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# Molecular Characterization of Water-Soluble Aerosol Particle Extracts by Ultrahigh-Resolution Mass Spectrometry: Observation of Industrial Emissions and an Atmospherically Aged Wildfire Plume at Lake Baikal

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ABSTRACT: Air pollution over Lake Baikal originating from anthropogenic emissions as well as wildfire events and secondary organic aerosol (SOA) formation poses a threat to this world heritage ecosystem. During a ship expedition in 2018, ambient aerosol particles were sampled on filters at different locations of Lake Baikal and extracted to obtain the fraction of water-soluble organic aerosol (WSOA). Subsequent analysis by Fourier transform ion cyclotron resonance (FTICR) mass spectrometry with direct-infusion electrospray ionization (ESI) in both ionization modes provides insights into the molecular composition of polar and high-molecular-weight species in WSOA. Light absorption spectral dependence determined by absorption Ångstrom exponent (AAE) is correlated to summed compound class abundancies to



identify light-absorbing compounds. Most detected species are heavily oxidized, associated with intense atmospheric aging, and contain significant amounts of nitrogen or sulfur, with the most abundant compound classes being CHO, CHON, and CHOS. Nitrogen-containing species are more frequently found in positive ESI and correlate well with AAE. Oxygen-to-nitrogen ratios (O/N) larger than 3 indicate organic nitrates, and also less oxidized nitrogen species can be linked to brown carbon (BrC). ESI in both ionization modes provides complementary molecular information with, on the one hand, more sensitive detection of high average carbon oxidation state ( $OS_C$ ) and low-volatility oxidized organic aerosol species in negative mode, and on the other hand, lower  $OS_C$  ( $OS_C < 0$ ) species as well as oligomers and potential biomass burning organic aerosol in positive mode. Additionally, a great overlap of sum formulae was found at all sampling sites along the expedition route, regardless of the potential primary emission sources, indicating strong atmospheric aging and mixing, leading to a similar oxidized organic aerosol (OOA) from different primary sources. **KEYWORDS:** *air pollution, Fourier transform ion cyclotron resonance mass spectrometry, electrospray ionization, solid-phase extraction, HULIS, biomass burning, BrC* 

# INTRODUCTION

Lake Baikal, the deepest lake in the world (1642 m), is the world's largest freshwater lake and contains approximately 20% of the global freshwater resources.<sup>1</sup> Baikal's waters are transparent, contain little suspended matter and amount of salts (96 mg/L) as well as high contents of oxygen (9–11 mg/L) at all depths.<sup>2,3</sup> This rift lake is located in Southern Siberia between the federal subjects Irkutsk Oblast and Buryatia and surrounded by the Baikal Mountains (north), the Barguzin Ridge (northeast), the Baykal'sky Ridge (northwest), Primorsky and Khamar Daban Ridges (south) with altitudes of more than 2000 m. In the greater region of Lake Baikal, steppe landscape in the West changes to boreal forest in the East, dominated by coniferous trees, such as larch and pine. Due to its outstanding variety of endemic flora and fauna, in 1996,

Lake Baikal was listed as UNESCO World Heritage Site. However, a number of integrity issues have been raised to now because of concerning pollution levels.<sup>4</sup> Particularly, anthropogenic emissions from the more populated southern basin have been shown to affect the water and air quality.<sup>5–7</sup> Moreover, it has been observed that the number of wildfires (WF), which naturally occur in that region, and the size of the

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area burned have increased over the past decades.<sup>6,8,9</sup> Hence, anthropogenic emissions pose directly and indirectly a threat to the ecosystem of Lake Baikal.

Air pollution in the Baikal region by means of elevated levels of fine particulate matter (PM), containing black carbon (BC) and organic aerosol (OA), as well as  $NO_x$  originates from midto long-range transport over more than 100 km.<sup>6,10,11</sup> Although typical products of incomplete combustion of fossil fuels or biomass, such as polyaromatic hydrocarbons (PAH), can be detected in OA,<sup>12</sup> primary aerosols, e.g., from combustion processes, have undergone substantial physical and chemical transformation, during its transport through the atmosphere.<sup>13</sup> Atmospheric aging, which is strongly driven by the availability of  $HO_{xy} O_{xy}$  and  $NO_{xy}^{14}$  is able to increase OA concentrations through gas-to-particle conversion. Organic vapors are oxidized to more polar compounds with decreased vapor pressure, condensing on ambient aerosol particles or nucleating as new particles (secondary organic aerosol, SOA).<sup>16,17</sup> In the further course, atmospheric aging proceeds in the condensed phase by, for example, oligomerization or heterogeneous oxidation.<sup>18–20</sup>

From a chemical perspective, aged OA is more functionalized and increased in its content of heteroatoms added to the hydrocarbon backbone.<sup>15</sup> Consequently, also the water solubility is increased, establishing the fraction of water-soluble organic aerosol (WSOA) or water-soluble organic carbon (WSOC). A significant fraction of WSOA (20–80%) is also referred to as humic-like substances (HULIS), but it is not strictly defined and therefore subject to the influence of the applied solid-phase extraction (SPE) method.<sup>21–23</sup>

Light-absorbing organic compounds in the atmospheric aerosol are often referred to as brown carbon (BrC) and show an important impact on the distribution of heat between atmosphere and surface.<sup>24,25</sup> A significant portion of lightabsorbing species is water-soluble (40% of total BrC absorption), e.g., nitro-aromatic compounds, but the chemical composition is not fully characterized.<sup>26,27</sup> Furthermore, WSOA contributes to aerosol hygroscopicity and may initiate cloud formation,<sup>28</sup> thus affecting the climate through direct and indirect aerosol radiative effects. Additionally, WSOA from aging of biogenic and anthropogenic SOA precursors as well as WSOA in ambient PM2.5 have been demonstrated to contain significant amounts of reactive oxygen species (ROS), which are linked to higher oxidative potentials and enhanced PM toxicity.<sup>29,30</sup> Moreover, the water-soluble fraction of wood tar, used as a proxy for biomass burning OA, showed enhanced production of total cellular ROS, decreased mitochondrial membrane potential, and induced oxidative damage in BEAS-2B cell exposure,<sup>31</sup> emphasizing the relevance of this OA fraction also for primary OA sources. Also for biomass burning plumes, increasing oxidative potentials were found for the fraction WSOA with increasing atmospheric transport time.<sup>32</sup>

In this study, PM was sampled near-water during a ship expedition in 2018, starting at the more populated South of Lake Baikal to the pristine region in its Northern part, as described in Popovicheva et al.<sup>6</sup> For molecular-level analysis and in-depth chemical characterization, electrospray ionization (ESI) is particularly suitable to investigate the chemical composition of the WSOA fraction because of its selectivity and sensitivity to polar compounds. While ESI in negative mode (ESI–) ionizes acidic compounds by deprotonation, ESI in positive mode (ESI+) affords access to molecules of higher proton affinity and complex forming tendencies with alkaline metals.<sup>33</sup> Ion detection by ultrahigh-resolution mass spectrom-

etry (UHRMS) allows accurate mass assignments of which sum formula and elemental composition may be derived. Thus, the analyses conducted are complementary to a previous study on aerosol optical properties and source attribution of PM,<sup>6</sup> providing molecular dimension in the composition of WSOA using parameters from sum formula attribution.

### EXPERIMENTAL SECTION

Samples and Sample Collection. For this study, 20 quartz microfiber filter samples (4.7 cm diameter, QM-A, Whatman, Maidstone, U.K.) collected during a ship-based expedition campaign on Lake Baikal in 2018 were analyzed. A detailed description of the filter sampling, methods, route (Figure S1), and other parameters of the campaign as well as backward air mass trajectories and data for nearby wildfire events can be found elsewhere.<sup>6</sup> Absorption Ångstrom exponents (AAE) of PM deposited on filters, using a multiple-wavelength light transmission instrument (seven wavelengths), are used to characterize the light-absorbing properties of aerosol samples.<sup>34-36</sup> Filter samples showed varying AAE values (Figure 2) ranging from 0.9, which was mainly attributed to industrial emissions and fossil fuel burning associated with black carbon (BC), to 3.6, which may be caused by, e.g., biomass burning and other sources of strong light-absorbing compounds (brown carbon, BrC).<sup>37</sup> Knowledge of backward air mass trajectories and the time of wildfire events in the area enabled the identification of samples influenced by wildfire plumes (samples 15-20, Table S1). More detailed data on the duration, size, and location of wildfire events that influenced the sampling in this study can be found elsewhere.<sup>6</sup> Additionally, equivalent BC concentrations were measured as an indicator of how intensely a filter sample was influenced by combustion aerosol emissions.

Extraction of WSOA. Each filter sample was cut with a cleaned blade, and one half was placed in a pre-baked extraction vial. WSOA was extracted by adding 10 mL of water (high-performance liquid chromatography (HPLC) grade) and gently shaking it for 30 min on a rotary shaker. The extracts were then filtered through a 0.2  $\mu$ m poly(tetrafluoroethylene) (PTFE) membrane (Sartorius, Goettingen, Germany) in a stainless-steel filter holder via a glass syringe. Finally, the filtered extracts were subjected to a preconditioned solid-phase extraction (SPE) cartridge (Oasis 60 mg HLB, Waters, Milford) for desalting and enrichment. For SPE, the cartridge was activated with 5 mL of methanol (LC-MS grade), equilibrated with 1 mL of 0.01 M hydrochloric acid, loaded with the filter extract adjusted to pH 2 with hydrochloric acid, and finally rinsed two times with 1 mL of water before drying with an applied vacuum.<sup>23</sup> After elution with 1.8 mL of methanol, the extracts were stored at -25 °C until further analysis. The limitations of the applied SPE method regarding the loss of low-molecular-weight and very hydrophilic compounds are described in detail elsewhere.<sup>21,23</sup> A field blank filter was extracted according to the same procedure and used for blank correction.

**Instrumentation.** Ultrahigh-resolution FTICR-MS measurements were carried out on a SolariX (Bruker Daltonik, Bremen, Germany) equipped with a 7 T superconducting magnet. The samples were analyzed in positive and negative ionization modes with a direct-infusion ESI ion source setup (Bruker Daltonik, API Ion Source). The following ionization parameters were selected for positive/negative-ion mode (ESI +/ESI-) respectively: Capillary voltage, -3.3/3.5 kV; drying



**Figure 1.** Relative abundance (intensity) variation of sum formula groups during the expedition of 2018, with samples heavily affected by wildfire plumes marked orange. (A) ESI– and (B) ESI+ relative abundance of CHO,  $CHON_1$ ,  $CHON_2$ , and CHOS compound classes. (C) ESI– and (D) ESI+ modes of AI, H/C, and O/C ratio-based sum formula classes. Sample numbers are assigned with the wind direction during their sampling (N: north, E: east, S: south, W: west, Table S1).

gas temperature, 180/200 °C; drying gas flow rate, 4.0 L/min; nebulizer gas flow rate, 1.4 bar; quadrupole mass, 120 m/z; and syringe flow rate, 200  $\mu$ L/h. A total of 200 scans were collected for each measurement with a 1.96 s (4M) transient with a resulting resolving power of >310 000 at m/z 400.

Mass Spectrometric and Statistical Data Analysis. External calibration of the Fourier transform ion cyclotron resonance (FTICR)-MS was performed using an arginine standard solution. An internal calibration of each mass spectrum was performed by characteristic and commonly abundant peaks from a self-generated calibration list (CHO<sub>x</sub>) CHNO<sub>x</sub> class compounds, manually verified) achieving subppm mass accuracies. Raw data were peak-picked (cutoff: S/N = 9) and exported with Bruker Data Analysis 5.1 (Bruker Daltonik, Bremen, Germany). The exported mass spectra were processed by self-written MATLAB algorithms and routines were combined in a graphical user interface named CERES Processing. After careful investigation and taking into account attribution boundaries from the literature, the following restrictions were deployed for elemental composition assignment in the range of  $120-1000 \ m/z$ :  $C_c H_h N_n O_o S_s Na_{nai}$ ,  $5 \le c \le 100, 5 \le h \le 200, n \le 3, o \le 20$ .<sup>38-40</sup> For ESI+:  $s \le 1, na \le 1$ 1 and a maximal error of 1 ppm or ESI-:  $s \leq 2$ , na = 0, with a maximal error of 1.5 ppm. Additional restrictions were applied for the H/C ratio: 0.4-2.4 and double-bond equivalents: DBE 0 - 40.

Attribution of the molecular formulae gives access to further descriptive parameters. Herein, DBE values were calculated from eq 1. Aromaticity index modified for high oxygen content (AI<sub>mod</sub>) was calculated from eq 2.<sup>41</sup> Average carbon oxidation state (OS<sub>C</sub>) was calculated from eq 3.<sup>42</sup> Saturation vapor pressure (C\*) was estimated from eq 4, and detailed parameters are described in Table S2.<sup>43-45</sup>

$$DBE = c - \frac{h}{2} + \frac{n}{2} + 1$$
(1)

$$AI = \frac{1 + c - 0.5o - s - 0.5h}{c - 0.5o - s - n}$$
(2)

$$\overline{OS_{\rm C}} = 2\frac{o}{c} - \frac{h}{c} \tag{3}$$

$$\log_{10} C^* = (n_{\rm C}^0 - n_{\rm C}) b_{\rm C} - n_{\rm O} b_{\rm O} - 2 \frac{n_{\rm C} n_{\rm O}}{n_{\rm C} + n_{\rm O}} b_{\rm CO} - n_{\rm n} b_{\rm n} - n_{\rm s} b_{\rm s}$$
(4)

Based on aromaticity index and O/C and H/C ratios, each sum formula can be classified in one of five groups representing an orientation for possible sources and structures:  $^{41,46,47}$  aliphatics and peptides (H/C 1.5–2.0), highly unsaturated and weakly oxygenated species (AI < 0.5, H/C < 1.5, O/C < 0.5), highly unsaturated and highly oxygenated species (AI < 0.5, H/C < 1.5, O/C > 0.5), vascular plant-derived polyphenols (AI 0.5–0.67, H/C < 1.5), and combustion-derived condensed aromatics (AI > 0.67, H/C < 1.5).

Spearman rank correlation coefficients were calculated by the MatLab R2020b Statistics Toolbox (The MathWorks, Inc., MA). Uncertainties of average values are given as the standard deviation.

Relative intensities of sum formulae are calculated by normalization to the sum of intensities of all assigned sum formulae of the respective sample.

#### RESULTS AND DISCUSSION

A previous study of Popovicheva et al.<sup>6</sup> based on the same expedition of Lake Baikal in 2018 investigated the aerosol optical properties including LIDAR sounding of the troposphere as well as particle number, particle size distribution, equivalent black carbon mass (eBC), and absorption Ångstrom exponent (AAE) over Lake Baikal. A nonuniform spatial–temporal variability of aerosol characteristics was found, indicating the impacts of various emissions from touristic and residential areas on the coast, remote wildfires, as well as industrial areas (Table S1). The most severe atmospheric pollution was associated with coal power plants in the region of Lake Baikal as well as residential coal and biomass burning. Hourly levels of PM10 during the ship expedition appeared in the range of  $2-33 \ \mu g \ m^{-3}$ .

Filter samples were categorized according to the wind direction during sampling, as the trajectories of the air masses are mostly straight. Air masses from northwest (NW) direction transport emissions from industrial and anthropogenic sources into habitat areas, especially during sampling in the southern part of Lake Baikal (Figure S1, samples 3-8, 22). Northeastern (NE) wind directions transport PM from less inhabited areas across the lake, and winds from the north (N) transport air masses affected by wildfire plumes from the pristine north of Lake Baikal (samples 15-20). Eastern (E) wind directions transport air masses affected by emissions from remote areas east of the lake (samples 11-14).

Molecular Composition of Ambient Aerosol WSOA with ESI-FTICR-MS. Measurements of all filter extracts show apparent differences in positive and negative ionization mode spectra because of different sensitivity and selectivity for basic and acidic compounds in both techniques.<sup>48</sup> In the respective ionization polarity, the samples show a similar distribution pattern of WSOA compounds, mainly observed in the range of m/z 150–800 in positive mode and m/z 150–650 in negative mode. The average number of assigned sum formulae with ESI- is 1400, ranging from 1700 to as low as 300 sum formulae (Figure S2). In ESI+, a significantly higher number of sum formulae could be attributed. The average number is 2900, ranging from 1900 to as many as 5500 sum formulae. Both possible adducts (Na<sup>+</sup> and H<sup>+</sup>) are counted as individual formulae. The high variation of sum formula number is likely a result of the substantial variation in sampling time and therefore volume as well as the inevitable variable character of ambient aerosol composition and its natural atmospheric concentration fluctuation over days and weeks.<sup>49,50</sup>

Figure 1 A and B show the relative intensity distribution of the compound classes in negative and positive modes, respectively. In both cases, CHO is the most abundant compound class ranging from 35 to 79% in ESI+ and 15 to 66% in ESI-. CHO species may contain typical products from incomplete combustion, e.g., thermal decompositions products of lignin or carbohydrates as well as from atmospheric aging. Detected WSOA sum formulae are in the range of 5-50 carbon atoms and 0-18 oxygen atoms. Oxidation reactions that add oxygen to a molecule may decrease its volatility and increase its polarity and therefore water solubility.43,51 Most detected compounds are heavily oxidized (average of around six and eight oxygen atoms in positive and negative modes, respectively) and belong to the CHO, CHON, or CHOS class, which is an expected result for ambient aerosol WSOA.<sup>52</sup> An overview of the distribution of oxygen atom numbers in ESI+ in each class for two exemplary samples, influenced by different primary emission (wildfire and industrial), shows similar maxima in the range of 4-6 oxygen atoms for nitrogen- and sulfur-containing molecules and a bimodal distribution with maxima at 6 and 11 oxygen atoms for CHO compounds (samples 6 + 16, Figure S3), indicating a comparable degree of oxidation through atmospheric aging, which will be discussed more in the following sections.

Other products of atmospheric aging belong to the class of CHON species, which may be formed by atmospheric reactions involving  $NO_x$  or  $NH_3$ . One of the frequently discussed species are organic nitrates which are formed by nitrate radical oxidation at nighttime or by reaction with hydroxyl radicals and NO during daytime.<sup>53,54</sup> Other nitrogencontaining functional groups like amines, imines, nitro groups, or ring structures are also possible products of atmospheric

aging reactions.<sup>55–58</sup> To evaluate the influence of reactions adding to the nitrogen backbone, the CHON compound class is separated into  $CHON_1$  and  $CHON_2$ , which represent most molecules that contain oxygen as well as nitrogen. The former is more abundant in this dataset, with relative intensities ranging from 18 to 52% in ESI+ and 3 to 28% in ESI-, while the latter displays intensities ranging from 3 to 16% and 2 to 28% respectively. The presence of significant portions of CHON compounds with two nitrogen atoms suggests a strong influence of nitrogen adding atmospheric aging reactions

CHOS compounds (relative intensity 2 to 15% and 8 to 80% ESI $\pm$ ), including organic sulfates, are also a well-known class in atmospheric aerosols due to their formation through secondary sulfonating reactions or oxidation of direct emission from the combustion of sulfur-containing fossil fuels like coal or fuel oils.<sup>59,60</sup> The formation is dependent on the presence of acidic sulfate-containing aerosol or the availability of SO<sub>2</sub> during photooxidation.<sup>61</sup> Also, sulfur is an essential nutrient in plants that can be taken up from the soil and also from the atmosphere as SO<sub>2</sub>, leading to the formation of, e.g., disulfide bonds in the plant-protein structure.<sup>62</sup> Different studies have also shown the occurrence of nitrooxy-organosulfates (CHNOS) in urban, rural, and forest aerosols.<sup>63–65</sup> However, this species was not identified in this study.

Generally, in ESI-, the abundance of CHOS is frequently higher than the summed CHON classes abundance, which is explained by the higher acidity of, e.g., sulfate or sulfonate functional groups compared to amine, nitro, or comparable nitrogen functional groups (excluding nitrate) and the concomitant selective ionization in ESI–.  $^{48}$  This observation highlights the need to account for both ionization modes and their respective selectivity (Table S3). Moreover, adding to the selectivity of ESI, another approach to categorize nitrogen- and sulfur-containing groups is to use the elemental ratios O/N and O/S.<sup>66</sup> An organic nitrate moiety  $(-(O)NO_2)$  has an O/ N of at least 3 or higher, depending on additional oxygencontaining functional groups, while an amine or nitro group can have an O/N ratio lower than 3 and a peroxyacetyl nitrate an O/N ratio of 5 or higher. The limitation of this approach becomes apparent when oxidation reactions, appearing at other reactive centers of a CHON species, can lead to an increase of the O/N ratio although the nitrogen-containing functional group is, e.g., an amine. Table S4 shows the relative number of sum formulae with O/N smaller than and equal to or larger than 3 and 5 in each sample. The variation between the samples is low in both ionization modes, with sum formulae of O/N < 3 making up 28 ± 5 and 11 ± 3% of CHON compounds in positive and negative modes, respectively. Together with the selectivity of the ionization modes, the higher relative abundance in ESI+ can be explained by the detection of nitro or amino groups as well as basic aromatic nitrogen (e.g., pyridine), which fit the limit of O/N and show sufficient proton affinity. Nitrogen compounds with C=N and C-N functional groups and low O/N ratio were identified as the two most important chemical bonding structures of BrC in summer in methanol filter extracts from a Chinese megacity.<sup>67</sup> On the other hand, in ESI-, the abundance of higher oxidized molecules is higher  $(O/N = 3-5, 52 \pm 3 \text{ and } 62 \pm 3\%, \text{ESI}\pm, 100 \text{ eV}$ respectively), which could be explained by the ionization of organic nitrates in combination with other acidic oxygencontaining functional groups. Sum formulae with an even higher O/N ratio of larger than 5 could be assigned to peroxyacetyl nitrate (PAN) compounds, which can act as a

way of transporting NO<sub>x</sub> to remote areas by long-range transport. Species with O/N ratios fitting this criterion are abundantly found in the dataset ( $20 \pm 3$  and  $27 \pm 3\%$ , ESI $\pm$ , respectively), suggesting the presence of PAN species transported from NO<sub>x</sub> emission sources.<sup>68,69</sup>

Looking at the O/S ratios, limits can be defined at ratios of 4 and 7. Organic sulfates  $(-OSO_3H)$  or sulfonates  $(-SO_3)$ , with additional oxygen-containing groups, are found at O/S > 4 or, for a better separation of highly oxygenated species, at O/S >7. At ratios below O/S = 4, less oxidized sulfur functional groups like sulfones  $(-SO_2-)$ , sulfonic acid  $(-SO_3H)$ , sulfinic acid (-SO<sub>2</sub>H), or sulfides are possible, among others.<sup>55,70</sup> Compared to the CHON compounds, CHOS species show a higher variation of relative abundance from sample to sample and the relative number of each O/S ratio group is more evenly distributed (ESI+: 28, 40, 33%, respectively, Table S5). Interestingly, in ESI-, most sum formulae have an O/S ratio below 4, which concludes that no sulfate group is present in these molecules, if only one sulfur atom is included. Therefore, other functional groups like sulfonate or sulfonic acid-type structures may be more likely, which is also in good agreement with the literature.55

Further classification of identified compounds based on the sum formulae was carried out as described above in the Experimental Section, based on aromaticity as well as H/C and O/C ratio. The most dominant groups in ESI+ are aliphaticand peptide-like compounds with a relative abundance of 71-91% with an average of 81% (Figure 1D). All other groups only account for a relatively small percentage, e.g., highly unsaturated species (high and low oxygen contents) with a combined average of 5%, plant-based polyphenols with 6–16% and condensed aromatics with 0.1-6% that may account for relevant light-absorbing properties as well as high carcinogenic potency.<sup>71</sup> However, it has to be mentioned that the overall abundance of the classified compounds does only account for  $32 \pm 11\%$  in ESI + and  $50 \pm 20\%$  in ESI- of the total abundance. In ESI-, a more homogeneous distribution between the samples can be observed (Figure 1C). It should be noted that the classification of sum formulae into groups like peptides or plant-based polyphenols is not necessarily equal to the real molecular structure or emission origin but serves as a proxy for classification. Although some filters were sampled partially during nighttime and sampling ended before sunrise, as described in Table S1, no clear influence of day/ night is observed due to atmospheric aging of several days.

BrC Species in WSOA. Compound classes, based on either elemental composition or chemical moieties, that show a significant correlation to AAE (Figure 2) indicate potential effects on light absorption properties (Figure S4). Despite the strong UV light-absorbing properties of condensed aromatics due to their conjugated double bonds,<sup>71</sup> they did not show a significant correlation with AAE in this study. We attribute these findings to the fact that aqueous extraction and electrospray ionization are not suited for the detection of a large fraction of nonpolar aromatic hydrocarbons. Moreover, partially oxidized aromatic compounds, which are more sensitively detected by ESI, can lose light-absorbing properties in the visible and UV-A range as the addition of functional groups often disrupts aromaticity, which is known as the 'photobleaching effect" on aerosols during atmospheric aging.<sup>72</sup> Thus, most BrC species are part of the water-insoluble fraction of BrC, which often shows greater light-absorbing properties than the water-soluble fraction.<sup>73</sup> Nevertheless,



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Figure 2. AAE values (bar) as well as equivalent black carbon mass (eBC) (blue dot) of filter samples with orange marked wildfire plume influenced samples. Samples are assigned with the wind direction during their sampling (Table S1).<sup>6</sup>

plotting of the summed CHON<sub>1</sub> class intensity (ESI+,  $r_S = 0.68$ , p < 0.05) as well as the CHOS class (ESI-,  $r_S = 0.62$ , p < 0.05) with AAE in Figure S5 shows how an increase in UV light absorption is related to the relative abundance of the CHON and CHOS compound classes. Especially nitrogen-containing compounds are in the focus for being a part of BrC responsible for a significant share of light absorption due to their molecular properties.<sup>67,74</sup> This formation of BrC species during atmospheric aging may be driven by the presence of ammonia or ammonium salts as found for laboratory aging of VOCs in the gas phase or aqueous phase, counteracting photobleaching.<sup>75,76</sup> Similar sum formulae are also found in this study.

Recently, it was found that sulfur-containing groups are not significant chromophores and therefore contribute negligibly to the light absorption properties of BrC. The correlation of CHOS compound intensity with AAE could be explained by the positive effect of SO<sub>2</sub> on the formation of nitrogen-containing BrC species under high NO<sub>x</sub> high-relative-humidity conditions, also seen by a significant correlation of CHON<sub>1</sub> and CHOS<sub>1</sub> compound classes (Figure S4).<sup>67</sup>

Chemical Characterization of Oxidized Organic Aerosols (OOA). Five of the 20 filter samples (samples 15–20) were identified to be impacted by wildfire plumes originating from long-range transport from areas north of Lake Baikal (Yakutia or Krasnoyarsk region).<sup>6</sup> The straight-line distance of wildfire events is in the range of a few hundred up to a thousand kilometers and the age of these air masses varies from 1 to 5 days. In contrast, the southwestern part of Lake Baikal is the location of larger industrial and urban areas, especially around the city of Irkutsk (Figure S1, samples 3–8, 22).

Although primary emissions like industrial fossil fuel burning or wildfires can be assigned to the sampling of each filter by means of, e.g., backward air mass trajectories, atmospheric aging during the transport from the emission sites to the sampling sites changes the chemical composition of the emitted compounds. With increasing oxidation of OA, the water solubility is also increased; hence, the WSOA fraction is well representing the aged aerosol. The OM/OC ratio of each sample was also calculated, which shows uniformly high values (Table S6), which is an indicator of high shares of SOA.<sup>77</sup> To examine the remaining differences of aged OA emitted from different sources, four exemplary samples, influenced by



**Figure 3.** ESI-(+)-FTICR mass spectra of exemplary industrial (left, sample 6) and WF-Yakutia-influenced (right, sample 16, long-range transport from wildfires in Yakutia) filter extract, intensity normalized to TIC, as well as pie charts of the relative abundance (number) of each compound class as insert. Separated CHO (black),  $CHON_{1-2}$  (dark/light blue), and  $CHOS_{1-2}$  (red) species as well as the whole spectra (gray) are shown.



**Figure 4.** Average  $OS_C$  vs carbon number plot of exemplary industrial (A) and Yakutia-wildfire (B)-affected ambient aerosol filter extract (sample 6/16, ESI+/ESI-: blue-green/red-black) with potential organic aerosol classes marked gray, the average value marked with a cross (ESI+/ESI-: blue/red) and *m/z* value indicated by the colormaps. ESI+ with a high abundance of molecules in the semivolatile oxidized organic aerosol (SV-OOA) and biomass burning organic aerosol (BBOA) classes. ESI- with the highest abundance in the low-volatility oxidized organic aerosol (LV-OOA) class.<sup>42,43,77</sup> The black dotted line indicates the trend of ESI+ signals towards the upper right corner.

wildfires in the Yakutia (sample 16) and Krasnoyarsk (sample 20) regions (long and short aging, respectively), as well as an industrial (sample 6) and a background sample (sample 10) were selected.

Figure 3 shows the ESI-(+)-FTICR mass spectra of two exemplary filter extracts from two different main primary emissions: industrial and WF-Yakutia (2703 and 2510 sum formulae, respectively). Only the main compound classes CHO, CHON, and CHOS are displayed in the mass spectra, accounting for above 90% of the overall response. A detailed description and discussion of the displayed mass spectra as well as additional ESI- data can be found in the Supporting Information (Figures S6 and S7).

Looking at single molecules and sum formulae of the wildfire-affected samples, some prominent marker molecules previously discussed in the literature are found in this dataset. One of the most frequently discussed compound classes of primary OA related to WF or biomass burning, in general, is the CHO class. Sum formulae that formally fit oxygenated aromatic compounds like 1-phenyl-1-penten-3-one  $(C_{11}H_{12}O)$ , 4-dimethyl-1,3-isobenzofurandione (C10H8O3), or (methyl)-1,3-dihydroxynapthalene  $(C_{10}H_8O_2)$  are part of the identified WF compounds and also of the studies on the chemical composition of Northern California wildfire plumes.<sup>78</sup> Wellknown biomass burning markers coniferylaldehyd  $(C_{10}H_{10}O_3)$ and sinapinic acid  $(C_{11}H_{12}O_5)$  were also detected here, although it has to be noted that these assignments are based on the sum formulae and no structural information was obtained. However, these relatively small molecules are at the lower end of the m/z detection range of the FTICR-MS instrument setup. Low intensities of the molecules in this study therefore do not accurately reflect the real concentration in the sample, as it is the case for all raw signal intensities measured by ESI. Their detection, despite the low sensitivity of the system for this case, suggests the presence in significant concentrations.

Average Carbon Oxidation State of Oxidized Organic Aerosol. The average carbon oxidation state  $(OS_C)$  of each sum formulae is calculated from eq 3 as a metric for the degree of oxidation of organic species and serves as an additional approach to describe the highly complex organic aerosol.<sup>42</sup>

For WSOA, an increase of carbon oxidation state is mainly based on one of two reasons: First, the formation of carbonheteroatom bonds (functionalization), and second, the breaking of carbon-hydrogen bonds (fragmentation).<sup>42</sup> Reactions that lead to an increase in carbon number (e.g., oligomerization), which are an important part of the aging of secondary organic aerosol, therefore do not necessarily change  $OS_C$  but increase the molecular mass. It should be mentioned that the OS<sub>C</sub> of all sum formulae was calculated the same by considering only O/C and H/C, although heteroatoms other than oxygen may lead to a small error, as the oxidation states of, e.g., sulfur and nitrogen differ from oxygen but are commonly not considered. Despite distinct abundancies of CHON and CHOS classes, the average N/C and S/C ratios in all samples are low (N/C < 0.05, S/C < 0.01); hence, the bias of the OS<sub>C</sub> is negligible. A more detailed discussion of this bias in OS<sub>C</sub> can be found elsewhere.<sup>42</sup>

Comparing positive and negative ESI data (Figures 4 and S8), it is apparent that the average carbon oxidation state is higher in ESI– (e.g., for WF-Yakutia, Figure 4B:  $OS_C = -0.23$ ) than in ESI+ ( $OS_C = -0.86$ ). In contrast, the average number of carbon atoms (#*C*) is higher in ESI+, and as discussed before, the overall number of sum formulae is higher. This suggests that in ESI–, ionization and detection of highly functionalized species, e.g., formed by atmospheric aging, is promoted because functional groups like carboxyl ( $-CO_2H$ ), hydroxyl (-OH), sulfate ( $-OSO_3H$ ), sulfonic acid ( $-SO_3H$ ), and nitrate ( $-NO_3$ ) increase the OS<sub>C</sub> and are potentially more efficiently ionized by ESI–.

ESI+ shows a much broader chemical space with high abundances of molecules with up to 40–50 carbon atoms and almost exclusively negative  $OS_C$ . Higher  $OS_C$  values would be a result of higher oxidation of carbon atoms, e.g., through atmospheric aging, which would at some point necessarily lead to the formation of acidic functional groups (e.g., carboxyl), which ESI+ does not ionize without the presence of other basic functional groups. Additionally, comparing both wildfire samples in ESI+ (Figures 4B and S8B), a divergent trend of intensity distributions is visible, with the WF-Yakutia sample showing a rising curve with increasing  $OS_C$  and decreasing #C, and the WF-Krasnoyarsk sample showing an ecliptic behavior not reaching positive  $OS_C$  values toward lower #C.

Higher carbon numbers indicate products of secondary reactions like oligomerization which are a point of focus for the characterization of SOA and the influence of atmospheric aging on aerosol emissions and BrC. Species in the area of semivolatile and low-volatile oxidized organic aerosol (average relative sum formula number in each area for ESI+/ESI-: SV-OOA  $(14 \pm 4)\%/(12 \pm 2)\%$ , LV-OOA  $(1 \pm 1)\%/(11 \pm 3)\%)$ can be attributed to differently aged secondary organic aerosol produced by several sequential oxidation steps, based on the observation that longer aging leads to higher oxidation states, higher oxygen content, and higher hygroscopicity.<sup>80,81</sup> Potential organic aerosol classes like SV-OOA and LV-OOA (e.g., gray areas in Figures 4 and S9) are based on AMS data as well as volatility measurements from the literature. 42,43,77 Products of prolonged aging were prominently found in ESIand, in combination, SV-OOA and LV-OOA are the most important organic aerosol classes that were assigned. The overall abundance weighted average of OS<sub>C</sub> and carbon number is also close to these areas. Primary emissions of biomass burning (average relative sum formula number biomass burning organic aerosol: BBOA ( $24 \pm 4.3$ )%/( $4 \pm 2.8$ )%) seem to be more readily detected with ESI+ as they display the highest relative number in these datasets. The average of OS<sub>C</sub> and carbon number is close to the BBOA area in ESI+ and shifted to higher OS<sub>C</sub> in ESI–.

Most sum formulae are not assigned to any of the defined organic aerosol classes, as they are shifted to higher carbon numbers and m/z values. Still, the OS<sub>C</sub> values of these formulae are like those in the lower-carbon-number region. This can be explained by the formation of thermodynamically stable oligomers in the particle phase. Oligomer formation is frequently observed in laboratory aging of SOA precursors like  $\beta$ -pinene and naphthalene in an oxidation flow tube reactor (OFR).<sup>82</sup> Figure S9 shows the #C vs OS<sub>C</sub> plots of methanol filter extracts from the photooxidation of  $\beta$ -pinene and naphthalene in an OFR. A distinct repetitive pattern along the carbon number axis is visible, resulting from oligomerization reactions of a single precursor. Comparable to the WSOA from Lake Baikal, higher masses are observed in ESI+ compared to ESI-. Also, the anthropogenic SOA precursor naphthalene shows higher oxidation states than the biogenic precursor  $\beta$ -pinene. When focusing on the molecular composition of the CHO class with a direct comparison of sum formulae found in the Baikal WSOA and in the precursor, anthropogenic and biogenic influences on the ambient WSOA may be examined more in detail (Figure S10). It is shown that the overlap with the SOA from a biogenic precursor is higher in each sample, but still, a significant overlap with the anthropogenic SOA precursor is present. Considering the sampling sites at Lake Baikal and the wind direction, some correlations with the SOA from the two precursors are observed. When sampling was influenced by air masses transported from the east of Lake Baikal, BPIN overlap was the highest in both ionization modes (ESI+/ESI-: 15%/25%, samples 11-14), which can be explained by the dominating forests and absence of human emission sources in the eastern region of Lake Baikal. The anthropogenic overlap was higher when air masses arrived from the northwest along the Angara River, especially for samples taken at the southwest part of the lake (samples 3-8, 22) and also in some of the wildfireinfluenced samples (samples 15-17). It should be noted that only CHO species are considered in this comparison and that identical sum formulae do not necessarily belong to the same molecular structures.

Since the organic aerosol classes discussed are closely related to the volatility of the compounds, it is useful to also consider a parameter like the saturation vapor pressure  $(C^*)$ , which depends on the molecular weight and chemical structure and can be approximated from the attributed elemental composition by the number of oxygen, nitrogen, sulfur, and carbon.<sup>43,45,51</sup> Combining C\* as a measure for volatility and OS<sub>C</sub> as a measure of oxidation enables the classification of molecular formulae into similar organic aerosol classes as described in Figure 4, with an additional layer of information. In the case of  $log(C^*)$  vs OS<sub>C</sub> (Figure S11) for the exemplary WF and industrial primary emission samples, there are apparent differences in positive and negative ionization modes and significant shifts of intensity in the respective organic aerosol classes BBOA, SV-OOA, and LV-OOA. Furthermore, these aerosol classes were connected to the compound classes from elemental analysis by UHRMS (Figure 5). As expected, all detect compounds have low volatility



**Figure 5.** Relative abundance (number) of molecules separated by compound class (CHO, CHON, CHOS) found in the respective areas of saturation vapor pressure ( $C^*$ ) and carbon oxidation state ( $OS_C$ ) chemical space in ESI– (top) and ESI+ (bottom).<sup>42,45</sup> Low-volatility oxidized organic aerosol (LV-OOA, blue) is more pronounced in ESI–, while biomass burning organic aerosol (BBOA, green) is more sensitively detected in ESI+, as well as semivolatile oxidized organic aerosol (SV-OOA, petrol) and hydrocarbon-like organic aerosol (HOA, red). Samples are assigned with the wind direction during their sampling. The relative abundance of compounds in the dominating oligomer area is not displayed; all data are found in Table S7 in the Supporting Information.

 $(\log(C^*) < 5)$  because the analytical approach aims to look at low-volatility and high-polarity compounds determined by their solubility in water and the selectivity of ESI and FTICR-MS.

The dominating OA class in all samples are the oligomers  $(OS_C < 0, log(C^*) < -2)$ , which are not displayed in Figure 5 for better visualization. The oligomer species are most likely an aging product of precursor molecules, which are assigned in one of the other aerosol classes. Oligomers show a similar carbon oxidation state as the precursor molecules, but a much lower vapor pressure. Therefore, the discussion will be focused on the other assigned classes. Numerical values of all OA classes are given in Table S7 in the Supporting Information. Next to oligomers, the highest abundance in ESI- is found for the low-volatility oxidized organic aerosol class (LV-OOA,  $OS_C 0-1$ ,  $log(C^*) < 0$ ), which shows the highest abundancy for each sample in the CHO and CHON class. It is less present in the CHOS class, but especially sample 9 shows a completely different distribution compared to any other sample with 50% biomass burning OA (BBOA,  $OS_C$  –0.75 to –1.75,  $log(C^*)$ -2 to 1.5) as well as 10% semivolatile oxidized OA (SV-OOA,  $OS_C - 1$  to 0,  $log(C^*) - 2.5$  to 1.5). Filter sampling for sample 9 took place on the Boyarsk-Selenga route in the southern part of Lake Baikal (Figure S1). Backward air mass trajectories show a shift in wind direction from northwest to northeast, transporting a few days aged air masses, affected by wildfires in the northern region of Lake Baikal, almost over the entire northern coast.<sup>6</sup> An explanation for the unusually high number of sulfur-containing BBOA (mostly  $CHO_rS_2$ ) could be the aging of wildfire emissions under the influence of acidic sulfate aerosol from oxidation of SO2 released from coal combustion.<sup>7,66</sup>

ESI– detects molecules with higher  $OS_C$  values compared to ESI+ because of higher functionalization with acidic functional groups, which leads to higher oxidation states. Those high  $OS_C$ compounds are consequently assigned to LV-OOA, also for the nitrogen-containing species. This observation is similarly confirmed by the second-highest OA class in most samples, SV-OOA, which also includes high  $OS_C$  values ( $OS_C - 1$  to 0).

In contrast, the dominating class in ESI+ is BBOA, with a lower range of  $OS_C$ , as well as SV-OOA to some degree. It is therefore suggested that ESI+ is more beneficial for the characterization of incomplete biomass burning emissions than ESI-. This is in good agreement with other studies that compared data of ESI in both polarities, as well as other ionization techniques like APPI.62,83,84 When comparing CHO, CHON, and CHOS data, the abundance of BBOA and SV-OOA is highest for all compound classes, but CHON and CHOS additionally show high abundancy of hydrocarbonlike OA (HOA,  $OS_C - 2$  to 1.5,  $log(C^*) - 2.5$  to 1.5). Sources for HOA are often identified as engine emissions from, e.g., diesel fuels or other fossil fuels.<sup>80</sup> The HOA, in this case, does not consist of pure hydrocarbons but of semi-/low-volatile species with low carbon oxidation state and apparently, nitrogen or sulfur, that are partially soluble in water and possess at least some amount of polarity to be ionized by ESI. Interestingly, the HOA class shows a high relative intensity for ESI+ CHON compounds, which suggests that these compounds contain nitrogen functional groups with significant proton affinity, e.g., basic nitrogen in aromatic structures or amines. CHOS compounds in both ionization modes are mostly found in the oligomer class: only small fractions of sum formulae are assigned to SV-OOA, BBOA, or LV-OOA. As CHOS compounds are supposed to be primarily a product of atmospheric aging reactions, the detection of oligomers formed by secondary aging reactions is in good agreement with this observation.

In general, no clear trend is observed when comparing the relative group abundance of samples with different primary emission sources. Over several days of atmospheric aging, the chemical composition of WSOA becomes more similar and seems to eliminate differences originating from individual primary OA sources. This phenomenon was previously described by aerosol mass spectrometric analysis in the so-called triangle plot.<sup>85</sup> Fresh and shot-aged OA may appear at a different position in the f43 (fraction of  $C_3H_7^+$  and  $C_2H_5O^+$ ) vs f44 (fraction of  $CO_2^+$ ) space, but move toward the upper vertex of the triangle. Considering the moderately low PM10



**Figure 6.** Van Krevelen plots of exemplary industrial (sample 6, top) and Yakutia-wildfire (sample 16, bottom) samples in ESI+. (A, D) O/C vs H/C ratios of all sum formulae found in industrial and wildfire filter extract in ESI+ with intensity weighted-average O/C and H/C ratio marked red. (B, E) N/C vs H/C ratios of nitrogen-containing sum formulae found in industrial and wildfire filter extract in ESI+. (C, F) S/C vs H/C ratios of sulfur-containing sum formulae. Dotted black lines indicate limits of  $AI_{mod}$ , and red lines indicate limits of  $OS_{C}$ .

concentrations analyzed by Popovicheva et al.<sup>6</sup> and high exposure of the aerosol to solar radiation, connected to the generation of OH radicals, intense atmospheric processing may be expected, supporting the finding of similarly high oxidized OA. However, despite high similarities in compound and OA classes, differences on a molecular level can still be discovered by ESI-UHRMS (Figure 3).

Fingerprints of Elemental Ratios. Almost all detected WSOA species are heavily oxidized under several individual conditions involving nighttime reactions with NO3 radicals, daytime photooxidation in the presence of NO<sub>x</sub>, ozonolysis, or reaction pathways including SO2.14 In the O/C ratio plot (Figures 6 and S12), sum formulae in specific areas (1 < H/C)< 2, 0.1 < O/C < 0.5) are often associated with phenolic and lignin-based species, which is also reflected in the aromaticity index and  $OS_C$  of formulae in this section.<sup>41,86</sup> This is based on the origin of the emitted particulate matter from biomass combustion. The modified aromaticity index (AI<sub>mod</sub>) is a useful tool for the classification of sum formulae.<sup>41</sup> Lignin degradation products or subunits are a known emission of incomplete biomass burning and commonly have AI values of 0.25 or higher.<sup>41</sup> Condensed hydrocarbons and condensed aromatics are commonly found at lower H/C ratios (H/C < 1)and therefore higher aromaticity  $(AI_{mod} > 0.5)$  and are also partially present in both datasets. Considering the calculated AI<sub>mod</sub> values of each molecular formula, it is shown that a significant fraction of compounds contains aromatic moieties. Hydrocarbons or polyaromatic hydrocarbons (PAH) are generally less abundant in the WSOA fraction due to low polarity and resulting in poor solubility in water as well as poor ionization efficiency in ESI.<sup>87</sup> Sulfur-containing species with a

high AI<sub>mod</sub> are likely a product of coal burning, while low AI<sub>mod</sub> species are linked to reactions of biogenic emissions with acidic sulfate sources.<sup>60,88</sup> In the Van Krevelen (VK) plot of sulfur species in ESI–, a distinct accumulation of low H/C and high AI<sub>mod</sub> compounds is observed. This fits the characterization of the industrial sample (sample 6, Figure 6 top) with fossil fuel burning as a main primary emission source. On the other end, high H/C ratios are also abundant, even with high O/C ratios up to O/C=1. Carbohydrate-like compounds with both high H/C and O/C of about 2 and 1, respectively, seem to terminate the maximum oxidation of ambient OA, while the area of lipid-like compounds of similar H/C, but lower O/C, might represent secondary species from less reactive, i.e., saturated, hydrocarbons.

#### CONCLUSIONS

The WSOA fraction of ambient aerosols collected over Lake Baikal was chemically characterized by electrospray ionization in positive and negative modes with ultrahigh-resolution FTICR-MS. The main compound classes of WSOA are CHO, CHON, and CHOS all revealing partial aromatic structures and high oxidation. This is a result of intense atmospheric aging of residential, industrial, wildfire, and biogenic primary emissions, identified by backward air mass trajectories during long-range transport, which were mixed with local and regional emission sources. A detailed description of the Van Krevelen diagrams can be found in the Supporting Information.

CHON species are positively correlated to light absorption properties (AAE) and functional groups are characterized by the selectivity of both ionization modes as well as the O/N ratio. Most of the nitrogen-containing compounds are highly oxidized and formally fit the classification as organic nitrates or products of nitrate radical reactions. Also, some less oxidized nitrogen species are identified, especially in ESI+, which could be assigned to amines or other products of atmospheric aging reactions with ammonia. Moreover, sulfur-containing compounds mostly show a high oxygen content that could be assigned to organic sulfates formed by secondary reactions of emissions from fossil fuel burning and SO2, or biogenic emissions with acidic sulfate seed aerosols. Atmospheric aging and long-range transport of aerosols lead to similar bulk properties of oxidized OA, despite different emission sources. However, UHRMS with ESI is still able to reveal differences in OA composition on a molecular level and link ambient OA data to laboratory aging of individual SOA precursors. As shown by Popovicheva et al.,<sup>6</sup> atmospheric processes and hydrosphere are connected by PM deposition in the lake at the air-water exchange interface. Combustion aerosol emissions deposited into the lake's ecosystem may alter its balance by the addition of nutrients as well as potential pollutants. Therefore, it is essential to monitor and understand processes related to the PM over Lake Baikal to preserve the unique freshwater ecosystem and UNESCO World Heritage Lake Baikal. Furthermore, the detection of aged biomass burning emissions in the WSOA fraction highlights the molecular complexity of these aged compounds, which indicates the need for further research regarding the chemical composition as well as the impact of aged biomass burning PM on the environment and human health.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspace-chem.2c00017.

Additional sample descriptions, sum parameters, and supporting mass spectrometric data discussion; sample list with eBC and AAE data from Popovicheva et al.,<sup>c</sup> details for calculating saturation vapor concentrations, and relative intensities of compound classes; relative number of sum formula with different O/N, O/S, and OM/OC; relative contributions of compound classes to organic aerosol classes; a list of elemental composition, double-bond equivalents, and modified aromaticity index; detailed description of the ESI-FT-ICR-MS method; discussion of compound classes in Van Krevelen space; map of the ship expedition at Lake Baikal; number of detected peaks in samples and molecular distribution of oxygen; Spearman rank correlation of data from UHRMS and aethalometer; relation of CHON<sub>1</sub> and CHOS<sub>1</sub> with AAE; negative ESI mass spectra of compound classes in samples "background," "industrial emissions," "wildfire Krasnoyarsk", and "wildfire Yakutia"; diagrams of carbon number or saturation vapor pressure vs average carbon oxidation state and comparison to naphthalene-SOA and  $\beta$ pinene-SOA; and Van Krevelen diagrams of O/C vs H/C, N/C, or S/C from negative ESI (PDF)

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### Notes

The authors declare no competing financial interest.

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