Hydrochemistry of the middle and upper reaches of the Yarlung Tsangpo River system: weathering processes and CO₂ consumption

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Abstract The study focuses on the chemical compositions of the river waters in the middle and upper reaches of the Yarlung Tsangpo river system. Samples were collected in two periods along the river system to analyze the spatio-temporal variation characteristics and to determine the weathering processes and CO₂ consumption. The results show that the chemical facies of river waters are dominated by Ca-HCO₃ type and the TDS values cover a wide range of 98.2–619.8 mg/l with an average value of 268.6 mg/l, which is higher than that of the global river waters. There are three major reservoirs (carbonates, evaporites, and silicates) contributing to the major ions, and the predominances of the reservoirs of different rivers show spatial heterogeneity. The chemical weathering rates of silicates and carbonates are 3.43 and 4.49 t/km²/year, respectively. Overall, the middle and upper reaches of Yarlung Tsangpo are responsible for 0.3 and 0.16 % of global atmospheric CO₂ consumption by silicates (1.7×10^5 mol/km²/year) and carbonates (1.27×10^5 mol/km²/year), respectively. In addition, the chemical weathering fluxes of the catchments consume atmospheric CO₂ of 0.5456 Tg C/year, accounting for 0.14 % of the total organic carbon flux to the oceans by rivers globally.

Keywords Yarlung Tsangpo · Hydrochemistry · Major ions · Weathering processes · CO₂ consumption

Introduction

Hydrochemistry is a function of natural factors, such as climate, geology, topography, and weathering of rocks and anthropogenic activities including industrial and agricultural activities, and domestic waste (Kumarasamy et al. 2013; Thomas et al. 2014). In addition, studies on hydrochemistry of rivers provide vital information on the sources of major chemical signatures, the environmental change, and on weathering processes and associated CO₂ consumption in a catchment (Dalai et al. 2002; Li et al. 2011). Chemical weathering is a major sink for atmospheric CO₂, thus knowing the chemical weathering rates is important for the determination of CO₂ consumption and its influence on global climate cooling and carbon cycle (Dalai et al. 2002; Galy and France-Lanord 2001; Wu et al. 2008b). Recently, those rivers originating in the southern slopes of the Himalaya have gained great concern. A number of arguments have suggested that the uplift of the Himalaya and heavy monsoonal precipitation promote rapid physical erosion and chemical weathering and thereby enhance CO₂ consumption (Dalai et al. 2002; Hren et al. 2007; Wu et al. 2008a).

The Yarlung Tsangpo River originates from the middle section of northern slope of the Himalaya Mountain, playing an important role in the regional water resources and eco-environment. However, there are only a few studies on the hydrochemistry of Yarlung Tsangpo, especially the middle and upper parts, due to the high elevation and oxygen-deficient atmospheres. Previous studies on the Yarlung Tsangpo have focused on water quality (Huang

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et al. 2011) and the data are mainly from the mainstream (Hren et al. 2007). No information is available on weathering processes and the associated CO₂ consumption rates about the reaches and tributaries in the middle and upper parts of Yarlung Tsangpo River.

In this study, extensive analysis of the mainstream and its major tributaries has been carried out to characterize the weathering reactions and the sources of dissolved elements in order to determine the CO₂ consumption in the middle and upper reaches of the Yarlung Tsangpo river system. Rates of weathering and CO₂ uptake are quantified and the spatial variations in the river system are also investigated.

Study area

The Yarlung Tsangpo River is the largest river system on the Tibetan Plateau. It originates from Jiemayangdrung glacier at the middle section of northern slope of the Himalaya Mountain (Huang et al. 2011). The upper reaches of the river, known as Maquan He, joined by Jiemayangdrung Qu, Kubizangbu and Mayum Tsangpo, run ~161 km to Lizi village through nomadic pastures with an elevation above 4400 m a.s.l. The middle reaches bring together many tributaries, such as Niduo Qu, Changguo Qu, Dargye Tsangpo, Dogxung Tsangpo, Xiang Qu, Nyang Qu, and Lhasa River, et al. Then the discharge increased several times than that of upper reaches. Along the middle reaches, floodplain and terrace are developed, constituting a broad river valley plain. The drainage area is ~153,000 km² and its annual water discharge is ~309 × 10⁸ m³ above Yangcun hydrology station (Liu et al. 2007). The study area is fed mainly by the Indian monsoon with its abundant moisture and high temperature. The catchment receives most of the rain between June and September, and has its maximum discharge during this period (Huang et al. 2011; Liu et al. 2007). What is more, the evaporation is high and the average potential evaporation is 2000–2500 mm/year (Zhang et al. 2003).

Geologically, Yarlung Tsangpo drains between the KailasRange-Nyainqentanglha Shanmai and the Himalaya-Laguigangri composed of different well-exposed strata, especially the Mesozoic strata. Siliceous rocks, harzburgite, dunite, and basalt are distributed along the Yarlung Tsangpo ophiolite zone (Zhu 2012). Generally, the terranes of the catchment mostly belong to the Tethian Sedimentary Series, which are composed of Palaeozoic–Mesozoic carbonate and clastic sedimentary rocks (Galy and France-Lanord 1999). Additionally, the bedrock in the study area consists mainly of schist/felsic volcanic and mafic volcanic rock, igneous granite/granitic gneiss, sedimentary and metamorphosed sedimentary units (Huang et al. 2011).

Sampling and analysis

River water samples were collected during two periods of time, May to June and October to November of year 2013, prior to and after the monsoon, respectively. The sampling was carried out along the entire stretch of the middle and upper reaches of the Yarlung Tsangpo River system from Maizhokunggar County (~100 km northeast of Lhasa) to Zhongba County (source of Yarlung Tsangpo) (Fig. 1; Table 1). The altitudes of the sampling locations range from ~3600 to ~4800 m a.s.l. The two sampling locations, covering the mainstream and major tributaries, have been identified and located by GPS. In total, 72 samples were collected at a depth of 10 cm. Samples were stored in pre-cleaned polyethylene bottles free of air and filtered through 0.45 μm Millipore filter. The pH, water temperature, and conductivity were measured in the field using Horiba U53 (HORIBA Ltd., Kyoto, Japan). HCO₃[−] of the first sampling samples was measured by titration using H₂SO₄ on the spot while that of the second was determined by charge balance from the other ions. Upon returning to the laboratory at the Institute of Geographic Sciences and Natural Resources Research (IGSNRR), CAS, pH of the samples were re-measured and the major cations (K⁺, Na⁺, Ca²⁺, Mg²⁺) were analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) of model ICP-OES 5300DV (PerkinElmer Inc., USA) with detection limit ranges of 0.1–1 ppb for K, Na and <0.1 ppb for Ca, Mg. Additionally, anions (F[−], Cl[−], NO₂[−], Br[−], NO₃[−], SO₄^{2−}, HPO₄^{2−}) were determined by ion chromatography of model ICS-2100 (Dionex Corporation, USA). The detection limits for Cl[−], SO₄^{2−}, and NO₃[−] are 0.006, 0.009, and 0.05 ppm, respectively.

Results and discussion

Major element chemistry

The fundamental statistics of the sampling data collected during two periods on river water chemistry are summarized in Tables 1 and 2 and Fig. 2. The pH values of all samples were in the range of 7.74–9.07 showing a fairly high buffering capacity. It was slightly alkaline in nature with average values of 8.41 and 8.43 in the respective periods. The pH values were relatively homogeneous spatially and temporally. The total dissolved solids (TDS) values vary greatly from 98.2 mg/l (S2) to 619.8 mg/l (S5). Comparatively speaking, the TDS was higher during October–November measurements than the former measurements, which is possibly attributed to the monsoon heavy rainfall. The average TDS value among the whole

Fig. 1 Map of the *middle* and *upper* reaches of the Yarlung Tsangpo River system and sampling locations (filled 5-stars)

catchment is 269 mg/l, which is more than two times higher than the global average value of 100 mg/l (Berner and Berner 2012). In addition, the TDS of Nyang Qu (i.e., Nianchu He) was the highest among the tributaries (342 mg/l and 388 mg/l during two periods' measurements). The total cationic charge ($TZ^+ = Na^+ + K^+ + 2Ca^{2+} + 2Mg^{2+}$) is a measure of total dissolved contents. There is a good correlation between TDS and TZ^+ ($r = 0.99$). It varies from 1253 to 8288 μeq and 1848 to 8976 μeq of two periods, respectively. And the averages are 3253 and 3829 μeq which are higher than the world weighted average of 1125 μeq (Meybeck 2003).

In general, the solutes of river water are from a complex interaction of atmosphere, hydrosphere, and lithosphere (Kumarasamy et al. 2013 and references therein). Natural Ca^{2+} and Mg^{2+} mainly originate from igneous and metamorphic rock minerals containing calcium and magnesium, especially chain silicates and plagioclase feldspars as well as carbonate sediments and gypsum (Thomas et al. 2014). The catchment is characterized by predominant Ca^{2+} cation and a high $(Ca + Mg)/TZ^+$ ratio (Figs. 2, 4a). Its concentration ranges from 23.24 to 137.8 mg/l and 14.57 to 128.4 mg/l during two periods' measurements. Mg^{2+} varies from 2.58 to 22.69 mg/l and 1.38 to 20.0 mg/l (Table 2). While the sources of Na^+ are atmospheric

inputs, besides mineral weathering (mainly plagioclase), the dominant source of K^+ is silicates (Dalai et al. 2002; Thomas et al. 2014). The average concentrations of Na^+ and K^+ are 12.98 and 1.17 mg/l, indicating a lower abundance in rivers compared to Ca^{2+} . On the ternary plots (Fig. 3a), sample clusters are close to the Ca apex, indicating dominance of carbonate weathering contribution to major ion concentration.

The boxplot of the selected parameters of all samples of the two periods indicates that HCO_3^- and SO_4^{2-} are pronounced anions (Fig. 2). During the two sampling measurements, HCO_3^- varies from 44.76 to 155.39 mg/l and 58.57 to 189.69 mg/l and SO_4^{2-} varies from 13.96 to 360.99 mg/l and 18.87 to 356.3 mg/l. From the ternary plots (Fig. 3b), it can be noted that almost all the samples focus near the HCO_3^- apex and fall along the mixing line between HCO_3^- and $(Cl + SO_4)$, suggesting carbonate and evaporite weathering in these catchments. The concentration of NO_3^- is low, except Nyang Qu, specifically, sampling site S10. The Nyang Qu drains Shigatse city, meaning manor of fertile soil and the second biggest city of the Tibet Autonomous Region and Gyangzê County which is well-known as the "Tibetan granary." The use of agricultural fertilizers may be responsible for the higher NO_3^- concentration in Nyang Qu.

Table 1 Sampling details

Code	River	Location	Elevation (m)	Sampling dates (mm.dd)	pH
Yarlung Tsangpo mainstream					
S3	Yarlung Tsangpo	D. of Lhasa River's confluence	3582	05.30/11.01	8.29/8.13
S4	Yarlung Tsangpo	U. of Lhasa River's confluence, beneath the Qushui bridge	3593	05.30/11.01	7.74/8.17
S13	Yarlung Tsangpo	D. of Xiang Qu's confluence	3818	05.31/11.02	8.19/8.39
S15	Yarlung Tsangpo	D. of Ji Qu's confluence	4003	06.01/11.03	8.15/8.37
S18	Yarlung Tsangpo	D. of Dargye Tsangpo's confluence	4480	06.01/11.03	9.07/8.47
S19	Yarlung Tsangpo	D. of Dargye Tsangpo's confluence	4485	11.03/–	8.50/–
S31	Yarlung Tsangpo	D. of Uyuma Qu's confluence	3782	06.08/11.07	8.16/8.62
S33	Yarlung Tsangpo	D. of Man Qu's confluence	3710	06.08/11.07	8.68/8.62
Tributaries					
S1	Lhasa River	Mainstream	3825	05.29/10.31	8.49/8.41
S2	Lhasa River	D. of the tributary-Xuerongzangbu	4032	05.29/10.31	8.08/8.22
S35	Lhasa River	Mainstream	3612	05.30/11.07	8.29/8.60
S36	Lhasa River	Middle of the tributary-Duilong Qu	3816	06.11/11.09	8.74/8.66
S5	Nyang Qu	Eastern source-Karuola glacier melt runoff	4857	05.30/11.01	8.49/7.95
S6	Nyang Qu	D. of the tributary-Xuedu ihe	4146	05.30/11.01	8.30/8.16
S7	Nyang Qu	Mainstream	4283	05.30/11.01	8.35/8.20
S8	Nyang Qu	D. of the tributary-Kangrupuqu	4158	05.30/11.01	8.12/8.20
S9	Nyang Qu	D. of Xueduihe's confluence	4021	05.31/11.01	8.35/8.23
S10	Nyang Qu	Before flowing into Yarlung Tsangpo	3848	05.31/11.02	8.13/8.27
S11	Xiang Qu	Middle of the mainstream	4066	05.31/11.02	8.31/8.41
S12	Xiang Qu	D. of the mainstream	3885	05.31/11.02	8.62/8.40
S14	Xiabu Qu	Mainstream, beneath the Xiabu Qu bridge	3912	05.31/11.02	8.46/8.36
S16	Dogxung Tsangpo	U. of mainstream	4734	06.01/11.03	8.29/8.31
S17	Dogxung Tsangpo	U. of mainstream, beneath 3# bridge	4731	06.01/11.03	8.85/8.48
S29	Dargye Tsangpo	D. of a tributary	4596	06.02/11.05	7.93/8.51
S28	Dargye Tsangpo	Middle of the mainstream	4568	06.02/11.05	8.79/8.60
S25	Chai Qu	Mainstream, beneath the bridge	4580	06.02/11.05	7.76/8.52
S23	Neu Tsangpo	Before flowing into Maquan He	4596	06.02/11.04	8.97/8.58
S21	Rongchuck Tsangpo	Before flowing into Maquan He	4640	06.02/11.04	8.44/8.61
S20	Rongchuck Tsangpo	Before flowing into Maquan He	4654	06.02/11.04	8.89/8.48
S22	Maquan He	D. of Rongchuck Tsangpo's confluence	4634	06.02/11.04	8.52/8.55
S24	Maquan He	Middle of the mainstream	4589	06.02/11.04	8.65/8.56
S26	Maquan He	U. of Niduo Qu's confluence	4559	06.03/11.05	8.61/8.58
S27	Niduo Qu	Before flowing into Maquan He, beneath the bridge	4571	06.03/11.05	8.53/8.60
S32	Man Qu	Before flowing into Yarlung Tsangpo	3764	06.08/11.07	8.41/8.52
S34	Nimuma Qu	Before flowing into Yarlung Tsangpo	3698	06.08/11.07	8.58/8.72
S30	Ji Qu	Before flowing into Yarlung Tsangpo	4130	06.07/11.06	8.11/8.59

D downstream, *U* upstream – not measured

Sources of solutes

Mechanisms controlling surface water chemistry include atmospheric input, rock weathering, evaporation-crystallization processes, and anthropogenic activity (Moon et al. 2007). Stoichiometry can provide some qualitative information for determining sources of several ions (Gao et al. 2009). The equivalent molar ratios of Na/Cl and (Na + K)/

Cl are marginally higher than one, indicating the excess of Na and K could source from atmospheric input and/or anthropogenic activity except chloride evaporite such as halite (Fig. 4a). The positive correlation between SO₄ with Mg (Fig. 4b) and Mg with Ca (Fig. 4f), and the low ratio of Mg/Ca (0.3, 0.14–0.5) indicate the weathering of dolomite through H₂SO₄. (Ca + Mg) by and large balance (SO₄ + HCO₃) (Fig. 4c), and they account for 82 % of the

Table 2 Summary of chemical composition of rivers

	Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	SiO ₂	Cl [−]	NO ₃ [−]	SO ₄ ^{2−}	HCO ₃ [−]	TDS
May–June measurements										
Mean	40.72	1.73	7.54	12.53	8.18	9.74	2.17	60.68	102.47	245.75
SD	21.69	0.92	4.45	8.59	2.40	12.16	1.87	69.36	28.88	101.69
Max	128.40	5.50	20.00	47.91	13.99	63.99	11.88	360.99	155.39	565.21
Min	14.57	0.26	1.38	2.27	3.75	0.18	0.65	13.96	44.76	98.17
October–November measurements										
Mean	49.35	1.70	8.81	13.43	8.56	9.33	2.25	66.12	129.58	290.90
SD	23.11	1.01	4.36	8.26	2.53	12.54	1.14	67.89	33.72	105.62
Max	137.80	5.64	22.69	46.96	17.06	58.02	6.89	356.30	189.69	619.80
Min	23.24	0.17	2.58	1.83	3.53	0.33	0.46	18.87	58.57	154.00
May–June and October–November measurements										
Mean	45.10	1.71	8.19	12.98	8.37	9.53	2.21	63.44	116.21	268.64
SD	22.68	0.96	4.42	8.38	2.46	12.26	1.53	68.18	34.06	105.44
Max	137.80	5.64	22.69	47.91	17.06	63.99	11.88	360.99	189.69	619.80
Min	14.57	0.17	1.38	1.83	3.53	0.18	0.46	13.96	44.76	98.17
All units are in mg/l; SD standard deviation; TDS = $\sum(\text{Ca}^{2+} + \text{K}^{+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{SiO}_2 + \text{Cl}^{-} + \text{NO}_3^{-} + \text{SO}_4^{2-} + \text{HCO}_3^{-})$

Fig. 2 Boxplot showing variations of major ions and TDS

total cations (Fig. 4e). This can be deciphered with regard to supply of these ions through weathering of calcium and magnesium carbonates by H_2CO_3 and H_2SO_4 (Fig. 4d).

Generally, the mass balance approaches are commonly used including forward/direct and inverse/indirect methods to quantify the sources. The direct method is a simple budget to apportion a chemical signature to each rock type by a series of steps (Gao et al. 2009; Meybeck 1987; Roy et al. 1999). To estimate the relative contribution of the different sources of the solutes, here, we apply the direct method suggested by Galy and France-Lanord (1999) with suitable assumptions. The budget equation for any element X in rivers can be written as follows:

$$[X]_{\text{river}} = X_{\text{cyclic}} + X_{\text{eva}} + X_{\text{car}} + X_{\text{sil}} + X_{\text{anth}}, \quad (1)$$

where the subscript ‘river’ indicates river water contribution, ‘cyclic’ represents atmospheric input, ‘eva’ represents contribution of evaporite dissolution, ‘car’ and ‘sil’ are inputs from carbonate and silicate weathering, respectively and ‘anth’ represents input of anthropogenic activity.

Atmospheric input

Generally, the chemistry of rain water is primarily derived from sea salt aerosols and dissolution of continental dust (Galy and France-Lanord 1999). Since the catchment of middle and upper reaches of the Yarlung Tsangpo is relatively far from marine influence, rainwater data derived from literature are used (Table 3) (Zhang et al. 2003). To address the additions of solute cations and Cl^{-} from atmospheric input, the method of multiplying the measured molar concentration of each cation by the corresponding ion/ Cl^{-} ratio measured in rainwater is adopted. The correction for rainwater input is performed under the assumption that rainwater has the Cl^{-} content of the drainage with the lowest Cl^{-} concentration in the catchment (Hren et al. 2007). The lowest Cl^{-} concentration at site S5 ($\text{Cl}^{-} = 5.0$ and $9.2 \mu\text{mol/l}$ during two periods, respectively) is taken as being supplied entirely by atmospheric input. The estimated results show that corrections for sodium, potassium, calcium, magnesium, sulfate, and chloride are close to 2.1 (0.3–13.4) %, 11.8 (1.9–39.4) %, 7.5 (1.6–16.1) %, 1.5 (0.3–2.0) %, 0.5 (0.04–1.3) % and 10.8 (0.3–29.0) %, respectively.

Fig. 3 Ternary plots for **a** cations and **b** anions on a molar (mol/l) basis (circles and triangles indicate samples collected during May–June and October–November, respectively)

Contribution from anthropogenic activity

Anthropogenic activity can modify the chemistry of river water (Galy and France-Lanord 1999). The middle reaches of the main river and the tributaries-Nyang Qu and Lhasa River are the integrated development areas for agriculture. And in recent years, industries and tourism are being rapidly developed (Huang et al. 2011). Anthropogenic activities have played an important role in the river chemistry. However, accurately quantifying the contribution of anthropogenic activity is somewhat difficult using only the major elements. Here, we assumed that the anthropogenic input is negligible in the reaches upstream because of sparse population and so we took SO_4^{2-} , Cl^- , and NO_3^- concentrations in these reaches as riverine geochemical backgrounds (Wu et al. 2008b). The results show that for all rivers, this contribution remains minor (e.g., $\text{NO}_3^-/\text{TZ}^- = \sim 1.6\%$). Thus, the anthropogenic input correction is ignored in this study.

Evaporite contribution

Evaporite contribution is mainly the result of dissolution of halite (NaCl) and gypsum/anhydrite (CaSO_4). After the correction of atmospheric input, Cl^- mainly came from halite and SO_4^{2-} from gypsum/anhydrite and/or pyrite oxidation. It is vital to discriminate the contribution of gypsum/anhydrite releasing SO_4^{2-} from that via pyrite oxidation. However, it is difficult to figure out through the available major ions. Considering the fact that in a few samples, SO_4^{2-} concentrations (on molar basis) exceed that of Ca^{2+} indicating the contribution of SO_4^{2-} to rivers via oxidation of pyrites, and the excess equivalent charge of

(Ca + Mg) over HCO_3^- also depicts this point (see “Sources of solutes”). Thus, we assumed that SO_4^{2-} derived from gypsum/anhydrite and pyrite oxidation in the ratio of 1:1. Then the chloride and sulfate can be calculated as follows (Noh et al. 2009):

$$\text{Cl}_{\text{eva}} = \text{Cl}_{\text{river}} - \text{Cl}_{\text{cyclic}} \quad (2)$$

$$\text{Na}_{\text{eva}} = \text{Cl}_{\text{eva}} \quad (3)$$

$$\text{SO}_{4\text{eva}} = 0.5(\text{SO}_{4\text{river}} - \text{SO}_{4\text{cyclic}}) \quad (4)$$

$$\text{Ca}_{\text{eva}} = \text{SO}_{4\text{eva}} \quad (5)$$

We estimated the contribution to riverine cations from halite dissolution ($\text{Na}_{\text{eva}}/\text{TZ}^+ = 7.3\%$, 0–29.7 %) and sulfate dissolution ($\text{Ca}_{\text{eva}}/\text{TZ}^+ = 16.1\%$, 5.4–45.4 %). If all SO_4^{2-} come from gypsum/anhydrite, then an upper limit of approximation for evaporite contribution will be 39.39 %. High sulfate dissolution is calculated, especially the samples S5 (90.7 and 82.6 % during two periods), S16 (74.9 and 65.1 % during two periods), S6 (58.7 and 57.6 % during two periods), and S29 (55.5 and 54.6 % during two periods). Halite contributions are slightly lower except sample S20 (28.7 and 29.7 % during two periods). In another extreme case, the evaporite contribution will be only 7.3 %.

Silicate weathering

Silicate weathering mainly contributes Na^+ and K^+ from sodium-feldspar and potassium-feldspar weathering, and Ca^{2+} and Mg^{2+} from calcium-magnesium silicate weathering. After the correction of atmospheric input and evaporite, remaining Na^+ in the river water is mainly derived from silicate weathering and K^+ after atmospheric

Fig. 4 Scatter plots showing analytical results with interrelationship among major ions

Table 3 Chemistry of rainwater in Tibet (in μmol) (Zhang et al. 2003)

Location	Data	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-
Lhasa	1998–2000	5.14	11.2	98.7	5.5	9.7	6.9	2.6	231.7
Amdo, Dingri, Dangxiong ^a	1998–2000	10.3	12.1	46.6	5.2	2.9	1.7	3.0	137.0

^a Weighted average of three area

input is from silicate. The calculation formula is as follows (Noh et al. 2009):

$$Na_{\text{sil}} = Na_{\text{river}} - Na_{\text{cyclic}} - Na_{\text{eva}} \quad (6)$$

$$K_{\text{sil}} = K_{\text{river}} - K_{\text{cyclic}} \quad (7)$$

Calcium and Mg^{2+} derived from silicate weathering can be written as follows (Moon et al. 2007; Noh et al. 2009):

$$Ca_{\text{sil}} = (Ca/Na)_{\text{sil}} \times Na_{\text{sil}} \quad (8)$$

$$Mg_{\text{sil}} = (Mg/Na)_{\text{sil}} \times Na_{\text{sil}} \quad (9)$$

where $(Ca/Na)_{\text{sil}}$ and $(Mg/Na)_{\text{sil}}$ are the molar ratios released to river waters from silicate weathering in the catchment.

Ideally, Ca^{2+} and Mg^{2+} derived from silicate should be estimated using data from monolithologic drainages within the study area, but this is rarely attainable in regional scale field studies (Moon et al. 2007; Noh et al. 2009). Therefore, we referred to previous studies of local silicate weathering to determine the ratios. In the following discussion, we assign 0.55 and 0.3 to Ca/Na , Mg/Na (Hren et al. 2007).

Then the shares of Ca^{2+} and Mg^{2+} from silicate weathering are 17.1 and 35.2 %.

Accordingly, the fraction of cation contributions from the silicates (%Silicate) could be estimated by the ratio of $\text{TZ}^+_{\text{sil}}/\text{TZ}^+$. The %Silicate values range from 1.9 to 67.7 % with an average of 27.2 %.

Carbonate weathering

Finally, we assume the remaining Ca^{2+} and Mg^{2+} are attributed to carbonate weathering. The fraction of cation contributions from carbonate weathering can be calculated as follows:

$$\frac{\text{TZ}^+_{\text{car}}}{\text{TZ}^+} = \frac{2 \times (\text{Ca}_{\text{river}} - \text{Ca}_{\text{cyclic}} - \text{Ca}_{\text{eva}} - \text{Ca}_{\text{sil}}) + 2 \times (\text{Mg}_{\text{river}} - \text{Mg}_{\text{cyclic}} - \text{Mg}_{\text{sil}})}{(\text{Na}_{\text{river}} + \text{K}_{\text{river}} + 2 \times \text{Ca}_{\text{river}} + 2 \times \text{Mg}_{\text{river}})} \quad (10)$$

The calculated Ca^{2+} and Mg^{2+} values are 0.56 mmol/l and 0.25 mmol/l, accounting for 50 and 63.2 %, respectively. The ratio of Mg/Ca can be obtained (0.39). The results show that the %Carbonate values range from 13.4 to 73.6 % and the average value is 46.8 %.

As a summary, according to the direct model, rain was 5.3 (1.4–11.5) %, evaporite 23.3 (9.0–51.7) %, silicate 26.7 (1.9–67.7) %, and carbonate 44.6 (13.4–73.6) % of total cations on equivalent in the whole catchment. However, attention should be given to local heterogeneity, and there exist pronounced differences among the tributaries (Fig. 5). For example, cations originating from carbonates account for 70.3 % in Niduo Qu basin, while those in Xiang Qu make up just 19.5 %, suggesting the difference of geological setting.

The weathering rate in the catchment

The silicate weathering rate (SWR) and carbonate weathering rate (CWR) can be calculated using data on silicate and carbonate components of cations, coupling with information of drainage area and discharge in their basins. The SWR and CWR are calculated as the sum of cations from silicate weathering and carbonate weathering as follows (Wu et al. 2008b):

$$\text{SWR} = (\text{Na}_{\text{sil}} + \text{K}_{\text{sil}} + \text{Ca}_{\text{sil}} + \text{Mg}_{\text{sil}}) \times \text{discharge/drainage area} \quad (11)$$

$$\text{CWR} = (\text{Ca}_{\text{car}} + \text{Mg}_{\text{car}}) \times \text{discharge/drainage area} \quad (12)$$

The calculated results are shown in Table 4. The SWR in the middle and upper reaches of Yarlung Tsangpo

catchment is 3.43 t/km²/year (1.32 mm/kyr), which is a little lower than the CWR, 4.49 t/km²/year (1.66 mm/kyr). Assuming all sulfates to be of evaporite origin, the values of CWR would be underestimated. It can be seen that the SWR and CWR are much higher than the others most likely resulting from higher precipitation and runoff.

The CO₂ consumption rate

The fluxes of CO₂ consumed during silicate and carbonate weathering have been calculated from the corresponding cations, discharges, and drainage area (Amiotte Suchet et al. 1995, 2003; Wu et al. 2008a):

$$\begin{aligned} \Phi[\text{CO}_2]_{\text{sil}} &= \Phi[\text{TZ}^+]_{\text{sil}} \\ &= (\text{Na}_{\text{sil}} + \text{K}_{\text{sil}} + 2\text{Ca}_{\text{sil}} + 2\text{Mg}_{\text{sil}}) \\ &\quad \times \text{discharge/drainage area} \end{aligned} \quad (13)$$

$$\begin{aligned} \Phi[\text{CO}_2]_{\text{car}} &= \Phi[\text{TZ}^+]_{\text{car}} \\ &= (\text{Ca}_{\text{car}} + \text{Mg}_{\text{car}}) \times \text{discharge/drainage area}. \end{aligned} \quad (14)$$

The study of (Qin et al. 2006) showed that the chemical weathering flux based on data sampled during peak flow months is in best agreement with annual time-series estimates and the worst during lean flow. Our data of major ions of water samples collected in June and November, which are comparatively water-rich periods, give the close approximation to the annual average weathering flux. The estimated results are shown in Table 4. The estimation of CO₂ consumption by silicate weathering may be overestimated, since sulfates could be from pyrite oxidation generating sulfuric acid which can dissolve silicates without consuming CO₂ (Noh et al. 2009). The middle and upper reaches of Yarlung Tsangpo are responsible for 0.3 and 0.16 % of global atmospheric CO₂ consumption by silicate and carbonate, respectively (Gaillardet et al. 1999), and the corresponding rates of CO₂ consumption are 1.7×10^5 and 1.27×10^5 mol/km²/year.

Comparison

The TDS values of river water are various according to different tributaries, showing conspicuous heterogeneity. Man Qu, Nyang Qu, Duoxung Tsangpo, and Dargye Tsangpo exhibit higher TDS values which exceed 300 mg/l

Fig. 5 Diagram showing the contribution of the different reservoirs for different rivers. The contribution corresponds to cations derived from different reservoirs

Table 4 Weathering rates and associated CO₂ consumption fluxes

River basin	SWR		$\Phi[\text{CO}_2]_{\text{sil}}$		CWR		$\Phi[\text{CO}_2]_{\text{car}}$		References
	t/km ² /year	mm/kyr	10 ⁵ mol/km ² /year	10 ¹⁰ mol/year	t/km ² /year	mm/kyr	10 ⁵ mol/km ² /year	10 ¹⁰ mol/year	
Yarlung Tsangpo (Yangcun)	3.43	1.32	1.7	2.6	4.49	1.66	1.27	1.94	This study
Lhasa River	4.66	1.79	2.28	0.74	6.95	2.57	1.94	0.63	This study
Nyang Qu	2.63	1.01	1.3	0.14	6.27	2.32	1.84	0.20	This study
Huang He	3.0	1.1	0.9	1.3	26.1	10.9	2.7	4.0	Wu et al. (2008a)
Yangtze River			3.81				0.72		Li and Zhang (2005)
Brahmaputra	10.3	3.8	1.5	8.7	35.4	14.8	3.4	19.9	Gaillardet et al. (1999)

during the two measurements. The analysis of ionic concentration indicates that the higher TDS values of these rivers result from relatively higher sulfate than other tributaries. These observations suggest the evaporite weathering and pyrite oxidation make large contributions to the TDS. Compared with other world rivers, the TDS of study rivers are relatively higher, averaging 269 mg/l, which is 2 times higher than that of the Brahmaputra (110 mg/l) (Singh et al. 2005) and ~1.5 times of the Indus Rivers (164 mg/l) (Karim and Veizer 2000) and the Ganges (130 mg/l) (Galy and France-Lanord 1999). While it is very similar to that of the Upper Huang He (274 mg/l) (Wu et al. 2005), it is lower than that of the rivers originating in the Qinghai–Tibet Plateau (Huang et al. 2009; Wu et al. 2008a). The water chemistry and TDS are strongly influenced by the lithology, hydroclimate, geography, and

human activities, etc. (Li et al. 2011 and references therein). The comparatively higher TDS is probably attributed to high weathering rates, intense evaporation, and the dissolution of evaporites.

The weathering rates of the Lhasa River are somewhat higher than the main stream of Yarlung Tsangpo river. Nevertheless, the weathering rates of the Lhasa River, Nyang Qu, and the main stream of Yarlung Tsangpo are comparatively lower than the Brahmaputra (Table 4). This can be interpreted by the fact that the Brahmaputra has the deepest gorge which has a very steep slope causing turbulent and rapid water flow. Besides, the intensive precipitation also leads to intense weathering (Wu et al. 2008b and references therein).

The atmospheric CO₂ consumption by silicates for the upper and middle reaches of the Yarlung Tsangpo is close

to the Brahmaputra reported by Gaillardet et al. (1999), while it is 2–3 times than that of Yangtze, Mackenzie, and the Indus (Gaillardet et al. 1999; Millot et al. 2003). The study area is about $0.15 \times 10^6 \text{ km}^2$, accounting for 0.1 % of the global land surface area. However, the chemical weathering fluxes of the catchment consume atmospheric CO_2 of 0.5456 Tg C/year, accounting for 0.14 % of the total organic carbon flux to the oceans by rivers globally (Cole et al. 2007; Ludwig et al. 1996).

Conclusions

The middle and upper reaches of Yarlung Tsangpo and its tributaries have been extensively sampled during the two periods. The analysis of the major elements in the rivers provides the following conclusions:

1. The waters are mildly alkaline, and the TDS values are relatively higher, from 98.2 to 619.8 mg/l with an average of 268.6 mg/l. Among the tributaries, TDS values of Man Qu, Duoxung Tsangpo, Nyang Qu, and Dargye Tsangpo are higher than 350 mg/l due to the excess of sulfate.
2. Carbonate dominates the water chemistry and contributes high Ca^{2+} and HCO_3^- to the rivers showing the dominant hydrochemical facies of Ca- HCO_3 type on the whole catchment scale.
3. Silicates contribute $\sim 27 \%$ (on molar basis) to the total cations on average in the whole catchments, the rest coming from carbonates, evaporites, and rain in decreasing order. Silicate weathering rate in the study area is $3.43 \text{ t/km}^2/\text{year}$ and that of carbonate is $4.49 \text{ t/km}^2/\text{year}$.
4. CO_2 consumption rates by silicate and carbonate weathering are $1.7 \times 10^5 \text{ mol/km}^2/\text{year}$ and $1.27 \times 10^5 \text{ mol/km}^2/\text{yr}$, which are responsible for 0.3 and 0.16 % of global atmospheric CO_2 consumption by silicate and carbonate respectively, reflecting a significant contribution considering the small area.

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