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Photoreaction of biomass burning brown carbon aerosol particles†

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The light-absorbing fraction of atmospheric organic particles, known as brown carbon (BrC) aerosol, can affect climate by influencing global radiative forcing. Regional effects arising from biomass burning BrC pollution are of particular interest, as they can have very high optical depth close to their sources. Due to the numerous fuel types, combustion conditions and reaction pathways encountered during the emission and lifetime of BrC, significant uncertainty arises from the impact that atmospheric aging can have on aerosol chemical composition and optical properties. Here, we investigate short-term aging processes driven by exposure to ultraviolet light (≈ 360 nm) that occur with primary BrC particles generated by smoldering pine wood. Suspended particles were aged in a chamber for a duration of 30 min. The single scattering albedo (SSA) at 405 nm decreased significantly by approximately 0.02 units (for example, from 0.98 to 0.96) during that time, due to an increase in absorption relative to scattering. This change was associated with an increase in oxygenation, represented by the signal fraction at $m/z = 44$ (f_{44}) from the aerosol mass spectrometer (AMS). Surprisingly, the SSA continued to decrease after light exposure stopped, pointing to the presence of long-lived reactive species, perhaps radicals, that we hypothesize to form from photosensitized reactions. While relative humidity (RH) had only a minor impact on the rate of aging during light exposure, the aging rate in the dark may have occurred faster under dry conditions than at 45% RH.

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Environmental significance

Brown carbon (BrC) aerosol particles from biomass burning events such as wildfires can significantly impact Earth's energy balance due to their ability to absorb light. The extent of this contribution, however, is not well understood, in part because of the complexity of BrC's composition and the various aging mechanisms that occur in the atmosphere. This work focuses on understanding one of these processes, which is short-term (30 min) light exposure of suspended particulate BrC. Improved understanding of the multiple aging processes of brown carbon will lead to more accurate modelling predictions of climate change.

1. Introduction

Biomass burning injects combustion compounds in enormous quantities into the atmosphere, including those that contribute to brown carbon (BrC) aerosol particles. Along with black carbon (BC), BrC is a component of carbonaceous aerosol that can significantly impact the Earth's radiative balance by its ability to absorb ultraviolet and visible light.^{1,2} It was estimated that the magnitude of BrC absorption is up to 25% the magnitude of BC absorption ($0.1\text{--}0.25\text{ W m}^{-2}$).³ Regional, near-

source absorption is also important for UV fluxes and photochemistry. Ground-based measurements have found varying contributions of BrC's absorption relative to BC depending upon proximity to the source.⁴ Global model predictions show large regional variations.⁵

The effects of BrC on climate remain uncertain, due to the complexity and variability of its chemical composition, and reactivity in the atmosphere.¹ Different fuels, including plant types from various locations (*e.g.*, litter, canopy), contribute to the complexity, as do burn conditions (*i.e.*, flaming *vs.* smoldering).^{6–10} All these factors lead to uncertainties in radiative forcing estimates. Thus, BrC aerosol optical properties and atmospheric behavior need to be better defined.¹¹

BrC molecules can exist in the atmosphere in the particulate phase or, *via* cloud scavenging, in the aqueous phase.^{1,12–14} Particulate BrC can be subject to a variety of aging mechanisms, including light exposure, and heterogeneous oxidation by OH radicals in daylight, nighttime NO₃ radicals, and ozone.^{12,15–19}

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experiment are shown in Fig. 2. The SSA is defined using the following equation:

$$\text{SSA}(\lambda) = \frac{\beta_{\text{scat}}(\lambda)}{\beta_{\text{scat}}(\lambda) + \beta_{\text{abs}}(\lambda)} \quad (1)$$

where β_{scat} and β_{abs} are the scattering and absorption coefficients, respectively. Before light exposure, the total absorption and scattering data both exhibit a decreasing trend, due to wall loss of particles in the chamber. The SSA, however, is more stable as a function of time (see also Fig. 3b and 4b). With exposure to light, the absorption experiences an initial increase, while the scattering continues to decrease. This translates into an SSA value with a strongly decreasing trend. The SSA data thus decreases as a result of an increase in absorption relative to scattering, and not solely from reduced scattering. In the subsequent figures, only SSA data will be presented.

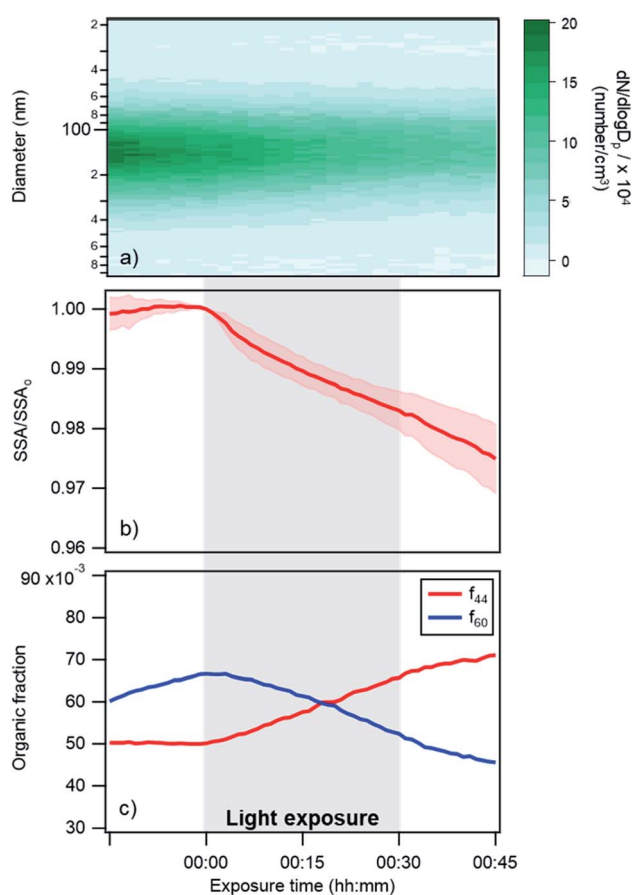


Fig. 3 Changes in (a) particle size distribution, (b) single scattering albedo at 405 nm, and (c) AMS f_{44} and f_{60} fractions over time for a typical photoreaction experiment in dry conditions. Darker shaded regions in panel (a) represent a higher number concentration of particles. In panel (b) the SSA is represented as the ratio of experimental SSA over the SSA at exposure time = 0, in order to directly compare different experiments. The shaded pink region in (b) represent the standard deviation (for 4 different replicates). Note that the changes in f_{44} and f_{60} during a control experiment (Fig. S4†) were much smaller than the changes shown in this figure; (a) and (c) are results for one replicate.

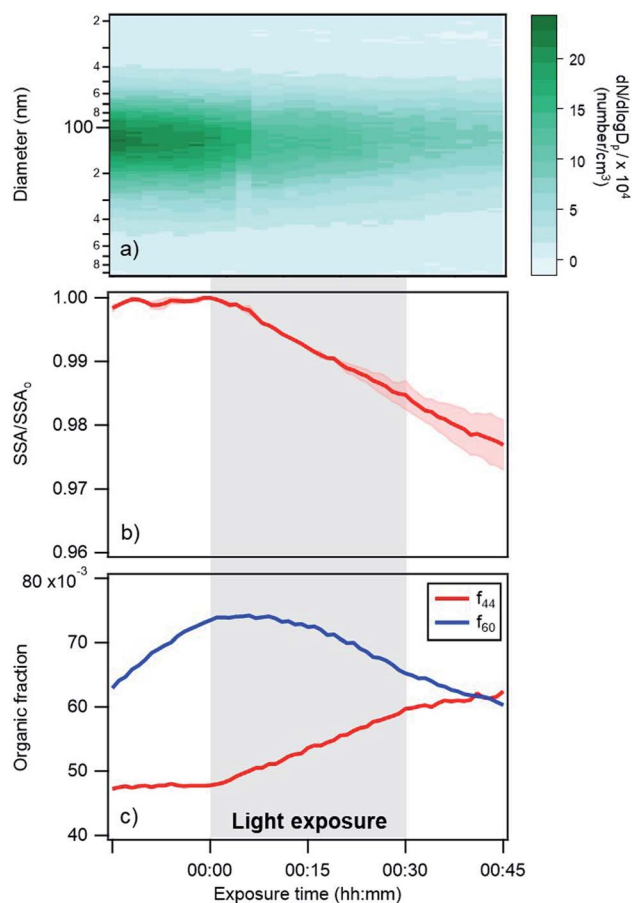


Fig. 4 Changes in (a) particle size distribution, (b) single scattering albedo at 405 nm, and (c) AMS f_{44} and f_{60} fractions over time for a typical photoreaction experiment at 45% RH. Darker shaded regions in panel (a) represent a higher number concentration of particles. In panel (b) the SSA is represented as the ratio of experimental SSA over the SSA at exposure time = 0 in order to compare multiple experiments. The shaded pink region represent the standard deviation (for 2 replicates). Note that the changes in f_{44} and f_{60} during a control experiment (Fig. S4†) were much smaller than the changes shown in this figure. (a) and (c) are results for one replicate.

Changes in the optical properties of primary brown carbon aerosols were investigated under 2 conditions, with average results presented for dry (Fig. 3b and S5†) and 45% RH (Fig. 4b and S5†) conditions. In these figures, in order to compare the single scattering albedo from different experiments, a normalized SSA was determined by initializing the SSA value at zero exposure time (SSA_0) to have a value of 1, to account for the inherent experimental variability in starting SSA values. The average absolute starting SSAs with their standard deviations are shown in Table S1.† While initially stable, the SSA starts to decrease upon light exposure with a total decrease of approximately 0.02 during 30 min of light exposure. An additional observation is that, surprisingly, the SSA continues to decrease after the lights were turned off. This continued aging persists for at least 30 minutes (Fig. S7†). As discussed below, this suggests that light induces the formation of sufficiently long-lived reactive species that are responsible for driving chemistry in the dark.



Also, shown in the figures are aerosol particle size distributions and select quantities from the AMS measurements. In particular, the particle size distributions (Fig. 3a and 4a) as a function of time show decreasing particle number concentrations due to losses to the chamber walls but they do not exhibit any abrupt changes in the shape of the distribution upon exposure or removal of light. However, the increase in absorption at exposure time zero is associated with an increase in a measure of the particle oxidation state, represented by the fraction of the AMS organic mass spectrum (f_{44}) (Fig. 3c and 4c). This m/z 44 mass spectral fragment arises from peroxides, esters and acids, often indicative of oxidation.⁷

The SSA is an important metric used to estimate aerosol absorption capability by taking into account scattering as well. To quantitatively compare the extent of SSA decrease for different experimental conditions and during the course of a photoreaction experiment, the linear regression slopes of the changing SSA values *versus* time are presented in Fig. 5. The more negative the slope, the faster and more significant the intrinsic absorption increase, *i.e.* increasing absorption relative to scattering.

In general, the SSA slopes before light exposure are close to zero for all conditions, including during a control experiment during which the lights were not turned on (Fig. S6†). During light exposure, the slopes were consistently negative, signifying a decrease in SSA. Two of the dry and 45% RH experiments were performed in pairs, one immediately after the other. While the results in Fig. 5 suggest that the relative humidity doesn't significantly affect the results when the lights are on, in the paired experiments the SSA slope was consistently more negative for 45% RH. This suggests that there is potentially a small influence of RH on the optical properties.

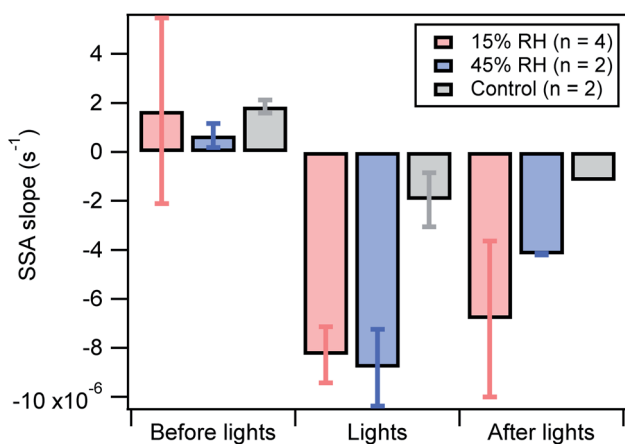


Fig. 5 Single scattering albedo slopes before, during, and after light exposure for dry (pink) and 45% RH (blue). The slopes were recorded for 15 min both before and after the lights were turned on. The slope during light exposure was for a duration of 30 min. The error bars represent the standard deviation. The control experiments are the SSA obtained from adding BrC aerosols to the chamber without any light exposure, where the data before lights were recorded for 10 min instead of 15 min. The absence of error bars for the control conditions after lights is due to absence of data for one of the two control experiments (Fig. S6†).

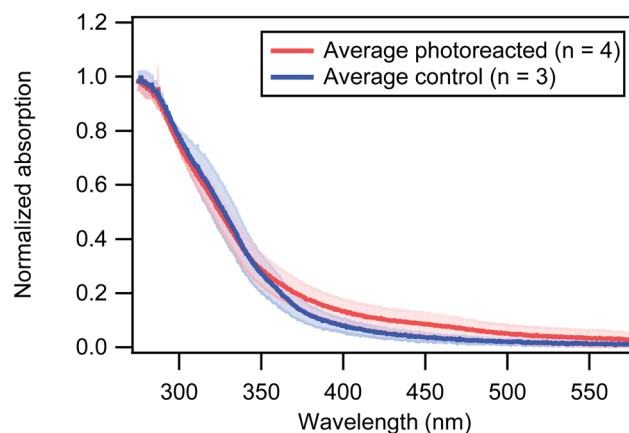


Fig. 6 Averaged normalized absorption spectra for photoreacted wood smoke (red) and control (blue) experiments. The absorption spectra were normalized to 1 at 275 nm in order to directly compare different experiments. The shaded regions represent the standard deviation obtained from the different replicates. The samples were taken at dry conditions (<15% RH).

When the lights are turned off, the photo-chemically initiated aging continues in the dark, but at a slower rate. Different environmental conditions yield different aging rates in the dark, where the higher relative humidity conditions may exhibit a slower decay than drier conditions with the caveat that the error bars are overlapping.

As described in the Methods section, filter samples were collected after light exposure for UV-vis analysis. The UV-vis absorption spectra were then measured of the DMSO extracts of the brown carbon material. Although these measurements require sample extraction, they allow us to observe shifts in the overall absorption spectrum whereas the absorption measurements described above were at a single wavelength (405 nm). In order to account for experimental variability and compare the shapes of the spectra from different experiments, the absorption was normalized to 1 at 275 nm which is approximately the maximum of the absorption spectrum. Results are shown in Fig. 6. In particular, it is shown that 30 minutes of photoreaction significantly increased the absorption at wavelengths > 350 nm.

4. Discussion

The major finding in this work is that primary wood smoke particles exhibit enhanced ultraviolet and visible absorption relative to scattering when exposed to atmospherically relevant wavelengths of ultraviolet light. This is in agreement with prior results from the literature, as discussed in the Introduction.^{13,14,26,28} This behavior is exhibited not only with the *in situ* measurements at 405 nm but also with the DMSO extracts, across the near-UV and visible parts of the spectrum. These changes occur without noticeable changes in the particles' size. As well, an intriguing observation is that the changes observed at 405 nm continue after the light exposure stops.

The results indicate that oxidation is occurring in the particles during the photoreactions. In particular, when the lights are turned on, we observe a pronounced increase in the m/z 44



fraction of the organic mass spectrum, which is indicative of oxidation (see Fig. 3c and 4c). The f_{60} AMS fraction also shows signs of oxidative aging during the experiment. This signal is representative of sugars such as levoglucosan and is a common biomass burning tracer. While f_{60} is rising before lights are turned on (likely because the increasing mass loading in the chamber at this time is driving increased partitioning of semi-volatile species to the particles), the signal abruptly starts declining when the lights are turned on. This collective behavior of a decrease in m/z 60 and an increase in m/z 44 (see also Fig. S2†) is characteristic of oxidative aging of biomass burning particles.²⁹ As well, levoglucosan decay from light exposure has been previously observed in chamber experiments and was attributed in part to OH oxidation arising from particles.²³ We note that levoglucosan does not absorb 360 nm light.³⁰

The mechanisms of formation of reactive species that lead to the f_{44} increase and f_{60} decrease are unclear. We do not believe that gas-phase OH radicals are being formed in substantial quantities, leading to heterogeneous oxidation. In particular, the flow from the wood smoke source passes through two diffusion denuders which will remove most potential gas-phase precursors, the wavelength of the UV light is high (≈ 360 nm), and we do not flame the wood to form NO_x . Most importantly, the character of the oxidation processes does not change after the light exposure is removed, *i.e.* removal of light would have instantly removed gas-phase OH sources.

When the lights are on, one possibility is that OH radicals are being generated within the particles. In particular, there is a report in the literature that OH radicals are present in the aqueous phase during light exposure of wood smoke extracts using UVB wavelengths.¹⁴ More generally, for many decades, there have been indications that indirect or photosensitized condensed-phase photochemistry can drive the formation of reactive species, such as singlet molecular oxygen.^{20,31} However, even if such short-lived species are forming during light exposure, such generation mechanisms would stop after light exposure.

To discuss potential light-driven mechanisms in more detail, we note that there is evidence for the formation of light-induced radicals in a variety of atmospheric particle samples.^{20,22,32} These radicals are believed to form through excited triplet states of specific, light-absorbing BrC molecules, referred to as photosensitizers. Once excited to their triplet state, these BrC compounds can generate radicals and catalyze radical chain reactions, thus affecting chemical composition and potentially inducing a change in absorption. For example, an excited photosensitizer may react with a neighboring organic compound to form a carbon-centered organic radical, or with O_2 to form reactive peroxy radicals.^{33,34} As well, in laboratory studies, reaction of a photosensitizer (specifically, imidazole-2-carboxaldehyde) with a fatty alcohol (1-octanol) revealed the possibility of forming a carbon centered radical, previously also observed to occur with limonene.^{34–36} Dimerization of organic radicals may give rise to larger, more absorbing species.^{21,22} If OH arises from higher levels of HO_x , then it may add to aromatic rings, increasing their electron densities and ability to absorb light.^{15,21,37} Observations of aqueous phase reactivity of

aromatic carbonyl photosensitizers with phenolic compounds have also been reported. Mechanistic insight into the reactivity of the excited triplet state revealed scavenging of the hydrogen atom from the alcohol functional group, forming an oxygen-centered radical.³⁸ Overall, we believe that the potential formation of both C- and O-centered radicals, and of OH radicals, all contribute to increased reactivity in the BrC particles, degradation of sugars such as levoglucosan, and the formation of more absorbing molecules through dimerization or functionalization. It is possible that the tight molecular confines of an aerosol particle promote intermolecular chemistry over the rate at which it occurs in a solvent extract. However, future experiments are needed to determine the details of the dominant mechanism.

We note that, during a light exposure event, we did not observe evidence in the AMS spectrum of higher molecular weight species forming (see Fig. S3†), only oxidation from the f_{44} fraction (Fig. 3c and 4c). However, this does not rule out dimerization of specific precursors to form stronger chromophores, given that the AMS is not well suited to the identification of low concentrations of higher molecular weight absorbing species. However, we do observe evidence of fragmentation, which has been previously demonstrated to occur as samples age.^{21,22}

As noted above, a novel observation in our experiments is the continued aging of the particles in the dark. While the lifetimes of excited triplet state photosensitizers are fractions of a second,^{39,40} the lifetime of some radicals formed in the condensed phase can be much longer. Indeed, the term “environmentally persistent free radicals” has been used to describe such species. There is considerable evidence in the literature for the presence of such radicals in biomass burning and combustion aerosol.^{41–44} As one example, Qin *et al.* recently determined a 100 day half-life of some radicals produced from light exposure of catechol, a common biomass burning aerosol component after mixing with ambient $\text{PM}_{2.5}$ particle material.⁴⁴ Yang *et al.* also observed the lifetime of radicals from PM_1 to be many days, with biomass burning being one of the sources of particulate matter.⁴³ While we cannot confidently say whether such long-lived radicals are driving continued oxidation in the particles, it is clear that some reactive intermediate with a lifetime of at least tens of minutes is present. It is interesting to note that experiments performed with the same chamber did not see evidence for continued oxidation in the dark when studying the photoreactions of water-soluble SOA generated from α -pinene ozonolysis.⁴⁵ Thus, the effect appears to be specific to biomass burning aerosol, perhaps related to its reactive, aromatic composition.

Another important parameter related to the conditions in which aging occurs is the relative humidity. Within the experimental uncertainty, the results obtained in Fig. 5 show that the SSA slope is just marginally (6%) larger at higher relative humidity than in dry conditions, indicating either no impact or a slightly more rapid aging process perhaps reflecting more rapid reactive intermediate generation or reaction. Past studies of atmospheric aerosol material surrogates have shown that photoreactions proceed more rapidly at higher RH, presumably



due to lower viscosity in the material and more molecular interactions.²⁶ Other photooxidation studies have been shown to occur more rapidly at higher RH values. For example, Zhong & Jang determined that photooxidation of hickory wood smoke, when exposed to sunlight, occurred at a faster rate at higher RH.²³ This was also demonstrated by Wong *et al.* where light exposure of SOA from α -pinene decreases the mass of total organics more rapidly at higher RH (85%) relative to mid-RH (60%) and low-RH (5%).⁴⁵ As well, Schnitzler *et al.* observed a more rapid and higher peak absorption at 60% RH relative to 15% RH during OH oxidation of primary pine wood smoke particles.¹²

By contrast to these photo-oxidation studies, aging may have continued in the dark more rapidly at lower RH than at high RH after light exposure was terminated. This suggests that particle viscosity may affect the sources and sinks of reactive intermediates in the particles in a different manner. With the sources of such species turned off in the dark, it is possible that the lifetimes of the reactive intermediates are lengthened when molecular motion is suppressed at low RH. There is also potential for concentration effects, given that low RH leads to more concentrated solutes.^{33,46} We note that previous studies on the effects of RH on radical production from photosensitized reactions have observed complex behavior, which may be driven by a variety of factors, including concentration and viscosity.³³

5. Atmospheric implications

The focus of this study was on aging by photoreaction of primary wood smoke brown carbon particles that will occur on a short timescale after injection into a sunlit atmosphere. Strong effects across the near UV and visible parts of the spectrum were observed after only 30 minutes with light levels lower than those typically present in the daytime atmosphere. While this aging effect has previously been investigated in the aqueous phase,^{13,14,24} the scope of this project differs from past studies by aging suspended aerosol particles using a UVA light source centered at 360 nm. Other studies have either employed stronger UV sources or performed aging measurements offline with solvent extracts or filters. Thus, we have demonstrated that darkening photoreactions occur in suspended particles that are held under steady environmental conditions.

We note that this project focuses on the aging of primary particles by removing the gas-phase compounds generated from wood burning prior to aging. It is known that the formation of secondary brown carbon aerosols from gas-phase precursors generates additional absorption.^{23,25} By removing the effects of secondary gas-to-particle conversion, we are able to constrain the effects of light on primary particles only. We note that there is possibility of evaporation from semi-volatile compounds within the chamber, however, there was no observation of significant changes to size distribution (Fig. 3a and 4a) and no impact on the optical properties.

We demonstrate that this photo-initiated effect persists in the dark, albeit at a slower rate than when light was present. This points to an aging mechanism that involves long-lived radicals or reactive intermediates.⁴⁴ This stands in contrast to

OH-driven aging which only occurs in the light.^{1,6} The persistent photo-initiated aging that we observe in the dark is relevant for atmospheric conditions where light levels are low. For example, particles generated from a biomass burning event can rapidly shift from direct sunlight exposure to a hazy or cloudy environment.

When placing this darkening photoreaction into an atmospheric context, it is important to consider the timescales involved. The aging mechanism studied here is relevant to short-term light exposure to primary BrC particles. A longer aging timescale would likely induce significant photobleaching subsequent to the photoenhancement observed at short times.¹⁴ For example, Wong *et al.* saw the initial increase of absorption from high molecular weight water-soluble BrC during the first 15 hours of aging, following by bleaching for 10 hours. Fleming *et al.* reported the decay lifetimes of BrC chromophores from different fuels to be on the order of days to a week.^{6,14} Furthermore, competition between other daytime aging processes, such as OH and O₃ heterogeneous oxidation, is likely to change the overall aging timescale as well.

Author contributions

CLK, PJG, JPDA conceptualized the project. CLK, PJG, TL conducted the measurements and analyzed the data. CLK, JPDA wrote the manuscript with contributions from all authors.

Conflicts of interest

There are no conflicts to declare.

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