

1 **Stream water quality in large glacierized catchments in Central Asia: a**
2 **perspective on cryosphere and land cover importance**

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24

25 **Highlights**

- 26 • Quantification of water quality in glacierized Central Asia catchments (> 485 km²).
- 27 • The cryosphere is a primary and secondary nitrogen source.
- 28 • Poor water quality occurs in hot spots rather than being uniformly good or bad.

- 29 • Shallow urban groundwater is contaminated by sewage.
- 30 • A dilution effect due to melt water was discernable at the lowest monitoring points.

31

32 **Abstract**

33 This work helps address recent calls for systematic water quality assessment in Central Asia and
34 considers how nutrient and salinity sources, and transport, affect water quality along the
35 continuum from glacier to lowland plain. Spatial and, for the first time, temporal variations in
36 stream water pH, temperature, salinity (electrical conductivity), and nitrate and phosphate
37 concentrations are presented for four catchments (485 – 13 500 km²), all with glaciers and
38 major urban areas. The catchments studied were: Kaskelen (Kazakhstan), Ala-Archa
39 (Kyrgyzstan), Chirchik (Uzbekistan) and the Kofarnihon (Tajikistan). Measurements were made
40 in cryosphere, stream water, groundwater, reservoir and lake samples over a 22-month period
41 at fortnightly intervals from 35 sites. The results highlight that glacier, permafrost and rock
42 glacier melt were primary and secondary nitrate sources ($> 1 \text{ mg N l}^{-1}$) to the headwaters, and
43 there are major increases in salinity and nitrate concentrations where rivers receive inputs from
44 agriculture and settlements. Overall, the water quality complies with national and World Health
45 Organization standards, however there were pollution hot-spots with shallow urban
46 groundwaters contaminated with nitrate ($> 11 \text{ mg N l}^{-1}$), and stream salinity above $800 \mu\text{S cm}^{-1}$
47 in some agricultural areas. Phosphate concentrations were generally low ($< 0.06 \text{ mg P l}^{-1}$)
48 throughout the catchments, and elevated ($> 0.2 \text{ mg P l}^{-1}$) only in urban areas due to effluent
49 contamination. A melt-water dilution effect along the main river channels was discernable in
50 the electrical conductivity and nitrate concentration seasonal dynamics, even at the lowest
51 monitoring points. Thus, the input of relatively clean water from cryosphere is an important
52 regulator of main channel water quality in the urban and farmed lowland plains adjacent to the
53 Pamir and Tien Shan, and improved sewage treatment is needed in urban areas.

54 **1. Introduction**

55 Over the past 50 years, glacier retreat has been observed and attributed to climate change,
56 with this trend projected to continue for the next 70 to 100 years (Hock et al., 2019).

57 Worldwide, approximately 1.9 billion people depend on the water supplied by glaciers for
58 domestic and commercial consumption, irrigation and hydropower, and therefore the
59 assessment of current and future mountain water resources is important (Hock et al., 2019).
60 Outside North America and Europe, relatively little attention has been given to water quality
61 assessment in glacier-fed catchments, and to the relationship with freshwater ecosystems and
62 the provision of clean water for downstream use. In part, this lack of attention on water quality
63 arises because of the practical difficulties and expense of sustained sample collection in remote
64 locations. When done, water chemistry studies of glacierized catchments tend to focus on the
65 spatial and temporal variations in the hydrochemistry with emphasis on water isotopes and the
66 major ions to quantify source water contributions to stream flow, and to assess weathering and
67 the release of potentially toxic elements (Tranter, 2003). Downstream changes in salinity and
68 nutrient concentrations and the seasonal dynamics remain poorly quantified and understood.

69 Central Asia (CA) is a largely arid region dependent on mountain snow and glacier melt for
70 water supply (Kaser et al., 2010; Viviroli et al., 2020). Model-based estimates of climate-change
71 impacts suggest a glacier-mass reduction, but that glaciers will remain (Farinotti et al., 2015;
72 Hock et al., 2019; Shahgedanova et al., 2020; Shannon et al., 2019; Van Tricht and Huybrechts,
73 2023). The mass reduction is expected to increase summer flows initially due to increased melt,
74 followed by a summer flow reduction as the melt water declines in the first quarter of this
75 century though the precise timing of 'peak water' remains uncertain (Duethmann et al., 2015;
76 Hagg et al., 2013; Huss and Hock, 2018; Kriegel et al., 2013; Shahgedanova et al., 2020;
77 Shahgedanova et al., 2018). As the catchment headwaters provide water that dilutes
78 downstream contaminant inputs, it is important to assess the salinity and nutrient
79 concentrations from the glacier to the plains to assess potable and irrigation water provision,
80 and eutrophication, along the continuum. As the high mountain cryosphere melts, headwater
81 solute concentrations in the vicinity of the glacier terminus will likely be affected through trace
82 element leaching from the exposed substrate due to weathering, and the release, in meltwater,
83 of legacy pollutants stored in snow, glacier ice, rock glaciers and permafrost (Bogdal et al.,
84 2009; Colombo et al., 2018; Liu et al., 2021). Shifts in the timing of snow and ice melt to earlier
85 in spring and a change precipitation form, from snow to rainfall, are anticipated which will likely

86 change solute release, including nitrate and phosphate, and stream temperatures (Brahney et
87 al., 2021). Headwater aquatic ecosystems are sensitive to small changes in meltwater
88 hydrochemistry and temperature because of the low stream water concentrations and
89 temperatures. Phosphate, for example, typically has very low stream water concentrations in
90 mountain areas as it is rapidly assimilated by the cryosphere (*e.g.*, cryoconite) and soil and
91 stream biota, and therefore increased concentrations could increase stream and lake
92 productivity (Bettinetti et al., 2008; Bogdal et al., 2009; Colombo et al., 2018; Milner et al.,
93 2017; Miner et al., 2019). Freshly comminuted glacier flour can contain high ion concentrations
94 that can lead to high fluxes with the ion composition dependent on the bedrock. Proglacial
95 streams have been assessed as generally nitrogen limited (Telling et al., 2011; Telling et al.,
96 2012), and increased nitrogen concentrations remain a eutrophication concern given possible
97 nitrogen and phosphorus co-limitation (Jarvie et al., 2018). Downstream, there has been little
98 consideration of lake and reservoir water quality used to supply drinking water and of stream
99 water used for irrigation. The mixing of surface and groundwater has been established as
100 important on the lowland plains around Bishkek with the city almost entirely dependent on an
101 unconfined aquifer fed by precipitation and meltwater for drinking water (Morris et al., 2006).
102 Work is therefore needed to assess aquifer water quality especially given the surface-
103 groundwater interaction.

104 A recent review of the hydrochemistry and water quality (HWQ) in glacierized CA mountain
105 catchments showed that river water quality mostly complies with national and World Health
106 Organization (WHO) standards, however studies are limited and not all are based on reliable
107 data (Yapiyev et al., 2021). Most publications on CA water quality focus on the middle and
108 lower reaches of the Amu Darya (Crosa et al., 2006) and its main tributary, the Zeravshan (Groll
109 et al., 2015; Olsson et al., 2012) showing that melt water dilutes pollutants released from urban
110 areas and farmland and regulates endorheic lake salinity (Jones and Deocampo, 2003; Orlovsky
111 et al., 2014; Wurtsbaugh et al., 2017). The review also noted that almost no information about
112 hydrochemistry and water quality in CA montane catchments was published after the 1980s
113 and, while the solute chemistry of snow and ice is understood relatively well, only one study
114 was found that described how solutes enter the hydrological system following snow and glacier

115 ice melt (You et al., 2015). A further recent study assessed nitrogen and phosphorus inputs to
116 the Aral Sea Basin and found that diffuse sources made the greatest contribution to the lower
117 reaches based on two longitudinal sampling campaigns in April and July, 2019 (Leng et al.,
118 2021). Thus, there is a need to build on these works to quantify the extent, dynamics and
119 severity of freshwater contamination in the lowland tributaries draining urban and agricultural
120 areas in CA in different water types, with an emphasis on the importance of the seasonal
121 meltwater dilution effect. Recent papers have highlighted the need for the systematic
122 measurement of contaminants, including nutrients, in CA catchments (Leng et al., 2021; Liu et
123 al., 2021).

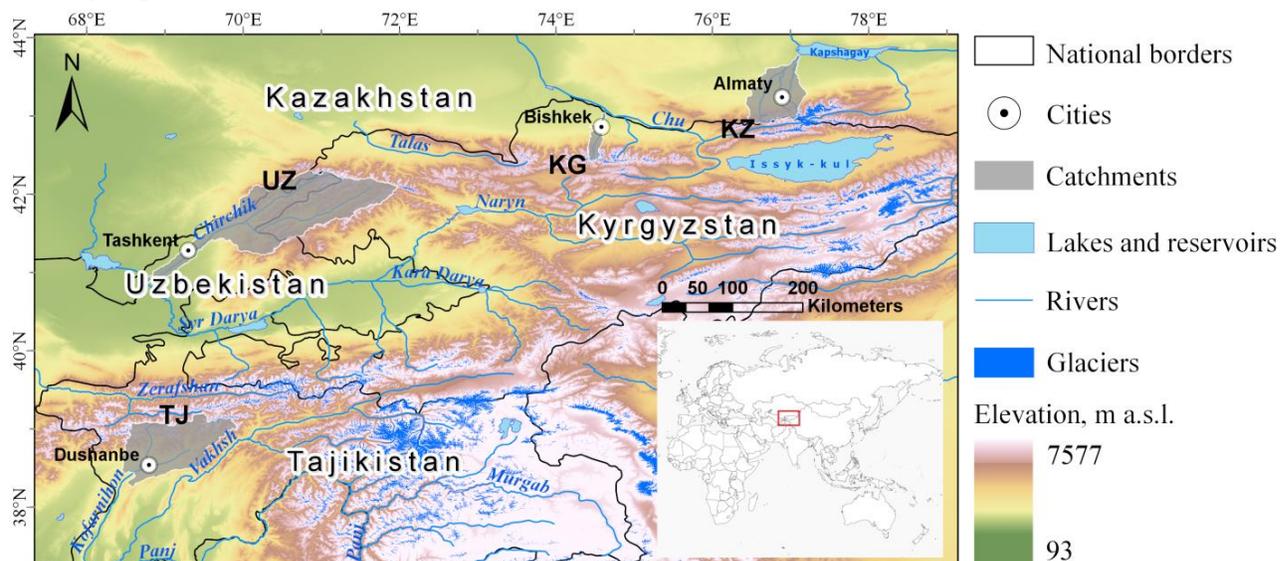
124 The aim of this work is to quantify the influence of the cryosphere on the proglacial zone and
125 downstream stream water quality along the elevation continuum, in lakes and reservoirs in the
126 arid lowlands, and on groundwater in large catchments with major urban centers. Specially,
127 four hypotheses were considered:

- 128 1. Weathering, rather than legacy contaminant release from snow and ice melt, is the
129 main nitrate and phosphate source in proglacial streams.
- 130 2. Land cover is the predominant control on stream salinity, nitrate and phosphate
131 concentrations, with higher concentrations associated with cropland and urban areas.
- 132 3. Urban groundwater is polluted with nitrate and phosphate through mixing with surface
133 waters.
- 134 4. Cryosphere melt, during June to August, maintains low stream water salinity, nitrate and
135 phosphate concentrations in the downstream urban and cropland areas.

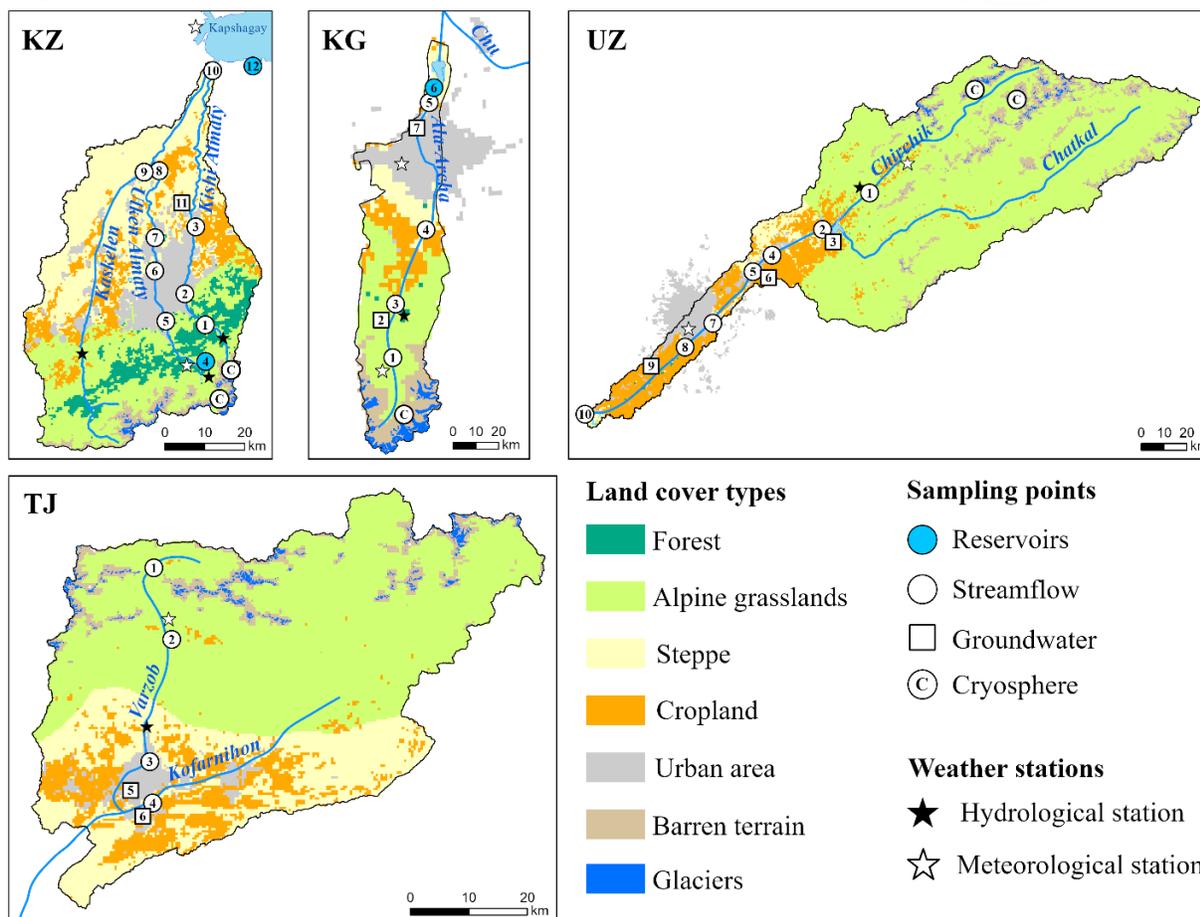
136 To achieve the overall aim and test the four hypotheses, fortnightly measurements of pH, water
137 temperature, salinity (electrical conductivity), and nutrient (nitrate, NO_3^- -N and phosphate,
138 PO_4^{3-} -P) concentrations were made in surface and groundwater along the elevation continuum
139 to determine the extent of urban and agricultural pollution, and the downstream effect of melt
140 water in the main channel, with samples taken every fortnight for 15-22 months, depending on
141 the site. The analytes were chosen because they are key indicators of water quality overall and
142 could be measured *in situ* or within 24 hours on return from the field to reduce sample

143 degradation effects. The sample collection and analysis were a major logistical effort given
144 catchment areas over 10,000 km², altitudes ranging from 200 to over 4000 m.a.s.l., the 2019
145 novel coronavirus (SARS-CoV-2) pandemic, and the large variation in environment including
146 glaciers, alpine grasslands, forests, cropland and dry steppe.

147 **2. Study region**



148



149

150 Fig. 1. The study catchments showing the land cover, sample site and weather station locations. The glacierized
 151 area shown was derived from the Global Land Ice Measurements from Space (GLIMS) database (Consortium 2017,
 152 Raup *et al* 2007). Here and in the subsequent figures: KZ – Kazakhstan, KG – Kyrgyzstan, TJ – Tajikistan, and UZ –
 153 Uzbekistan.

154 Table 1. Study catchment characteristics. The streamflow gauging site locations are shown in Fig. 1. Potential evaporation is from the
 155 Climate Research Unit CRU TS 4.01 data set (Harris et al 2014). The glacierized area was calculated for the following years: 2011
 156 (Varzob/Kofarnihon), 2014 (Chirchik), 2017 (all Kazakhstan catchments), 2018 (Ala-Archa). The proportion of the glacierized area is
 157 expressed as a percentage of the total catchment area. *The catchment area, glacierized area, elevation range and mean of the
 158 Kaskelen catchment includes the Kaskelen River, Ulken Almaty and Kishi Almaty basins.

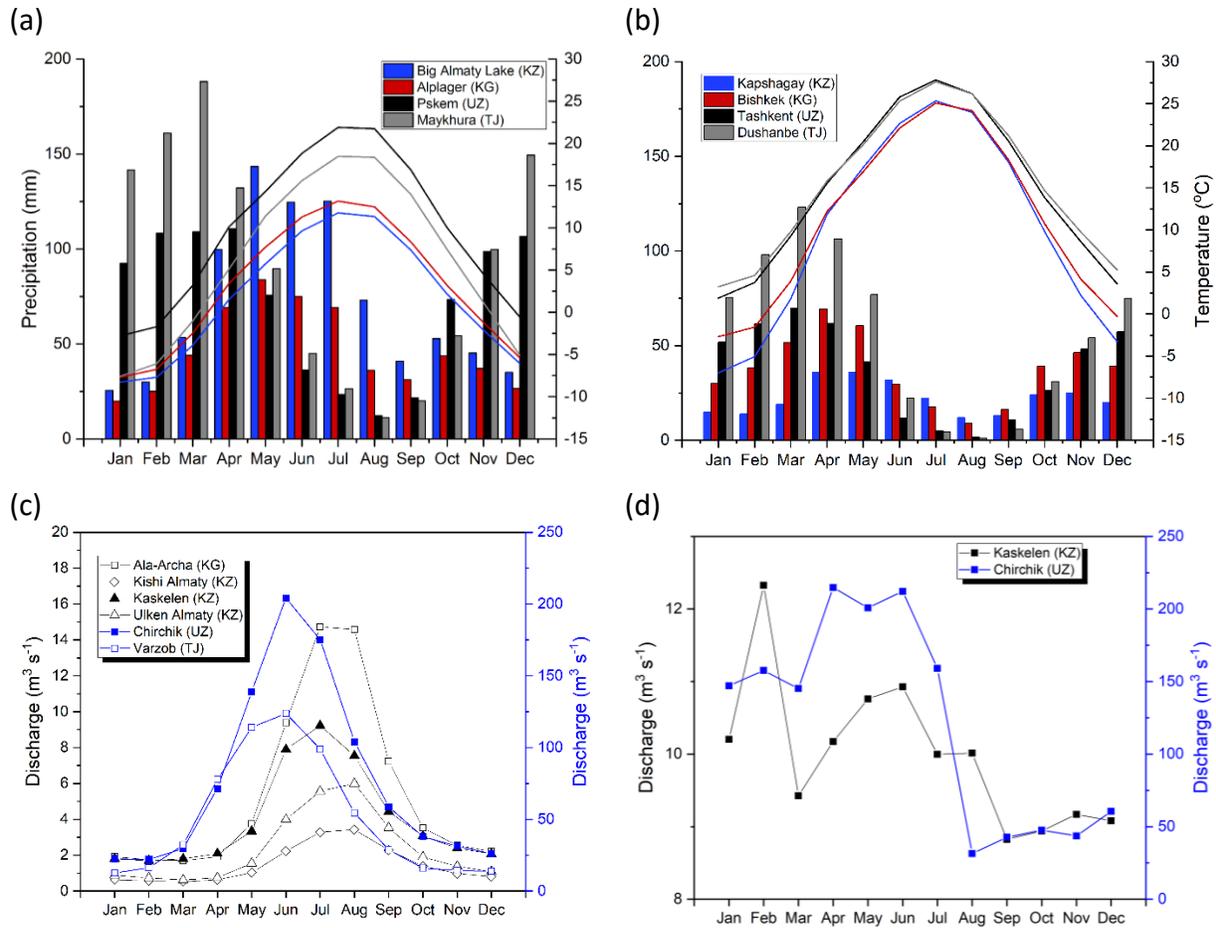
| Country | Catchment | Catchment area (area to upper gauging site) km ² | Potential evaporation (1991-2010) mm year ⁻¹ | Catchment elevation min – max (mean) m.a.s.l. | Glacial area km ² (%) | Gauging site name, Lat., Long., (elevation) Decimal degrees (m.a.s.l.) | Discharge (Years) m ³ s ⁻¹ | Specific discharge m ³ s ⁻¹ km ⁻² | Major city (population) million |
|------------|-------------------|--|--|--|-------------------------------------|---|---|---|------------------------------------|
| Kazakhstan | Kishi Almaty | 1048 (43) | 900 | 447 – 4361 (1051) | 4.5 (0.4) | Below Sarysai inflow, 43.1396; 77.0684, (1942) | 1.5 (2005-2013) | 0.034 | |
| | Ulken Almaty | 485 (74) | | 547 – 4355 (2033) | 13.8 (2.8) | Upstream of Big Almaty Lake, 43.0389; 76.9947, (2559) | 2.3 (2000-2013) | 0.031 | Almaty (1.78) |
| | Kaskelen* | 3792 (294) | | 447 – 4361 (1360) | 34.0 (0.9) | Kaskelen town, 43.134260, 76.612036, (1129) Kaskelen downstream, 43.7219, 77.0716, (502) | 4.0 (2001-2013) 10 (2000-2013) | 0.013 NA | |
| Kyrgyzstan | Ala-Archa | 701 (238) | 887 | 608 – 4746 (1940) | 31.5 (4.5) | Baityk, 42.647609 74.495405, (1560) Mullala, 41.771928, | 5.5 (1990-2015) 76.9 | 0.019 | Bishkek (0.98) |
| Uzbekistan | Chirchik | 13464 (2506) | 1129 | 226 – 4455 (2251) | 142.9 (1.1) | 70.190761, (925) Chinaz, 40.909312, 68.7593287, (253) | (1980-2010) 121.9 (2004-2010) | 0.031 0.009 | Tashkent (2.52) |
| Tajikistan | Varzob/Kofarnihon | 7536 (1275) | 1056 | 673 – 4835 (2170) | 98.8 (1.3) | Dagana, 38.702; 68.79, (1056) | 50.81 (1990-2011) | 0.040 | Dushanbe (0.92) |

159

160

161 Water quality monitoring was done during 2019 and 2020 in four glacierized catchments in
162 each of Kazakhstan (KZ), Kyrgyzstan (KG), Tajikistan (TJ) and Uzbekistan (UZ, Fig. 1; Table 1). The
163 Kishi Almaty and Ulken Almaty (KZ) are tributaries of the Kaskelen which flows into the
164 Kapshagay reservoir which the Ile river flows into and from. The other three catchments are
165 also the headwaters of major rivers: the Ala-Archa (KG) – of the River Chu; the Chirchik (UZ) – of
166 the Syr Darya, and the Kofarnihon and its tributary, the Varzob (TJ) – of the Amu Darya. All
167 rivers drain large ($> 250 \text{ km}^2$) areas and have a glacial-nival regime, and the relative glacial area
168 ranges from 0.4 to 4.5 % of the catchment area. The Kaskelen, Ala-Archa and Chirchik drain
169 from the Tien Shan mountains and the Kofarnihon and Varzob from the Pamir. The Chirchik and
170 Kofarnihon are an order of magnitude larger in area than the Kaskelen and Ala-Archa and
171 longer. All rivers flow through irrigated farmland and cities, with populations of 0.9 – 2.5
172 million, which rely on river flow, typically stored in mountain reservoirs, for water supply (Table
173 1). Bishkek in the Ala-Archa basin is an exception as it relies on groundwater almost entirely
174 (Morris et al., 2006) and Dushanbe (TJ) has an approximately even ratio of abstraction from
175 ground and surface water (Finaev et al., 2017). The regional geology and hydrogeology are
176 described in detail elsewhere (Gao et al., 2009; Koronovsky, 2003; Li et al., 2019). In brief, the
177 Tien Shan mountains are comprised of granitoids mainly, and the downstream plains of
178 cropland and dry steppe in the Kaskelen, Ala-Archa and Chirchik are primarily on Quaternary
179 deposits on Meso-Cenozoic sedimentary rocks. The Kofarnihon and Varzob rivers drain from
180 the Devonian volcanic rocks and Carboniferous conglomerates and sandstones of the Pamir,
181 and then also cross Quaternary deposits on Meso-Cenozoic sedimentary rocks. The soils in the
182 four catchments are thin Leptosols in the mountains, and Calcisols around the cities at the
183 mountain base in Kaskelen, Ala-Archa and Chirchik which are characterized by calcium
184 carbonate accumulation. Gleysols occur around Kapchagay in Kaskelen where the soils are wet,
185 and Anthrosols occur in the lowest reaches of the Chirchik near Tashkent modified by farming.
186 In TJ, there are Cambisols in mountain base which are weakly to moderately developed soils,
187 and Anthrosols in the lowest reaches downstream of Dushanbe where the Varzob flows into
188 the Kofarnihon (FAO/IIASA/ISRIC/ISSCAS/JRC, 2012).

189



190 Fig. 2. Air temperature and precipitation at the (a) middle mountain (1200 – 2500 m a.s.l) and (b) plains and
 191 foothill (500 – 800 m a.s.l) stations, and streamflow in the (c) middle mountains and on the (d) plains. The blue
 192 lines show the catchments in the south and west (UZ, TJ) and the black lines those in the north and north-east (KZ,
 193 KG) and the difference between the timing of the peak flow (June in the south and west, July and August in the
 194 north and north-east). The meteorological and streamflow gauging site locations are shown in Figure 1. The
 195 meteorological data are for the 1980-2020 period if not indicated otherwise and the station elevations are: Big
 196 Almaty Lake (2500 m a.s.l.), Alplager (2100 m a.s.l., 1992-2010), Pskem (1256 m a.s.l.), Maykhura (1921 m a.s.l.),
 197 Kapshagay (492 m a.s.l., 1971-2000), Bishkek (828 m a.s.l., 1980-2000), Tashkent (488 m a.s.l.), Dushanbe (803 m
 198 a.s.l.). The coordinates and elevation of the streamflow gauging sites, and observation period are given in Table 1.

199 All catchments have large altitudinal gradients in air temperature and precipitation, and distinct
 200 seasonal precipitation with a spring maximum (Fig. 2a, b). In the KZ and KG catchments in the
 201 north of the region, and in the high mountains, the Köppen climate classification is subarctic
 202 and tundra with a humid-continental climate on the lower slopes that transitions to semi-arid
 203 grassland steppe (Fig. 1). In UZ and TJ, to the south, the Köppen climate classification changes

204 from subarctic in the high mountains to humid-continental and then to a Mediterranean
205 climate as the altitude decreases to semi-arid grasslands and desert. Discharge is an order of
206 magnitude higher in the Chirchik and Varzob which have larger headwater areas than the Ulken
207 Almaty, Kishi Almaty and Ala-Archa though the specific discharge is similar in the Ulken Almaty,
208 Kishi Almaty Chirchik and Varzob (Table 1). The discharge peaks in summer (JJA) in all
209 catchments in the middle mountain sites, although the maximum occurs in June in the south
210 and west (Chirchik, Varzob) compared to July in the north and north-east (Kaskelen, Ulken
211 Almaty, Kishi Almaty and Ala-Archa) catchments and in the catchments where seasonal
212 snowmelt dominates over the runoff from glaciers (Fig. 2c). During winter, in November
213 through to February, stream and river flows are at a minimum.

214 In this article, *'upland'* or *'high-elevation'* refers to those sites above the transition from forest
215 and alpine grassland to cropland and dry grassland steppe in each catchment (Fig. 1), and
216 *'lowland'* or *'low-elevation'* to the areas downstream of this transition point. *'High-flow'* refers
217 to the surface water flows augmented by glacier and snow melt in JJA (MJJA in Chirchik and
218 Varzob) and *'low-flow'* to the relatively dry-period dominated by baseflow during winter. In the
219 lowlands, the stream flow is heavily modified everywhere except Chon Kyzyl-Suu, with the
220 flows in the lower Kaskelen particularly affected by reservoir storage in the Ulken Almaty and
221 the flows in the lower Chirchik by irrigation abstractions (Fig. 2d). Weathering at the glacial ice-
222 rock interface, is considered a *primary* source of ions, whilst legacy ion release from snow and
223 glacial ice is considered a *secondary* source with, in the case, the primary source distant and the
224 material transported to the cryosphere through the atmosphere and deposited (Chen et al.,
225 2022; Painter et al., 2012).

226

227 **3. Materials and methods**

228 *3.1. Surface and groundwater samples*

229 Once every two weeks for 22 months, water samples were collected at fixed locations along the
230 main channel from the periglacial headwaters to the lowlands, from large tributaries, and from
231 three deep wells, two wells that were artesian and three springs to characterize the

232 groundwater water chemistry (Fig. 1, Table 2). The samples were analyzed for NO_3^- -N, and PO_4^{3-}
233 -P and dissolved Fe concentrations (section 3.3). Sample collection started between April and
234 July 2019 and ended between October 2020 and January 2021 dependent on the country (Table
235 2). The water was sampled using a plastic syringe and filtered through a $0.45\mu\text{m}$ syringe filter
236 (Fisher Scientific, part No. 15216869) in the field into a 30 ml universal plastic screw cap tube.
237 The samples were stored in a portable fridge and analyzed in a laboratory within 24 hours at
238 room temperature. Water temperature, electrical conductivity (EC), pH and total dissolved
239 solids (TDS) were measured in the field using a hand-held field meter (Hanna Instruments Inc,
240 model HI 9812-5) and combination probe (Hanna Instruments Inc, model HI 1285-5). The
241 portable meters were calibrated before each day of sampling. The sampling locations were
242 chosen to represent different land uses, the headwater to lowland continuum, and the main
243 water sources: glacial headwaters, main channel and tributaries, groundwater, lakes and
244 reservoirs (Fig. 1; Table 3). The TDS measurements, which are derived from the EC data, did not
245 compare well with ion balances made using major cation and anions measured in a companion
246 hydrochemistry study, and further investigation of the TDS data is needed and therefore it is
247 not reported here. The cold water temperatures meant that water samples had to be returned
248 to the laboratory for nitrate and phosphate analysis; *in situ* measurement, to minimize sample
249 degradation, using portable spectrophotometers was not possible as the samples were too cold
250 for analysis.

251

252 3.2. Cryosphere samples

253 Snow and glacial melt water samples were collected during the summers of 2019 and 2021 at
254 the Tuyuksu (KZ) and Golubin (KG) glaciers, and at the Barkrak and Tekesh glaciers (UZ) in 2020
255 (see Table S2 for detailed cryosphere sampling sites information, Fig. 1). Sampling in TJ in 2020
256 was prevented by Covid-19 travel restrictions. The snow samples were collected from snow pits
257 using plastic scoops, placed in plastic bags, melted at room temperature, and filtered and
258 stored as the other water samples. The snow pit sampling was most extensive in KZ where, in
259 2019, samples were collected from 6 cm layers from the top to the bottom of the snow pit (See
260 Table S2). In 2020, the snow pit was divided into three equal vertical layers of the overall depth

261 of 162 cm and one sample was taken from each layer (see Table 2, Table S2). In Kyrgyzstan, the
 262 cryosphere samples (snow, glacial ice and glacial melt) were collected in 2019 and 2020 (see
 263 Table S2). In Uzbekistan, 13 cryosphere samples were collected from the Tekesh and Barkrak
 264 glaciers in June and July 2020 (Table 2, Table S2). In Kazakhstan, at least three glacial melt-
 265 water samples were collected in immediate proximity of the Tuyuksu glacier terminus. Water
 266 samples were also collected from the Gorodetskiy and Morenniyi rock glaciers and melting
 267 permafrost in the Ulken and Kishi Almaty headwaters. In total cryosphere samples were taken
 268 at 39 unique locations, and the pH, EC and water temperature were measured *in situ* except
 269 were samples required melting, and NO₃⁻-N and PO₄³⁻-P was measured on return to the
 270 laboratory. Not all analytes could be measured in every sample (see Table S2 for details and
 271 data).

272

273 Table 2.

274 A summary of the sampling program. Kaskelen includes the Ulken and Kishi Almaty sub-
 275 catchments.

| Catchment | Kaskelen (KZ) | Ala-Archa (KG) | Chirchik (UZ) | Varzob/ Kafoinon (TJ) |
|--|--|------------------------------------|------------------------------------|-------------------------------------|
| <i>Fortnightly stream water sampling (n=812)</i> | | | | |
| Sample type | Monitoring period and number of samples (n) | | | |
| Stream water | April 2019 to January 2021 (n=410) | June 2019 to December 2020 (n=135) | June 2019 to November 2020 (n=153) | July 2019 to September 2020 (n=114) |
| <i>Cryosphere sampling (n=128)</i> | | | | |
| Mountain snow | June 2019, May 2020 and 2021 (n=70) | August 2019 and 2020 (n=2) | July and August 2020 (n=3) | NA |
| Glacier melt | August 2019, August and September 2020, August 2021 (n=16) | August 2019 and 2020 (n=4) | July and August 2020 (n=6) | NA |

| | | | | |
|-----------------------|--|----|----------------------------------|----|
| Permafrost melt | August and September 2020, August 2021 (n=7) | NA | NA | NA |
| Rock glacier melt | August and September 2020, August 2021 (n=7) | NA | August 2020 (n=2) | NA |
| Proglacial streams | August 2019, September 2020, August 2021 (n=8) | NA | July and August 2020 (n=3) | NA |

276

277 *3.3 Laboratory analysis*

278 Nitrate and phosphate concentrations were measured using a laboratory spectrophotometer
 279 (Hach Lange Ltd., model DR3900) and the manufacturer's reagent kits: nitrate cuvette test (part
 280 Nr. LCK 339), phosphate ortho/total cuvette test (part Nr. LCK 349) and iron trace cuvette test
 281 (part Nr. LCK521). Calibration of the spectrophotometer was checked using manufacturer
 282 standards (part Nr. LCA 721) before each analysis using a one-point calibration. Every two
 283 months, a set of three standard solutions for each analyte was prepared to check calibration
 284 drift with a $\pm 10\%$ deviation considered acceptable. Nitrate and phosphate concentrations were
 285 reported in mg l^{-1} of NO_3^- -N and PO_4^{3-} -P. The detection limits were 0.23 mg N l^{-1} , 0.05 mg P l^{-1}
 286 and $0.01 \text{ mg Fe l}^{-1}$. Dissolved iron concentrations were found to be very close to, or below, the
 287 limit of detection at all sites, and therefore dissolved iron measurement was stopped after six
 288 months given cuvette and standard costs.

289

290 *3.4 Land cover, glacial area and potential evaporation*

291 The Moderate Resolution Imaging Spectroradiometer (MODIS) Land cover product (MCD12Q1,
 292 Type 1) was used for land cover classification of the study catchments with a 500 m pixel
 293 resolution (Friedl and Sulla-Menashe, 2019). The product, using 2018 imagery, identified 17
 294 land cover classes of which 13 were present and merged as follows for use in this study: forest
 295 (class 1-9); grasslands (10-11), and croplands (12 and 14) (see Supplementary Material Table 1).
 296 Grasslands were divided into alpine grasslands and steppe based on elevation. Land cover area
 297 was calculated for each sub-catchment using the 'Calculate geometry' function in ArcGIS Pro,

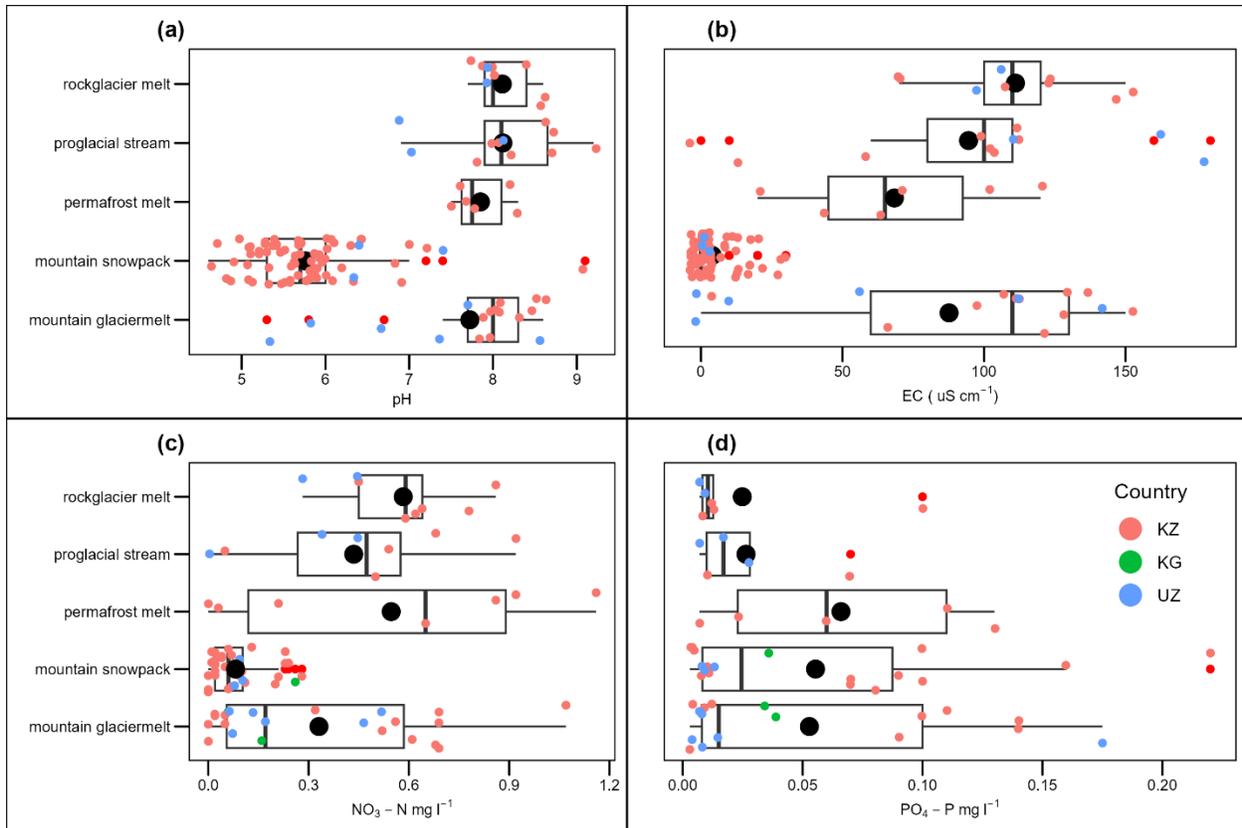
298 and the sub-catchment boundary was delineated using the Spatial Analyst Hydrology tool using
299 the sampling point as the pour point. Glacier extent was delineated using the semi-automated
300 glacier mapping method using Landsat 5 and 8 TM and Sentinel 1 and 2 imagery (Narama et al.,
301 2010; Severskiy et al., 2016). CRU potential evapotranspiration (PET) data were obtained for
302 1991-2010 (grid resolution 0.5°; CRU TS v. 4.03) (Harris et al., 2020).

303 *3.5 Statistical methods*

304 The differences between cryosphere melt measurements for each catchment were visualized
305 using stacked box and whisker diagrams (Fig. 3) with one-way ANOVA done on the means using
306 parametric (Welch) and non-parametric (Kruskal-Wallis) tests (R package: ggstatplot,
307 Supplementary material, Fig. S1). The spatial variations in the surface water and groundwater
308 quality mean values were plotted with the land cover as a background for initial visual
309 inspection (Figs. 4 and 5) and summary statistics calculated for each site (Table 1). The
310 differences between the upland and lowland surface water and groundwater for each
311 catchment were also visualized using stacked box and whisker diagrams (Fig. 6) with one-way
312 ANOVA done using the same methods as used with the cryosphere measurements
313 (Supplementary material, Fig. S2). Paired scatterplots were drawn and the Spearman's
314 correlation co-efficient and the associated significance calculated to determine the correlation
315 between analytes and with land cover using all data (Fig. 7a) and by catchment (Fig. 7b) to test
316 the strength and significance of the correlations. Many of the sample sites were located on the
317 same tributaries and therefore data from the same channel are autocorrelated and dependent.
318 For this reason, no regression analysis was done and two land cover types only, cropland and
319 urban, are shown and discussed because of the high, negative correlation between these and
320 the land covers associated with the uplands: glaciers, barren terrain, forests and alpine
321 grassland.

322 **4. Results and Discussion**

323 *4.1. Cryosphere water quality*



324
 325 Fig. 3. Cryosphere water quality: (a) pH, (b) EC, (c) NO₃⁻-N and (d) PO₄³⁻-P in rock glacier melt, proglacial streams,
 326 permafrost melt, mountain snowpack and mountain glacier melt. Black points are mean values and red values are
 327 extremes. Parametric and non-parametric ANOVA tests are presented in the Supplementary Material.

328
 329 The water quality (pH, EC, NO₃⁻-N and PO₄³⁻-P) of the cryosphere samples, rock glacier melt,
 330 permafrost melt, mountain snowpack, glacier melt and proglacial stream water, is presented in
 331 Figure 3. The mountain snowpack was acidic with a mean pH of 5.8, which was significantly
 332 lower than the mean pH for the glacier, proglacial stream, permafrost and rock glacier melt (Fig.
 333 3a, Welch, $p < 0.001$, See Supplementary Materials for full details). The lower snow pH reflects
 334 the interaction between precipitation and atmospheric carbon dioxide, and sulphur and
 335 nitrogen oxides, to form weak carbonic acid and sulphuric and nitric acids, and the further
 336 absorption of carbon dioxide during snow melt. In contrast, other melt and proglacial stream
 337 waters were neutral or slightly alkaline with a mean pH of 7.3, 7.6 and 8.1 for permafrost, rock
 338 glacier and glacier melt respectively, and 8.1 for the proglacial streams; all indicative of greater
 339 contact with soil and bedrock, which likely contain carbonates mostly as CaCO₃ (Fig. 3a)

340 (Yapiyev et al., 2021). Three glacial melt samples were acidic, reaching as low as 5.4, which was
341 attributed to fresh snow melt.

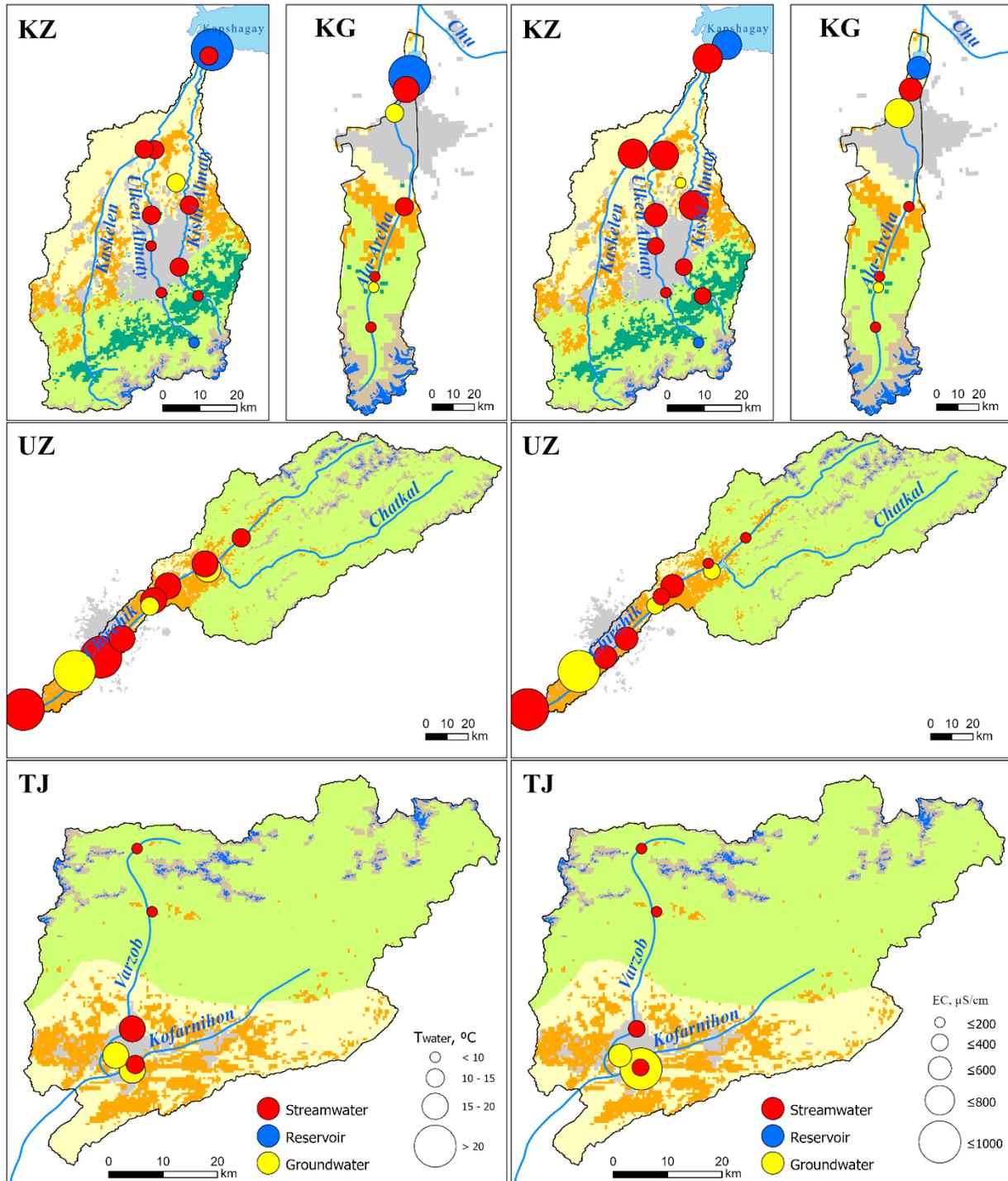
342

343 The EC of the cryosphere samples was lowest for the mountain snowpack ($n = 73$) with a mean
344 of approximately $4 \mu\text{S cm}^{-1}$ and varied most in glacier melt ($n = 17$) from zero to $150 \mu\text{S cm}^{-1}$ (with
345 mean and median values of 90 and $120 \mu\text{S cm}^{-1}$) (Fig. 3b). Rock glacier ($n = 9$) and permafrost
346 melt ($n = 6$) were relatively rich in ions with a mean EC of approximately 110 and $70 \mu\text{S cm}^{-1}$,
347 respectively, again likely due to greater rock: water ratios and rock-water contact times. The rock
348 glacier and permafrost melt had higher mean nitrate concentrations (*c.* $0.5 - 0.6 \text{ mg N l}^{-1}$)
349 compared to glacier melt, though the glacier melt nitrate concentrations were highly variable,
350 ranging from zero to 1.16 mg N l^{-1} (Fig. 3c). Mountain snowpack nitrate concentrations were
351 lowest among all the cryosphere samples with a mean value of 0.1 mg N l^{-1} . The nitrate
352 concentrations measured in the glacier melt, permafrost melt and the proglacial streams were
353 all highly variable, and only the mean nitrate concentrations in the rock glacier melt were
354 significantly higher ($\rho < 0.01$) than those in the snow melt when using the parametric Welch test.
355 Using the non-parameter Kruskal-Wallis test, all melt and proglacial stream nitrate
356 concentrations were significantly higher ($\rho \leq 0.05$) than those in snow melt. The large variation
357 in the proglacial stream nitrate and EC concentrations suggests mixing at the glacier terminus of
358 nitrate derived from basal debris and rock weathering, a primary nitrate source, and nitrate
359 derived from the release of legacy wet and dry nitrate deposition stored in snow, a secondary
360 nitrate source. The cryosphere phosphate concentrations were all low with means of
361 approximately $0.05 \pm 0.03 \text{ mg P l}^{-1}$ which was close to the detection limit. The highest phosphate
362 concentrations observed in the mountain snowpack and glacier melt with a maximum
363 concentration of 0.22 mg P l^{-1} in the Tuyuksu snow melt (Fig. 3d). No significant differences
364 between group means were identified. This suggests less distinction between the phosphate
365 concentrations in wet and dry deposition and those derived from melt water contact with rock
366 and basal debris, with any available phosphate rapidly taken up by the biota (Darcy and Schmidt,
367 2016; McCutcheon et al., 2021).

368

(a)

(b)



370

371 Fig. 4 Stream water, reservoir and groundwater mean (a) water temperature and (b) EC concentrations.

372 The background shading shows the land cover classes as defined in Fig. 1.

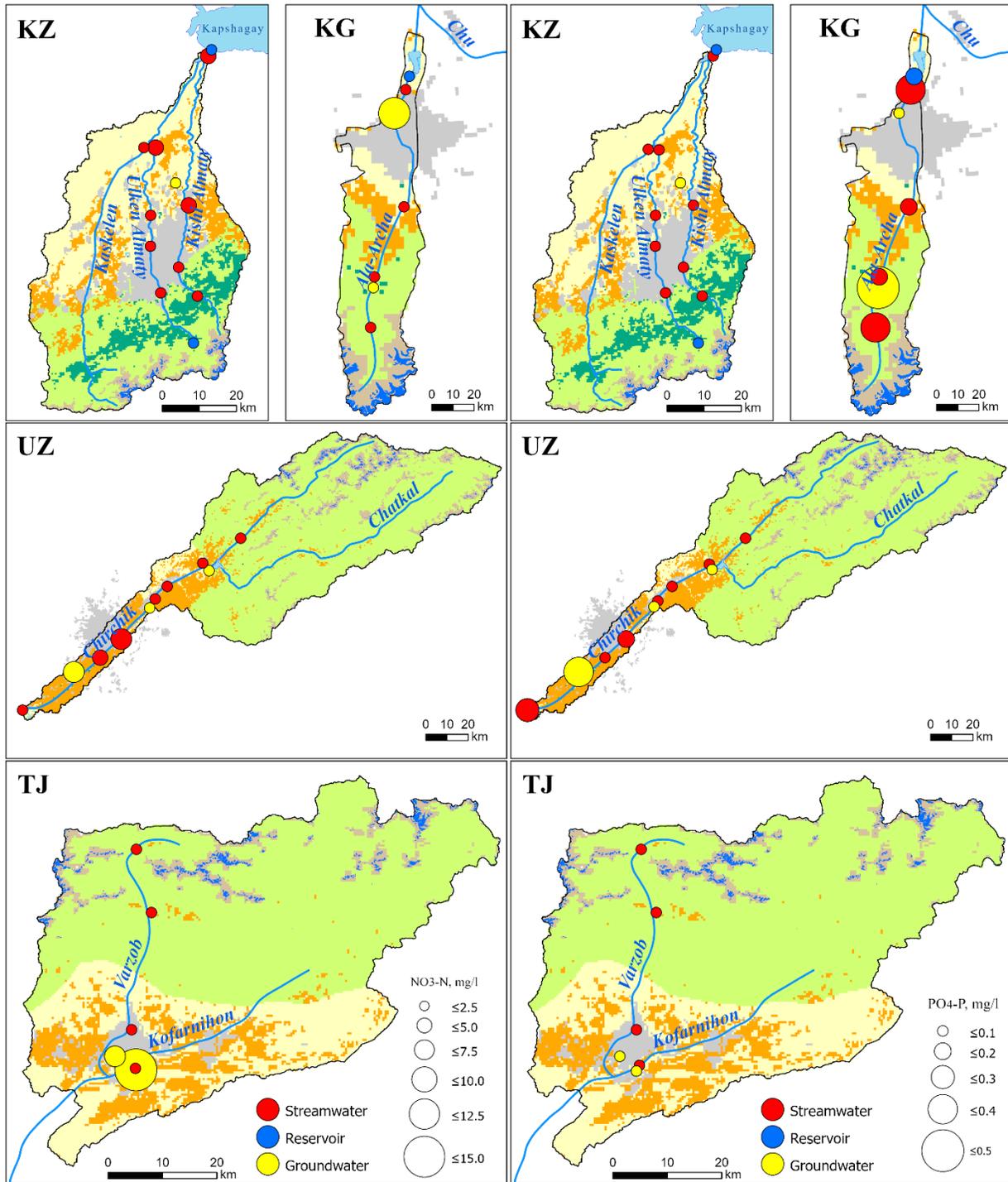
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374

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(a)

(b)



376

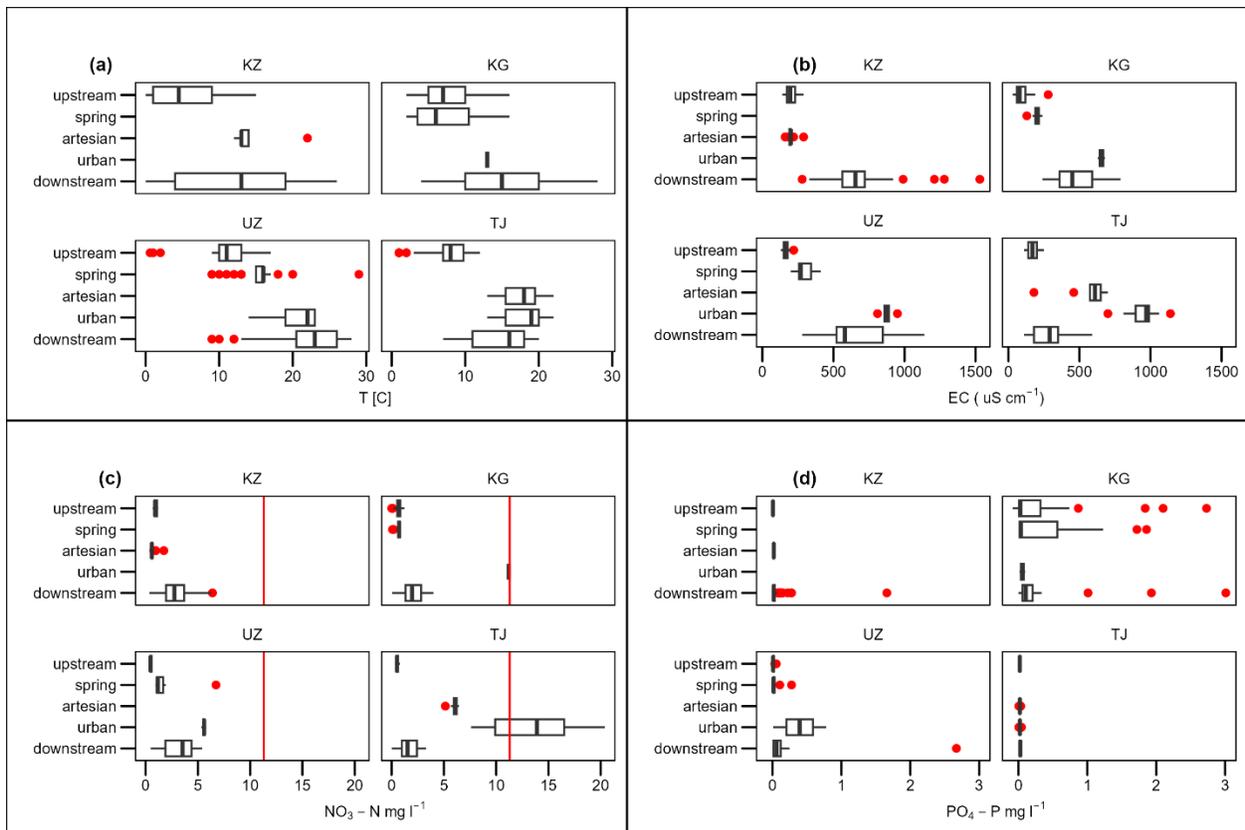
377 Fig. 5. Stream water, reservoir and groundwater mean (a) NO₃⁻-N and (b) PO₄³⁻-P concentrations. The

378 background shading shows the land cover classes as defined in Fig. 1.

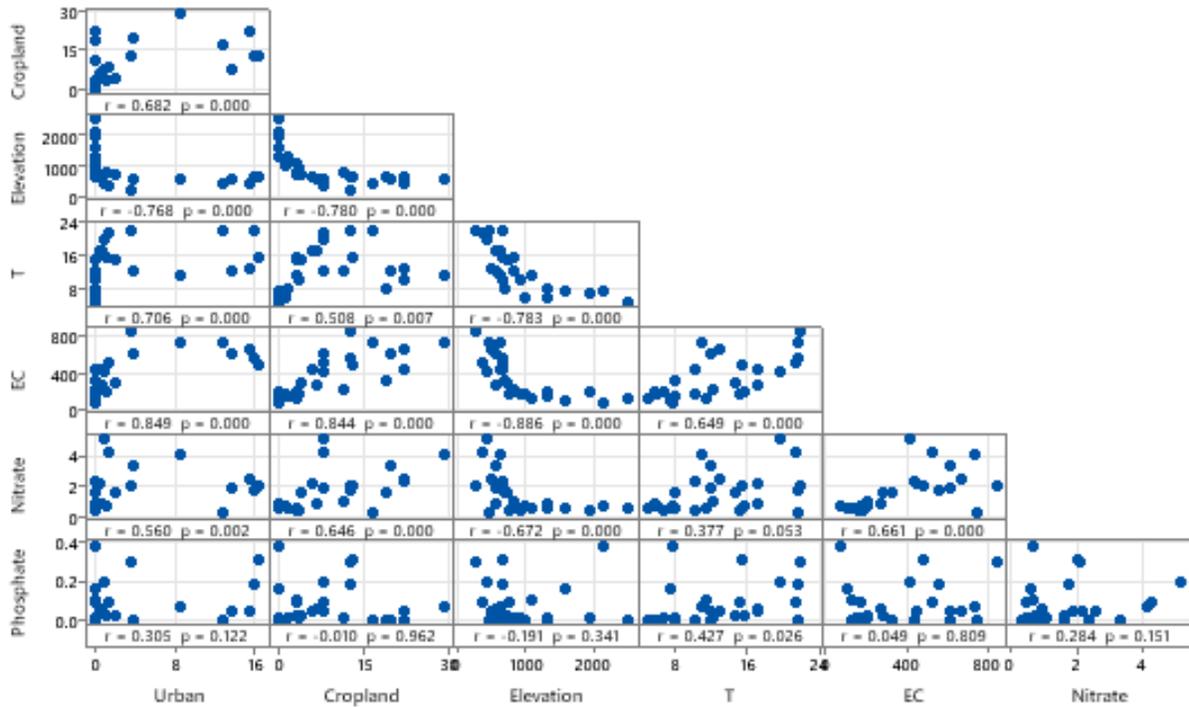
379 Table 3. Stream water quality descriptive statistics (mean, maximum and minimum): water temperature (°C), pH, EC ($\mu\text{S cm}^{-1}$), pH,
 380 NO_3^- -N (mg l^{-1}), PO_4^{3-} -P (mg l^{-1}). The detection limits were 0.23 mg N l^{-1} and 0.05 mg P l^{-1} and therefore many phosphate
 381 measurements were below detection. Abbreviations: Elev. = elevation (m.a.s.l), Ground = groundwater, us = upstream, ds =
 382 downstream, gs = gauging station.

| Location | Site code | Lat, N | Lon, E | Elev. (m) | Sample type | n | Mean | | | | | Max | | | | | Min | | | | |
|-----------------------|-----------|--------|--------|-----------|-------------------|----|--------|-----|------------------------------|---|--|--------|-----|------------------------------|---|--|--------|-----|------------------------------|---|--|
| | | | | | | | T (°C) | pH | EC ($\mu\text{S cm}^{-1}$) | NO_3^- -N (mg l^{-1}) | PO_4^{3-} -P (mg l^{-1}) | T (°C) | pH | EC ($\mu\text{S cm}^{-1}$) | NO_3^- -N (mg l^{-1}) | PO_4^{3-} -P (mg l^{-1}) | T (°C) | pH | EC ($\mu\text{S cm}^{-1}$) | NO_3^- -N (mg l^{-1}) | PO_4^{3-} -P (mg l^{-1}) |
| Kishi Almaty, us | KZ-1 | 43.174 | 77.015 | 1333 | Stream | 38 | 5.7 | 8.0 | 201 | 0.95 | 0.009 | 15 | 8.4 | 290 | 1.20 | 0.021 | 0.0 | 7.6 | 140 | 0.68 | 0.000 |
| Kishi Almaty, Almaty | KZ-2 | 43.251 | 76.959 | 826 | Stream | 18 | 12.3 | 8.2 | 212 | 1.08 | 0.018 | 20 | 8.5 | 350 | 4.02 | 0.129 | 3.0 | 7.6 | 150 | 0.59 | 0.003 |
| Otegen Batyr | KZ-3 | 43.406 | 77.015 | 628 | Stream | 38 | 11.1 | 8.2 | 725 | 4.11 | 0.067 | 24 | 8.6 | 990 | 6.39 | 1.660 | 1.0 | 8.0 | 540 | 0.93 | 0.000 |
| Big Almaty Lake | KZ-4 | 43.057 | 76.986 | 2516 | reservoir | 40 | 4.9 | 8.1 | 133 | 0.65 | 0.006 | 10 | 8.5 | 220 | 0.95 | 0.033 | 0.0 | 7.7 | 90 | 0.54 | 0.000 |
| First President Park | KZ-5 | 43.192 | 76.890 | 993 | Stream | 38 | 5.9 | 8.0 | 174 | 0.72 | 0.008 | 19 | 8.6 | 310 | 1.31 | 0.016 | 0.0 | 7.6 | 130 | 0.20 | 0.000 |
| Darhan | KZ-6 | 43.312 | 76.870 | 700 | Stream | 40 | 8.1 | 8.0 | 328 | 1.60 | 0.007 | 18 | 8.4 | 750 | 3.45 | 0.029 | 0.0 | 7.7 | 170 | 0.69 | 0.000 |
| Kazcık | KZ-7 | 43.390 | 76.881 | 658 | Stream | 40 | 10.2 | 8.1 | 440 | 2.36 | 0.009 | 20 | 8.9 | 720 | 5.28 | 0.033 | 0.0 | 7.6 | 200 | 0.77 | 0.000 |
| Kosozen, Ulken Almaty | KZ-8 | 43.561 | 76.908 | 558 | Stream | 38 | 12.1 | 8.2 | 616 | 3.28 | 0.009 | 26 | 8.5 | 1530 | 5.46 | 0.026 | 0.0 | 7.8 | 280 | 1.45 | 0.000 |
| Kaskelen | KZ-9 | 43.562 | 76.898 | 558 | Stream | 38 | 12.1 | 8.3 | 613 | 1.88 | 0.045 | 23 | 8.5 | 780 | 3.14 | 0.278 | 0.0 | 8.0 | 460 | 0.54 | 0.000 |
| Arna village | KZ-10 | 43.778 | 77.134 | 482 | Stream | 40 | 13.0 | 8.3 | 667 | 2.54 | 0.045 | 26 | 8.6 | 810 | 4.24 | 0.152 | 0.0 | 7.8 | 370 | 0.36 | 0.002 |
| AgroBioCenter | KZ-11 | 43.466 | 76.978 | 609 | Ground (artesian) | 37 | 13.4 | 8.2 | 198 | 0.65 | 0.019 | 22 | 8.8 | 290 | 1.74 | 0.028 | 12.0 | 7.8 | 160 | 0.51 | 0.004 |
| Kapshagay | KZ-12 | 43.794 | 77.147 | 476 | Reservoir | 5 | 21.8 | 8.4 | 740 | 0.33 | 0.005 | 26 | 9 | 960 | 1.16 | 0.010 | 10.0 | 8.0 | 470 | 0.03 | 0.002 |
| Alplager | KG-1 | 42.565 | 74.480 | 2135 | Stream | 26 | 7.7 | 7.6 | 72 | 0.68 | 0.381 | 13 | 8.3 | 190 | 1.23 | 2.730 | 3.0 | 6.7 | 30 | 0.05 | 0.003 |
| Spring, Ala Archa | KG-2 | 42.630 | 74.491 | 1690 | Ground (spring) | 15 | 7.7 | 8.0 | a | 0.67 | 0.421 | 16 | 8.1 | 240 | 0.90 | 1.860 | 2.0 | 7.9 | 130 | 0.08 | 0.006 |
| Baityk | KG-3 | 42.648 | 74.495 | 1589 | Stream | 29 | 7.6 | 7.7 | 109 | 0.63 | 0.165 | 16 | 8 | 280 | 1.18 | 0.741 | 2.0 | 7.2 | 50 | 0.01 | 0.000 |
| Zarechnoe | KG-4 | 42.759 | 74.571 | 1080 | Stream | 28 | 11.4 | 7.8 | 132 | 0.66 | 0.109 | 26 | 8.1 | 220 | 2.46 | 0.633 | 1.0 | 7.3 | 16 | 0.00 | 0.004 |
| Bridge | KG-5 | 42.950 | 74.592 | 663 | Stream | 29 | 15.4 | 8.0 | 481 | 2.05 | 0.316 | 28 | 8.4 | 790 | 4.01 | 3.010 | 4.0 | 7.3 | 240 | 0.04 | 0.001 |
| Ala Archa reservoir | KG-6 | 42.971 | 74.602 | 660 | Reservoir | 6 | 21.8 | 8.0 | 558 | 1.74 | 0.191 | 29 | 8.5 | 720 | 3.12 | 0.390 | 14.0 | 7.4 | 360 | 0.39 | 0.022 |

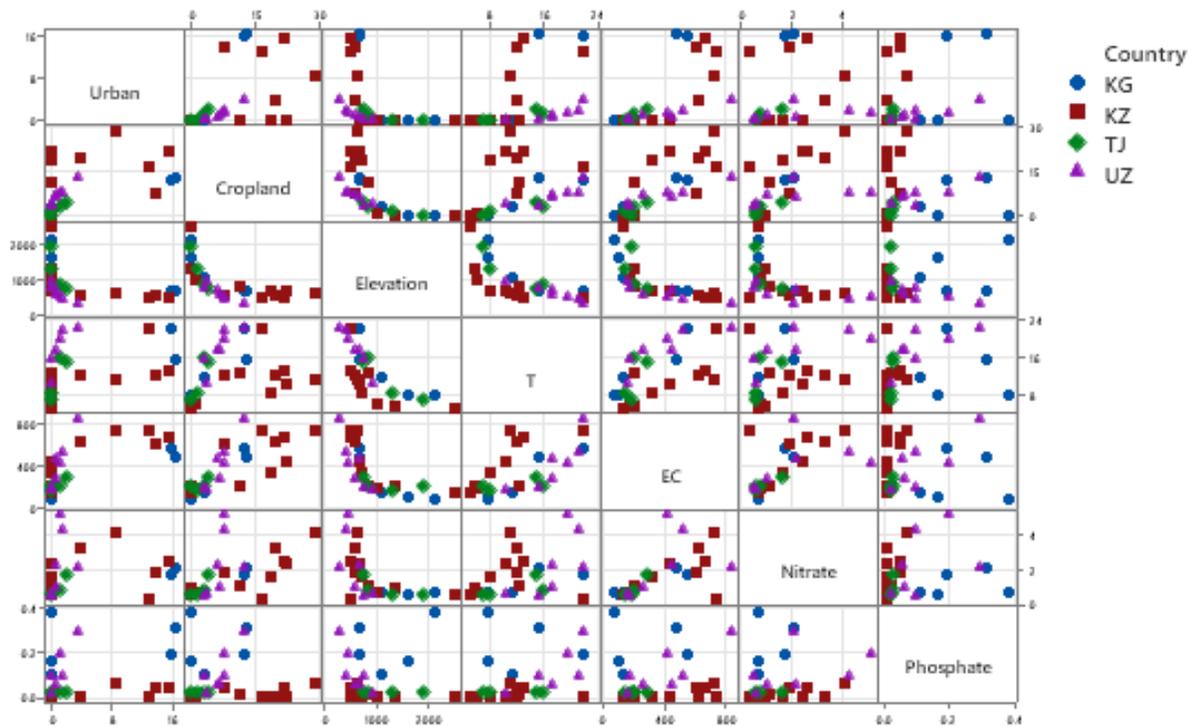
| | | | | | | | | | | | | | | | | | | | | | |
|---------------------------------------|-------|--------|--------|------|----------------------|----|------|-----|-----|-------|-------|----|-----|------|-------|-------|------|-----|-----|-------|-------|
| Household well | KG-7 | 42.913 | 74.563 | 702 | Ground (urban) | 2 | 13.0 | 7.3 | 655 | 11.20 | 0.058 | 13 | 7.3 | 680 | 11.20 | 0.098 | 13.0 | 7.3 | 630 | 11.20 | 0.017 |
| Pskem, Mulala | UZ-1 | 41.772 | 70.191 | 929 | Stream | 18 | 10.3 | 8.2 | 166 | 0.50 | 0.017 | 17 | 8.6 | 220 | 0.64 | 0.056 | 0.6 | 8.1 | 130 | 0.42 | 0.001 |
| Chirchik, ds Charvak reservoir | UZ-2 | 41.630 | 69.953 | 748 | Stream | 18 | 15.2 | 8.3 | 178 | 0.47 | 0.094 | 20 | 8.8 | 240 | 0.70 | 0.707 | 5.0 | 8.0 | 130 | 0.36 | 0.005 |
| Hodjakent | UZ-3 | 41.623 | 69.940 | 769 | Ground (spring) | 18 | 16.0 | 8.2 | 256 | 1.43 | 0.030 | 29 | 8.4 | 290 | 6.73 | 0.107 | 9.0 | 7.9 | 200 | 0.97 | 0.008 |
| Chirchik, ds Gazalkent | UZ-4 | 41.530 | 69.688 | 636 | Stream | 18 | 17.3 | 8.1 | 449 | 2.16 | 0.050 | 23 | 8.4 | 640 | 3.58 | 0.290 | 5.0 | 7.6 | 150 | 0.81 | 0.004 |
| Chirchik | UZ-5 | 41.431 | 69.583 | 561 | Stream | 18 | 17.2 | 8.3 | 268 | 0.93 | 0.058 | 22 | 8.5 | 450 | 1.76 | 0.304 | 8.0 | 8.1 | 180 | 0.56 | 0.000 |
| Spring, Chirchik | UZ-6 | 41.431 | 69.583 | 561 | Ground (spring) | 10 | 15.0 | 7.6 | 355 | 1.68 | 0.050 | 20 | 7.7 | 410 | 1.92 | 0.277 | 11.0 | 7.5 | 290 | 1.41 | 0.010 |
| Chirchik, us Tashkent | UZ-7 | 41.262 | 69.375 | 444 | Stream | 17 | 19.8 | 8.1 | 420 | 5.14 | 0.200 | 27 | 8.7 | 520 | 6.56 | 0.965 | 8.0 | 7.6 | 30 | 1.48 | 0.010 |
| Chirchik, ds Tashkent | UZ-8 | 41.168 | 69.232 | 375 | Stream | 16 | 21.4 | 7.9 | 523 | 4.27 | 0.095 | 28 | 8.1 | 610 | 5.39 | 0.248 | 9.0 | 7.6 | 280 | 1.75 | 0.005 |
| Borehole near Yangiyul | UZ-9 | 41.094 | 69.053 | 344 | ground (urban) | 5 | 20.2 | 7.4 | 876 | 5.57 | 0.396 | 23 | 7.6 | 950 | 5.80 | 0.780 | 14.0 | 7.4 | 810 | 5.33 | 0.011 |
| Chirchik, near inflow to Syr Darya | UZ-10 | 40.900 | 68.709 | 253 | Stream | 15 | 21.9 | 8.0 | 842 | 2.08 | 0.295 | 28 | 8.3 | 1140 | 3.93 | 2.670 | 10.0 | 7.8 | 500 | 0.48 | 0.001 |
| Maykhura | TJ-1 | 39.027 | 68.785 | 1934 | Stream | 19 | 6.8 | 8.2 | 189 | 0.51 | 0.020 | 10 | 8.3 | 250 | 0.66 | 0.033 | 1.0 | 8.0 | 120 | 0.36 | 0.006 |
| Varzob, gs | TJ-2 | 38.872 | 68.833 | 1307 | Stream | 19 | 8.0 | 8.1 | 152 | 0.54 | 0.020 | 12 | 8.6 | 200 | 0.79 | 0.032 | 1.0 | 8.0 | 110 | 0.32 | 0.009 |
| Luchob | TJ-3 | 38.587 | 68.772 | 822 | Stream | 19 | 15.8 | 8.3 | 206 | 0.74 | 0.021 | 23 | 8.6 | 290 | 1.23 | 0.042 | 4.0 | 7.9 | 110 | 0.34 | 0.006 |
| Kofarnihon | TJ-4 | 38.493 | 68.784 | 719 | Stream | 19 | 14.8 | 7.8 | 285 | 1.64 | 0.027 | 20 | 8.1 | 590 | 3.29 | 0.056 | 7.0 | 7.0 | 110 | 0.01 | 0.009 |
| Drinking water facility | TJ-5 | 38.522 | 68.720 | 747 | Ground (artesian) | 19 | 17.6 | 7.2 | 592 | 6.04 | 0.021 | 22 | 7.7 | 700 | 6.44 | 0.033 | 13.0 | 7.0 | 180 | 5.14 | 0.006 |
| Potable well | TJ-6 | 38.490 | 68.785 | 728 | Ground (urban) | 19 | 17.7 | 6.9 | 941 | 13.27 | 0.022 | 22 | 7 | 1140 | 20.40 | 0.045 | 13.0 | 6.4 | 700 | 7.59 | 0.006 |



384
 385 Fig. 6. Surface and groundwater water quality: (a) water temperature, (b) EC, (c) NO₃-N and d) PO₄-P
 386 upstream and downstream of urban areas, and in urban springs (springs), artesian boreholes (artesian)
 387 and urban wells (urban). The red vertical line in panel c shows the drinking water limit of 11.3 mg N l⁻¹
 388 adopted by the World Health Organization.



389
390



391

392 Fig. 7. Matrix scatterplot of (a) mean water quality values across all four catchments with Spearman's
 393 correlation co-efficient values and p-values shown, and (b) the same data grouped by catchment. The
 394 units are urban and cropland (% catchment area), elevation (m.a.s.l), mean air temperature (T, °C),
 395 mean electrical conductivity (EC, $\mu\text{S cm}^{-1}$), mean nitrate (mg N l^{-1}), and mean phosphate (mg P l^{-1}).

396 *4.2. Spatial variations in surface water and groundwater quality*

397 Along all the rivers, the predominant land cover changes from barren, mountain terrain to
398 alpine grassland and forest and then to cropland and dry grassland steppe (Fig. 1, Table S1). In
399 the Ala-Archa, Bishkek is located on the steppe, downstream of cropland. The Kaskelen is
400 different as Almaty is located at the mountain base and upstream of the cropland and steppe,
401 whilst Tashkent in the Chirchik and Dushanbe in the Kofarnihon are surrounded by cropland.
402 The pH data show little variation either between stream water sites or with season and are
403 generally within the range 7 to 8.6 (Table 3) suggesting any pH differences between cryosphere
404 sources are eliminated as waters mix. There are two notable outliers. The first is the Kapshagay
405 reservoir where the pH reaches 9, likely due to the wash-in of catchment soils enriched in
406 calcium carbonate and bicarbonate. The second outlier is an urban well in Dushanbe where the
407 pH is slightly acidic with a minimum pH of 6.4 most likely reflecting a more acidic geology.

408

409 *4.2.1 Water temperature*

410 The mean stream water temperature increased downstream in all catchments moving from the
411 glaciers to the plains, reflecting the decreasing influence of glacial meltwater and the increasing
412 air temperatures at lower elevations (Figs. 4a, 6 and S2, Table 3). Immediately downstream of
413 the glaciers, in the Kaskelen, Ala-Archa and Kofarnihon catchments, the mean water
414 temperatures were approximately 5 - 7 °C and the water temperature remained in this range in
415 these catchments until the forest and alpine grassland transition to cropland and steppe when
416 the water temperatures increased markedly in the Ala-Archa, Kaskelen and Kofarnihon. In
417 Kaskelen and Ala-Archa, the urban groundwater temperatures were in a similar range to the
418 surface water temperatures with a mean of approximately 13 °C indicative of groundwater and
419 surface water mixing (Figs. 3a and 5). In Tashkent and downstream, the surface water and
420 groundwater temperatures of the Chirchik were similar, but higher (median c. 22 °C), again
421 indicative of surface-subsurface mixing.

422 The highest water temperatures were found in the two reservoirs, Kapshagay and Ala-Archa,
423 with mean water temperatures of approximately 22 °C and summer maximums of 29 °C. These
424 mean and maximum temperatures were approximately equal to those at the lowest

425 measurement points on Kaskelen at Arna village and Ala-Archa at the main road bridge north of
426 Bishkek, which are immediately upstream of the reservoir inflows, demonstrating the influence
427 of the rivers on the reservoir water quality close to the inflow. The Chirchik water temperatures
428 were generally higher than in the other catchments because the catchment area is much larger,
429 and the highest water quality sampling point at Mulala was further away from the glacial
430 headwaters than elsewhere, and the lowest reaches of the Chirchik were located furthest (80 –
431 160 km) into the cropland and steppe.

432 *4.2.2 Electrical conductivity (EC)*

433 Stream water EC, a measurement of salinity, increased downstream in all catchments and was
434 correlated with water temperature and the percentage of urban area and cropland, which all
435 increase downstream (Figs. 4b, 6b and 7). In Kaskelen, the EC increased from approximately 130
436 - 200 $\mu\text{S cm}^{-1}$ in Big Almaty Lake (KZ-4), a reservoir formed from a proglacial lake, to
437 approximately 500 - 700 $\mu\text{S cm}^{-1}$ downstream in the Kishi Almaty, Ulken Almaty and Kaskelen
438 rivers and the Kapshagay reservoir (Figs. 4b and 6, Table 3). The EC measured at the upland
439 stream water sites had a similar range to glacier melt (0 – 200 $\mu\text{S cm}^{-1}$, Section 4.1; Table 3)
440 suggesting few additional solute inputs and instream processing until the transition from the
441 forest and alpine grassland to cropland and steppe. High (> 800 $\mu\text{S cm}^{-1}$) EC concentrations
442 were observed at Kosozen (KZ-8) on the Ulken Almaty, Arna on the Kaskelen (KZ-10),
443 downstream of Bishkek on the Ala-Archa and on the Chirchik near the inflow to the Syr Darya
444 (UZ-10), however these were lower than the World Health Organization TDS standard of 1000
445 mg l^{-1} (approximately equivalent to 1564 $\mu\text{S cm}^{-1}$, Yapiyev et al., 2021). Groundwater inputs to
446 the surface water also likely increase along the continuum and groundwater has elevated EC
447 concentrations relative to upstream surface waters due to contact time with the geology and
448 urban pollution (Fig. S2). Thus, when groundwater enters the surface waters, this will increase
449 the EC also, and this increase is further amplified in the lowest river reaches by
450 evapoconcentration and soil leaching and irrigation return flow inputs. The mean EC
451 concentrations in the Kaskelen at Arna Village and the Kapshagay reservoir were both
452 approximately 700 $\mu\text{S cm}^{-1}$ and in the Ala-Archa at the bridge and the Ala-Archa reservoir

453 approximately $500 \mu\text{S cm}^{-1}$ indicating, as for water temperature, the regulating effect of the
454 river on the reservoir water quality at least close to the inflow (Fig. 4b).

455 4.2.3 Nitrate

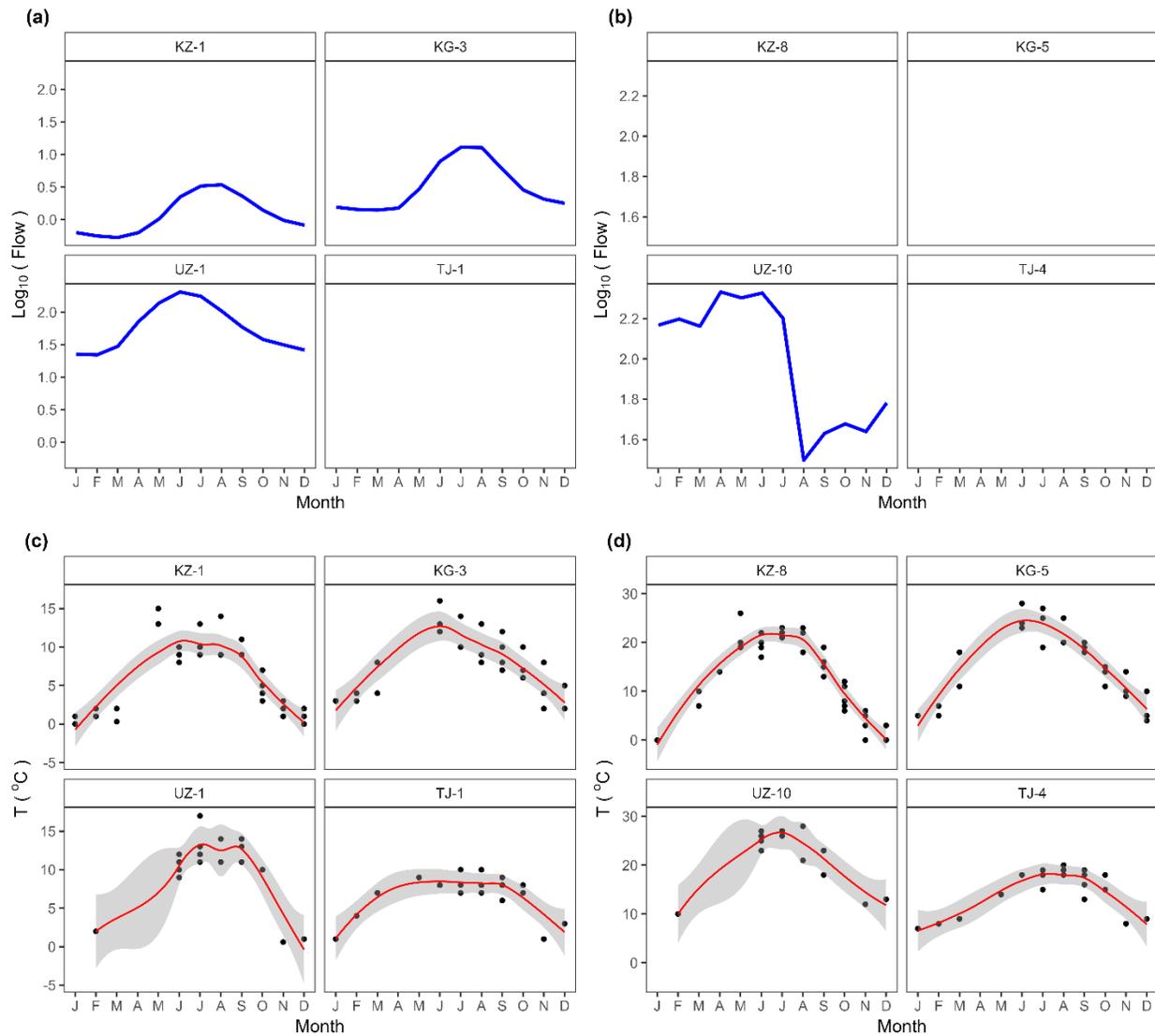
456 Mean surface-water nitrate concentrations ranged from 0 to 1.25 mg N l^{-1} at the upstream
457 stream water sites in all four study catchments and between 0 to 6 mg N l^{-1} at the sample
458 locations in, and downstream of, the major cities (Figs. 5a and 6c, Table 3, Fig. S2). Stream
459 water nitrate concentrations were correlated with EC ($r = 0.6, p < 0.001$) which indicates that
460 nitrate is a key component of the ion balance (Fig. 7). The greatest spatial variability was
461 observed in the Chirchik catchment with concentrations ranging from 0.5 mg N l^{-1} in the
462 headwaters (UZ-1) to over 5 mg N l^{-1} near Tashkent (UZ-7). The nitrate concentrations showed a
463 marked increase downstream of the cities in each catchment (Welch, $p < 0.0001$, Fig. S2), and
464 whilst there is a strong correlation between cropland area and stream water nitrate
465 concentration in all catchments ($r = 0.65, p < 0.001$, Fig. 7a), there is also a correlation between
466 nitrate concentrations and urban area ($r = 0.56, p < 0.01$, Fig. 7a). The highest nitrate
467 concentrations were measured in shallow well-water samples in Bishkek (approximately 11 mg
468 N l^{-1}) and Dushanbe (approximately 13 mg N l^{-1}) indicating urban groundwater pollution with
469 concentrations above the national drinking water standards of 10 mg N l^{-1} adopted in KZ, KG
470 and TJ and 9 mg N l^{-1} adopted in UZ, and the 11.3 mg N l^{-1} set by WHO (Yapiyev et al., 2021). In
471 the croplands upstream of Bishkek and Dushanbe, lower nitrate concentrations were observed
472 in springs, and an artesian well, which suggests lower pollution from farming compared to
473 urban areas (Fig. 6c). The stream water nitrate concentrations were lower than those in the
474 urban groundwater (Welch, $p < 0.0001$, Fig. S2) suggesting the groundwater contamination was
475 from urban effluent rather than the surface waters.

476 4.2.4 Phosphate

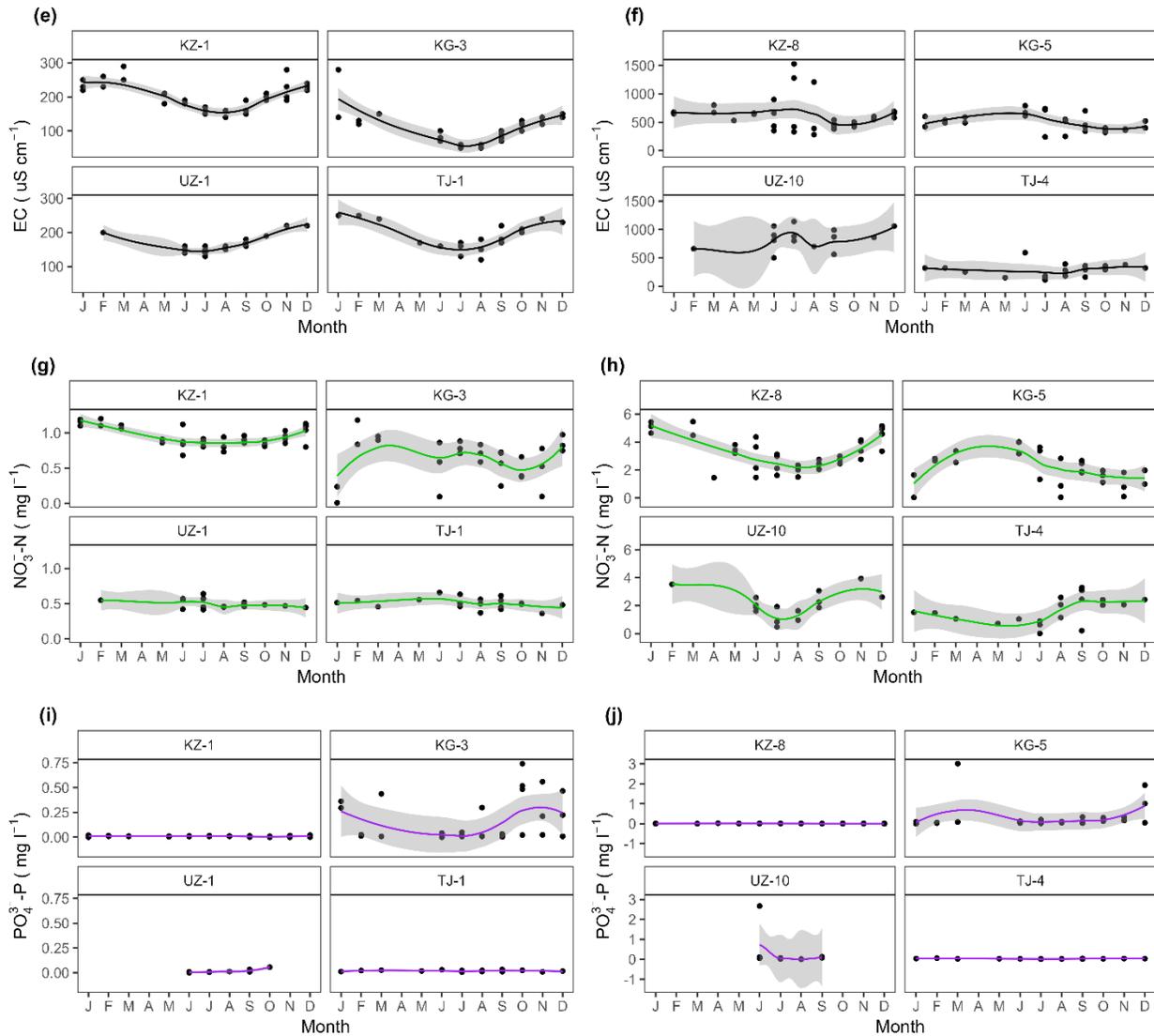
477 Overall, river and groundwater $\text{PO}_4\text{-P}$ concentrations are low above the urban centers, with
478 mean stream water concentrations below the detection limit of 0.05 mg P l^{-1} . Downstream of
479 the urban areas the concentrations increase to approximately 0.2 mg P l^{-1} indicating effluent
480 inputs to the lower reaches (Figs. 5b and 6d, Table 3). Very high phosphate concentrations

481 were measured throughout the Ala-Archa catchment with mean and maximum phosphate
482 concentrations of 0.38 and 2.7 mg P l⁻¹ (KG-1) respectively, upstream of Bishkek, with a
483 measurement of 1.8 mg P l⁻¹ in a headwater groundwater spring possibly indicating a geological
484 source (KG-2, Figs. 5b and 6d, Table 3). The corresponding EC concentrations were variable with
485 some high EC values equating to high phosphate concentrations and with some samples having
486 low EC but high phosphate. Large spikes, as high as 3 mg P l⁻¹, were also measured in the
487 phosphate concentrations in Bishkek (KG-5) which may be due to contamination by untreated
488 sewage (Figs. 1, 5b and 6d, Table 3). Relatively high phosphate concentrations of approximately
489 0.3 mg P l⁻¹ were also observed in an urban well (UZ-9) in the Chirchik catchment and at the
490 surface water sampling point immediately downstream of Tashkent indicating an urban source
491 of the contamination (UZ-10; Figs. 5b and 6d, Table 3). The stream water phosphate
492 concentrations were only weakly correlated with urban area ($r = 0.3$, *not significant*) and not
493 correlated with cropland ($r = 0.0$, *not significant*), and there was little correlation with stream
494 water nitrate ($r = 0.28$, *not significant*), suggesting phosphate was limited in the soils and
495 stream water whilst nitrate, which is much more soluble and abundant, was leached.

496 4.3 Seasonal water quality dynamics



497
 498 Fig. 8. Seasonal (a) Flow – high elevation, (b) Flow – low elevation (from Fig. 1), (c) Stream water temperature –
 499 high elevation, (d) Stream water temperature – low elevation in selected upstream and downstream points in each
 500 catchment (see also Fig. 1a and Table 3). The measurements were made in 2019-2020. *Continued.*



501
 502 *Continued from* Fig. 8. Seasonal (e) EC - high elevation, (f) EC - low elevation, (g) NO₃-N - high elevation, (h) NO₃-N
 503 – low elevation, and (i) PO₄-P – high elevation, (j) PO₄-P – low elevation in selected upstream and downstream
 504 points in each catchment (see also Fig. 1a and Table 3). The measurements were made in 2019-2020.

505

506 4.3.1 Stream flow

507 The seasonal variations in stream flow are described in section 2 and are drawn in Fig. 8a and
 508 8b to allow comparison with the observed water quality dynamics. The stream measurement
 509 locations on the Kishi Almaty (KZ-1), Ala-Archa (KG-3) and Chirchik (UZ-1 and UZ-10) are co-
 510 located with stream water sampling points.

511

512 4.3.2 Water temperature

513 Stream water temperatures at the upland and lowland sites have a strong seasonal pattern
514 with temperature maximums in summer (JJA) and minimums in winter (NDJF). In the uplands of
515 the Kishi Almaty (KZ-1), Ala-Archa (KG-3) and Chirchik (UZ-1), the maximums are in the range of
516 10 to 15 °C, compared to the Maykhura River which is a headwater tributary of the Varzob
517 where the maximum is lower between 5 and 10 °C (Fig. 8b). This difference is sustained in the
518 lowland reaches with the summer stream water maximum temperatures between 20 to 30 °C
519 in the Kaskelen, Ala-Archa and Chirchik, but approximately 18 °C in the Kofarnihon perhaps
520 indicative of a greater melt water contribution.

521

522 *4.3.3 Electrical conductivity*

523 Seasonal changes in electrical conductivity (EC) were evident with EC lower under the summer
524 high flow conditions at all upstream sites suggesting solute dilution (KG-3, KZ-1, TJ-1 and UZ-1,
525 Fig. 8c and 8d). The lowest EC concentrations occurred one month after peak flow, suggesting a
526 dilution effect in the river due to the input of water with relatively low EC from glacier and
527 snow melt (see section 4.1). At the downstream-lowland locations, the meltwater inputs
528 reduced the mean EC at all sites in July and August relative to the June values commensurate
529 with an increased input of melt water (Figs. 7a and 7e). In the snowmelt dominated Kofarnihon
530 River at Dushanbe (TJ-4), the EC seasonal variation was low with a mean value of 285 $\mu\text{S cm}^{-1}$
531 demonstrating a sustained dilution even at the most downstream site below a large urban area
532 (Fig. 7b and 7f, Table 3). However, variations in EC were evident around these mean EC values
533 and in the downstream-lowlands of Ala-Archa (KG-5), the EC peaked at approximately 800 $\mu\text{S cm}^{-1}$
534 in July and August. This result demonstrates that the dilution effect on water quality can
535 be diminished downstream, but not eliminated, as the main channel becomes dominated by
536 urban and agricultural sediment and nutrient inputs. A large annual variation in EC was
537 observed at the lowest sample site on the Ulken Almaty (KZ-8), downstream of Almaty, and was
538 probably dependent on the amount of summer glacier and snow melt and altered hydrological
539 connections between soil leaching and the main river during the summer months in different
540 years. In the Ulken Almaty at Kosozen (KZ-8), the summer EC varied from 300 - 1600 $\mu\text{S cm}^{-1}$ in
541 July due to differences in discharge between 2019, with high summer discharge which

542 associates with an EC of $300 \mu\text{S cm}^{-1}$, and 2020 characterised by a delayed melt due to cloudy
543 conditions and lower air temperatures resultant in lower discharge in summer, which with an
544 EC of $1600 \mu\text{S cm}^{-1}$ (Fig. 7f).

545 *4.3.4 Nitrate*

546 In the Kishi Almaty (KZ-1) and Ala-Archa rivers (KG-3) at high-elevation, there is some evidence
547 that nitrate is higher during the winter low-flow period and lower during the summer, though
548 little seasonal variability in nitrate concentrations was observed particularly for the Chirchik
549 (UZ-1) and Varzob (TJ-1) rivers (Fig. 8g). This suggests that the in Ala-Archa and Kishi Almaty
550 headwaters, the nitrate flux is dominated by a steady, albeit small, supply of nitrate from the
551 cryosphere which is diluted by summer snow melt. The cryosphere samples nitrate
552 concentrations range from 0 to 1.2 mg N l^{-1} (section 4.1), which are close to the values observed
553 in the upstream stream water sites. Though the concentrations are lower during the high flows
554 in the summer, the total flux could be significant due to higher glacier melt (July-August, Fig.
555 2c). Further work is needed to measure flow and concentrations simultaneously. Seasonal
556 variations in the lowland nitrate concentrations were also evident though the patterns were
557 complex. In the lowlands, nitrate concentration peaks were observed in June and July (c. 4 mg
558 N l^{-1}) in Ala-Archa (KG-5), whereas in the Kofarnihon (TJ-4) the peak occurred in September (c. 3
559 mg N l^{-1}), and in Ulken Almaty River (KZ-8) in the winter, December-March, period (c. 5 mg N l^{-1})
560 and there was a notable variation in nitrate concentration in June (Fig. 8h). These differences
561 probably indicate variations in the relative inputs of nitrate from urban and cropland areas,
562 groundwaters, the evapoconcentration effect and the timing of the meltwater input.

563

564 *4.3.5 Phosphate*

565 Both high- and low-elevation phosphate concentrations exhibited little seasonal variation (Fig. i
566 and 8j), though concentration spikes were evident and there was some evidence for meltwater
567 dilution or summer uptake of phosphate in the high-elevation Ala-Archa (KG-3). In the Ala-
568 Archa River, spikes in the phosphate concentrations were measured in March (3 mg P l^{-1}) and
569 December (1.9 mg P l^{-1}) at the downstream KG-5 site. The increase of phosphate at the upper
570 site (KG-1) observed from August to November 2020 (from 1.8 to 2.7 mg P l^{-1} , respectively)

571 suggested some subsurface inputs to the stream water while the biggest phosphate spike in
572 March 2020 downstream (KG-5) that reached 3.0 P l^{-1} was likely due to effluent input or
573 possibly a deeper groundwater source (Fig. 8i). High phosphate concentrations were also
574 measured in the Chirchik (UZ-10) in June with maximum values of 0.97 and 2.7 mg P l^{-1} for UZ-9
575 and UZ-10 respectively suggesting an agricultural or urban source (Table 3, Fig. 8j). The
576 measurements of the phosphate standards were good suggesting the phosphate spikes were
577 real and not due to analytical error.

578

579 **5. Key findings and wider implications**

580 For the first time, an extensive spatial and temporal dataset describing key water quality
581 parameters has been created for four glaciated catchments in Central Asia and made available.
582 Whilst some data were available for KZ and UZ, this study extends water quality measurement
583 to KG and TJ, increases the measurement frequency from monthly to fortnightly to better
584 capture seasonal variations, links the cryosphere to the downstream stream water, and
585 includes groundwater and high mountain and lowland reservoirs; all using methods common to
586 all catchments and water types. Thus, the work begins to address recent calls for better
587 systematic quantification of contaminants in the catchments of Central Asia through the
588 initiation of a water quality monitoring network (Beard et al., 2022a; Beard et al., 2022b; Leng
589 et al., 2021; Liu et al., 2021).

590 Our data show that nutrients can be present in significant concentrations in mountain
591 cryosphere melt, particularly nitrate in Ulken Almaty headwaters which contained over 1 mg
592 $\text{NO}_3^- \text{-N l}^{-1}$. The nitrate concentrations were especially high in rock glacier and permafrost melt
593 and the subsequent melting of these is a concern for input fluxes to downstream streams and
594 lakes. Considering hypothesis one, the proglacial stream nitrate concentrations were found to
595 be significantly lower than those in rock glacier melt and significantly higher than those in the
596 snowpack melt. Given this, and the large variation in the proglacial stream nitrate
597 concentrations, then the nitrate measured at the glacier terminus seems likely derived from a
598 mixture of weathering and atmospheric deposition. In 1999, Vilesov and Uvarov (2001)
599 measured elevated nitrate concentrations (up to 3.9 mg l^{-1} of $\text{NO}_3^- \text{-N}$) in Tyuksu glacier melt

600 samples, and these linked to the air pollution of Almaty from fossil fuel combustion. We did not
601 find concentrations as high and more detailed study is required to better understand the
602 relative contribution of nitrate to proglacial streams from weathering and atmospheric
603 deposition, especially as air pollution of large cities in Central Asia is a growing concern
604 (Tursumbayeva et al., 2023). The relative contributions of supraglacial, englacial and subglacial
605 melt, including snow and firn melt, also require quantification to confirm if nitrate in CA glaciers
606 is derived from a mix of primary and secondary sources.

607 Low dissolved phosphate concentrations at the high elevation sample sites suggest that the
608 soils and stream waters were phosphorus limited with any available phosphorus rapidly
609 assimilated by the soil or stream biota or, alternatively or in addition, that phosphorus was in a
610 particulate form. Phosphorus can be derived from the glacier flour (Tranter, 2003) but the low
611 phosphate concentrations in the cryosphere samples suggests that this is not an important
612 source in the Ala-Archa. Rather the elevated concentrations may be due to small, localised
613 sewage inputs, upstream of the sampling locations or spring water. Further measurements are
614 required for resolution.

615 The water stored in upland lakes and reservoirs was clean in terms of the analytes measured
616 and of high quality for drinking when transferred to the cities downstream. There was neither
617 evidence of lake or reservoir acidification nor eutrophication. Based on field observations, the
618 cold water-temperatures in the mountains, typically less than 6 °C, combined with the
619 turbulent stream flows, appear to keep primary productivity low in streams and limited to
620 biofilm and microbial growth, which is similar to other high mountain ecosystems (Milner et al.,
621 2017). However, the productivity of the lakes and reservoirs requires a more complete
622 assessment to determine eutrophication risk.

623 Overall, the water quality in all four catchments complied with national and World Health
624 Organization standards along the continuum from the source to the plains. In all four
625 catchments, there was a marked transition in water quality where the land cover changed from
626 forest and alpine grassland to cropland, urban and grassland steppe, and there was strong
627 evidence that land cover explained the spatial variations in the EC and nitrate concentrations

628 (hypothesis two). The observed longitudinal variations in stream water nitrate and phosphate
629 concentrations were found to be similar to previous studies, being very low close to the
630 glaciers, and higher in urban and cropland areas (< 0.23 to 6 mg N l^{-1} ; < 0.05 to 3 mg P l^{-1}) (Leng et
631 al., 2021; Yapiyev et al., 2021). The general increase in EC was caused by pollutant inputs from
632 cropland and urban areas, higher evapoconcentration resultant from higher air temperatures
633 and longer water residence times, and inflows of irrigation return water and soil leaching.
634 Downstream of the land cover transition, contamination hotspots were also evident. The
635 stream water EC remained within accepted standards for good quality drinking and irrigation
636 water though higher ($> 1000 \mu\text{S cm}^{-1}$) values occurred near the river mouths, lowland reservoirs
637 and groundwaters but still below levels that become problematic for human and livestock
638 consumption (i.e., c. $2500 \mu\text{S cm}^{-1}$). The groundwater had higher EC than the surface waters due
639 to higher dissolved solutes and urban pollution, however it was not saline.

640 Whilst EC and $\text{NO}_3\text{-N}$ concentrations were correlated, the increase in stream water $\text{NO}_3\text{-N}$
641 concentrations at the land cover transition was less marked than for EC. This may reflect that
642 nitrogen inputs from agriculture remain low even following economic recovery in the post-
643 Soviet era, or that farms and farmland are managed to maintain a balance between nitrogen
644 inputs and outputs. World Bank fertilizer application data suggest the former, with fertilizer-
645 application rates generally low except in Uzbekistan which may explain the higher stream water
646 $\text{NO}_3\text{-N}$ concentrations observed in the Chirchik (Yapiyev et al., 2021).

647 The phosphate concentrations generally do not breach national drinking water standards;
648 however, they are a concern for eutrophication in the lower river reaches with concentrations
649 measured above nutrient thresholds for eutrophication ($\text{TP} > 0.1 \text{ mg P l}^{-1}$ and $\text{TN} > 1 \text{ mg N l}^{-1}$)
650 (Figs. 4b and 5, Table 3) (Bowes et al., 2012; Poikane et al., 2022). There was no evidence of
651 surface-groundwater mixing diluting groundwater EC, nitrate and phosphate concentrations
652 from bedrock contact (hypothesis three). Instead, the higher nitrate and phosphate ($> 0.2 \text{ mg P}$
653 l^{-1}) concentrations observed in urban wells indicate the contamination of urban groundwater
654 with sewage effluent and, whilst not measured, this suggests likely microbial contamination
655 given the lack of sewage treatment, particularly in Tashkent and Bishkek. Comparison of the

656 water temperature, EC and nitrate data all suggest that local contamination, by sewage, in the
657 urban areas rather than by mixing with surface waters. Leng et al. (2021) modelled high total
658 dissolved phosphorus inputs in urban locations from effluent discharges. There is some
659 evidence of high phosphate concentrations in a groundwater spring in the Ala-Archa
660 headwaters indicating a geological source.

661 In the mountains, seasonal dynamics in the water temperatures and EC were evident in all four
662 catchments indicating ion dilution during the summer (JJA) melt. At the most downstream sites
663 on the main river channels, a dilution effect is discernable with lower EC and $\text{NO}_3\text{-N}$
664 concentrations during JJA (hypothesis four). However, the effect is variable and likely
665 dependent on the wash-in of contaminants from croplands and urban groundwater and inter
666 and intra-year variations in snow and ice melt. The meltwater dilution effect is difficult to
667 quantify with the data collected because of the integration of sources, pathways, and instream
668 processes including evapoconcentration, nitrification and denitrification, and further work to
669 use water stable and nitrogen isotopes and models is recommended to quantify the melt water
670 dilution effect along the main channel, and determine how higher air temperatures, an early
671 melt season and greater spring precipitation will affect biogeochemical cycling and contaminant
672 wash-in and dilution (Mueller et al., 2016). Any assessment should include the effect of lakes
673 and reservoirs which control water release.

674 Given projected population growth in the region and the reliance on glacial melt water for
675 irrigation and drinking, and transboundary contaminant transport in both the atmosphere and
676 water then continued regional collaboration is required to maintain and expand the monitoring
677 network established. The transport and release from snow and ice of trace organics, potentially
678 toxic elements and radionuclides, now needs to be considered given projected increases in dust
679 storms in the region (Nobakht et al., 2021), and such assessment should also include
680 bioaccumulation and biomagnification assessments for lake and reservoir ecology and
681 measurement of sediment transport and associated contamination (Liu et al., 2021). Our data
682 showed that there is likely a substantial nitrate flux from the cryosphere given the relatively
683 high concentrations measured, however, concurrent flow and concentration measurements are

684 required to determine accurate flux estimates for a range of solutes and particulates.
685 Enhanced primary productivity depends on residence time, light and water temperature, and
686 further work is needed to assess these in lakes and the lower river reaches to better assess
687 eutrophication with consideration of organic nitrogen, phosphorus and carbon.

688 **6. Conclusion**

689 The first dataset to describe the water quality in four catchments in Central Asia in a systematic
690 way for high and low flow conditions is presented. Overall, the water quality is good upstream
691 and downstream of the transition point in land cover from alpine grassland and forest to
692 cropland and steppe when compared with national and World Health Organization standards,
693 and glacier and snow melt provide dilution to the downstream sections of the catchments.
694 Shallow urban groundwater is contaminated by nitrate and phosphate, most probably from
695 urban sewage, and these pollution hot spots are a primary concern given the use of
696 groundwater for drinking in Bishkek and Dushanbe. The data provide a baseline against which
697 to assess future changes in spatial and seasonal concentrations, and the newly established
698 network of environmental research institutes in Kazakhstan, Kyrgyzstan, Uzbekistan and
699 Tajikistan provides a basis for further systematic, water quality measurement across the region.
700 Whilst a melt water dilution effect is discernable in the seasonal data even at the lowest
701 monitoring points close to the river mouths, an exact quantification of the dilution effect is
702 required, probably using stable water isotopes and modelling to determine the melt water
703 contribution along the continuum and the implications of a reduced future melt water input on
704 water quality.

705

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715

716 **Appendix A. Supporting information.**

717

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