

Revised chapter – Dietze et al., ClimPastDisc 2020

4.1.2 Potential source areas and degradation pathways from source to sink

5 While certain formation and transport mechanisms are still uncertain (Suciu et al., 2019), MAs are thought to be produced as gases during pyrolysis under low burning temperatures, but quickly condensate on co-emitted particulate matter in the smoke plume. A small fraction of MAs can remain at the site and potentially adsorb to char during higher burning temperatures (c. 600° C), becoming available for subsequent transport by overland flows (Suciu et al., 2019). MAs oxidize via several degradation pathways during atmospheric transport and/or get lost by wet or dry deposition within hours to few days (see Suciu et al. (2019) for a review). Hence, we expect higher influxes when fires happen close to the lake because under atmospheric conditions, several degradation pathways limit chemical stability of MAs during aeolian transport to a few hours to days (Sang et al., 2016; Suciu et al., 2019). In central European lake sediments, large fire episodes c. 20-100 km away from the deposit could be traced by robust MA peaks (Dietze et al., 2019). Here, we discuss the potential local and regional to extra-regional MA source areas, transport pathways and post-depositional degradation in El'gygytyn lake sediments.

15 Local sources would require biomass burning within the lake catchment, which is rather small (183 km²) compared to the 110 km² large lake (Nolan and Brigham-Grette, 2007). In the period 2000 to 2018, no fires have occurred in the El'gygytyn catchment and only a few in the estimated pollen source area covering several hundreds of kilometres (based on remote sensing data, after Nitze et al. (2018)). The sparse tundra vegetation is currently limited to slopes below 5° (Nolan and Brigham-Grette, 2007), which is c. 70 % of the catchment. Hence, we suggest that during interglacials of similar or cooler conditions (e.g. during MIS 7e) catchment fires were highly unlikely. During warmer interglacials with a potential spread of boreal tree taxa towards the lake (Melles et al., 2012), we cannot exclude a certain contribution from local fires, but given the size of the lake we assume that the majority of MAs in El'gygytyn sediments derives from extra-local aeolian transport.

25 Our HYPSPPLIT backward trajectories (Fig. 6) show that MAs attached to aerosols would derive from modern day tundra and larch taiga in the Chukotka region, several hundreds of km away from the lake, transported by north- to south-westerly winds during the main fire season in July and August, in agreement with modern climatology (Mock et al., 1998). Yet, El'gygytyn MA influx records represent centennial-scale averages integrating over multiple fire events under multiple synoptic conditions that varied in the past, such as changing jet stream position and orientation (Herzschuh et al., 2019). Hence, the potential source area could have been even larger during past interglacials, but still be located in the vegetated realm of eastern Siberia. We assume that shifts in geographic source areas associated with shifts in atmospheric circulation would affect the variability of MA influxes within rather than between interglacials.

30 *Fig. 6*

35 Next to dry deposition, rain and snowfall can deposit MAs directly on the (frozen or unfrozen) lake surface and/or within the lake catchment. Snow and lake ice were found to be covered with partially black particulate matter (V. Wennrich, pers. communication), with snowmelt and ice-break up currently happening from mid-May to early July (Nolan et al., 2002), i.e. overlapping with the onset of the boreal fire season. Snowmelt causes high-energetic fluvial transport across the alluvial fans that drain the catchment for few days and provide most of the detrital

40 sediments to lake El'gygytyn (Nolan and Brigham-Grette, 2007). The amount of local aeolian reworking of sediment from barren to sparsely vegetated surfaces during the snow-free season is unknown, but wind intensities are high throughout the year (Nolan and Brigham-Grette, 2007; Fedorov et al., 2013). Hence, a certain amount of MAs from within the catchment could have reached the lake in either dissolved or particulate form, e.g. adsorbed to clays (Suciu et al., 2019). Rather short residence times on snow and quick transport of MAs as part of the turbulent discharge of suspended matter in the main channels (Wennrich et al., 2013) could have a) prevented an important contribution (and potential loss) of dissolved MAs to the local groundwater and b) limited degradation during short distance fluvial transport (Hunsinger et al., 2008; Suciu et al., 2019). During warmer interglacials (MIS 5e and MIS 11c), a denser local vegetation coverage would have prolonged the snowmelt period and reduced the fluvial transport energies, also during rainstorms in summer. These effects would reduce the absolute fluvial and aeolian influxes of MAs from the catchment in warmer compared to cooler interglacials, which might be counterbalanced by an increased likelihood for more local fires during warmer interglacials. During glacial, climate and vegetation reconstructions suggest a dry and windy climate with a multi-year to perennially frozen lake surface and limited local runoff (Nolan et al., 2002; Melles et al., 2007; Melles et al., 2012), limiting also the influxes of MAs. Aeolian material, including extra-regional MAs, would experience much slower deposition times via moats and cracks as currently observed in Antarctica (Rivera-Hernandez et al., 2019), with enough time for certain, not well-constrained cryogenic processes to degrade MAs (Suciu et al., 2019).

55 MA degradation ~~could still~~can also happen in the lake water column or after deposition. Recently, Schreuder et al. (2018) found that LVG was transported and settled attached to organic matter, which might have prevented its degradation within the marine water column, despite its water-solubility. ~~whereas~~In contrast, Norwood et al. (2013) suggested ~~there is a~~ substantial MA degradation in well-oxygenated river water, which, however, could have been limited when MAs deposit quickly (Suciu et al., 2019). Yet, degradation and desorption of MAs at the sediment–water interface could still be substantial (Schreuder et al., 2018), especially under aerobic conditions (Knicker et al., 2013), as MAs are anhydrous sugars and, thus, potentially more labile and mobile than other organic compounds.

65 Monitoring and sediment properties of Lake El'gygytyn suggest rapid depositional processes in a turbulent, wind-mixed water column (Wennrich et al., 2013) and well-oxygenated bottom waters during summers and past warm periods (Wennrich et al., 2013; Melles et al., 2012); whereas during glacial periods long-term lake stratification led to rather anoxic bottom water conditions that improved the preservation of total organic carbon (Melles et al., 2007; Melles et al., 2012). Assuming that dissolved MAs degrade within days or weeks in oxic, turbulent water (Norwood et al., 2013), the MAs recorded from previous warm periods may rather derive from MAs in particulate phase, which probably did not migrate post-depositionally and which also cannot be produced by diagenesis (Suciu et al., 2019). If we assume a constant influx of particulate phase MAs and high organic matter degradation at the lake bottom, we would expect higher preservation during glacial than interglacials – but we find higher MA influxes in interglacial sediments (Fig. 2b), similar to total organic carbon percentages (Melles et al., 2012). Hence, we assume that MA degradation was limited ~~even~~ over longer time, when occluded within or adsorbed to a mineral matrix or iron oxides (Lalonde et al., 2012; Hemingway et al., 2019). MAs are known to adsorb well to minerals and organic particles such as co-emitted soot and are chemically prone to form organo-metal complexes via chelation (Tobo et al., 2012; Suciu et al., 2019). Adsorption (protecting) and desorption (destabilizing) processes can happen already during emission, transport and at the sediment-water interface, most likely in rather short time

of days to weeks (Suciú et al., 2019) and may vary with climate conditions, as described above. These short-term processes would affect all isomers in a similar way. ~~MAAs are known to adsorb well to particles (Tobo et al., 2012; Suciú et al., 2019),~~ and all isomers show indeed the same trends ~~with~~ over centennial and orbital time scales (Fig. 2b), which is indicative for bound and protected compounds (Hemingway et al., 2019). Hence, we assume propose that MA influxes from El'gygytgyn sediments ~~based MA influxes~~ represent particle-bound MAAs that are only marginally affected by degradation on centennial to orbital timescales, and, instead, represent relative changes in biomass burnt from a similar-regional source during low-intensity fires.

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