pu et al., 2019), the specific impacts of WSOC have not been studied. Consequently, ours is the first study to report on the impact of WSOC on snow albedo and radiative forcing in northeastern China and to compare these data with BC results to highlight the non-negligible role of WSOC.

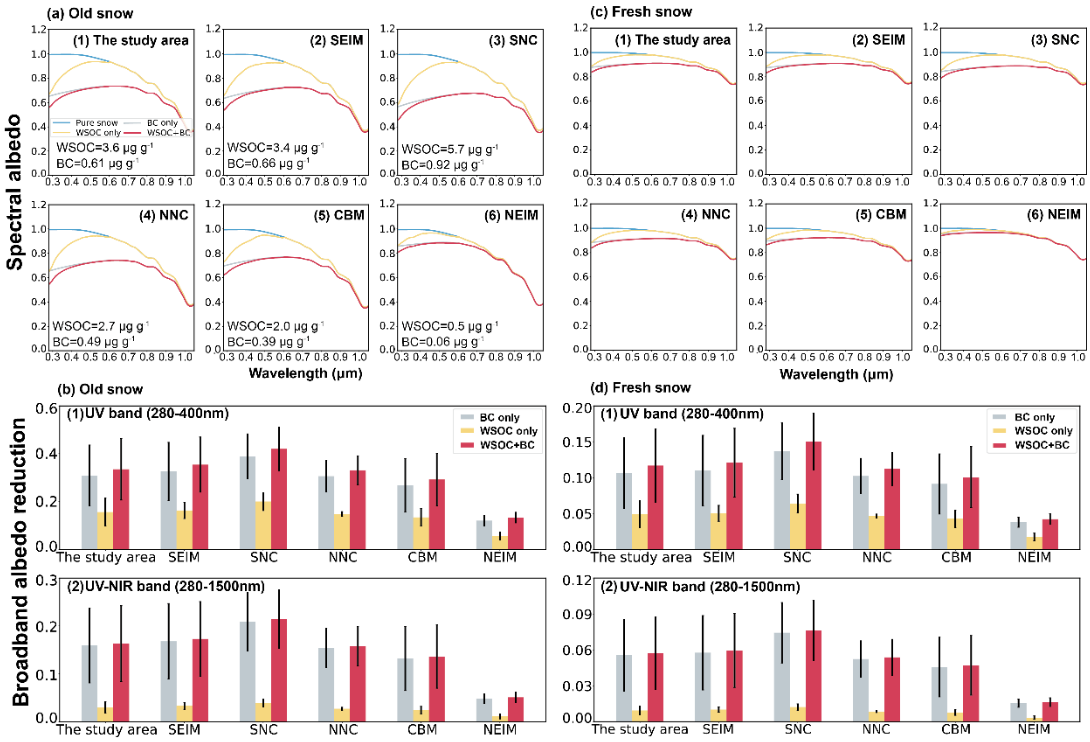

Figure 8: (a) and (b): Simulated snow spectral albedo and broadband albedo reductions—under various contamination scenarios and for different regions—for old snow (radius = 1000 μm). (c), (d) Simulated snow spectral albedo and broadband albedo reductions—under various contamination scenarios and for different regions—for fresh snow (radius = 100 μm). Colors represent the different types of snow (pure snow, BC- or WSOC-contaminated snow, and snow polluted by both WSOC and BC).

Figure 8 shows the regional-mean spectral snow albedo as well as the reduction in albedo due to WSOC, BC, and WSOC + BC. We assume a snow radius of 100 μm for fresh snow and 1000 μm for old snow. Our findings reveal that WSOC induces a marked decline in albedo within the UV and short-wave VIS bands, with the magnitude of albedo reduction growing rapidly as wavelength shrinks owing to the large AAE value of WSOC. In comparison, BC induces a widespread albedo reduction spanning the UV to NIR bands, and wavelength-dependent variations are significantly smaller than those of WSOC. For VIS and NIR, the reduction in albedo is dominated by BC, whereas the impacts of WSOC and BC are comparable in UV wavelengths, a pattern that is consistent with the results of studies of atmospheric aerosols (Shamjad et al., 2016). We note that these characteristics persist throughout northeastern China despite regional variability in environmental conditions and snowpack types (old vs. fresh snow).

For broadband wavelengths, our results indicate that the WSOC-induced (mean = 3.6 μg g^{-1}) albedo reduction for 280–400 nm wavelength in old (fresh) snow is 0.16 (0.05) across the whole study area, which corresponds to approximately 50.3 % (46.3 %) the impact of BC (mean = 0.6 μg g^{-1}). Regionally, the greatest decline in albedo occurred in SNC, where a mean WSOC of 5.7 μg g^{-1} resulted in a reduction of 0.20 (0.06) in the 280–400 nm range for old (fresh) snow. In contrast, the smallest decline in albedo was observed in NEIM, with reductions of 0.06 (0.02) resulting from an average WSOC concentration of 0.5 μg g^{-1}. Compared with the UV bands, a WSOC-induced albedo reduction of 0.03 (0.009) over the UV–NIR range (280–1500 nm) accounts for only ~18.8 % (16.7 %) of that due to BC in our study area. The regional mean for old (fresh) snow falls in the range of 0.01–0.04 (0.003–0.012), with the highest (lowest) values occurring in SNC (NEIM). However, we observed the highest ratio of WSOC- to BC-induced albedo reduction in NEIM. Together, these results indicate that WSOC plays a potentially important role in altering UV snow albedo in NEIM, despite its relatively low concentrations in the regional snowpack.

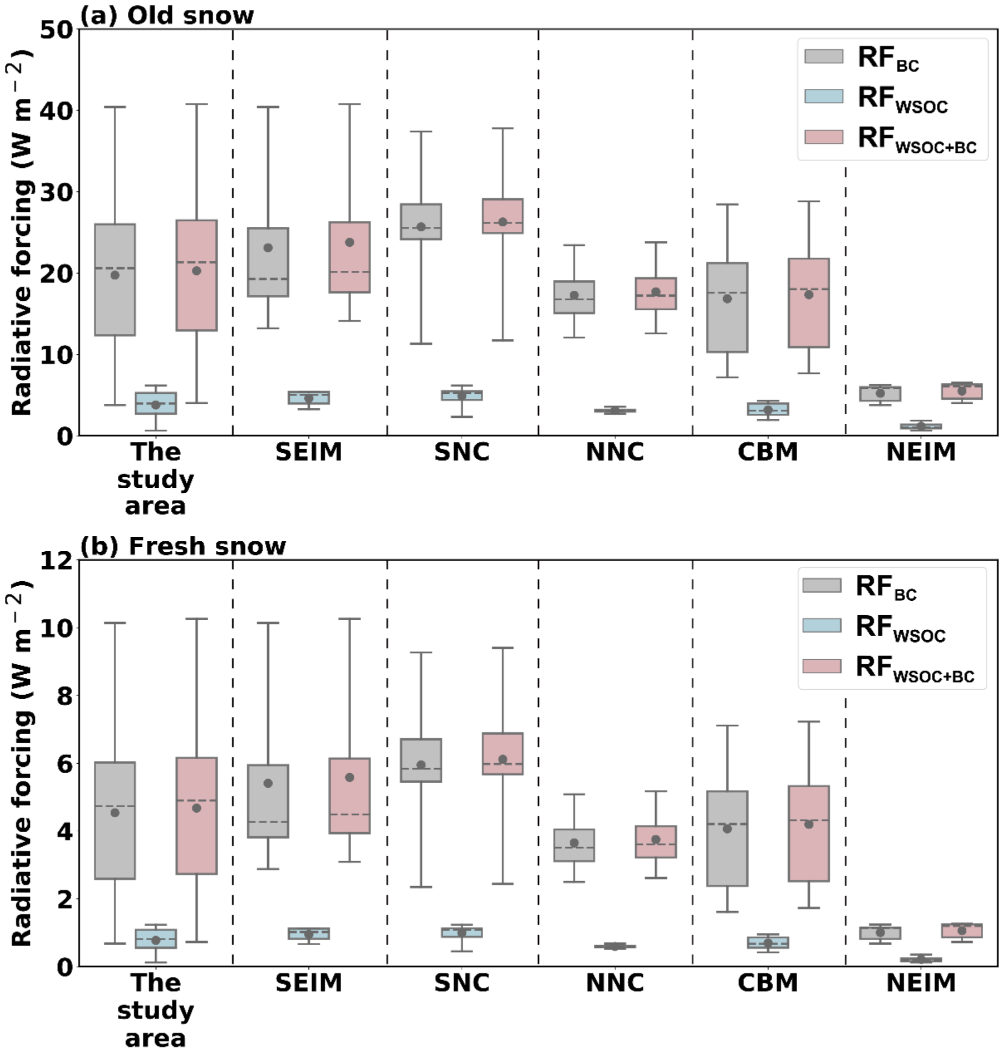

Figure 9: Radiative forcing due to different pollutants in (a) old or (b) fresh snow. Gray, blue, and red indicate the radiative forcing of BC, WSOC, and BC + WSOC, respectively.

Radiative forcing is an important index that directly reflects the impact of snowpack WSOC on the regional radiation balance and climate (Beres et al., 2020). Previous studies have tended to focus on calculating instantaneous radiative forcing values; however, in reality, time-averaged results are more valuable for climate research. Here, we present data on the daily mean radiative forcing due to WSOC, BC, and WSOC + BC (Fig. 9). In general, for northeastern China we found the mean radiative forcing of WSOC in old (fresh) snow to be 3.78 (0.77) W m^{-2}, with regional mean values varying from 1.15 (0.21) to 4.88 (1.0) W m^{-2}. Zhou et al. (2021) reported daily mean radiative forcing by regional WSOC

(0.6–7.1 μg g^{-1}) of between ~0.04 and ~0.59 W m^{-2} for northwestern China, which is comparable to our values in fresh snow. Furthermore, the ratio of WSOC-driven to BC-driven radiative forcing varies within the range of 10.3 %–32.0 % (9.8 %–30.8 %) for old (fresh) snow, which is consistent with the results of our calculated albedo reductions. These results confirm that the role of WSOC must not be ignored in discussions about radiative balance in northeastern China. Similarly, the sizeable impact of WSOC on the absorption of UV radiation has the potential to influence biogeochemistry (Helms et al., 2013; Seekell et al., 2015), snow photochemical processes (e.g., photolysis of nitrate (NO_3^-) and nitrite (NO_2^-) in snow, in addition to the release of NO_x (NO + NO_2 and HONO). Snow photochemistry is beyond the scope of this study, however, the high concentrations of WSOC and nitrate (not shown) pollution in northeastern China make this a logical next step for research in this field.

4 Conclusions and atmospheric implications

During 2020 and 2021, we collected 34 surface samples of seasonal snow from sites throughout northeastern China to investigate the fluorescence characteristics, optical properties, and radiative effects of snowpack WSOC. With an average concentration of WSOC of 3.6 ± 3.2 μg g^{-1}, our results returned regional mean values of 3.4 ± 1.5 μg g^{-1} (SEIM), 5.7± 3.7 μg g^{-1} (SNC), 2.7 ±0.8 μg g^{-1} (NNC), 2.0 ± 1.3 μg g^{-1} (CBM), and 0.5 ± 0.2 μg g^{-1} (NEIM), indicating a considerable degree of regional variability of WSOC mass loadings. Measured values of WSOC fluorescence intensity (690–18600 RU nm^2) and light absorption (0.4–17.0 m^{-1}) are also highly variable.

Moreover, we also used EEMs and PARAFAC to identify three fluorescence WSOC components prevalent in northeastern China, and analyzed their regional differences. In SEIM, which is characterized by desert and bare soil surfaces, the signal of high-oxygenated and terrigenous HULIS-1 is dominant (47 %). The high degree of humification and minimal bioavailability of WSOC, indicating that snowpack

WSOC originates primarily from soil sources. In contrast, the autochthonous PRLIS signal (58 %) dominates in remote and clean NEIM. Low-oxygenated and anthropogenic HULIS-2 dominates the densely populated and intensively farmed SNC (51 %) and NNC (57 %) regions, leading us to conclude that the snowpack WSOC in SNC and NNC are influenced more by anthropogenic source. In CBM of forest environment, the impact of long-distance transport of pollutants is greater than that of the background environment. The above conclusions are also verified by fluorescence-derived indices.

We employed multiple regression analysis to estimate the fractional contributions of different WSOC components to snowpack light absorption. Throughout our study area, HULIS-1 tends to be the greatest contributor (~56 %–65 %) over the 280–400 nm range, followed by HULIS-2 (~19 %–30 %) and PRLIS (~12 %–17 %). In contrast to its primary role in fluorescence, the contribution of HULIS-2 to light absorption is relatively low across all regions, potentially reflecting the variable molecular structure of different components. Finally, we highlighted that the average RF due to WSOC in old (fresh) snow in northeastern China is 3.8 (0.8) W m^{-2}, which is equal to 19 % (17 %) of the BC-induced radiative forcing. Therefore, we demonstrated the important impacts of WSOC on the snow energy budget and potentially on triggering snow photochemistry. We indicate that our study could contribute to the understanding of carbon cycling processes, regional air quality, hydrological processes, and climate change in the earth systems. For example, the abundant WSOC concentrations measured in this study implied the significant carbon input from the atmosphere to the snowpack through wet or dry depositions in northeastern China. While the complex chemical compositions of snowpack WSOC could further influence the carbon balance of the snow environment by affecting microbial activities (Stedmon et al., 2007). The strong absorption properties of WSOC in the UV–Vis band also implied its important role in initiating snow photochemistry (McNeill et al., 2012). It will change the composition of organic compounds in the snow in turn (Grannas et al., 2007), and affect the surrounding air quality by releasing oxidizing gas like NO_x into the atmosphere (Zatko et al., 2013). Moreover, the non-negligible influence of WSOC on the snow albedo and radiative effect indicated that it could not only accelerate snow melting, change the periods and mass of water and carbon exchange between snowpack and underlying soils or vegetation (Meyer and Wania, 2008), but also potentially affect regional climate through changing the surface radiative balance (Beres et al., 2020).

Data availability. Data presented and used throughout this study can be accessed through the following data repository: https://doi.org/10.5281/zenodo.6541956.

Supplement. The supplement related to this article is available online at:

Author contributions. XN and WP designed the study and wrote the first draft with contributions from all coauthors. XN designed and conducted the lab experiments with the assistance of YZ and HW. XN processed the data with the assistance of DW and TS. XN, WP, YC, YX, TS designed and conducted the field campaign. XW supervised this study. All co-authors commented on the paper and improved it.

Competing interests. The authors declare that they have no conflict of interest.

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