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Tracing total and dissolved material in a western Canadian basin using quality control samples to guide the selection of fingerprinting parameters for modelling

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1 **Tracing total and dissolved material in a western Canadian basin using quality control samples to**
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13

14 **Abstract**

15 The source dynamics of total and dissolved material in riverine systems are being affected by
 16 anthropogenic activities resulting in the degradation of waterways worldwide. Identifying the main
 17 sources of total and dissolved material is thus central to the management of increasingly scarce water
 18 resources. Here, we utilize data generated from water quality monitoring programs to investigate the
 19 sources of total and dissolved material in a large, semi-arid basin in western Canada. Our research focuses
 20 on the confluence of two major tributaries in the South Saskatchewan River Basin (SSRB) in the Province
 21 of Alberta: the Bow River (25,611 km²) and the Oldman River (28,270 km²). A tributary tracing technique
 22 coupled with a Deconvolutional-MixSIAR (D-MIXSIAR) modelling approach is used to estimate the
 23 potential source contributions of total and dissolved material from major tributary sites to target node
 24 sites on the main stem of the Bow River and Oldman River in addition to target nodes downstream of
 25 their confluence. In total, 812 samples were taken from 29 sites across the SSRB. A novel approach to
 26 selecting fingerprints for modelling is presented based on the analyses of additional quality control
 27 samples (146 duplicate and 172 blank samples). Overall, the Rocky Mountain headwater catchments were
 28 found to dominate the supply of material modelled using total recoverable (68%) and dissolved (76%)
 29 metals. There were seasonal fluctuations in source dynamics evident where the Bow River dominated the
 30 supply of total (69%) and dissolved (57%) material during the ice-covered season (November-March), and
 31 the Oldman River dominated the supply of total (73%) and dissolved (59%) material during the open water
 32 season (April-October). On the one hand, these seasonal dynamics are potentially the result of the
 33 extensive regulation of flow, particularly along the Bow River. On the other hand, the intensification of
 34 agriculture in the prairie/plain catchments may also facilitate the excess supply of total relative to
 35 dissolved material. For example, the Little Bow River, with ~70% agricultural land cover, contributed ~14
 36 times more total material than anticipated based on discharge and 1.6 times more than anticipated based
 37 on unit area during the open water season. Overall, this research has improved our understanding of the
 38 source dynamics of total and dissolved material in the SSRB, providing the foundation for focussed studies
 39 targeting the main sources of total and dissolved material in this large, semi-arid basin in western Canada.
 40 In addition, our research highlights the potential of using existent data generated from water quality
 41 monitoring programs along with quality control best practices to help improve our understanding of the
 42 source dynamics of total and dissolved material in waterways around the world.

43 **Keywords:** Alberta; waterways; sediment; water resources; conservation; geochemistry

44

45 **Highlights:** *3 to 5 bullet points, maximum 85 characters, including spaces, per bullet point*

- 46 • The source dynamics of total and dissolved material were investigated
- 47 • Water quality monitoring data was modelled with Deconvolutional-MixSIAR
- 48 • A novel approach to select tracers based on quality control samples was presented
- 49 • Future research should examine source dynamics in reservoirs and lakes

50 **1. Introduction**

51 Anthropogenic activities (e.g. grazing, clearing, agriculture, and logging) have affected more than half
52 of the Earth's terrestrial surface (Hooke et al., 2012; Richter and Mobley, 2009) impacting fundamental
53 critical zone processes and resulting in major changes in the cycling of particulate and solute material in
54 riverine systems (Meybeck, 2003). Elevated total and dissolved material may be indicative of the
55 downstream transfer of contaminants transported either in the dissolved phase or bound to particulate
56 matter (Bainbridge et al., 2012; Elbaz-Poulichet et al., 2006; Gateuille et al., 2014). Accordingly, it is
57 important to identify and understand the source dynamics of both total and dissolved material in riverine
58 systems in order to develop and implement best management practices that mitigate the degradation of
59 freshwater systems (Collins et al., 2011; Gellis and Walling, 2011; Grasby et al., 1997).

60 Sediment source fingerprinting is a field-based technique that estimates the main sources of sediment
61 in riverine, lacustrine and coastal systems (Douglas et al., 2003; Hatfield and Maher, 2008; Jalowska et al.,
62 2017). This technique capitalizes on differences in physical and biogeochemical parameters between
63 potential sources to trace sediment provenance (Klages and Hsieh, 1975; Lewin and Wolfenden, 1978;
64 Oldfield et al., 1979). A wide variety of fingerprinting parameters have been used to investigate sediment
65 sources (e.g. fallout radionuclides, mineral magnetic properties, major and trace element geochemistry)
66 through being incorporated into end-member mixing models that are solved stochastically in frequentist
67 (Collins et al., 2012; Tiecher et al., 2019; Walling et al., 1993) or Bayesian frameworks (Cooper and
68 Krueger, 2017; Davies et al., 2018; Small et al., 2002) to apportion source contributions to target material.

69 Developed for stable isotope research in ecology, Bayesian mixing models such as Stable Isotope
70 Analyses in R (SIAR) (Parnell et al., 2008) and MixSIAR (Semmens et al., 2013) are increasingly being used
71 to model sediment sources (Boudreault et al., 2019; Garzon-Garcia et al., 2017; Koiter et al., 2013). One
72 advantage of using these stable isotope mixing models is that they are inherently designed to include the
73 concentration dependency of isotope ratios during end-member modelling (Mabit et al., 2018; Reiffarth
74 et al., 2019; Upadhayay et al., 2018a). A second advantage is the relative straightforwardness of running
75 complex Bayesian end-member mixing models in a R coding environment or with the provided graphical
76 user interface (Stock and Semmens, 2013).

77 Accordingly, there has been a significant uptake of stable isotope mixing models in sediment
78 fingerprinting research (e.g. Astorga et al., 2018; Bahadori et al., 2019; Barthod et al., 2015; Brandt et al.,
79 2016; Bravo-Linares et al., 2018; Dutton et al., 2013; Glendell et al., 2018; Jantzi et al., 2019; Liu et al.,

2017; McCarney-Castle et al., 2017). One key innovation has been the development of functions in the R programming language that allow for the ‘de-convoluted un-mixing’ of sediment sources (Blake et al., 2018). Notably, the Deconvolutional-MixSIAR (D-MIXSIAR) model facilitates the downstream propagation of source contributions to sediment for multiple target sampling locations (Blake et al., 2018), which holds significant potential to generate comprehensive information on sediment source dynamics. As the development of D-MIXSIAR in the literature has predominantly focussed on small catchments (Blake et al., 2018; Upadhayay et al., 2018b), there remains a gap in our knowledge regarding the utility of D-MIXSIAR in larger catchments.

Here, we apply the D-MIXSIAR model in a large watershed in Alberta, western Canada. In particular, our research focuses on the confluence of two major tributaries in the South Saskatchewan River Basin (SSRB), the Bow River (25,611 km²) and the Oldman River (28,270 km²) (Figure 1). Snowmelt and precipitation runoff in the Rocky Mountain headwaters are hypothesized to drive the downstream transfer of total and dissolved material in this region. To test this hypothesis, a D-MIXSIAR modelling approach, using dissolved and total recoverable metals analyzed on surface water grab samples (n = 812) taken monthly for approximately three years (2016-2018), was run for target sampling sites on the main stem (i.e. nodes) upstream and downstream of the confluence of the Bow and Oldman Rivers. A tributary tracing technique is employed where surface water grab samples from 22 different tributaries are used as source samples that are de-convoluted with the D-MIXSIAR model through seven main stem node sites (i.e. target samples) to provide a comprehensive understanding of the source dynamics of total and dissolved material in the SSRB.

Our research design includes the sampling and analyses of 318 quality control samples. In particular, field blank samples (n = 172) estimate the potential bias (i.e. contamination) in the dataset whereas duplicate samples (n = 146) assess the variability (i.e. precision) of the potential fingerprinting parameters. Results from a comprehensive statistical analysis of the duplicate and field blank samples, based on best practices developed by the United States Geological Survey (i.e. Bender et al., 2011; Mueller et al., 2015) are used to develop a novel approach to select fingerprinting parameters to be included in end-member mixing models based on quality control samples.

The overall objective of this research is to investigate the source dynamics of total and dissolved material from tributaries in the SSRB in order to help understand and manage these waterways in the context of land use intensification and a changing climate. In particular, the modelling results may highlight tributaries that disproportionately contribute total and dissolved material, which require

111 targeted management. Our research also highlights a particularly powerful approach to utilize data
112 generated from water quality monitoring programs, coupled with an appropriate quality control
113 framework, to investigate total and dissolved material dynamics worldwide. To best of our knowledge,
114 this is one of the first attempts to use regional water quality monitoring data, including quality control
115 best practices, to simultaneously trace both the total and dissolved fractions with the sediment source
116 fingerprinting technique.

117 **2. Material and Methods**

118 **2.1 Study Site**

119 In south eastern Alberta, Canada, the Bow (25,611 km²) and Oldman Rivers (28,270 km²) merge to
120 form the South Saskatchewan River, which flows eastward towards Lake Winnipeg and discharges
121 eventually into Hudson's Bay as part of the Nelson River basin (Figure 1). The headwaters of the Bow and
122 Oldman Rivers are situated on the eastern side of the Continental Divide in the Rocky Mountains. These
123 watersheds transition from alpine and foothill landscapes in their montane headwaters (maximum
124 elevation: ~3500 m) to prairie and grassland plains as they cross the province of Alberta (minimum
125 elevation: ~600 m). The geology of the Bow and Oldman watersheds, in their montane headwaters, is
126 mainly calcareous limestone, dolomite and shale predominantly of Paleozoic age. The geology transitions
127 downstream to calcareous feldspathic sandstone, siltstone, mudstone and coal beds predominantly of
128 Cretaceous and Tertiary age in the foothills and prairie landscapes (Hamilton et al., 1999). During the last
129 glaciation, between ~18,000 to 13,000 years before present, the Laurentide Ice Sheet retreat left behind
130 varying thicknesses of glacio-fluvial, glacio-lacustrine, Aeolian and till deposits across the Albertan prairies
131 (Dyke and Prest, 1987). These deposits continue to exert a strong control on the source dynamics of total
132 and dissolved material throughout Alberta.

133 Land use and land cover in the study watershed, as delineated from the outlet sampling site (SSR2 -
134 Figure 1), are dominated by agriculture (ca. 40% of the total area) followed by 21% grassland, 16% forest,
135 5% exposed rock, 5% water, reservoirs and wetlands, 4% shrub, 3% linear transport, 3% disturbed
136 (including urban land covers), 1% forestry and 1% mining including oil and gas operations. Overall, land
137 use and land cover are highly variable in the tributary source watersheds, progressing from catchments
138 dominated by relatively natural land cover in the Rocky Mountain headwaters to agriculturally dominated
139 watersheds in the lower reaches of the study basin. The main agricultural crops or activities in the outlet
140 sampling site (SSR2) watershed, according to the Agriculture and Agri-food Canada, Annual Crop Inventory

141 (AAFC, 2018) were spring wheat (36%), canola / rapeseed (22%), barley (16%), peas (8%) and pasture /
142 forage (6%).

143 The SSRB has a predominantly semi-arid climate with a mean annual precipitation of 435 mm (Kerr,
144 2017) and a precipitation gradient across the catchment from the Rocky Mountains headwaters (~600
145 mm annually) to the drier downstream prairie region (~300 mm annually) (Halliday, 2009). In most of the
146 non-montane headwater regions, evapotranspiration exceeds precipitation (Schindler and Donahue,
147 2006). Although there is sufficient rainfall in the region to sustain crop production with irrigation, little to
148 no runoff is generated from the grassland and prairie landscapes that include dead drainage areas
149 (Godwin and Martin, 1975; Halliday, 2009). In fact, 71% of Canada's irrigated land is found in the Province
150 of Alberta (Statistics Canada, 2017), the majority of which is in the SSRB. As such, there is an extensive
151 regulation of rivers in this region, including 13 dams, four weirs and eight reservoirs in the Bow River
152 watershed (AMEC, 2009) along with three major reservoirs and more than a dozen other water control
153 structures in the Oldman River watershed (Koning et al., 2006).

154 The SSRB basin is characterized by short summers and cold winters with a mean annual temperature
155 of ~3°C (Downing and Pettapiece, 2006). This seasonal pattern results in the rivers being predominantly
156 covered with ice during winter (November-March) followed by periods of snow-melt runoff, first from the
157 prairies and then from the mountain snowpack (Pomeroy et al., 2005). Snowmelt and rainfall during
158 snowmelt generates most of the annual runoff and flow (Halliday, 2009). Accordingly, the region's
159 dominant hydrological event is the annual melting of the Rocky Mountain snowpack starting in early May
160 and lasting for approximately 40 days (Grasby and Hutcheon, 2000). Discharge is greatest in June when
161 the peak in montane runoff coincides with the month with the most rainfall. Although there can be
162 significant rainfall events in May and June, the mountain snowmelt runoff generally dominates the
163 hydrograph. For example, snowmelt from the Rocky Mountains may produce between 70-90% of the
164 annual discharge in the Oldman River, depending on annual variation in snowpack (Byrne et al., 2006).

165 **2.2 Sample Design**

166 Water quality data was obtained from two Alberta Environmental and Parks (AEP) monitoring
167 programs: the long-term river monitoring network (LTRN) and the tributary monitoring network (TMN).
168 The LTRN program generally has monitored sites on the main stems of Alberta's major rivers for the last
169 30+ years. In 2016, AEP initiated the TMN program to investigate water quality dynamics in smaller
170 tributaries across the province. Here, we capitalize on data generated by these programs, to illustrate how

171 water quality data from monitoring programs are often naturally suited to be used in tributary tracing
172 research designs (i.e. where samples from potential tributaries are incorporated into end-member mixing
173 models as potential sources) and incorporated into sediment fingerprinting research. Water quality
174 monitoring data has the potential to be particularly powerful when coupled with the D-MIXSIAR model
175 that allows for the propagation of downstream tributary site source contributions to total and dissolved
176 material through multiple main stem target sites, or nodes, in large river basins.

177 Dissolved and total recoverable metals were analyzed for one-litre grab samples of surface water
178 taken monthly in pre-cleaned, high-density polyethylene bottles at surface water quality monitoring sites
179 as part of the TMN and LTRN programs between April 2016 and December 2018 (Table 1). An illustration
180 of the timing of the sampling regime on the main stem sites plotted with discharge can be found in Figure
181 S1. In total, 812 samples were obtained, 224 during the winter ice-covered season (November – March)
182 and 588 during the open water season (April – October). For some tributary sites (n = 9), it was not possible
183 to sample during the winter. For the majority of the target site nodes, there were 21 samples obtained
184 during the open water season and 12 during the ice-covered season (Table 1). In the Bow River catchment,
185 samples were obtained at 15 sites, including three target site nodes (Figure 1). In the Oldman River
186 catchment, samples were taken at 10 sites, including two target nodes. Finally, there were four sampling
187 sites, including two nodes, in the South Saskatchewan River sub-basin downstream of the confluence of
188 the Bow and Oldman Rivers. In total, 29 sites were sampled, of which 22 were potential sources, along
189 with seven target site nodes. For the final D-MIXSIAR model, the source contributions from the 22
190 potential source sites are estimated for the outlet site of this study basin on the South Saskatchewan River
191 downstream of Medicine Hat (SSR2 – Figure 1).

192 No particle size fractionation was undertaken owing to the fact that we are comparing tributary site
193 water quality grab samples to water quality grab samples from main stem node sites with the major
194 particle size sorting effects generally occurring during sediment generation, mobilization and initial
195 transport phases which have been assumed to have already materialized (Lacey et al., 2017; Lacey et
196 al., 2015a). Additionally, to address the potential solubility of various metals (e.g. Ca, K, Mg, Sr)(Kraushaar
197 et al., 2015), which may be transported primarily in the dissolved phase (Meybeck and Helmer, 1989), D-
198 MIXSIAR models were run on both the dissolved and total recoverable metal datasets to compare
199 differences in their modelled contributions to dissolved and total material across the SSRB.

200 Twenty-nine metals were analyzed by Innotech Alberta's Environmental Analytical Laboratory in
201 Vegreville, Alberta (Table 2) for both the total recoverable fraction (i.e. the total water sample) and the

202 dissolved fraction which was filtered with 0.45 µm cellulose acetate filter paper. Total water samples and
203 the dissolved filtrate were preserved in Vegreville by staff at Innotech with 1% concentrated SeaStar high
204 purity nitric acid for at least 16 h, thereafter ~50 ml of the preserved sample was digested for 20 m at
205 180°C and 200 PSI. A portion of the digested solution was then introduced directly to an inductively
206 coupled argon plasma-mass spectrometer with internal standards added online. Although Se and Cl are
207 not metals, they will be referred to in the results and discussions as metals as they are included in the
208 metal analysis results provided by Innotech. We use the term total material, rather than total suspended
209 solids, as total material includes both suspended and dissolved material, which is representative of how
210 the total recoverable metals were analyzed in our water samples. Additionally, we use the term dissolved
211 material rather than total dissolved solids to emphasise the fact that the dissolved metals are likely
212 representative of only a fraction of total dissolved solids (e.g. inorganic salts, nutrients, etc.). Our objective
213 of using the term material is to indicate that modelling results are illustrative of the main sources of the
214 bulk of the material being sampled and analyzed rather than identifying sources of individual constituents
215 of the dissolved or total material.

216 **2.3 Quality Control Samples**

217 **2.3.1 Blank samples**

218 Blank samples quantify the potential positive or negative bias in environmental data resulting from
219 contamination (Mueller et al., 1997; Riskin et al., 2018). In general, positive bias is introduced from
220 contamination in sampling and analyses which may result in environmental data being reported at a
221 higher level than actual levels present in the environment (Mueller et al., 2015). Here, field blank samples
222 are used to assess the positive bias (i.e. contamination) that may result from the entire process of sample
223 collection through sample storage and laboratory analyses. Blank water, obtained from Innotech, was
224 used to rinse the sample containers three times prior to being used to fill these containers with a field
225 blank water sample for analyses. In total, 172 field blank samples were collected by staff at the Calgary
226 field office during the sampling period.

227 The frequency and magnitude of potential contamination in the field blank samples is directly related
228 to 2,015 similar one-litre grab samples of surface water collected by AEP's Calgary field office from January
229 2016 to December 2018. After Mueller et al. (2015), the 90 percent upper confidence limit (UCL) for the
230 95th percentile concentration of the field blank dataset, is representative of the maximum contamination
231 anticipated, with a 90% confidence, in 95% of the sample population. Accordingly, this provides 90%

232 confidence that this contamination level would not be exceeded in more than 5% of the sample
233 population, including both the environmental and field blank datasets. Following Mueller et al. (2015), a
234 binomial function calculates a distribution-free UCL for the field blank percentiles, ranks the data in
235 ascending order, and then uses a binominal probability function (B) to calculate the UCL with equation 1:

$$B(p, n, U - 1) \geq 1 - \alpha \quad (\text{Eq. 1})$$

236 Where p is the percentile/100, n is the number of samples, U is the rank, and α is the significance level of
237 the confidence interval. The $100(1-\alpha)$ -percent UCL for the $(100)p^{\text{th}}$ percentile of potential extraneous
238 contamination in the population is estimated by the analytical value of a given parameter at rank U in a
239 set of n field blanks. As an example, for 100 field blank samples, the UCL (90%) at the 95^{th} percentile,
240 hereafter referred to as the B95-90 value, is:

$$B(0.95, 100, U - 1) \geq 0.90 \quad (\text{Eq. 2})$$

241 Solving for U yields $U=99$; therefore, the B95-90 value is the analytical result for the 99^{th} ranked blank
242 sample.

243 An example of this statistical procedure is outlined in more detail in Mueller et al. (2015) and a
244 comprehensive report on field blank analyses for samples taken across the province of Alberta is
245 presented in Laceby et al. (in press). The difference between the environmental data and the B95-90 value
246 is used to calculate the potential for environmental contamination based on relating the percent of field
247 blanks above the detection limit and the amount of environmental data within one order of magnitude of
248 the B95-90 value with this procedure again outlined comprehensively in both Mueller et al. (2015) and
249 Laceby et al. (in press).

250 **2.3.2 Duplicate samples**

251 Duplicate samples are used to estimate random error in environmental data potentially generated
252 during sample collection, storage and laboratory analyses (Mueller et al., 2015; Riskin et al., 2018). In
253 particular, duplicate samples assess the overall variability (i.e. precision) of environmental monitoring
254 programs, whereas field blank samples investigate the potential bias (i.e. accuracy). During our study
255 period, 146 duplicate samples were collected by the Calgary field office. The majority of duplicate samples
256 were collected concurrently (i.e. simultaneously within 1 m distance), with some duplicates obtained
257 sequentially (i.e. within 2 minutes and 1 m distance) in limited instances owing to logistical constraints.
258 Prior to sampling, duplicate bottles were rinsed three times with river water.

259 The variability in analyte detection and the variability relative to environmental data were both
 260 determined from the duplicate sample analyses. Variability in analyte detection is calculated by first
 261 determining the percent of duplicate sets with inconsistent detections (i.e. duplicate sets that contain
 262 both a non-detect and a detected value) (Mueller et al., 2015). Second, the number of duplicate sets with
 263 inconsistent detections is divided by the total amount of duplicate sets minus the number of pairs with
 264 consistent non-detects (i.e. two MDLs). Following Mueller et al. (2015), a one-sided UCL is calculated for
 265 the percentage of inconsistent duplicate sets with equation 3:

$$P_U = 100 \left\{ 1 + \frac{n - x}{(x + 1)F_{1-\alpha, df_1, df_2}} \right\}^{-1} \quad (\text{Eq. 3})$$

266 where P_U is the UCL (%), n is the total number of duplicate pairs, x is the number of duplicate pairs having
 267 inconsistent detects, and F is a percentage point derived from the F distribution for a $100(1-\alpha)$ percent
 268 confidence with the degrees of freedom being: $df_1 = 2x + 2$ and $df_2 = 2n - 2x$ (Mueller et al., 2015).

269 To relate duplicate variability to the environmental data, the variability in analyte concentrations is
 270 evaluated. Here, we use a bias-corrected log-log regression model, which is based on the approximate
 271 linear relationship in the logarithms of the duplicate mean and standard deviation concentrations, to
 272 evaluate duplicate variability across their concentration range (Mueller et al., 2015). For a comprehensive
 273 discussion on the suitability of this approach to analyze duplicate samples and detailed examples, see
 274 Mueller et al. (2015). The regression model is based on equation 4:

$$\log(SD) = B_0 + B_1 \log(C) \quad (\text{Eq. 4})$$

275 where $\log(SD)$ is the logarithm of the standard deviation (SD) of the paired duplicate sample
 276 concentrations, B_0 is the y-axis intercept of the regression line, which is estimated by the least squares
 277 method, B_1 is the regression line slope, and $\log(C)$ is the logarithm of the mean of the paired duplicate
 278 concentrations.

279 The residuals from this regression equation are then back-transformed to their original scaling. The
 280 mean of these residuals is included in equation 5 as a bias correction factor (BCF) to compensate for
 281 transformation bias when the SD is calculated in original units (e.g. mg/L):

$$SD = BCF \{ 10^{[B_0 + B_1 \log(C)]} \} \quad (\text{Eq. 5})$$

282 Equation 5 is then used to determine duplicate variability as the mean bias-corrected SD for any given
 283 parameter concentration, C (Mueller et al., 2015).

284 To relate the variability in the duplicate samples to the environmental data, we estimate the
285 uncertainty of analyte values measured in environmental samples through constructing confidence
286 intervals for environmental sample concentrations with equation 6 (Mueller et al., 2015):

$$[C_L, C_U] = C \pm Z_{(1-\alpha/2)}\sigma \quad (\text{Eq. 6})$$

287 where C is the measured environmental analyte value, C_L and C_U are the lower and upper confidence limits
288 (CL) of the analyte value for the 100(1- α /2) confidence interval percent, Z is the percentage point of a
289 normal standard curve containing an area of 100(1- α /2) percent, α represents the probability of the
290 confidence interval not including the true analyte value (i.e. α is 0.9 for the 90% CL), and σ is the SD of the
291 analyte value calculated with equation 5. To contextualize this duplicate analysis, we calculate the mean
292 confidence interval (M-CI), which is the average C_L and C_U when applying equation 6 to each percentile of
293 the environmental data ($n = 2,015$). Of note, both the duplicate and blank analyses include all LTRN and
294 TMN samples taken by the Calgary field office, including several sites not included as nodes or tributary
295 source sites in this fingerprinting research in order to comprehensively quantify the overall potential bias
296 and contamination of samples obtained during the study period as a larger sample size should
297 theoretically result in improved estimates of potential bias and variability.

298 **2.4 Source Fingerprinting**

299 The results from the quality control analyses were used to remove metals that have a high potential
300 for bias (i.e. contamination) or variability. First, metals were removed if they had a potential for
301 contamination greater than 20% based on the field blank analyses. Second, metals were removed that
302 had an upper confidence limit for inconsistent detection greater than 20% and/or a duplicate variability
303 (i.e. M-CI) across the concentration range greater than 20%. The 20% upper limit of bias and variability
304 was selected because it is the maximum acceptable relative percent difference between laboratory
305 duplicates and the maximum allowable bias on laboratory spike samples, which if exceeded, the batch of
306 samples requires reanalysis. After removing metals based on the quality control analyses, a mean and
307 standard deviation (SD) conservative bracket/range test (e.g. the mean of the target material falls within
308 one SD of the source tributary material) was used to select metals for modelling. A separate bracket/range
309 test was conducted for each individual MixSIAR model. Owing to MixSIAR's capacity to handle correlated
310 data, no further tracer selection steps were included following the work of Smith et al. (2018).

311 The D-MIXSIAR model was run in the R-programming Language using MixSIAR as the model engine
312 based on code published as supplementary information in Blake et al. (2018) with MixSIAR's mathematical

313 formulation outlined in Stock et al. (2018). All models were run first with normal distributions as Smith et
314 al. (2018) illustrated that the removal of tracers with non-normal distributions may reduce the overall
315 accuracy of MixSIAR results. Additionally, we applied log-normal, square root and cube root
316 transformations to our source data in very-short and very long MixSIAR model runs to investigate the
317 sensitivity of MixSIAR to assumptions around the normality of source data, which was assessed after the
318 transformations, or the lack there of for normal distributions, with Shapiro-Wilks tests.

319 The NADA package in R implemented regression on order statistics (ROS) to estimate the mean and
320 standard deviation of the source metal concentrations with censored data (e.g. below minimum detection
321 limits) to generate the normal distributions that were modelled with MixSIAR. In total, there were seven
322 data points in the dissolved modelled data that were below detection limits whereas there was no
323 censored data in the total recoverable modelled data.

324 MixSIAR was run with the residual error model structure, an uninformative prior, all Dirichlet
325 hyperparameters set to one, and the Markov Chain Monte Carlo (MCMC) set to a very long chain length
326 of 1,000,000, with a burn in of 700,000, and a thinning of 300 for three chains (following Blake et al., 2018).
327 Additionally, a very short chain length of 10,000 with a burn in of 5,000 and a thinning of 5 for three chains
328 was used to investigate the impact of the source distributions. The Gelman-Rubin diagnostic was used to
329 assess model convergence and none of the variables modelled had a Gelman-Rubin diagnostic > 1.01 with
330 the very long run times.

331 Owing to the strong seasonal influence on hydrological dynamics in the region, we ran three model
332 scenarios. First, all annual data was modelled. Second, we ran models for the open water season (April to
333 October). Third, we ran models for the ice-covered season (November to March). In summary, the D-
334 MIXSIAR framework de-convolutes the posterior proportion contributions sequentially for each node
335 progressing downstream while propagating the uncertainty through estimating full posterior distributions
336 for the model results for each potential source (Blake et al., 2018). All analyses, modelling and plotting of
337 results for this manuscript were conducted in the R programming language (R Development Core Team,
338 2011) with multiple packages (i.e. devtools, ggplot2, R2jags, RGtk2, ggord, data.table, tidyverse, Hmisc,
339 matrixStats, MASS, klaR, reshape2, psych, foreach, Rsolnp, MixSIAR, rjags, NADA, tidyhydat, cowplot, plyr,
340 stringr, tibble, scales, gridExtra, egg, forcats, tidyhydat and dplyr).

341 **3. Results**

342 **3.1 Fingerprint Selection for modelling**

343 For the 29 total recoverable metals analyzed, including Cl and Se, only 12 passed the quality control
344 screening. From the field blank analysis, there were four metals with a potential for environmental
345 contamination greater than 20% (Cl, Cu, Pb, and Zn - Table 2). Regarding the duplicate analyses, only Bi
346 had a greater than 20% UCL in inconsistent detections. In addition, 14 metals had an M-Cl greater than
347 $\pm 20\%$ (Ag, Al, Be, Bi, Cd, Co, Cr, Ni, Pb, Th, Tl, Se, Sn and Zn) including four metals with an M-Cl greater
348 than $\pm 50\%$ (Ag, Bi, Cd, and Sn). Overall, the quality control screening removed 59% of the metals analysed
349 with 12 (41%) moving on to the bracket/range test (As, B, Ba, Ca, Fe, Li, Mn, Mo, Sb, Sr, U and V). Between
350 five and 12 total recoverable metals were selected for modelling the three scenarios (i.e. ice, open & all
351 samples) for each target node based on the conservative bracket/range test requiring the mean node
352 concentrations to plot within one standard deviation of source concentrations (Table 3). Box plots of all
353 total recoverable metals modelled are provided in the supplementary information (Figures S2 to S13).

354 For the 29 dissolved metals analyzed, including Cl and Se, only 11 passed the quality control screening.
355 Regarding the field blank analysis, there were three metals with a potential for environmental
356 contamination greater than 20% (Al, Cu, and Ti - Table 4). Regarding the duplicate analyses, five metals
357 had a greater than 20% UCL in inconsistent detections (Ag, Be, Bi, Cr and Pb). In addition, 15 metals had
358 an M-Cl greater than $\pm 20\%$ (Ag, Al, Bi, Cd, Co, Cr, Fe, Ni, Mn, Pb, Th, Tl, Se, Sn and Zn) including four metals
359 with an M-Cl greater than $\pm 50\%$ (Ag, Pb, Th and Sn) and one that was greater than 100% (Cr). Overall, the
360 quality control screening removed 62% of the dissolved metals analysed with 11 (38%) moving on to the
361 bracket/range test (As, B, Ba, Ca, Cl, Li, Mo, Sb, Sr, U and V). Between four and 11 dissolved metals were
362 selected for modelling the three scenarios (i.e. ice, open & all annual samples) with the conservative
363 bracket/range (Table 3). Box plots of all dissolved metals modelled are provided in the supplementary
364 information (Figures S14 to S24).

365 **3.2 Total Verses Dissolved Metals**

366 On average, 64% (SD 30%) of the total recoverable metals were dissolved material. For the total
367 recoverable metals selected for modelling, this increased to 76% (SD 33%). There were only three
368 modelled metals with a dissolved to total recoverable ratio below 50% (Fe: 8%, Mn: 16% and V: 49%),
369 whereas the other total recoverable metals modelled were predominantly comprised of dissolved
370 material (i.e. $>80\%$) (Table 5). The dominance of dissolved material in the modelled dataset was evident
371 for the majority of TSS concentrations (TSS <50 mg: Mean (M) 78%, SD 33%, TSS between 50-100mg: M
372 70%, SD 37%, and TSS between 100-1000 mg/L: M 59%, SD 37%). The dissolved fraction constituted the
373 minority of material for TSS concentrations >1000 mg/L, where it only comprised a mean of 38% (SD 36%)

374 of the metal concentrations modelled, although there were only 4 samples with TSS concentrations >
375 1000 mg/L. The metal concentrations in the one litre water grab samples are thus predominantly
376 comprised of dissolved material.

377 Accordingly, the modelled source contributions with total recoverable and dissolved metals should
378 theoretically be similar as the majority of the material is dissolved. Any deviations between the modelled
379 source contributions with the total recoverable and dissolved metals should highlight differences between
380 the source dynamics of total and dissolved material across the SSRB. For example, in situations where
381 sites have relatively similar modelled source contributions with both total recoverable and dissolved
382 metals, it can be assumed that model results from both of these metals datasets are representative of the
383 dissolved fraction. In contrast, for situations where model results from the total recoverable metals data
384 are greater than those estimated with dissolved metals, the source contributions modelled using the total
385 recoverable metals are likely to be representative of suspended material (e.g. particulate matter,
386 sediment, etc.).

387 **3.3 MixSIAR Sensitivity to Source Data Transformations**

388 Overall, 834 and 821 respective total recoverable and dissolved metal source distributions were
389 incorporated into MixSIAR when modelling the ice-covered (n 265, 300), open water (n 277, 259), and all
390 annual samples (n 279, 275). A log-10 transformation achieved the greatest degree of normality in the
391 source dataset with a mean (M) of 61% (SD 3%) for dissolved metals (DM) and 56% (SD 0.2%) for total
392 recoverable metals (TRM) when including the ice-covered, open water and all annual source distributions,
393 followed by the cube root (DM: 55% SD 2.1%; TRM: 47% SD 0.8%) and square root transformations (DM:
394 54%, SD 0.9%; TRM: 43%, SD 0.8%). In the absence of any transformation, the source distributions of 48%
395 (SD 0.3%) of the dissolved metals and 37% (SD 0.2%) of the total recoverable metals were distributed
396 normally. Transformations to the source data prior to modelling with D-MIXSIAR had little to no impact
397 on source apportionment results with a very long run time. The average standard deviation for all source
398 contributions for all models (i.e. ice, open and all annual samples) with normal, log-normal and square
399 root and cube root transformations was only 0.1% when modelling with a very long run time. In fact, the
400 maximum standard deviation for modelled source contributions to target material was only 0.8%,
401 indicating that the nature of the source data had limited impact on the model outputs with the very long
402 run times. In contrast, the transformations resulted in a significantly higher standard deviation in results
403 for models with very short run times (paired t-test results: $t = -6.041$, $df = 131$, $p\text{-value} = <0.001$), which
404 had an average standard deviation of 0.7% and a maximum standard deviation of 7.8%. Accordingly, the

405 results presented below are from models with very-long run times and the conventional normal
406 distributions, although any of the four approaches to the source data would provide nearly identical
407 results using dissolved and total recoverable metals data modelled with very long run times.

408 **3.5 D-MIXSIAR model results**

409 For the D-MIXSIAR model run using the dissolved metals dataset, the Bow River headwaters were
410 estimated to contribute the most material (M 31%, SD 6%) for all annual samples followed by Belly River
411 (M 15%, SD 5%) and the Oldman River headwaters (M 14%, SD 4-5%) (Table 6). Although the Belly River's
412 modelled contributions using the dissolved metals data were relatively stable over the ice-covered and
413 open water seasons (M ~15%), the Bow River headwaters modelled contribution decreased from 29% (SD
414 7%) in the ice-covered season to 22% (SD 8%) in the open water season. In contrast, the Oldman River
415 headwaters contribution, modelled using the dissolved metals, increased from 10% (SD 5%) during the
416 ice-covered season to 21% (SD 7%) during the open-water season. The Little Bow River (M 7%, SD 3% for
417 annual samples), the only other catchment with a noteworthy source contribution >5%, modelled using
418 the dissolved metals, fluctuated from a 2% (SD 2%) contribution during the ice-covered season to 9% (SD
419 4%) during the open water season. As anticipated, seasonal fluctuations in the mean contribution ratios
420 (MCRs) reflected these source contributions modelled using dissolved metals with the Belly River
421 contributing approximately twice (MCRs between 1.94 – 2.04) as much material as anticipated based on
422 unit area across all seasons. The Oldman River headwaters also contributed twice as much material as
423 anticipated during the open water season (MCR 2.04) relative to essentially an expected contribution
424 based on watershed area during the ice-covered season (MCR 1.02). The Bow River headwaters were
425 modelled to contribute 1.78 times more material using dissolved metals than anticipated based on unit
426 area during the ice-covered season compared to 1.38 times more during the open water season. The Little
427 Bow River fluctuated from contributing almost 85% less than anticipated based on unit area in the ice-
428 covered season (MCR 0.16) to only ~30% less during the open water season (MCR 0.68). Overall, the
429 montane headwater catchments in the Bow and Oldman Rivers were modelled to contribute 77% using
430 the dissolved metals dataset in the open water season, compared to 70% during the ice-covered season,
431 and 76% when modelling all annual samples. This results in the montane headwaters being modelled
432 using dissolved metals to contribute ~30% more material than anticipated in the open water season (MCR
433 1.30) and for all annual samples (MCR 1.29) versus ~20% more material than anticipated during the ice-
434 covered season (MCR 1.19) based on their watershed area.

435 The modelling results using the total recoverable metals also had pronounced seasonal variations.
436 When modelling all annual samples using the total recoverable metals, the Bow River headwaters were
437 estimated to provide the most material to the SSR2 outlet node, contributing 27% (SD 8%), followed by
438 the Oldman River headwaters (M 12%, SD 5%), the Belly River (M 9%, SD 5%), the Little Bow River (M 9%,
439 SD 4%), the Saint Mary River (M 8%, SD 4%) and New West Coulee (M 7%, SD 4%) (Table 6). During the
440 ice-covered season, the Bow River headwaters were deconvoluted using the total recoverable metals to
441 contribute the most material (M 31% SD 8%), followed by the Belly River (M 9%, SD 6%), New West Coulee
442 (M 7%, SD 6%) and the Highwood River (M 7%, SD 5%). During the open water season, the Little Bow River
443 was modelled using the total recoverable metals to contribute the most material (M 20%, SD 7%),
444 followed by the Oldman River headwaters (M 18%, SD 6%), the Saint Mary River (M 14%, SD 6%), the Belly
445 River (M12%, SD 5%) and the Bow River headwaters (M 11%, SD 7%). This seasonal variation in modelled
446 source contributions is again clearly evident in the MCRs. The Bow River headwaters shift from an MCR of
447 0.69 in the open water season to 1.94 in the ice-covered season. In contrast, several catchments in the
448 OMR have major increases in their MCRs in the open water season with the Little Bow River shifting from
449 0.09 in the ice-covered season compared to 1.61 in the open water season. The Oldman headwaters
450 (OMR1) shifts from an MCR of 0.48 in the ice to 1.97 in the open season, the Saint Mary River from 0.3 in
451 the ice to 1.85 in the open season and the Belly River shifting from 1.18 in the ice to 1.5 in the open season.
452 Overall, montane headwater catchments in the Bow and Oldman Rivers were modelled using the total
453 recoverable metals to contribute 68% of the material for all annual samples compared to 64% in the open
454 water season and 62% during the ice-covered season. Accordingly, the montane headwaters were
455 modelled to contribute between 5-15% more material than anticipated based on watershed area with an
456 MCR of 1.05 for the ice-covered season, 1.08 in the open-water season and 1.15 for all annual samples.

457 Clearly, there was a major shift in the estimate of tributary contributions between the two main
458 seasons. When summing all tributary D-MIXSIAR model contributions, the Bow River was estimated to
459 contribute 57% and 69% using the dissolved and total recoverable models respectively in the ice-covered
460 season compared to 38% and 24% during the open water season. In contrast, the Oldman River's summed
461 modelled contributions increased from 34% and 22% using the dissolved and total recoverable metals
462 respectively in the ice-covered season to 59% and 73% during the open water season. This seasonal
463 variation in material modelled using total recoverable metals is predominantly driven by a 20% decrease
464 in contributions from the Bow River headwaters site in the open water season relative to the ice-covered
465 season, with multiple tributaries in the Oldman River all contributing more material in the open water
466 season relative to the ice-covered season (i.e. increases of 19% in the Little Bow River, 14% in the Oldman

467 River headwaters, and 11% in the Saint Mary River). The seasonal variation in source contributions
468 modelled using dissolved metals was more muted with only a 6% decrease in contributions from the Bow
469 River headwaters site in the open water season relative to the ice-covered season with multiple tributaries
470 in the Oldman River basin modelled to contribute more dissolved material in the open water season
471 relative to the ice-covered season (i.e. increase of 11% in the Oldman River headwaters, 7% in the Little
472 Bow River and 7% in the Saint Mary River).

473 **4. Discussion**

474 **4.1 Quality Control Analyses**

475 As MixSIAR is not limited by a three-step selection process (e.g. bracket/range test, Kruskal-Wallis h-
476 test, and discriminant function analyses) (Smith et al., 2018), it facilitates the development of alternative
477 approaches to identify appropriate fingerprints to include in end-member mixing models. Accordingly, we
478 presented a novel approach using quality control samples to guide fingerprint selection for modelling.
479 Overall, we found that the majority of the metals (total recoverable 59%, dissolved 62%) analyzed in one-
480 litre grab samples of surface water had a bias (i.e. blank sample contamination) and/or a variability (i.e.
481 duplicate replicability) greater than 20%. In particular, our results highlight the fact that routinely
482 measured metals data may not have equivalent uncertainty. As sediment mixing models advance (e.g.
483 Cooper and Krueger, 2017; Lizaga Villuendas et al., 2018; Pulley and Collins, 2018; Sanisaca et al., 2017),
484 ideally the quality of data (i.e. bias and variability) could be incorporated directly into mixing models in
485 addition to the reporting of results.

486 Importantly, the potential for bias and variability evident in our metals data is likely present in other
487 research programs analyzing particulate material collected with discrete, low volume grab samples of
488 water, or potentially even automated stage samplers. Of note, the M-CI value used to select metals
489 represents the mean confidence interval (e.g. $\pm 20\%$) across all percentiles of environmental data. This
490 mean value is masking elevated variability at lower concentrations. For example, the average M-CI for the
491 50th percentile of dissolved and total recoverable metals that were not modelled was $\pm 40\%$ and $\pm 35\%$
492 respectively, whereas it was $\pm 55\%$ and $\pm 53\%$ for the 10th percentile (Figure 2). In contrast, the average M-
493 CI for dissolved and total recoverable metals that were modelled was $\pm 6\%$ and $\pm 7\%$ respectively for the
494 50th percentile versus $\pm 9\%$ and $\pm 8\%$ for the 10th percentile. Clearly the quality of the data generated for
495 individual metals varies greatly (i.e. Figure 2) and the bias and variability of environmental data ideally
496 should be accounted for more regularly in sediment fingerprinting research.

497 Whether similar levels of bias and variability are evident in soil and sediment samples (e.g. lag deposits,
498 time integrated samplers) requires further research and analyses. The challenge with soils and sediments
499 will likely revolve around metals with low abundances (e.g. rare earth elements / lanthanides) where the
500 potential for bias and variability may arise in the field (e.g. sampling design and device contamination),
501 laboratory (e.g. sieving, grinding and drying samples), and/or during analytical analyses (e.g. digestion
502 procedures). As such, it would be beneficial for researchers to analyze replicate soil and sediment samples,
503 along with some variant of consistent blank reference soils (e.g. Fernandez et al., 2014; Guzmán et al.,
504 2010), to improve our understanding of the potential for variability and bias in these media. Although
505 there will be obvious trade-offs with respect to increased analytical costs, we feel it is important for
506 sediment fingerprinting researchers to start to entertain the notion of incorporating quality control best
507 practices into their research design, end-member mixing models and reporting of results.

508 **4.2 Total and Dissolved Source Dynamics**

509 Watersheds originating in the Rocky Mountains or foothills region, with >25% of their landscapes
510 having a slope >10%, were modelled to supply 76% of the material using dissolved metals and 68% using
511 total recoverable metals to the outlet node (Site SSR2). The Bow River watershed was modelled to
512 contribute more dissolved (53%) and total material (53%) than the Oldman River watershed (DS 46% and
513 TS 44%) for all annual samples. For dissolved and total material, there was a clear shift in source
514 contributions from these two major river systems during the ice-covered and open water seasons. During
515 the ice season, the Bow River supplied the majority of total (69%) and dissolved material (57%) modelled
516 for the outlet node, whereas the Oldman River supplied the majority of total (73%) and dissolved material
517 (59%) during the open season. Seasonal fluctuations for total material contributions from the Bow and
518 Oldman Rivers were more pronounced (i.e. 12-14% greater) than for dissolved material. This seasonal
519 fluctuation is highlighted by a decrease in total material contributions from all but one of the Bow River
520 sites during the open season and an increase from all but two Oldman River sites during the open water
521 season. In particular, the Bow River headwater site (BR1) contributions to total material declined ~20%
522 and three Oldman River tributaries had major increases in source contributions including the Little Bow
523 River (19%), the Oldman River headwaters (14%), and the Saint Mary River (11%). Of these latter
524 tributaries, the 19% increase in the Little Bow River source contributions stands out as this tributary has
525 a relatively gentle topography (i.e. only 5% of the watershed has a slope >10%) compared to the other
526 three sites with montane headwaters.

527 To facilitate the interpretation of these results, we compiled the mean monthly discharge for 20 of
528 the sites from 1988 to 2018, for which there was a nearby gauging station where the watershed area for
529 the gauging station did not differ from our sites area by more than 11% (Area Ratio (AR) in Table 5). As
530 many of the smaller waterways in this region are essentially frozen or inaccessible during the winter,
531 discharge data was only available for eight of the sites during the ice-covered season. Accordingly, we
532 calculated the annual, ice-covered and open water season mean monthly discharge to contextualize the
533 modelling results where data was available. During our study period, the Bow River supplied 52% of the
534 annual discharge to the South Saskatchewan River relative to the Oldman River's 46%, which is remarkably
535 similar to the contributions modelled with D-MIXSIAR for both total recoverable metals (TRM) and
536 dissolved metals (DM) for the Bow (TRM: 53%, DM 53%) and Oldman Rivers (TRM: 44%, DM: 46%).
537 Additionally, during the ice season, the Bow River supplied 67% of the discharge compared to 69% of the
538 modelled supply of total material and 57% of the supply of dissolved material, whereas in the open
539 season, the Bow River supplied 52% of the discharge compared to only 24% of the modelled total material
540 and 38% of the dissolved material.

541 Discharge along with the D-MIXSIAR source contributions modelled using total recoverable and
542 dissolved metals for the Bow and Oldman Rivers were relatively similar when examining all annual
543 samples and the ice-covered samples, whereas they clearly deviated during the open water season. In
544 particular, the Oldman River contributed more total material than anticipated based on both watershed
545 area (MCR: 1.58) and more than 1.53 times more than expected based on discharge during the open water
546 season. Much of this increase in total material supply appears to be originating from the Little Bow River
547 which had a 20% increase in its supply of total material during the open season, delivering 1.6 times more
548 total material than its catchment area and ~14 times more than anticipated based on its discharge (Table
549 7).

550 One hypothesized driver of the source dynamics of total and dissolved material is the extent of river
551 regulation and irrigation infrastructure in this region. The Bow River watershed is the most regulated
552 catchment in Alberta with 13 dams, four weirs and eight reservoirs (AMEC, 2009). Of note, there are three
553 major impoundments on the main stem of the Bow River between nodes BR1 and BR4. The last major
554 impoundment on the Bow River, Bassano dam, is upstream of node BR4 (the most downstream Bow River
555 sampling node), whereas for the Oldman River, the last main stem impoundment is upstream of the
556 Oldman River headwaters site. There are also several irrigation canals diverting flow along the Bow River
557 from sites BR1 through to BR4 (Figure 1), which are evident as the overall discharge actually decreases in

558 the open water season between site BR2 (357 million m³ per month) and site BR4 (297 million m³ per
559 month).

560 The decrease in flow and disconnectivity introduced by multiple impoundments on the Bow River
561 logically facilitates the directly related and relative increase in total material supplied to the outlet SSR2
562 site by the Oldman River. This elevated contribution is likely enhanced by agriculture activities supported
563 by water diversions and irrigation in the Little Bow River watershed and other similar catchments. In
564 particular, there were eight tributary sites with watersheds that had agricultural land uses greater than
565 50% (Table 8). From these sites, the Little Bow River was found to be a significant contributor of total
566 material in the study area, contributing 20% in the open water season to the downstream outlet site
567 (SSR2) compared to only 1% in the ice-covered season. This high open season contribution from the Little
568 Bow River, which is ~14 times more than expected based on its discharge, is further supported by high
569 total suspended solids (TSS) measurements at this site. During the open season, the Little Bow River had
570 the highest median TSS concentration of all monitored tributary sources (57 mg/L), which is more than
571 double the site with the second highest median open season TSS concentrations (Twelve Mile Coulee - 25
572 mg/L) (Figure 3). Although the Little Bow River catchment is the largest of the prairie/plain source
573 tributaries, the contribution of total material from the Little Bow River during the open water season is
574 particularly noteworthy when taking into consideration that there is a major reservoir (Travers Reservoir
575 – surface area 22.5 km²) located ~50 km upstream of the sampling site that is potentially trapping material
576 from ~70% of the Little Bow River watershed. It is likely that enhanced hydrological connectivity derived
577 from agricultural development is facilitating the downstream transport of sediment in the Little Bow River
578 and other similar catchments.

579 Although the dissolved material source dynamics still varied among the ice-covered and open water
580 seasons, variations were less pronounced. This pattern suggests that the changes in flow conditions and
581 the extensive river regulation throughout the SSRB may have less of an impact on the dissolved material
582 compared to total material. The approach taken to fingerprint sources with dissolved metal
583 concentrations likely only incorporates a fraction of the overall solute load. Ions, nutrients and other
584 dissolved solids likely constitute the majority of material in the dissolved material that was sampled.
585 Although there are likely significant challenges to directly tracing dissolved material with only dissolved
586 metals, this approach has several analogies with tracing the suspended sediments with sediment source
587 fingerprinting techniques. For example, multiple processes occurring in-stream (e.g. sorption, desorption,
588 settling, scouring, etc.) occur within a 'biogeochemical black box' that could affect both the total

589 recoverable and dissolved metal concentrations potentially adding uncertainty to model results.
590 Nonetheless, the fact that both models behave relatively similarly provides increased confidence in the
591 results, particularly with regards to the potential effect of the major reservoirs trapping potential
592 suspended material relative to the more straightforward downstream migration of the dissolved fraction.

593 **4.3 Perspectives and limitations**

594 This research illustrates a powerful approach to use data generated from water quality monitoring
595 programs to investigate sources of dissolved and total material across large spatial areas (>60,000 km²).
596 In particular, the D-MIXSIAR model of Blake et al. (2018) is naturally suited to be used with data generated
597 by water quality monitoring programs. Here, the D-MIXSIAR model effectively demonstrated that the
598 majority of the dissolved (76%) and total material (68%) sampled at the outlet of this large catchment is
599 generated in the montane headwater catchments. In addition, it highlighted an interesting seasonal
600 dynamic, where some of the prairie/plains catchments dominated by agriculture, such as the Little Bow
601 River, were modelled to generate a significant and disproportionate amount of total material during the
602 open water season. The results from this research may be used to help optimize Alberta's water quality
603 sampling networks to be more representative of the watersheds that may potentially contribute the
604 majority of total material in this region, and develop targeted focus studies in watersheds that
605 disproportionately contribute material transiting these river systems.

606 As suspended and dissolved material often act as a proxy for hydro-geomorphological processes
607 operating over multiple scales, this research provides insight into how hydro-geomorphic processes in the
608 Rocky Mountain headwaters drive the flux of dissolved and total material downstream coupled with the
609 disconnectivity introduced by water supply and management infrastructure and the agriculture activities
610 supported by this infrastructure. With multiple dams and reservoirs creating disconnectivity in the
611 downstream transfer of particulate material, future research should analyze metals and fallout
612 radionuclides (i.e. ¹³⁷Cs, ²¹⁰Pb_{xs}, and ⁷Be) on sediment cores collected in these lentic systems to quantify
613 depositional dynamics and understand how source dynamics have changed over time (e.g. Foucher et al.,
614 2015; Le Gall et al., 2017; Le Gall et al., 2016). The use of next generation tracers such as compound
615 specific stable isotopes (Blake et al., 2012; Mabit et al., 2018; Reiffarth et al., 2019), or even environmental
616 DNA (Evrard et al., 2019; Foucher et al., 2020), may provide more insight into the dominant processes
617 supplying total material in this region.

618 The interdependencies between dissolved and total metal concentrations, along with potential
619 relationships with TSS, may influence model results. There could be situations where variations in TSS may
620 affect estimated source contributions when modelling dissolved and total metal concentrations. These
621 affects will likely be most pronounced for models that unmix individual target samples or those populated
622 with a limited number of source samples. The approach taken in the current research was to capitalize on
623 three years of existent monitoring data to comprehensively model dissolved and total metal distributions
624 for both tributary sources and target material, directly incorporating the variation of TSS throughout the
625 study period. Additionally, we use a distribution approach to address potential non-conservative
626 behaviour in modeled parameters requiring the mean node metal concentrations to plot within one
627 standard deviation of source metal concentrations (Wilkinson et al., 2013). Nonetheless, there are likely
628 situations where non-conservative tracers are still modelled. To help address these non-conservative
629 tracers, our approach was to maximize the number of tracers included in the models (Smith et al., 2018;
630 Wynants et al., 2020), which has been demonstrated to be effective in limiting the affect of non-
631 conservative tracers with Bayesian un-mixing models (Sherriff et al., 2015).

632 Unfortunately, gauging stations were not located near each site and therefore we cannot calculate
633 sediment budgets, sediment loads nor a comprehensive water balance. In the future, water isotopes ($\delta^{16}\text{O}$
634 and $\delta^2\text{H}$) could be utilized to help understand if the water that is driving the generation and transportation
635 of dissolved and total material, is derived from surface runoff due to snowmelt or rainfall, or importantly
636 groundwater sources (Gibson et al., 2005; Stadnyk et al., 2005). The development of multi-tracer
637 approaches that capitalize on a variety of different isotopic fingerprints could provide significant
638 additional information on potential anthropogenic drivers of dissolved and total material source dynamics
639 across the SSRB (Kruk et al., 2020; Lacey et al., 2015b; Tanna et al., 2020).

640 One important caveat when using water quality monitoring data in source fingerprinting research is
641 that quality control data are necessary when analyzing total recoverable and dissolved metals for one-
642 litre grab samples of surface water or potentially even automated stage samples. In particular, not all
643 metals used in mixing models will have equivalent bias or variability. It would be beneficial if future
644 research investigated the potential for bias and variability in sediment and soil samples for a variety of
645 parameters used in sediment source fingerprinting analyses.

646 A second important caveat when utilizing data from water quality monitoring programs in a
647 fingerprinting framework is that the monitoring design will inherently bias model results. For example, in
648 the SSRB, the ice-covered season constitutes five months resulting in essentially ~40% of the annual

649 samples being taken in near base flow conditions. Additionally, ambient water quality monitoring
650 programs are typically not designed to sample different stages of the hydrograph. On the one hand, field
651 staff likely schedule their monthly grab sample campaigns on factors unrelated to streamflow. On the
652 other hand, for basins as large as the SSRB, field staff may at times sample different stages of the
653 hydrograph for different sites in any given month. As such, the base-flow dominance of the ice-covered
654 and the non-hydrograph specific sampling may result in a relatively insignificant portion of the dissolved
655 and total material being modelled to generate the source apportionment results (Horowitz et al., 2008).
656 Although, the model results presented above are likely biased towards the dissolved fraction, differences
657 between the total recoverable and dissolved fraction model results highlight areas that are potentially
658 important sources of particulate matter such as the Little Bow River. Installing multiparameter probes
659 (Clifford et al., 1995; Orwin and Smart, 2005) and time-integrated samplers (Phillips et al., 2000) would be
660 required to thoroughly characterize particulate matter (e.g. sediment) source dynamics across the SSRB.
661 Nonetheless, existent data generated by water quality monitoring programs can be effectively modelled
662 with sediment source fingerprinting approaches to generate a broad-scale understanding the source
663 dynamics of dissolved and total material providing a concrete foundation to develop focus studies
664 addressing issues of concern across a large region such as the SSRB.

665 Future research should investigate the accuracy of the D-MIXSIAR model and the potential
666 conservative behaviour of suspended and dissolved tracing parameters. The generation of synthetic or
667 hypothetical mixtures could help illustrate whether the D-MIXSIAR approach is mathematically robust. In
668 particular, it is important to know how uncertainty in the source contribution in one node may impact
669 other modelled source contributions as they are de-convoluted. Additionally, it would be valuable to
670 understand how the impact of tracer selection affects source contributions modeled by D-MIXSIAR. As
671 the de-convolution of source contributions with D-MIXSIAR is a relatively novel approach in the sediment
672 source fingerprinting literature, we focussed our attention on a new application of the D-MIXSIAR model
673 using data generated by water monitoring programs. Nonetheless, it would be valuable for future
674 research to assess the strengths and limitations of D-MIXSIAR with a robust sensitivity analysis.

675 More research is warranted into the interactions between dissolved and total metals as a multitude of
676 processes occur within the in-stream 'biogeochemical black box' (i.e. exchange processes, sorption,
677 desorption, etc.), which all may affect metal concentrations. In particular, there may be in-stream
678 processes, undocumented sources, and/or other factors driving the non-conservative behaviour of the
679 modelled dissolved and total metals. When modelling source contributions with the sediment

680 fingerprinting technique, there remains significant uncertainty regarding what actually drives the
681 potential conservative behaviour of parameters populating mixing models (e.g. Motha et al., 2002).
682 Uncertainty in model results driven by the non-conservative behaviour of selected parameters is arguably
683 an under researched theme in the sediment fingerprinting literature. In fact, it is debatable as to whether
684 we should be more or less concerned regarding non-conservative behaviour in the dissolved and total
685 fractions modelled in this current research relative to the potential for the non-conservative behaviour in
686 suspend sediments, sediment cores, lag deposits and rising stage samples. Hopefully, our modelling of the
687 dissolved and total metal parameters in a sediment fingerprinting framework will help instigate more
688 research regarding the potential drivers of non-conservative behaviour in all these various media and
689 present unique opportunities to develop interdisciplinary research collaborations and approaches
690 engaging with surface water and/or groundwater researchers.

691

692 **5. Conclusion**

693 A significant contribution from this research was the novel use of a water quality monitoring data to
694 investigate the source dynamics of both dissolved and total material in a large-mixed use basin. In
695 particular, a comprehensive quality control program facilitated the inclusion of water quality monitoring
696 data directly into a sediment source fingerprinting framework. As long as researchers have a strong
697 understanding of the quality of their data, particularly for discrete, low volume grab samples of surface
698 water and automated stage samplers, there is significant potential to use water quality data generated
699 from monitoring programs to investigate the source dynamics of dissolved and total material.
700 Additionally, sediment source fingerprinting research could benefit from incorporating quality control
701 best practices from water quality monitoring research and elsewhere to propagate information regarding
702 the uncertainty the data generated (i.e. bias and variability) through mixing models and into the reporting
703 of results. Overall, we believe it is time for researchers fingerprinting sediment sources and those tracing
704 the more soluble fraction to exchange best practices and embark on collaborative research projects
705 investigating source dynamics of the particulate and dissolved loads simultaneously. These collaborations
706 could help further our understanding of how anthropogenic activities may be affecting fundamental
707 critical zone processes and resulting in major changes in the cycling of particulate and dissolved material
708 in riverine systems worldwide.

709

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Figures

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Tables

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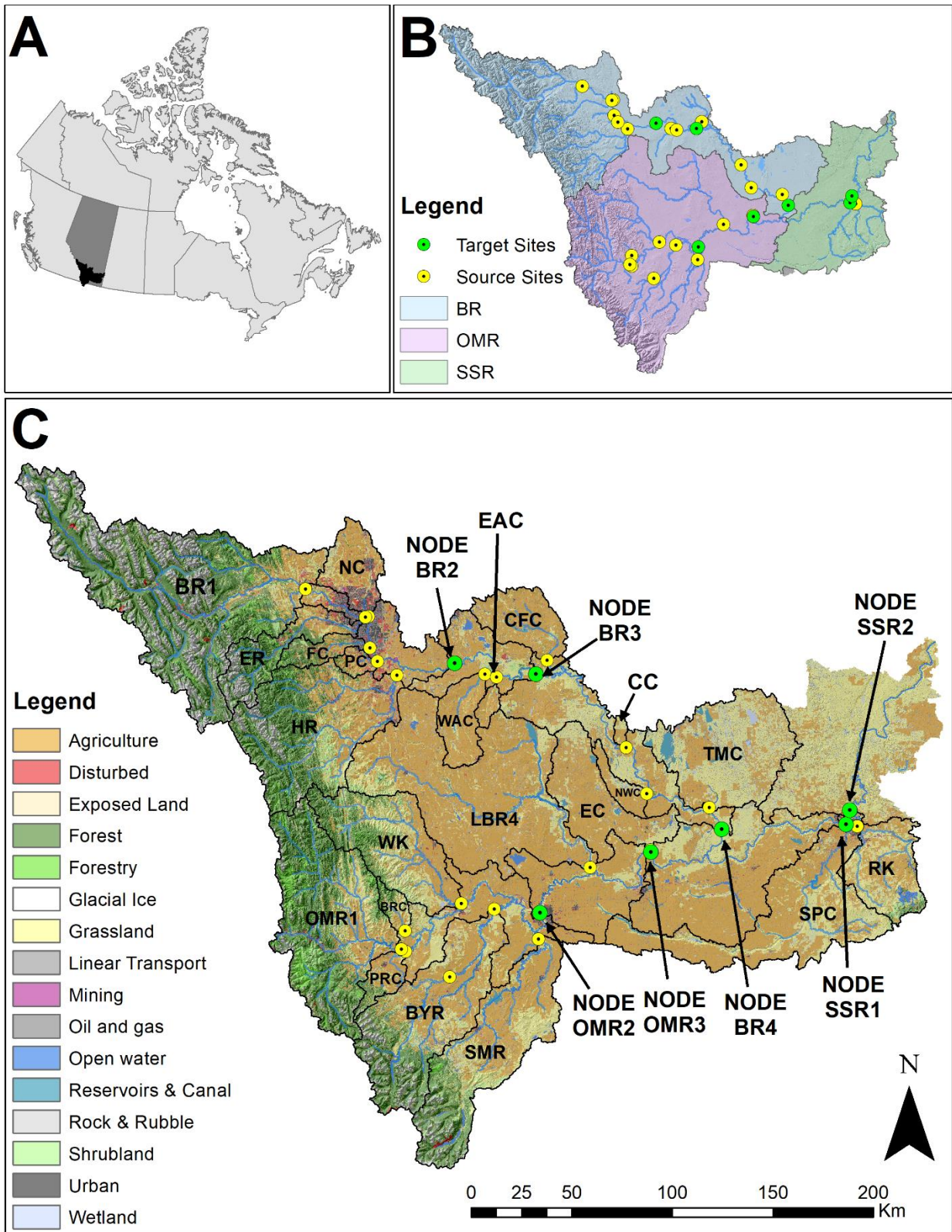


Figure 1: Location of the SSRB in Canada (inset A), the confluence of the Bow River (BR) and the Oldman Rivers (OMR) (inset B), along with the tributary and node sites / watersheds overlain on land use / land cover for the study region (C).

Table 1: Summary of sampling information for each site including site name, site identification (ID), basin, latitude, longitude, node information and the number of samples taken at each site including the ice-covered (November – March) and open-water (April – October) seasons.

Site Name	Basin	ID	Area (km2)	Latitude	Longitude	Mix	Node	<i>n samples</i>		
								Total	Ice	Open
Bow River @ Cochrane	BR	BR1	7543	51.1831	114.4871		1	33	12	21
Bow River D/S Carseland Dam	BR	BR2	15585	50.8306	113.4167	1	1	33	12	21
Elbow River	BR	ER	1240	51.0448	114.0419		1	33	12	21
Fish Creek	BR	FC	443	50.9052	114.0110		1	26	6	20
Highwood River	BR	HR	3948	50.7823	113.8259		1	32	12	20
Nose Creek	BR	NC	948	51.0464	114.0189		1	31	11	20
Pine Creek	BR	PC	210	50.8450	113.9619		1	27	7	20
Bow River @ Cluny	BR	BR3	17826	50.7731	112.8455	2	2	33	12	21
East Arrowwood Creek	BR	EAC	165	50.7647	113.1239		2	21	1	20
West Arrowwood Creek	BR	WAC	813	50.7792	113.2036		2	15	1	14
Bow River @ Ronalane Bridge	BR	BR4	24766	50.0478	111.4248	3	3	33	12	21
Coal Creek	BR	CC	76	50.4306	112.2278		3	21	1	20
Crowfoot Creek	BR	CFC	1068	50.8333	112.7611		3	21	1	20
New West Coulee	BR	NWC	352	50.2167	112.0208		3	21	1	20
Twelve Mile Creek	BR	TMC	2958	50.1500	111.6667		3	20	1	19
Beaver Creek	OMR	BRC	256	49.6393	113.7952		4	23	2	21
Belly River	OMR	BYR	3614	49.7275	113.1781		4	32	11	21
Oldman River @ Brocket	OMR	OMR1	4369	49.5586	113.8222		4	33	12	21
Oldman River U/S Lethbridge	OMR	OMR2	16800	49.7067	112.8629	4	4	32	11	21
Pincher Creek	OMR	PRC	425	49.5463	113.7945		4	28	8	20
St. Mary River	OMR	SMR	3440	49.5889	112.8806		4	31	10	21
Willow Creek	OMR	WK	2506	49.7572	113.4069		4	23	2	21
Little Bow River	OMR	LBR4	5890	49.9017	112.5067		5	32	11	21
Oldman River @ Taber	OMR	OMR3	24691	49.9611	112.0847	5	5	32	11	21
Expanse Coulee	OMR	EC	1859	49.9717	112.0833		6	23	2	21
Ross Creek	SSR	RK	1452	50.0311	110.6431		6	30	10	20
Seven Persons Creek	SSR	SPC	3473	50.0311	110.6439		7	30	10	20
SSR U/S Medicine Hat	SSR	SSR1	55345	50.0433	110.7222	6	7	33	12	21
SSR D/S Medicine Hat	SSR	SSR2	60330	50.1048	110.6911	7	7	30	10	20

Table 2: Results from the analysis of blank and duplicate samples for total recoverable metals in the SSRB including the field blank detection (detect) frequency, the potential environmental contamination, the 90-percent UCL for the percentage of inconsistent detects, and the mean confidence interval (M-CI) for the duplicate samples. Any variable with greater than 20% for the potential environmental contamination, the UCL of inconsistent detections or the M-CI was not selected for modelling which is denoted by the asterisks (*) beside the percentages.

Metal	Detection Frequency (%)	Pot. Env. Cont. (%)	90-percent UCL for % Inconsistent Detects	M-CI (%)	Modelled
Aluminum (Al)	88	9	2	21*	
Antimony (Sb)	20	1	2	6	Yes
Arsenic (As)	20	0	2	10	Yes
Barium (Ba)	40	0	2	3	Yes
Beryllium (Be)	2	4	20*	32*	
Bismuth (Bi)	7	12	28*	59*	
Boron (B)	40	0	2	4	Yes
Cadmium (Cd)	4	8	17	54*	
Calcium (Ca)	38	0	2	3	Yes
Chlorine (Cl)	57	21*	2	7	
Chromium (Cr)	21	2	19	40*	
Cobalt (Co)	20	4	2	21*	
Copper (Cu)	52	31*	2	18	
Iron (Fe)	52	4	2	15	Yes
Lead (Pb)	51	20*	2	23*	
Lithium (Li)	18	0	2	4	Yes
Manganese (Mn)	41	0	2	11	Yes
Molybdenum(Mo)	54	0	2	5	Yes
Nickel (Ni)	42	5	3	28*	
Selenium (Se)	5	2	3	23*	
Silver (Ag)	10	4	17	81*	
Strontium (Sr)	37	0	2	3	Yes
Thallium (Tl)	11	8	3	45*	
Thorium (Th)	19	7	4	41*	
Tin (Sn)	36	2	12	52*	
Titanium (Ti)	46	14	2	21*	
Uranium (U)	9	0	2	3	Yes
Vanadium (V)	28	6	2	15	Yes
Zinc (Zn)	63	37*	2	33*	

* Indicates percentage greater than 20 resulting in these metals not being modelled

Table 3: Metals that passed the conservative bracket/range test for each of the seven nodes in the SSRB and for each of the three different modelling scenarios (i.e. all samples, the open season and the ice season). Metal abbreviations are provided in Table 2 or the periodic table.

Type	Node 1 - BR2			Node 2 - BR3			Node 3 - BR4			Node 4 - OMR2			Node 5 - OMR3			Node 6 - SSR1			Node 7 - SSR2		
	All	Open	Ice	All	Open	Ice	All	Open	Ice	All	Open	Ice	All	Open	Ice	All	Open	Ice	All	Open	Ice
Total R. Metals	As	As	As	As	As	As	B	As	B	As	As	As	As	As	As	As	B	As	As	As	B
	B	B	B	B	B	B	Ca	B	Ba	B	B	B	B	Ba	B	B	Ca	B	B	B	Ba
	Ba	Ba	Ba	Li	Ba	Ca	Li	Ba	Ca	Ba	Ba	Ba	Ba	Ca	Ba	Ca	Li	Ba	Ba	Ba	Ca
	Ca	Ca	Ca	Sb	Fe	Fe	Mo	Li	Li	Ca	Ca	Ca	Ca	Mo	Ca	Li	Mo	Ca	Ca	Ca	Mo
	Fe	Fe	Fe	U	Li	Li	Sb	Mn	Mn	Fe	Fe	Fe	Li	Sb	Fe	Mn	Sb	Fe	Fe	Fe	Sb
	Li	Li	Li		Mn	Mo	Sr	Mo	Mo	Li	Li	Li	Mo	Sr	Li	Mo	Sr	Li	Li	Li	Sr
	Mn	Mn	Mn		Sb	Sb	U	Sb	Sb	Mn	Mn	Mn	Sb		Mn	Sb		Mn	Mn	Mn	U
	Mo	Mo	Mo		Sr	Sr		Sr	Sr	Mo	Mo	Mo	Sr		Mo	Sr		Mo	Mo	Mo	V
	Sb	Sb	Sb		U	U		U	U	Sb	Sb	Sb	U		Sb	U		Sr	Sb	Sb	
	Sr	Sr	Sr		V	V		V		Sr	Sr	Sr			Sr			U	Sr	Sr	
	U	U	U							U	U	U			U			V	U	U	
	V	V	V							V	V	V			V			V	V	V	
	Dissolved Metals	As	As	As	As	As	As	B	As	As	As	As	As	As	As	As	As	As	As	As	As
B		B	B	B	Ba	B	Ba	B	B	B	B	B	B	B	B	B	B	B	B	B	B
Ba		Ba	Ba	Cl	Li	Cl	Ca	Ba	Ba	Ba	Ba	Ba	Ba	Ba	Ba	Ba	Ba	Ba	Ba	Ba	Ba
Ca		Ca	Ca	Li	V	Li	Li	Ca	Ca	Ca	Ca	Ca	Ca	Cl	Ca	Ca	Ca	Ca	Ca	Ca	Ca
Cl		Cl	Cl	Sb		Sb	Mo	Li	Li	Cl	Cl	Cl	Li	Li	Li	Cl	Cl	Cl	Li	Li	Li
Li		Li	Li	U		U	Sb	Mo	Mo	Li	Li	Li	Mo	Mo	Mo	Li	Li	Li	Mo	Mo	Mo
Mo		Mo	Mo	V		V	Sr	Sb	Sb	Mo	Mo	Mo	Sb	Sb	Sb	Mo	Mo	Mo	Sb	Sb	Sb
Sb		Sb	Sb				U	Sr	Sr	Sb	Sb	Sb	Sr	Sr	Sr	Sb	Sb	Sb	Sr	Sr	Sr
Sr		Sr	Sr					U		Sr	Sr	Sr	U	U	U	Sr	Sr	Sr	U	V	U
U		U	U							U	U	U	V	V	V	U	U	U	V		V
V		V	V							V	V	V			V	V	V	V	V	V	

Table 4: Results from the analysis for blank and duplicate samples for dissolved metals the SSRB including the field blank detection (detect) frequency, the potential environmental contamination, the 90-percent UCL for the percentage of inconsistent detects, and the mean confidence interval (M-CI) for the duplicate samples. Any variable with greater than 20% for the potential environmental contamination, the UCL of inconsistent detections or the M-CI was not selected for modelling which is denoted by the asterisks (*) beside the percentages.

Metal	Detection Frequency (%)	Pot. Env. Cont. (%)	90-percent UCL for % Inconsistent Detects	M-CI (%)	Modelled
Aluminum (Al)	58	28*	5	38*	
Antimony (Sb)	0	0	3	8	Yes
Arsenic (As)	17	0	2	10	Yes
Barium (Ba)	2	0	2	2	Yes
Beryllium (Be)	2	3	94*	9	
Bismuth (Bi)	0	0	92*	38*	
Boron (B)	35	0	2	4	Yes
Cadmium (Cd)	2	3	11	47*	
Calcium (Ca)	0	0	2	4	Yes
Chlorine (Cl)	30	14	3	9	Yes
Chromium (Cr)	0	0	55*	111*	
Cobalt (Co)	6	0	4	32*	
Copper (Cu)	24	20*	2	14	
Iron (Fe)	26	0	9	42*	
Lead (Pb)	13	2	20*	58*	
Lithium (Li)	17	0	2	4	Yes
Manganese (Mn)	41	2	2	35*	
Molybdenum (Mo)	27	0	2	4	Yes
Nickel (Ni)	32	2	3	30*	
Selenium (Se)	3	0	5	24*	
Silver (Ag)	7	0	40*	91*	
Strontium (Sr)	3	0	2	3	Yes
Thallium (Tl)	16	0	12	45*	
Thorium (Th)	19	6	19	56*	
Tin (Sn)	27	0	18	51*	
Titanium (Ti)	38	21*	3	18*	
Uranium (U)	7	0	2	3	Yes
Vanadium (V)	4	1	2	18	Yes
Zinc (Zn)	41	9	9	42*	

* Indicates percentage greater than 20 resulting in these metals not being modelled

Table 5: The dissolved to total recoverable ratio (DTR) for all analyzed metals across a range of total suspended solids concentrations (Low TSS: <50 mg/L, Medium TSS: 50-100 mg/L, High TSS (100-1000 mg/L) and very high TSS (>1000 mg/L). For example, Ag for all samples has a DTR of 51% indicating that half of the material in the total recoverable ratio is in dissolved form.

Metal	n	All DTR (%)	n Low TSS	Low TSS DTR (%)	n Medium TSS	Medium TSS DTR (%)	n High TSS	High TSS DTR (%)	n Very High TSS	Very High TSS DTR (%)
Ag	229	51	188	59	16	19	23	11	2	3
Al	816	6	725	7	42	1	45	0	4	0
As*	848	80	756	84	43	64	45	38	4	12
B*	848	95	756	96	43	96	45	90	4	70
Ba*	848	89	756	92	43	74	45	57	4	11
Be	49	54	39	64	4	18	5	16	1	1
Bi	100	81	88	86	7	45	4	52	1	3
Ca*	848	98	756	99	43	97	45	85	4	33
Cd	604	50	515	55	42	21	43	12	4	2
Cl	844	97	754	97	43	98	43	97	4	97
Co	780	48	689	53	42	18	45	8	4	1
Cr	232	61	206	67	14	17	11	12	1	1
Cu	847	72	755	77	43	40	45	27	4	6
Fe*	725	8	639	9	40	2	42	1	4	0
Li*	848	94	756	96	43	90	45	70	4	32
Mn*	844	16	752	18	43	6	45	2	4	0
Mo*	848	98	756	98	43	98	45	100	4	99
Ni	813	67	723	71	42	51	44	30	4	7
Pb	501	20	437	22	29	4	31	2	4	0
Sb*	720	96	636	97	41	97	39	87	4	93
Se	835	90	747	91	43	85	41	81	4	45
Sn	321	81	283	83	17	69	20	64	1	100
Sr*	848	96	756	97	43	96	45	89	4	57
Th	641	39	559	44	37	14	41	5	4	1
Ti	821	25	731	27	41	9	45	5	4	5
Tl	779	64	694	70	37	24	44	18	4	6
U*	848	95	756	97	43	93	45	79	4	50
V*	847	49	755	53	43	23	45	10	4	3
Zn	794	48	710	52	40	13	40	9	4	1

* indicates metals may have been selected in the modelling of total recoverable metals

Table 6: D-con model results including the mean (M) and standard deviation (SD) of the 22 tributary site contributions to total and dissolved material sampled at outlet node sample SSR2 including the mean contribution ratio (MCR).

Site	Total - All samples			Dissolved - All samples			Total – Ice-covered			Dissolved – Ice-covered			Total - Open Water			Dissolved - Open Water		
	M	SD	MCR	M	SD	MCR	M	SD	MCR	M	SD	MCR	M	SD	MCR	M	SD	MCR
BR1	27%	8%	1.68	31%	6%	1.92	31%	8%	1.94	29%	7%	1.78	11%	7%	0.69	22%	8%	1.38
ER	1%	1%	0.38	1%	1%	0.53	4%	4%	1.52	4%	4%	1.48	0%	1%	0.15	1%	1%	0.46
FC	1%	1%	0.64	1%	1%	0.64	1%	1%	1.49	1%	1%	1.28	0%	0%	0.32	1%	1%	0.53
HR	6%	3%	0.72	5%	3%	0.62	7%	5%	0.86	6%	5%	0.73	2%	2%	0.19	3%	2%	0.33
NC	2%	1%	0.99	1%	1%	0.65	3%	2%	1.34	2%	1%	0.84	1%	1%	0.40	1%	1%	0.40
PC	1%	1%	1.12	1%	1%	2.46	2%	2%	4.93	2%	2%	4.26	0%	0%	0.67	1%	1%	1.57
EAC	0%	0%	0.86	0%	0%	0.86	1%	1%	3.42	1%	1%	3.14	0%	0%	1.14	1%	1%	2.00
WAC	0%	0%	0.17	0%	0%	0.12	1%	1%	0.75	1%	1%	0.46	0%	0%	0.12	0%	0%	0.23
CC	2%	1%	9.85	2%	2%	12.3	4%	3%	24.0	3%	3%	17.9	1%	1%	6.16	2%	2%	10.5
CFC	3%	2%	1.50	2%	1%	0.75	2%	2%	1.01	2%	2%	0.84	2%	2%	1.01	1%	1%	0.62
NWC	7%	4%	9.22	5%	3%	6.41	7%	6%	9.75	5%	4%	6.14	3%	3%	3.74	3%	2%	3.61
TMC	4%	3%	0.62	3%	2%	0.51	4%	4%	0.70	3%	2%	0.45	3%	3%	0.41	3%	2%	0.43
BRC	1%	1%	0.92	1%	1%	1.10	0%	1%	0.74	0%	0%	0.74	1%	1%	2.02	1%	1%	1.84
BYR1	9%	5%	1.22	15%	5%	1.94	9%	6%	1.18	16%	7%	2.02	12%	5%	1.50	16%	8%	2.04
OMR1	12%	5%	1.28	14%	5%	1.55	5%	4%	0.48	10%	5%	1.02	18%	6%	1.97	21%	7%	2.22
PC1	2%	2%	2.65	3%	2%	2.88	2%	2%	1.66	2%	2%	2.54	4%	3%	3.98	2%	2%	2.32
SMR	8%	4%	1.11	5%	4%	0.70	2%	2%	0.30	2%	2%	0.31	14%	6%	1.85	9%	6%	1.27
WK	1%	1%	0.23	1%	1%	0.13	1%	1%	0.11	1%	1%	0.11	2%	2%	0.41	1%	1%	0.23
LBR	9%	4%	0.71	7%	3%	0.53	1%	1%	0.09	2%	2%	0.16	20%	7%	1.61	9%	4%	0.68
EC	2%	1%	0.51	1%	1%	0.15	3%	2%	0.73	1%	1%	0.30	3%	2%	0.73	1%	1%	0.23
RK	1%	1%	0.29	1%	1%	0.26	4%	3%	1.26	4%	3%	1.26	1%	1%	0.42	1%	1%	0.45
SPC	1%	1%	0.18	1%	1%	0.12	5%	4%	0.61	5%	4%	0.65	2%	2%	0.26	2%	1%	0.20

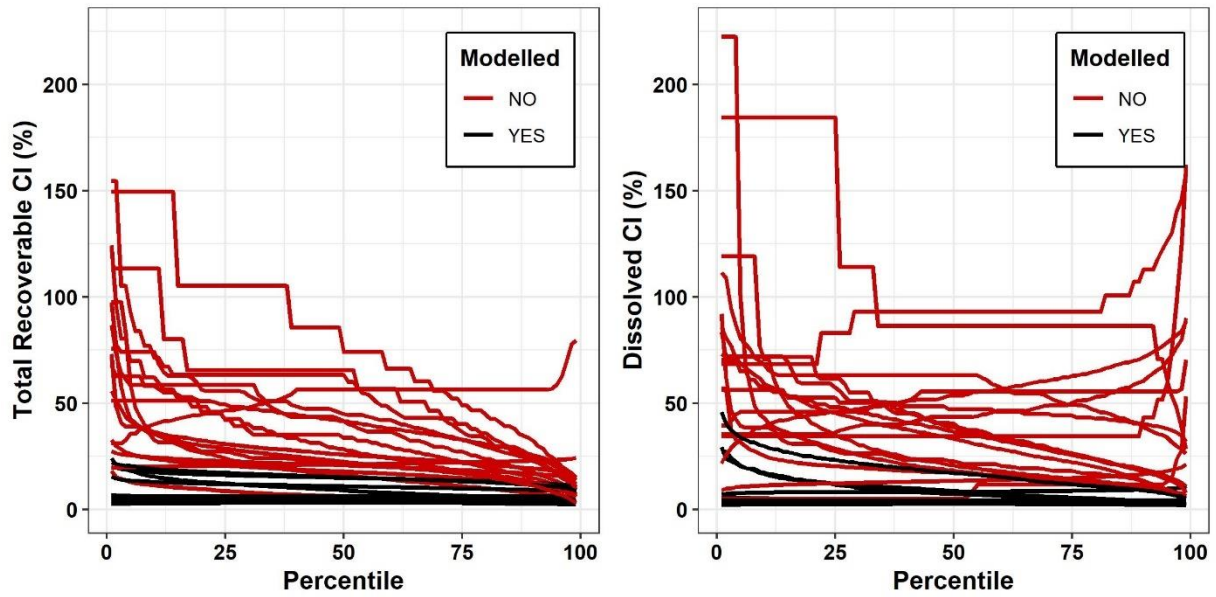
Table 7: Mean monthly discharge for the open water and ice-covered seasons from the closest available gauging station operated by the Water Survey of Canada with an area ratio (AR) maximum between the gauging station and the sampling site of 11%.

Site Name	ID	Gauge Stations		n samples (1998-2018)		Discharge (in million m ³ per month)	
		ID	AR (%)	Open	Ice	Open	Ice
Bow River @ Cochrane	BR1	05BH005	2	374	71	312	--
Bow River D/S Carseland Dam	BR2	05BM002	0	611	6	357	--
Elbow River	ER	05BJ001	0	581	575	30	7
Fish Creek	FC	--	--	--	--	--	--
Highwood River	HR	05BL024	0	581	575	86	11
Nose Creek	NC	--	--	--	--	--	--
Pine Creek	PC	--	--	--	--	--	--
Bow River @ Cluny	BR3	--	--	--	--	--	--
East Arrowwood Creek	EAC	--	--	--	--	--	--
West Arrowwood Creek	WAC	05BM014	4	581	229	1	--
Bow River @ Ronalane Bridge	BR4	05BN012	2	642	635	298	164
Coal Creek	CC	--	--	--	--	--	--
Crowfoot Creek	CFC	05BM008	3	642	133	5	--
New West Coulee	NWC	05BN006	10	642	5	3	--
Twelve Mile Creek	TMC	05BN002	6	556	2	5	--
Beaver Creek	BRC	05AB013	0	611	126	1	--
Belly River	BYR	05AD934	1	316	56	77	--
Oldman River @ Brocket	OMR1	05AA024	1	581	575	147	32
Oldman River U/S Lethbridge	OMR2	05AD007	1	642	635	249	72
Pincher Creek	PCR	--	--	--	--	--	--
St. Mary River	SMR	05AE006	2	581	575	47	15
Willow Creek	WK	05AB046	0	590	124	18	--
Little Bow River	LBR4	05AC023	0	555	1	8	--
Oldman River @ Taber	OMR3	05AG006	11	642	635	265	78
Expanse Coulee	EC	05AG003	1	555	1	2	--
Ross Creek	RK	--	--	--	--	--	--
Seven Persons Creek	SPC	05AH005	8	642	252	3	--
SSR U/S Medicine Hat	SSR1	--	--	--	--	--	--
SSR D/S Medicine Hat	SSR2	05AJ001	7	642	635	570	244

Table 8: Land use and topography of the sampling sites in the SSRB basin including the percent slope greater and less than 10%, land use (i.e. human footprint) and land cover for areas without a human footprint, with short forms in the table including agriculture (Ag.), oil and gas (O&G), and linear transportation (L. Trans) .

Site Name	ID	Slope (%)		Land Use (%)							Natural Land Cover (%)						
		<10	>10	Ag.	Forestry	Mining	O&G	L.Trans.	Urban	Wetland	Water	Ice	Rock	Exposed	Shurb	Grass	Forest
Bow River @ Cochrane	BR1	26	74	4	2	0	0	1	1	0	3	1	27	0.1	7	8	45
Bow River D/S Carseland Dam	BR2	43	57	16	2	0	0	3	5	1	2	1	16	0.1	7	10	37
Elbow River	ER	41	59	12	3	0	0	4	6	0	2	0	19	0.1	5	8	42
Fish Creek	FC	66	34	24	3	0	0	6	8	0	1	0	0	0.0	4	8	44
Highwood River	HR	42	58	21	2	0	0	2	3	1	1	0	6	0.1	10	13	41
Nose Creek	NC	94	6	48	0	1	0	10	19	2	1	0	0	0.0	0	17	1
Pine Creek	PC	75	25	46	0	0	0	8	14	3	1	0	0	0.1	2	12	12
Bow River @ Cluny	BR3	50	50	22	2	0	0	3	5	1	2	1	14	0.1	6	11	32
East Arrowwood Creek	EAC	97	3	79	0	0	1	3	1	3	0	0	0	0.0	3	10	0
West Arrowwood Creek	WAC	99	1	82	0	0	1	3	1	2	0	0	0	0.0	1	9	0
Bow River @ Ronalane Bridge	BR4	63	37	28	1	0	1	3	4	2	3	0	10	0.1	4	19	23
Coal Creek	CC	100	0	55	0	0	3	2	1	3	0	0	0	0.0	0	35	0
Crowfoot Creek	CFC	97	3	78	0	0	2	3	1	2	1	0	0	0.2	1	10	1
New West Coulee	NWC	100	0	71	0	0	1	3	1	7	1	0	0	0.0	0	15	1
Twelve Mile Creek	TMC	99	1	26	0	0	7	3	1	7	5	0	0	0.1	0	50	0
Beaver Creek	BRC	34	66	17	5	0	0	1	0	2	0	0	0	0.1	9	42	22
Belly River	BYR	67	33	36	0	0	0	2	1	3	4	0	7	1.1	6	21	20
Oldman River @ Brocket	OMR1	25	75	9	9	0	0	1	1	1	1	0	5	0.2	13	16	43
Oldman River U/S Lethbridge	OMR2	56	44	30	3	0	0	2	1	2	3	0	4	0.6	8	23	23
Pincher Creek	PRC	72	28	45	1	0	0	3	3	3	1	0	2	0.1	5	19	18
St. Mary River	SMR	65	35	35	1	0	0	2	1	2	4	0	4	1.3	7	26	17
Willow Creek	WK	51	49	26	1	0	0	2	1	2	1	0	0	0.1	11	35	20
Little Bow River	LBR	95	5	72	0	0	1	3	1	4	2	0	0	0.2	1	15	0
Oldman River @ Taber	OMR3	68	32	44	2	0	0	2	2	2	3	0	3	0.5	6	20	16
Expanse Coulee	EC	100	0	68	0	0	2	3	1	4	3	0	0	0.0	0	19	0
Ross Creek	RK	86	14	37	0	0	1	2	2	2	4	0	0	0.1	3	43	5
Seven Persons Creek	SPC	94	6	59	0	0	1	2	2	3	2	0	0	0.2	0	31	0
SSR U/S Medicine Hat	SSR1	69	31	39	1	0	1	3	3	2	3	0	6	0.3	5	20	17
SSR D/S Medicine Hat	SSR2	71	29	40	1	0	1	3	2	2	3	0	5	0.3	4	21	16

Figure 2: The confidence interval (CI) (i.e. +/- 150%) for total recoverable metals (left) and dissolved metals (right) that were modelled (black) or were not modelled (red) based on the analyses of the duplicate quality control samples for all percentiles of environmental data sampled by the Calgary field office.



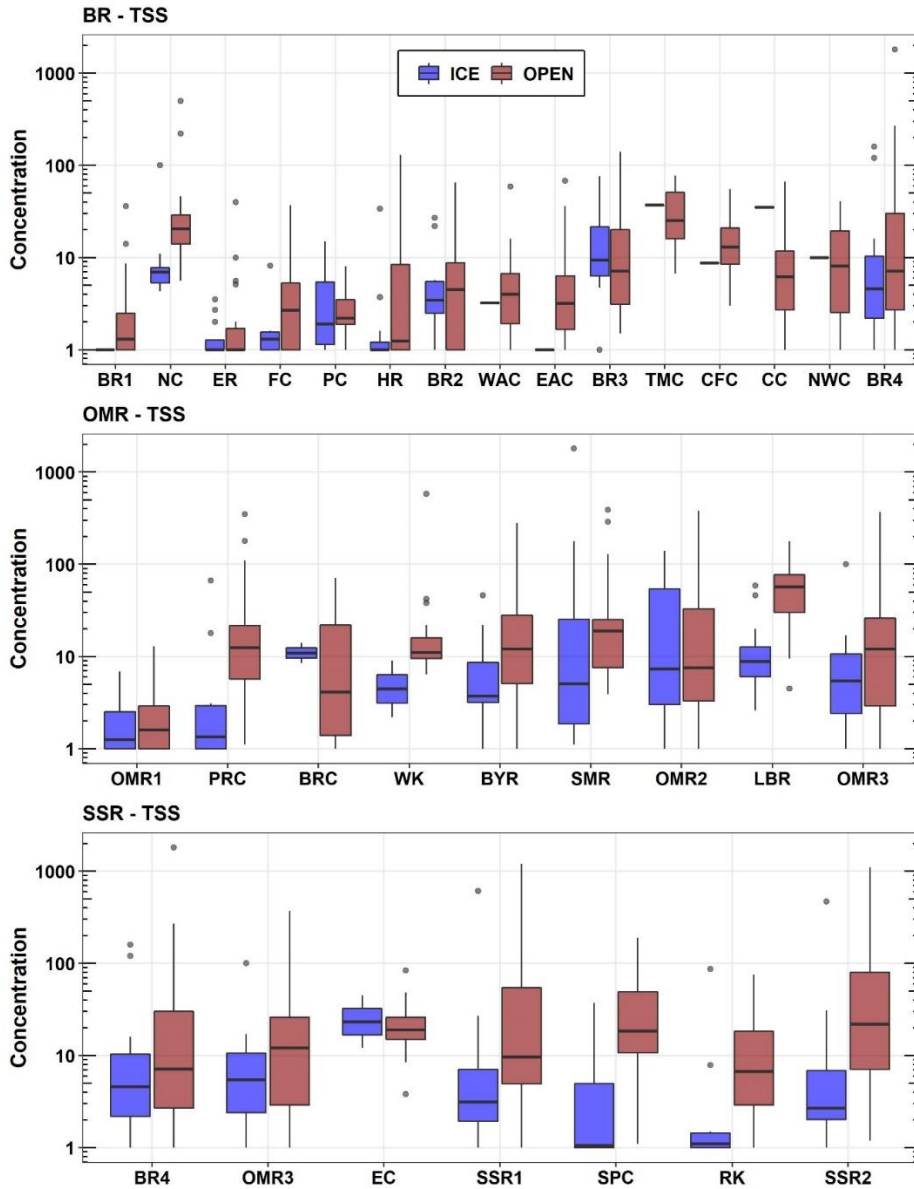


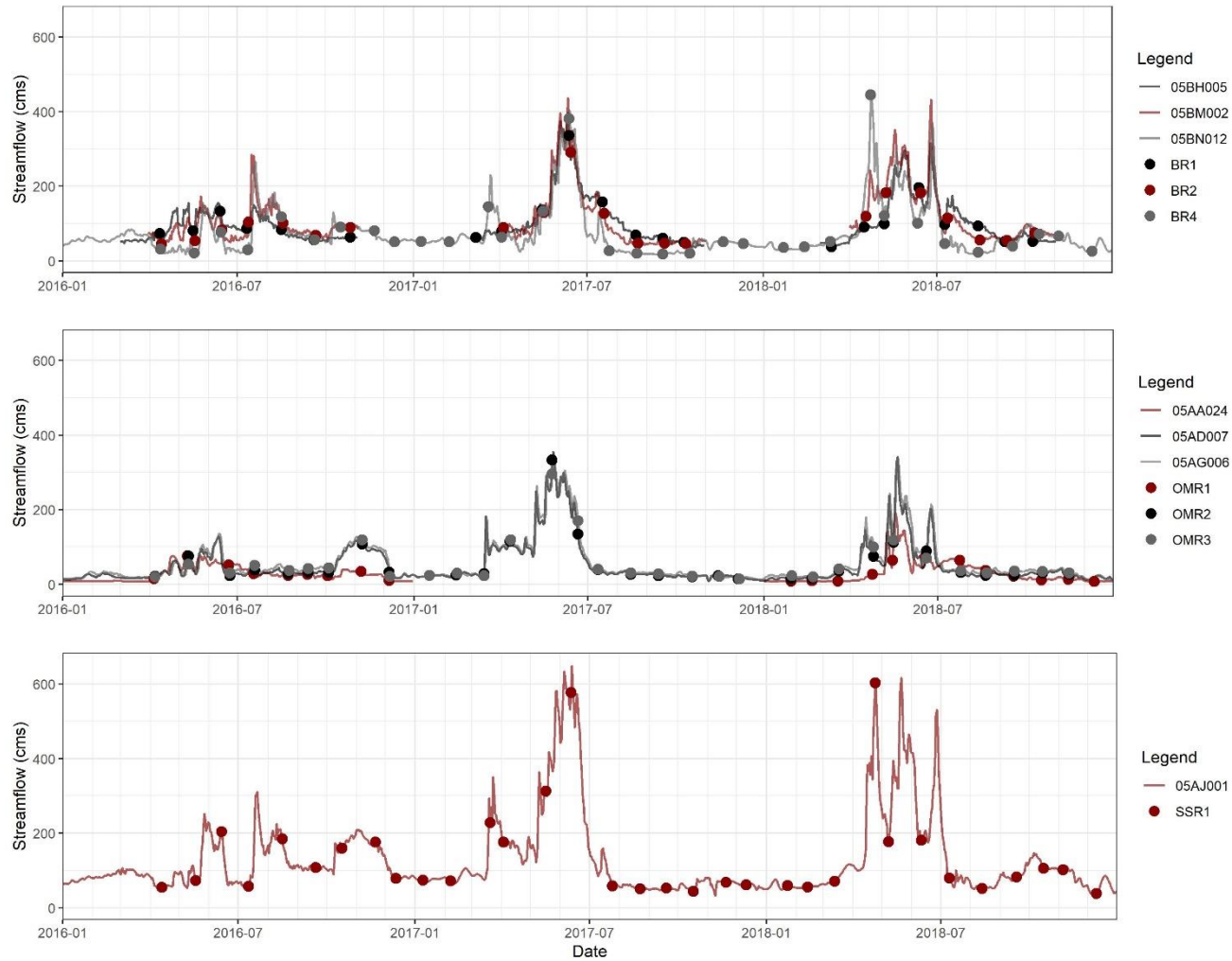
Figure 3: Total suspended sediment (TSS) concentrations for the Bow (BR), Oldman (OMR) and South Saskatchewan River (SSR) systems for the ice-covered (blue – November to March) and open water (red – April to October) seasons. Of note it is often not possible to sample all sites in the winter.

0

1 **Supplementary Information**

2

Figure S1: Discharge in cubic metres per second (cms) for mainstem sites where streamflow data was available streamflow for the sampling dates.



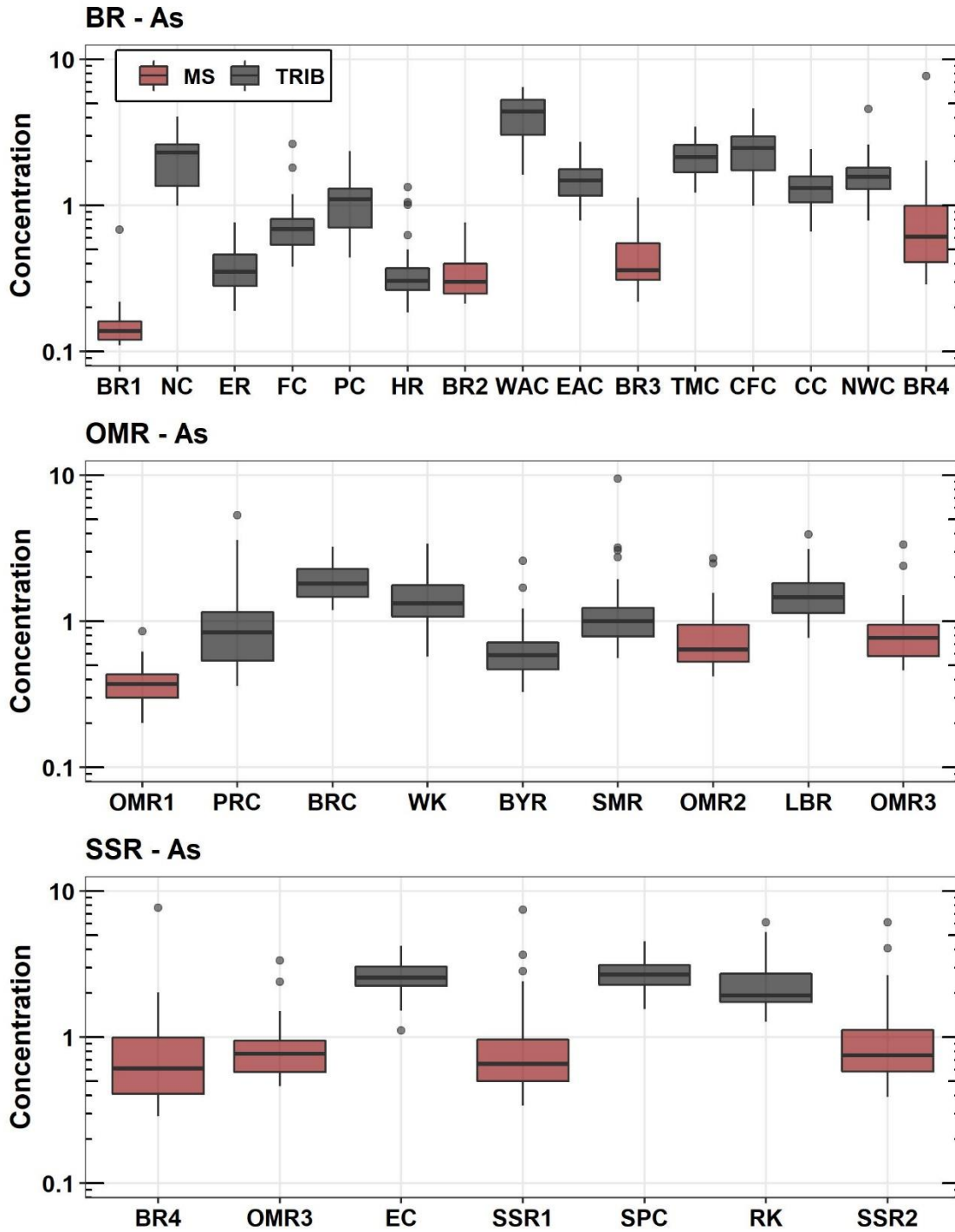


Figure S2: Box plots of the modelled total recoverable Arsenic (As) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

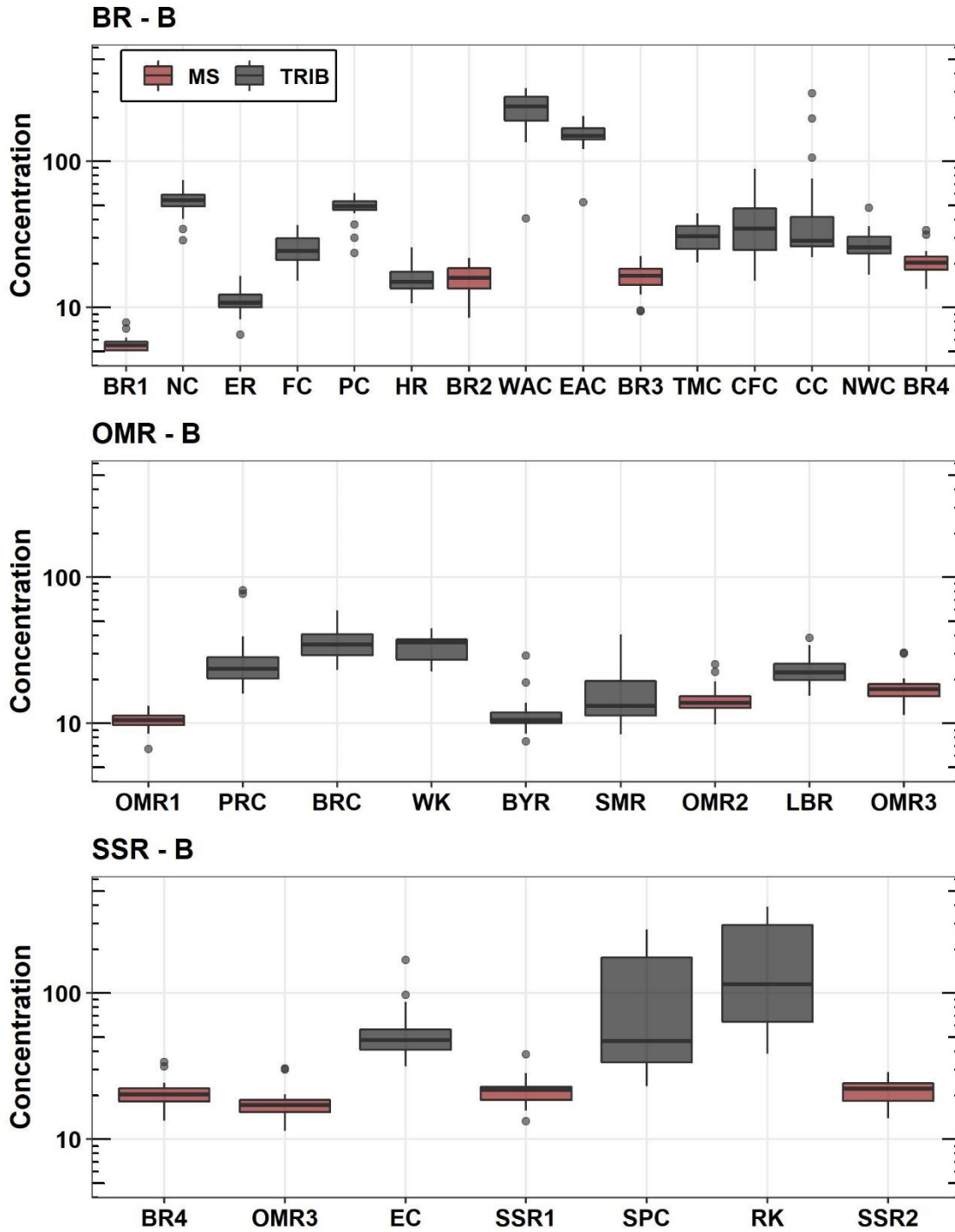


Figure S3: Box plots of the modelled total recoverable Boron (B) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red)) and tributary (TRIB – grey) sites for all annual samples.

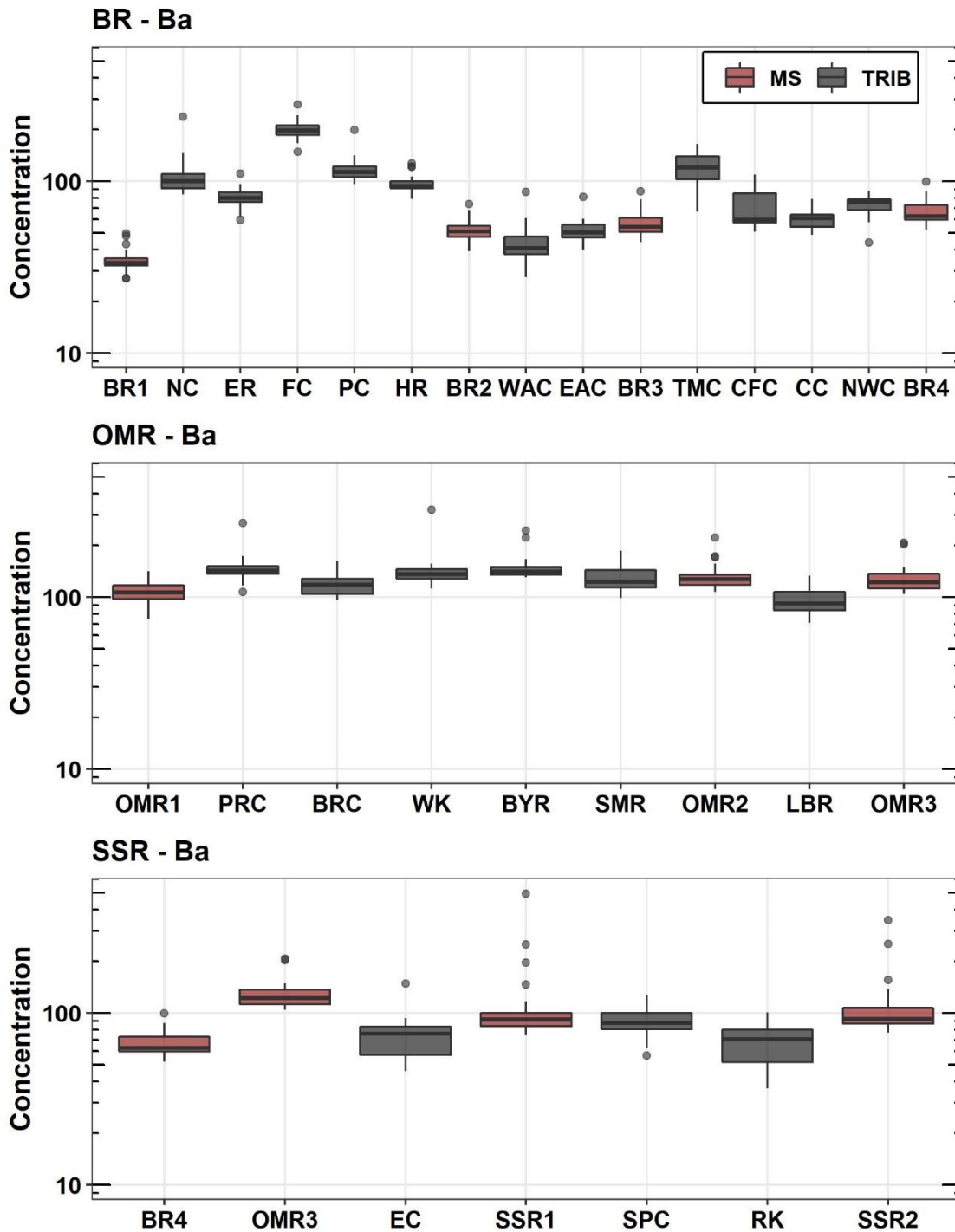


Figure S4: Box plots of the modelled total recoverable Barium (Ba) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

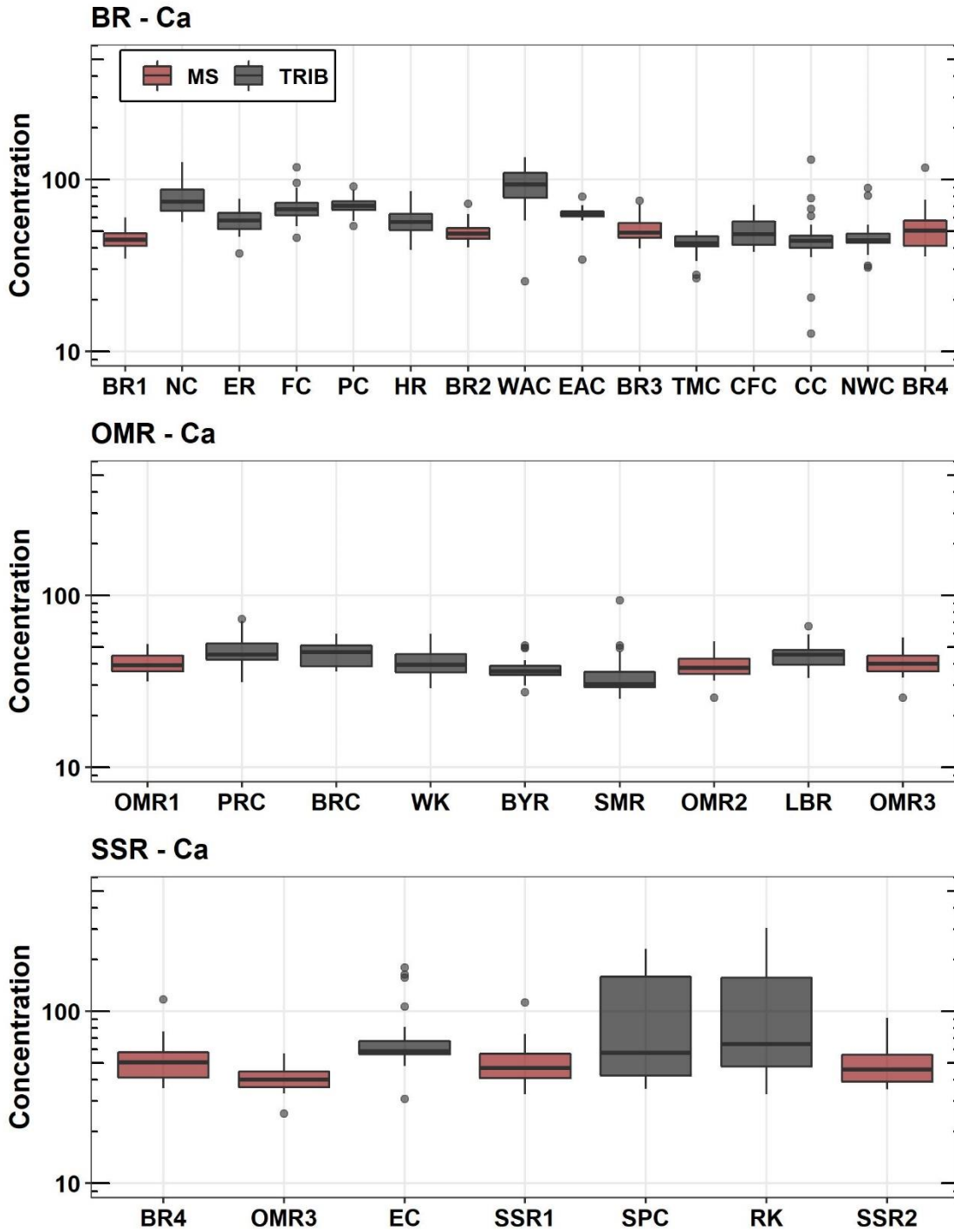


Figure S5: Box plots of the modelled total recoverable Calcium (Ca) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

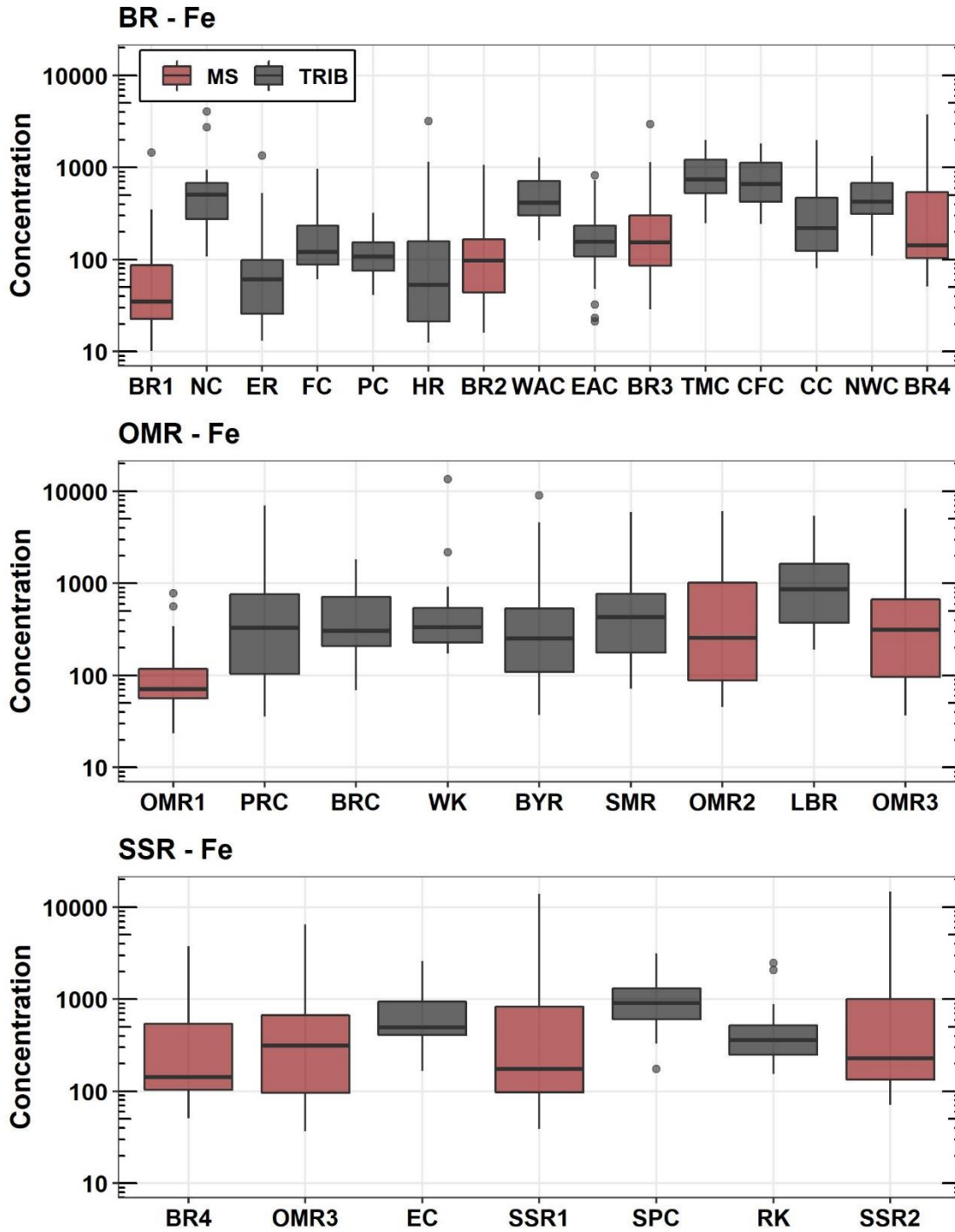


Figure S6: Box plots of the modelled total recoverable Iron (Fe) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red)) and tributary (TRIB – grey) sites for all annual samples.

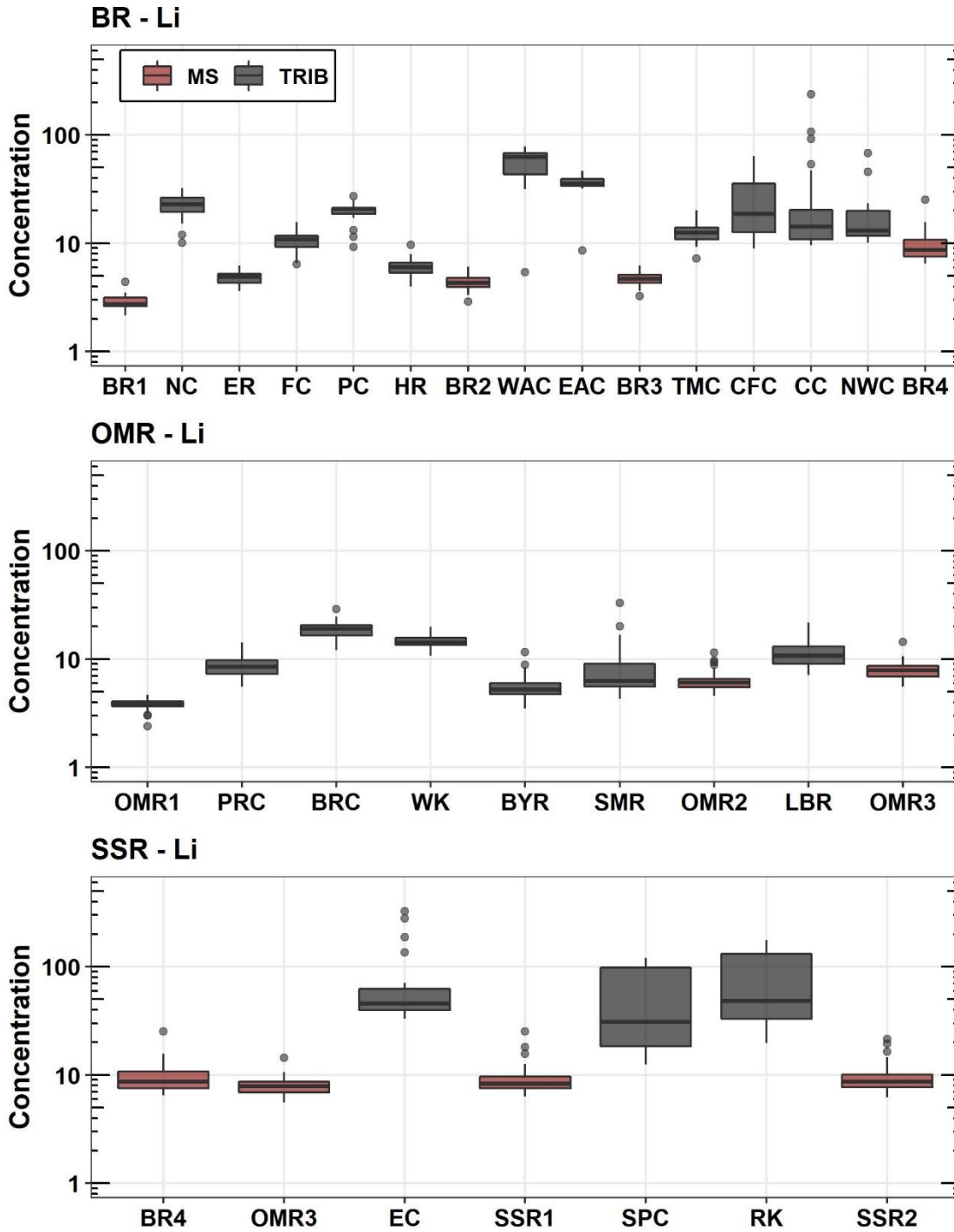


Figure S7: Box plots of the modelled total recoverable Lithium (Li) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

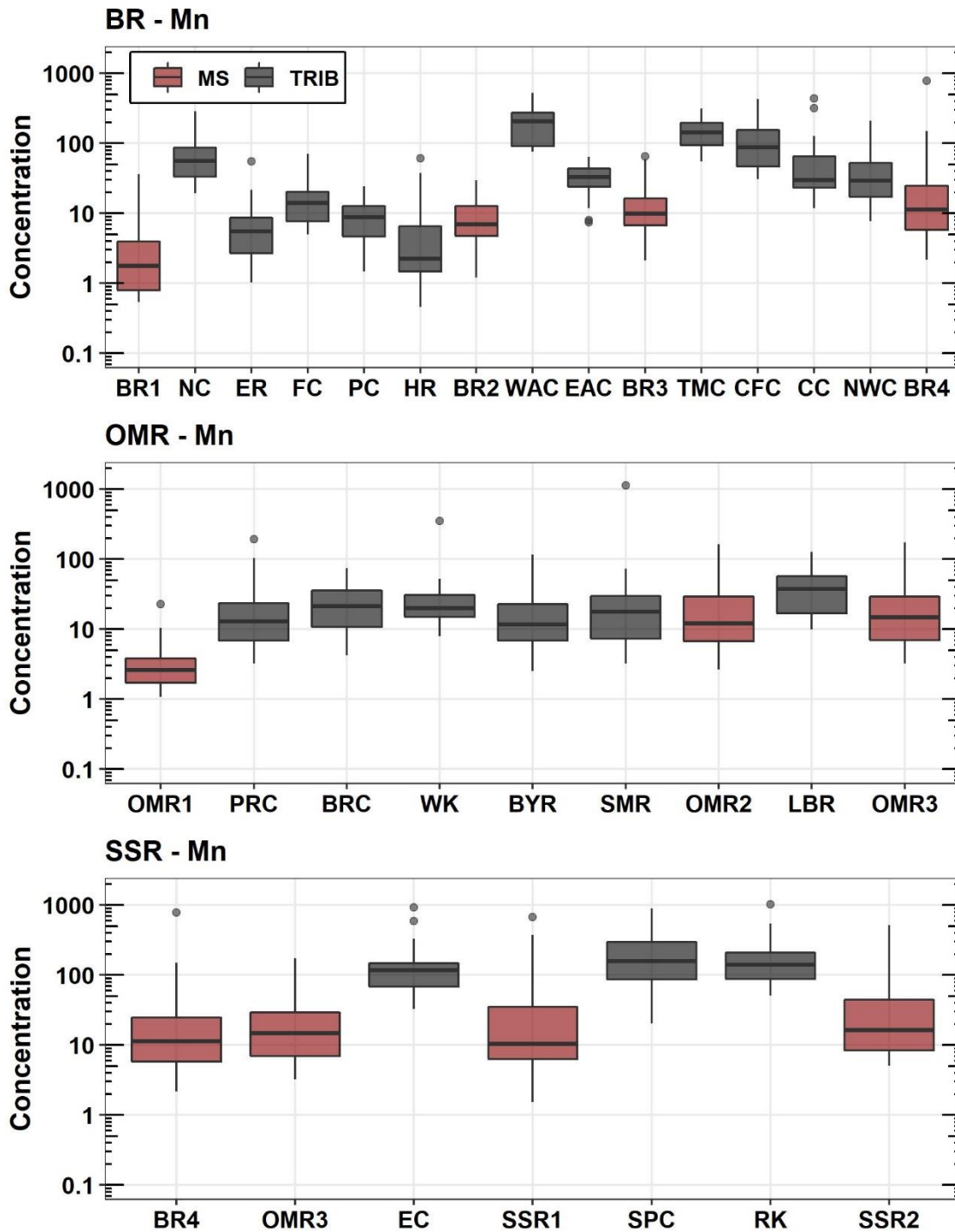


Figure S8: Box plots of the modelled total recoverable Manganese (Mn) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

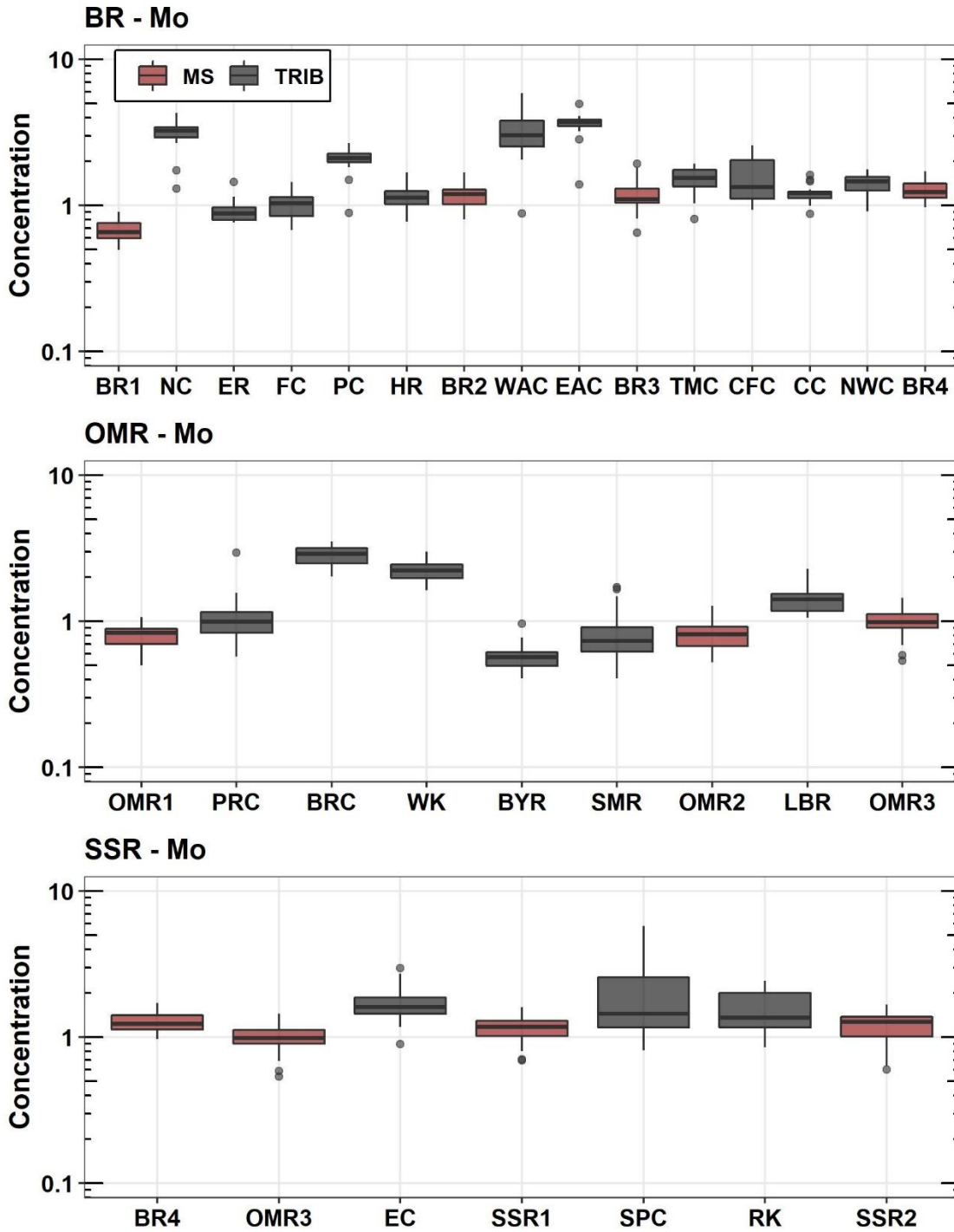


Figure S9: Box plots of the modelled total recoverable Molybdenum (Mo) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red)) and tributary (TRIB – grey) sites for all annual samples.

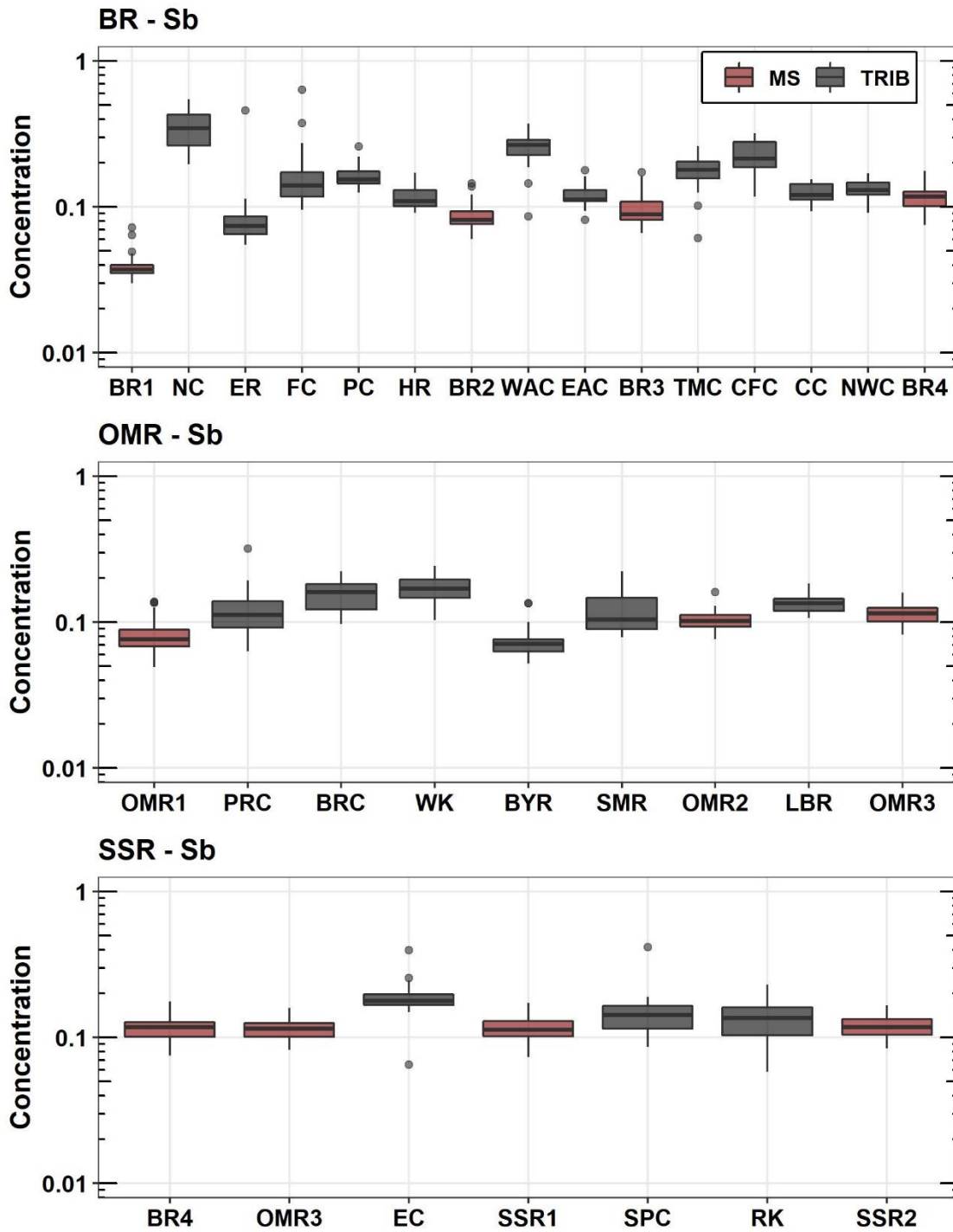


Figure S10: Box plots of the modelled total recoverable Antimony (Sb) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

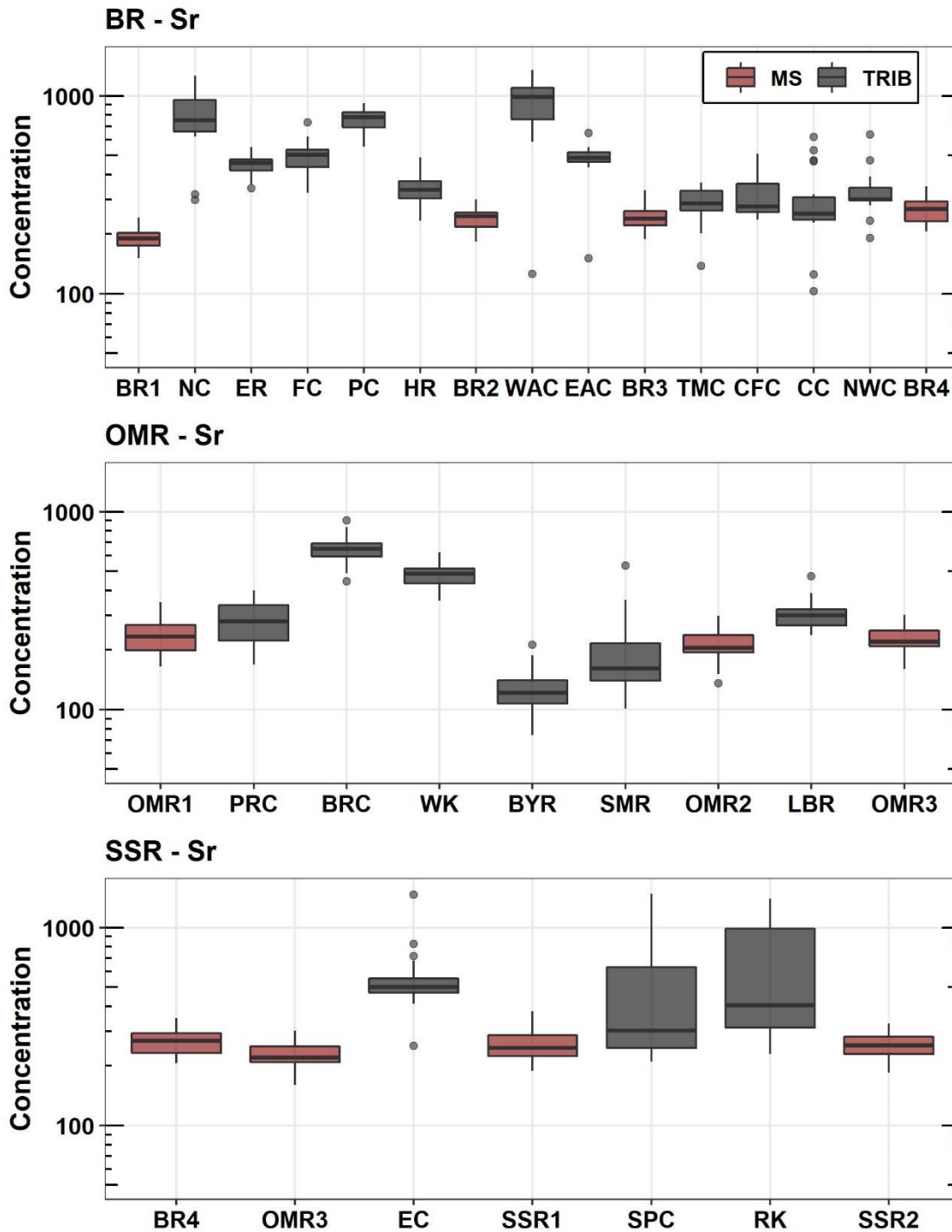


Figure S11: Box plots of the modelled total recoverable Strontium (Sr) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

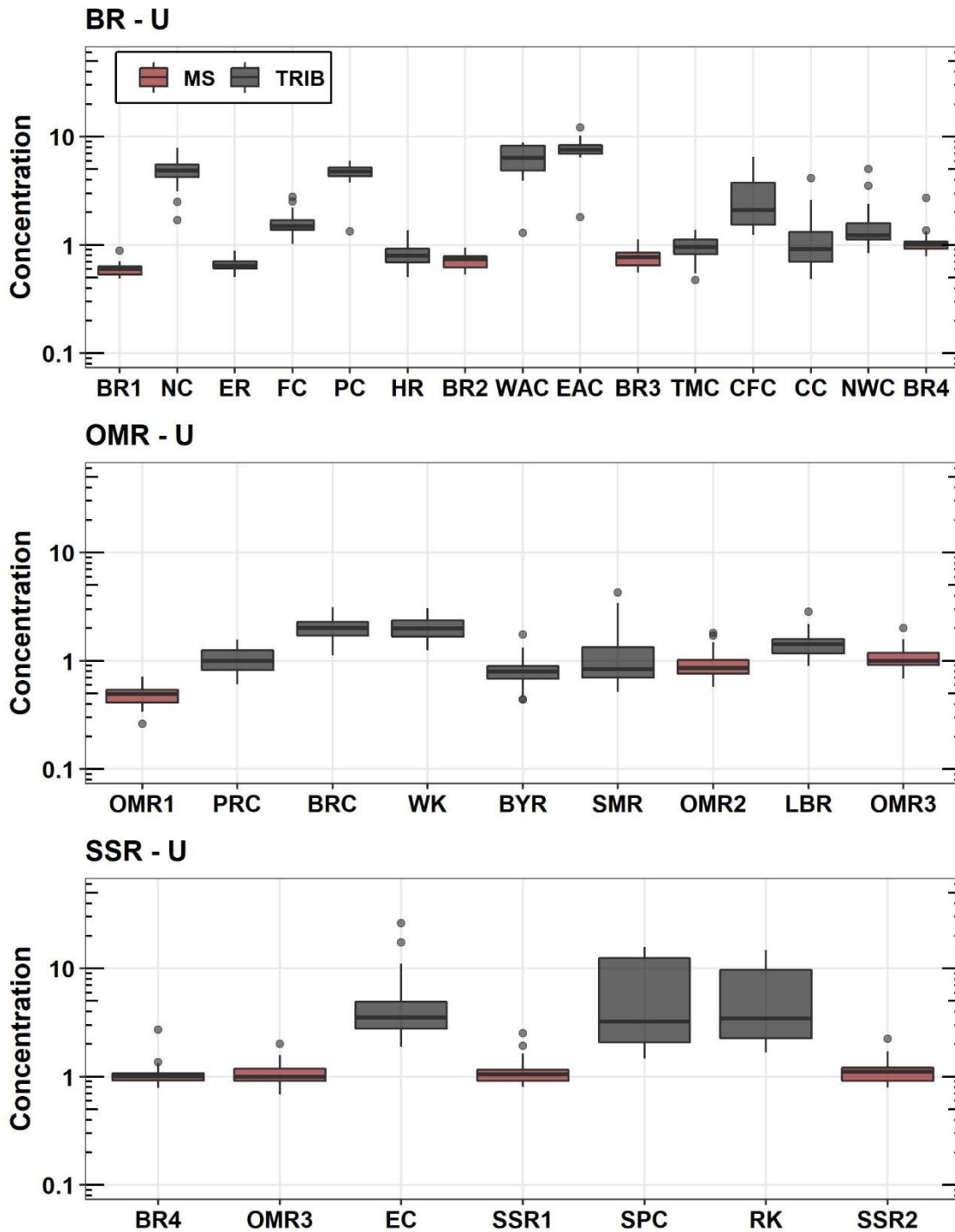


Figure S12: Box plots of the modelled total recoverable Uranium (U) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

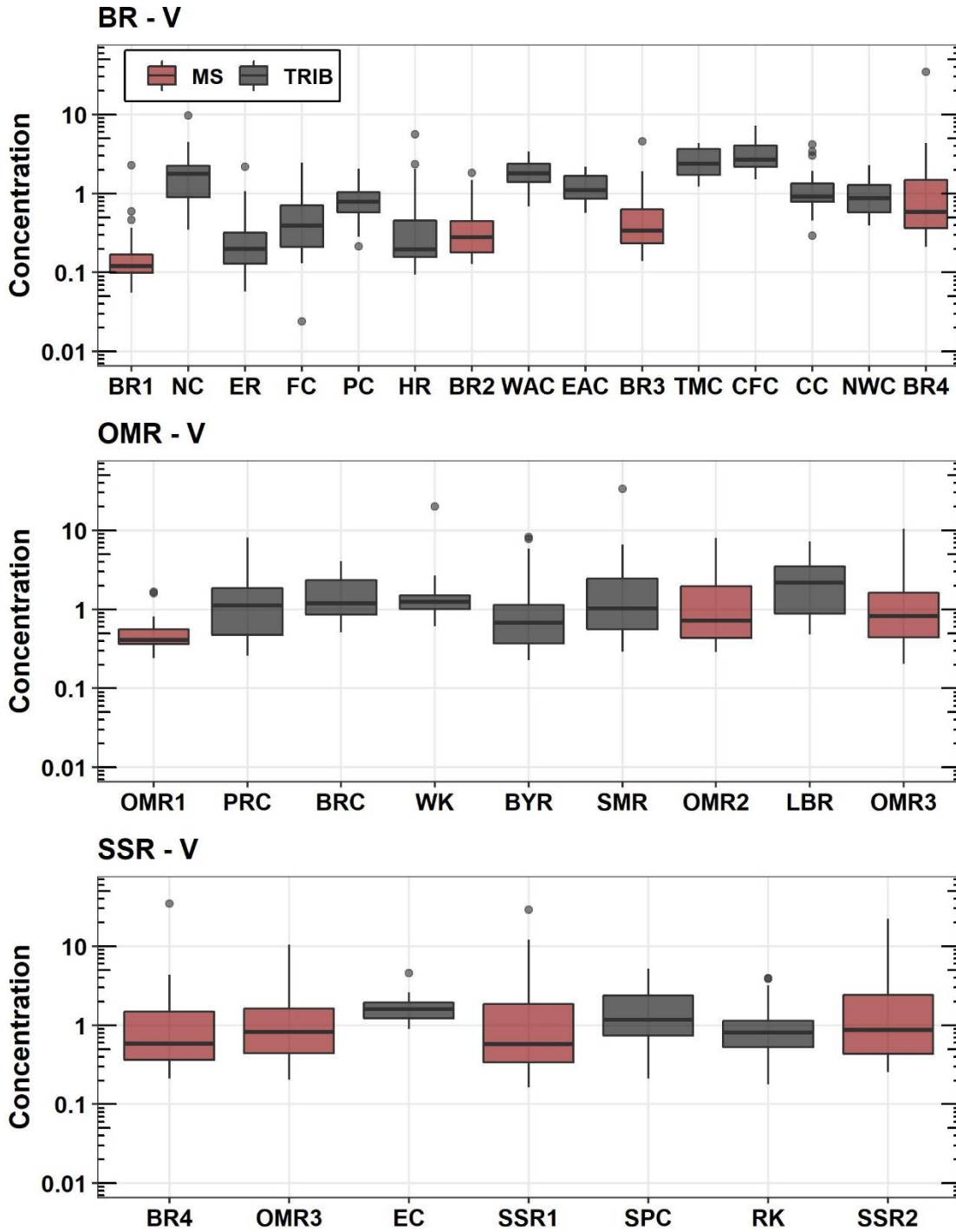


Figure S13: Box plots of the modelled total recoverable Vanadium (V) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

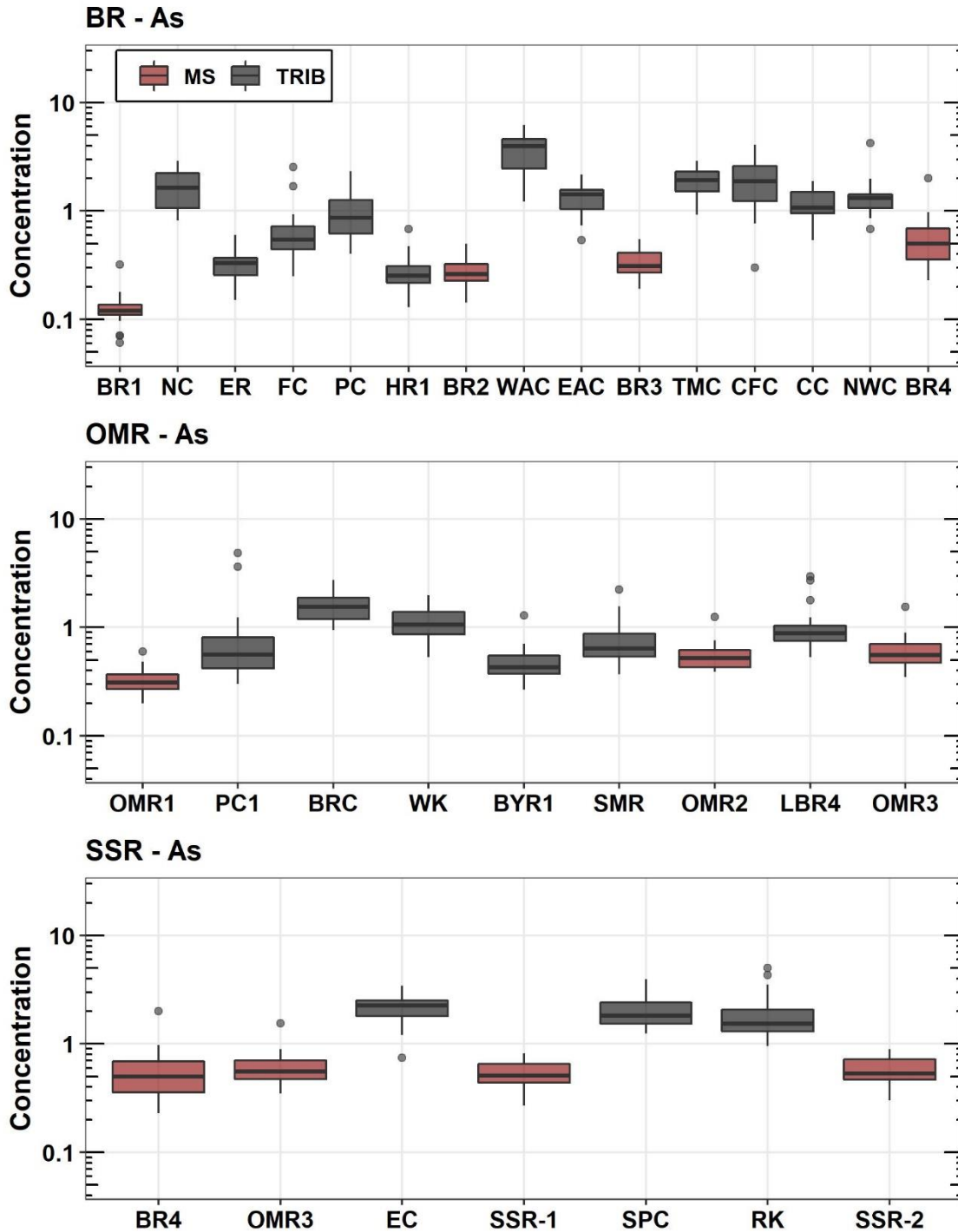


Figure S14: Box plots of the modelled dissolved Arsenic (As) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

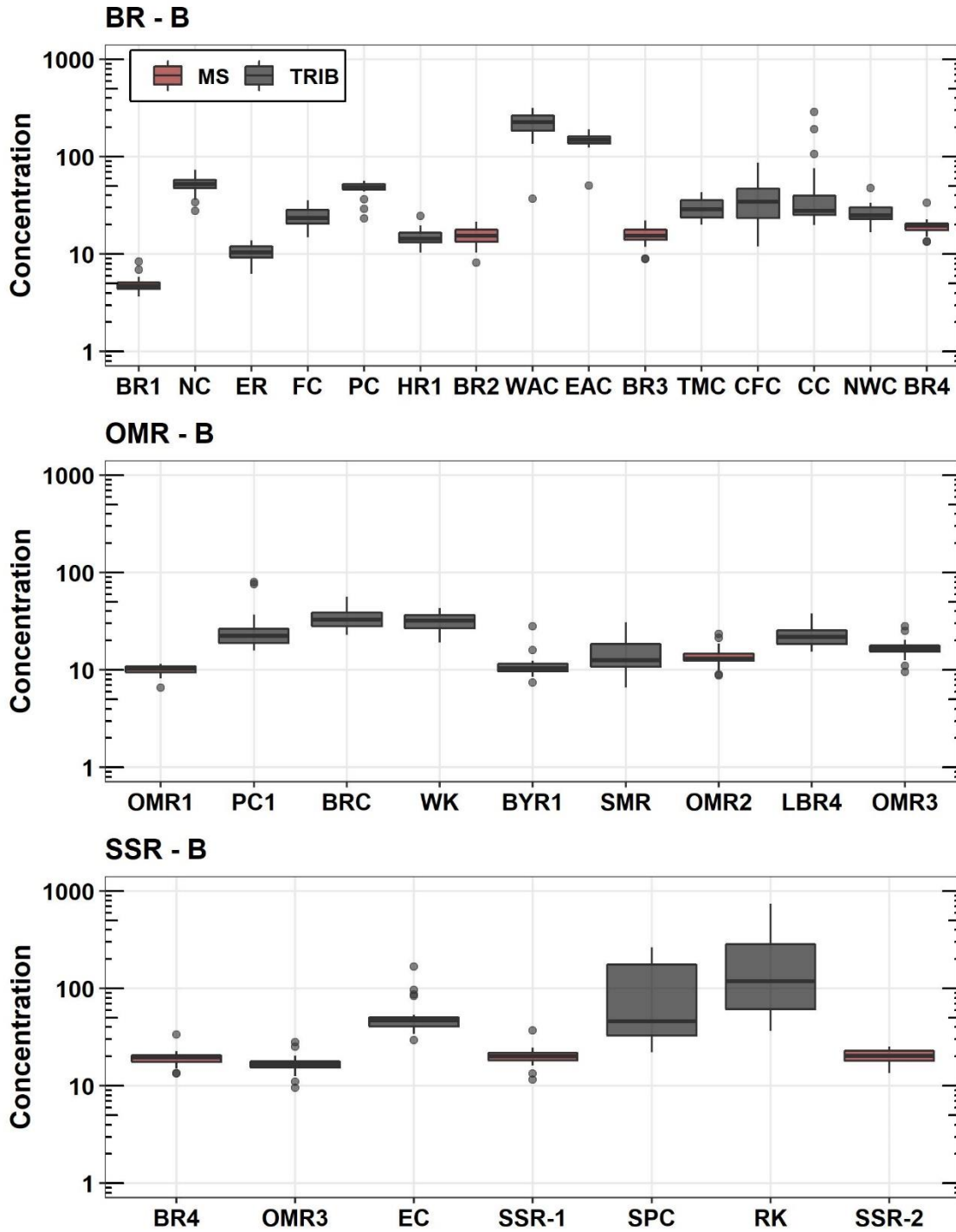


Figure S15: Box plots of the modelled dissolved Boron (B) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

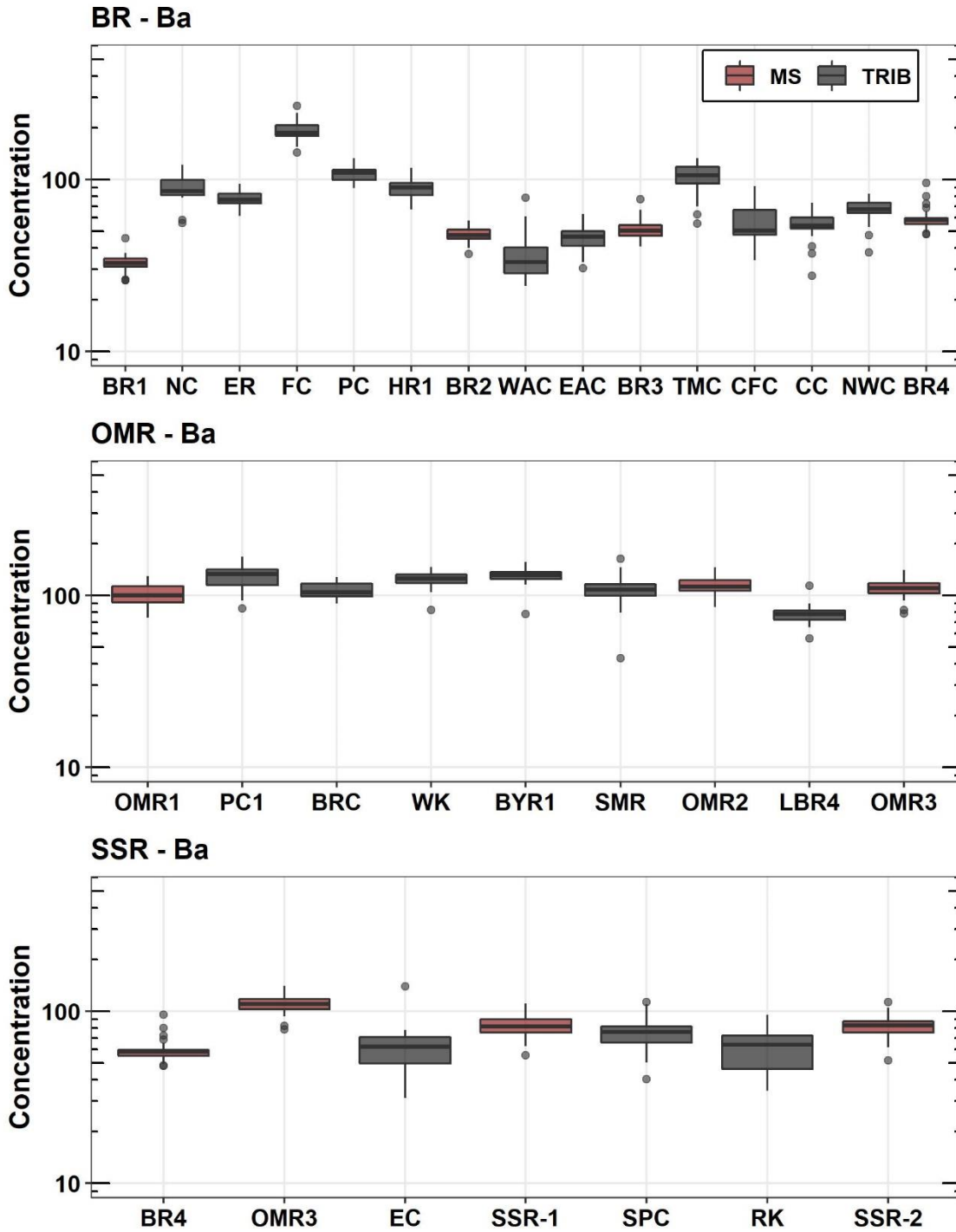


Figure S16: Box plots of the modelled dissolved Barium (Ba) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

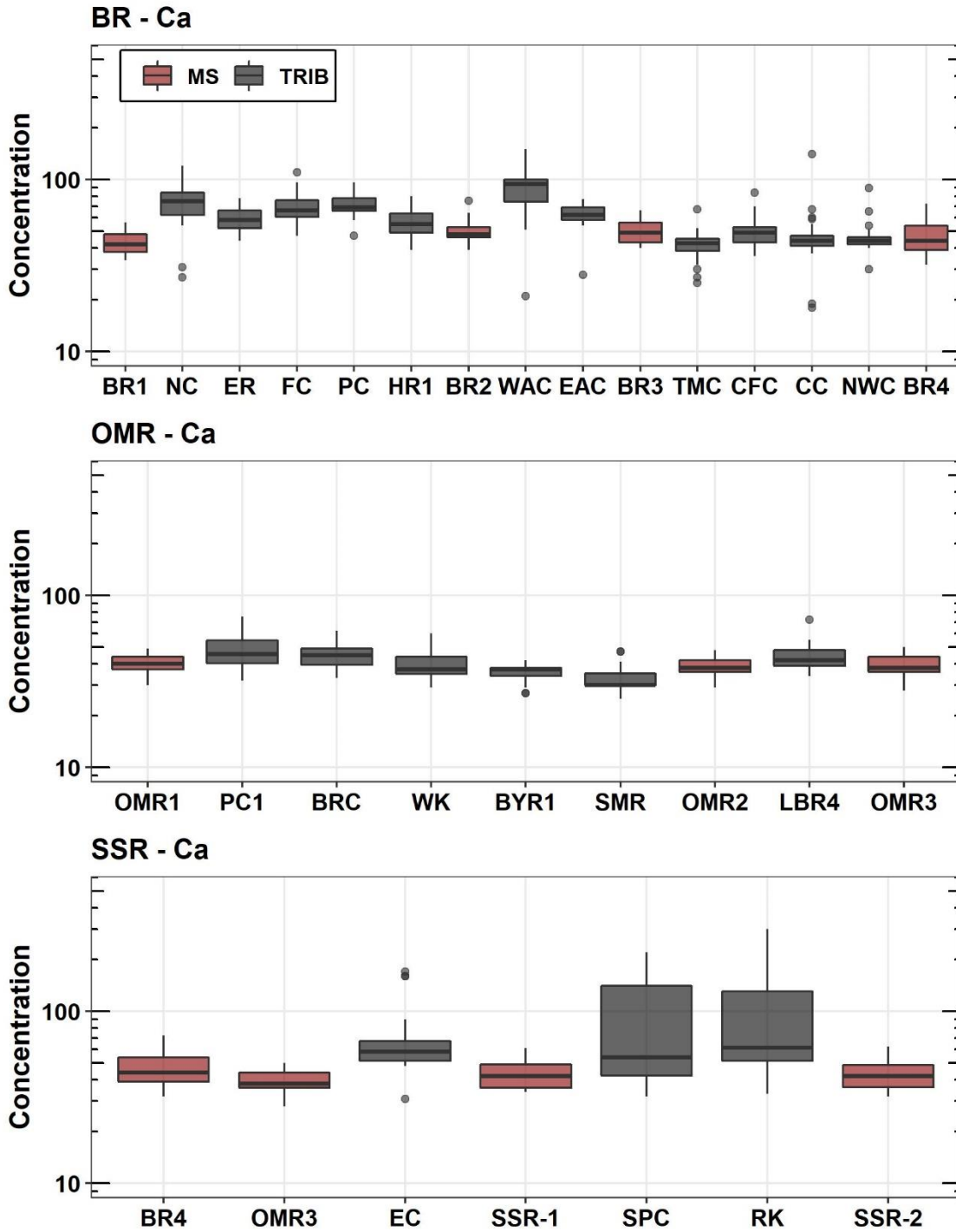


Figure S17: Box plots of the modelled dissolved Calcium (Ca) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

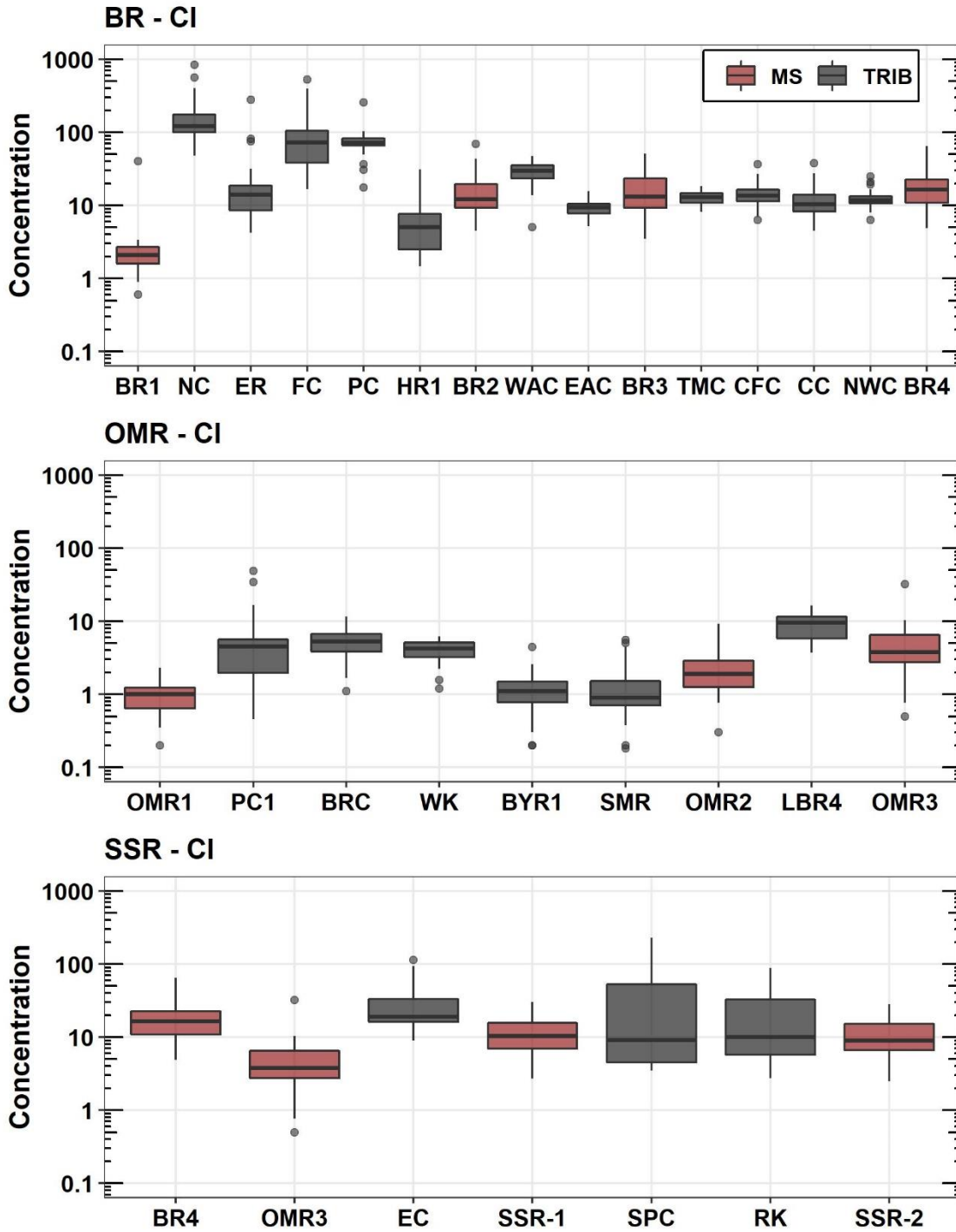


Figure S18: Box plots of the modelled dissolved Chloride (Cl) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

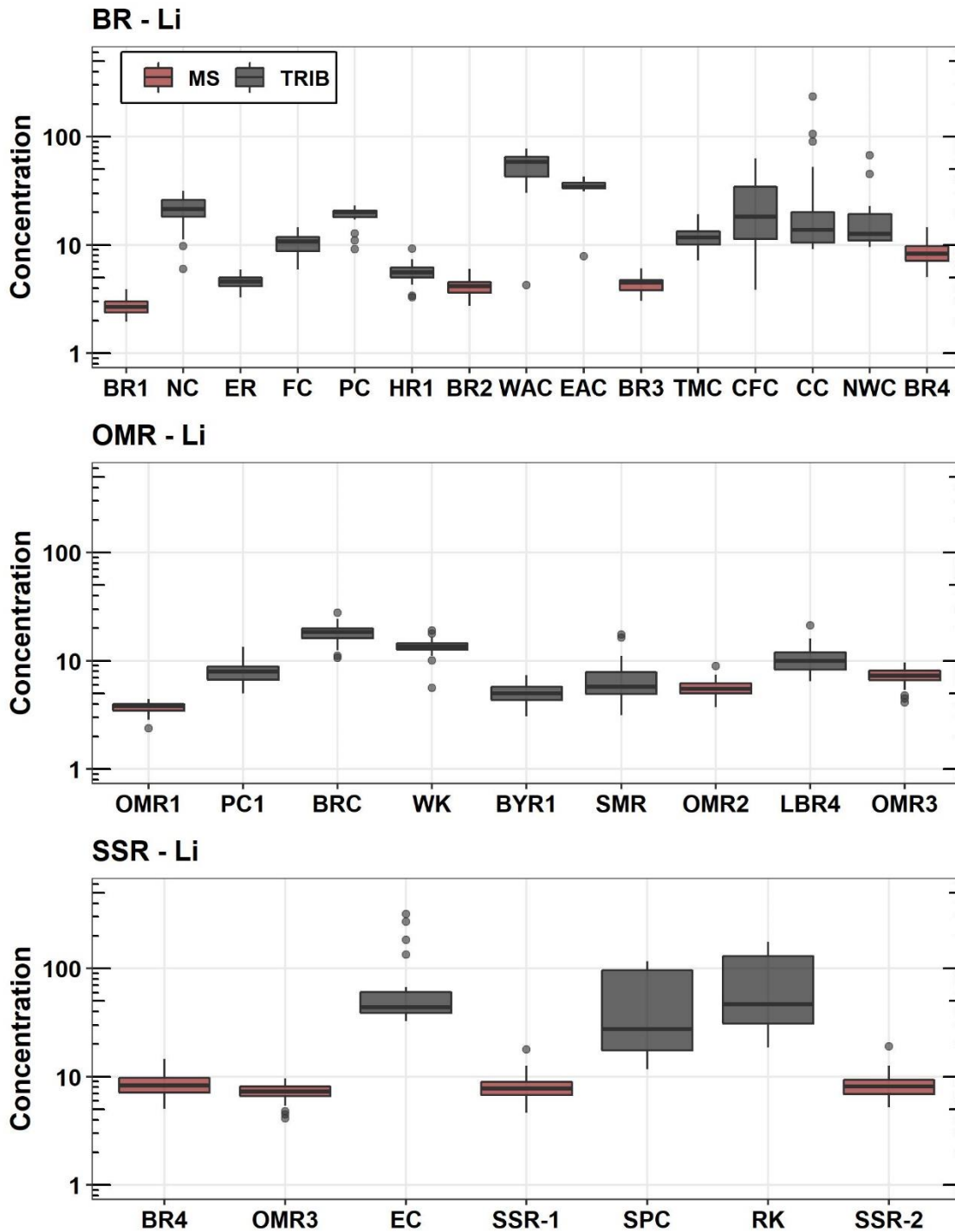


Figure S19: Box plots of the modelled dissolved Lithium (Li) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

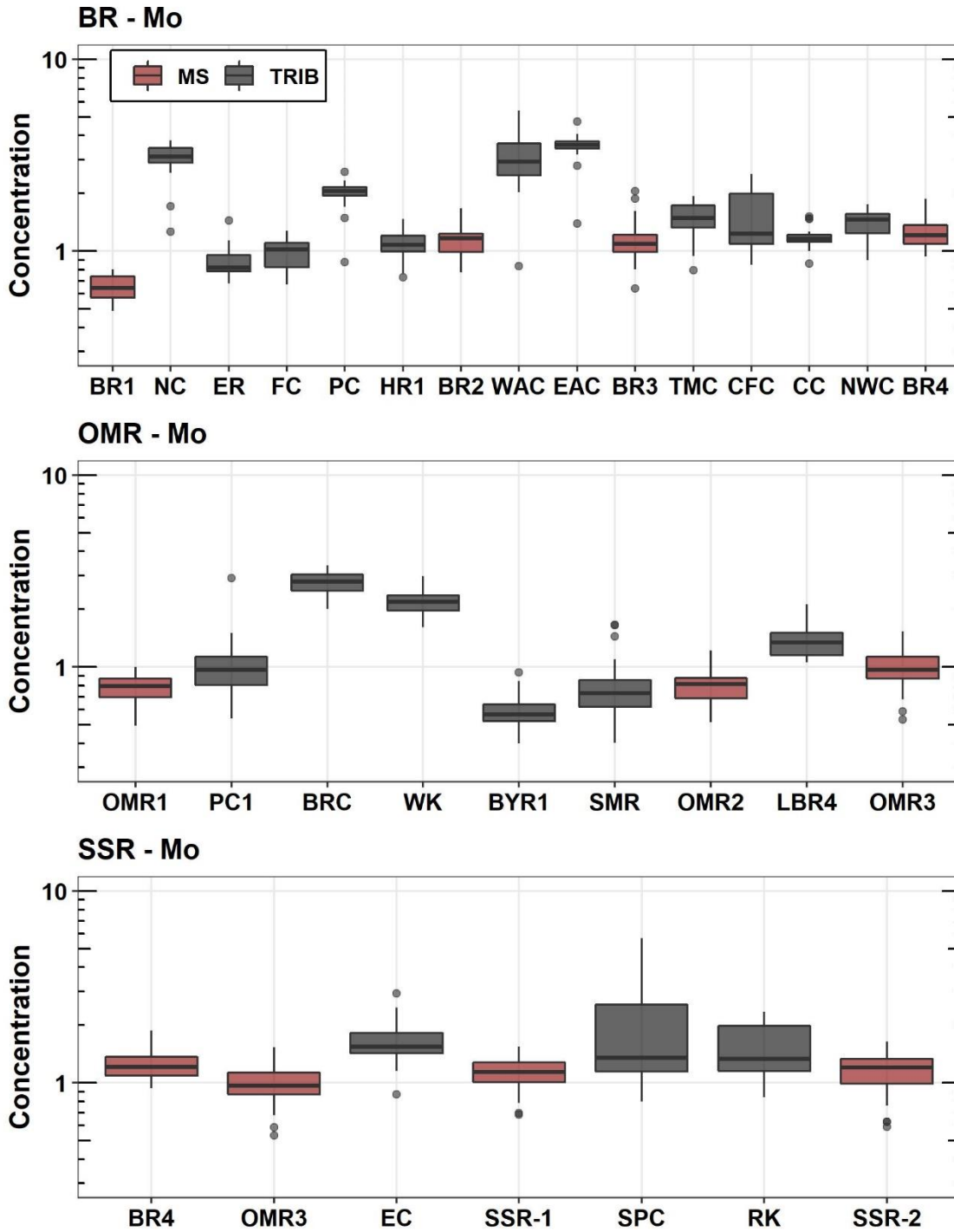


Figure S20: Box plots of the modelled dissolved Molybdenum (Mo) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

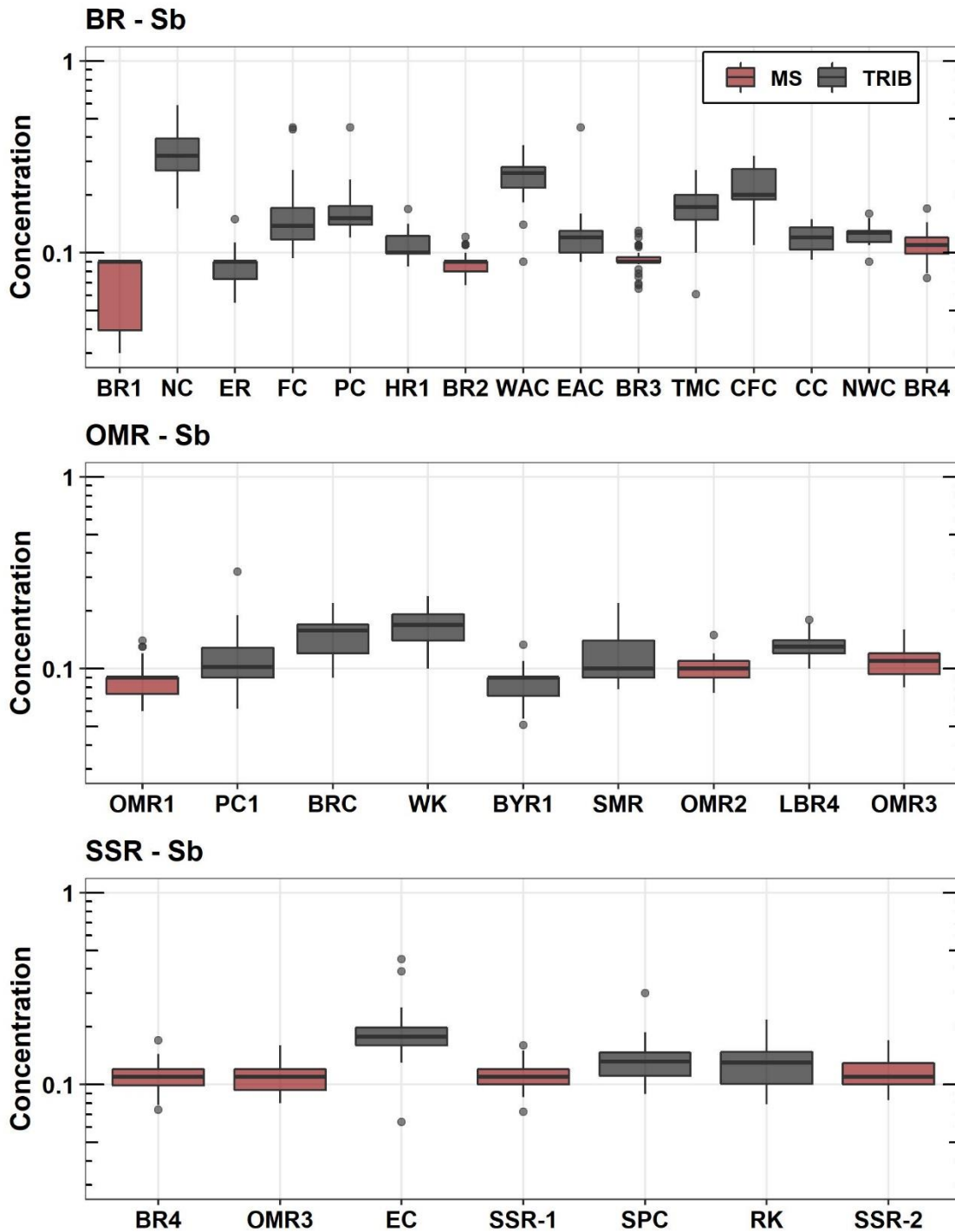


Figure S21: Box plots of the modelled dissolved Antimony (Sb) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red)) and tributary (TRIB – grey) sites for all annual samples.

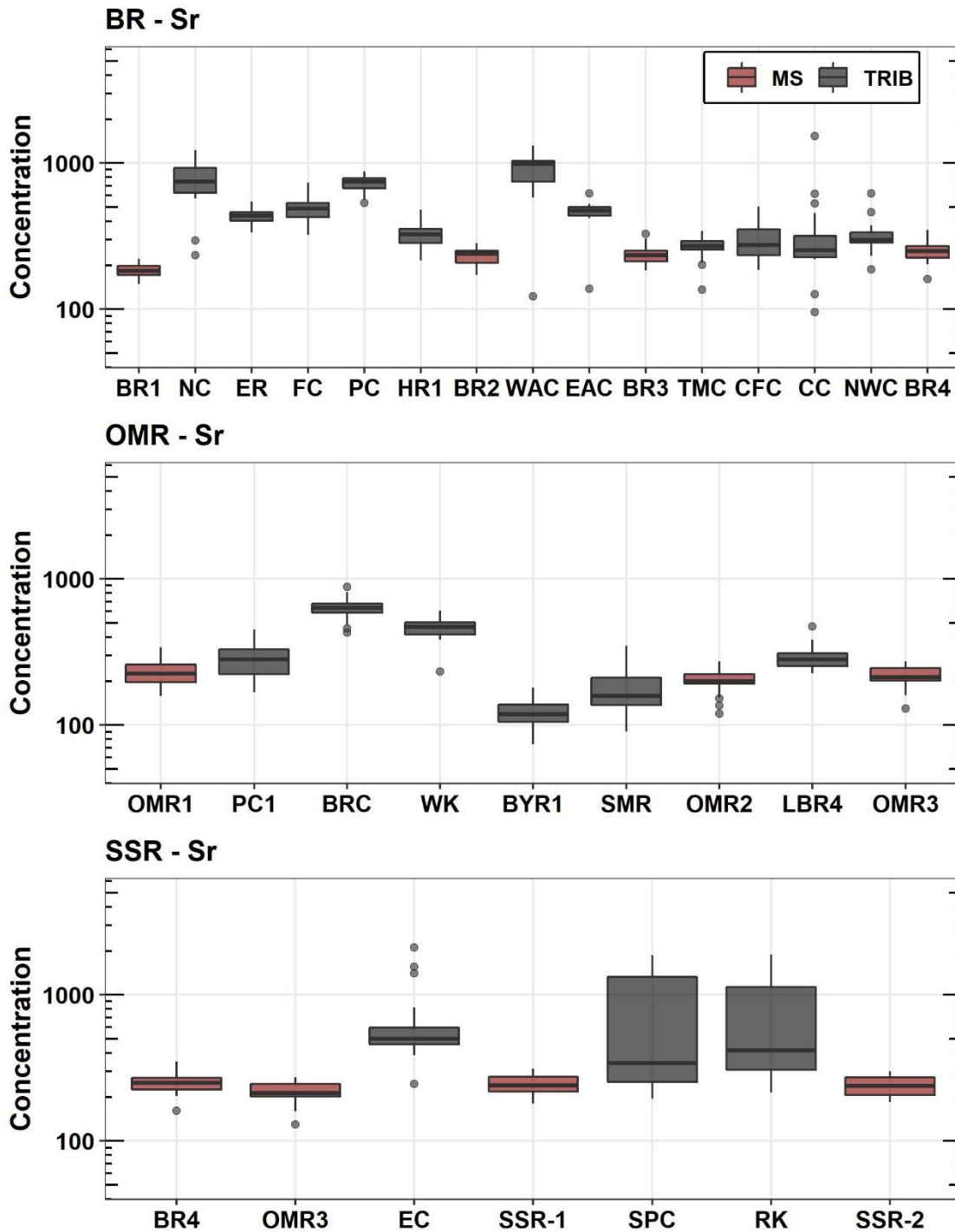


Figure S22: Box plots of the modelled dissolved Strontium (Sr) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

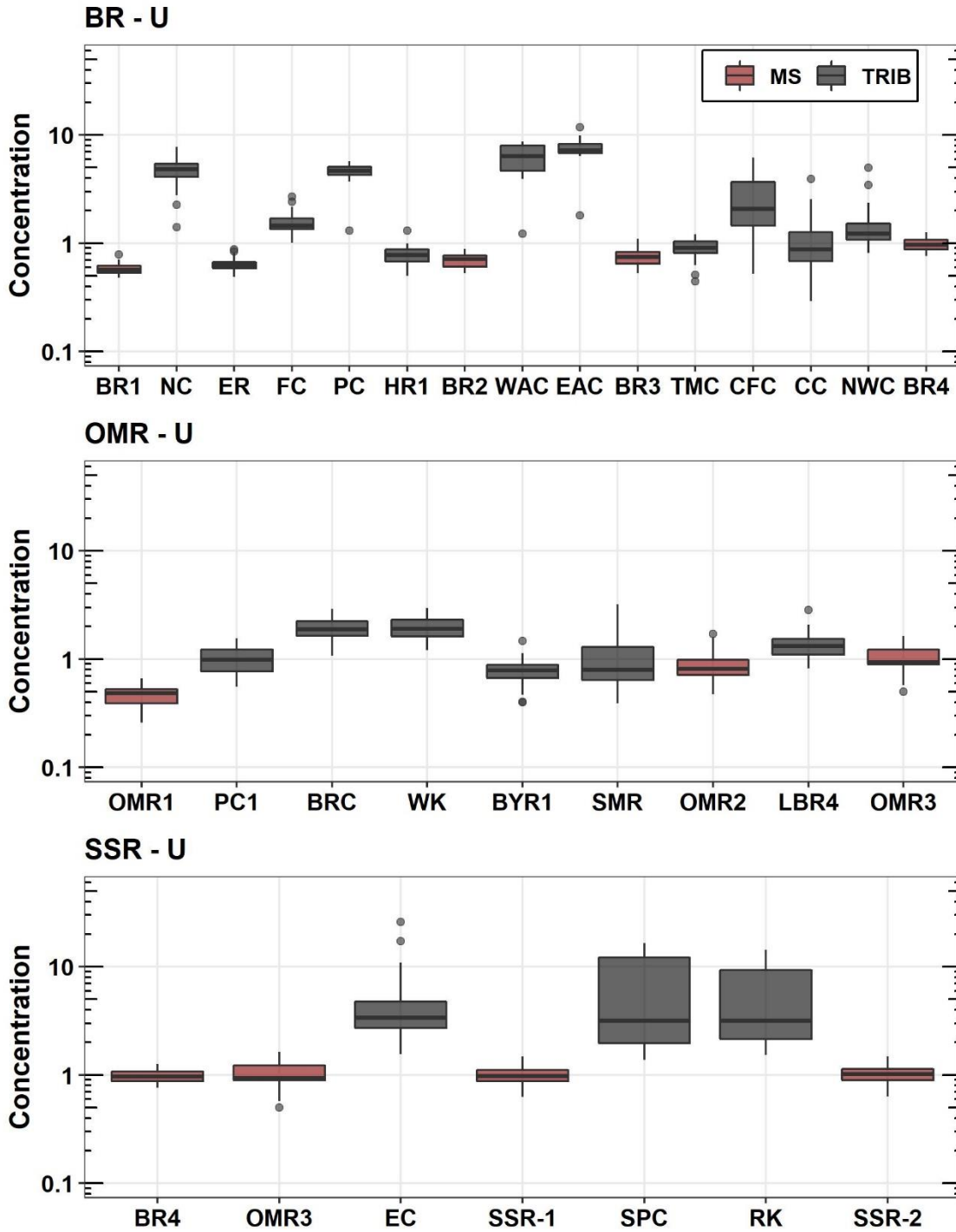


Figure S23: Box plots of the modelled dissolved Uranium (U) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red) and tributary (TRIB – grey) sites for all annual samples.

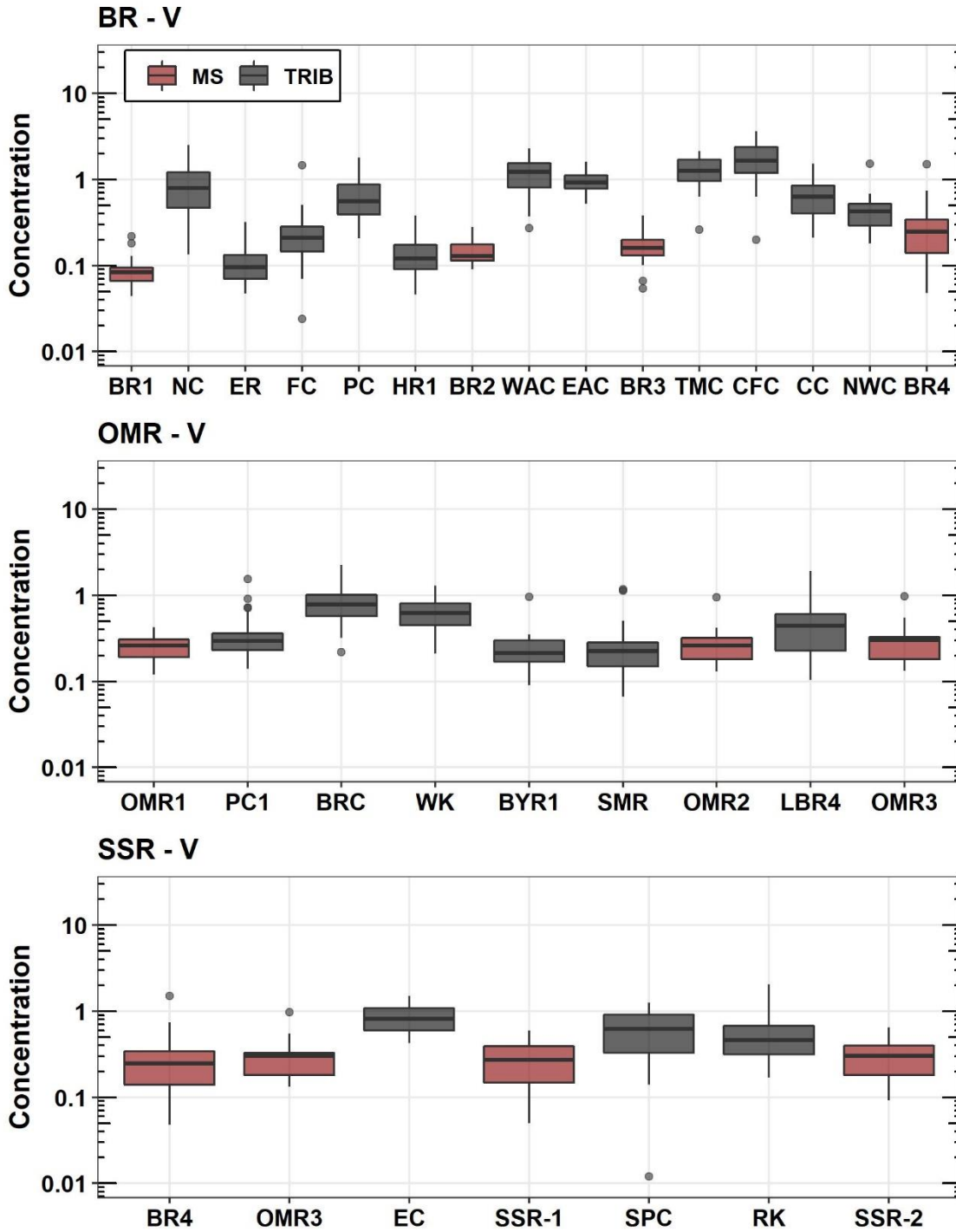


Figure S24: Box plots of the modelled dissolved Vanadium (V) concentrations for the Bow River (BR – Top), Oldman River (OMR – middle) and South Saskatchewan River (SSR) including main stem (MS – red)) and tributary (TRIB – grey) sites for all annual samples.