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Geochemistry and sediment in the main stream of the Ca River 2 basin, Vietnam: weathering process, solute-discharge 3 relationships, and reservoir impact 4

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8 Abstract In this study, we investigated the chemical 9 composition of dissolved solids in the Ca River basin, North-Central Vietnam. Water samples were collected 11 from August 2017 to July 2018 at three hydrological sta-12 tions located in the main stream of the Ca River. Carbonate 13 weathering was found as the dominant process controlling 14 the water chemistry in that area. The average concentra-15 tions of dissolved solids generally decreased from upstream 16 to downstream, resulting in low concentrations of the major 17 ions in the downstream basin. Variations in the concen-18 trations of major chemical ions and suspended solids at 19 discharge were also investigated. Major chemical weath-20 ering products were found to behave chemostatically with 21 increasing discharges upstream. However, dilution behav-22 iors of solutes were shown in both midstream and down-23 stream. Primary evidence shows that water storage in 24 reservoirs impacts a variety of suspended solids and dis-26 AQ1 solved solids in the Ca River.

27 Keywords Ca River · Dissolved solids · Geochemistry ·

28 Carbonate weathering · Suspended solids

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1 Introduction

The natural chemical compositions and transport fluxes in 30 rivers depend on multiple environmental factors such as 31 sources (lithosphere, atmosphere, biosphere), sinks (vege-32 tation uptake, settling), rate-controlling factors (tempera-33 ture, water circulation), and drainage basin area (Meybeck 34 1994; Milliman and Farnsworth 2011). Atmospheric pol-35 lution and human activity can have significant effects on 36 the natural geochemistry of river basins (Chetelat et al. 37 2008; Li et al. 2009; Li and Zhang 2008; Roy et al. 1999). 38 Detailed geochemical studies have quantified major ion 39 compositions (Li and Zhang 2008; Maharana et al. 2015), 40 weathering processes (Chetelat et al. 2008; Sarin et al. 41 1989), long-term fluxes (Negrel et al. 2007; Sarin et al. 42 1989), and controlling factors in solute exports from vari-43 44 ous scales of basins (Godsey et al. 2009; Musolff et al. 2015). Some have researched natural river geochemistry, 45 where basins with minimal human activity-such as hilly 46 headwater basins (Bruijnzeel 1983) and unpolluted or less-47 polluted river basins (Meybeck 1994)-were considered. 48 However, establishing natural background values is chal-49 50 lenging because most major rivers are already polluted or exposed to long-range transport of atmospheric pollutants 51 (Meybeck and Helmer 1989). 52

Rivers in Vietnam, like many other rivers around the 53 world, have been impacted by economic development. 54 55 Reservoirs of various sizes have been constructed along the rivers for power generation, water supply, and flood control 56 (Amos et al. 2017). In addition, other anthropogenic 57 58 activities (e.g., intensive agriculture, land-use change, and industrial development) can have significant impacts on 59 how natural river materials move. However, geochemical 60 data for Vietnamese rivers are sparse. Thus, we investi-61 gated the geochemistry of the Ca River, one of the large 62

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basins in north-central Vietnam, covering an area of 63 27,200 km². Major ion chemistries were determined at 64 65 sites upstream of the reservoirs, which were primarily 66 under forest cover, and at sites mid- and downstream, 67 below the reservoirs. Weathering processes controlling the 68 major geochemistry were also determined. Additionally, 69 variations in the concentrations of major chemical ions and 70 suspended solids in the discharge were investigated.

71 2 Study area

72 The Ca River is an international river located between 73 18°15′00″N to 20°10'30"N and 103°45′20″E to 74 105°15'20"E (Fig. 1). The basin covers 27,200 km², 75 including 17,730 km² in Vietnam's territory and 9470 km² 76 in Laos. The main river originates from Mt. Muong Khut 77 and Muong Lap (1800-2000 m) in Laos, flows from 78 northwest to southeast, enters into the Nghe An, Thanh 79 Hoa, and Ha Tinh provinces of Vietnam, and flows out to 80 the Eastern Sea at the Hoi estuary. Total river length is 81 531 km, of which 170 km runs through Laos and 361 km 82 is in Vietnam. Forests in the Ca River basin are largely 83 located upstream of three Laos provinces (Bolikhamxay, 84 Xieng Khouang, and Houaphanh). In Vietnam, forests are 85 concentrated north, northwest, and southwest of the basin 86 at elevations of 150-1500 m (IWRP 2012). The catchment 87 is covered primarily by forest (44%) and agricultural crops 88 (18%) (Chikamori et al. 2012). Area soils are formed from 89 parent rocks, Ferralsol in particular (83.51%) (IWRP 2012; 90 Nauditt and Ribbe 2017). Other soil types are Fluvisol and 91 Acrisol. The Ca River basin is located in a monsoon cli-92 mate, and rainfall is distributed over the year, which has 93 two distinct seasons: the dry season and the rainy season. In 94 the upper reaches of the river, the rainy season is from May 95 to October, but downstream, it is from June to November.



Fig. 1 Map of the Ca River basin

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Average precipitation in basin 96 annual the is 97 1100-2500 mm.

Multiple reservoirs have been constructed in the Ca 98 River basin, namely Ban Ve, Khe Bo, Thac Muoi, and Sao 99 reservoirs. These multi-purpose reservoirs are used for hydropower generation, water supply, irrigation, and flood and drought control. Ban Ve is the largest among them and 102 is located at approximately 100 m elevation. Its gross 103 capacity is 1835×10^6 m³, and its effective capacity is 104 $1383 \times 10^6 \text{ m}^3$. 105

Samples were obtained from the main stream of the Ca 106 River at My Ly (104°18'54"E and 19°36'51"N), Dua 107 (105°02'20"/E and 18°59'20"N), and Yen Thuong 108 (105°23'00"E and 18°41'10"N). My Ly is located 109 approximately 215 m above the Ban Ve reservoir (70 km). 110 It covers 1190 km^2 or 4.4% of the total drainage basin. 111 Located in the high mountains and covered primarily by 112 forest, the My Ly basin is sparsely populated and is subject 113 to little human impact. Both Dua and Yen Thuong are 114 downstream of all reservoirs, covering 20,800 km² and 115 23,000 km² (76.5% and 84.6% of the river basin), 116 respectively. Both are strongly influenced by human 117 activity (e.g., agriculture and mining activities). Addition-118 ally, water storage and reservoir operations impact the Ca 119 River and its resources. 120

3 Sampling and analytical methods

From August 2017 to July 2018, 121 water samples were 122 collected from three hydrological stations in the main 123 stream of the Ca River basin. During the flood season, 124 water samples were collected four to six times monthly, 125 126 and during the dry season, they were collected one to four times monthly. Samples were representative of the range of 127 discharge rates. 128

Each sample of 2 L, collected from an average depth of 129 10 cm at the river bank, was placed in high-density poly-130 ethylene containers then immediately cooled and main-131 tained at a low temperature until analysis. Concentrations 132 of the major cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+), anions 133 $(HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, and PO_4^{3-})$, and dissolved silica 134 (SiO₂) were determined in the laboratory. Cation and most 135 anion concentrations were found using ion chromatography 136 (Shimadzu, Japan). Dissolved silica and phosphate were 137 measured using a DR900 (HACH) colorimeter. Water 138 samples were filtered through pre-washed 0.45-µm Milli-139 pore membrane filters before ion concentrations were 140 141 determined. Additionally, the concentration of suspended solids was determined by filtering 100 mL sample through 142 a 0.45-µm membrane filter (Whatman). Finally, the total 143

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144 concentration of all dissolved solids was the sum of the145 major elements plus dissolved silica.

146 4 Results and discussion

147 4.1 Contributions of chemical compositions

148 The concentration of each major chemical in the main 149 stream of the Ca River basin is given in Table 1. Total 150 dissolved solids (TDS) varied from 77 to 205 mg/L, 151 averaging 144 mg/L, higher than the world average, 100 mg/L (Milliman and Farnsworth 2011). The average 152 153 value for TDS is comparable to that reported for the Hong 154 (176 mg/L) in Vietnam, but it is lower than that reported 155 for the Son in India (227 mg/L) and the Upper Han River 156 in China (248 mg/L) (Li and Zhang 2008; Maharana et al. 157 2015; Moon et al. 2007). Compared with the rivers drain-158 ing in areas dominated by silicate rock, such as the upper 159 Ganjiang (63 mg/L) and rivers in the Southeast Coastal 160 Region of China (75.2 mg/L), TDS in the Ca River is much 161 higher (Liu et al. 2018; Ji and Jiang 2012). However, it is 162 much lower compared to the Huanghe (557 mg/L) and Tarim (1000 mg/L), both of which drain in areas domi-163 164 nated by evaporite dissolution (Fan et al. 2014; Xiao et al. 165 2012). Bedrock lithology plays a critical role in controlling the character and quantity of the total delivered (Meybeck 166 167 1987; Milliman and Farnsworth 2011). Human activity also 168 significantly influences TDS values [e.g., in the Liao River 169 of China (400 mg/L) and several European rivers (Ding 170 et al. 2016; Milliman and Farnsworth 2011)].

The total cationic charge $(Tz^+ = 2Ca^{2+} + 2Mg^{2+} + K^+)$ 171 172 +Na⁺) ranged from 1145–2981 µeq/L, averaging 2119 μ eq/L. The total anionic charge (Tz⁻ = HCO₃⁻ + 2SO₄²⁻+ 173 $Cl^{-} + NO_{3}^{-} + 3PO_{4}^{3-}$) ranged from 811 to 2271 µeq/L, 174 175 averaging 1567 μ eq/L. The extent of Tz⁺ – Tz⁻ charge 176 imbalance, characterized by the normalized inorganic charge balance [NICB = $(Tz^+ - Tz^-)/Tz^+$], is related to 177 178 the contributions of other anions (Li et al. 2009; Ji and 179 Jiang 2012).

180 Calcium was the dominant cation, ranging in concen-181 tration from 381 to 1005 µM, accounting for an average of 182 62.0% of the total cation charge. Magnesium followed, 183 ranging from 102 to 368 µM, accounting for an average of 184 23.2% of the total cation charge, then sodium (12.3%) and 185 potassium (2.4%) followed. Bicarbonate was the dominant 186 anion, ranging from 600 to 2039 µM, accounting for 84.4% 187 of the total anion charge. Chloride and sulfate together 188 comprised 12.6% of the total anion charge in nearly equal 189 proportions. Nitrate and phosphate contributed negligible 190 proportions (2.7 and 0.3%, respectively).

Dissolved Si ranged in concentration from 133 to 191 192 250 µM, averaging 202 µM, comprising an average of 8.6% of the TDS. It ranked third in abundance after HCO_{2}^{-} 193 (55.8%) and Ca²⁺ (18.3%). Compared to other major ions, 194 dissolved Si was relatively independent of lithology, 195 remaining constant between 80 and 160 umol/L SiO₂(ex-196 197 cept in streams draining volcanic rocks, where it reaches 350 µmol/L SiO₂) (Meybeck 1987). Dissolved Si content 198 is, however, controlled by the climate (temperature and 199 rainfall) (White and Blum 1995). 200

4.2 Spatial and seasonal variations of major solutes 201 and suspended solids 202

203 The total concentrations of major solutes at My Ly ranged from 142 to 205 mg/L, averaging 168 mg/L. At Dua, TDS 204 varied from 85 to 171 mg/L, averaging 138 mg/L. On the 205 other hand, the TDS value at Yen Thuong ranged from 77 206 to 167 mg/L, averaging 128 mg/L. Generally, the total 207 solute concentration decreased from upstream to down-208 stream, consistent with decreased concentrations of the 209 major ions Ca²⁺, Mg²⁺, Na⁺, Cl⁻, HCO₃⁻, SO₄²⁻, and SiO₂ 210 in the downstream basin. The observed spatial variations in 211 solute concentrations in the main stream of the Ca River 212 could be related to the effects of tributary inflows, resulting 213 in dilution. A downstream trend in K⁺ concentration was 214 not significant, reflecting its conservative behavior in the 215 basin. An increase in NO₃⁻ concentration in the down-216 stream basin might have been from anthropogenic sources 217 such as agricultural activity and untreated sewage (Maha-218 rana et al. 2015). 219

The study period was divided into two sub-periods: the 220 wet season (June to November for Dua and Yen Thuong 221 and May to October for My Ly) and the dry season (De-222 cember to May and November to April, respectively) 223 (Fig. 2). Trends in seasonal solute variations were similar 224 between Dua and Yen Thuong. The concentrations of 225 almost all tested ions increased from the wet to dry sea-226 227 sons, indicating the dilution effect of greater atmospheric precipitation during the rainy season. For that reason, at 228 Dua and Yen Thuong, the total solute concentration 229 increased from the wet to dry seasons. At My Ly, however, 230 231 TDS decreased slightly from the wet to dry seasons, a result of decreased concentration in the major ion HCO₃. 232 Other elements remained constant when comparing the two 233 seasons. Phosphate concentration increased in the wet 234 season at all stations, indicating the contribution of organic 235 matter degradation (at My Ly) or human activity (at Dua 236 and Yen Thuong). 237

Normally, suspended sediment concentration (SSC) 238 decreases from upstream to downstream and from the wet 239 to dry seasons (Fig. 2). In our case, it greatly varied from 240



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Table 1 Chemical compositions of the rivers in the Ca River basin

Stations	Date	Discharge m ³ /s	Na ⁺ mg/l	K ⁺ mg/l	Ca ²⁺ mg/l	Mg ²⁺ mg/l	Cl ⁻ mg/l	SO ₄ ^{2–} mg/l	HCO ₃ mg/l	NO ₃ mg/l	PO ₄ ^{3–} mg/l	SiO ₂ mg/l	NIBC	TSS mg/l
My Ly	13/08/2017	172	4.65	1.30	30.43	7.89	1.15	4.28	120.80	_	0.13	12	0.12	54
	20/08/2017	154	13.87	1.73	18.74	6.68	7.93	6.00	97.60	_	0.16	13	0.08	41
	27/08/2017	198	14.20	2.76	24.51	7.90	12.24	6.76	107.40	-	0.14	12	0.12	81
	03/09/2017	152	6.69	1.70	29.40	7.37	2.89	4.16	95.16	_	0.17	13	0.28	183
	10/09/2017	148	6.29	1.83	28.86	8.55	2.82	5.45	101.30	_	0.15	13	0.25	59
	16/09/2017	400	5.97	1.83	22.74	6.74	3.11	4.61	100.00	2.82	0.25	13	0.06	576
	17/09/2017	380	4.39	1.64	30.54	6.92	2.19	5.93	118.30	2.54	0.19	12	0.07	502
	24/09/2017	108	5.46	2.30	24.34	5.45	3.69	5.78	102.50	1.78	0.13	13	0.01	46
	01/10/2017	128	7.67	1.39	26.86	8.87	3.79	3.86	96.38	0.85	0.17	13	0.27	25
	08/10/2017	132	13.63	3.16	27.55	7.67	10.65	6.14	91.50	10.11	0.17	13	0.22	46
	22/10/2017	348	11.78	1.78	28.42	6.94	5.45	9.46	93.94	1.06	0.20	13	0.25	15
	05/11/2017	328	8.19	1.63	26.99	7.56	3.85	5.43	96.38	2.23	0.12	12	0.22	5
	12/11/2017	132	4.65	1.17	27.82	7.09	1.01	4.56	97.60	0.38	0.19	13	0.21	6
	19/11/2017	132	6.65	2.31	28.51	8.66	2.32	5.43	93.94	0.93	0.12	13	0.30	5
	26/11/2017	130	4.93	1.31	28.23	7.64	0.62	4.97	97.60	0.54	0.11	14	0.24	7
	03/12/2017	130	6.77	2.23	26.98	8.27	3.08	5.87	96.38	2.14	0.13	13	0.23	3
	10/12/2017	132	6.24	1.25	23.11	7.33	0.57	5.32	90.28	5.39	0.12	13	0.18	7
	17/12/2017	132	8.38	2.20	25.04	7.24	3.16	4.87	96.38	2.27	0.10	14	0.20	9
	24/12/2017	129	4.57	1.21	24.65	6.11	1.97	4.83	93.94	1.29	0.04	13	0.12	3
	30/12/2017	129	5.64	1.90	29.36	7.72	3.25	5.50	97.60	1.87	0.15	13	0.23	12
	21/01/2018	80	4.76	1.62	27.79	5.23	2.47	4.25	79.30	4.05	0.19	12	0.26	5
	28/01/2018	50	11.08	1.68	29.94	8.95	6.60	6.28	98.82	6.30	0.08	12	0.26	7
	04/02/2018	42	9.54	1.87	28.24	8.92	5.97	6.52	96.38	2.43	0.11	13	0.26	3
	04/03/2018	40	6.35	1.93	26.38	6.44	3.70	3.94	102.50	3.12	0.04	13	0.12	4
	11/03/2018	40	7.12	1.78	31.39	8.20	3.39	5.27	102.50	1.98	0.11	13	0.26	23
	01/04/2018	40	10.83	2.49	30.75	8.15	4.98	6.28	97.60	1.02	0.10	14	0.31	39
	08/04/2018	40	5.06	2.14	31.51	8.03	1.43	5.90	97.60	1.48	0.23	14	0.28	360
	16/04/2018	72	8.62	2.01	32.65	8.33	4.50	5.06	98.82	3.27	0.09	12	0.30	265
	29/04/2018	48	13.17	3.08	27.06	7.53	8.85	6.62	87.84	6.09	0.17	14	0.26	632
	06/05/2018	94	5.96	2.27	26.77	7.29	2.00	4.89	95.16	2.39	0.20	12	0.22	410
	13/05/2018	72	5.02	2.13	34.24	7.74	1.49	6.20	98.82	1.01	0.23	15	0.31	414
	27/05/2018	60	5.15	2.17	30.41	6.07	2.28	4.94	81.74	1.64	0.36	12	0.33	200
	03/06/2018	160	6.70	2.31	34.31	8.37	3.41	5.67	109.80	3.45	0.40	12	0.24	536
	17/06/2018	240	4.49	3.14	40.27	8.46	2.00	6.12	124.40	2.37	0.33	13	0.24	3727
	24/06/2018	87	4.29	1.47	35.91	8.02	0.94	5.25	112.20	0.96	0.11	12	0.25	338
	08/07/2018	72	5.25	1.64	28.60	7.51	1.23	2.62	103.70	0.31	0.12	12	0.22	197
	16/07/2018	160	5.59	2.78	23.19	5.50	3.88	5.97	106.10	2.57	0.08	12	- 0.05	387
	22/07/2018	2100	3.33	1.27	26.42	5.95	2.86	7.35	89.06	5.35	0.16	12	0.10	2310



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Dua	06/08/2017				0	mg/1	mg/1	mg/i	1115/1	mg/1	mg/1	mg/1		mg/l
		869	4.16	1.75	23.39	4.35	2.68	2.87	84.18	_	0.20	12	0.13	77
	14/08/2017	463	3.47	1.45	23.89	5.12	1.24	3.20	85.40	_	0.19	13	0.16	57
	20/08/2017	860	8.65	1.97	23.04	4.84	5.47	3.88	63.44	_	0.13	12	0.35	106
	27/08/2017	882	3.76	1.83	26.77	4.98	2.43	3.30	78.08	_	0.19	11	0.27	85
	04/09/2017	565	3.99	1.54	21.73	5.23	2.30	3.29	70.76	_	0.15	12	0.25	58
	10/09/2017	562	3.94	1.43	24.98	5.49	1.92	3.41	73.20	_	0.18	11	0.30	42
	17/09/2017	2688	3.77	1.83	18.41	3.86	2.37	3.26	51.24	3.60	0.25	10	0.28	621
	24/09/2017	610	4.59	2.10	23.47	5.39	2.06	4.11	75.64	3.35	0.15	12	0.23	62
	01/10/2017	749	10.14	1.63	26.80	5.78	10.82	3.06	81.74	2.14	0.14	13	0.24	33
	08/10/2017	1241	6.13	2.25	20.97	4.55	4.72	3.60	63.44	5.79	0.20	12	0.23	174
	10/10/2017	1772	3.45	1.70	18.75	3.09	2.51	2.71	54.90	3.91	0.19	11	0.21	395
	11/10/2017	3564	2.91	1.77	16.98	3.40	2.41	2.51	61.00	3.81	0.18	12	0.09	411
	12/10/2017	4393	2.55	1.82	16.08	2.89	2.00	2.58	43.90	4.43	0.24	9	0.24	465
	22/10/2017	700	8.65	1.76	26.22	6.37	5.06	5.68	78.08	3.78	0.17	14	0.29	40
	05/11/2017	336	8.22	1.89	27.37	6.22	4.34	3.99	80.52	3.42	0.10	13	0.31	17
	12/11/2017	440	9.51	2.30	27.86	6.68	5.99	4.34	84.18	3.12	0.16	14	0.30	8
	20/11/2017	283	4.80	1.97	27.70	6.18	1.97	4.20	78.08	2.40	0.13	13	0.32	36
	26/11/2017	246	3.73	1.45	24.71	5.30	0.97	4.21	80.52	2.38	0.14	14	0.21	17
	03/12/2017	259	4.65	1.59	24.31	5.39	1.92	3.75	75.64	2.69	0.14	14	0.25	12
	10/12/2017	494	4.28	1.57	23.88	5.30	1.71	3.73	84.18	3.00	0.11	13	0.16	10
	18/12/2017	195	14.05	4.47	27.62	7.82	8.94	10.08	79.30	5.97	0.08	13	0.32	8
	24/12/2017	170	4.98	1.45	24.14	5.45	2.22	4.41	81.74	2.08	0.09	13	0.20	4
	31/12/2017	240	8.64	2.55	25.80	7.01	7.62	4.84	78.08	4.61	0.13	13	0.27	5
	21/01/2018	289	5.66	1.59	27.85	6.08	2.45	4.00	81.70	1.95	0.12	11	0.30	9
	27/01/2018	169	8.85	2.20	30.37	7.28	6.93	4.72	93.94	2.93	0.06	11	0.26	12
	04/02/2018	154	4.37	1.51	28.35	6.04	1.23	4.37	86.62	1.42	0.14	13	0.27	8
	04/03/2018	56	4.65	1.86	27.27	5.55	2.68	3.75	87.84	2.82	0.04	12	0.21	8
	11/03/2018	185	4.43	1.62	30.77	6.45	1.53	4.56	87.84	1.97	0.13	12	0.30	8
	02/04/2018	117	10.39	2.39	31.33	7.77	5.79	5.52	86.60	3.27	0.08	12	0.35	3
	07/04/2018	345	4.50	1.62	31.64	6.29	2.37	4.45	86.62	1.64	0.08	12	0.31	139
	17/04/2018	300	5.59	1.86	31.70	6.80	2.74	4.34	86.62	2.11	0.10	12	0.33	6
	01/05/2018	275	4.31	1.92	28.14	5.79	2.10	4.34	80.52	1.81	0.09	13	0.29	14
	06/05/2018	294	7.28	2.04	28.62	6.64	4.79	3.60	73.20	3.80	0.23	12	0.37	76
	13/05/2018	339	8.69	2.21	27.00	5.59	5.69	4.66	74.42	4.46	0.19	12	0.31	44
	20/05/2018	356	4.67	2.01	28.29	6.38	2.14	5.20	73.00	2.21	0.19	11	0.36	557
	27/05/2018	252	4.38	2.03	29.49	5.64	2.09	3.05	76.86	1.05	0.20	11	0.35	9
	03/06/2018	319	5.87	2.71	29.79	5.79	3.70	4.27	84.18	1.43	0.35	11	0.30	13
	17/06/2018	316	6.95	2.37	27.14	5.46	4.99	4.70	73.20	2.63	0.13	13	0.31	157
	24/06/2018	420	4.08	1.84	25.76	5.22	1.92	3.90	70.76	1.40	0.13	12	0.32	40
	08/07/2018	455	8.85	2.34	30.31	6.70	4.82	5.43	84.18	2.30	0.19	12	0.33	13
	16/07/2018	747	5.69	1.36	22.24	2.87	5.69	3.29	84.18	2.26	0.10	11	- 0.01	72
	22/07/2018	4210	2.22	1.79	20.71	4.30	1.26	4.58	70.76	3.83	0.26	11	0.11	867

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Table 1 continued

Stations	Date	Discharge m ³ /s	Na ⁺ mg/l	K ⁺ mg/l	Ca ²⁺ mg/l	Mg ²⁺ mg/l	Cl ⁻ mg/l	SO ₄ ²⁻ mg/l	HCO ₃ mg/l	NO ₃ ⁻ mg/l	PO ₄ ³⁻ mg/l	SiO ₂ mg/l	NIBC	TSS mg/l
Yen Thuong	06/08/2017	752	3.39	1.44	21.74	4.15	1.51	3.27	74.42	_	_	_	0.17	158
	14/08/2017	430	3.39	1.60	22.97	4.69	1.72	3.20	86.62	_	0.23	12	0.10	77
	20/08/2017	862	3.97	1.72	18.73	4.19	1.98	2.91	62.22	_	0.13	11	0.24	187
	27/08/2017	750	4.80	1.97	24.02	4.46	3.65	3.56	68.32	_	0.25	11	0.29	117
	04/09/2017	475	3.80	1.82	24.77	4.27	3.02	3.03	65.88	_	0.14	11	0.31	107
	10/09/2017	514	3.83	1.58	25.53	4.98	2.29	3.56	68.32	-	0.14	12	0.33	66
	17/09/2017	2910	3.42	1.80	15.36	2.95	3.02	2.98	37.82	4.14	0.18	9	0.30	343
	18/09/2017	2625	6.42	1.80	18.03	2.48	5.34	2.29	50.02	5.28	0.20	10	0.22	369
	24/09/2017	750	5.26	2.17	17.98	4.73	3.59	4.11	53.68	3.68	0.13	12	0.28	85
	01/10/2017	690	5.16	1.91	27.33	5.17	4.23	3.72	75.64	2.57	0.15	12	0.28	95
	08/10/2017	2045	4.43	2.09	17.08	3.16	3.81	2.89	46.36	4.61	0.20	9	0.26	75
	10/10/2017	3150	2.58	2.17	15.29	2.60	2.58	3.10	36.60	4.08	0.25	8	0.29	200
	12/10/2017	4422	2.88	2.07	15.99	2.65	2.47	2.90	51.20	4.10	0.20	10	0.13	186
	22/10/2017	735	5.53	1.63	25.39	4.72	3.01	4.19	65.88	3.34	0.16	13	0.32	56
	05/11/2017	480	5.65	1.65	27.58	5.57	3.02	4.31	73.20	2.93	0.12	13	0.33	18
	12/11/2017	420	6.03	1.84	26.64	5.22	3.54	3.56	82.96	2.63	0.14	13	0.24	22
	20/11/2017	400	4.44	1.22	25.01	4.56	2.88	4.37	67.01	2.38	0.15	13	0.29	17
	27/11/2017	327	3.86	1.45	22.46	4.69	1.81	3.25	58.56	2.64	0.15	13	0.34	7
	03/12/2017	375	8.50	2.00	21.65	6.42	6.69	4.70	69.54	4.58	0.12	12	0.26	4
	10/12/2017	260	5.61	1.71	24.48	5.69	3.42	4.34	57.34	3.52	0.10	13	0.40	13
	18/12/2017	326	5.79	2.14	24.39	5.38	4.50	5.03	69.54	2.72	0.09	13	0.28	10
	24/12/2017	287	7.04	1.84	24.89	6.65	3.79	4.48	76.86	4.08	0.07	13	0.29	6
	31/12/2017	255	4.60	1.68	26.27	5.37	2.64	3.80	74.42	2.26	0.13	12	0.29	13
	21/01/2018	310	6.72	1.45	28.38	8.43	2.63	5.37	95.20	1.18	0.12	12	0.27	5
	27/01/2018	235	7.45	3.49	27.94	6.19	2.88	3.85	64.66	2.05	0.04	11	0.46	9
	04/02/2018	275	8.30	2.09	28.76	6.84	5.80	5.67	73.20	3.77	0.12	11	0.36	6
	04/03/2018	260	4.18	1.73	27.21	5.33	2.38	4.35	78.08	2.23	0.03	12	0.27	3
	11/03/2018	180	4.89	2.18	30.04	6.16	3.30	4.87	78.08	4.76	0.08	11	0.32	23
	02/04/2018	148	10.15	2.34	30.54	7.58	7.63	5.80	57.30	2.97	0.06	11	0.50	14
	07/04/2018	120	5.21	1.58	30.06	6.55	2.68	4.24	82.96	2.09	0.11	12	0.32	18
	17/04/2018	142	4.72	1.85	29.25	6.25	1.88	4.05	73.20	1.92	0.20	13	0.38	7
	06/05/2018	119	8.91	2.17	23.71	5.69	6.59	4.78	62.22	5.48	0.25	11	0.33	211
	13/05/2018	335	6.60	2.05	27.64	5.50	4.01	4.61	73.20	3.64	0.25	12	0.32	55
	20/05/2018	180	5.29	2.87	27.21	5.81	2.66	5.58	62.00	2.82	0.21	12	0.41	33
	28/05/2018	176	7.10	2.30	31.14	7.70	3.69	8.85	93.94	2.04	0.22	10	0.27	25
	02/06/2018	149	5.22	2.05	27.49	5.51	2.62	3.80	74.42	2.13	0.25	12	0.33	13
	17/06/2018	240	11.81	3.21	28.47	8.15	9.51	8.73	73.20	3.16	0.21	13	0.36	12
	24/06/2018	370	5.07	1.78	24.02	5.48	2.26	4.20	75.64	0.90	0.11	12	0.26	24
	08/07/2018	300	5.25	2.16	28.80	6.26	2.44	4.28	81.74	1.28	0.25	12	0.32	52
	16/07/2018	350	3.35	1.82	22.31	4.34	2.93	5.47	65.88	1.70	0.09	10	0.21	246
	22/07/2018	1410	2.32	1.24	18.13	3.27	1.37	5.56	54.90	5.95	0.13	10	0.12	228

241 month to month (Fig. 3), showing the opposite trend of that
242 seen for solute concentration, except at My Ly (for
243 example, in June and July). The highest SSCs occurred
244 during September, October, and July at Dua and Yen

Thuong (135–317 mg/L). Peak SSC occurred in June at245My Ly (1534 mg/L), indicating significant erosion in the246upper basin due to heavy rain.247

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Fig. 2 Seasonal variations in the concentration of major ions (μM) , TDS, and SS (mg/l)



Fig. 3 Monthly variations in the concentration of TDS and SS (mg/l)

4.3 Weathering processes controlling the major ion chemistry

250 Major natural processes determining the ion chemistry of water can be identified by plotting variations in the weight 251 252 ratio between Na⁺ and Na⁺ + Ca²⁺ as a function of TDS (Gibbs 1970). The sources of major ions were divided into 253 254 three groups: precipitation dominance, rock dominance, 255 and evaporation-crystallization dominance. Figure 4 shows 256 weathering dominance for most of the samples drawn. 257 Rock weathering controls the water composition in the Ca River basin, producing a TDS value between 77 and 258 205 mg/L and a $Na^+/(Na^+ + Ca^{2+})$ ratio ranging from 259 0.10 to 0.43. 260

The three primary lithologies undergoing chemical 261 262 weathering were silicates, carbonates, and evaporites 263 (Gaillardet et al. 1997). Carbonate weathering (calcite, dolomites) produces Ca2+, Mg2+, and HCO3-. Silicate 264 weathering results in HCO₃⁻, Na⁺, K⁺, Mg²⁺, Ca²⁺, and 265 SiO₂. Evaporite dissolution results in Na⁺, K⁺, Cl⁻, and 266 SO₄²⁻ (Han and Liu 2001; Meybeck 1987; Sarin et al. 267 1989). The relationships between Ca^{2+}/HCO_3^{-} , 268 $(Ca^{2+} + Mg^{2+})$ /total cations, and $(Na^{+} + K^{+})$ /total cations 269 for the Ca River were determined to evaluate the contri-270 bution of rock weathering. The Ca^{2+} and HCO_3^{-} for most 271 samples fell along a 1:1 equiline (Fig. 5a), implying that 272



Fig. 4 The Gibbs graph of Ca River between the ratio of Na/ $(\mathrm{Na}+\mathrm{Ca})$ and total dissolved solids

carbonates dissolution dominates in this drainage basin273(Roy et al. 1999). The HCO_3^- is slightly more enriched than274 Ca^{2+} at My Ly, possibly consistent with a silicate weathering source for some of this anion (Holland 1978). The276

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scatter plot (Fig. 5b) of $(Ca^{2+} + Mg^{2+})$ against total 277 278 cations indicates a significant contribution of these two 279 cations (approximately 85% of the total). Any deviation of $(Ca^{2+} + Mg^{2+})$ from the 1:0.85 line was attributed to 280 increasing proportions of $Na^+ + K^+$) (Fig. 5b, c), implying 281 282 contributions from silicate weathering or evaporite disso-283 lution (Li and Zhang 2008; Maharana et al. 2015). The 284 correlations among geochemistry parameters and their 285 correlations with suspended solids were investigated for 286 each station (Table 2). The significant relationships Ca^{2+}/Mg^{2+} , Ca^{2+}/HCO_3^- , Mg^{2+}/HCO_3^- , 287 between Ca^{2+}/TDS , Mg^{2+}/TDS , and HCO_3^-/TDS at all stations 288 support the finding of carbonate weathering dominance in 289 290 the Ca River basin. Significant correlations between SiO₂ 291 and Na^+ , K^+ , or HCO_3^- were not found, implying minimal 292 silicate weathering. However, moderate correlations between Cl⁻, SO₄²⁻, Na⁺, K⁺, and TDS were found, 293 indicating that evaporite weathering was the source (Li and 294 295 Zhang 2008).

The Piper diagram is widely applied to determine the 296 297 classification of water on the basis of its chemical character (Maharana et al. 2015; Negrel et al. 2007; Ji and Jiang 298 2012). The triangular cationic fields of the Piper diagram 299 (Fig. 6) revealed that most of the water samples fell into 300 the Ca^{2+} field, whereas in the anion triangle, the majority 301 fell into the HCO_3^- field. Chemical data plotted on the 302 diamond-shaped central field revealed the dominance of 303 the $Ca^{2+} - HCO_3^-$ type. Therefore, $Ca^{2+} - HCO_3^-$ is the 304 dominant hydrogeochemical species in the Ca River basin. 305 The Piper diagram for our Ca River samples is similar to 306 that for the Son River (Maharana et al. 2015) and the 307 upstream Huanghe River (Fan et al. 2014), dominated by 308 carbonate weathering. However, it differs from the mid-309 and downstream sections of the Huanghe River (Fan et al. 310 2014), where evaporite dissolution dominates. They also 311 differ from the Liao River, Daling River, Hun-Tai River 312 (Ding et al. 2016), Ou River, and Min River (Liu et al. 313 2018), where silicate weathering dominates. In many 314



Fig. 5 Scatter plots between a Ca^{2+} and HCO_3^{-} , b Ca^{2+} , Mg^{2+} , and total cations, and c Na^+ , K^+ , and total cations

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$\begin{array}{llllllllllllllllllllllllllllllllllll$	0.17 0.40**		0.01	-0.10	0.12	0.06	0.00	1.00			
$\begin{array}{llllllllllllllllllllllllllllllllllll$	V 10**	0.01	0.17	-0.03	0.15	-0.19	-0.16	-0.04	1.00		
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C+-0	0.54^{**}	0.55**	0.37*	0.34*	0.76^{**}	0.18	0.15	-0.03	1.00	
$\begin{array}{llllllllllllllllllllllllllllllllllll$	0.28	0.43 **	- 0.01	- 0.12	0.23	0.35*	0.13	0.44^{**}	-0.07	0.36^{*}	1.(
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$\begin{array}{llllllllllllllllllllllllllllllllllll$	0.56^{**}	0.22	0.37*	1.00							
$\begin{array}{llllllllllllllllllllllllllllllllllll$	0.77^{**}	0.46^{**}	0.68^{**}	0.41^{**}	1.00						
$\begin{array}{llllllllllllllllllllllllllllllllllll$	0.03	0.78^{**}	0.65^{**}	0.16	0.33*	1.00					
PO ³⁻ – 0.30 SiO ₂ 0.35* TDS 0.69** TSS – 0.42**	0.49^{**}	-0.47^{**}	-0.10	0.39*	0.28	- 0.47**	1.00				
SiO ₂ 0.35* TDS 0.69** TSS – 0.42** <i>Yen Thuone</i>	0.00	-0.35*	-0.39*	-0.20	- 0.30	-0.48^{**}	0.13	1.00			
TDS 0.69** TSS – 0.42** <i>Yen Thuong</i>	0.06	0.28	0.43^{**}	0.19	0.32*	0.45**	- 0.03	-0.41^{**}	1.00		
TSS – 0.42** Yen Thuong	0.40^{**}	0.86^{**}	0.86^{**}	0.50^{**}	0.62^{**}	0.88^{**}	- 0.19	-0.49^{**}	0.51^{**}	1.00	
Yen Thuong	-0.10	-0.59^{**}	-0.53^{**}	-0.25	-0.18	-0.66^{**}	0.28	0.49**	-0.53^{**}	-0.66^{**}	
0											
Na^{+} 1.00											
K^+ 0.56**	1.00										
Ca^{2+} 0.50**	0.23	1.00									
Mg^{2+} 0.73**	0.34*	0.84^{**}	1.00								
Cl ⁻ 0.87**	0.50^{**}	0.19	0.41^{**}	1.00							
${ m SO}_4^{2-}$ 0.60**	0.39*	0.53 **	0.71^{**}	0.49**	1.00						
HCO_3^- 0.25	-0.09	0.76^{**}	0.70^{**}	- 0.06	0.40 **	1.00					

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	Na^+	\mathbf{K}^+	Ca^{2+}	${\rm Mg}^{2+}$	Cl-	SO_4^{2-}	HCO_3^-	NO_3^-	PO_4^{3-}	SiO_2	TDS	TSS
NO_3^-	0.02	- 0.03	- 0.55**	-0.45^{**}	0.31	- 0.16	-0.58^{**}	1.00				
PO_4^{3-}	- 0.08	0.09	-0.19	-0.24	0.02	-0.06	-0.12	0.16	1.00			
SiO_2	0.29	- 0.13	0.55**	0.51^{**}	0.04	0.15	0.54^{**}	$- 0.41^{*}$	-0.23	1.00		
TDS	0.59**	0.16	0.90^{**}	0.89^{**}	0.28	0.63^{**}	0.92^{**}	-0.48^{**}	-0.15	0.59^{**}	1.00	
TSS	- 0.37*	- 0.17	- 0.72**	- 0.72**	- 0.07	-0.36^{*}	-0.60^{**}	0.51^{**}	0.30	-0.69^{**}	- 0.69**	1.00
**Corr	elation is signific	cant at the 0.01	level									
*Corre	lation is significa	ant at the 0.05 le	svel									

Table 2 continued

watersheds around the world, carbonate weathering play an315important role in controlling river water chemistry because316carbonate is more susceptible to weathering than silicate317(Fan et al. 2014; Roy et al. 1999).318

4.4 Variations in major solute concentrations319at discharge320

The relationships between solute concentration and its321discharge were investigated at each hydrological station.322Concentrations of the weathering-derived solutes were323plotted against instantaneous discharge on logarithmic axes324(Fig. 7), yielding the approximate relationships between325concentration and discharge using a power law (Baronas326et al. 2017; Herndon et al. 2015; Musolff et al. 2015):327

$$C = a \times Q^b \tag{1}$$

329 where C is solute concentration, Q is discharge, and a and b are constants. The exponent b is the slope of the C-Q330 relationship on logarithmic axes. When concentration does 331 not change with changing discharge, the relationship is said 332 to be chemostatic (Moatar et al. 2017; Musolff et al. 2015). 333 When this is the case, b is between -0.1 and 0 (Herndon 334 et al. 2015; Hunsaker and Johnson 2017). When discharge 335 increases, solute concentrations can either increase (en-336 richment behavior, b > 0) or decrease (dilution behavior, 337 b < -0.1), and the relationship is said to be chemody-338 namic (Herndon et al. 2015). 339

Our results show that the upstream catchment (My Ly) 340 behaved chemostatically for the major chemical weather-341 ing products except for Na⁺ (b = -0.11), NO₃⁻ (b = 0.11), 342 and PO_4^{3-} (b = 0.15). The large store/high production rate 343 of weathering products can lead to chemostatic behavior 344 for major ions (Musolff et al. 2015). Nutrient increases 345 with increasing discharge at My Ly indicated the source 346 was organic matter degradation in the forest area. Similar 347 trends for the major ions at discharge were seen at Dua and 348 Yen Thuong. Negative slopes were found for Ca^{2+} , Mg^{2+} , 349 and HCO_3^- (b = -0.12 to -0.28) with low variability 350 $(R^2 \ge 0.5)$ and for Na⁺ and SO₄²⁻ (b = -0.13 to -0.22) 351 with moderate variability ($R^2 \ge 0.3$). The concentrations of 352 NO_3^- and PO_4^{3-} were constant or increasing, indicating 353 enrichment in nutrient sources in the basin (Musolff et al. 354 2015). Meanwhile, K⁺ and Cl⁻ behaved chemostatically, 355 increasing in the discharge at all basins, indicating 356 important biogeochemical influences (Saunders and Lewis 357 1989) or exogenous sources (atmospheric deposition) 358 (Musolff et al. 2015). For the major solutes (Ca^{2+} , Mg^{2+} , 359 Na^+ , and HCO_3^-), the dilution slopes at the downstream 360 361 station were greater than those found midstream, indicating that catchments with higher water yields were more likely 362 to express dilution (Moatar et al. 2017). The negative 363



Fig. 6 Piper trilinear diagram of Ca River water in comparison with other river basins (data from Ding et al. 2016; Fan et al. 2014; Liu et al. 2018; Maharana et al. 2015)

364 correlation between major elements and runoff increased (higher R^2 values) with decreasing elevation (Torres et al. 365 2015). Less-reactive elements $(Ca^{2+}, Mg^{2+}, and HCO_3^{-})$ 366 exhibited strong correlations with discharge and indicated 367 368 various degrees of dilution with increasing runoff (Baronas et al. 2017). However, low correlations found for PO_4^{3-} , 369 NO₃⁻, Cl⁻, and K⁺ reflected biological processes, atmo-370 371 spheric input, or anthropogenic impacts (i.e., fertilizer 372 application) (Bluth and Kump 1994; Moatar et al. 2017).

4.5 Primary evidence of reservoir impact on concentrations of suspended solids and dissolved solids

376 Located above the largest reservoir of the Ca River basin, 377 My Ly is significantly influenced by the operation of the 378 Ban Ve reservoir. The impact of water storage at the Ban 379 Ve reservoir on the correlation between SSC and discharge 380 at My Ly is shown in Fig. 8a. In August and September 381 (the rainy season), SSC increased with increasing dis-382 charge. Water storage starts at the end of the rainy season 383 (October), leading to increased water levels behind the

384 reservoir. The water level was raised until it was over the My Ly station. Consequently, runoff was delayed during 385 November and December. As a result, the SSC gradually 386 decreased as suspended sediment settled, and sediment 387 suspension was deferred during this period. The reservoir 388 opened at the beginning of January, but SSC remained low 389 until March because it was the dry season. Rain in April 390 and May can wash out the settled sediment surrounding the 391 upper part of My Ly, resulting in the steep increases in 392 SSC. Thereafter, SSC increases with increasing discharge 393 in June and July, consistent with increases seen in August 394 395 and September.

Dua and Yen Thuong, located in the lower part of the 396 main reservoirs in the Ca River basin, showed similar SSC 397 behaviors in their discharges (Fig. 8b, c): decreasing SSCs 398 399 with increasing discharge when comparing the rainy to dry seasons. This reflects the impact of suspended sediment 400 settling in the reservoirs. Upstream sediment erosion also 401 402 influenced that seen downstream; this is implied by the high SSC found in May. Generally, SSCs are positively 403 correlated with streamflow (Moore and Anderholm 2002). 404



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dilution. However, inverse correlations between ion con-

centrations and discharges were seen at Dua and Yen

Thuong, indicating dilution effects (Zhang et al. 2015).

When discharge exceeded 1000 m³/s, ion concentrations

decreased sharply, for example, on 17 December 2017, 8-

12 October 2017, and 22 July 2018. The correlations

between TSS and geochemical parameters are shown in

Table 2 and indicate that suspended solids are negatively

correlated with all ions (except NO_3^- and PO_4^{3-}) and TDS at

Dua and Yen Thuong. This is common with increases in

sediment, whereas chemical ions become diluted with

increasing discharge. In contrast, positive correlations

between TSS and K⁺, Ca²⁺, SO₄²⁻, HCO₃⁻, NO₃⁻, PO₄³⁻,

and TDS were identified at My Ly. These results imply a



Fig. 7 Variation of river elements concentration with discharge at My Ly (a, b), Dua (c, d), and Yen Thuong (e, f)

However, reservoir operations lead to a variety of SSCbehaviors in the discharge.

407 Dam closure not only affects suspended sediment but also river water quality (Muigai et al. 2010; Castilla-Her-408 nandez et al. 2014). Variations in solute concentrations 409 410 with discharge at My Ly were quite different from the 411 fluxes with discharge at Dua and Yen Thuong. Differences 412 could be the results of the impacts of the reservoir. During 413 the wet season, when water is stored at My Ly, most ion 414 concentrations were less variated than in other periods. 415 When the reservoir was open, ion concentrations increased 416 with discharge during the dry season until the highest 417 concentration was reached at the first flash flood on 17 June 418 2018. Since then, ion concentrations decreased due to

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433 significant geochemical impact of water storage in the My 434 Ly basin. When the water level at My Ly rises, My Ly can 435 act as a reservoir, resulting in sediment suspension and 436 sediment settling. Dam closures lead to increased water 437 residence time, causing increased interaction between 438 sediment particles and solutes. Dam closures also change 439 the environmental water conditions (low oxygen content 440 and high temperature), favoring biogeochemical processes 441 (Moatar et al. 2017). Muigai et al. (2010) indicated that the 442 reservoir leads to decreases in dissolved oxygen content 443 due to eutrophication and increases the TDS value. Moore 444 and Anderholm (2002) found that, in downstream reser-445 voirs, TDS concentrations increase from evapotranspira-446 tion while nutrient concentrations decrease from settling 447 and nutrient uptake, and SSCs decrease due to settling. In 448 this study, it was not easy to assess the impact of the 449 reservoir on the downstream basin because TDS values 450 showed small seasonal variations. Moreover, the TDS 451 concentration and composition were significantly influ-452 enced by multiple factors such as human activity, 453 groundwater discharge, and tributary inflow. Therefore, the 454 impact of dam closure on TDS in the downstream basin 455 requires further investigation.

456 **5 Conclusions**

From 121 Ca River water samples collected from August 457 2017 to July 2018 at three stations, cations (Ca²⁺, Mg²⁺, 458 Na⁺, and K⁺), anions $(HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, and$ 459 PO_4^{3-}), dissolved silica, SSCs, and TDS values showed that 460 carbonate weathering is dominant. Bicarbonate and cal-461 cium are the prevailing chemical species, accounting for 462 463 84.4% and 62.0% of the total anionic and cationic charges, 464 respectively. The TDS values varied from 77 to 205 mg/L, averaging 144 mg/L and decreasing in the downstream 465 466 basin with decreases in major solute concentrations.

467 The relationships between solute concentrations and 468 discharge show that the upstream catchment (My Ly) behaves chemostatically for the major chemical weathering 469 products. Similar negative trends for Ca^{2+} , Mg^{2+} , HCO_3^- , 470 Na^+ , and SO_4^{2-} with discharge at Dua and Yen Thuong 471 472 indicate dilution behaviors for those ions. The constant or increasing ion concentrations of NO_3^- and PO_4^{3-} in the 473 three basins reflect enrichment of nutrients from organic 474 475 matter degradation or human activity.

Relationships between SSC and discharge show that the
reservoirs along the Ca River trigger sediment suspension
and sediment settling at the My Ly station and decreasing
SSCs at the Dua and Yen Thuong stations. Delays in water
flow can lead to greater interactions between sediment and
solutes and can allow biogeochemical processes that result



Fig. 8 Variation of suspended sediment concentration with discharge at My Ly (a), Dua (b) and Yen Thuong (c)

in unusual changes in the concentrations of major ions and 482 TDS with increasing discharges at My Ly. 483

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