

Response to Reviewer #1 Comments

General and Major Comments and Responses

General Comment 1 and Major Comment 3

This manuscript presented an extensive experimental data set for both fresh and aged PM_{2.5} source profiles of smoldering-dominated combustions of peat collected from six geographically different areas, representing four main climate regions. The reported results could provide a good reference for the emission factors especially of organic and elemental carbon species before and after atmospheric aging processes, facilitating better constrained modelling studies based on receptor-oriented source apportionment analysis. However, the reasons for the similarities and differences in the corresponding source profiles of the six types of peat seem to be not well explained. The analysis for PM_{2.5} Florida peat source profiles suggested that the two subtropical profiles should not be combined with other biomes. In this sense, how should the readers understand the equivalence measures for combined ‘Subtropical + Temperate’, or rather ‘Florida + Alaska’ in Table 2, where a high P-value was also reported? Consequently, how about the related experimental data for these two types of peat source profiles? Related clarification is needed.

Response 1

Three performance measures (i.e., correlation coefficient [r]; percent distributions of weighted difference -- residual [R]/uncertainty [U], the R/U ratios; and Student *t*-test) are used to provide guidance in grouping or compositing the 40 sets of fresh vs aged source profiles for further comparison. These measures are useful for qualitative data interpretations. The first comparison was made between the two Florida (subtropical) profiles to examine within region variations (Table S4). This is followed by the comparisons among the four biomes (i.e., boreal, temperate, subtropical, and tropical) in Table 2 which yielded statistical differences on paired comparisons except when combining the two fresh Florida profiles.

As pointed out by the Reviewer, the two Florida profiles should not be combined with the other biomes. The revised Table 2 shows the comparisons that separate the “Subtropical” into Subtropical 1 and 2 regions to represent peats from Putnam County Lakebed (Florida-1 [FL1]) and Everglades National Park (Florida-2 [FL2]) regions. The equivalence measures show similar results with or without separating the two Florida peats, except for the abnormalities found in Putnam (FL1) peats.

Among the six tested peats, the Putnam (FL1) peat fuel with the highest carbon content ($56.6 \pm 0.37\%$) and lowest oxygen content ($31.4 \pm 0.36\%$) (see Table 1 of Watson et al. (2019)) exhibited species abundance different from the other peats. As noted in the revised text, the “sum of species” to PM_{2.5} ratios decreased by 6–11% after atmospheric aging except for Putnam (FL1) peat, which shows similar mass fractions between the fresh and aged profiles. This is attributed to the lack of variations in organic carbon (OC), the largest PM_{2.5} component. After atmospheric aging, the OC abundance in PM_{2.5} for Putnam (FL1) peat only changes by ~0.5–1.5 %, much lower than the ~12–33% decreases for other peats; these are explained in different sections of the revised text.

Additional text revisions are added (Lines 233-265) to clarify the comparisons for “Section 3.1 Similarities and differences among peat profiles”:

The equivalence measures are used to provide guidance in compositing and comparing the 40 sets of fresh vs. aged profiles. The first comparison is made between two Florida samples from locations separated by ~485 km (i.e., Putnam County Lakebed [FL1] and Everglades National

Park [FL2]), representing different geological areas and land uses. Panel A of Table S4 shows that the two profiles yield high correlations ($r > 0.994$), but are statistically different ($P < 0.002$); with over 93 % of the chemical abundance differences within $\pm 3\sigma$. However, when combining both fresh Florida profiles (i.e., all Fresh 2 vs. all Fresh 7 in Panel B), statistical differences are not found, with over 98 % of abundance differences within $\pm 1\sigma$ and $P > 0.5$. Notice that statistical differences are found between the two fresh Florida profiles (i.e., FL1 Fresh 2 vs. FL2 Fresh 2 and FL1 Fresh 7 vs. FL2 Fresh 7 in Panel A) with few ($< 0.81\%$ and 5.6%) R/U ratios exceeding 3σ ; combining the two Florida profiles may cancel out some of the differences. However, paired comparisons of other combined profiles show statistical differences with low P -values ($P < 0.002$). To further demonstrate the differences, these two Florida profiles are classified as Subtropical 1 and Subtropical 2 to compare with other biomes.

Similarities and differences in peat profiles by biome are summarized in Table 2. Comparisons are made for: 1) paired fresh vs. aged profiles (i.e., All Fresh vs. All Aged; Fresh 2 vs. Aged 2; and Fresh 7 vs. Aged 7); 2) different experimental tests (i.e., Fresh 2 vs. Fresh 7); and 3) two aging times (i.e., Aged 2 vs. Aged 7). Equivalence measures show that most of these profiles are highly correlated ($r > 0.97$, mostly > 0.99) but statistically different ($P < 0.05$), with a few exceptions.

Group comparisons between fresh and aged samples (Panel A of Table 2) show statistical differences for all but Putnam (FL1) peat ($P > 0.94$). This is consistent with Watson et al (2019) where atmospheric aging (7 days) reduced organic carbon EFs (i.e., EF_{OC}) by $\sim 20 - 33\%$ for all but Putnam (FL1) peats (EF_{OC} remained within $\pm 0.5\%$). As OC is a major component of $PM_{2.5}$, no apparent changes in OC and carbon fractions abundances may dictate the lack of statistical differences between the fresh and aged profiles.

Paired comparisons for 2-day aging (Panel B of Table 2) show no statistical differences between the Fresh 2 vs. Aged 2 Putnam (FL1) and Malaysian profiles ($P > 0.30$ and 0.95), which may be due to the low number of samples ($n=2$) in the comparison; this results in no statistical differences for combined Putnam (FL1) and Malaysian peat comparison ($P > 0.62$). Similar to the findings of combining both fresh Florida profiles (i.e., all Fresh2 vs. all Fresh 7 in Table S4), the two fresh Alaskan profiles (Fresh 2 vs. Fresh 7 in Panel D of Table 2) do not show statistical differences ($P > 0.12$).

General Comment 2

Discrepancies between 2-day and 7-day aging which relate to the influence of photochemical aging on the evolution of chemical characteristics of biomass burning particles are lack of further interpretation. Details about the oxidation experiments using the PAM-OFR are insufficiently provided, although which might have been described elsewhere. The OH exposure or the photochemical age is definitely important, while other parameters such as the initial concentration of gaseous precursors, humidity, and seed particles are also key to the heterogeneous oxidation processes.

Response 2

Details on oxidation experiments using the PAM-OFR are addresses in Cao et al. (2019) and have been summarized in the revised supplemental material (Section S.1). Refer to Reviewer #2 comments and responses that address this issue. Reviewer #1 is correct in that initial gaseous precursor concentrations, humidity, and seed particles are key to the heterogeneous oxidation process. However, this manuscript emphasizes the variations between fresh and aged profiles after the oxidation process, not the fundamental chemical mechanisms that control the oxidative aging.

The PAM-OFR is used to provide sufficient oxidation to enhance gas-to-particle conversion over a short time period.

Although there are many source profiles available for fresh source contributions to PM_{2.5} concentrations, there is a dearth of regional source profiles to estimate pollution impacts from regional-scale sources. As smoldering peat fires produce long-lasting smoke that extend from urban- (~100 km) to regional- (~1,000 km) scales, the potential environmental impacts need to be investigated, especially in southeast Asia. As no information on PM_{2.5} speciated source profiles for peat combustion is available, this manuscript pioneers the use of PAM-OFR to simulate profile aging and illustrates the changes between fresh vs. aged source profiles. As noted by the Reviewer, this work contains a large amount of chemical data characterizing the emissions of laboratory-generated peat smoke particles, which could be useful for air quality modeling and further application on biomass-burning-aerosol-related research fields.

The selected aging times are limited to the maximum flow rate through the OFR (~10 L min⁻¹); relatively consistent dilution ratios (~3 to 5); and short sampling duration (~50–70 minutes) to achieve optimal particle loadings (~500 µg/filter) for subsequent chemical analyses (see Table S1 for operation condition). The manuscript intends to contrast the species abundances among fresh (diluted and unaged), intermediate-aged (~2 days), and well-aged (~7 days) source profiles that mimic source profile changes during atmospheric transport between source and receptor. The actual impact on source contribution estimates using fresh vs. aged profiles in chemical mass balance (CMB) or positive matrix factorization (PMF) (e.g., Watson et al., 2016) receptor models can be calculated based on the sensitivity tests.

Differences between 2- and 7-day aging times varied by peat types. These are discussed in Sections 3.1 to 3.6 for PM_{2.5} mass; sum of species to PM_{2.5} mass ratios; carbon abundances (i.e., OC and thermally evolved carbon fractions), organic mass [OM]/OC ratios, water-soluble organic carbon [WSOC], carbohydrates, and organic acids); nitrogen species, sulfate, and chloride abundances; and mass reconstruction. The “ratio of average” comparison in Figure 3 depicted that longer aging time (from 2- to 7-days) resulted in additional increases in ionic species (e.g., ammonium, sulfate, and nitrate) and organic acids, but decreases in low-temperature carbon fractions (e.g., OC1 and OC2 thermally evolved at 140 and 280 °C). Since species abundances are much lower for ionic species (~0.1% of PM_{2.5} mass) than those of carbon abundance (~1–10 %, see Figure 2), most of the data analyses are focused on carbon.

As much of the decreases (7–22 %) in OC abundance is attributed to changes in low temperature OC1 and OC2, new Figures S2 and S3 are added to highlight the additional degradation from 2- to 7-days of atmospheric aging. The following text are revised (Lines 328–342):

High temperature OC3 and OC4 contain more polar and/or high molecular-weight organic components (Chen et al., 2007) that are less likely to photochemically degrade. Large fractions of pyrolyzed carbon (OP of 7–13 %) are also found, indicative of higher molecular-weight compounds that are likely to char (Chow et al., 2018; Chow et al., 2004; Chow et al., 2001).

Reduction in OC abundances after atmospheric aging is attributed mostly to decreases in low temperature OC1 and OC2 abundances in the OFR as shown in the fresh vs. aged ratios of average abundances (Fig. 3). Figure S3a shows reductions in OC1 abundances after 2- and 7-days of atmospheric aging is apparent but at a similar level: ranging from 2–10 % and 3–14 %, respectively. Additional OC1 reductions from 2- to 7-days are most apparent for Russia and

Everglades (FL2) peats at the 6–10 % level. Similar reductions are found for OC2 (Fig. S3b): ranging from 3–11 % and 3–12 % after the 2- and 7-days of aging, respectively. Prolonged aging times resulted in additional 4–8 % OC2 reduction for all but Russian and Putnam (FL1) peats. As oxidation of organic compounds with OH radicals is an efficient chemical aging process (Chim et al., 2018), some of the VOCs and SVOCs may have been liberated (Smith et al., 2009).

General Comment 3 and Major Comment 1

How can the authors conclude that the volatilization of SVOCs during longer aging processes would serve as the main cause for the reduction of OM abundance in PM_{2.5}? One of the major concerns is the determinant reason behind the reduction of OM abundance in PM_{2.5} after an even longer photochemical aging. Further discussion would be required for the identification of the crucial influence from volatilization of SVOCs.

Response 3

Oxidation of organic compounds with gas-phase OH radicals is an efficient chemical aging process (Chim et al., 2018). The losses of low temperature OC1 and OC2 after atmospheric aging suggest volatilization of low-molecular weight and high vapor pressure OC components. These are further evidenced by field and laboratory chamber experiments that showed prominent mass spectrometric wood combustion markers (e.g., fragments of levoglucosan or other anhydrous sugars, pentene, butenal, and furfuryl alcohol) in OC1 and OC2 fractions that are likely degraded during atmospheric aging (Diab et al., 2015; Grabowsky et al., 2011). This is consistent with the flow tube reactor study of squalene by Smith et al. (2009) that particles lose carbon leading to particle volatilization.

However, as profiles age, reduction in “sum of species” and OC abundances can be offset by the formation of oxygenated organics. The increases on OM/OC ratios are further clarified with the addition of new Figure S4.

As OC abundances change by oxidation and varied by peat type, OM in this study represent unmeasured mass in organic compounds. It is determined by subtracting other components (i.e., mineral, ions, and EC) from PM_{2.5} mass. Therefore, the reduction of OM abundance in PM_{2.5} (Figure 6) by 3–18% after 7-days of aging can be attributed to effects of increased oxygenated organics, SVOC volatilization; and an increase in ionic species. The following sentences are revised to clarify:

--Lines 354–359:

Table 3 shows that OM/OC ratios ranged from 1.1–1.7 and 1.3–2.2 for fresh and aged profiles, respectively. The lower OM/OC ratios in fresh emissions are consistent with those reported for other types of biomass burning (Chen et al., 2007; Reid et al., 2005). Figure S4 shows a general upward trend in OM/OC ratios after atmospheric aging with additional 14–21 % increases from 2- to 7-days for all but Putnam (FL1) peat. The increase in OM/OC ratios with aging are likely due to an increase in oxygenated organics.

--Lines 483–486:

Although the 7-day aging time increased the OM/OC ratios (by 12–19 %), the abundances of OM in PM_{2.5} are reduced (3–18 %). This can be attributed to the combined effects of increased oxygenated organics; SVOC volatilization (Smith et al., 2009); and an increase in ionic species as shown in the average aged/fresh ratios in Fig. 3.

Major Comment 2

Why the mass fraction of WSOC in PM_{2.5} decreased after experiencing 2-day or 7-day aging for most of the peat samples?... the WSOC fraction Aged 7 was almost lower than that of Aged 2; what is the reason?...in previous studies which suggest that the oxygenated organic fraction tends to increase with atmospheric aging processes, contributing to a higher water-soluble organic fraction as the oxygenated organics are normally more polar/water-soluble than fresh biomass burning organic compounds.

Response 4

The WSOC/PM_{2.5} ratio is not a good indicator to understand the changes in WSOC abundances during atmospheric aging as PM_{2.5} also contains non-water-soluble and non-carbonaceous aerosol. The WSOC/PM_{2.5} ratios of Malaysian peat are used in the text to compare with past studies, not for paired comparison between fresh and aged profiles. To further explore changes of WSOC during aging, a new Table (now Table S6) is added. The large variabilities associated with the differences in WSOC abundance (i.e., aged minus fresh) suggest that no differences exist within ± 3 standard deviations, with the exceptions of the 7-day Putnam (FL) and 2-day Malaysian peats.

As WSOC is part of the OC, the WSOC/OC ratio is a better indicator to illustrate the effect of atmospheric aging. Irrespective of decreases in levoglucosan carbon/WSOC ratios and increased oxalic acid carbon/WSOC ratios after atmospheric aging (see Figure 4), the new Figure S5 shows apparent increases in WSOC/OC ratios with higher ratios after 7-day aging for all but the two Florida peats where similar WSOC/OC ratios were found between 2- and 7-days aging. This is consistent with the analogy pointed out by the Reviewer that "... atmospheric aging results in higher fractions of WSOC". The following text is revised to clarify this (Lines 376–388).

However, the WSOC/PM_{2.5} ratio is not a good indicator of changes in WSOC abundances during atmospheric aging as PM_{2.5} also contains non-water-soluble and non-carbonaceous aerosol. Table S7 shows large variabilities associated with the differences (i.e., aged minus fresh), suggesting that no differences exist within ± 3 standard deviations. The only exceptions are for the 7-day Putnam (FL1) peat and 2-day Malaysian peat, where aging resulted in 7–8 % increases of WSOC abundances in PM_{2.5}.

As WSOC is part of the OC, the WSOC/OC ratio is a better indicator of atmospheric aging. WSOC/OC ratios (Table 3) vary between fresh (0.18–0.64) and aged (0.31–0.71) profiles. Figure S5 shows a general increase of WSOC/OC ratios from fresh to aged profiles. Longer aging time from 2- to 7-days results in 5–10 % higher WSOC/OC ratios for all but the two Florida peats. OC water-solubility also varies by peat type. Russian peat OC emissions are largely water-soluble, whereas Malaysian peat emissions are mostly water-insoluble, with WSOC/OC ratios of 0.59–0.71 and 0.18–0.40, respectively.

Specific Comments

Specific Comment 1

Abstract: The expression of '5 orders of magnitude' sounds confusing. Is it supposed to be the discrepancy between reactive/ionic species and the carbon content, within ~ 3 orders of

magnitude? Following this, the authors mentioned about ‘the two distinguishable clusters’ in Sect. 3.3 of Line 244, Page 10. I would agree that species abundance in PM_{2.5} mass percent > 1% or 10% are distinct. However, it’s not clear to me why the results around 0.1% were regarded as one distinguishable cluster, as quite few data were actually covered within this range as displayed in Figure 2. Please clarify this point accordingly.

Response 5

Table 1 shows large variations of species abundance in PM_{2.5} from 10⁻⁵ to 10¹. However, the Reviewer is right that most species varied within ~three orders of magnitude. This is clarified in the revised text.

Because of the low abundances in reactive/ionic species, only a few species were included in original Figure 2. To demonstrate the two distinguished clusters, the revised Figure 2 included additional three ions (i.e., Na⁺, Cl⁻, and NO₂⁻) and three organic acids (i.e., formic acid, acetic acid, and propionic acid) that are below 1 % abundances. A 1:1 line and two circles are added to each graph in Figure 2 to delineate the two clusters. This is explained in the revised Figure 2 caption as well as in Abstract and text.

Specific Comment 2

Abstract: It’s a bit strange to say ‘low temperature OC’; are you trying to mean ‘highly volatile OC’?

Response 6

The low temperature OC1 and OC2 are referred to thermally-evolved carbon at 140 and 280 °C following the IMPROVE_A carbon analysis protocol (Chow et al., 2007) that is applied in long-term U.S. PM_{2.5} networks. This low temperature carbon is likely considered highly volatile OC. The sentence is revised (Lines 32–35) as:

Organic carbon (OC) accounted for 58–85 % of PM_{2.5} mass in fresh profiles with low EC abundances (0.67–4.4 %). OC abundances decreased by 20–33 % for well-aged profiles, with reductions of 3–14 % for the volatile OC fractions (e.g., OC1 and OC2, thermally evolved at 140 and 280 °C).

Specific Comment #3

What is the relationship between “Elemental Carbon (EC) and “EC1, EC2, EC3” in this study? I assumed the EC here was the sum of EC1+2+3, similar to that of OC; however, the mass fraction of EC is much lower than that of EC1 or EC2, as summarized in Table 1. Please provide the corresponding discussion.

Response 7

Elemental carbon (EC) is the sum of EC1+EC2+EC3 minus pyrolyzed carbon (i.e., OP) whereas organic carbon (OC) is the sum of OC1+OC2+OC3+OC4 minus OP. Since a large fraction of OP (7–13%) are found--indicative of higher molecular-weight compounds that are likely to char, the resulting EC may be lower than those of EC fractions after OP correction. This explanation is added to the footnote of Table 1.

Specific Comment 4

Figure 3: Why does the ratio of EC of Borneo, Malaysia increase for the A2/F2 but decrease for the A7/F7 scenario, which is different from all the other types of peat? Additionally, do you have any idea on the increase of EC ratio for the A7/F7 case of Pskov, Siberia?

Response 8

For smoldering dominant peat emissions, the abundance of EC in PM_{2.5} are low in the range of 0.82 to 4.4 % with no apparent changes between fresh and aged profiles. Figure 3 shows large uncertainties are associated with the A2/F2 and A7/F7 ratios. The decrease in A7/F7 ratio for Malaysian peats is mainly due to the low and variable EC abundances (0.67 ± 0.94) in aged profiles. Similarly, the increase in A7/F7 ratio for Siberian peat is also due to the low and variable EC abundance (0.83 ± 1.30) in aged profiles.

Specific Comment 5

In Sect. 3.4.2, the authors used the IMPROVE soil formula by Malm et al. (1994) to calculate the mass of mineral components. How do you think of the uncertainty in such an estimation, considering that large variabilities in the corresponding mineral species even exist for the six different types of peat? Further, is it appropriate to apply an empirical equation for the US country into the conditions for different origins representing various climate regions (i.e., boreal, temperate, subtropical, and tropical)? Corresponding details are preferred.

Response 9

As shown in Figure 6, mineral components only account for a small fraction (0.07–2.9 %) of PM_{2.5}. These variations may be due to the extent of the degraded peats (Miettinen et al., 2017) used in the experiments. The IMPROVE soil formula from Malm et al. (1994) is selected as it has been applied in many other studies (e.g., Chan et al., 1997; Pant et al., 2015; Rogula-Kozłowska et al., 2012) which provides an adequate estimate of geological mineral in reconstructed mass.

Since geological minerals are not a major component of PM_{2.5}, variations in the assumption regarding metal oxides or multipliers do not contribute to large variations in reconstructed mass (Chow et al., 2015). The following revisions are made to clarify this (Lines 494–498):

The IMPROVE soil formula has been applied in many other studies (e.g., Chan et al., 1997; Pant et al., 2015; Rogula-Kozłowska et al., 2012) which provides an adequate estimate of geological mineral in reconstructed mass. Since geological minerals are not a major component of PM_{2.5}, variations in the assumption regarding metal oxides or multipliers do not contribute to large variations in reconstructed mass (Chow et al., 2015).

Technical Corrections

1. Abstract, line 37: "...the reduction of OM abundances in PM_{2.5} by 3–18 % after 7 days aging". A similar issue exists in some other sentences (e.g., Lines 238, 279, 287, 478, 502, etc.), since the 7-day here is just an equivalent duration for laboratory oxidation but not a real time period. Please check through the manuscript.

Response 10: The Reviewer is correct that 7-days is an equivalent duration of laboratory oxidation, not a time period. This is clarified in the "Abstract" (Lines 25–28) and in the "Introduction" (Lines 116–118):

Lines 25–28:

Smoke from laboratory chamber burning of peat fuels from Russia, Siberia, U.S.A. (Alaska and Florida), and Malaysia representing boreal, temperate, subtropical, and tropical regions was sampled before and after passing through a potential aerosol mass-oxidation flow reactor (PAM-OFR) to simulate intermediate-aged (~2 days) and well-aged (~7 days) source profiles.

Lines 116–118:

Comparisons between fresh (diluted and unaged) and aged (represent intermediate-aged [~2 days] and well-aged [~7 days] laboratory simulated oxidation with an OFR) PM_{2.5} speciated profiles are made to highlight chemical abundance changes with photochemical aging.

2. Page 5, line 95: "...and elsewhere ~~where~~ it is transported over long distances".

Response 11: Corrected

3. Page 7, line 161: "...A portion (0.5 cm²) of the other half quartz-fiber filter ~~half~~ ..."

Response 12: Corrected

4. Page 17, line 477: "... the majority of the TC is ~~in~~ OC..."

Response 13: Corrected

References

- Cao, J.J., Wang, Q.Y., Tan, J., Zhang, Y.G., Wang, W.J., Zhong, B.L., Ho, S.S.H., Chen, L.-W.A., Wang, X.L., Watson, J.G., Chow, J.C., 2019. Evaluation of the oxidation flow reactor for particulate matter emission limit certification. *Atmos. Environ.*, submitted.
- Chan, Y.C., Simpson, R.W., McTainsh, G.H., Vowles, P.D., Cohen, D.D., Bailey, G.M., 1997. Characterisation of chemical species in PM_{2.5} PM₁₀ aerosols in Brisbane, Australia. *Atmos. Environ.* 31, 3773-3785.
- Chen, L.-W.A., Moosmüller, H., Arnott, W.P., Chow, J.C., Watson, J.G., Susott, R.A., Babbitt, R.E., Wold, C.E., Lincoln, E.N., Hao, W.M., 2007. Emissions from laboratory combustion of wildland fuels: Emission factors and source profiles. *Environ. Sci. Technol.* 41, 4317-4325.
- Chim, M.M., Lim, C.Y., Kroll, J.H., Chan, M.N., 2018. Evolution in the reactivity of citric acid toward heterogeneous oxidation by gas-phase OH radicals. *ACS Earth and Space Chemistry* 2, 1323-1329.
- Chow, J.C., Lowenthal, D.H., Chen, L.-W.A., Wang, X.L., Watson, J.G., 2015. Mass reconstruction methods for PM_{2.5}: A review. *Air Qual. Atmos. Health* 8, 243-263.
- Chow, J.C., Riggio, G.M., Wang, X.L., Chen, L.-W.A., Watson, J.G., 2018. Measuring the organic carbon to organic matter multiplier with thermal/optical carbon mass spectrometer analyses. *Aerosol Science and Engineering* 2, 165-172.
- Chow, J.C., Watson, J.G., Chen, L.-W.A., Arnott, W.P., Moosmüller, H., Fung, K.K., 2004. Equivalence of elemental carbon by Thermal/Optical Reflectance and Transmittance with different temperature protocols. *Environ. Sci. Technol.* 38, 4414-4422.
- Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., Merrifield, T.M., 2001. Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Sci. Technol.* 34, 23-34.
- Diab, J., Streibel, T., Cavalli, F., Lee, S.C., Saathoff, H., Mamakos, T., Chow, J.C., Chen, L.-W.A., Watson, J.G., Sippula, O., Zimmermann, R., 2015. Hyphenation of a EC/OC thermal-optical carbon analyzer to photo ionization time-of-flight mass spectrometry: A new off-line aerosol mass spectrometric approach for characterization of primary and secondary particulate matter. *Atmos. Meas. Tech.* 8, 3337-3353.
- Grabowsky, J., Streibel, T., Sklorz, M., Chow, J.C., Mamakos, A., Zimmermann, R., 2011. Hyphenation of a carbon analyzer to photo-ionization mass spectrometry to unravel the organic composition of particulate matter on a molecular level. *Analytical and Bioanalytical Chemistry* 401, 3153-3164.
- Malm, W.C., Trijonis, J.C., Sisler, J.F., Pitchford, M.L., Dennis, R.L., 1994. Assessing the effect of SO₂ emission changes on visibility. *Atmos. Environ.* 28, 1023-1034.
- Miettinen, J., Hooijer, A., Vernimmen, R., Liew, S.C., Page, S.E., 2017. From carbon sink to carbon source: Extensive peat oxidation in insular Southeast Asia since 1990. *Environmental Research Letters* 12.
- Pant, P., Shukla, A., Kohl, S.D., Chow, J.C., Watson, J.G., Harrison, R.M., 2015. Characterization of ambient PM_{2.5} at a pollution hotspot in New Delhi, India and inference of sources. *Atmos. Environ.* 109, 178-189.
- Reid, J.S., Eck, T.F., Christopher, S.A., Koppmann, R., Dubovik, O., Eleuterio, D.P., Holben, B.N., Reid, E.A., Zhang, J., 2005. A review of biomass burning emissions part III: intensive optical properties of biomass burning particles. *Atmos. Chem. Phys* 5, 827-849.
- Rogula-Kozłowska, W., Klejnowski, K., Rogula-Kopiec, P., Mathews, B., Szopa, S., 2012. A study on the seasonal mass closure of ambient fine and coarse dusts in Zabrze, Poland. *Bulletin of Environmental Contamination and Toxicology* 88, 722-729.

Smith, J.D., Kroll, J.H., Cappa, C.D., Che, D.L., Liu, C.L., Ahmed, M., Leone, S.R., Worsnop, D.R., Wilson, K.R., 2009. The heterogeneous reaction of hydroxyl radicals with sub-micron squalane particles: a model system for understanding the oxidative aging of ambient aerosols. *Atmos. Chem. Phys* 9, 3209-3222.

Watson, J.G., Cao, J., Wang, Q., Tan, J., Li, L., Ho, S.S.H., Chen, L.-W.A., Watts, A.C., Wang, X.L., Chow, J.C., 2019. Gaseous, PM_{2.5} mass, and speciated emission factors from laboratory chamber peat combustion. *Atmospheric Chemistry and Physics Discussion*, online.

Table S6
Differences of WSOC abundances^a in PM_{2.5} between the aged and fresh profiles

Peat Location	Differences and associated uncertainties between aged and fresh WSOC abundances in PM _{2.5}	
	2-day aging	7-day aging
Odintsovo, Russia	-5.17 ± 4.16 ^b	-6.56 ± 6.72
Pskov, Siberia	6.04 ± 7.34	-2.62 ± 8.91
Northern Alaska, USA	-0.97 ± 9.80	-5.81 ± 11.93
Putnam County Lakebed, (FL1), USA	3.18 ± 6.44	6.82 ± 1.86
Everglades National Park, (FL2), USA	-2.82 ± 9.30	-11.05 ± 5.57
Borneo, Malaysia	8.26 ± 2.51	5.75 ± 2.90

^aSee Table 1 for WSOC abundances in PM_{2.5}.

^bDifference in WSOC abundance= Aged minus Fresh. Plus or minus signs indicate the increase and decrease, respectively in WSOC/PM_{2.5} ratios after atmospheric aging; the uncertainty of the difference is based on square root of the sum of the squared uncertainties associated with each averaged profile.

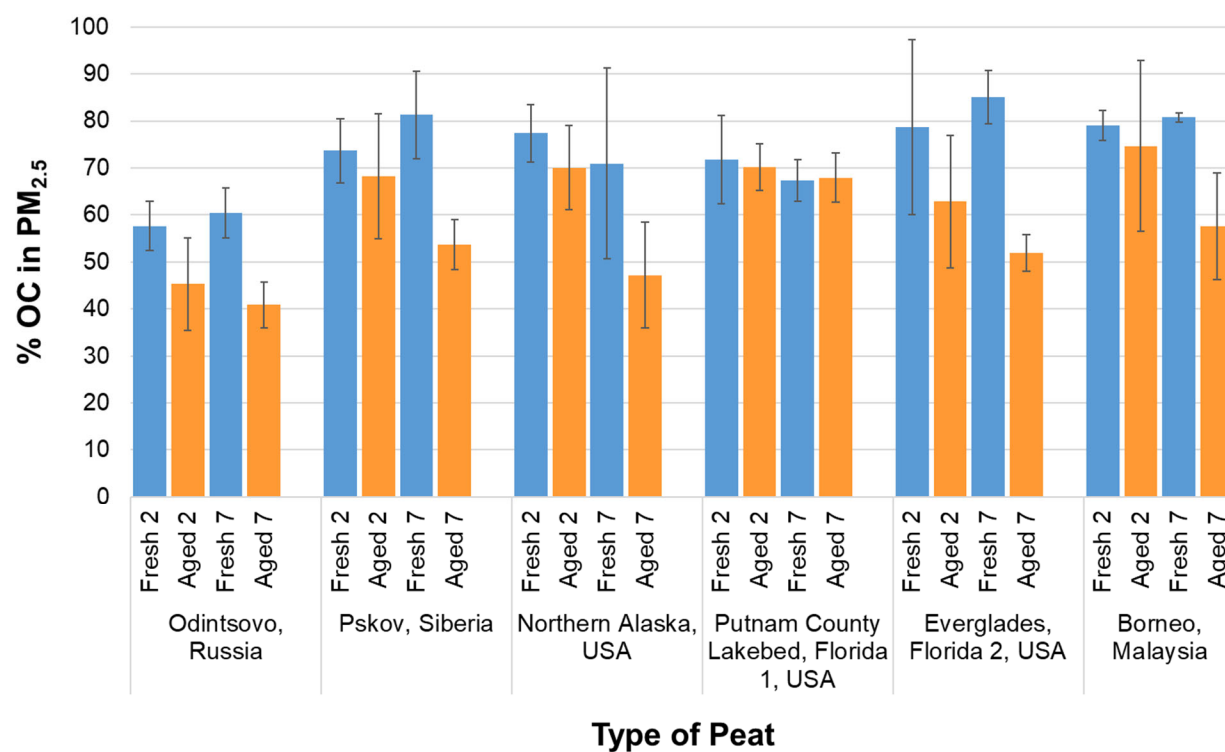
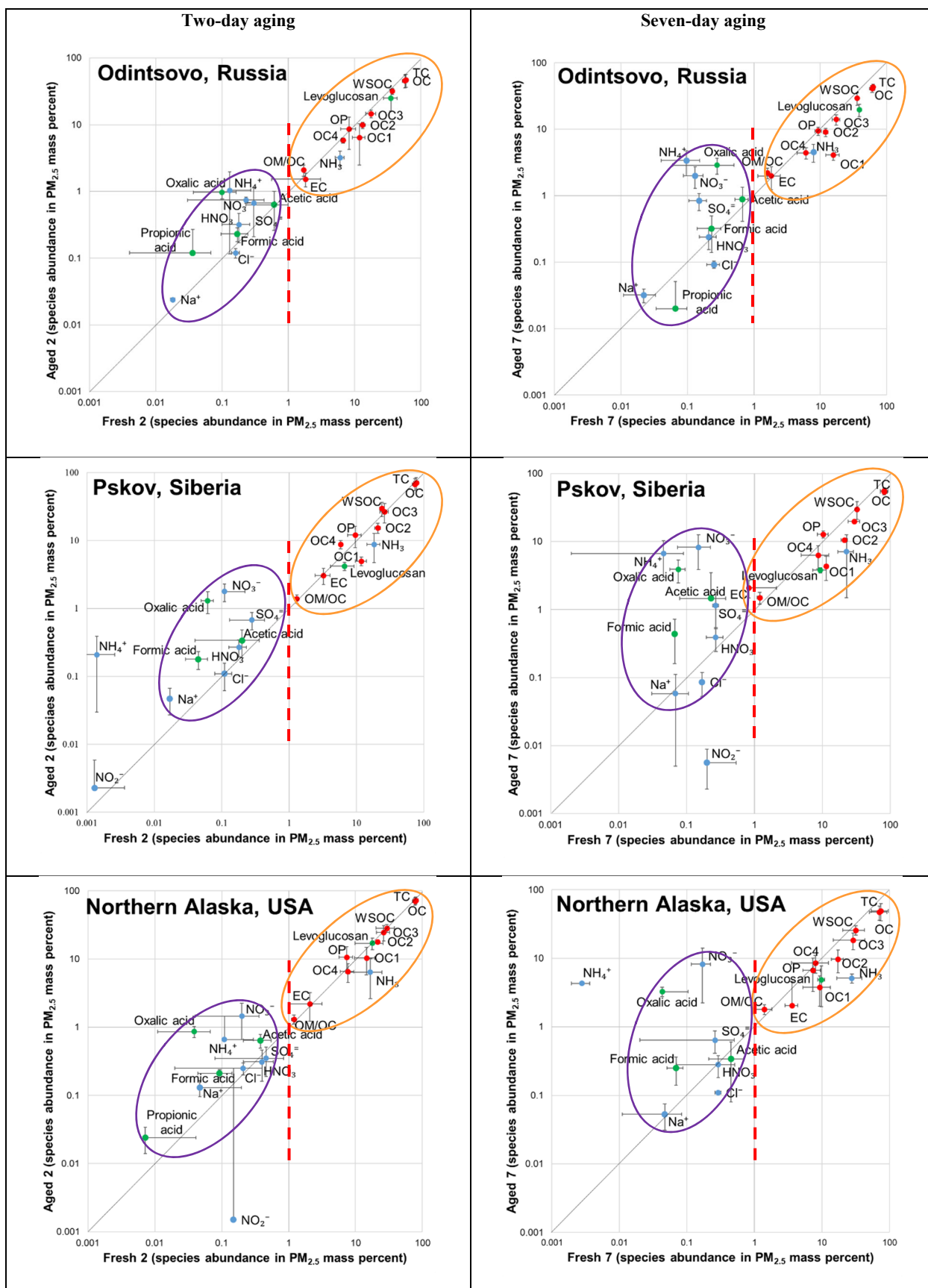
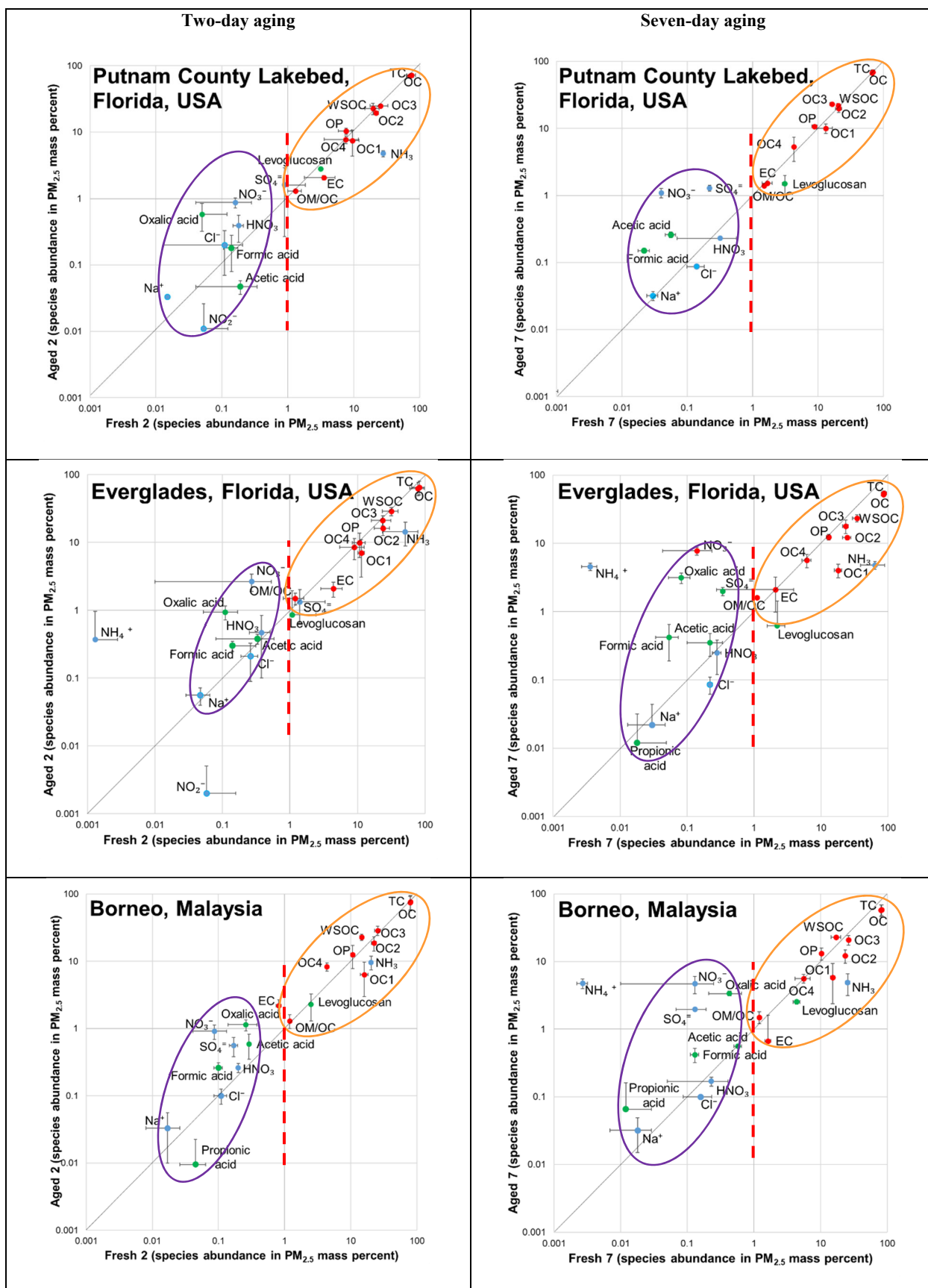


Figure S2. Further reduction of OC abundances in PM_{2.5} (~7–22%) from 2- to 7-days of aging are found for all but Putnam (FL1) peat profiles (Fresh 2 vs. Aged 2 and Fresh 7 vs. Aged 7 represent the comparison of 2- and 7-days of atmospheric aging, respectively).





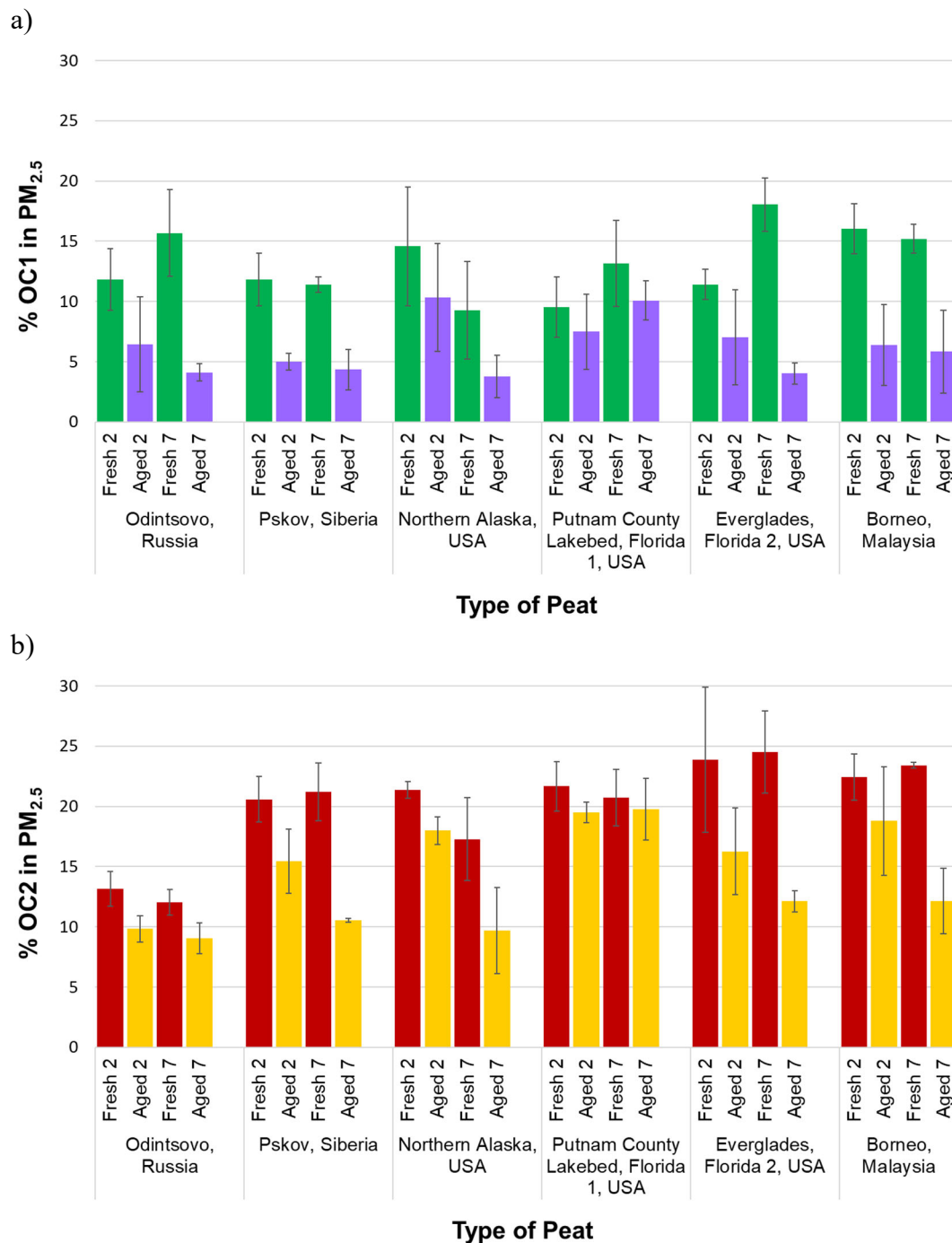


Figure S3. Reduction of low temperature OC1 (a) and OC2 (b) after 2- and 7-days of atmospheric aging. The OC1 and OC2 are carbon fractions thermally evolved at 140 and 280 °C in a helium atmosphere following IMPROVE_A thermal/optical reflectance protocol (Chow et al, 2007) that are applied in U.S. long term IMPROVE network and Chemical Speciation Network (CSN). (Fresh 2 vs. Aged 2 and Fresh 7 vs. Aged 7 represent the comparison of 2- and 7-days of atmospheric aging, respectively).

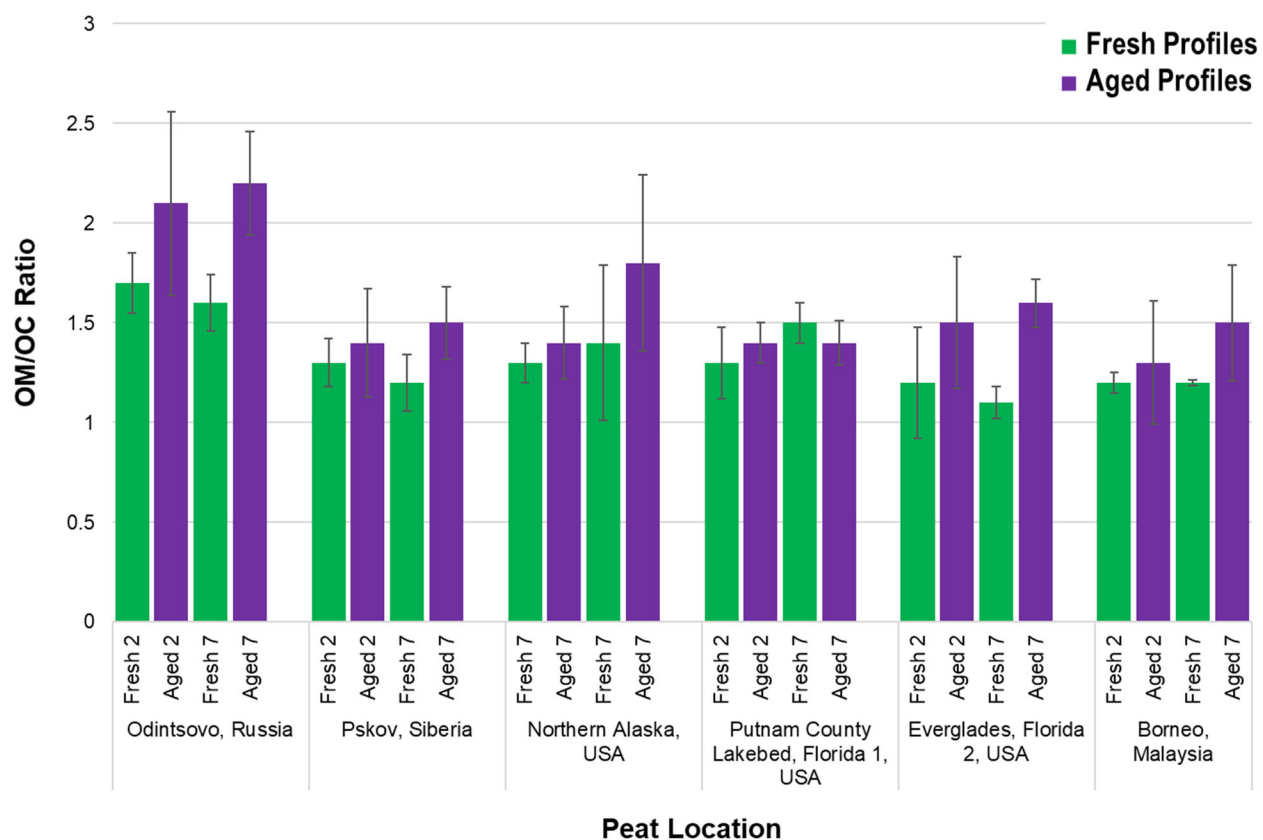


Figure S4. The OM/OC ratios between fresh and aged aerosol (Fresh 2 vs. Aged 2 and Fresh 7 vs. Aged 7 represent the comparison of 2- and 7-days of atmospheric aging, respectively).

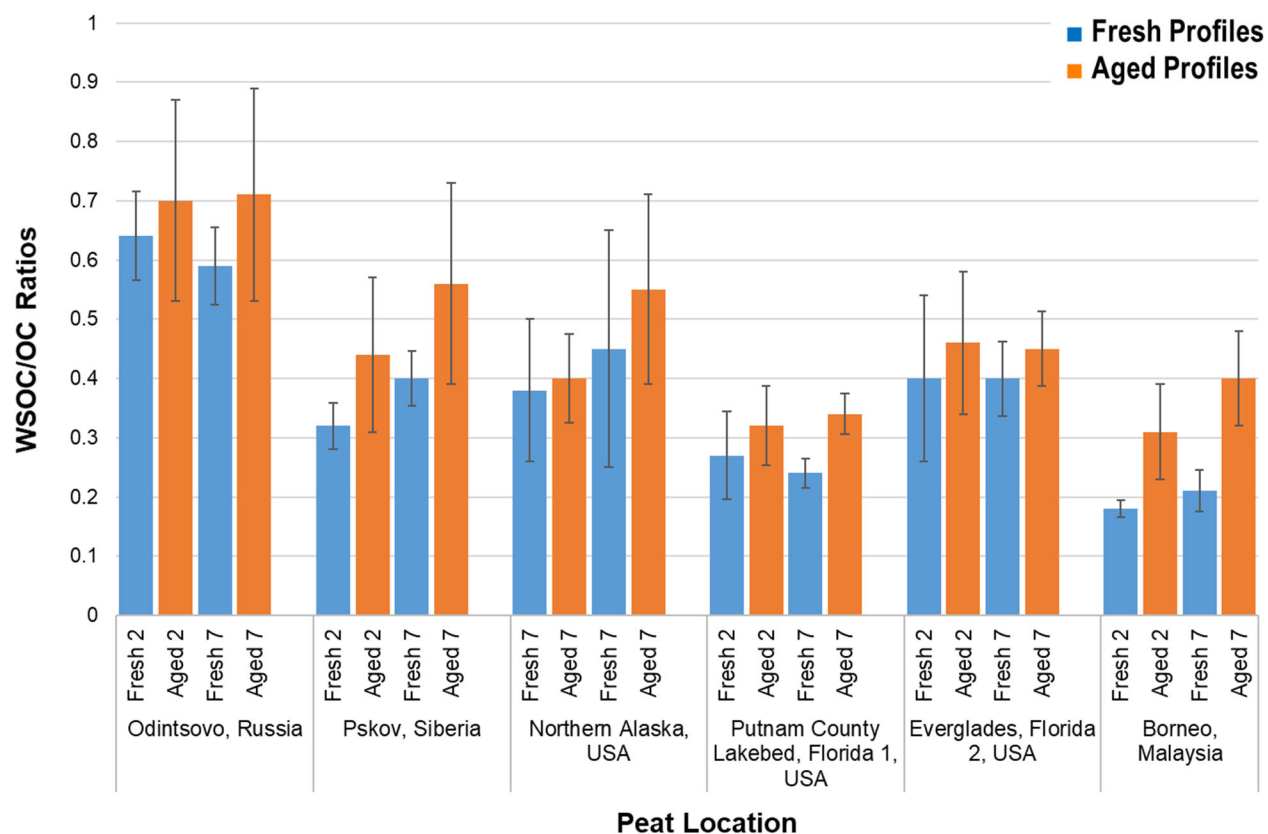


Figure S5. Ratios of water-soluble organic carbon (WSOC) OC between fresh and aged peat profiles (Fresh 2 vs. Aged 2 and Fresh 7 vs. Aged 7 represent the comparison of 2- and 7-days of atmospheric aging, respectively)