



1 **A DOM continuum from the roof of the world – Tibetan molecular dissolved organic**
2 **matter characteristics track sources, land use effects, and processing along the**
3 **fluvial-limnic pathway**
4

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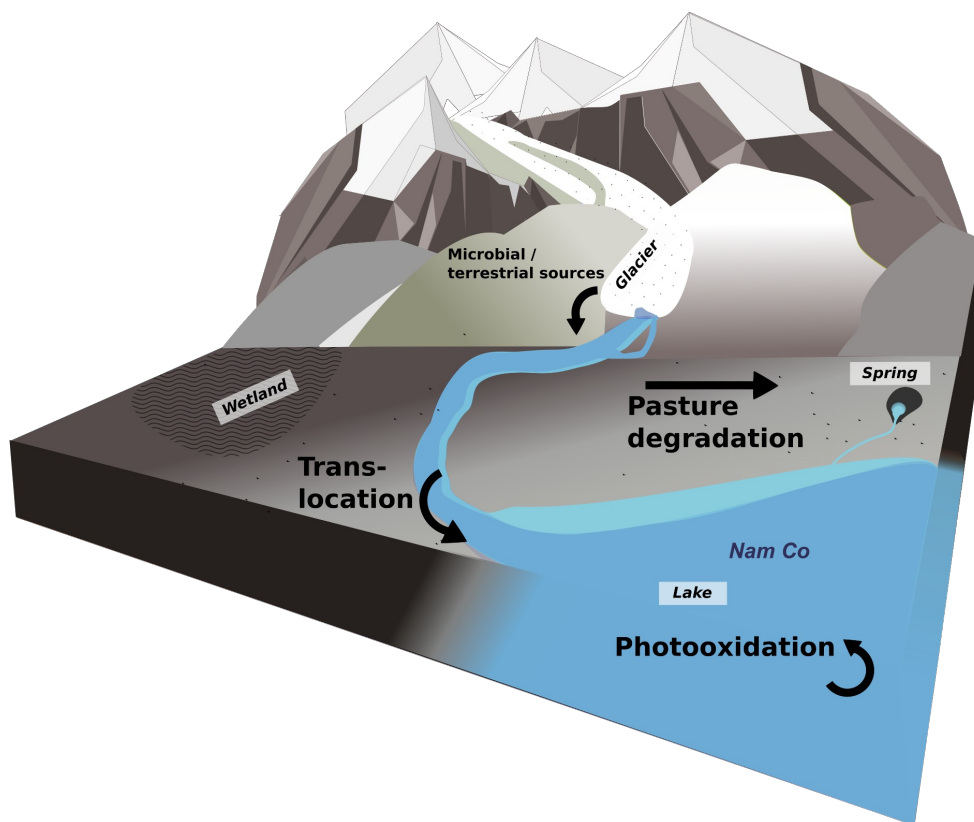
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24 Abstract

25 The Tibetan Plateau (TP) is the world largest and highest plateau, also comprising the biggest
26 connected alpine pasture system of the world. Like other alpine systems, it is sensitive to impacts by
27 climate change and increasing anthropogenic pressure. Carbon cycling at the TP is complex, including
28 sources such as primary production in lakes, glaciers, and terrestrial plants, agricultural land use but
29 also organic matter (OM) from aeolian deposition. Dissolved organic matter (DOM) connects these
30 carbon reservoirs in the network, following the hydrological cycle from precipitation, glaciers, and
31 headwaters to lakes. DOM is highly complex, its molecular composition holds information from its
32 diverse sources and transformations during transport. However, due to its complexity, DOM cycling
33 along the headwater-fluvial-limnic pathway and how terrestrial change can impact carbon cycling in
34 the diverse water bodies is still not well understood. Here, we study DOM molecular transformations
35 using ultrahigh-resolution mass spectrometry (FT-ICR-MS) along the TP alpine continuum from
36 glacial, groundwater springs, and wetland biomes including pastures and alpine steppe, to the large
37 saline endorheic Lake Nam Co. DOM molecular composition differed with respect to allochthonous
38 sources between endmembers, as well as between stream samples, the brackish mixing zone, and
39 the lake. Glacial meltwater DOM contained autochthonous signatures of low-oxidised, unsaturated
40 molecular formulae together with terrestrial-like, dust-borne DOM sources. Glacial-fed streams were
41 characterised by fresh autochthonous, probably algal DOM, and aromatic compounds likely
42 originating from pastoral land sources. DOM from a groundwater spring had a highly degraded,
43 strongly oxidised signature, probably related to the shallow upper aquifer, and degraded pastoral
44 land sources. Wetland and stream DOM were characterised by less oxidised and less degraded inputs
45 from vascular plants and soils. At the brackish zone of the lake shore, DOM contained a mixture of
46 lake- and terrestrial DOM inherited from the streams. At Lake Nam Co, depletion of aromatic
47 terrestrial molecular formulae suggested photooxidation at the surface, and relative enrichment of
48 potentially recalcitrant DOM within the lake. Additionally, a relative enrichment of more aliphatic,
49 nitrogen-containing DOM suggests autochthonous algal and microbial DOM sources in the lake. Our
50 study revealed that DOM composition was largely influenced by local sources and transformations in
51 glaciers, wetlands, and groundwater springs, also incorporating molecular signatures of pasture
52 degradation. Streams with less glacial influence had plant- and soil borne aromatic-rich DOM sources,
53 while the endorheic Lake Nam Co had a recalcitrant DOM composition comparable to millennial-
54 scale stable marine DOM. This suggests that there is no typical high-alpine DOM signature, but that
55 complex processes form DOM characteristics in the fluvial-limnic continuum. Small-scale catchment
56 properties, land degradation and aquatic domains shape the differences. Alpine DOM compositions
57 hence appear to be closely linked to landscape properties suggesting their susceptibility to changes in
58 water quality and OM cycling in sensitive High Asian ecosystems.



59 **Graphical Abstract: Main processes shaping DOM molecular characteristics and transformation in**
60 **the high-alpine Nam Co watershed.**

61 **1. Introduction**

62 The Tibetan Plateau (TP) comprises the largest alpine pasture system of the world (Miehe et al.,
63 2019). It is also known as Asia's water tower (Bandyopadhyay, 2013), forming the source of many
64 large river systems, providing freshwater resources to billions of people in East and South-East Asia.
65 Large quantities of the water are stored in the ice masses of the TP, forming the largest frozen
66 freshwater reservoir outside the Polar Regions. This third pole environment is well investigated (Qiu,
67 2008; Yao et al., 2012), revealing that High Asia's ecosystems are threatened (Hopping et al., 2018)
68 by climate change (Yao et al., 2019) and by intensification and other changes of land use (Harris,
69 2010). Emerging freshwater quality issues (Qu et al., 2019) and the unknown consequences of peak
70 water (McDowell et al., 2022) highlight the utmost importance of the TP for up- and downstream
71 societies. Nutrient and energy cycles of ecosystems are connected by dissolved organic matter
72 (DOM) fluxes (Spencer et al., 2014). Biogeochemical processes in the source area shape the
73 molecular composition of DOM (Liu et al., 2020; Roebuck et al., 2020; Seifert et al., 2016; Wilson and
74 Xenopoulos, 2009). We hypothesize that DOM molecular characteristics entail markers for climatic



75 and land use changes on the TP and that these markers can be used to differentiate between
76 landscape units and endmembers. Understanding the marker function of DOM will allow to better
77 foresee carbon processing at present and under changing environmental conditions. Lastly, this will
78 be key to assess the potential vulnerability and responses of high alpine ecosystems to the challenges
79 of the Anthropocene.

80 DOM connects fluvial ecosystems over several hundreds of kilometres (Seidel et al., 2015), and links
81 terrestrial and aquatic biomes (Goodman et al., 2011). Changes in catchment properties might
82 therefore trigger effects in distanced, fragile ecosystems (Wilson and Xenopoulos, 2009), showing
83 that action and response of land use or climatic changes can be temporally and spatially detached
84 (Goes et al., 2020; Roulet and Moore, 2006). The molecular diversity and complexity of DOM calls for
85 the employment of advanced techniques (Fellman et al., 2010; Nebbioso and Piccolo, 2013). This led
86 to analytical advancements such as electrospray ionization Fourier-transform ion cyclotron
87 resonance mass spectrometry (FT-ICR-MS), an ultrahigh-resolution mass spectrometry method
88 allowing to identify thousands of molecular formulae in samples of natural organic matter (NOM),
89 thus offering a unique opportunity to understand molecular DOM characteristics, sources and
90 transformations (Hawkes et al., 2020).

91 Here, we used FT-ICR-MS to gain insight about molecular information and elemental composition of
92 DOM, to understand characteristics and processing of stream DOM of different catchments, glacier,
93 groundwater spring and alpine wetlands endmembers and DOM of an endorheic lake. The Nam Co
94 watershed, located in the southern/central part of the TP lies in the transition zone of the *Kobresia*
95 *pygmaea* (*K. pygmaea*) dominated alpine pasture biome (Miehe et al., 2008) and the alpine steppe.
96 The area's unique positioning in this transition zone is expressed between the south, with a more
97 humid, glacial-influenced high-mountain ecosystem contrasting the hilly northern margin of the
98 catchment, with more arid climate and alpine steppe dominated vegetation, where clear signs of
99 pasture degradation are visible (Maurischat et al., 2022). DOM characteristics and transformation in
100 this complex natural interplay were only investigated to limited extent. Spencer et al. (2014) found
101 complex OM sources in glaciers, streams and Lake Nam Co, while a recent study highlighted
102 transformation of DOM in pro-glacial streams (Li et al., 2021). This leaves important questions of 1)
103 how DOM signatures are influenced by the diverse biotic and abiotic inventories of the watershed
104 with differing degree of glaciation, alpine wetlands, and groundwater sources as well as land
105 degradation, and the alpine pasture alpine steppe ecotone, and 2) how DOM is processed during the
106 fluvial pathway and in the lake. The Nam Co watershed is a sentinel for changes and a natural
107 laboratory (Anslan et al., 2020), suited to test whether DOM characteristics can be employed as a
108 precursor for changes in this sensitive alpine environment, representative for larger parts of the TP.



109 In this context we hypothesized: I) Catchments of the Nam Co watershed, having different DOM
110 sources, differ in their molecular composition of DOM, where the effect of intensified land use and
111 pasture degradation drives a degraded, terrestrial signature rich in recalcitrant molecular formulae.

112 II) The endmembers (glacial effluents, groundwater springs and alpine wetlands) along the glacier-to-
113 lake continuum possess unique DOM signatures compared to the integrated DOM of streams.

114 III) DOM transformations along the stream path are limited by cold water temperatures, large
115 discharge, high turbidity, and short residence times in the stream. In contrast, signatures of DOM
116 transformations in the clear and deep lake are expected to be dominant.

117 In consequence, IV) DOM signatures of lake water are chemically distinct compared to the terrestrial
118 sources and reveal photodegradation and biological utilisation induced processing of DOM.

119 2. Materials and methods

120 2.1 Site description and sampling

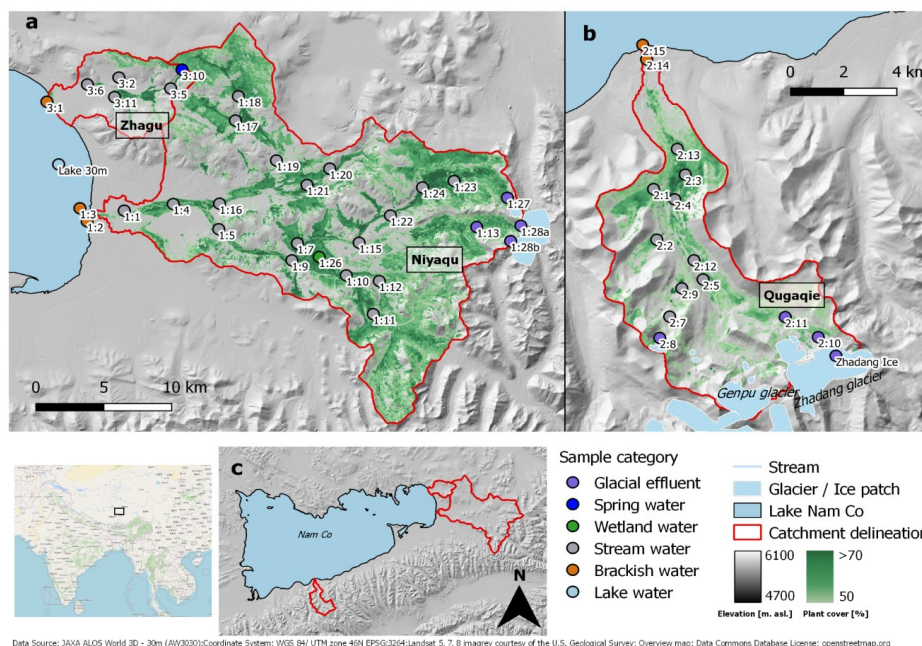
121 The Nam Co watershed has a total size of 10789 km². Two main landscape units can be distinguished,
122 the southern mountainous and the northern upland zone. The south of the watershed is
123 characterised by the Nyainqentanglha mountain ridge (NMR) with highest elevations of more than
124 7000 m. asl., which are glaciated (Bolch et al., 2010). Glacial meltwater is the dominating water
125 source of the streams here (Adnan et al., 2019b). Sparse vegetation dominates the glacial zone, while
126 *K. pygmaea* pastures are being developed at lower elevations (Miehe et al., 2019). Close to the lake
127 shore and on lake terraces, alpine steppe vegetation is developed (Nieberding et al., 2021). The
128 southern part of the watershed is characterised by higher precipitation compared to the north. Up to
129 530 mm y⁻¹ are measured in the NMR (Anslan et al., 2020). In the northern margin hilly uplands a less
130 steep relief dominates (Yu et al., 2021), lower annual precipitation of around 300 mm y⁻¹ are reported
131 (Anslan et al., 2020). Alpine pasture is developed on north-exposed hill-flanks and in the valley
132 bottoms, while alpine steppe grows on south exposed flanks, in the upland, and at the lake shoreline
133 (Maurischat et al., 2022). Along with the aridity gradient from south to north a degradation gradient
134 occurs (Anslan et al., 2020). The climate of the watershed is biannual. The summer months are
135 dominated by the Indian Summer Monsoon from May until early September (Chen et al., 2019).
136 More than 80% of the annual precipitation falls during the monsoon season with mean day-time air
137 temperature up to 11°C (Chen et al., 2019). During winter and spring, the climate is dry and cold with
138 minima of around -20°C between December and February and fewer precipitation (Nieberding et al.,
139 2021). The endorheic Lake Nam Co with an elevation of 4726 m. asl. has a total size of 2000 km². The
140 lake is dimictic, oligotrophic, and lightly saline with 0.9 g l⁻¹ (Keil et al., 2010), and has a maximum
141 depth of 99 m. It is well supplied with oxygen and has a clear water column (Wang et al., 2020).



142 Three catchments of the Nam Co watershed were selected to represent its natural diversity (Fig. 1 a,
143 b). The Niyaqu catchment (sample IDs 1:n in Fig. 1a) in the east has a total area of 406 km². Two
144 streams drain the catchment, the southern stream receives meltwater from a glacial outcrop of the
145 NMR located 700 m above lake level. This river runs through extensive alpine pastures and feeds a
146 large alpine wetland (Fig. 1b). The northern stream drains a hilly upland area in the transition of
147 alpine steppe and alpine pasture. Herding of yak takes place throughout the year. The Zhagu
148 catchment (sample IDs 3:n Fig. 1a) in the arid north of the watershed is the smallest investigated
149 catchment. It has a size of 46 km² and is mostly characterised by hilly upland relief (Keil et al., 2010).
150 There is no glacial influence and only a small altitudinal gradient in this catchment, with the highest
151 elevation at 5230 m. asl. Two creeks drain the catchment, both fed by groundwater springs. During
152 investigation the catchment was arheic, clear signs of degradation of *K. pygmaea* pastures were
153 visible (Maurischat et al., 2022), alongside alpine steppe is developed and also used for animal
154 husbandry. In the south, the Qugaqie catchment (sample IDs 2:n Fig. 1b) represents the high-altitude
155 zone of the NMR. The catchment has a size of 58 km² and is characterised by steep relief and a valley
156 course in south-north direction (Keil et al., 2010). The altitudinal difference between lake and summit
157 is 2200 m. This catchment is used as summer pasture along the stream that drains the catchment.

158 Water samples were taken in September 2019 following the stream paths from the source until the
159 terminus. Potential endmembers were sampled directly, identified by following the stream discharge
160 routes upstream.

161 We identified three endmember groups (glacial effluents, groundwater springs, and alpine wetlands)
162 and three additional sampling units (stream water, brackish water, and lake water), resulting in six
163 sample categories (Fig. 1). Glacial effluents were drawn directly at or close to the glacial terminus,
164 while groundwater samples were drawn directly at springs. Alpine wetland samples were taken from
165 the standing water column of areas characterised by bogs and aquatic plants. Brackish water samples
166 were taken in the mixing zone of stream and lake water at the stream mouth at the shoreline of Lake
167 Nam Co. Lake samples were taken offshore. Details on the characteristics of the catchments and the
168 sampling can be obtained from Maurischat et al. (2022).



169

Data Source: JAVA ALOS World 3D - 30m (AW3300); Coordinate System: WGS 84/ UTM zone 46N EPSG:3264; Landsat 5, 7, 8 imagery courtesy of the U.S. Geological Survey; Overview map: Data Commons Database License; openstreetmap.org

170 **Figure 1: Overview map of the investigated catchments and sampling locations with sample**
171 **categories. Plant cover estimations from Maurischat et al. (2022.) (a+b) represent *K. pygmaea***
172 **pastures, the zones of most prominent yak grazing. © OpenStreetMap contributors 2022.**
173 **Distributed under the Open Data Commons Open Database License (ODbL) v1.0.**

174 Samples were taken from the middle of the stream profile using a telescopic sampling device. Lake
175 waters were sampled from 30 m depth with a submersible sampling device. All water samples were
176 taken in seven subsamples with a volume of one litre each, mixed and a 500 mL aliquot of this was
177 taken for final processing. Samples were filtered on-site using a 0.45 µm mesh size polyethersulfone
178 membrane (Supor, Pall, Port Washington, USA), a vacuum filtration device and a portable electric
179 pump. Samples were stored in pre-cleaned high-density polyethylene bottles (Rotilabo, Carl Roth,
180 Karlsruhe, Germany) and kept at -21°C until analysis.

181 2.2 Solid phase extraction

182 Filtered DOM samples were acidified to pH 2 using 32 % HCl (Rotipuran p.a., Carl Roth, Karlsruhe,
183 Germany). Dissolved organic carbon (DOC) concentrations were measured from 20 mL of sample by
184 high-temperature oxidation on a total organic analyser (varioTOC Cube, Elementar, Langenselbold,
185 Germany). DOM samples were then diluted with ultrapure water to a concentration of 1.5 mg C L⁻¹,
186 and 250 mL of diluted sample was used for extraction. Cartridges with 100 mg of styrene divinyl
187 benzene polymer (PPL) resin (Bond Elut, Agilent Technologies, Santa Clara, USA) were used for
188 extraction. Solid phase extracted (SPE) DOM was prepared following Dittmar et al. (2008). The SPE



189 elute was transferred in cauterized brown glass flasks (Neochrom, Neolab Migge, Heidelberg,
190 Germany) sealed with polytetrafluorethylen caps (Neochrom, Neolab Migge, Heidelberg, Germany)
191 and stored at -18°C until further analysis. Extraction efficiency was assessed by drying 0.2 mL of SPE-
192 DOM under an N₂ atmosphere and resolving the aliquot in 20 mL of ultrapure water. The samples
193 were then analysed for carbon concentration by high-temperature oxidation (varioTOC Cube,
194 Elementar, Langenselbold, Germany) and the volumetric proportion of initial DOC to extracted SPE-
195 DOC was calculated. Reference material (Suwannee River / IHSS) (Green et al., 2015) was compared
196 to routine assays. Blank samples with ultrapure water were used to check process-induced
197 contamination.

198 2.3 Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry

199 SPE-DOM samples were diluted in 1:1 methanol/ultrapure water to a final concentration of 5 mg C L⁻¹
200 for analysis. Samples were analysed on a Solarix XR 15 Tesla FT-ICR-MS (Bruker Daltonik, Bremen,
201 Germany). Duplicate sample electrospray ionization (ESI) was carried out in negative mode at a flow
202 rate of 122 µL h⁻¹. 200 broadband scans (masses of 92.14 to 2000 Da) were acquired per sample,
203 accumulation time was 0.2 s per scan. Internal calibration standards from the Northern Equatorial
204 Pacific Intermediate Water (NEqPIW) (Green et al., 2015) were used to assign mass spectra to mass
205 error < 0.1 ppm. Data processing followed routines of ICBM-OCEAN (Merder et al., 2020). Method
206 detection limits (MDL) were applied (Riedel and Dittmar, 2014) with the ICBM-OCEAN default
207 elemental composition and a minimum signal-to-noise ratio (S/MDL) of 2.5. Minimum signal to MDL
208 ratio as backbone for recalibration was 5 using mean recalibration mode. Molecular formulae were
209 assigned with a tolerance of 0.5 ppm as C₁₋₁₀₀H₁₋₁₂₅O₁₋₄₀N₀₋₄S₀₋₂P₀₋₁ in the mass range 95 to 1000 Da.
210 Molecular formulae assignments were accepted if they were present in more than 5% of the
211 samples. Contaminants were identified and excluded using the contaminant reference mass list.
212 Detection limits for peaks were normalised to sample peak intensities. Overall peak intensities were
213 scaled to the local sample maxima by using the sum of peaks. Isotope (¹³C, ¹⁸O, ¹⁵N, ³⁴S) mass effects
214 were corrected to the naturally most abundant form of each isotopologue. Molecular formulae with
215 molar ratios of oxygen-to-carbon (O:C) = 0, O:C ≥ 1, and hydrogen-to-carbon (H:C) > 2.5 were
216 removed. Duplicate samples were normalised, molecular formulae were retained only, when present
217 in both duplicates. NEqPIW DOM was used as an in-line calibration to measure instrument drift.

218 2.4 Molecular descriptive classes, counts and indices

219 Molecular formulae were assigned to molecular compound classes (Leyva et al., 2020). The original
220 compound classification was suggested by Šantl-Temkiv et al. (2013), compound class names were
221 modified according to the descriptive classes used by ICBM-OCEAN (Merder et al., 2020). The



222 modified aromaticity index (AI_{mod}) and double bond equivalents index (DBE), representing aromaticity
223 and unsaturation, respectively in DOM, were calculated for each formula as proposed by Koch and
224 Dittmar (2006; 2016). AI_{mod} indices > 0.5 were assigned as aromatic, while indices ≥ 0.67 were
225 considered as condensed aromatic compounds. The degradation index (I_{deg}) was calculated as a
226 measure of degradation state of OM (Flerus et al., 2012) and the terrestrial index (I_{terr}) was
227 calculated, as a measure of terrestrial DOM sources (Medeiros et al., 2016). We further assessed the
228 island of stability (I_oS) (Lechtenfeld et al., 2014) to gain insights into the relative share of recalcitrant,
229 i.e. millennial-scale stable molecular compounds. The CHO index was calculated as a measure of
230 organic carbon oxidation stage (Mann et al., 2015). Low CHO values indicate highly reduced
231 (relatively low O content) and high CHO values indicate highly oxidized (relatively high O content)
232 molecular formulae. Molecular diversity was interpreted as α -diversity by depicting the intra-
233 community molecular diversity (Thukral, 2017), here we use the total number of molecular formulae
234 on catchment or endmember scale as a representative.

235 2.5 Environmental variables

236 Relative DOM fluorescence (FDOM) as the product of co-correlated microbial-like and terrestrial-like
237 FDOM, DOC, dissolved inorganic carbon concentration (DIC), $\delta^{13}C$ of DOC, mean plant cover at the
238 sampling point and the concentration of nitrate (NO_3^-) were taken as environmental predictor
239 variables from Maurischat et al. (2022) and tested for statistical correlations with the molecular DOM
240 data.

241 2.6 Statistics

242 Molecular formula intensities were rescaled between 0 and 1 and expressed in percentage. The
243 analysis was conducted by grouping with two independent factors. 1) The three catchments: Niyagu,
244 Qugaqie, Zhagu and Lake Nam Co and 2) sample categories: endmember water (glacial effluents,
245 spring, and wetland) as well as site groups (stream water, brackish water, and lake water). Two
246 endmember groups, spring, and wetland, as well as the site group Lake Nam Co was excluded from
247 statistical analysis due to small sample size. Intensity weighted arithmetic means and standard
248 deviation were calculated for AI_{mod} , number of formulae with $AI_{mod} > 0.5$, number of formulae with
249 $AI_{mod} > 0.67$, DBE, and number of formulae containing heteroatoms nitrogen (N), phosphorous (P) and
250 sulphur (S), the total number of assigned formulae and for compound classes.

251 Data were tested for normal distribution and homoscedasticity by application of Kolmogorov-
252 Smirnov test and Levene test (Brown and Forsythe, 1974). Due to violations of normal distribution in
253 combination with unbalanced sample sizes per group, parametrical tests were considered unreliable
254 (Bortz and Schuster, 2010). Multiple pairwise comparisons were conducted using Kruskal Wallis and



255 Mann Whitney tests (Birnbau, 1956) for pairwise comparisons with Bonferroni post-hoc correction
256 for multiple testing. Significance levels (α) of 0.05 were set as threshold (Supplementary material,
257 Table S1 and Table S2).

258 Non-metric multidimensional scaling (NMDS) was used for dimensionality reduction and ordination
259 (Anderson et al., 2006; Faith et al., 1987). Data for NMDS were scaled and mean-centred (Jolliffe,
260 2002). NMDS was conducted for both independent factors (site and sample category), while sites and
261 sample categories with low statistical power ($n < 3$) were not incorporated to avoid confounding.
262 The Bray-Curtis dissimilarity index with $k = 3$ was used. Loadings, scores, and R^2 -coefficients of
263 determination are provided in the supplementary material (Table S3 – S7). The following compound
264 classes were combined because of co-correlation: aromatic O-rich and aromatic O-poor = ARO, highly
265 unsaturated O-rich and highly unsaturated O-poor = HUSAT, unsaturated O-rich, unsaturated O-poor
266 and unsaturated with N = USAT (Fig. 4). Collinear external predictor variables were removed from the
267 NMDS. R software (The R project for statistical computing, v3.6.3, GNU free software) was used for
268 statistics. The R base packages (R Core Team, 2013) and *tidyverse* (Wickham et al., 2019) were used
269 for data organisation and pre-processing, as well as non-parametric statistics. The packages *ggplot2*
270 (Wickham et al., 2019) and *vegan* (Oksanen et al., 2020) were used for graphical illustration and for
271 NMDS analysis, respectively.

272 3. Results

273 3.1 Sample treatment

274 SPE-DOM extraction efficiencies were $61.4 \% \pm 18.6 \%$ (Supplementary material, Table S8). There was
275 no sufficient statistical explanatory power between the extraction efficiency and the retrieved
276 number of molecular formulae of the samples ($R^2 = .08$, $F(1, 43) = 5.144$, $\beta = -0.007$, $p = 0.02$) to expect
277 systematic methodological failure.

278 3.2 Group counts and statistics

279 Samples were grouped by two independent factors, site (the three investigated catchments Niyaqu,
280 Qugaqie, Zhagu, or the Nam Co Lake) and sample category (the three endmembers (glacial,
281 groundwater spring and wetland waters) as well as stream, brackish and lake water samples). For
282 sites, the total number of assigned molecular formulae decreased in the order Qugaqie > Zhagu >
283 Niyaqu > Lake Nam Co, latter had 50 % less assigned formulae compared to the catchments (Table 1).
284 Water samples from wetland and brackish environments had highest numbers of assigned formulae,
285 followed by glacial effluents, spring and stream water, while lake water samples had the lowest
286 molecular diversity (Table 2).



287 Heteroatom-containing molecular formulae (N, S, P) had different relative abundances in sites and
288 sample categories. Lake Nam Co had relatively more N-heteroatoms than the three catchments
289 (Table 2). The relative abundance of sulphur containing formulae significantly decreased in Niyaqu
290 compared to Qugaqie ($p=0.005$), lowest mean values were found in DOM of Zhagu and Lake Nam Co.
291 P-containing molecular formulae were enriched in DOM of the lake water relative to DOM of the
292 three catchments (Table 1, Table S1).

293 N-containing molecular formulae were most abundant in wetland water and brackish water samples.
294 Spring, stream, and glacial effluents formed a group of medium N distribution and lake samples had
295 the lowest count of formulae associated with N. DOM and glacial DOM had the highest relative
296 abundances of S-containing molecular formulae, followed by wetland and stream DOM with lower
297 amounts, while groundwater springs and lake DOM had the lowest number of molecular formulae
298 associated with S. Molecular formulae containing P were least abundant in glacial and groundwater
299 spring DOM, followed by the order stream < lake < brackish water < wetland DOM. A high abundance
300 of P was visible in lake DOM at relative numbers (Table 2).

301 DOM of Lake Nam Co had lowest AI_{mod} , DBE and I_{terr} values, while DOM from Niyaqu, Qugaqie and
302 Zhagu exhibited no differences (Table 1). For sample categories, brackish DOM had higher I_{terr} and
303 DBE values but no significant differences were visible between DOM of terrestrial systems (Table 2).
304 No significant differences were visible for O/C ratios, but the H/C ratios were highest in Lake DOM
305 (Table 1). Significantly higher relative numbers of hydrogen in samples of Qugaqie were found
306 compared to Niyaqu ($p=0.005$). Additionally, the CHO index showed that Lake DOM and DOM of the
307 Qugaqie catchment were significantly less oxidized compared to DOM of the degraded, arheic Zhagu
308 catchment ($p=0.042$). Correspondingly, I_{deg} values, indicating relatively more degraded DOM, were
309 significantly higher for Zhagu compared to both the Niyaqu and Qugaqie catchment DOM ($p=0.0002$).
310 DOM of Lake Nam Co had Lowest values of I_{deg} . IoS values, indicating recalcitrant DOM, showed a
311 significantly higher contribution in Zhagu and Lake Nam Co compared to Niyaqu and Qugaqie
312 ($p=0.04, 0.05$, respectively). In the sample categories (Table 2). H/C ratios were higher in glacial and
313 lake DOM and lower in wetland DOM. The CHO index showed less oxidized DOM originating from
314 glacial effluents and the lake compared to terrestrial sources (Fig. 5). I_{deg} values were lower in the
315 lake compared to glacial, stream and wetland DOM. Highest I_{deg} values were observed in DOM in the
316 brackish intermixing zone and in groundwater springs. The percentage of IoS values increased in the
317 order glacial effluents > brackish water > stream water > wetland water > lake > groundwater springs
318 indicating differences in the contribution of recalcitrant DOM.

319 Assigned compound classes (Fig. 2) give an overview about the composition of DOM. Largest
320 differences among the sites were found for the aromatic DOM groups. Lake Nam Co had five times



321 fewer aromatic oxygen (O)-rich molecular classes compared to catchment DOM. For aromatic O-poor
322 compounds, the lake had almost 20 times fewer compound abundance. For highly unsaturated O-
323 rich molecular formulae Lake Nam Co showed higher values compared to catchment DOM, while
324 highly unsaturated O-poor molecular formulae were slightly decreased. Further, the unsaturated O-
325 poor and unsaturated N-containing DOM classes were higher in lake DOM compared to DOM
326 sampled in terrestrial systems. Within catchments, highly unsaturated O-rich formulae were more
327 abundant in glacial influenced DOM of Qugaqie. Significantly more unsaturated O-rich molecular
328 formulae were found in Niyaqu DOM compared to Qugaqie ($p=0.02$), while unsaturated O-poor
329 molecular formulae were significantly less abundant in DOM of Zhagu compared to both Niyaqu and
330 Qugaqie samples ($p=0.007$). Relative abundances of saturated molecular formulae were overall low
331 (Fig. 2).



332 **Table 1: Overview on mean and standard deviation of indices and elemental composition ratios and**
 333 **mean and standard deviation of molecular formulae counts for sites.**

Variable	Niyaqu		Qugaqie		Zhagu		Lake Nam Co ‡
	Mean	SD (±)	Mean	SD (±)	Mean	SD (±)	Value
Al _{mod}	0.33 ^a	0.05	0.32 ^a	0.02	0.36 ^a	0.02	0.25
DBE	9.43 ^a	1.05	9.52 ^a	0.93	10.22 ^a	0.32	8.14
O/C	0.46 ^a	0.02	0.45 ^a	0.02	0.45 ^a	0.02	0.44
H/C	1.12 ^a	0.08	1.17 ^b	0.05	1.13 ^{ab}	0.08	1.20
CHO	-0.21 ^{ab}	0.11	-0.26 ^b	0.08	-0.17 ^a	0.04	-0.29
I _{org}	0.55 ^a	0.15	0.59 ^a	0.10	0.77 ^b	0.02	0.33
I _{ter}	0.32 ^a	0.13	0.35 ^a	0.03	0.34 ^a	0.04	0.08
IoS [%]	14.4 ^a	1.7	14.7 ^a	1.6	18.0 ^b	2.2	17.2
Number of formulae containing N	1412 ^a (49.2)	941	1928 ^a (54.9)	1083	1933 ^a (56.5)	951	1284 (58.8)
Number of formulae containing P	143 ^a (4.9)	112	129 ^a (3.6)	96	130 ^a (3.8)	54	196 (8.9)
Number of formulae containing S	69 ^a (2.4)	96	146 ^b (4.1)	101	46 ^{ab} (1.3)	43	37 (1.6)
Total number of molecular formulae	2867 ^a	1060	3509 ^a	1340	3416 ^a	848	2183

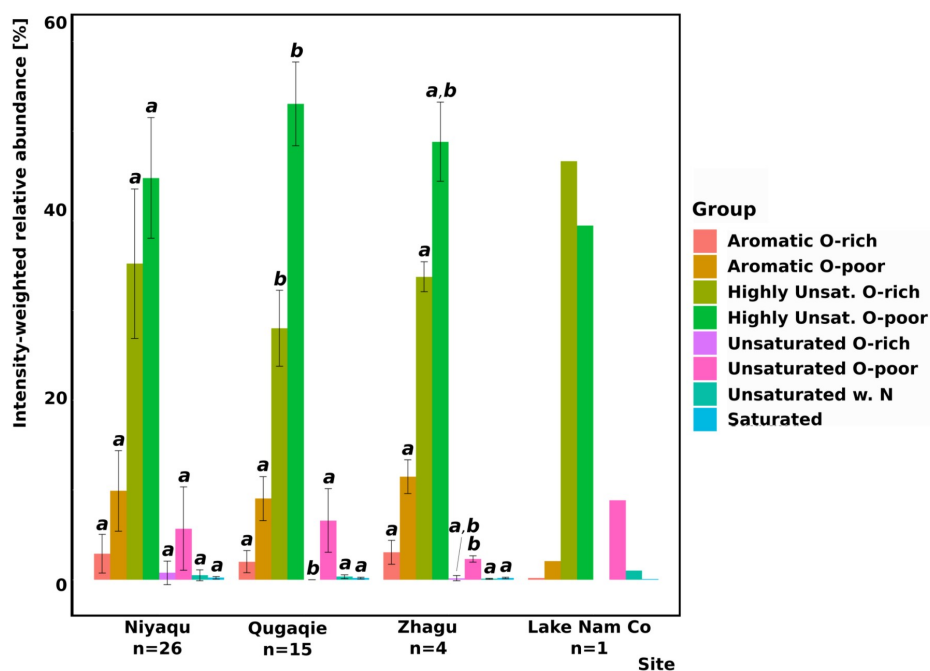
334 *Significant differences are indicated by superscript letters (a,b,c) ‡ indicates sample size n<3, here no*
 335 *standard deviations are given and no statistical tests were performed. For heteroatoms (N, P, S)*
 336 *percentages of the total number of molecular formulae are given in brackets. Boxplots of data are*
 337 *presented in the supplementary materials (Fig. S2).*

338 **Table 2: Overview on mean and standard deviation of indices and elemental composition ratios and**
 339 **mean and standard deviation of formulae counts for sample categories (including endmembers).**

Variable	Glacial effluent		Spring ‡	Wetland ‡	Stream water		Brackish water		Lake water ‡
	Mean	SD (±)	Value	Value	Mean	SD (±)	Mean	SD (±)	Value
Al _{mod}	0.31 ^a	0.04	0.35	0.33	0.33 ^a	0.05	0.35 ^a	0.02	0.25
DBE	9.15 ^a	1.06	9.76	9.70	9.51 ^a	0.97	10.39 ^a	0.73	8.14
O/C	0.45 ^a	0.03	0.44	0.46	0.46 ^a	0.02	0.46 ^a	0.01	0.44
H/C	1.17 ^a	0.08	1.15	1.09	1.13 ^a	0.07	1.13 ^a	0.07	1.20
CHO	-0.28 ^a	0.14	-0.18	-0.19	-0.22 ^a	0.09	-0.18 ^a	0.07	-0.29
I _{org}	0.53 ^a	0.13	0.77	0.53	0.58 ^a	0.15	0.66 ^a	0.02	0.33
I _{ter}	0.34 ^a	0.06	0.32	0.34	0.32 ^a	0.11	0.39 ^a	0.04	0.08
IoS [%]	13.7 ^a	2.24	17.4	16.0	15.1 ^a	1.9	14.5 ^a	1.33	17.2
Number of formulae containing N	1548 ^a (52.2)	1135	1261 (44.7)	2549 (62.3)	1511 ^a (44.2)	922	2586 ^a (57.5)	1231	1284 (58.8)
Number of formulae containing P	103 ^a (3.4)	90	117 (4.1)	291 (7.1)	130 ^a (3.8)	91	231 ^a (5.1)	160	196 (8.9)
Number of formulae containing S	134 ^a (4.5)	125	9 (0.3)	68 (1.6)	77 ^a (2.2)	90	163 ^a (3.6)	126	37 (1.6)



340 *Significant differences are indicated by superscript letters (a,b,c) † indicates sample size < n=3, here no*
 341 *standard deviations are given and no statistical tests were performed. For heteroatoms (N, P, S)*
 342 *percentages of the total number of molecular formulae is given in brackets. Boxplots of data are*
 343 *presented in the supplementary materials (Fig. S3).*



344

345 **Figure 2: Mean relative intensity-weighted counts of descriptive compound classes for stream waters**
 346 **of the three catchments and Lake Nam Co. For sample sizes < n=3, no standard deviations are given.**
 347 **Error bars indicate standard deviations, significant differences are indicated by superscript letters**
 348 **(a,b,c).**

349 Lake water samples contained only one fourth of aromatic O-rich compounds compared to stream
 350 water samples. Also, for aromatic O-rich compounds, large differences exist between lake water and
 351 water samples assigned to other sample categories, with samples from Nam Co having smallest
 352 abundances in this class. Brackish waters had significantly more aromatic O-poor compounds compared
 353 to glacial effluents (p=0.05). The relative abundances of highly unsaturated O-poor were highest in
 354 glacial effluents and groundwater spring waters, while wetland waters and samples from Lake Nam Co
 355 had the smallest relative values. Water samples from the Nam Co Lake had the highest relative
 356 abundances of highly unsaturated O-poor DOM compared to all other groups, especially glacial effluents
 357 had 40% less relative abundances in this class.



358 Unsaturated O-rich compounds had a very low proportion, but were more abundant in stream,
359 glacial and groundwater compared to wetland, brackish and lake waters, while unsaturated O-poor
360 compounds were more frequent in lake waters and glacial effluents compared to the other
361 categories. Spring water exhibited the least relative contribution of unsaturated O-poor compounds,
362 being almost 20 times lower compared to water from Lake Nam Co. Lake and glacial DOM were rich
363 in these molecular formulae, followed by stream, brackish and wetland waters which showed 50%
364 less abundance in unsaturated N-containing formulae compared to lake DOM. Spring water had
365 fewest of this compound class, being 75% lower compared to Lake Nam Co (Figure 3). Saturated
366 compounds were overall low, slightly higher values were only encountered in stream, spring, and
367 brackish waters.

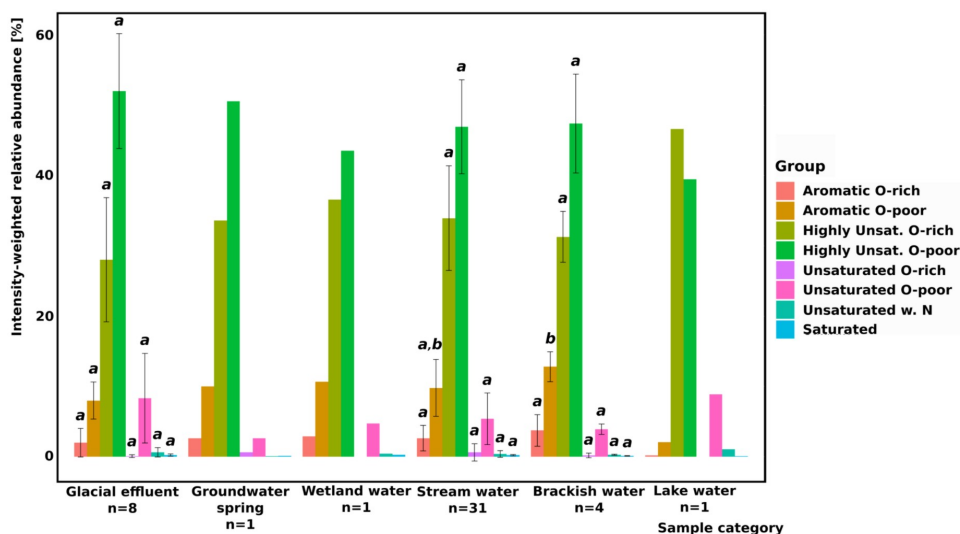


Figure 3: Mean relative intensity-weighted counts of descriptive compound classes sorted for sample categories. Error bars indicate standard deviations. For sample sizes $n < 3$, no standard deviations are given. Error bars indicate standard deviations, significant differences are indicated by superscript letters (a,b,c).

368 3.3 NMDS ordination

369 NMDS ordination was conducted with an overlay for both independent factors. NMDS stress value of
370 0.14 is in line with accepted stress measures (< 0.2 ; Dexter et al., 2018). The NMDS showed an
371 expansion of molecular formulae in the ordination plane in a funnel-shaped circumference above the
372 coordinate origin. The clustering of samples was within the scatter of formulae separated in two
373 smaller groups above the origin of coordination and more closely to the origin (Fig. 4a). AI_{mod} values
374 increased towards the negative direction of the first NMDS dimension and decreased towards the



375 positive direction, respectively (Fig. 4a). In the positive direction of dimension 1 of the NMDS biplot
376 (Fig. 4b), unsaturated and saturated compound classes are resolved together with sulphur for the
377 internal variables. DIC and EC explained this direction as external variables (black vectors in Fig. 4b).
378 In the negative direction of dimension 1 aromatic compound classes, the AI_{mod} , DBE , I_{Deg} and I_{Terr}
379 indices were loading. For external variables: plant cover, DOC and FDOM and partly $\delta^{13}C$ of DOC were
380 loading in this direction. The positive direction of dimension 2, distinguished samples with high
381 abundances in highly unsaturated and saturated compounds, together with the heteroatoms N, P
382 and S. The external variable of NO_3 concentration also loaded in this direction. The negative direction
383 of dimension 2 clustered samples close to the origin of the ordination which were related to IoS
384 values. Water samples of the Zhagu catchment were located around the centre of the ordination
385 plane in figure 4b, while DOM of Qugaqie was placed below and above the centre of the dimension
386 plane. Water samples from the Niyaqu catchment were more uniformly positioned below the centre.
387 The sampling categories showed that stream water samples were scattered over a wide plane of the
388 ordination, while brackish DOM samples were placed in the upper right corner of the plane, except
389 for one sample with less negative $\delta^{13}C$ of DOC. Glacial DOM clustered around the top-right to
390 bottom-right half of the ordination, indicating glacial DOM to be associated with heteroatoms,
391 saturated and unsaturated molecular compounds but as well with the external variables DIC
392 concentration and less depleted $\delta^{13}C$ of DOC. Glacial DOM signatures from Niyaqu and Qugaqie were
393 distinct in the ordination.

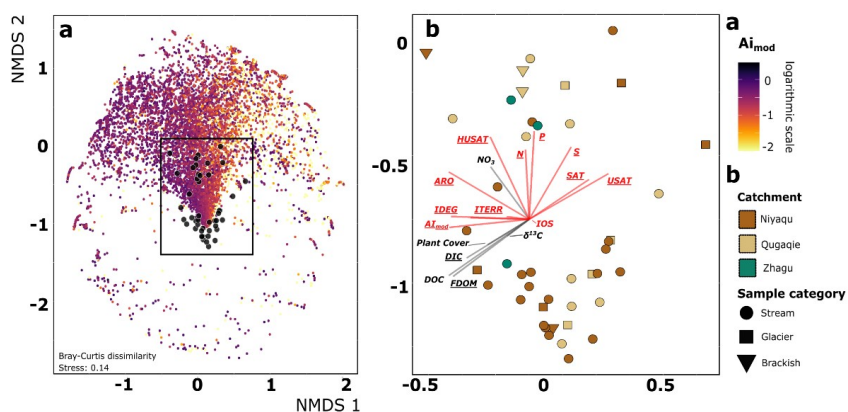
394 4. Discussion

395 4.1 Catchment properties shape DOM composition in the Lake Nam Co watershed

396 The three investigated catchments of the Nam Co watershed differed significantly in their molecular
397 DOM composition. The Qugaqie catchment showed the largest number of chemical formulae
398 identified, together with a higher abundance of formula containing S heteroatoms. The large α -
399 diversity of Qugaqie DOM can be influenced by the productivity of the glacial ecosystem hotspot
400 (Hodson et al., 2008) adding to the alpine pasture signature. The strong influence of S heteroatoms is
401 likely related to the local weathering processes by sulphate oxidation in the Zhadang glacier (Yu et
402 al., 2021). Anaerobic metabolism of sulphate reducing bacteria is known to take place in glacial
403 sediments and ice (Wu et al., 2012). After biotic reduction, sulphate is abiotically incorporated into
404 DOM, forming dissolved organic sulphur compounds (Pohlabein et al., 2017). Unsaturated O-rich and
405 highly unsaturated O-rich molecular formulae were relatively depleted compared to the other
406 catchments, while highly unsaturated O-poor and unsaturated O-poor formulae were increased.
407 Correspondingly, the CHO index indicated a comparably low degree of C oxidation. This shows that
408 higher complex compounds originating from plants and soils dominated the DOM of Qugaqie.



409 Correspondingly, the degree of microbial breakdown was lower compared to the other two
410 catchments, explaining the larger abundance of O-poor molecular formulae as also found in
411 incubation studies (D'Andrilli et al., 2019).



412

413 **Figure 4: Non-metric multidimensional (NMDS) scaling for a) samples and elemental composition**
414 **of compounds (elements C, H, O, N, P and S) plotted with the colour-coded logarithmic scale of the**
415 **aromaticity index AI_{mod} (Koch and Dittmar 2006; 2016). And b) for samples and environmental**
416 **variables: internal explanatory variables (red) and external explanatory variables (black).**
417 **Underscores indicate significant ($\alpha = 0.05$) relation of environmental parameters with the NMDS**
418 **dimensions. Stress = 0.14, $k = 3$, dissimilarity index = Bray-Curtis. ARO= aromatic O-rich and**
419 **aromatic O-poor, HUSAT =highly unsaturated O-rich and highly unsaturated O-poor, USAT =**
420 **unsaturated O-rich, unsaturated O-poor and unsaturated with N, SAT = saturated. Sites are**
421 **represented by the colour of sample points, while sample categories are represented by point**
422 **shapes.**

423 The Qugaqie catchment is mostly defined by its steep altitudinal gradient (>2000 m) and its glacial
424 influence, with glacial meltwater as the dominating water source (Bolch et al., 2010; Gao et al.,
425 2015), relatively low water temperatures of the meltwater hamper the microbial oxidation of DOM,
426 while water turbidity and turbulence shields against photooxidation. The higher relative abundance
427 of unsaturated low-molecular compounds makes microbial DOM derived from the glacial ecosystem
428 probable (Anesio et al., 2009; Hood et al., 2009; Spencer et al., 2014) and further suggests its
429 preservation through low water temperatures (Adams et al., 2010).

430 The contribution of glacial meltwater was smaller in the Niyaqu catchment and absent in Zhagu.
431 Here, the streams were less turbid and flowing slower (Maurischat et al., 2022). The main water
432 sources are precipitation and groundwater (Adnan et al., 2019a; Anslan et al., 2020; Tran et al.,
433 2021). In the arctic Zhagu catchment, a stronger indication of aromaticity with higher AI_{mod} and
434 higher relative abundance of aromatic compounds was found, alongside with a relatively low
435 contribution of lower-molecular mass unsaturated compounds. Furthermore, the higher oxidation



436 state indicated by CHO index (Fig. 5b, Table 2) and higher degradation index (Table 2) suggest an
437 intense microbial processing of biopolymers. This was also corroborated by the higher share of the
438 IoS, underlining that relatively more complex highly unsaturated O-rich molecular formulae are left
439 behind and by this enriched as recalcitrant DOM, as was shown in incubation studies (Mann et al.,
440 2015). The Niyaqu catchment in comparison showed a high contribution of aromatic compounds
441 together with a high contribution of unsaturated compounds and low H/C ratios. This catchment is
442 largely influenced by DOM originating from plants such as lignin and its degradation products
443 (Roebuck et al., 2018; Seifert et al., 2016), underlining the existence of a terrestrial – fluvial pathway.
444 In comparison, the high-altitude Qugaqie catchment also comprises of a glacial-borne microbial DOM
445 source highlighting compositional changes in the glacial – fluvial pathway. All catchments,
446 irrespective of the composition of the water source show influences of terrestrial allochthonous
447 organic material in DOM. This is visible by equally high aromatic indices (AI_{mod} , DBE, I_{terr}) and similar
448 contributions of aromatic compound classes. This serves as a strong indication of a land use control
449 on DOM signatures, namely by the human-induced *K.pygmaea* plagioclimax. There appears to be a
450 steady input of terrestrial DOM along the streampath from pastoral land as also demonstrated for
451 other agricultural systems (Roebuck et al., 2018). Notably, this influence became smaller, when
452 glacial, microbial DOM sources were more dominant on catchment level (Fig. 3b).

453 4.2 Abiotic and biotic controls on DOM composition are superimposed by pasture degradation

454 Our data show, that molecular diversity and DOM characteristics can be pinpointed to landscape
455 units and endmembers (summarized in the conceptual model in Fig. 7). NMDS analysis (Fig. 4)
456 suggested that glacial effluents were diverse in chemical composition, but differed between glacial
457 ecosystems, as was also shown by Spencer et al. (2014). But generally, glacial DOM from Qugaqie and
458 Niyaqu contained two different signatures from different sources. These were, 1) high abundances in
459 unsaturated compounds with and without nitrogen as well as a low oxidation state of carbon (Fig.
460 5a), high ratios of H/C and lowest percentage of recalcitrant DOM as demonstrated by comparatively
461 low IoS abundances. These parameters indicated a relatively fresh, reduced (oxygen-poor) DOM of
462 low-molecular mass derived from autotrophic microbial activity at the partly anoxic ice shield and are
463 in-line with findings from other glacial environments worldwide (Hood et al., 2009; Telling et al.,
464 2011; Anesio et al., 2009). 2) aromatic and highly unsaturated compound classes and aromatic and
465 terrestrial indices (I_{terr} , AI_{mod} , DBE) were in-line with other terrestrial DOM sources in our dataset,
466 despite the absence of plant cover in the glacial zones (Maurischat et al., 2022). Glaciers are
467 understood to receive compounds with higher molecular mass from aeolian deposition, either
468 condensed (poly)aromatics, e.g. from the burning of fossil fuels (Takeuchi, 2002) or compounds
469 uncondensed but rich in phenols, usually associated with vascular plants and soils (Singer et al.,
470 2012). The investigated coexistence of autochthonous and allochthonous DOM sources in glacial



471 DOM make them diverse and complex and render the understanding of glacial DOM reactions on
472 climatic changes and its downstream lability difficult (Singer et al., 2012).

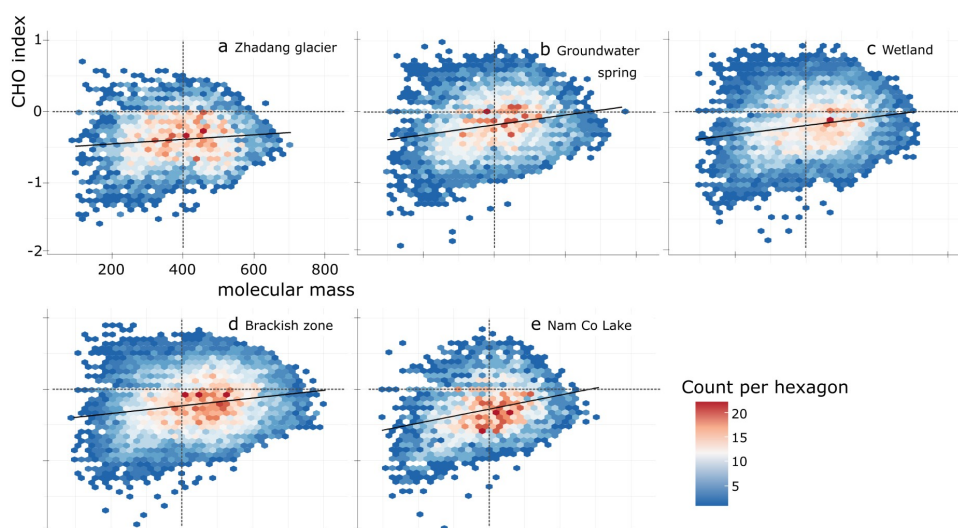
473 Groundwater spring DOM from the upland of the Zhagu catchment mainly comprised aromatic and
474 highly unsaturated DOM compounds. Molecular diversity and the number of N, P and S heteroatoms
475 was low. Concurrently, spring DOM suggested a strong degradation by high I_{Deg} and CHO indices (Fig.
476 5b) and a large contribution of recalcitrant organic matter as indicated by IoS values. Spring water is
477 generally expected to inherit aquifer and catchment characteristics in its DOM signature, also
478 preserving terrigenous DOM (Osterholz et al., 2022; Yoo et al., 2020). The shallow groundwater table
479 as found in Zhagu (Tran et al., 2021), was shown to be in contact with soil organic matter and yak
480 faeces (Maurischat et al., 2022), both of which can leach soil-borne OM to the groundwater table
481 (Connolly et al., 2020) and re-emerge at groundwater springs. The low molecular diversity of
482 groundwater spring DOM responds to an enrichment in aromatic and highly unsaturated formulae,
483 given the high degradation and recalcitrant nature of DOM, these compounds likely originated from
484 the degraded pedosphere and have been transported with the groundwater. The connection of over-
485 used, degraded pastures of Zhagu (Fig. 1 & 4b) with groundwater spring DOM indicated that a highly
486 modified DOM signature is emitted from springs and retrieved in streams. While investigations of the
487 effects of pasture degradation on Tibetan soil OM stocks are receiving much attention (Liu et al.,
488 2017), degradation induced changes of DOM composition have fallen short. DOM as a marker for
489 *K.pygmaea* degradation should generally receive more attention when studying degradation effects
490 on landscape-scale.

491 DOM from an extensive alpine wetland of the Niyaqu catchment shows a high α -diversity (>4000
492 assigned molecular formulae), was rich in N and P heteroatoms and in terrigenous highly unsaturated
493 O-rich and unsaturated O-poor compounds. In a study from the same site, wetland DOM was
494 enriched in mineralized nitrogen and DOC compared to the surrounding streams (Maurischat et al.,
495 2022). It was reported that alpine wetlands are highly productive and contain large amounts of
496 nutrients in the organic biomass and organic matter. Accordingly, the degradation of wetlands can
497 pose a nutrient threat to downstream ecosystems (Bai et al., 2010; Zhang et al., 2020).

498 Stream samples cluster relative widely around the NMDS ordination space but are concentrated in
499 the lower centre (Fig. 4b). Most samples had a predominance of aromatic compounds either
500 associated with highly unsaturated O-poor or highly unsaturated O-rich formulae, suggesting an
501 input of terrestrial compounds, such as lignin and tannin and their degradation products (Mann et
502 al., 2015), corroborated by depleted $\delta^{13}C$ DOC signatures (Maurischat et al., 2022). The *K. pygmaea*
503 biome spreads as an azonal pasture along the streams (Fig. 1). Roebuck et al. (2020) pointed out that
504 agricultural sites provide terrestrial inputs to surface waters. Correspondingly, Lu et al. (2015) found



505 predominance of aromatic and highly unsaturated compounds in watersheds dominated by pastoral
506 activity. The *K. pygmaea* biome is a large alpine yak pasture with potential influence of faeces, known
507 for their high biolability (Du et al., 2021), suggesting low molecular mass and negative CHO. The
508 scattering of stream samples can therefore also be explained by changing inputs from the pasture
509 biome. Faeces input and products of their microbial utilisation, will be associated with increases of N-
510 containing unsaturated formulae and saturated formulae (Vega et al., 2020). Still, the input from soil
511 and terrestrial plant material dominated stream samples.



512

513 **Figure 5: Hexagon scatter plots show the count of chemical formula in the space of CHO index**
514 **(Mann et al., 2015) and molecular mass. Black lines represent the linear model of CHO index and**
515 **molecular mass of the respective sample, grey dashed lines split the plot in quadrants for**
516 **orientation. Regression and orientation lines are printed to guide the eyes only. a) Ice from a**
517 **glacier in Qugaqie, b) groundwater spring from the upland of Zhagu (3:10), c) water from the**
518 **standing water column of a Niyaqu wetland (1:26), d) water from the brackish zone of Lake Nam**
519 **Co and the Qugaqie stream (2:15) and e) water sample from 30 m depth of the Lake Nam Co. Axis**
520 **scales are fixed.**

521 4.3 The Lake reactor: photooxidation changes DOM molecular composition

522 Brackish water samples showed the overall highest molecular diversity, highest number of N and S
523 heteroatoms and as well highest number of aromatic O-poor compounds together with high AI_{mod} ,
524 I_{terr} and DBE indices (Tab. 2). These samples were mostly dominated by aromatic and highly
525 unsaturated O-poor formulae and by this retained and accumulated the terrestrial signal of streams.
526 Van Dongen et al. (2008) described brackish waters as a zone of gradual mixing. Several studies
527 found a connection of terrestrial-derived DOM signatures from streams to be exported to marine
528 systems and showed gradual mixing in the brackish zone (Benner et al., 2004; Dittmar and Kattner,
529 2003; Pettersson et al., 1997; Ruediger, 2003). More so, the relative increase of aromatic compounds



530 suggests to some extent a selective degradation and oxidation of lower-molecular mass compounds
531 in the wash of the waves as suggested by the CHO index (Fig. 5d) and I_{Deg} , as shown for estuaries
532 (Asmala et al., 2014). We suggest that the high molecular diversity in brackish samples represents
533 both, the terrestrial input from catchment streams mixing with the DOM signature of lake water and
534 selective degradation of DOM, which is visible for the exemplary mass-to-charge (m/z) region
535 between 565.5 and 567.5 Da when comparing the evolution of molecular compounds from Zhadang
536 and Qugaqie mid-stream towards its brackish zone (Fig. 6a-c).

537 Lake water differed in its DOM composition compared to all other samples (summarized in the
538 conceptual model in Fig 7). Lake DOM was relatively enriched in unsaturated and saturated
539 compounds, which can include lipids and carbohydrates, but depleted in aromatic and highly
540 unsaturated O-rich formulae. Correspondingly, Al_{mod} , DBE and I_{Terr} decreased, likely as a result of
541 photooxidation (Helms et al., 2014) given the clear water column and high irradiation (Wang et al.,
542 2020). Spencer et al. (2009) reported photooxidation to remove aromatic DOM such as lignin phenols
543 from a large river system and Helms et al. (2014) investigated the loss of DOM optical properties
544 after light exposition. This process can hence explain the depletion of phenolic constituents
545 corresponding to decreased Al_{mod} , I_{Terr} and DBE indices and becomes visible in the excerpt of mass
546 spectra between 565.5 to 567.5 Da when comparing brackish and lake DOM (Fig. 6c-6d). In a stream-
547 estuary-lake gradient the terrigenous brackish DOM likely underwent a transformation when
548 entering deeper in the lake, leaving more recalcitrant DOM behind (Goldberg et al., 2015) as
549 corroborated by the higher percentage of IoS compared to stream and brackish DOM (Table 2).
550 Miranda et al. (2020) found that highly unsaturated and aromatic compounds are not only degraded,
551 but partly transformed to unsaturated (N-containing) compounds by UV radiation. This can further
552 explain the increase in unsaturated and unsaturated N-containing compound classes and the more
553 negative CHO with lower molecular mass (Fig. 5e) in lake DOM (Figure 3). Along with degradation and
554 transformation of allochthonous DOM, autochthonous DOM production plays a large role for the
555 natural OM characteristics of Lake Nam Co. Microbial autochthonous DOM sources have been
556 suggested for Lake Nam Co (Spencer et al., 2014; Maurischat et al., 2022) and other large lakes of the
557 Himalayas (Liu et al., 2020). Hu et al. (2016) report from a Nam Co food web study that mainly
558 autochthonous organic carbon sources are utilised by zooplankton, further corroborating the
559 importance of an autochthonous DOM source. The comparably low CHO index (Fig. 5e) underlines
560 the existence of autochthonous low molecular mass, reduced carbon species, while higher molecular
561 masses of allochthonous origin are more oxidised in the lake environment compared to other
562 systems (Fig. 5), indicative of strong processing. The DOM signature of water samples of Lake Nam Co
563 from 30 m depth were drawn below the dimictic thermocline (Wang et al., 2009). This DOM
564 resembled characteristics of the open ocean, being low in aromatic compounds and terrigenous



565 indices (Seidel et al., 2017) and had a larger percentage of IoS, suggesting higher recalcitrance and
566 millennial scale stability. Comparably DOM recalcitrance of Lake Nam Co was not on the level of large
567 arctic rivers (Behnke et al., 2021) or the deep ocean (Lechtenfeld et al., 2014), but clearly increased
568 compared to the watershed stream network. Lake DOM further exhibited autochthonous DOM
569 sources derived from algal and microbial production (Zark and Dittmar, 2018; Seidel et al., 2015).
570 DOM of this large endorheic Tibetan lake is evidently not influenced by DOM of inflowing streams,
571 since the lake is a functional reactor in processing terrigenous aromatic DOM.

572

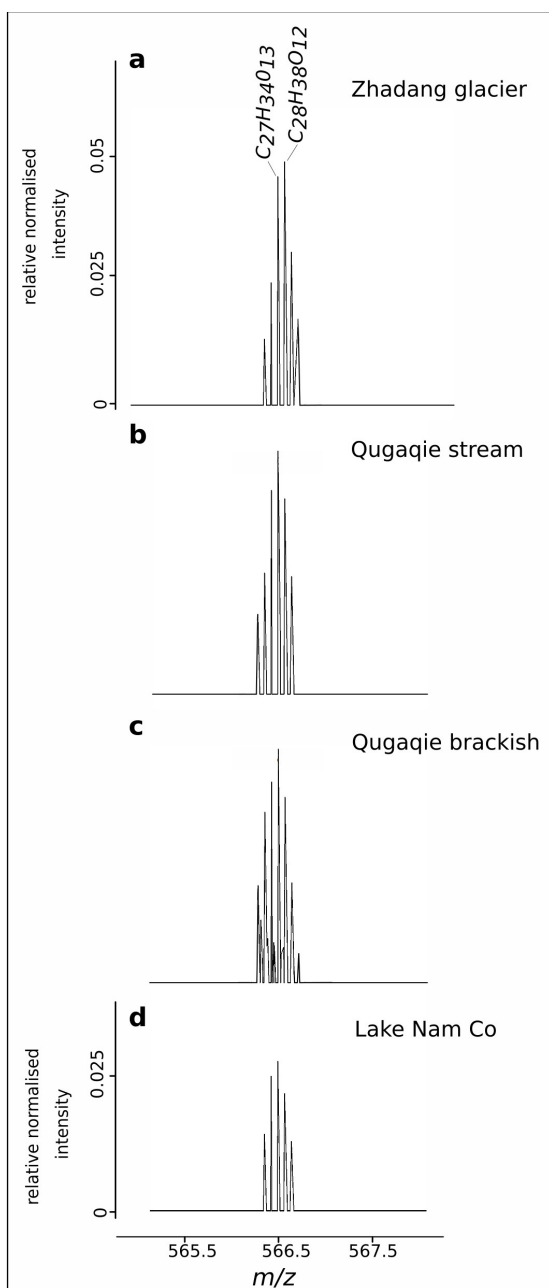


Figure 6: Molecular cross-section through the Qugaqie catchment with the termination in Lake Nam Co. Presented mass spectra between 565.5 and 567.5 m/z are noise reduced and normalised for intensity. A) Ice from a glacier in Qugaqie, b) mid-stream sample from Qugaqie (2:12), c) water from the brackish zone of Lake Nam Co (2:15) and the Qugaqie stream and e) water sample from 30 m depth of the Lake Nam Co. Axis scales are fixed.



573 5. Conclusions

574 We elucidated the composition and the processing of DOM along the flow path in the High Asian
575 endorheic Nam Co watershed. We investigated different endmembers of three catchments, including
576 DOM samples of glaciers, groundwater springs, alpine wetlands, streams, the brackish mixing zone
577 and the saline lake.

578 Catchments of the Nam Co watershed differed in their chemical composition of DOM irrespective of
579 the spatial distances. Conversely, endmembers, and degradation of alpine pastures, were found to
580 influence these differences by releasing degraded terrestrial DOM signatures. Water sources
581 influence DOM signatures in streams of the Lake Nam Co watershed. Molecular diversity was large in
582 glacial influenced streams, which were also characterized by the largest proportion of low molecular
583 mass compounds. In the glaciated Qugaqie catchment, we identified a unique dual source, on the
584 one hand, a microbial, low-molecular mass DOM fraction relatively rich in S heteroatoms and
585 unsaturated compounds with and without nitrogen, possibly including degradation products of
586 peptides and amino sugars, suggesting high biolability and autotrophic DOM production in the glacial
587 ice shield. On the other hand, DOM with high aromaticity and high abundances of highly unsaturated
588 compounds, such as plant-derived lignin, hinting at a depositional source of aeolian transported local
589 dust, derived from soil. Polycondensed aromatics probably including black carbon with high an Al_{mod}
590 and large number of C-atoms derived from the combustion of fossil fuels or household burning of yak
591 dung may also enter the ice shield via the atmospheric pathway. The large influence of glacial
592 meltwater in the Qugaqie catchment greatly modifies DOM signatures along the whole stream of the
593 catchment and probably delivers bio-available compounds to the southern lake shoreline,
594 underlining the existence of a glacial – lacustrine pathway. The Niyaqu and Zhagu catchment
595 comprised a lower molecular diversity, and had a mainly allochthonous DOM source of highly
596 unsaturated and aromatic compounds, attributed to the input of surrounding plants and soils of the
597 pastoral *K.pygmaea* biome to the streams.

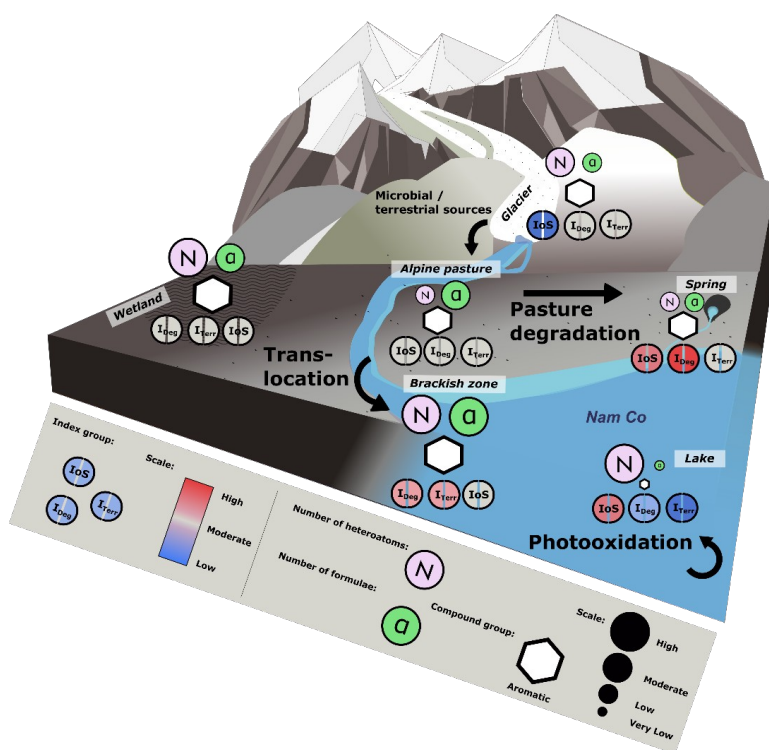
598 Groundwater spring DOM had a low molecular diversity and was enriched in plant and soil-derived
599 aromatic and highly unsaturated compounds alongside with an increase in P heteroatoms and
600 saturated formulae. This suggests that spring DOM of the Zhagu upland constitutes background DOM
601 signatures but also inherits highly degraded, oxidized, and probably recalcitrant DOM from the
602 degrading pastures and potentially yak faeces. Wetland DOM exhibited a high molecular diversity
603 and was especially rich in N-heteroatom compounds, alongside with aromatic and highly unsaturated
604 formulae. Wetland DOM likely represents a broad range of terrestrial DOM signatures from the
605 catchment, driven by the high productivity, water-logging and the basin topography of the wetlands.
606 The latter lead to a steady inflow of water and OM by lateral movement. If the reported degradation



607 of alpine wetlands in High Asia drives a larger release of DOM to the streams, this can be considered
608 a threat for oligotrophic terminal aquatic systems, such as Lake Nam Co, but especially for smaller
609 lakes.

610 Stream samples were mostly associated with the input of allochthonous materials, originating from
611 vascular plants and soils. These are attributed to the predominant *K. pygmaea* biome and pastoral
612 practise stretching along the path of streams. From these zones terrestrial-borne DOM is constantly
613 refuelled into the streams.

614 Brackish samples represented the mixing zone of stream and lake water, showing that the terrestrial
615 DOM signal is being transported with stream waters into the lake. In this cold, fast flowing streams
616 with short water residence times and high turbidity transformation along the pathway is arguably
617 smaller compared to other ecosystems. Lake DOM, however, was chemically diverse compared to all
618 other sources, its molecular composition suggests intense photooxidation and transformation of
619 imported allochthonous stream DOM, alongside with an autochthonous DOM source from microbial
620 and algal in-situ production in the large oligotrophic lake. These DOM signatures can be compared to
621 terminal signatures encountered in the open ocean. Our study shows that DOM cycling in the Nam
622 Co catchment needs a thorough assessment, since it can be diverse between catchments and
623 landscape units. In order to safeguard water resources and related ecosystem services, knowledge
624 about the different sources and their later processing is indispensable. DOM properties have proven
625 here as a selective proxy, suitable to be implemented as a monitoring agent in the Nam Co
626 watershed, representative for processes on the larger southern TP.



627

628 **Figure 7: Overview of the molecular DOM information along the water network continuum of the**
629 **TP. The number of N-heteroatoms are indicated relative to the total number of molecular**
630 **formulae. Island of stability (I_{oS}), degradation index (I_{Deg}) and terrestrial index (I_{Terr}) are ranging in a**
631 **red colour code for high blue in the opposite case. Alpine steppe and groundwater spring samples**
632 **are spatially correlated, and thus subject of a common evaluation. Main processes and sources are**
633 **added and indicated by black arrows.**

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641

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