- 1 A-Complex dissolved organic matter DOM continuum fromon the roof of the world
- 2 Tibetan <u>DOM</u> molecular dissolved organic matter characteristics track sources,
- 3 land use effects, and processing along the fluvial-limnic pathwaycontinuum
- 4
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- 15 **Keywords:** Non-metric multidimensional scaling (NMDS), Alpine pastures, Natural organic matter
- (NOM), Land use controls, Molecular NOM composition, Fourier-transform ion cyclotron resonance
   mass spectrometry (FT-ICR-MS)

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# 25 Abstract

The Tibetan Plateau (TP) is the worldworld's largest and highest plateau, also comprising the earth's 26 biggest connected alpine pasture system of the world. Like other alpine systems, lit is sensitive to 27 28 impacts of climate change and increasing anthropogenic pressure. Carbon cycling aton the TP is 29 determined influenced in particular by glaciation and degradation of the pasture ecosystem is complex, 30 including sources such as primary production in lakes, glaciers, and terrestrial plants, agricultural land use but also organic matter (OM) from aeolian deposition. Dissolved organic matter (DOM) connects 31 these carbon reservoirs in the network, following the hydrological cycle continuum from precipitation, 32 33 glaciers, and headwaters to lakes. DOM is highly complex, complex: its molecular composition 34 holdscontains information from the its diverse sources and transformations during transport. 35 However, Due due to its complexity, complexity, the DOM cycling of DOM cyclingDOM along the 36 headwater fluvial-limnicaguatic pathway-continuum and how-the impact of terrestrial-land use and climate change can impact organic matter on DOM carbon characteristics cycling in the diverse water 37 bodies isare still not well understood. Here, we study solid phase extracted (SPE) DOM molecular 38 transformations characteristics using ultrahigh-resolution mass spectrometry (FT-ICR-MS) along the TP 39 40 hydrological continuum from glaciglaciersal, groundwater springs, and wetlands-biomes including pastures and alpine steppe, steppes, to the large saline endorheic Lake Nam Co. Our study revealed 41 that the SPE-DOM composition of DOM was largely influenced by local sources of glaciers, wetlands, 42 and groundwater springs and also incorporateding molecular signatures of as well as pasture 43 degradation. Intensive transformation of DOM was visible betweenDOM molecular composition 44 45 differed with respect to allochthonous sources between endmembers, as well as between stream 46 samples, the brackish mixing zone, and the lake. Glacial meltwater SPE-DOM contained showed 47 contained more saturated compounds suggesting microbial sources together with dust-borne condensed (?) aromatic compounds probably derived from aeolian deposition. autochthonous 48 signatures of low-oxidised, unsaturated molecular formulae together with terrestrial like, dust borne 49 50 DOM sources. Glacial fed streams were characterised by fresh autochthonous, probably algal DOM, and aromatic compounds likely originating from pastoral land sources. DOMDOM from of a g which we 51 52 related to the shallow upper aquifer, and degraded pastoral land sources. In comparison, wetland and stream SPE-DOM were characterised by a higher percentage of highly unsaturated and aromatic 53 54 molecular formulae. These were likely derived from less oxidised and less degraded inputs of vascular 55 plants and soils. Groundwater spring SPE-DOM from degraded pastures differed from intact pasture samples. In degraded systems Here a strongly oxidised signature with lowest counts of P heteroatoms, 56 lower O/C ratio and higher aromaticity of SPE-DOM together with a high degradation index suggested 57 58 a strong transformation of SPE-DOM, probably. SPE-AtDOM of the endorheic Lake was richer in unsaturated molecular formulae compared to the tributaries. This suggest algorithm and microbial 59 2

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60	DOM-sources and production in the lake. The SPE-DOM rich in aromatic and highly unsaturated
61	formulae visible in the brackish zone of the lake shore contrasted highly sharply Nam C with the lake
62	samples. depletion Aromatic aromatic terrestrial molecular formulae- were strongly depleted in the
63	lake deep water suggesting suggested photooxidation of riverine SPE-DOM-at the surface, and relative
64	enrichment of potentially recalcitrant DOM within the lake. Additionally, a relative enrichment of more
65	aliphatic, nitrogen-containing DOM suggests. Our study revealed that DOM composition was largely
66	influenced by local sources and transformations in glaciers, wetlands, and groundwater springs, also
67	incorporating molecular signatures of pasture degradation. Streams with less glacial influence had
68	plant-and soil borne aromatic rich DOM sources, while the endorheic Lake Nam Co had a recalcitrant
69	DOM composition comparable to millennial scale stable marine DOM. This suggests indicates that
70	there is no typicalsing the alpine SPE-DOM signature, high alpine DOM signature, but that complex
71	processes form <u>different_DOM characteristics in the fluvial limnicaguatic</u> continuum. <u>iss are</u> shaped by
72	Small-scaleSsmall-scale catchment properties, land degradationdegradation, and aquatic domainsthe
73	influence of glaciers and wetlands-these differences. Alpine The close link of alpine SPEDOM
74	composition -compositions hence appear to be closely linked to -landscape properties is
75	indicative for suggestinga strong their susceptibility to changes in water quality and OM cycling in
76	sensitive High Asian ecosystems, susceptibility of DOM characteristics to climatic and land use changes
77	in High Asia.
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- Graphical Abstract: Main processes shaping SPE-DOM molecular characteristics and transformations
   in the high-alpine Nam Co watershedcatchment. DOM pPMain processesing and sources are added
- 80 and indicated by black arrows. Pasture degradation is indicated by a dashed arrow.
- 81

82	1. Introduction
02	-
83	How the characteristics of natural organic matter (NOM) are innuenced by different ecosystems and
84	$ the \ degradation \ of \ land \ on \ the \ TP \ is \ still \ not \ fully \ understood. \ While \ T\_tT he \ Tibetan \ Plateau \ (TP)$
85	comprises the largest alpine pasture system ofin the world (Miehe et al., 2019) and is-It is also known
86	as Asia's water tower (Bandyopadhyay, 2013), formingforming the source of many-large river systems,
87	providing freshwater resources to billions of people in East and South-East Asia. Large
88	quantitiesamounts of the water are stored in the ice masses of the TP, forming the largest frozen
89	freshwater reservoir outside the Polar Regions. polar regions. This third pole environment is well
90	investigated (Qiu, 2008; Yao et al., 2012), revealing that High Asia's ecosystems are threatened
91	(Hopping et al., 2018) by climate change (Yao et al., 2019) and by intensification and other changes of
92	land use (Harris, 2010). <u>Furthermore, Ee</u> merging freshwater quality issues give reason for concern (Qu

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93	et al., 2019)-and the unknown consequences of peak water (McDowell et al., 2022) highlight the
94	utmost importance of the TP for up- and downstream societies.
95	-Nutrient and energy cycles of ecosystems are connected by dissolved organic matter (DOM) fluxes
96	(Spencer et al., 2014). DOM can connect fluvial ecosystems over hundreds of kilometres (Seidel et al,
97	2015) and links terrestrial and aquatic ecosystems (Goodman et al., 2011). Biogeochemical
98	processesing inand DOM-the sources area are known to shape the molecular composition of DOM (Liu
99	et al., 2020; Roebuck et al., 2020; Seifert et al., 2016; Wilson and Xenopoulos, 2009). But how the DOM
100	characteristics isare influenced by different ecosystems and how itDOM responds to ecosystem
101	degradation is yet not well understood. We hypothesize that DOM molecular characteristics ental
102	markers for climatic and land use changes on the TP and that these markers can be used to
103	differentiate between landscape units and endmembers. Understanding the marker function of DOM
104	will allow to better foresee carbon processing at present and under changing environmental
105	conditions. Lastly, this will be key to assess the potential vulnerability and responses of high alpine
106	ecosystems to the challenges of the Anthropocene.
107	DOM connects fluvial ecosystems over several hundreds of kilometres (Seidel et al., 2015), and links
108	terrestrial and aquatic biomes (Goodman et al., 2011). Changes in catchment properties might
109	therefore trigger effects in distanced, fragile ecosystems (Wilson and Xenopoulos, 2009), showing that
110	action and response of land use or climatic changes can be temporally and spatially detached (Goes et
111	al., 2020; Roulet and Moore, 2006). The molecular diversity and complexity of DOM calls for the
112	employment of advanced techniques (Fellman et al., 2010; Nebbioso and Piccolo, 2013). This led to
113	analytical advancements such as electrospray ionization Fourier transform ion cyclotron resonance
114	mass spectrometry (FT-ICR-MS), an ultrahigh resolution mass spectrometry method allowing to
115	identify thousands of molecular formulae in samples of natural organic matter (NOM), thus offering a
116	unique opportunity to understand molecular DOM characteristics, sources and transformations
117	(Hawkes et al., 2020).
118	Here, we used Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) is FT-ICR-
119	MS-an ultrahigh-resolution method allowing the identification of elemental composition in thousands
120	of molecular formulae-of NOM, offering an opportunity to better understand molecular, solid phase
121	extracted (SPE) DOM characteristics, sources, and transformations (Hawkes et al., 2020; Leyva et al,
122	2020; Šantl-Temkiv et al., 2013). Here we used FT-ICR-MSto gain insight about molecular information
123	and elemental composition of DOM, to understand decipher characteristics and processing of stream
124	SPE-DOM of different subcatchments, glaciers, <u>a</u> groundwater spring, and an alpine wetland as well
125	ass endmembers and SPE-DOM of an endorheic lake on the TP.

126 The Nam Co watershedcatchment, located in the southern/central part of the TPTP, lies in the 127 transition zone of the K. pygmaea (K. pygmaea) dominated alpine pasture biomeecosystem (Miehe et 128 al., 2008) and the alpine steppe. The area's The unique positioning in this transition zone is expressed 129 between the south, with a more humid, humid glacial-influenced high-mountain ecosystem contrasting 130 the hilly northern margin of the catchment, with more arid climate and and vegetation dominated by 131 alpine steppe dominated vegetation, steppe, where clear signs of pasture degradation are visible 132 (Maurischat et al., 2022). This makes the Nam Co catchment a suitable natural laboratory (Anslan et 133 al., 2020)-to test for effects on organic matter (OM) characteristics and the cycling of organic matter 134 OM in different ecosystems (Anslan et al., 2020). The effects of pasture degradation of Tibetan soils 135 on\_OM stocks are receiving much attentionabundant have been studied previously (Liu et al., 2017), 136 but investigations on degradation induced changes of DOM composition have fallen short. when studying degradation effects on landscape scale.DOMAlso\_DOM characteristics and transformation in 137 this complex natural interplay werehave only been only investigated to limited extent. Spencer et al. 138 139 (2014) found complex OM sources in glaciers, streamsstreams, and Lake Nam Co. A recent study 140 highlighted transformation highlighted a coupled decrease of "protein-like" DOM with an increase of 141 "humic-like" DOM along the flowpath (Li et al., 2021), whereas other works found indications for less reactive stream DOM due to the cold and fast flowing water (Maurischat et al., 2022). This leaves 142 143 important questions of 1) howhow DOM signatures are influenced by the diverse biotic and abiotic inventories processes of in the watershedcatchment with differing degreedegrees of glaciation, alpine 144 145 wetlands, and groundwater sources, as well as land degradation, and the alpine pasture alpine steppe ecotone, and 2) how DOM is processed during the fluvial pathwayalong the streams and in the 146 147 lake.

148 We hypothesize that DOM molecular characteristics entail markers for climatic and land use 149 changesOur investigations of DOM will on the TP and that these markers can be used to differentiate 150 between landscape units and endmembers. Understanding the marker function of DOM will allow to 151 better aim at a better understanding of SPE-controlling factors of DOM processing at present 152 conditions which will help to better understand the potential and to foresee carbon processing at 153 present and underconsequences of changing environmental conditions in the future, Lastly, tIt will be 154 keyis important -to assess the potential vulnerability and responses of high alpinehigh-alpine 155 ecosystems to the Anthropocene anthropogenic challenges changes of the Anthropocene. The Nam Co watershed is a sentinel for changes and a natural laboratory (Anslan et al., 2020), suited 156 157 to test whether DOM characteristics can be employed as a precursor for changes in this sensitive alpine 158 environment, representative for larger parts of the TP. In this respect, we In this context we

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160	having different DOM sources	differ in their molecular	composition of DOM	where the effect of
100	, naving amerene bow sources,	unce in their molecului	-composition of Dow,	where the chect of

161 intensified land use and pasture degradation drives a degraded, terrestrial signature rich in recalcitrant

- 162 molecular formulae.
- I) SPE-<u>DOM derived from different eThe endmembersEcosystems</u>— <u>(glaciers, glacial effluents,</u>
   groundwater springs and <u>alpine</u>-wetlands) <u>and streams in degraded land along the glacier to lake</u>
   <u>continuum</u> possess unique DOM signatures compared to the integrated DOM of <u>subcatchment</u>
   streams.
- 167 III) The SPE-DOM ttransformations along the stream path are is limited by cold water temperatures
- 168 large discharge, high turbidity, and short residence times in the stream. I, no major compositional shift
- 169 is expected in-stream.n contrast, signatures of DOM transformations in the clear and deep lake are
- 170 expected to be dominant.
- 171 In consequence, IV)[II] The SPE-DOM signatures characteristics of lake water are chemically disting
- 172 compared to the from the terrestrial DOM sources and integrated stream SPE-DOM composition.reveal
- 173 photodegradation and biological utilisation induced processing of DOM.

#### 174 2. Materials and methods

# 175 2.1 Site description and sampling

176 The Nam Co watershedcatchment has a total size of 10870089 km<sup>2</sup>. Two main landscape units can be 177 are distinguished, the southern mountainous and the northern upland zone. The south of the 178 watershedcatchment is characterised by the Nyaingentanglha mountain ridge (NMR) with glaciation at highest elevations of more than 7000 m.m asl. , which are glaciated (Bolch et al., 2010). Glacial 179 180 meltwater is the dominatingdominant water source of southern the streams here (Adnan et al, 181 2019b). Sparse vegetation dominates the glacial zone, while K.K. pygmaea pastures are being 182 developed fromat 5300 m asl. downward lower elevations (Anslan et al., 2020 Miehe et al., 2019) and are associated with a felty organic-rich topsoil (Kaiser et al., 2008). Closer to the lake shore and on lak 183 184 terraces, alpine steppe vegetation is developed-prevailing (Nieberding et al., 2021). The southern part 185 of the watershed<u>catchment</u> is characterised by higher precipitation compared to the north. Up to 530mm y<sup>-1</sup> are measured <u>atin</u> the NMR (Anslan et al., 2020). In the northern marginthe hilly uplands a less 186 steep relief dominates (Yu et al., <del>2021),2021), and an lower annual precipitation of around 300 mm y</del> 187 188 <sup>1</sup> are is reported (Anslan et al., 2020). Alpine pasture is developed onin north-exposed hill-flanks and 189 inand the valley bottoms, while alpine steppe grows on south exposed flanks, in the upland, upland 190 and at the lake shoreline (Maurischat et al., 2022). Along with thise aridtivaridity gradient from south 191 to northhan degradation, land degradation gradient occursis increasing (Anslan et al., 2020). Th 192 climate of the watershed is biannual. The summer months are dominated by the Indian Summer

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193 Monsoon from May until early September (Chen et al., 2019). More than 80% of the annual 194 precipitation falls during the monsoon season with mean day time air temperature up to 11°C (Chen 195 et al., 2019). During winter and spring, the climate is dry and cold with minima of around 20°C 196 between December and February and fewer precipitation (Nieberding et al., 2021). The endorheic Lake 197 Nam Co with an elevation of 4726 m- asl. has a total size of \_2000 km<sup>2</sup>-<sup>2</sup>. The lake is dimictic, 198 oligotrophic, and lightly lightly-saline (0.9 g salt l<sup>-1</sup>; Keil et al., 2010),2010) and has a depth of 99 m. It is 199 well supplied with oxygen and has a clear water column (Wang et al., 2020).

200 Three subcatchments of the Nam Co watershedareaNam Co catchment were selected to represent 201 theits natural diversity (Fig. 1 a, b). The Niyaqu catchment (sample IDs 1:n in Fig. 1a, low glaciation) -in 202 the east has a total area of 406 km<sup>2</sup>. Two streams drain the subcatchment, the southern stream 203 receives meltwater from a glacier of the NMR located 700 m above lake level. This river runs through 204 extensive alpine pastures and feeds a large alpine wetland (Fig. 1b, point 1:26). The northern stream drains a hilly upland area in the transition of of the alpine steppe and and the alpine pasture. 205 206 HerdingThe herding of yakyaks takes place throughout the year. The Zhagu subcatchment (sample IDs 207 3:n Fig. 1a, no glaciation - degraded) is located -in the arid north-of the watershed is the smallest 208 investigated catchment. It has a size of 46 km<sup>2</sup> and is mostlymainly characterised by hilly upland relief 209 (Keil et al., 2010). There is no glacial influence and only a small altitudinal gradient in this catchment, 210 with the highest elevation at 5230 m. asl. Two creeks drain the catchment, both fed by groundwater 211 springs. During investigation sampling, the streams were arheic, and showed clear signs of degradation 212 of K. pyqmaea pastures were visible (Maurischat et al., 2022), -, -Besides degraded pastures, alpine 213 steppe is developed and used for animal husbandry. In the south, the Qugagie subcatchment (sample 214 IDs 2:n Fig. 1b, <u>high glaciation</u>) represents the high altitude <u>NMR</u> zone of the NMR. The catchment has 215 a size of 58 km<sup>2</sup> and is characterised by steep relief and a valley course in south-north direction (Keil 216 et al., 2010). The altitudinal difference betweenbetween the lake and and the summit is 2200 m. This 217 catchment is used as summer pasture-along the stream that drains the catchment. 218 Water samples were taken in September 2019 following the streams from source until-to\_terminus. 219 Potential endmembers Glaciers, wetlands wetlands, and groundwater springs were sampled directly.

220 identified by following the stream discharge routes upstream.

We identified\_<u>T</u>three endmember\_source\_groups (glacial effluents, groundwater springs, and alpine wetlands) and three-<u>additional</u> sampling units (stream water, brackish water, and lake water) were <u>distinguished</u>, resulting in six sample categories (Fig. 1). Glacial effluents were drawn directly at or close to the glacial terminus, while groundwater was sampled directly at springs. Alpine wetland samples were taken from the standing water column-<u>in the wetlands</u>of areas characterised by bogs and aquatic plants. Brackish water<u>s</u> samples were samples were taken taken <u>sampled</u>-in the mixing

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- 227 zone of stream and lake water at the stream mouth at the shoreline offshore in of Lake Nam Co. Lake
- 228 samples were taken offshore. Details on the characteristics of the catchments and the sampling can
- 229 be obtained from Maurischat et al. (2022).



<sup>230</sup> 

Figure 1: (a) Overview map (by-Stamen Design, under CC BY 3.0. Data by Open Street Map contributors 2022, under CC BY SA, © OpenStreetMap contributors 2022. Ddistributed under the Open Data Commons Open Database LicenseLicence, { ODbL}, v1.0). The rectangle represents the sampling area.A+B}\_Overview\_m (b) Shows the Ooutline of the Nam Co Lake and the three subcatchments. (c) and (-Dd) Map of the investigated subcatchments and sampling locations with sample categories. Plant cover estimations from Maurischat et al. (2022.)(2022) (a+b) represent K. pygmaea pastures, the zones of most prominent yak grazing.

Samples were taken from the middle of the stream profile using a telescopic sampling device. Lake waters wasere sampled from 30 m depth with a submersible sampler. All samples were taken in seven subsamples with a volume of <u>1 of ne litre</u> each, mixed and a <u>500 0.5 mL</u> aliquot of this was taken for final processinganalysis. Samples were filtered on-site using a 0.45 µm mesh size polyethersulfone membrane (Supor, Pall, Port Washington, USA), a vacuum-filtration device and a portable electric pump. Samples were stored in pre-cleaned high-density polyethylene bottles (Rotilabo, Carl Roth, Karlsruhe, Germany) and kept at -21°C until analysis.

245 2.2 Solid\_phase extraction

Data Source: JAXA ALOS World 3D - 30m (AW3030); 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 License; openstreetmap.org (OSM)

246 Filtered DDOM samples were acidified to pH 2 using 32 % HCl (Rotipuran p.a., Carl Roth, Karlsruhe, 247 Germany). Dissolved organic carbon (DOC) concentrations were measured from 20 mL of sample by 248 high-temperature oxidation on a total organic carbon analyser (varioTOC Cube, Elementar, 249 Langenselbold, Germany). DOM samples were-then diluted with ultrapure water toatto a concentration of 1.5 mg C L<sup>-1</sup>, L<sup>1</sup>, and 250 mL of diluted sample waswere used for extraction. Cartridges 250 with 100 mg of styrene divinyl benzenedivinylbenzene polymer (PPL) resin (Bond Elut, Agilent 251 Technologies, Santa Clara, USA) were used for extraction. SPE-DOM was prepared following Dittmar 252 253 et al. (2008). The SPE elute was transferred into cauterized brown glass flasks (Neochrom, Neolab 254 Migge, Heidelberg, Germany) sealed with polytetrafluorethylen caps (Neochrom, Neolab Migge, 255 Heidelberg, Germany) and stored at -18°C until further analysis. Extraction The extraction efficiency 256 was assessed evaluated by drying 0.2 mLmL of SPE-DOM under an-N2 atmosphere and resolving the 257 aliquot in 20 mL of ultrapure water. The samples were then analysed for their its-Dearbon-OC 258 concentrations by high-temperaturehigh temperature oxidation (varioTOC Cube, Elementar, 259 Langenselbold, Germany) and the volumetric proportion of initial DOC to extracted SPE-DOC 260 concentrations was calculated. Reference material (Suwannee River / IHSS) (Green et al., 2015) was compared towith routine assays. Blank samples with ultrapure water were used to checkcheck for 261 262 contaminationa.

# 263 2.3 Fourier\_-Transform Ion Cyclotron Resonance Mass Spectrometry

SPE-DOM samples were diluted in 1:1 methanol/ultrapure water to a final concentration of 5 mg C L<sup>-1</sup> 264 265 for analysis. Samples were analysed in duplicates on a SolariX XR 15 Tesla FT-ICR-MS (Bruker Daltonik, Bremen, Germany). Duplicate sample eElectrospray ionization (ESI) was carried out in negative mode 266 267 and samples were injected at a flow rate of 122 µL h<sup>-1</sup>. 200 broadband scans (masses range of 92.14 to 268 2000 Da) were acquired per sample, accumulation time was 0.2 s per scan. Mass spectra were 269 internally calibrated with a list of known CxHyOz molecular formulae over the mass range in the 270 samples, achieving a mass error of < 0.1 ppm. Instrument variability was assessed with an in-house 271 standard of SPE-DOM from North Equatorial Pacific Intermediate Water (NEqPIW) collected near 272 Hawaii (Natural Energy Laboratory of Hawaii Authority, NELHA)Internal calibration standards from the 273 Northern Equatorial Pacific Intermediate Water (NEqPIW) (Green et al., 20145).- were used toto a 274 assign mass spectra to mass error < 0.1 ppm.\_Molecular formula attribution was done with ICBM-275 OCEAN (Merder et al., 2020). The Mmethod detection limits (MDL) wereas applied (Riedel and Dittmar, 276 2014) with thethe default ICBM-OCEAN defaultICBM-OCEAN elemental composition and with a a 277 minimum signal-to-noise ratio (S/MDL) of 2.5. Minimum signal to MDL ratio as backbone for 278 recalibration was 5 using mean recalibration mode. Molecular formulae were assigned with a tolerance 279 of 0.5 ppm as  $C_{1-100}H_{1-125}O_{1-40}N_{0-4}S_{0-2}P_{0-1}$  in the mass range 95 to 1000 Da. Molecular formulae Formatiert: Hochgestellt

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280	assignments wereformulae assignments was were accepted if the molecular formula was they were
281	present in more than 25% of the samples. Contaminants were identified and excluded using the
282	contaminant reference mass list and in additional conformity with the SPE-DOM process blanks.
283	Detection limits for peaks were normalised to sample peak intensities. OverallThe overall peak
284	intensities were scaled to the local sample maxima by maxima using the sum of peaks. Molecular
285	formulae containing lisotopes (13C, 18O, 15N, 34S) were removed mass effects were corrected to the
286	naturally most abundant form of each isotopologuefrom the data table for further processing and
287	Mmolecular formulae with molar ratios of oxygen-to-carbon (O:C) = 0, O:C ≥ 1, and hydrogen-to-
288	carbon (H:C) > 2.5 were removed <u>as well</u> . Duplicate samples were normalised, normalised, and
289	molecular formulae were retained only, only when present in both duplicates. NEqPIW DOM was used
290	as an in-line calibration to measure instrument drift.
291	2.4_SPE-DOM Mmolecular descriptive classes, countscounts, and indices
292	Molecular formulae were assigned to SPE- <u>DOM</u> molecular compound classes (Leyva et al., 2020). The
293	original compound classification was <del>suggested <u>taken from</u>by</del> Šantl-Temkiv et al. (2013) <u>, and </u> SPE-DOM
294	compound class names-labels were modified according to the descriptive classes used by ICBM-OCEAN
295	$\frac{1}{2}$ (Merder et al., (2020). The modified aromaticity index (Al <sub>mod</sub> ) representing SPE-DOM aromaticity in $\frac{1}{2}$
296	DOM, was calculated for each formula as proposed by Koch and Dittmar (2006; 2016). Almod indices >
297	0.5 were-was assigned as aromatic, while $\underline{AI_{mod}}$ indices-> 0.67 were-was considered as condensed
298	aromatic compounds. The degradation index ( $I_{\text{Deg}}$ ) was calculated as a measure of degradation state of
299	SPE-DOM (Flerus et al., 2012) and the terrestrial index ( $I_{\text{Terr}}$ ) was calculated, as a measure of terrestrial
300	SPE-DOM sources (Medeiros et al., 2016). Molecular formulae that were part of We further assessed
301	ŧ <u>∓t</u> he island of stability (IO <mark></mark> ₽S) <del>(Lechtenfeld et al., 2014) <u>was</u>were evaluated</del> to gain <del>insights<u>i</u>nsight</del> into
302	the relative <u>abundance of recalcitrant SPE-DOM (Lechtenfeld et al., 2014)</u> , This is based on the
303	assumption that share of comparably intrinsically stable recalcitrant, i.e. millennial scale stable
304	molecular compoundsTthise_IOS_contains_SPE-DOM_molecular_formulae_representing_recalcitrant
305	oceanic SPE-DOM that is empirically stable on millennial time scales was defined with an age of 4 to 5
306	ky and a lifetime from months to millennia in oceanographic contexts (Lechtenfeld et al., 2014)The
307	CHO index was calculated as a measure <del>of<u>of</u> organic carbon oxidation stage<u>oxidation</u> (Mann et al,</del>
308	2015). Low CHO values indicate highly reduced reduced molecular formulae (relatively low O content)
309	and high CHO values indicate highly <del>oxidized<u>oxidised</u> (relatively high O content)</del> molecular formulae.
310	Molecular diversity was interpreted as $\alpha$ -diversity by depicting the intra-community intracommunity
311	molecular diversity (Thukral, 2017). <sub>7</sub> 뉴 <u>H</u> ere we use <u>d</u> the total number of molecular formulae <del>on<u>on the</u></del>
312	catchment or endmember group scale of subcatchments and sample categories as a representative.

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#### 313 2.5 Environmental variables

314	Relative DOM fluorescence (FDOM) as the product of co-correlated microbial-like and terrestrial-like
315	EDOM, DOC, dissolved inorganic carbon concentration (DIC), $\delta$ <sup>43</sup> C of DOC, mean plant cover at the
316	sampling point and the concentration of nitrate (NO <sub>2</sub> <sup>3</sup> ) were taken as environmental predictor variables
317	from Maurischat et al. (2022) and tested for statistical correlations with the molecular DOM data.
318	2. <u>5</u> 6 Statistic <u>al analyses</u>
319	Molecular formula intensities were rescaled between 0 and 1-and expressed in percentage. The
320	analysis was conducted by <u>G</u> grouping was conducted with two independent factors: 1) $\pm the three$
321	subcatchments: Niyaqu (low glaciation), Qugaqie (high glaciation), Zhagu (degraded) and Lake Nam
322	Co; and 2) the sample categories: : endmember water (glacial effluents, spring, and wetland as well as)
323	<del>as well as site groups (</del> stream water, brackish water, and lake water <del>)</del> . <u>Samples from <del>Two <mark>endmember</mark></del></u>
324	groups, sSspring, and wetland, as well as the site group-Lake Nam CoCo, was were excluded from
325	statistical group comparisons analysis due toto the small sample sizes. Intensity weighted arithmetic
326	$\underline{means}\underline{means}_{means}, \text{ and standard deviation} \underline{s} \text{ were calculated for } AI_{mod}, \text{ number of formulae containing} \underline{the}$
327	heteroatoms nitrogen (N), phosphorous (P) and sulphur (S), as well as the total number of assigned
328	formulae and for compound classes.
329	Data were tested for normal distribution and homoscedasticity by application of Kolmogorov Smirnoff

test and Levene test (Brown and Forsythe, 1974). Due to violations of normal distribution\_and homoscedasticity in combination with unbalanced sampling designe sizes per group, parametrical tests were considered unreliable (Bortz and Schuster, 2010). Multiple pairwise comparisons were conducted using Kruskal WallisKruskal-Wallis tests in combination with Bonferroni post hoc corrected Dunn tests and Mann Whitney tests (Birnbaum, 1956).- for pairwise comparisons with Bonferroni post hoc correction for multiple testing. Significance levels of  $\alpha = 0.05$  were set as threshold applied (Supplementary material, Table S1 and Table S2).

Non-metricNonmetric multidimensional scaling (NMDS) was used for dimensionality reduction and 337 338 ordination (Anderson et al., 2006; Faith et al., 1987) based on a Bray-Curtis dissimilarity index matrix 339 (k = 3). Data for NMDS were scaled and mean-centred (Jolliffe, 2002). NMDS was conducted performed 340 for both independent factors (sites and sample categoriesy), while sites and sample categories those with low statistical power (n < 3) were not incorporated to avoid confounding. -The Bray Curtis 341 dissimilarity index with k = 3 was used. Loadings, scores, and R<sup>2</sup>-coefficients of determination are 342 343 provided in the supplementary material (Tables S3 – S7). Co-correlation was checked visually and by 344 Pearson's correlation coefficient, defined as:  $|\mathbf{r}| > 0.75$ . The following compound classes were 345 combined because of co-correlation: aromatic O-rich and aromatic O-poor = ARO, highly unsaturated O-rich and highly unsaturated O-poor = HUSAT, unsaturated O-rich, unsaturated O-poor and 346 12

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347 348	unsaturated with N = USAT (Fig. 4). Collinear external predictorvariables (section 2.6) were remove	ł		
540	non ale node.			
349	R software (The R project for statistical computing, v3.6.3, GNU free software) was used for statistics	•		
350	The R base packages (R Core Team, 2013) and tidyverse (Wickham et al., 2019) were used for data	a		
351	organisation, and pre-processing pre-processing, and, as well as non-parametric statistics. The	9		
352	packages ggplot2 (Wickham et al., 2019) and vegan (Oksanen et al., 2020) were used for graphica	I		
353	illustration and for NMDS analysis, respectively.			
354	2.65 Environmental variables for statistical analysis			
355	Several parameters were used as predictor variables in the NMDS. Internal predictor variables were	2		
356	generated from the SPE-DOM FT-ICR-MS-dataset obtained by FT-ICR-MS (SPE-DOM indices, compound	<u>t</u>		
357	class percentages and heteroatom counts; described in section 2.4). External predictor variables wer	2		
358	taken from a previous study of the same site and the same sampling campaign (Maurischat et al. 2022	)		
359	and tested for statistical correlations with this SPE-DOM dataset. The selected external variable	<u>s</u>		
360	showed evidence as functional predictors in the prior study and are acknowledged as key parameter	<u>s</u>		
361	for DOM characterisation in numerous applications.: The variables included fluorescent DOM (FDOM	)		
362	components (here used as the product of co-correlated microbial and terrestrial-like FDON	1		
363	components) (Fellman et al., 2010), DOC concentrations (Eklöf et al., 2021), δ- <sup>13</sup> C of DOC (Guo et al			
364	2006), dissolved inorganic carbon concentration (DIC) concentrations, as a catchment geolog	L		
365	parameter (Wang et al., 2016), nitrate concentrations (NO <sub>3</sub> ) (Harms et al., 2016), and the mean plan	<u>t</u>		
366	cover at the sampling point as a land use indicator (Sankar et al., 2020) were used.			
367	<u>3. Results</u>			
368	Relative DOM fluorescence (FDOM) as the product of co-correlated microbial-like and	•	_	Formatiert: Schriftart: Fett. Schriftfarbe: Text 1
369	terrestrial-like FDOM, DOC, dissolved inorganic carbon concentration (DIC), δ 13C of DOC,			Formatiert: Überschrift 3, Links, Abstand Nach: 8 Pt.,
370	mean plant cover at the sampling point and the concentration of nitrate (NO3-) were taken as			Zeilenabstand: einfach
371	environmental predictor variables from Maurischat et al. (2022) and tested for statistical correlations with the molecular DOM data			
272				
3/3				
374	<del>, Kesuits</del>		$\langle$	Formatiert: Schriftart: 11 Pt.
375	3.1 Sample treatment and quality assessment			Formatiert: Uberschrift 3
376	SPE-DOM extraction efficiencies were 61.4 $\% \pm$ 18.6 $\%$ (Supplementary material, Table S8). DON	1		Tormatiert, Schnitart, FFT, Fett, Schnitarbe, Text I
377	extraction efficiencies and the number of SPE-DOM molecular formulae (detected by FT-ICR-MS) were	2		
378	only weakly correlated (R <sup>2</sup> =0.08, F (1, 43) =5.144, $\beta$ =-0.007, p=0.02) indicating that There was non-	<u>&gt;</u>		
379	sufficient statistical explanatory power <u>relationship</u> between the <u>between</u> extraction efficiency and th	•		
	13	2		
	1.			

380	retrieved <u>the</u> number <u>of of retrieved</u> molecular formulae of the <u>of</u> samples (R <sup>2</sup> =.08, F (1, 43) =5.144, $\beta$ =-	
381	0.007, p=0.02) to expect systematic methodological failur extraction efficiency was not an important	
382	driver of molecular variability in our samples $\frac{R^2=.08}{R^2=.08}$ , F (1, 43) =5.144, $\beta$ = 0.007, p=0.02). SPE-DOM	
383	process blanks and reference material (Suwannee River / IHSS) were runDuplicate SPE-DOM process	
384	blanks had below 1000 molecular formulae assigned and the Suwannee River / IHSS reference material	
385	had ~3500. Minimum molecular formulae count to accept NOM samples was set to 2000, roughly in	
386	the range of the number of molecular formulae expected from terrestrial aquatic samples (Seidel et	
387	al., 2017; Spencer et al., 2014). The in house-control standard 38 in-line drift control standards	
388	(NEqPIW_SPE-DOM) wereas_run_repeatedly_during_analysis (n = 38) to account for instrument	
389	variability. In meanOn average, 3558 (± 218) molecular formulae were assigned: no significant	
390	instrument drift was detected (Supplementary material Figure S1).	
301	3.2 Molecular group counts and statistics	
551		
392	Samples were grouped by two independent factors, site (the three investigated catchments Niyaqu,	
393	Qugaqie, Zhagu, or the Nam Co Lake) and sample category (the three endmembers (glacial,	
394	groundwater spring and wetland waters) as well as stream, brackish and lake water samples). TFor	
395	sites, the total number of assigned molecular formulae, here termed $\alpha\text{-diversity},$ decreased in the	
396	order Qugaqie_ <u>(high glaciation)</u> > Zhagu_ <u>(degraded)</u> > Niyaqu_ <u>(low glaciation)</u> > Lake Nam Co <sub>ur</sub> Lake	
397	Nam CO SPE-DOM latter had 50 % less assigned molecular formulae compared to the subcatchments	$\overline{\ }$
398	(Table 1). Water-SPE-DOM samples from wetland and brackish environments hadhad the highest	
399	numbers of assigned molecular formulae, followed by glacial effluents, spring and stream water,	
400	contrasting molecular diversity (Table 2), compositional shifts in the H/C and O/C ratio of brackish and	
401	lake SPE-DOM are displayed in Figure 6a with a zoom on one example mass range (371 <u>-</u> 371.3 <u>m/z</u> , Fig.	
402	6b).	
403	Heteroatom containing molecular formulae (N. S. P.) bad different relative abundances in sites and	
404	sample categories - Lake Nam Co SPE-DOM had relatively more N-containing molecular formulae -N-	
405	sumple categories, take rain of <u>site bown</u> had relatively more two ontaining more categories. The of the	
405	neteroatoms than compared to SPE-DUM water samples from the subthree catchments (Table 2). The	

<u>low glaciation</u> Niyaqu compared to <u>high glaciation</u> Qugaqie <u>SPE-DOM (p=0.005)</u>, lowest mean values

were found in DOM of Zhagu and Lake Nam Co. P-containing molecular formulae were enriched in the 408 DOM of the lake water relative to compared to SPE-DOM of the three subcatchments (Table 1, Table 409 410 S1).

relative abundance of sulphurS--containing molecular formulae was significantly decreased-lower in

406

407

411 N-containing molecular formulae were mostmore abundant in wetland water and brackish water-SPE-412 DOM samples, while - Spring, stream, and glacial effluents formed a group of medium N distribution 413 and groundwater springlake SPE-DOM samples had the lowest count. GDOM and glacial SPE-DOM had 14 Formatiert: Nicht Hervorheben Formatiert: Nicht Hervorheben

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414 the highest relative abundances of S-containing molecular formulae, followed by wetland and stream 415 DOM with lower amounts, while groundwater springs and lake DOM had the lowest number 416 molecular formulae associated with S. Molecular formulae containing P were least abundant in glac 417 and groundwater spring DOM, followed by the order stream < lake < brackish water < wetland DO 418 A high abundance of P was visible in lake DOM at relative numbers (Table 2). 419 SPE-DOM of Lake Nam Co had lowest-lower\_AImod\_-DBE and Iterr values, while DOM from Niyaqu, Qugaqie and Zhagucompared to the subcatchments -exhibited no differences (Table 1). For For the 420 421 sample <del>categories, categories, \_</del>-brackish SPE-DOM had higher I<sub>Terr</sub> and DBE values but no significant 422 differences were visibleobserved -between DOM of terrestrial systems-(Table 2). -The No significar 423 differences were visible for O/C ratios, but the H/C ratios were highest in Lake SPE-DOM (Table 1) with 424 - Ssignificantly higher relative numbers of hydrogen in samples of Qugagiehydrogen compared to Niyagu (p=0.005). Additionally, the CHO index showed that Lake SPE-DOM and SPE-DOM of the high 425 <u>glaciated</u> -Qugagie catchment were significantly less oxidized compared to SPE-DOM of the degraded, 426 427 arheic Zhagu catchment (p=0.042 statistically tested only for subcatchments). Correspondingly, IDe 428 values, were significantly higher for <u>degraded</u> Zhagu compared to <del>both</del> the <u>glaciated</u> Niyaqu and 429 Qugagie subcatchments SPE-DOM (p=0.0002). DOM of Lake Nam Co had Lowest values of Ipee-IOS 430 values, indicatingive\_of recalcitrant SPE-DOM with relatively long residence timesmore recalcitrant 431 intrinsically stable DOM, showed a significantly higher contribution in-<u>degraded</u> Zhagu and Lake Nam 432 Co compared to low glaciated - Niyaqu and high glaciated Qugaqie (p= 0.04, 0.05, respectively 433 statistically tested only for subcatchments). In theFor sample categories (Table 2)2- H/C ratios were higher in glacial and lake SPE-DOM-and lower in wetland DOM and . The CHO index suggested less 434 435 oxidized SPE-DOM in originating from glacial effluents and the lake compared to terrestrial sources 436 (Fig. 5). Correspondingly Iner values were lower in the lake compared to glacial, stream and wetla DOM. Hhighest I<sub>Deg</sub> values were observed in SPE-DOM of the brackish zone and in groundwater springs 437 438 The percentage of IOS values values increased in lake and groundwater springs compared to the order glacial effluentseffluents, > brackish water > stream water > wetland water > lake > groundwater 439 springs-indicating differences in the contribution of intrinsically recalcitrant-stable recalcitrant-SPE 440 441 DOM.

Assigned cCompound classes (Fig. 2) give an overview aboutof the composition of SPE-DOM. Largest differences among the sites were were found for the aromatic classes DOM groups. Lake Nam Co had 80 % less aromatic (O)-rich molecular classes compared to the subcatchment-sDOM. For aromatic C poor compounds, the The lake had only 5 % of the almost 20 times fewer compound abundance of aromatic O-poor compounds compared to subcatchment SPE-DOM. For highly unsaturated O-rich molecular formulaeformulae, Lake Nam Co had higher values compared to subcatchment SPE-DOM,

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- 448 while highly unsaturated O-poor molecular formulae wereformulae slightly decreased in the lake.
- 449 Further, Furthermore, the unsaturated O-poor and unsaturated N-containing SPE-DOM classes were
- 450 higher in lake SPE-DOM compared to the terrestrial systems. Within catchments, hH ighly unsaturated
- 451 O-rich formulae were more abundant in glacial influenced-SPE-DOM of high glaciation Qugagie
- 452 <u>compared to low glaciation Niyaqu</u> Significantly more unsaturated O-rich molecular formulae were
- 453 found in Niyaqu DOM compared to Qugaqie (p=0.02), while unsaturated O-poor molecular formulae
- 454 were significantly less abundant in DOM of Zhagu compared to both Niyaqu and Qugaqie samples
- 455 (p=0.007). Relative abundances of saturated molecular formulae were overall low (Fig. 2).

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	Niyaqu <u> (low</u>	<u>glaciation)</u>	Qugaqie (hig	<u>h glaciation)</u>	Zhagu (d	egraded)	Lake Nam Co	ŧ
Variable	<u>n=</u> 2	<u>n=26</u>		<u>n=15</u>		-4	<u>n=1</u>	
	Mean	SD (±)	Mean	SD (±)	Mean	SD (±)	Value	
$AI_{mod}$	0.33 ª	0.05	0.32 ª	0.02	0.36 ª	0.02	0.25	
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 <u>b</u>	0.05	1.13 <u>a.b</u>	0.08	1.20	
СНО	-0.21 ab	0.11	-0.26 b	0.08	-0.17ª	0.04	-0.29	
I <sub>Deg</sub>	0.55 <u>n</u>	0.15	0.59 ª	0.10	0.77 <u>b</u>	0.02	0.33	
I <sub>Terr</sub>	0.32 <sup>a</sup>	0.13	0.35 <sup>a</sup>	0.03	0.34 <sup>a</sup>	0.04	0.08	
100S [%]	14.4 ª	1.7	14.7ª	1.6	18.0 <sup>b</sup>	2.2	17.2	
Number of formulae containing N	1412 ° (49.2)	941	1928 ° (54.9)	1083	1933 ° (56.5)	951	1284 (58.8)	
Number of formulae containing P	143 ° (4.9)	112	129 ° (3.6)	96	130° (3.8)	54	196 (8.9)	
Number of formulae containing S	69 ª (2.4)	96	146 <sup>b</sup> (4.1)	101	46 <sup>ab</sup> (1.3)	43	37 (1.6)	
Total number of molecular formulae (α-diversity)	2867 ª	1060	3509 <sup>a</sup>	1340	3416ª	848	2183	

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

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458  $\frac{a,b}{b}$  Significant differences ( $\alpha$ =0.05) are indicated by superscript letters  $\frac{(a,b,c)}{b}$ ,  $\frac{b}{c}$  Significant differences ( $\alpha$ =0.05) are indicated by superscript letters  $\frac{(a,b,c)}{b}$ ,  $\frac{b}{c}$  Significant differences ( $\alpha$ =0.05) are indicated by superscript letters  $\frac{(a,b,c)}{b}$ ,  $\frac{b}{c}$  Significant differences ( $\alpha$ =0.05) are indicated by superscript letters  $\frac{(a,b,c)}{b}$ ,  $\frac{b}{c}$  Significant differences ( $\alpha$ =0.05) are indicated by superscript letters  $\frac{(a,b,c)}{b}$ ,  $\frac{b}{c}$  Significant differences ( $\alpha$ =0.05) are indicated by superscript letters  $\frac{(a,b,c)}{b}$ ,  $\frac{b}{c}$  Significant differences ( $\alpha$ =0.05) are indicated by superscript letters  $\frac{(a,b,c)}{b}$ ,  $\frac{b}{c}$  Significant differences ( $\alpha$ =0.05) are indicated by superscript letters.

460 no standard deviations are given and no statistical tests were performed. For heteroatoms (N, P, <del>S)</del><u>S)</u>,
 461 percentages of the total number of molecular formulae are given in brackets-parentheses. Boxplots of
 462 heteroatom (N, P, S)

462 data are presented in the supplementary materials (Fig. S2).

# Table 2: Overview on mean and standard deviation of indices and elemental composition ratios and mean and standard deviation of formulae counts for sample categories <del>(including endmembers)</del>.

	Glacial effluent <u>n=8</u>		effluent Spring † Wetland †		Stream w	ater	Brackish w	ater	Lake water ‡	T
Variable			<u>n=1</u>	<u>n=1</u>	<u>n=38</u>		<u>n=4</u>		<u>n=1</u>	
	Mean	SD (±)	Value	Value	Mean	SD (±)	Mean	SD (±)	Value	ļ
$AI_{mod}$	0.31 ª	0.04	0.35	0.33	0.33 <sup>a</sup>	0.05	0.35 °	0.02	0.25	
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	1.17ª	0.08	1.15	1.09	1.13 °	0.07	1.13 ª	0.07	1.20	
СНО	-0.28 ª	0.14	-0.18	-0.19	-0.22 ª	0.09	-0.18 ª	0.07	-0.29	
I <sub>Deg</sub>	0.53 <sup>a</sup>	0.13	0.77	0.53	0.58 *	0.15	0.66 ª	0.02	0.33	
I <sub>Terr</sub>	0.34 ª	0.06	0.32	0.34	0.32 ª	0.11	0.39 °	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 ° (52.2)	1135	1261 (44.7)	2549 (62.3)	1511 °(44.2)	922	2586°(57.5)	1231	1284 (58.8)	
Number of formulae containing P	103 ° (3.4)	90	117(4.1)	291 (7.1)	130°(3.8)	91	231 ° (5.1)	160	196 (8.9)	
Number of formulae containing S	134ª (4.5)	125	9(0.3)	68(1.6)	77 ° (2.2)	90	163° (3.6)	126	37(1.6)	
Total number of formulae	2965 a	1132	2819	4091	3416 ª	1053	4492 <sup>a</sup>	1639	2183	

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465  $\frac{a_{-b}}{b_{-}}$  Significant differences ( $\alpha$ =0.05) are indicated by superscript letters <u>(a,b,c),  $\frac{1}{2}$  Single sample, indicates</u> 466 sample size < n=3, here no <u>s</u> tandard deviations <u>were not calculated and are given and no</u>-statistical tests 467 were <u>not</u> performed. For heteroatoms (N, P, <del>S)S),</del> percentages of the total number of molecular formulae 468 isare given in <del>brackets-parentheses.</del> Boxplots of data are presented in the supplementary materials (Fig. 469 S3).

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471 Figure 2: Mean rRelative intensity-weighted <u>averages counts</u> of <u>descriptive</u> SPE-DOM\_compound classes
472 for stream water of the three <u>sub</u>catchments and Lake Nam Co (sites). For sample sizes n<3, no standard</li>
473 deviations are given. Error bars indicate standard <u>deviations, deviations</u>, significant differences (α=0.05)
474 are indicated by superscript letters (a, b,c).

475 The relative abundances of Also\_Lake water samples contained only one fourth of aromatic O-rich 476 compounds compared to stream water samples. Also, fEfor agromatic O-rich-compounds ,were 477 differencest exist between SPE-Dom of the lake water and water SPE-DOM samples assigned to other 478 sample categories, with samples from Nam Co having the smallest lowest relative abundances (Fig\_3) in 479 this class. Brackish waters-SPE-DOM had significantly more aromatic O-poor compounds compared to glacial effluents (p=0.05). The relative abundances of highly unsaturated O poor were highest in glacial 480 481 effluents and groundwater spring waters, while wetland waters and samples from Lake Nam Co had the allest relative values. Water <u>SPE-DOM samples</u> from the Nam Co Lake had the highest relative 482

483 abundances of highly unsaturated O-poor-rich\_DOM- compounds compared to all other groups, especially

484 glacial SPE-DOM had <u>in mean-on average</u> 40% less <u>O-rich compoundsrelative abundances in this class</u>.

485 Unsaturated O-rich compounds had a very low proportion, but were more abundant in stream, glacial 486 and groundwater compared to wetland, brackish and lake waters, while unsaturated O-poor 487 compounds were relatively more abundant more frequent in lake waterswater-SPE-DOM and glacial 488 effluents compared to the other environmental sample categories categories; this class was especially depleted in .- Sspring water-SPE-DOM. Alongside exhibited the least relative contribution of 489 490 unsaturated O-poor compounds, being almost 20 times lower compared to water from Lake Nam Co. Lake and glacial SPE-DOM were relatively rich in these molecular formulae, followed by stream, 491 492 brackish and wetland waters which showed 50% less abundance in unsaturated N-containing formulae compared to lake DOM. Spring water hadhad the fewest of this compound class, being 75% lower 493 494 compared to Lake Nam Co (Figure 3). Saturated compounds were overall low, slightly higher values 495 were only encountered in stream, spring, and brackish waters.





496 3.3 NMDS ordination Multivariate statistical analysis

497 NMDS ordination was conducted with an overlay with a graphical overlay for sites and sample
498 categories. <u>NMDS-The</u> stress value of 0.14 is in line within stress measurestolerance (< 0.2; Dexter et</li>
499 al., 2018). In NMDS ordination (Fig. 4a) molecular formulae expanded in the ordination plane above

500 the coordinate origin. The clustering of <u>S</u>amples were distributed in as within the scatter of formulae

501	separated in-two groups depending on aromaticity and related indicators (AI <sub>mod</sub> , I <sub>Deglpeg,</sub> and I <sub>tref</sub>
502	Izerrindices-). AImod values increased from the positive towardsto the negative direction of the first
503	NMDS-dimension-and decreased towards the positive direction, respectively (Fig. 4a). In the positive
504	direction of dimension 1, samples containing relatively more (Fig. 4b), unsaturated and saturated SPE-
505	DOM_compound classes as well as S-containing compounds awere resolved loading together with
506	<del>sulphur_distributed (Fig. 4b) these<u>.</u> for the internal variables<u>, sS</u> samples <u>in this dimension</u>also <u>have</u>had</del>
507	lower_Almod, HDeglper, and HTerr-LTerrindices DIC and EC explained this direction as external variables (black
508	vectors in Fig. 4b). In the negative direction of dimension 1, samples with a higher abundance of
509	aromatic compound classes_ <u>were awere loadingdistributed</u> . For external variables <u>The external</u>
510	predictors: DIC and plant coverplant cover, DOC and FDOM and partly 8 <sup>13</sup> C of DOC were loading in this
511	direction along with DOC concentrations and values of FDOM and $\delta^{13}$ C of DOME -(black vectors in Fig.
512	4b) suggesting that these samples were influenced by This all indicates-DOM inputs of plants and soils
513	influence is indicated here. The second dThe positive direction of dimension 2 of the NMDS ordination
514	separated samples according to the <u>points on</u> , distinguished samples with high abundance in <u>of</u> highly
515	unsaturated and saturated SPE- <u>DOM</u> compounds, together with the <u>N, P and S</u> heteroatoms <del>N, P and</del>
516	S. These samples were also characterized by elevated The external predictor variable of NO3
517	concentration <u>s</u> also loaded in this direction_Samples located closer to the origin of predictor variable
518	vectors were related to higher_IOS valuespercentages and suggested a higher abundance of more
519	intrinsically stable_recalcitrant_SPE-DOM.
520	Samples of the <u>degraded</u> Zhagu <u>sub</u> catchment were located close to the centre of predictor variable
521	vectors <del>plane in (F</del> fig.ure 4b), while <del>DOM</del> -samples of <u>high glaciation</u> Qugaqie was-were scattered on
522	the dimension plane. SPE-DOM from the <i>low glaciation</i> Niyaqu subcatchment as more uniformly
523	placedositioned in the lower part. The sampling categories showed that sStream water water SPE
524	DOM wassamples were scatteredover, indicating large chemical diversity. while Most brackish DOM
525	SPE-DOM_samples were placed in the upper left of the plane, associated with higher terrestrial
526	indicators (AI <sub>mod</sub> , heelpeer, and hereform) and more abundance of N and P heteroatoms, except for one
527	sample with less negative $\delta^{13}$ C of DOC. Glacial DOM_SPE-DOM_was associated with heteroatoms,
528	saturated and unsaturated molecular compounds <u>compounds</u> , but as well with the external variables
529	DIC concentration and less depleted $\delta$ <sup>13</sup> C of DOMC, visible by its positioning in the bottom left to top
530	right of the ordination plane. to beGlacial DOM signatures from Niyaqu and Qugaqie were distinct in
531	the ordination.

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# 532 4. Discussion

4. 1 Catchment properties shape SPE-DOM composition at Lake Nam Co watershed 533 The three investigated subcatchments (high glaciation, low glaciation and degraded) of the Lake Nam 534 Co watershed catchment (high glaciation, low glaciation and degraded) differed significantly in their 535 536 molecular SPE-DOM composition. The high glaciation subQugaqie catchment had the largest chemical 537 molecular α-diversity and , together with a larger abundance of formula containing. S heteroatoms (Table 1). This DOM can be influenced by the productivity of the glacial ecosystem hotspot (Hodson et 538 539 al., 2008). S heteroatoms in DOM are likely related to high the sulphide contents in the runoff of Zhadang glacier (Yu et al., 2021). SulAnaerobic metabolism of sulphate reducing bacteriation is known 540 541 to-takes place in glacial sediments and ice (Wu et al., 2012). Under sulfidic conditions,- aAfter biotic biotic reduction, sulphateide can beis abiotically incorporated into DOM ("sulfurization"), forming 542 543 dissolved organic sulphur compounds (Pohlabeln et al., 2017). Correspondingly, the CHO index 544 indicated a comparably low degree of C oxidation. This shows that higher complex compounds 545 originating from plants and soils dominated the DOM of Qugaqie. Correspondingly, the degree of 546 microbial breakdown was lower compared to the other two catchments, The higher abundance of O-547 poor compounds, namely with depleted unsaturated O-rich and highly unsaturated O-rich molecular formulae and compared to the other catchments, increased highly unsaturated O-poor and 548 549 unsaturated O-poor formulae alongside with negative CHO values, indicates a-lowerless intensively 550 microbial breakdown\_transformed of\_SPE-DOM-borne compounds (Anesio et al., 2009; Hood et al., 551 2009; Spencer et al., 2014)- compared to the degraded and low glaciation subcatchments. This is corroborated by Accrodingly Accordingly, D'Andrilli et al. (2019) : In their study, observed the relative 552 553 increase of production of mostly O-enriched molecular formulae were produced after bio-incubations 554 of DOM-substrates, while fresh substrates initially had more O-poor formulae. Likely, ILow water temperatures of the glacial meltwater in Qugagie hamper the microbial decomposition of DOM 555 556 (Adams et al., 2010).

explaining the larger abundance of O poor molecular formulae as also found in incubation studies
 (D'Andrilli et al., 2019).

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560 Figure 4: Non-metric multidimensional (NMDS) scaling analysis based on the relative abundances of 561 SPE-DOM molecular formulae (calculated on Bray–Curtis dissimilarity matrix) for-(a) samples ar 562 elemental composition of compounds (elements C, H, O, N, P a nd S) plotted with the colour-coded 563 logarithmic scale of the modified aromaticity index: (Almod-, logarithmic scale) (Koch and Dittma 564 2006; 2016). And b) Zoom of -NMDS analysis based on the relative abundances of SPE-DOM 565 molecular formulae with post-hoc fitted SPE-DOM parameters (internal predictor variables, red) and environmental parameters (external predictor variables, black) shown as vectorsfor samples an 566 environmental variables: internal explanatory predictor variables (red) and external explanator 567 568 predictor variables (black). UnderscoresThe underscoresUnderlined parameters wer 569 indicate indicate a significantly ( $\alpha p$  =  $\leq$  0.05) relationed of the environmental parameters predictor variables with to the NMDS dimensions dimensions of the NMDS ordination (Stress = 0.14, <u>k</u> k 570 571 3, dissimilarity index - Bray-Curtis). ARO= aromatic O-rich and aromatic O-poor, HUSAT-\_highly unsaturated O-rich and highly unsaturated O-poor, USAT = unsaturated O-rich, unsaturated O-poor 572 573 and unsaturated with N,N, and SAT = saturated. Sites Subcatchments are represented by the colour 574 of sample points, while sample categories are represented by point shapes. Compared to the Qugaqie catchment, t<del>The Qugaqie catchment is mostly defined by its steep altitudin</del> 575 576 gradient (>2000 m) and its glacial influence, with glacial meltwater as the dominating wate (Bolch et al., 2010; Gao et al., 2015), relatively low water temperatures of the meltwater hamper the 577 microbial oxidation of DOM, while water turbidity and turbulence shields against photooxidation. Th 578 579 higher relative abundance of unsaturated low-molecular compounds makes microbial DOM from the glacial ecosystem probable (Anesio et al., 2009; Hood et al., 2009; Spencer et al., 2014) ar 580 581 further suggests its preservation through low water temperatures (Adams et al., 2010he contribution 582 of glacial meltwater was smaller in the Niyaqu subcatchment and absent in Zhagu. Here, the stream were less turbid and flowing slower (Maurischat et al., 2022). The main water sources for Zhagu are 583 precipitation and groundwater (Adnan et al., 2019a; Anslan et al., 2020; Tran et al., 2021). In the 584 degraded Zhagu subcatchment, a stronger indication of aromaticity with higher Almod and higher 585 586 relative abundance of aromatic compounds was found, alongside with a relatively low contribution lower-molecular mass unsaturated compounds. Likewise, the higher oxidation state indicated by the 587

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CHO index (Fig. 5b, Table 2) and higher degradation index (Ipeg, Table 2) suggest a larger share of soilborne, aromatic DOM compoundsintense biopolymers This was also corroborated by the higher share percentage of the IOS (+ ~3 %), indicating a larger input of degradation productsunderlin. The <u>low</u> <u>glaciation</u> Niyaqu catchment in comparison had a higher contribution of aromatic and unsaturated compounds together with a lower H/C ratio, suggesting less oxidised DOM. In combination with the Al<sub>mod</sub> and I<sub>Terr</sub> indices -this suggests inputs of soils and plants, with e.g. such as lignin and hemicellulose and <u>its-their</u> degradation products (Roebuck et al., 2018; Seifert et al., 2016)<sub>37</sub>

The *high altitude high glaciation* Qugaqie catchment also comprises of a signature rich in highly 595 596 unsaturated O-poor and unsaturated O-poor formulae likely derived from a glacial-borne microbial 597 source. Furthermore, the high aromatic indices (AImod, ITerr) and high percentages of aromatic 598 compound classes are indicative of SPE-DOM derived from soil and plant material. This is vThis serves 599 as a strong indication of a land use control on DOM signatures, namely by the human-induced 600 K.pygmaea plagioclimax.-Likely, there is a steady input of soil-derived material into the streams from pastoral land as demonstrated for other grassland systems (Seifert et al., 2016; Lu et al., 2015). 601 602 Notably, this influence became smaller, when glacial-borne more unsaturated DOM was more 603 dominant on subcatchment level (Fig. 3b).

#### 604 4.2 The effect of pasture degradation on SPE-DOM composition

605 <del>Our data show, that m<u>M</u>olecular  $\alpha$ -diversity defined by the number of molecular formulae and SPE-</del> 606 DOM characteristics can be pinpointed to landscape units / environmental sample categories and endmembers-(summarized in the conceptual model in Fig. 7). NMDS analysis (Fig. 4) suggested that 607 glacial effluents were diverse in chemical composition, but differed between glacial ecosystems, as 608 609 was also shown by Spencer et al. (2014). But generally, Gglacial SPE-DOM from Qugaqie and Niyaqu 610 subcatchments contained two different signatures from different sources. First, with high abundances 611 of unsaturated compounds with and without nitrogen as well as a low oxidation state of carbon (Fig. 612 5a), high ratios of H/C and lowest percentages of recalcitrant SPE-DOM visible by the of recalcitrant 613 DOM as demonstrated by comparatively low-IOS-abundances. These parameters indicate a relatively fresh, reduced (oxygen-poor) SPE-DOM of low-molecular mass\_probably derived from microbial 614 615 activity at the partly anoxic ice shield. This is in-line with findings from other glacial environments 616 worldwide (Hood et al., 2009; Telling et al., 2011; Anesio et al., 2009). Second, 2)-aromatic and highly 617 unsaturated compound classes and aromatic and terrestrial indices (I<sub>Terr</sub>, AI<sub>mod</sub>) were suggesting plantand soil-borne SPE-DOM sources, despite the absence of plant cover in the glacial zones (Maurischat 618 619 et al., 2022). Glaciers are understood to receive compounds with higher molecular mass from aeolian 620 deposition, either condensed (poly)aromatics, e.g. from the burning of fossil fuels (Takeuchi, 2002) or 621 compounds uncondensed but rich in phenolics, usually associated with dust from degraded -vascular Formatiert: Tiefgestellt

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plants\_material and soils (Singer et al., 2012). Local dust formation on the TP is projected to increase
with ongoing pasture degradation (Wang et al., 2008), likely affecting the DOM composition of glaciers.
The investigated coexistence of microbial produced, autochthonous DOM and airborne aromatic,
allochthonous DOM sources in glacial DOM make them diverse and complex and renders the
understanding of the downstream fate of glacial DOM reactions on climatic changes and its
downstream lability difficult (Singer et al., 2012).

Groundwater spring SPE-DOM from the *upland of the degraded* Zhagu subcatchment mainly 628 comprised contained aromatic and highly unsaturated DOM compounds. Molecular  $\alpha$ -diversity and 629 the number of N, P and S heteroatoms was were low. Together with this, high IDeg and CHO indices 630 631 spring DOM-suggesteded a strong degradation\_of <u>spring\_</u>SPE-DOM\_<del>by high l<sub>beg</sub> and CHO indices</del> (Fig. 632 5b) further\_17% of DOM\_being IOS DOM indicates a large contribution of recalcitrant-recalcitrant DOMas indicated by IoS values. Spring water is generally expected to inherit aquifer and catchment 633 634 characteristics in its DOM signature, also partly preserving its terrigenous source (Osterholz et al, 2022; Yoo et al., 2020). The shallow groundwater table as found inof Zhagu (Tran et al., 2021), wa 635 636 shown to beis in contact with soil organic matterOM and yak faeces (Maurischat et al., 2022), both 637 which can leach soil-borne OM to the groundwater table (Connolly et al., 2020) which re-emerge at 638 groundwater springs. The low molecular diversity of groundwater spring DOM responds to a 639 enrichment in aromatic and highly unsaturated formulae, Ggiven the high degradation and recalcitrar 640 nature of this DOM, these Hence, the highly degraded SPE-DOM compounds likely originated from the 641 degraded pedosphere and have been transported with the groundwater. The connection of over-use 642 degraded pastures of Zhagu (Fig. 1 & 4b) with the molecular composition of groundwater spring SPE-DOM indicatesed that a-highly modified SPE-DOM signatures is are emitted from transported with the 643 644 springs water and retrieved in streams. While studies on investigations of t SPE-DOM from of an extensive alpine wetland of the Niyaqu catchment showshadeds a high  $\alpha$ -diversity 645 646 (>4000 assigned\_molecular formulae), was rich in N, and P heteroatoms, as well as in esand in 647 terrigenous-highly unsaturated O-rich, and unsaturated O-poor compounds. In a study from tThe wetland was also e same site, wetland DOM was enriched in ammonium and DOC compared to the 648 649 surrounding streams (Maurischat et al., 2022). It was reported that a Alpine wetlands are highly productive and contain large amounts of nutrients in the organic biomass and organic mattersoil ON 650 651 (Bai et al., 2010; Zhang et al., 2020).- Wetlands on the TP have been massively degrading (Zhang et al. 2011), enhancing microbial decomposition in wetland mire soils (Ma et al., 2018) and driving 652 subsequent release of nutrients into adjacent streams (Gao, 2016). For Nam Co Lake this of wetlan 653 654 canwould pose a severe biodiversity nutrient threat to oligotrophic streams and the sensitive lake 655 shore (Hu et al., 2016). downstream ecosystems (Bai et al., 2010; Zhang et al., 2020).

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656 Stream samples cluster relative widely around the NMDS ordination space but are concentrated in the 657 lower centre of the NMDS (Fig. 4b). these samples had had a predominance of aromatic compounds 658 either associated with highly unsaturated O-poor or highly unsaturated O-rich formulae, suggesting 659 mostlyan inputs of terrestrial compounds, such as lignin and tannin and their degradation products (Mann et al., 2015), further corroborated by depleted  $\delta^{13}$ C DOC signatures\_-(Fig. 4b; Maurischat et al., 660 661 2022). The K. pygmaea biomeecosystem spreads as an azonal pasture along the streams (Fig. 1). Lu et 662 al. (2015) pointed out that grassland sites provide terrestrial inputs of aromatic and highly unsaturated 663 compounds to surface waters.-The K. pygmaea biome is a large alpine yak pasture browsed by yak has 664 potential influence of their biolabile faeces (Du et al., 2021), known for their high biolability (Du et al., 665 2021), suggesting lower molecular mass and negative CHO inputs due to the reductive conditions in 666 the yak gastrointestinal tract and decomposition of plant-borne material therein (Fahey et al., 1983). The scattering of sStream samples can therefore also be under influence of explained by changing 667 668 inputs from the pasture biomeecosystem. Faeces inputs and products of their microbial 669 utilisation, Faeces inputs and products of their microbial utilisation are likely associated with increases 670 of N-containing unsaturated formulae and saturated formulae (Vega et al., 2020). Pastoral land-use and pasture degradation both had a considerable impact on stream SPE-DOM composition. While 671 intact pastures released a highly unsaturated and aromatic signature related to the pasture soils and 672 673 plants, streams close to degraded pastures were characterised by highly oxidized aromatic signatures and low molecular  $\alpha$ -diversity. Still, the input from soil and terrestrial plant material dominated stream 674 675 samples.



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 Figure 5: Hexagon scatters plot the count of of the chemical formula in the space of of the CHO index

 678
 (Mann et al., 2015) and m/z. Black The black dotted lines represent the linear model of of the CHO

679 680 681 682 683 684	index and <i>m/z</i> of the respective sample, <u>greyand the grey</u> dashed lines split the plot <u>ininto</u> quadrants for orientation. <u>RegressionThe regression</u> and <u>orientation-ledger</u> lines are printed to guide the eyes only. a) Ice from a glacier in <i>high glaciation</i> Qugaqie, b) groundwater spring from the upland of <i>degraded</i> Zhagu (3:10), c) water from the standing water column of a wetland (1:26), d) water from the brackish zone of Lake Nam Co and a tributary stream (2:15) and e) water sample from 30 m depth <del>of the of</del> Lake Nam Co. Axis scales are fixed.
685	4.3 The Lake reactor: photooxidation changes the SPE-DOM molecular composition
686	Brackish SPE-DOM_samples had the highest molecular $\alpha$ -diversity, highest number of N and S
687	heteroatoms and <del>as well</del> highest number of aromatic O-poor compounds together with high Al <sub>mod</sub> and,
688	I <sub>Terr_</sub>
689	aromatic and highly unsaturated O-poor formulae and by this retained and accumulated the terrestrial
690	signal of streams. Brackish regions are not only zones of gradual mixing of different water masses (Van
691	Dongen et al. (2008)-described brackish waters as a zone of gradual mixing, where a connection of
692	terrestrial-derived DOM of signatures from streams is to be exported to marine lakes and the ocean
693	(Benner et al., 2004; Dittmar and Kattner, 2003; Ruediger, 2003) but are also zones of chemical
694	transformation and uptake of riverine DOM, e.g. by flocculation and osmotrophy (Hoikkala et al. 2015).
695	More so, the The relative increase of aromatic compounds in brackish SPE-DOMs
696	streams_SPE-DOM_(Fig. 3)_suggests to some extent-a relative enrichment, for example, by selective
697	degradation and oxidation of lower-molecular mass compounds in the wash of the waves as suggested
698	indicated by the increased CHO index (Fig. 5d) and IDegr values (Fig. 5d) as shown for estuaries
699	(Asmala et al., 2014). We suggest conclude that the high molecular $\alpha$ -diversity in brackish samples
700	represents both, the terrestrial input from catchment streams mixing with the SPE-DOM signature of
701	lake water and selective degradation of SPE-DOM in the high-energy wave zone, which is visible for
702	the exemplary mass to charge (m/z) region between 565.5 and 567.5 Da when comparing the
703	evolution of molecular compounds from Zhadang and Qugaqie mid-stream towards its brackish zone
704	<del>(Fig. 6a-c)</del> .
705	Lake water differed in its SPE-DOM composition most strongly as compared to all other samples
706	categories (summarized in the conceptual model in Fig 7). Lake SPE-DOM was relatively enriched in
707	unsaturated and saturated compounds, which can include lipids and carbohydrates, but it was
708	relatively depleted in aromatic and highly unsaturated O-rich molecular formulae. Correspondingly,
709	AI <sub>mod</sub> and I <sub>Terr</sub> decreased. Spencer et al. (2009)-reported pPhotooxidation and microbial degradation
710	can both to-remove aromatic DOM, such as lignin-derived phenolics-from a large river system and
711	(Spencer et al. {2009}; Helms et al. (2014; Vähätalo and Wetzel, 2004) investigated the loss of DOM
712	optical properties after light exposition. Given the clear water column and high irradiation at the TP
713	(Wang et al., 2020), photooxidation can take place down to greater depths in the lake, making it a

714 probable important mechanism. <u>Photooxidation in combination with microbial degradation most likely</u>

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- 715 <u>to-can</u> explain the depletion of <u>aromatic phenoliconstituents when comparing brackish and lake SPE-</u>
- 716 DOM : globally\_corresponding to decreased Almost, large and DBE indices and becomes visible in the van
- 717 Krevelen plot {(blue points in Fig. 6a) and the in excerpt of one mass spectra between in {Fig. 6b)565.5
- 718 to 567.5 Da when comparing brackish and lake DOM (Fig. 6c-6d).

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719	In thea stream-estuary-lake gradient_riverine the_terrigenous-brackish SPE-DOM likely
720	underwent a transformation when entering deeper in th, Jeaving more recalcitrant recalcitrant.
721	SPE-DOM behind (Goldberg et al., 2015) as corroborated by the 2.1% and 2.7% increase.
722	of IOS compared to stream and brackish SPE-DOM, respectively. (Table 2). Along with
723	degradation and transformation of imported riverine SPE-DOM, primary
724	production in the lake plays a large key role for the SPE-DOM characteristics of Lake Nam
725	Co. The increase in unsaturated and unsaturated N-containing compound classes and the more
726	negative CHO with lower molecular mass (Fig. 5e) in lake SPE-DOM (Figure Fig. 3, ) yellow points in
727	Fig. 6a) act as indicators for bacterial and algal primary production in the
728	lake. MMicrobial DOM sources have been suggested for Lake Nam Co (Spencer et al., 2014;
729	Maurischat et al., 2022) and other large lakes of the TPA (Liu et al., 2020). Performing a food
730	web study in Lake Nam Co, Hu et al. (2016) reported from a Nam Co food web study of
731	Nam Co, that mainly that mainly lake-borne organic carbon sources are utilised by zooplanktor,
732	further corroboratingshowing the importance of an autochthonousthis type of pom as
733	substrate source. The comparably low CHO index (Fig. 5e) underlines the existence of low
734	molecular mass <del>,</del> reduced <del>carbon species DOM</del> produced in the lake, while higher molecular
735	masses <u>, here</u> of aromatic and highly unsaturated riverine origin originate
736	more oxidised in the lake environment compared to other systems (indicated by the
737	greatest steepness of the regression line in Fig. 5C), indicative of the strong
738	processing described beforehandabove, Lake SPE-DOM, further-exhibited sources derived from
739	algal and microbial production Also it This DOM resembled characteristics of the open ocean, being
740	low in aromatic compounds and terrigenous indices and had a <u>much</u> larger percentage of IOS as
741	compared to subcatchment streams SPE-DOM, suggesting higher recalcitrance
742	and millennial scale stabilitymore recalcitrant compounds. A comparably his compound DON
743	recalcitrance <u>fraction of Lake Nam Co was not on the level of large arctic rivers (Behnke et al., 2021)</u> 29

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or the deep ocean (Lechtenfeld et al., 2014), but clearly increased compared to the catchment

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756	5. Conclusions	•	Formatiert: Schriftart: +Textkörper (Calibri),
757	We elucidated the molecular composition and the processing of SPE-DOM along the flow path in th	e 🔪	Schriftfarbe: Automatisch
758	High Asian endorheic Nam Co watershedcatchment. We investigated three subcatchments: high	<u>1</u>	Abstand Nach: 0 Pt.
759	glaciation, low glaciation, no glaciation / glagraded, different endmembers of three catchment	7	Formatiert: Schriftart: Kursiv
760	including SPE-DOM samples of glaciers, groundwater springs, alpine wetlands, streams, the brackis	ı	Formatiert: Schriftart: Kursiv
761	mixing zone, and the weakly saline lake.		
762	Catchments of the The subNam Co watershedcatchments differed in their chemical molecula	r	
763	composition of SPE-DOM-of DOMirrospectiv	-	
,			
764	Molecular diversity was large in glacial influenced streams, which were also characterized by th	e	
765	largest proportion of low molecular mass compounds. In the high glaciationglaciated Qugaqi	•	Formatiert: Schriftart: Kursiv
766	catchment, we identified a unique dual source, source on the one hand, of a microbial, low-molecula	r	
767	mass SPE-DOM fraction-relatively rich-enriched in S heteroatoms and unsaturated compounds with	n	
768	and without nitrogen, possibly including degradation products of peptides and amino sugar	,	
769	suggesting high biolability and autotrophic production sources in the glacial ice shieldMeanwhileO	<del>,</del>	
770	the other hand, aromatic SPE-DOM with high aromaticity and high abundances of highly unsaturate	ł	
771	compounds, such as plant-derived lignin_degradation products or polycondensed aromatics derive	<u>t</u>	
772	from the combustion of fossil fuels or household burning of yak faeces, hinting at a depositional source	e	
773	of-by aeolian transported local dust, derived from soil. Polycondensed aromatics probably includin	3	
774	black carbon with high an Almost and large number of C atoms derived from the combustion of foss	4	
775	fuels or household burning of yak dung may also enter the ice shield via the atmospheric pathway. Th	5	
776	large influenceinfluence of glacial meltwater in the Qugaqie catchment greatly modifiesd SPE-DOM	1	
777	signatures along the whole stream high glaciation Qugagie stream, probably and of the catchmer	ŧ	Formatiert: Schriftart: Kursiv
778	and probably deliversing more bio-available compounds to the southern lake shoreline, underlining	3	
779	the existence of a glacial – lacustrine pathway. The <u>low glaciation</u> Niyaqu and Zhagu catchmer	t	Formatiert: Schriftart: Kursiv
780	comprised a lower molecular $\alpha$ -diversity, diversity and had a mainly terrestrial-borne SPE-DOM source	2	
781	of highly unsaturated and aromatic compounds, attributed to the input of the surroundin	3	
782	surroundingplants and soils of the pastoral K. pygmaea biomepastures -to the streams.		
783	Groundwater spring SPE-DOM had a low molecular $\alpha$ diversity and was <u>relatively</u> enriched in plant an	ŧ	
784	soil-derived aromatic and highly unsaturated compounds-In comparison, salongside with an increas	÷	
785	in P heteroatoms and saturated formulae. This suggests that spring SPE-DOM of the degraded Zhag	<u> </u>	Formatiert: Schriftart: Kursiv
786	subcatchment was influenced by degradation of K. pyqmaea pastures visible by the Zhagu uplan	ł	
787	constitutes background DOM signatures but also inherits highly degraded, and oxidized , and probable	¥	
788	recalcitrant DOMsignatures with a higher percentage of recalcitrant compounds. DOM signatures ca	n	
789	thus be used to trace pasture degradationfrom the degrading pastures and potentially yak facee	÷	
	3	1	

790 Wetland SPE-DOM exhibited aexhibited high molecular  $\alpha$ -diversity and was relatively enespecially 791 riched inwith N-heteroatoms compounds, alongside with aromatic and highly unsaturated formulae. 792 Wetland SPE-DOM reflectsed likely represents a broad range of terrestrial DOM signatures from the 793 catchment, driven by the comparably high primary productivity of these systems, water logging and 794 the basin topography of the wetlands. The latter lead to a steady inflow of water and OM by lateral 795 movement. If the reported degradation of alpine wetlands in HighHigh Asia can drives a large larger release of DOM to the streamsstreams;- at Nam Co this can be considered a threat forto the 796 797 oligotrophic\_lake. terminal aquatic systems, such as Lake Nam Co, but especially for smaller lakes.

5. Stream<u>The stream</u> samples were mostly associated with the input of terrestrial-borne materials, originating from vascular plants and soils. These are attributed to the <u>predominant *K. pygmaea\_K.*</u> *pyamaea\_biomeecosystem* and pastoral practise\_stretching along the paths of streams. From these zones\_the pastures\_aromatic and highly unsaturated SPE-DOM was constantly refuelled into the streams.

803 \_Brackish <del>samples</del>-SPE-DOM\_represented the mixing zone of stream and lake water\_<del>\_\_showing that <u>Here</u></del> 804 riverinethe terrestrial DOM entered thesignal is being transported with stream waters into the lake, 805 indicating that- DOM In this cold, fast flowing streams with short water residence times and high 806 turbidity transformation along the pathway stream was limited arguably smaller compared to other 807 ecosystems. LakeHowever, lake DOM, however, SPE-DOM was different compared to-the tributariesall 808 other sources, -\_\_\_\_\_its molecular composition suggesteds intense photooxidation and microbial 809 degradation as well as transformation of imported stream DOM, alongside together with a DOM source from<u>of</u> microbial and algal in-situ production in the oligotrophic lake. 810

811

812 These DOM signatures can be compared to terminal signatures encountered in the open ocean. Our 813 study shows that that -DOM cycling in the Nam Co catchment needs a thorough assessment, sinceas it 814 can be diverse between on subcatchment level and betweens and landscape units. In order to 815 safeguard water resources and related ecosystem services, knowledge about the different sources and 816 the fate of DOM their later processing is indispensable. SPE-DOM molecular properties properties have 817 proven to be selective for the source systems and hence allow to decipher landscape processes. In the case of here as a selective proxy, suitable to be implemented as a monitoring agent in the Nam Co 818 819 watershed, representative for processes on the sensitive larger TPTP, they might be a way forward to better understand the local effects of global change.-820



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Figure 7: Overview of the molecular molecular information from DOM informationSPE-DOM along 822 the water network continuum of the TP. The number of N-heteroatoms areis indicated relative to 823 824 the total number of molecular formulae. Island The island of stability (IOS), degradation index 825 (H<sub>Deg</sub>)(Ipeg), and terrestrial index (ITerr) are ranging in a red-blue colour code for high blue in the opposite case. Alpine steppe and groundwater spring samples are spatially correlated, and thus 826 827 subject of a common evaluation. The local pasture degradation gradient is indicated by a dashed 828 arrow.Main processes and sources are added and indicated by black arrows. Acknowledgements 829

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