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1 **Establishment of background water quality conditions in the Great Zab River catchment: influence**
2 **of geogenic and anthropogenic controls on developing a baseline for water quality assessment and**
3 **resource management**

4

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ABSTRACT

The Great Zab River catchment is a major left-bank tributary of the River Tigris and drains a substantial part of the Kurdistan Region, an autonomous region of Northern Iraq. Within Kurdistan, the water resources of the Great Zab River catchment are under pressure from population increase and are utilized for potable, domestic and agricultural and industrial supply. As with many parts of the world, effective management of water resources within Kurdistan is hindered by a lack of water quality data and established background concentrations. This study therefore represents the first regional survey of river water chemistry for the Great Zab River catchment and presents data on the spatial and temporal trends in concentrations of As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Sr, Zn, NO_3^- , SO_4^{2-} , F^- , Cl^- , and PO_4^{3-} , in addition to pH, electrical conductivity, dissolved oxygen and turbidity. As a tool for underpinning the management and monitoring of water quality, background concentrations were defined for the Great Zab catchment using three methods. The influences of geogenic and anthropogenic controls upon spatial and temporal trends in water chemistry are also evaluated. The influence of geogenic loading from underlying bedrock was identifiable within the observed spatial trends, with the most notable differences found between waters sampled from the relatively more volcanic-rich Zagros Zone to the north and those sampled from the lower catchment underlain by younger clay-, sand- and siltstones. The greatest anthropogenic influence, identifiable through elements such as Cl^- and NO_3^- , is present in the more highly-populated lower catchment. The background concentrations identified in the Great Zab catchment would be those expected as a result of geogenic loading with some anthropogenic influence and represent a more conservative value when compared to those such as the World Health Organization Maximum Admissible Concentration. However, background concentrations represent a powerful tool for identifying potential anthropogenic impacts on water quality and informing management of such occurrences.

KEY WORDS: ambient background; water quality; management; Kurdistan

INTRODUCTION

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As noted by Adams and Chapman (2007), compared to organic substances, metals in surface waters pose significant regulatory challenges given that they may be sourced from natural geogenic loading as well as anthropogenic inputs, and that the latter may be highly spatially variable and diffuse in nature. Furthermore, anthropogenic inputs may stem from historical activities long-since ceased (e.g. Alpers et al., 2005).

A major step in developing a regulatory framework for surface water quality is the derivation of background concentrations (Oste et al., 2012). Determining a background concentration may be used to set a threshold value, which may allow instances of contamination of water to be identified (Panno et al., 2006). Background can be considered to be a concentration of a substance resulting from natural processes, uninfluenced by human activity (Reimann and Garrett, 2005). Given the spatial variability in factors determining geogenic metal loading to surface waters, 'global' background values are therefore of limited use (Oste et al., 2012). As a result, developing regional background concentrations can be seen as preferable. Given the difficulty in finding waters that have no anthropogenic 'signal' (Smith et al., 2003), the term 'ambient background concentrations' has been developed, whereby concentrations represent natural and low level anthropogenic inputs (Peters et al., 2012). Approaches to defining background concentrations in surface waters have been reviewed by detail by Oste et al. (2012).

Ensuring water quality is a key component of ensuring sufficient water supply as part of water resources management. This is particularly relevant to the provision of potable water supplies. Pressures on water quality have been noted in catchments and regions experiencing population and industrial growth (McDonald et al., 2011; McDonald et al., 2014).

The Kurdistan region is experiencing rapid increase in population. This combined with an increased urban population and improvements in living standards have resulted in pressures on water resources through impacts upon water quality (Alobaidy et al., 2010). These pressures are being felt, in conjunction with the threat posed from climate change, across the globe (Vörösmarty et al., 2000). The Great Zab River catchment represents one of the largest catchments in the Kurdistan Region, covering an area of approximately 40,643 km² and surface waters in the catchment provide water supply to a population of 1.8 million. Effective management of water resources through legislative control on water quality is currently being restricted by a lack of national water quality guidelines (Shareef and Muhamad, 2008). Whilst there has been some study of water quality in particular parts of the catchment (e.g. Abdulwahid, 2013; Shareef et al., 2009; Shareef and Muhamad, 2008; Toma, 2011a; Toma, 2011b), there has been no attempt to establish baseline water chemistry and define

94 background concentrations that may act as a means of evaluating water quality, and which may form
95 the basis for the development of appropriate legislative guidelines.

96 The aims of this study are therefore to address this knowledge gap by determining ambient
97 background concentrations for the Great Zab River catchment for 16 metals, 5 anions, pH, electrical
98 conductivity (EC), dissolved oxygen (DO) and turbidity and to evaluate the spatial and seasonal trends
99 in water quality within the catchment.

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STUDY AREA

102 Kurdistan occupies an area of 40,643 km² and a population growth rate is 2.7% per annum (Ministry of
103 Planning, 2011), notably in the cities of Erbil, the capital city, Sulaimaniya and Dohuk, is placing
104 pressure upon water resources. Stevanovic and Lurkiewicz (2009) report that that population growth
105 has led to the decline in the per capita availability and use of water resources. According to the
106 Ministry of Planning/KRG (2011), the quantity of water produced on a daily basis is 924,600 m³, while
107 daily demand totals approximately 1.25 million m³. Therefore, the present water supply deficit is
108 325,400 m³ per day, i.e. 26% of total demand and 35% of total quantity produced at present.

109 The Great Zab River catchment covers an area of approximately 40,300 km², with 13,708 km² within
110 Kurdistan and the remainder in Turkey. The Great Zab River is a left bank tributary of the River Tigris,
111 with confluence downstream of Mosul. The flow regime of the Great Zab River is strongly influenced
112 by annual snowmelt, with the highest monthly mean discharges occurring in the early summer months
113 (Saleh, 2010). Within Kurdistan, the Great Zab catchment sits within three major geological zones
114 (Figure 1). To the northeast, the Zagros Zone comprises predominantly folded limestones with some
115 felsitic volcanics. The Imbricated and High-fold zones comprise Cretaceous-age carbonates in a range
116 of different formations. A detailed description of these has been produced by Sissakian (2013),
117 however, in summary these formations comprise predominantly limestone that has been variably
118 pervaded by dolomite, marl and shale. The lower portion of the catchment lies within the Foothill zone
119 (Figure 1), dominated by late Miocene to Pleistocene-aged sandstones, siltstone and claystone
120 (Sissakian, 2013). The region at the boundary of the High-fold and Foothill zones comprises a number
121 of formations of generally Paleocene and Eocene age that comprise dolomitic limestones and,
122 particularly to the northwest, thick basaltic lavas (Sissakian, 2013).

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METHODS

127 Samples of river water were collected from 62 sites in February 2014 and June 2014 (Figure 1). Sample
128 sites were selected to best balance the demands of ease of access and spatial coverage, with sample
129 sites focusing mainly upon road-river intersections (c.f. Bird et al., 2010). In the field, samples were
130 filtered through 0.45 μm cellulose nitrate filter membranes, acidified with 50% HNO_3 and placed on
131 ice in acid-washed Nalgene bottles. Samples were stored below 5°C prior to analysis. Concentrations
132 of As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Sr, Zn were determined by Inductively Coupled
133 Plasma Mass Spectrometry (Agilent Technologies 7700). Analytical accuracy was assessed through the
134 analysis of the NIST1643 certified reference material and analytical precision through the repeat
135 analysis ($n = 10\%$ of total sample number) of a randomly selected sample. Data for analytical quality
136 control are given in Table 1. Samples were analysed by ion chromatography for their NO_3^- , SO_4^{2-} , F^- ,
137 Cl^- , and PO_4^{3-} content. A Thermo Fisher AS22 anion exchange column was used for the separation of
138 SO_4^{2-} , F^- , Cl^- , and PO_4^{3-} . The mobile phase was 4.5 mM sodium carbonate/1.4 mM sodium bicarbonate
139 and flow rate 1.2 ml/min. Suppression was achieved using a Metrohm Suppressor Module, supplied
140 with a 150 mM sulphuric acid/0.1 M oxalic acid/acetone mix and ultrapure water. Inorganic anions
141 were detected using a suppressed conductivity detector. All solutions were prepared in ultrapure
142 water with a specific resistance of (18.2) $\text{M}\Omega\text{ cm}$ (Millipore, Molsheim, France). Analytical accuracy on
143 anion analyses (Table 1) was assessed through the analysis of standard solutions and analytical
144 precision through the repeat analysis ($n = 10\%$ of total sample number) of a randomly selected sample.

145 In the field, measurements of pH (Hanna Instruments HI991003), electrical conductivity (Hanna
146 Instruments HI8733), dissolved oxygen (PDO520) and turbidity (Hanna Instruments HI93703) were
147 made at the time of sampling.

148

RESULTS AND DISCUSSION

149 Water chemistry

150 A summary of minimum, mean, median and maximum values is provided for cations (Figure 2),
151 anions (Figure 3) and pH, EC, DO, turbidity (Figure 4). Global median and World Health Organization
152 (WHO) Maximum Admissible Concentrations (MACs) also plotted in order to provide context for the
153 data from Kurdistan. WHO MACs are appropriate for potable water, which is consistent with the
154 Great Zab River, and provides an indication of water quality in relation to human health. In addition,
155 percentage cumulative frequency plots of the water chemistry data for cations (Figure 5) and anions,
156 pH, EC, DO, turbidity (Figure 6) show the frequency distribution of the parameters in summer and
157 winter. Arsenic, and Hg were non-detectable in all samples.

158 In comparison to world median values, cation concentrations in the Great Zab catchment vary by
159 metal (Figure 2). All Li and Ca concentrations are greater than the world median value, whilst the
160 third quartile concentration for Ba is greater than the world median concentration. Third quartile
161 concentrations for Cu, Zn and Pb are lower than the respective world median concentrations. For
162 metals for which a WHO MAC has been defined, all concentrations in the Great Zab catchment fall
163 below these.

164 All anion concentrations measured in the Great Zab catchment fall below their respect WHO MACs
165 (Figure 3). All F^- and NO_2^- concentrations measured in the Great Zab catchment fall below world
166 median concentrations, however a majority of sites had SO_4^{2-} concentrations in excess of the world
167 median. The median Cl^- concentration in the Great Zab (6.7 mg l^{-1}) is largely similar to the world
168 median concentration of 8.3 mg l^{-1} .

169 The pH of river water ranges from mildly acidic (5.6) to mildly alkaline (8.9). The turbidity of water
170 ($1.7\text{-}65 \text{ NTU}$) indicate that in general river water in Great Zab River catchment contains relatively low
171 concentrations of suspended organic and inorganic material. Electrical conductivity ranges from 200
172 to $1028 \mu\text{S cm}^{-1}$ with a median value of $375 \mu\text{S cm}^{-1}$.

173 A Pearson Product Moment correlation was performed to evaluate bivariate relationships between
174 water chemistry parameters. The full correlation matrix is included as Supplementary Material and
175 Fe, As and Hg were not include in the analysis due to the high number of non-detectable
176 concentrations. Statistically significant correlations between cations and anions are relatively rare,
177 notable exceptions being between SO_4^{2-} ($r = 0.408$) and NO_3^- ($r = 0.441$) and Ba; both significant at α
178 = 0.01. Statistically significant correlation between cations and between anions are more frequent.
179 With respect to cations, significant correlations exist between metals in the same groups, such as
180 between the transition metals. Particularly strong correlations exist between Ni and Co ($r = 0.801$),
181 Cu ($r = 0.659$) and Zn ($r = 0.816$). For alkaline earth metals, strong correlation relationships exist
182 between Ca and Sr ($r = 0.822$) and Ba ($r = 0.349$). Significant correlations exist between a number of
183 anions (see supplementary data), being strongest between F^- and SO_4^{2-} ($r = 0.637$). There are
184 relatively few significant correlations between elemental concentrations and pH; Ca, Ba, Cl^- and NO_3^-
185 being exceptions. Dissolved oxygen concentrations are correlated with PO_4^{3-} and SO_4^{2-} ($\alpha = 0.01$).

186 In order to establish whether water chemistry differs significantly between summer (lower flow
187 conditions) and winter (generally higher flow conditions), data collected in February 2014 and June
188 2014 were compared using a one way ANOVA on log-transformed data, using a significance
189 threshold of $\alpha = 0.05$. Results (Table 2) indicate that concentrations of Ca, Li, Mo are higher in the

190 winter than summer (statistically significant at $\alpha = 0.05$), whilst concentrations of Zn, SO_4^{2-} , F^- , Cl^- ,
191 and PO_4^{3-} are higher in the summer than winter (statistically significant at $\alpha = 0.05$). Seasonal
192 differences for other analytes were not statistically significant. Higher concentrations of a number of
193 elements during winter (higher discharge conditions) in the Great Zab catchment suggests enhanced
194 delivery from the riparian zone via a combination of surface and sub-surface flows. Calcium, Li and
195 SO_4^{2-} concentrations have been found to be consistently higher than world median concentrations.

196 The relationship between water quality and river discharge is a potentially complex scenario.
197 Previous studies (e.g. Garbarino et al., 1995) have reported generally higher concentrations of
198 metals under low flow conditions due to a lower degree of physical dilution that occurs during
199 periods of low discharge. In addition, higher discharge conditions can result in a reduction in
200 dissolved concentrations due an increase in sorption process due to higher suspended sediment
201 concentrations. However, conversely other studies (e.g. Gundersen and Steinnes, 2001) have
202 demonstrated that periods of higher discharge can yield higher metal concentrations due to
203 enhanced delivery of substances to the river channel from run-off and the potential activation of
204 point sources. What is apparent is that different elements can display different relationships with
205 discharge, as noted in a study of Southeast Asian rivers by Chanpiwat and Sthiannopkao (2014).

206 In an attempt to evaluate the spatial trends in water quality, samples were grouped based upon the
207 major underlying geological units identified in the Great Zab catchment. The groups were identified
208 as: 1) Zagros Zone, 2) the Imbricated/High-folded Zone and 3) the Foothill Zone (Figure 1). The
209 grouping by underlying geology, reflects the importance of geogenic loading in determining surface
210 water chemistry (Drever, 1997). Log-transformed data were analysed using a one way ANOVA, using
211 a significance threshold of $\alpha = 0.05$. The most frequent differences were found between water
212 chemistry in samples collected from the Zagros and Foothill Zones, with 13 parameters showing a
213 statistically significant difference (Table 2). Five and 7 parameters, respectively showed statistically
214 significant differences between the Zagros and Imbricated/High-fold Zones and Imbricated/High-fold
215 and Foothill Zones. The greater statistical similarity of water chemistry sampled in the
216 Imbricated/High-fold and Foothill Zones will reflect the greater similarity in bedrock geology
217 between these areas than compared with the Zagros Zone. The influence of geology on water
218 chemistry is exemplified by Ca and Sr concentrations; these are found to be significantly higher in
219 waters within the Imbricated/High-fold and Foothill Zones than in the Zagros Zones (Table 2).
220 Average Sr concentrations in water with the Imbricated/High-fold ($542 \mu\text{g l}^{-1}$) and Foothill Zones (683
221 $\mu\text{g l}^{-1}$) are at least twice as high as in the Zagros Zone ($243 \mu\text{g l}^{-1}$). Average Ca concentrations are c.
222 10 mg l^{-1} lower in the Zagros Zone compared to the Imbricated/High-fold and Foothill Zones. This

223 reflects the abundant carbonate bedrocks, notably limestone and dolomitic limestone, which are the
224 main sources of Sr to stream water in particular, whilst the bedrock of Zagros Zone is relatively
225 carbonate poor.

226 Chloride and NO_3^- show a statistically significant difference between the Foothill Zone (the lower
227 Great Zab catchment) and the two upstream zones (Table 2). Concentrations of Cl^- and NO_3^- are
228 significantly higher in the lower catchment (Figure 7), as indicated by mean concentrations of 14.2
229 and 6.8 mg l^{-1} , respectively, which are twice as high as those for the Zagros and Imbricated/High-fold
230 Zones upstream. Chloride and NO_3^- are two elements for which higher concentrations in river water,
231 and particularly within-catchment variability, can be the result of anthropogenic inputs, such as from
232 agricultural activity in the case NO_3^- (Randall and Mulla, 2001). Importantly, the amount of
233 anthropogenic activity is greatest in the lower Great Zab catchment, the part of the catchment
234 containing the highest Cl^- and NO_3^- levels. Whilst concentrations are below respective WHO MACs,
235 the data exemplify and indicate that whilst geogenic inputs are important in explaining large scale
236 variability in water chemistry, the spatially variable influence of anthropogenic activity is an
237 important contributor to the water chemistry of the Great Zab catchment.

238 **Quantifying background conditions**

239 Establishing background geochemical conditions, provides a potentially valuable regulatory tool for
240 evaluating water quality. However, given the difficulty in locating 'pristine' water bodies that have
241 no anthropogenic influence, as reviewed by Peters et al. (2012), a range of approaches have been
242 utilized to quantify background conditions in river catchments. Peters et al. (2012) used a low
243 percentile of water quality data to provide a relatively conservative estimate of background, or what
244 can be termed 'ambient background'. In contrast, other approaches have utilized higher percentile,
245 such as the 90th percentile value (Fraters et al., 2001).

246 To evaluate the potential influence of the approach used, three different approaches were taken.
247 Firstly, background conditions were calculated as the 10th percentile value (Peters et al., 2012) of the
248 whole dataset from the Great Zab River catchment (Table 3). Secondly, based upon the analysis of
249 Q-Q plots of NO_3^- concentrations, utilized as an anthropogenic marker, and other water quality
250 parameters (Figure 8), the 95th percentile was identified as a point where the distributions differ
251 (Helsel and Hirsch, 2002). Therefore this is indicative of a different sample population above the 95th
252 percentile and can be interpreted as a separation of geogenic and anthropogenic components (Table
253 3). Finally, following the method of Davies (1983) background concentrations were estimated using

254 regression analysis of % cumulative frequency curves of log₁₀ concentrations from the sample
255 population (Table 3).

256 Generally, of the three approaches, the 10th percentile concentrations are always the lowest (Table
257 3), with the exception of Ca and Sr, for which the regression-derived concentrations are lowest. The
258 10th percentile concentrations have been described by Peters et al. (2012) as reflecting ambient
259 background conditions that, in relation to the Great Zab catchment, would be expected resulting
260 from natural, geogenic inputs and low level anthropogenic activity. However, utilizing NO₃⁻
261 concentrations as an anthropogenic marker, suggest that the proportion of the sample population
262 that could be considered as geogenic is much larger, equating to the 95th percentile value, and that
263 background concentrations could potentially be established at higher concentrations.

264 Given that background concentrations may be used as an indicator of water quality, the background
265 concentrations can be compared to WHO MACs (Table 3). All background concentrations in the
266 Great Zab, determined by the three methods used, are lower than WHO MACs. In some case,
267 background concentrations are orders of magnitude lower, for example in the case of Cu and Zn
268 (Table 3). The comparison to WHO MACs suggests that the background concentrations defined by
269 this study can be viewed as very conservative if used as a guide for water quality based upon risks
270 posed to human health. It is not suggested that the background concentrations derived here are
271 adopted as a measure to protect human health, however, the concentrations quantified may act as
272 valuable guide for identifying instances for anthropogenic pollution within the Great Zab catchment.

273 Variations in water chemistry within the catchment would mean that the instances of enrichment
274 above background concentrations varies between waters from the Zagros, Imbricated/High Fold and
275 Foothill Zones. By way of example, comparison of Li, Ba, F⁻ and NO₃⁻ concentrations, which have
276 been shown to differ significantly between the three zones (Table 2), suggests that instances of
277 elevation above background concentrations vary between zone and element (Figure 9). Highest
278 NO₃⁻ concentrations occur in the Foothill Zone, in waters from the Great Zab River itself, but also its
279 tributaries, the Khazir River and the Gomal. NO₃⁻ concentrations in 7% of samples from Foothill zone
280 exceed the 95th percentile-defined background value, but samples from the Zagros and
281 Imbricated/High Fold Zones do not. Conversely, Li and F⁻ concentrations in the Zagros Zone, in 9%
282 and 7% of samples respectively, exceed the 95th percentile-defined background value, with all
283 samples in the two downstream zones falling below. These data further highlight that spatial trends
284 in water chemistry, including the occurrence of relative elevation in concentrations, are likely to
285 reflect both geogenic influences operating at larger spatial scales and site-specific conditions,

286 particularly point sources associated with anthropogenic activity, that vary between different water
287 quality parameters.

288 **CONCLUSIONS**

289 This study has conducted and presented data for the first regional survey of river water chemistry
290 for the Great Zab River catchment, a major left-bank tributary of the River Tigris. Data analysis has
291 shown that concentrations in river water of Ca, Li, Mo, Zn, F⁻, Cl⁻, SO₄²⁻ and PO₄³⁻ are significantly
292 different during summer and winter sampling periods, however, there are variations in terms of
293 when concentrations are highest for different elements. The Great Zab catchment can be divided
294 into three major geological units, and the influence of bedrock geology upon surface water
295 chemistry is evidenced by differences in elemental concentrations in waters sampled from the
296 different units. In addition, whilst elemental concentrations in the Great Zab are below WHO MACs,
297 a potential anthropogenic influence on water chemistry is identifiable through the location of
298 highest elemental concentrations. The lower catchment, which is most highly populated contains
299 highest elemental concentrations and represent areas of concern for water resources management.

300 Background concentrations for the Great Zab catchment have been quantified using the 10th and
301 95th percentile concentrations and a regression analysis. These concentrations could be used as the
302 basis for establishing water quality norms for the catchment and potentially the broader Kurdistan
303 region. Comparison to WHO MACs, which provide human-health oriented guidelines for water
304 quality, indicates that the use of a background concentration as a guide for water quality
305 management, would produce much more conservative and stricter quality limits. This suggests that
306 there is a potentially significant difference between background concentrations, which may be used
307 to identify instances of contamination within a catchment and guidelines that establish potential
308 threats to human health. The use of a guideline such as a WHO MAC as a measure of water quality
309 in water quality assessments may actually mask instances of poor water quality that are identified
310 via the establishment of a catchment-wide background concentrations.

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312

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315 Research.

316

317 **FIGURE CAPTIONS**

318 Figure 1. Location map showing the Great Zab catchment within Kurdistan, major study rivers,
319 sample sites and major geological units.

320 Figure 2. Minimum, median and maximum concentrations for cations in river water plotted with
321 global median and World Health Organization (WHO) Maximum Admissible Concentrations (MACs),
322 where determined.

323 Figure 3. Minimum, median and maximum concentrations for anions in river water plotted with
324 global median and World Health Organization (WHO) Maximum Admissible Concentrations (MACs),
325 where determined.

326 Figure 4. Minimum, median and maximum values for pH, EC, DO and turbidity in river water plotted
327 with global median and average values and World Health Organization (WHO) Maximum Admissible
328 Concentrations (MACs), where determined.

329 Figure 5. Cumulative frequency plots of cation concentrations in the Great Zab catchment during
330 winter and summer seasons.

331 Figure 6. Cumulative frequency plots of anion concentrations and pH, EC, DO and turbidity in the
332 Great Zab catchment during winter and summer seasons.

333 Figure 7. NO_3^- and Cl^- concentrations in the Great Zab catchment plotted as proportional circles.

334 Figure 8. Q-Q plots of NO_3^- (as an anthropogenic tracer) and Li, Zn and Sr concentrations in the Great
335 Zab catchment.

336 Figure 9. Minimum, median and maximum concentrations of Li, F^- , Ba and NO_3^- determined in the
337 river water from three geological zones within the Great Zab catchment. Background concentrations
338 determined by three different methods are also plotted.

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434 Table 1. Analytical quality control data for laboratory analyses.

	Certified	Measured	% Accuracy	% Precision
As	60.5±0.7	40.5	33	6.6
Ba	544.2±5.8	504	7.3	1.9
Ca	32300±110	34100	5.6	3.6
Cd	6.6±0.07	5.7	13.8	n.d.
Co	27.1±0.32	20.4	24.5	1
Cr	20.4±0.24	15.9	21.7	1.8
Cu	22.8±0.31	39.6	74	1.8
Fe	98.1±1.4	97.6	0.5	4.9
Hg	-	-	-	n.d.
Li	17.4±1.7	9.3	46.3	0.9
Mn	38.9±0.45	34.9	10.4	3.6
Mo	121.4±1.3	120.9	0.4	0.7
Ni	62.4±0.69	62.4	0	0.7
Pb	19.6±0.21	18.7	4.8	n.d.
Sr	323.1±3.6	298.6	7.6	0.2
Zn	78.5±2.2	32.3	58.8	2.2
NO ₃ ⁻	-	-	4.4	2.5
SO ₄ ²⁻	-	-	7.9	2.1
F ⁻	-	-	3.5	5.8
Cl ⁻	-	-	11.5	3.4
PO ₄ ³⁻	-	-	0.5	1.9

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445 Table 2. Results of a one-way ANOVA for temporal trends. Bold indicates significant at $\alpha = 0.05$. *
 446 denotes mean summer concentration is higher than mean winter concentration. ** denotes mean
 447 winter concentration is higher than mean summer concentration.

Parameter	P value (Seasonal)	P value (Spatial)		
		Z ¹ vs I/HF ²	Z v FZ ³	I/HF v FZ
As	N/A	N/A	N/A	N/A
Ba	0.486	0.888	0.000	0.000
Ca	0.000**	0.009	0.001	0.625
Cd	0.224	0.210	0.944	0.275
Co	0.986	0.711	0.299	0.025
Cr	0.719	0.063	0.653	0.270
Cu	0.487	0.210	0.772	0.500
Fe	0.224	0.233	0.455	0.726
Hg	N/A	N/A	N/A	N/A
Li	0.029**	0.000	0.000	0.855
Mn	0.223	0.980	0.455	0.726
Mo	0.036**	0.000	0.000	0.596
Ni	0.256	0.169	0.946	0.212
Pb	N/A	0.424	0.708	0.792
Sr	0.642	0.019	0.001	0.441
Zn	0.031*	0.311	0.801	0.629
NO ₃ ⁻	0.180	0.746	0.000	0.000
SO ₄ ²⁻	0.000*	0.651	0.000	0.000
F ⁻	0.000*	0.024	0.005	0.734
Cl ⁻	0.017*	0.771	0.008	0.000
PO ₄ ³⁻	0.000*	0.886	0.735	0.936
Turbidity	0.769	0.650	0.963	0.764
DO	0.000*	0.801	0.996	0.686
EC	0.563	0.119	0.021	0.626
pH	0.000**	0.413	0.014	0.000

448 ¹Zagros Zone

449 ²Imbricated/High-folded Zone

450 ³Foothill Zone

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456 Table 3. Background conditions defined for the Great Zab catchment. WHO MAC and world median
 457 concentrations also given for comparison. Concentrations in $\mu\text{g l}^{-1}$ unless stated.

	10 th percentile	95 th percentile	Regression analysis	WHO MAC	World median
Li	0.7	11.5	2.3	-	0.2 ¹
Ca	26.1 mg l ⁻¹	67 mg l ⁻¹	22 mg l ⁻¹	-	¹ 12 mg l ⁻¹
Cr	0.2	1.7	0.3	50	0.7 ¹
Mn	1.4	14.6	3.6	400	4 ¹
Fe	0.8	26.9	2.1	300	40 ¹
Co	0.1	0.5	0.1	-	0.3 ¹
Ni	0.9	7.2	1.7	70	0.3 ¹
Cu	0.2	14.8	0.5	2000	3 ¹
Zn	1.2	17.7	8.1	3000	15 ¹
As	n/d	n/d	n/d	10	4 ¹
Sr	161	1650	154	-	500 ¹
Mo	0.2	3.3	0.4	70	0.5 ¹
Cd	<0.01	0.01	<0.01	3	0.02 ¹
Ba	21	108	21	700	20 ¹
Hg	n/d	n/d	n/d	6	0.05 ¹
Pb	0.1	1.8	0.2	10	3 ¹
Cl ⁻	2.2 mg l ⁻¹	31.5 mg l ⁻¹	3.2 mg l ⁻¹	² 250 mg l ⁻¹	³ 7.8 mg l ⁻¹
SO ₄ ²⁻	13.6 mg l ⁻¹	105 mg l ⁻¹	15.9 mg l ⁻¹	² 250 mg l ⁻¹	⁴ 8.3 mg l ⁻¹
F ⁻	0.04 mg l ⁻¹	0.4 mg l ⁻¹	0.1 mg l ⁻¹	1.5 mg l ⁻¹	³ 0.1 mg l ⁻¹
NO ₃ ⁻	1.2 mg l ⁻¹	11.2 mg l ⁻¹	6.9 mg l ⁻¹	50 mg l ⁻¹	³ 1 mg l ⁻¹
PO ₄ ³⁻	<0.01 mg l ⁻¹	0.3 mg l ⁻¹	mg l ⁻¹	-	³ 0.03 mg l ⁻¹

458 ¹Reimann and de Caritat (1998)

459 ²Based upon acceptable taste. A health-based limit has not been established.

460 ³Ivanov (1996)

461 ⁴Berner and Berner (1996)

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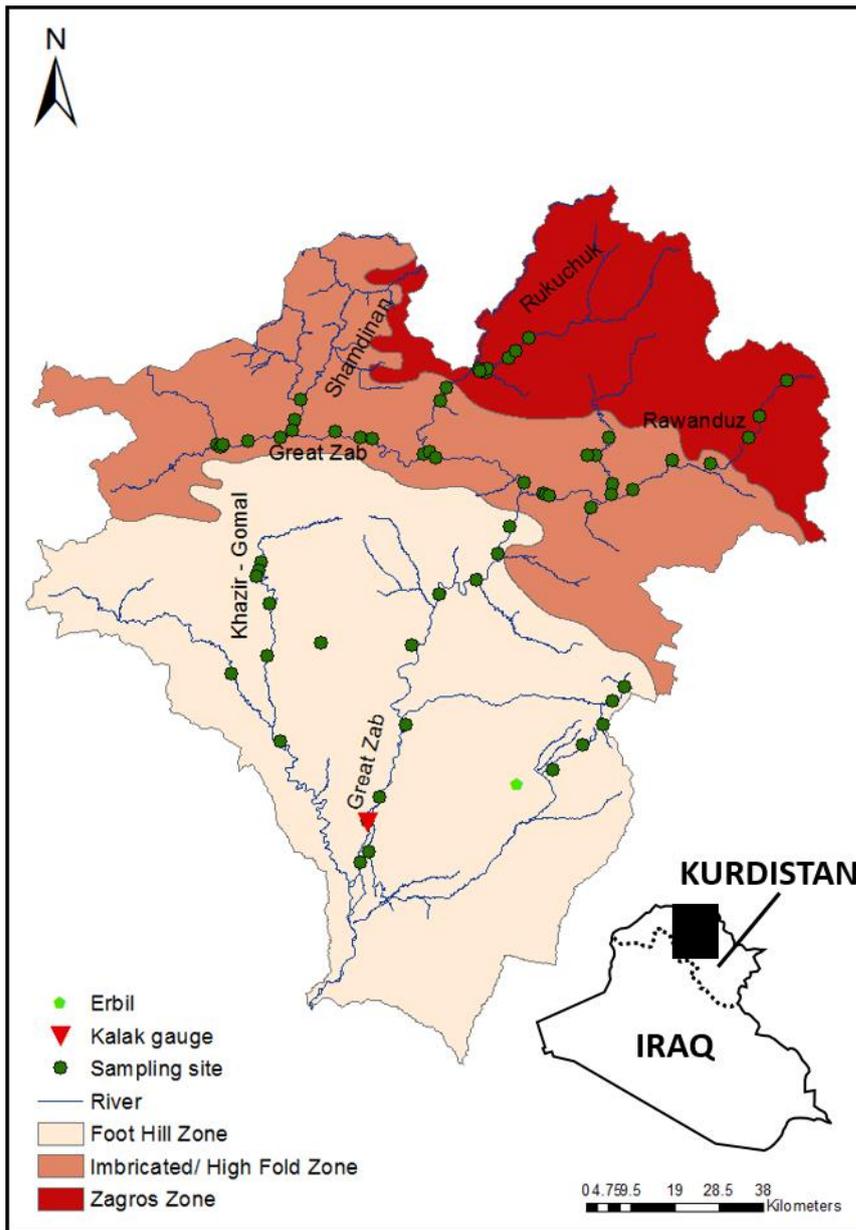
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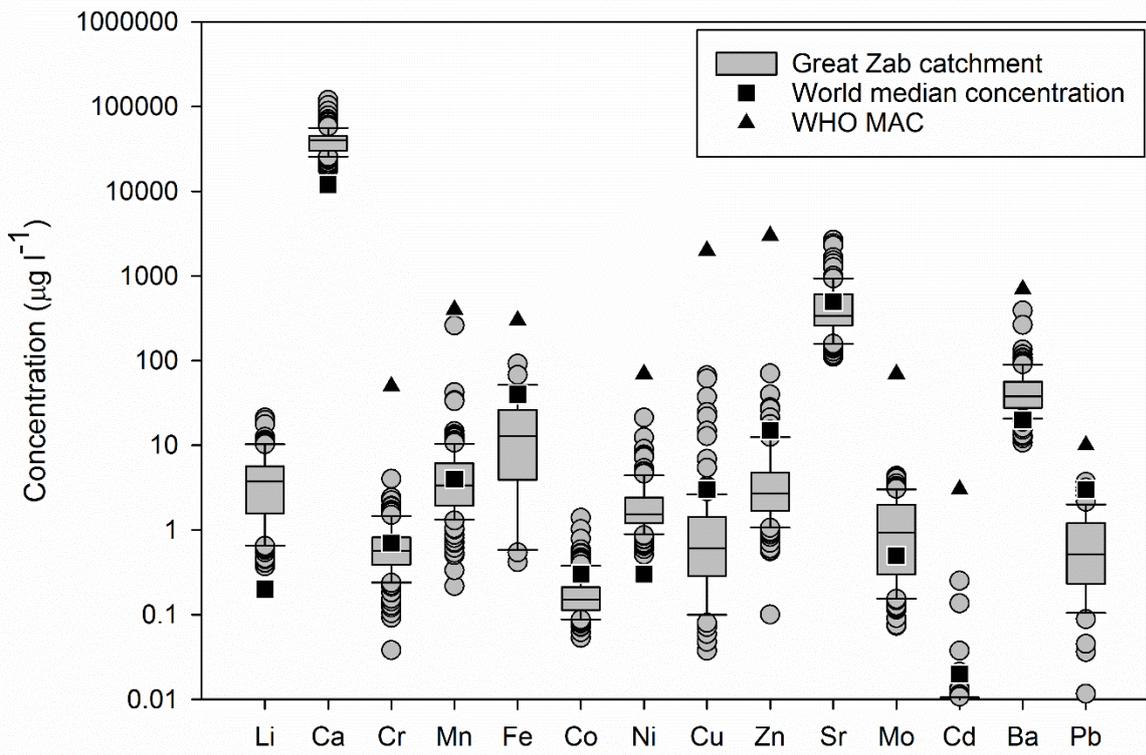
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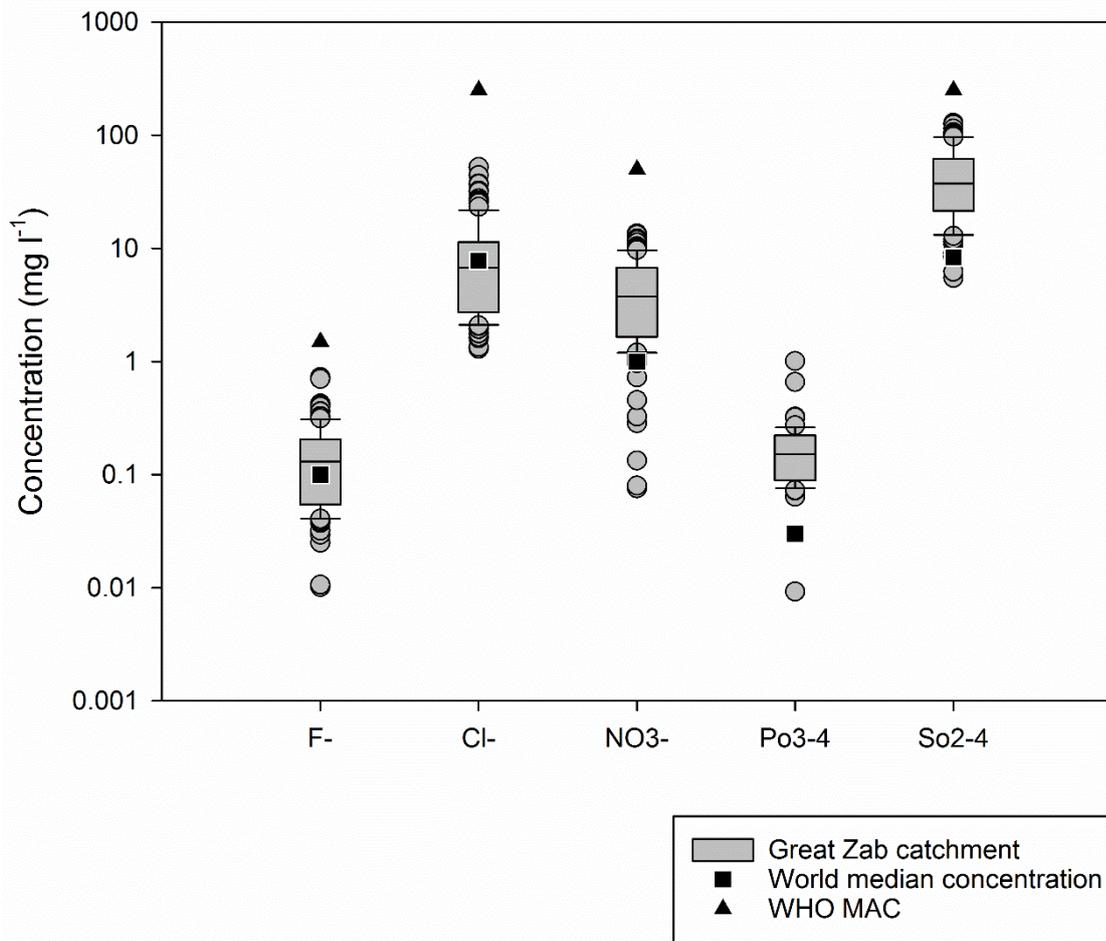
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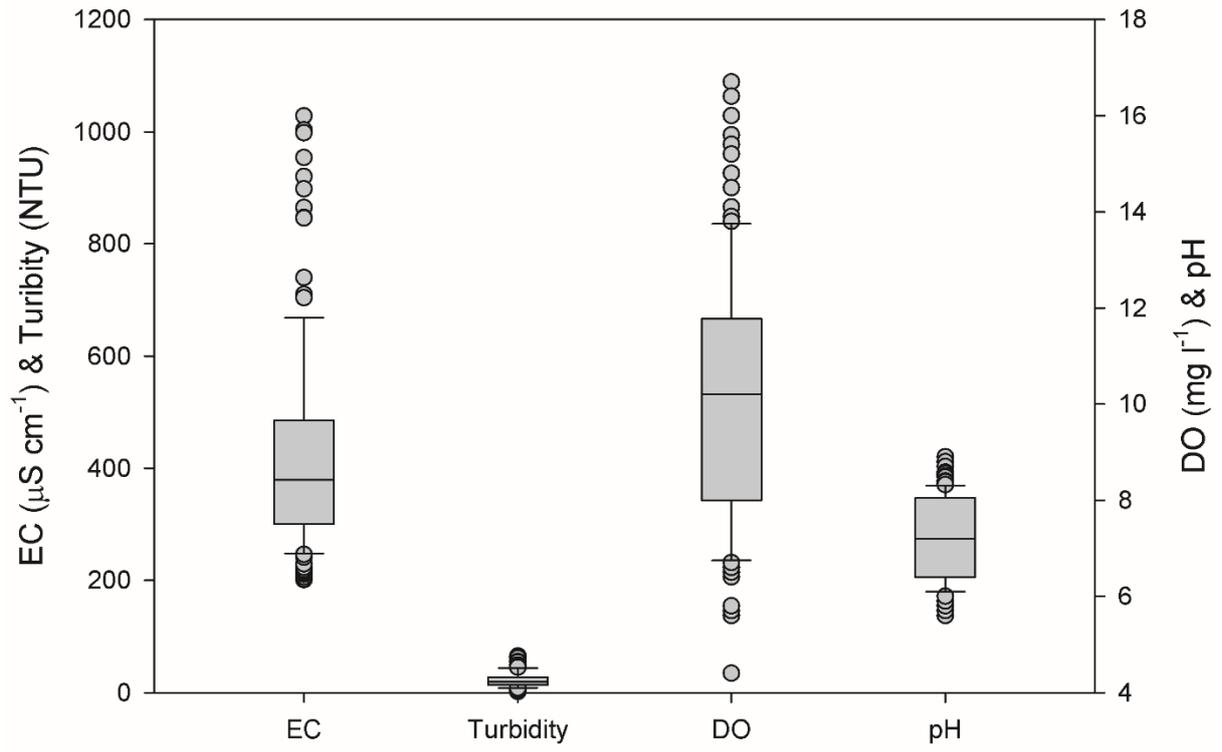
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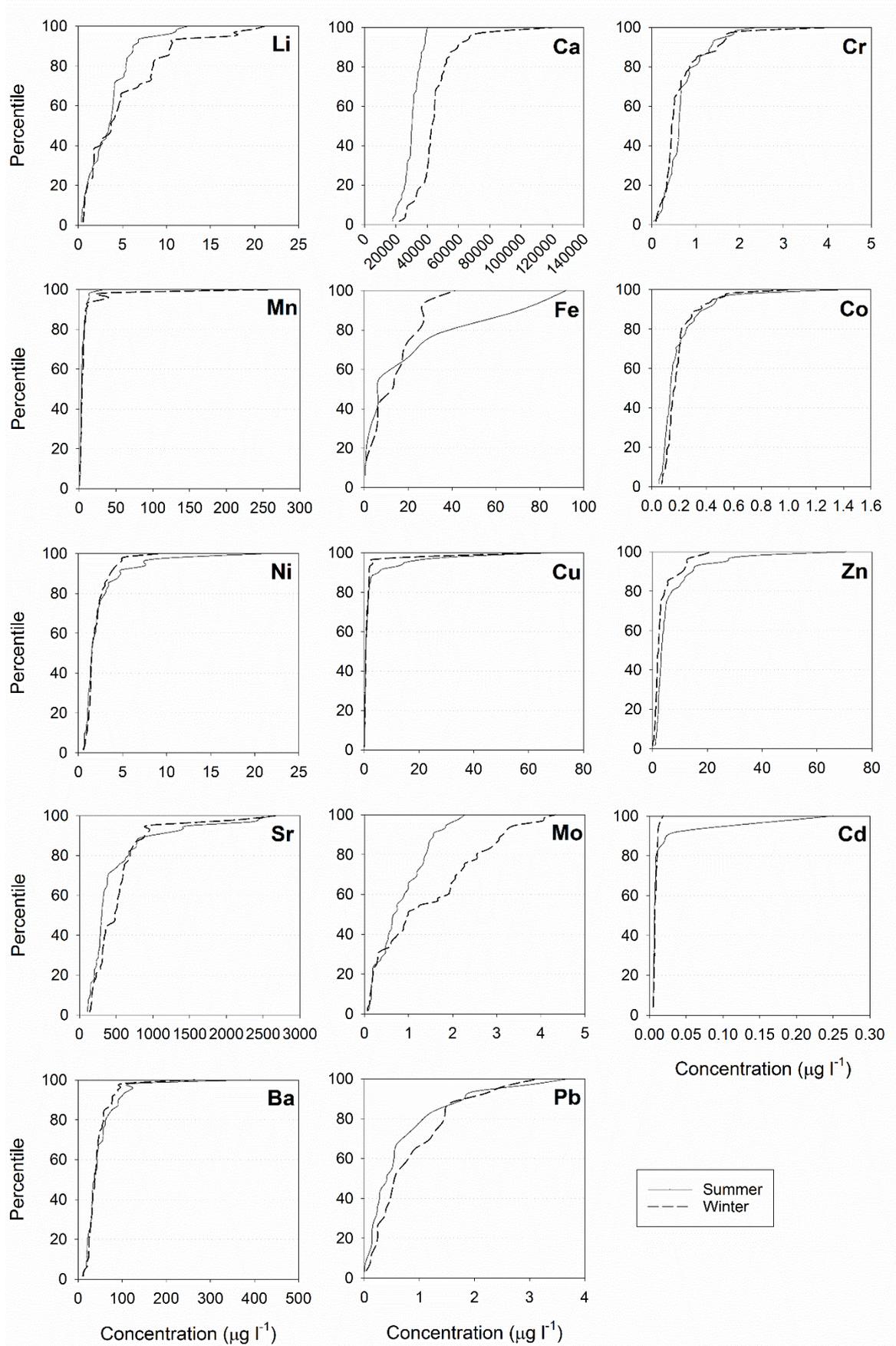
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 490 Figure 3
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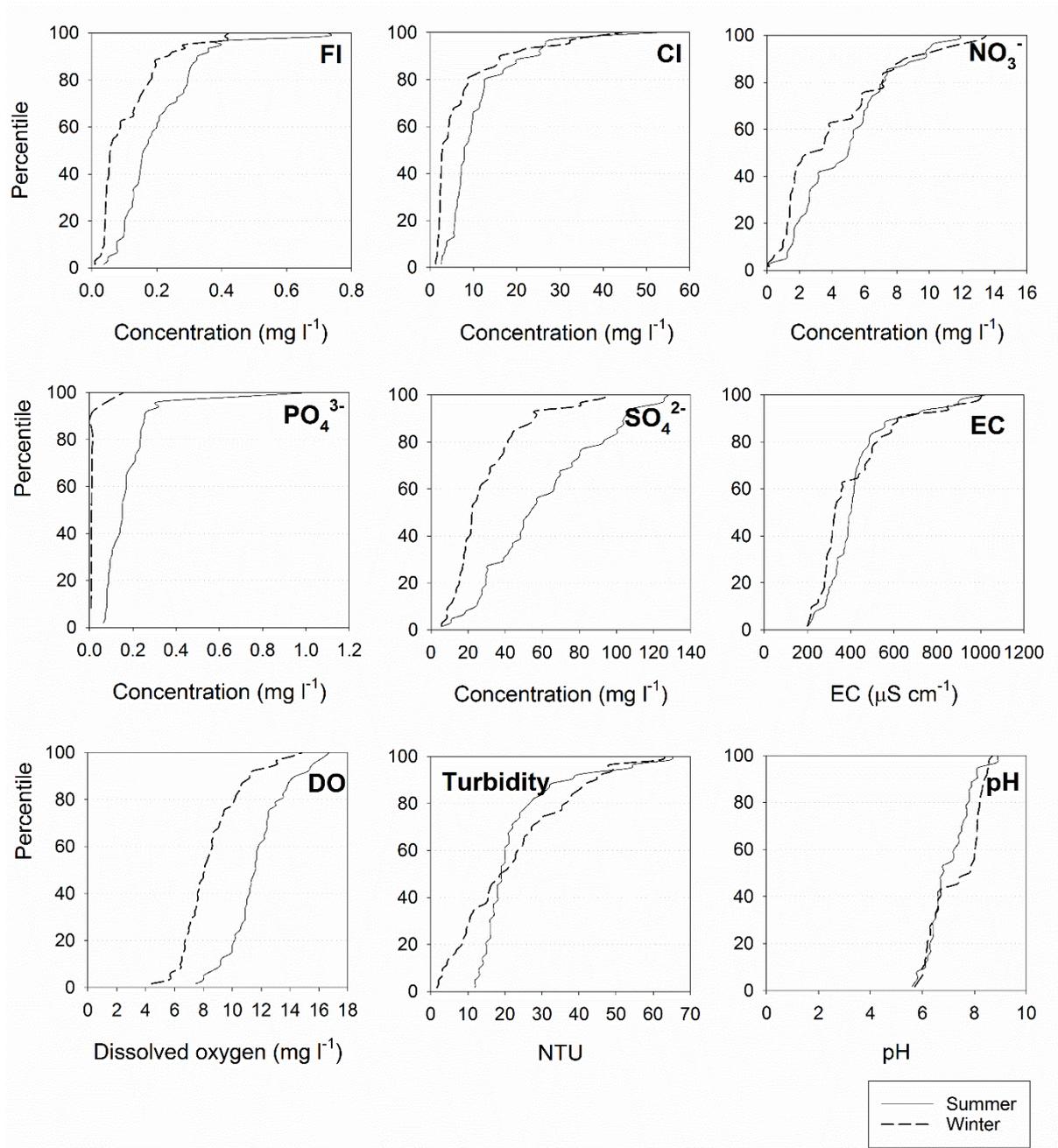


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 493 Figure 4
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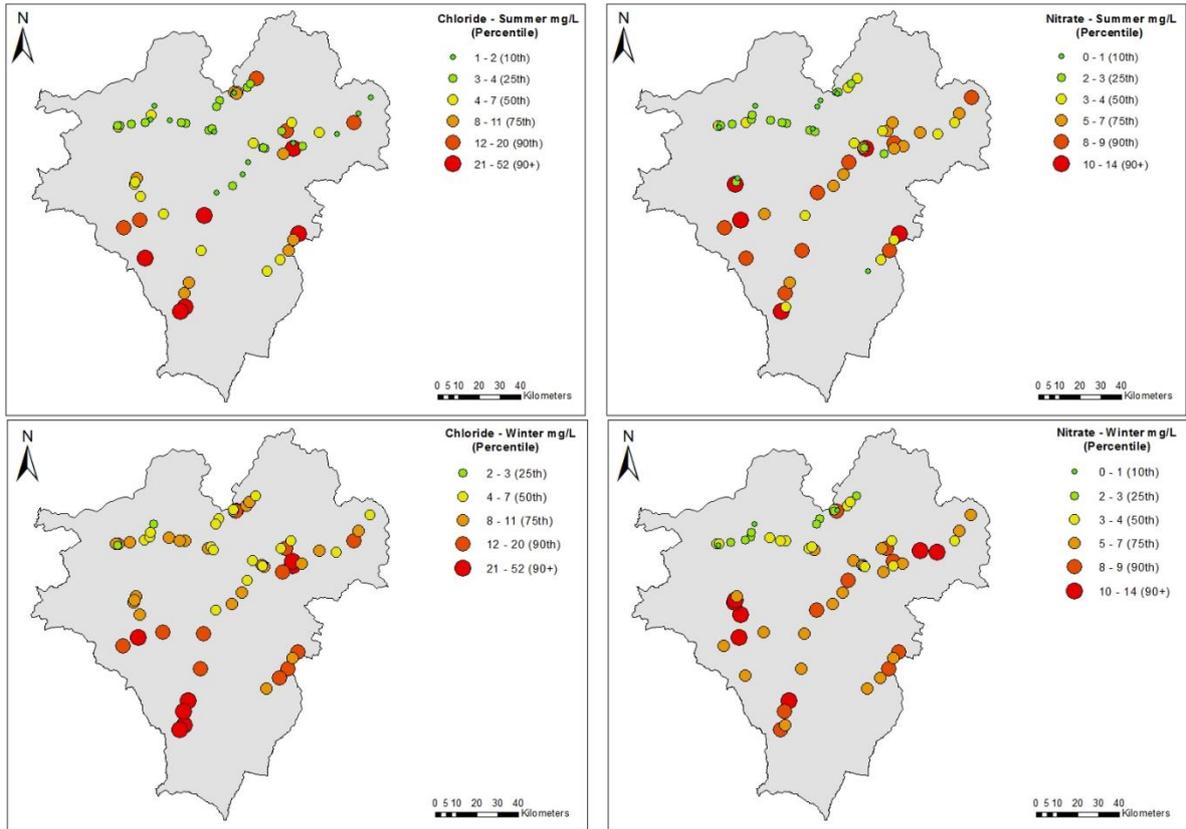
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Figure 5

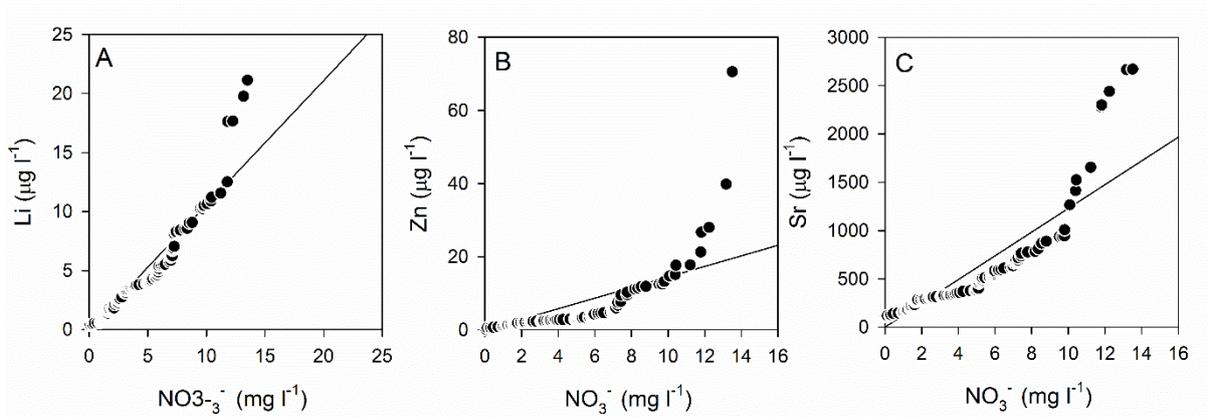


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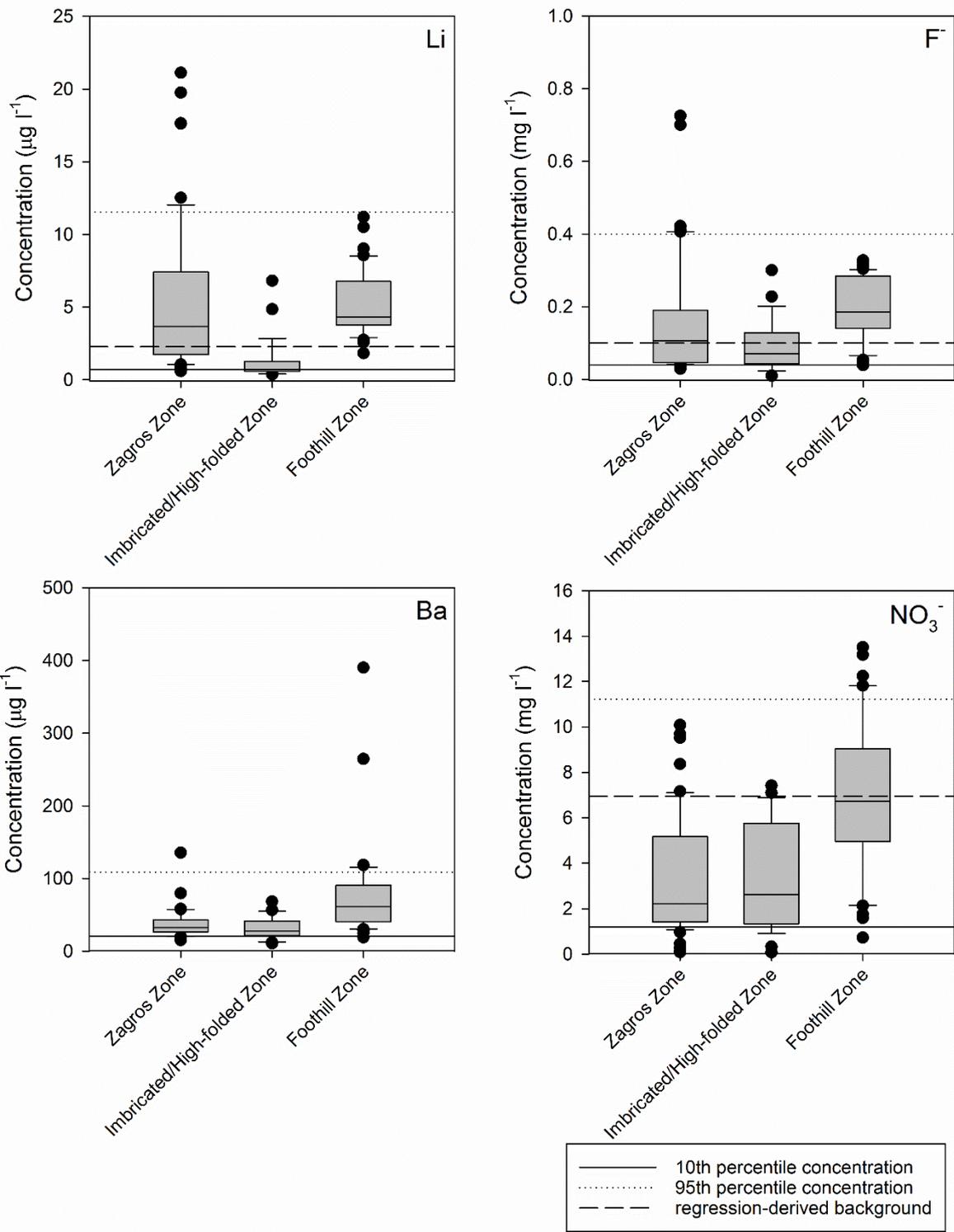
Figure 6



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