

Mechanisms Controlling the Dissolved Load, Chemical Weathering and CO₂ Consumption Rates of Cauvery River, South India: Role of Secondary Soil Minerals

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1 **Mechanisms controlling the dissolved load, chemical weathering**
2 **and CO₂ consumption rates of Cauvery river, South India: Role of**
3 **secondary soil minerals**

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1 **Abstract**

2 Hydrochemical assessment of the Cauvery River Basin (CRB), an east flowing Western
3 Ghats (WG) river is carried out to understand the dissolved load sources and controlling
4 mechanisms along with quantification of source-wise input to the dissolved load. Silicate
5 weathering rates (SWR) and associated CO₂ consumption rates (CCR) are evaluated on account
6 of silicate basement of CRB comprising of granulites and supracrustal rocks. The source-wise
7 solute load contributions estimated using the chemical mass balance model signify that 68% of
8 total load is from chemical weathering followed by 18.5% and 13.5% from anthropogenic and
9 atmospheric inputs respectively, implying that chemical weathering is the major solute load
10 controlling mechanism for CRB. The intensity of silicate chemical weathering occurring in the
11 CRB is measured by index (Re) and found to be > 3, suggesting an incomplete weathering of
12 drainage rocks (primary minerals) resulting in formation of soils comprising of secondary
13 minerals including oxides, alumino-silicates and clay minerals (smectite, kaolinite and
14 montmorillonite). Detailed understanding of chemical weathering mechanisms is carried out
15 using Ca/Na and Mg/Na elemental ratios of different end-members including primary minerals
16 from rocks and secondary minerals from soils. The Na-normalized mixing diagram reveals that
17 chemical weathering of secondary minerals is dominating and the solute load contribution to
18 the total dissolved load is significantly higher from secondary minerals (35.5%) than primary
19 minerals (23.5%). The SWR and associated CCR are estimated to be 13 t.km⁻².y⁻¹ and 3.3 ×
20 10⁵ mole.km⁻².y⁻¹ respectively at outlet (Musiri) of the CRB. Results also indicate that SWR of
21 the east flowing WG river, Cauvery are several times (~4) lower than the average SWR of west
22 flowing WG rivers even though the associated CCR are comparable for both river systems.

23 **Key words:** solute load, source-wise input, anthropogenic activities, primary rock minerals,
24 secondary soil minerals, silicate weathering rates.

25

1. Introduction

Dissolved solutes in river waters are acquired by various natural and anthropogenic sources as a result of diverse biogeochemical processes. Among the natural sources, continental weathering and subsequent erosion are the major processes that controls the solute load of river there by transporting materials to ocean realm and geochemical cycling of elements at the Earth's surface. Rock minerals (primary minerals) of Earth's crust can undergo chemical weathering coupled with physical weathering by the action of water in presence of CO₂, NO₂, SO₂, and O₂ resulting in the formation of weathered materials from parent rock consisting of soils with chemically altered minerals (secondary minerals) such as oxides, alumino-silicates, and clay minerals (smectite/kaolinite/montmorillonite) depending on the intensity of weathering. Analogous to primary minerals, secondary minerals in soils can further undergo chemical weathering with higher rates as the surface area of water-soil mineral interaction is higher than the water-rock mineral interaction¹⁻². Chemical weathering of both primary and secondary minerals consumes atmospheric CO₂ as dissolved bicarbonates and the amount of CO₂ intake depend on the weathering rate of minerals. Silicate weathering has been recognized as the controlling factor on long-term evolution of atmospheric CO₂ and hence on Earth's climate³⁻⁵. The silicate weathering rates (SWR) and associated CO₂ consumption rates (CCR) need to be estimated for the global carbon cycle budget modelling and are generally computed from geochemical mass balances of river systems⁶.

In Indian subcontinent, studies related to chemical weathering mainly focus on major ion and isotope characterization as well as the estimation of SWR and associated CCR values for Himalayan rivers⁷⁻¹⁰ and for smaller rivers draining the deccan basalt¹¹⁻¹². Studies on peninsular rivers comprise of Braun *et al.*² (Kabini), Gupta *et al.*¹³ (Narmada), Gurumurthy *et al.*⁵ (Netravati), Pattanaik *et al.*¹⁴ (Cauvery) and Thomas *et al.*¹⁵ (Pambar), carried out the hydrochemical characterization along with estimation of SWR and associated CCR. However,

1 studies related to understanding the importance of secondary minerals in chemical weathering
2 and quantification of their contribution to the dissolved load at river basin scale are sparse.
3 Violette *et al.*¹⁶ attempted to understand the role of secondary minerals in chemical weathering
4 through modelling approach in an experimental watershed, the Mule hole. Gurumurthy *et al.*¹⁷
5 used Sr isotope ratios to assess the role of secondary minerals in chemical weathering of
6 Netravati river and proposed that solute contribution from secondary minerals is significant to
7 the river load during monsoon season compared to the pre-monsoon.

8 The study area, Cauvery River Basin (CRB) comprise of varying lithological
9 compositions, elevations and climatic conditions which play a crucial role in rock (primary
10 minerals) weathering that underpins the formation of weathered materials consisting of soils
11 highly characterized by secondary minerals from upstream to downstream¹⁸⁻¹⁹. Many studies
12 reported that industrial and urban waste are polluting the tributaries of Cauvery river along its
13 course at many places due to increased developmental activities²⁰⁻²². Pattanaik *et al.*^{14,23} studied
14 the Sr isotopic ratios and major ion chemistry of Cauvery river, concluded that more than 90%
15 of the total dissolved load is derived from weathering of silicate rocks and also estimated the
16 SWR and associated CCR values. However, previous studies have not elaborated the
17 anthropogenic impacts on the dissolved load and the role of secondary minerals in chemical
18 weathering. Present study emphasizes the source-wise solute load quantification, role of
19 secondary minerals and anthropogenic activities in controlling the dissolved load of CRB
20 followed by the estimation of weathering index (Re), SWR and associated CCR.

21 **2. Materials and methods**

22 **2.1 Study area**

23 The Cauvery river (Fig. 1) originates from Brahmagiri hill range of Western Ghats
24 (WG) at an elevation 1341m situated in the Coorg district of Karnataka, South India and drains
25 an area of 81,155 sq.km with a total length of 800 km from origin to outfall. In South India,

1 the CRB possess high socio-economic significance as the river basin drains through several
2 hectares of agricultural land. Temperature of the CRB varies from upper reaches to the plain
3 regions mainly due to altitude variations²⁴. Rainfall varies considerably across the basin,
4 western side of basin receives higher rainfall during southwest monsoon (Jun to Sep) up to
5 Mettur dam, while southeastern portion receives higher rainfall during the northeast monsoon
6 (Oct to Dec) seasons²⁵. Water balance study²⁶ of the CRB reveals that evapo-transpiration is
7 higher than water yield during February to June months due to higher temperatures during
8 summer. Land use land cover analysis of CRB in 2005 reveals that agricultural land is dominant
9 in the basin (66.21%) followed by forest area (20.5%), built up area (4.01%) and waste land
10 (3.86%). However, the land use land cover analysis of CRB in 2014 claims that, forest land has
11 reduced due to agricultural activities while built up area increased due to rapid socio-economic
12 developments²⁴. Soil types vary across the basin, mostly possessing red soils followed by black,
13 mixed, alluvial and lateritic soils http://karenvis.nic.in/Databse/Natural_Resources_7958.aspx.
14 Moreover, trivial amounts of pedogenic carbonate accumulation is found at some places
15 characterized by lower than average rainfall of WG within the CRB²⁷⁻²⁸.

16 The CRB forms the part of South Indian shield that constitute the igneous and
17 metamorphic rocks of Precambrian age and sedimentary rocks (Fig. S1) of late Jurassic to
18 recent age²⁹⁻³⁰ and possess geological significance as the river basin undergo several tectonic-
19 sedimentary evolutionary phases. Geologically, CRB constitutes two geological terrains –
20 northern greenstone terrain (Dharwar Craton) and southern granulite terrain (SGT) separated
21 by a transition zone. Northern greenstone terrain comprises of rocks of granitic composition
22 included with supracrustal belts metamorphosed to lower than amphibolite facies such as
23 tonalite–trondhjemite and granodiorite. Southern granulite terrain comprises of granitic and
24 supracrustal belts that are metamorphosed to granulite grade resulting in rock like charnockite,
25 pyroxene granulite and high-grade metamorphic assemblages. Closepet granite intruded into

1 gneiss, charnockites as large block mountain masses at the south of transition zone^{18,31}.
2 Carbonatites hosted within pyroxenite dikes intruded into the charnockites are found in a
3 smaller area of Hogenakkal region³². Lower part of the basin (below Musiri) comprises of
4 faunal rich sedimentary rocks such as limestone, sandstones and quaternary sediments³³.

5 **2.2 Hydrochemical data**

6 Present study uses the multiannual hydrochemical data of Cauvery river provided by the
7 Central Water Commission (CWC), an organization of Ministry of Water Resources,
8 Government of India. CWC has a large number of river monitoring sites called hydrological
9 observatory (HO) stations for Indian rivers. The hydrological as well as hydrochemical data
10 obtained from these stations are available with Water Resources Information System of India
11 <http://indiawris.gov.in/wris/#/SWQuality>. There are six HO stations that exist along the main
12 channel of the Cauvery river from upstream to downstream²⁴ (Cauvery basin report, 2014) and
13 their locations are shown in the base map, Figure 1. Among these HO stations, ‘Kudige’ is
14 located in the upstream region and ‘Musiri’ is located at farthest downstream region covering
15 an area of 66,243 km² which is almost 82% of the CRB³⁴. Hydrochemical data of these six
16 HO stations are considered for the present study, where the parameters like Na, K, Ca, Mg,
17 SiO₂, Cl, SO₄ and HCO₃, pH, EC, TDS and discharge data collected on monthly basis for the
18 years 2011 – 15 are used and their seasonal average values are provided in Table 1. Further,
19 this hydrochemical data is validated by using the normalized inorganic charge balance (NICB)
20 test, using the following equation.

$$21 \text{ NICB} = [(Tz^+ - Tz^-) / (Tz^+ + Tz^-)] \times 100\% \text{ ----- (1)}$$

22 NICB is the extent of deviation between sum of cations charge (Tz⁺) and sum of anions charge
23 (Tz⁻) expressed in equivalents. The NICB values (Table 1) are generally within 10% for all the
24 data points used, suggesting that major ions are by and large balanced. In addition, the scatter
25 plot between Tz⁺ and Tz⁻ shows good correlation (Fig. 2a), indicating that the data is highly

1 reliable³⁵. Variation in the multiannual hydrochemical data presented in the box plot of Fig. 2b,
2 shows significant variations among all the dissolved solutes, indicating the prominent spatio-
3 temporal differences in the river water chemistry.

4 In following sections, the validated hydrochemical data is used for appraising the
5 dissolved load sources, controlling factors and chemical weathering mechanisms along with
6 the quantification of source-wise input, silicate weathering index (Re), chemical weathering
7 and CO₂ consumption rates. Relative importance of various solute acquisition mechanisms viz.
8 atmospheric precipitation, water-mineral interaction, evaporation-crystallization and
9 anthropogenic activities are deciphered by different ionic ratios and relations perceived through
10 scatter diagrams including the Gibbs model of TDS vs Na/(Na+Ca). The source-wise input to
11 the total dissolved load is determined by using the chemical mass balance model based on the
12 major ion concentrations. Silicate weathering index is used for measuring the intensity of
13 silicate chemical weathering occurring in the drainage basin. Mixing analysis of Na-normalized
14 elemental ratios of different end-members is followed to understand chemical weathering input
15 from various geochemical species to the dissolved load. Further, the implications of chemical
16 weathering in the drainage basin are realized by estimating the SWR and associated CCR.

17 **3. Results and discussions**

18 **3.1 Sources and mechanisms controlling the dissolved load**

19 Sources of dissolved solutes in the river waters³⁶⁻³⁷ are mainly (1) Cyclic salts which are
20 precipitation inputs carried from ocean to land and modified by the atmospheric processes (2)
21 Anthropogenic inputs including solid and liquid wastes from settlements, seepages, agricultural
22 and industrial activities, etc. (3) Water-mineral interaction products including the chemical
23 weathering of drainage minerals.

1 Gibbs³⁸ model demonstrate the relative importance of solute acquisition mechanisms like
2 precipitation, water-rock/soil interaction and evaporation. Gibbs diagram for the CRB waters
3 (Fig. 3a) shows the dominance of water-rock/soil interaction. Nevertheless, samples are not
4 clustered at one point due to increasing TDS concentrations from upstream to downstream,
5 rather range from precipitation-dominated to evaporation-dominated region with most samples
6 are classified under water-rock/soil interaction. This resembles the impact of excessive
7 chemical weathering, influence of anthropogenic activities and climatic conditions in the
8 drainage basin (sub-humid climate in upstream region to semi-arid in downstream). In addition,
9 the scatter plot (Fig. 3b) of HCO₃ and Na+K+Ca+Mg (total cations) shows good correlation
10 among them ($R^2 = 0.815$), suggesting that the common source for all these ions is most possibly
11 the chemical weathering of drainage minerals. However, the deviation from 1:1 towards total
12 cation concentrations indicate the sources other than chemical weathering, most probably the
13 anthropogenic activities yielding significant concentrations of Na. Thus, both Gibbs model and
14 scatter plot of HCO₃ vs total cations emphasize that water-rock/soil interaction thereby the
15 chemical weathering of drainage minerals is the major solute acquisition mechanism for CRB.

16 Scatter plot of Na/Cl versus Cl is used to characterize the relative importance of solute
17 sources like cyclic salts, anthropogenic activities and silicate weathering. Na/Cl ratio below
18 0.86 indicates cyclic salt sources, whereas the ratio close to 1:1 indicates the addition of both
19 Na and Cl due to a common source (evaporite dissolution or anthropogenic activities) and the
20 ratios greater than 1:1 generally interpreted as the addition of Na by silicate weathering. Fig.
21 4a shows Na/Cl versus Cl plot for the CRB, indicates the presence of all the aforesaid processes.
22 Considering the study area, significant amount of Cl is being added up linearly from upstream
23 (Kudige) to downstream (Musiri) region as shown in Fig 4b. Since there are no evaporite
24 minerals present in the study area, these higher concentrations of Cl most likely originated from
25 the anthropogenic activities that are markedly increase downstream along the river course.

1 Moving from the upstream to the downstream, Cauvery river is flowing through industrial,
 2 agricultural and settlement areas. The middle and downstream regions of Cauvery main stream
 3 is merges with its most polluted tributaries, Amaravathi and Noyyal which are the carriers of
 4 industrial and sewage effluents to the main streams of Cauvery²⁰⁻²². Thus, impact of
 5 anthropogenic activities can be clearly seen on the solute load of CRB moving to down reaches.

6 **3.2 Degree of chemical weathering - evidence for secondary soil minerals**

7 To account for the intensity of silicate rock weathering occurring in the CRB, degree of
 8 silicate chemical weathering is determined by using the index (Re) proposed by Tardy³⁹. This
 9 index is based on the number of cations released into water relative to silica and alumina which
 10 is in turn related to the mean chemical composition of bed rock minerals and is as follows⁴⁰.

$$11 \quad \text{Re} = \frac{3\text{Na} + 3\text{K} + 2\text{Ca} - \text{SiO}_2}{\text{Na} + \text{K} + \text{Ca}} \text{-----} (2)$$

12 In the above equation (2), coefficients are derived from the chemical composition of minerals
 13 present in the drainage basin excluding the Mg minerals as the entire basin is composed of
 14 felsic minerals. However, present study uses slightly modified equation in order to incorporate
 15 Mg minerals like biotite, hypersthene and hornblende found in CRB along with the felsic
 16 minerals present in the granite substratum. The modified weathering index equation is likely;

$$17 \quad \text{Re} = \frac{3\text{Na} + 3\text{K} + 2\text{Ca} + 3.6\text{Mg} - \text{SiO}_2}{0.5 \text{Na} + 0.5 \text{K} + \text{Ca} + 1.46\text{Mg}} \text{-----} (3)$$

18 In this equation (3), coefficients are derived based on following mineral compositions; feldspar
 19 minerals including orthoclase, anorthite, albite and mafic minerals covering biotite,
 20 hypersthene and hornblende. Re values of 0, 2 and 4 corresponds to allitization (formation of
 21 Gibbsite and Goethite), monosiallitzation (formation of Kaolinite) and bisiallitzation
 22 (formation of Smectites) respectively³⁹⁻⁴⁰. If the value of Re > 2, but varies between 2 to 4,
 23 indicating formation of chlorite, montmorillonite, illite, vermiculite, and sericite. Considering
 24 CRB, the Re values vary between 2 to 4 over different parts of the study area with a discharge

1 weighted average of 3.3 indicating bisiallitization stage of weathering (less intense weathering)
2 i.e., incomplete weathering with formation of kaolinite, chlorite, montmorillonite and smectite
3 mineral assemblages in soils. Further, abundance of these secondary minerals in CRB
4 evidenced by studies of Sharma and Rajamani¹⁸; Tripathi and Rajamani³¹; Rajamani *et al.*¹⁹.

5 **3.3 Elemental ratios of different end-members- mixing analysis**

6 In order to account for the chemical weathering input from different geochemical end-
7 members, present study uses the modified Na-normalized Ca versus Mg mixing diagram by
8 defining ‘3’ different geochemical end-members in terms of Ca/Na and Mg/Na molar ratios -
9 primary silicate minerals from rocks, secondary silicate minerals from soils and carbonate
10 minerals. The primary (rock) minerals end-member is developed following Rao *et al.*⁴¹;
11 Sharma and Rajamani¹⁸; Jayananda *et al.*⁴²; Tomson *et al.*⁴³; Rajamani *et al.*¹⁹; Braun *et al.*².
12 The carbonate end-member is developed from geochemical composition of Hogenakkal
13 carbonatite by Pandit *et al.*³² and from the study by Violette *et al.*²⁸ about the geochemistry of
14 calcretes (pedogenic carbonates). Finally, the secondary soil minerals end-member is
15 developed by using the weathered profile geochemical data provided by Sharma and
16 Rajamani¹⁸; Tripathi and Rajamani³¹; Rajamani *et al.*¹⁹. The molar ratios of Ca/Na and Mg/Na
17 estimated for various end-members from the previous studies are provided in Table 2.

18 The Na-normalized mixing diagram thus developed along with the river water samples is
19 shown in Fig. 5, which is slightly different from the Na-normalized mixing diagram used by
20 various researchers^{5,14,44} as it involves an additional end-member, ‘secondary minerals’
21 representing the secondary silicate minerals in soils. Accordingly, the Na – normalized Ca
22 versus Mg mixing diagram of CRB shows the aforementioned ‘3’ general end-members.
23 Primary minerals end-member is generated by taking into account all the major silicate rocks,
24 while the carbonate end-member is determined by taking all the carbonate sources and the
25 secondary minerals end-member is developed by considering the silicate minerals in soils of

1 each major lithology exposed from upstream to downstream. In the Na-normalized mixing
2 diagram, granite and granodiorite show the lowest Ca/Na and Mg/Na values while the other
3 silicate rock types gneiss, biotite gneiss, charnockite and felsic granulites are lying almost
4 closely. The average Ca/Na and Mg/Na values of these silicate rocks is handled as primary
5 minerals end-member which is similar to the silicate end-member range developed by
6 Gaillardet *et al.*⁴⁵. The carbonate end-member shows the highest Ca/Na and Mg/Na values and
7 is similar to the carbonates end-member range developed by Gaillardet *et al.*⁴⁵. Third end-
8 member secondary minerals which is exclusive to the CRB, not falling in the mixing line
9 between primary minerals and carbonate end-members rather follows a triangular relation with
10 the latter two end-members indicating that secondary minerals end-member is characterized by
11 rather higher Mg/Na values than the Ca/Na values. The Na-normalized diagram of CRB with
12 water samples (Fig. 5) show a mixing between primary and secondary mineral end-members
13 along the Mg/Na axis, with most of the samples showing a trend more towards the secondary
14 minerals end-member than the carbonate. This emphasize that most of the Mg in CRB is
15 derived from the weathering of primary and secondary minerals with negligible contribution
16 from carbonates. This leads to the inference that Mg sources in CRB river water is entirely
17 from silicate minerals not exclusively from primary silicate minerals but with significant
18 contribution from secondary silicate minerals. This can be due to higher rates of chemical
19 weathering of secondary minerals present in soils than that of primary minerals in rocks. Apart
20 from the Mg acquisition processes, the Na-normalized mixing diagram (Fig. 5) also infer that
21 Ca in CRB is derived from chemical weathering of all the '3' end-members - primary rock
22 minerals, secondary soil minerals and carbonates.

23 **4. Quantification of source-wise input to the dissolved load**

1 The chemical mass balance model^{19,46-48} is used to decipher the contribution of different
2 sources to the total dissolved load. Accordingly, chemical mass budget equation for any solute
3 'X' in the dissolved load of CRB is given by:

$$4 X_{rw} = X_{atm} + X_{anthro} + X_{chem.weath} ; \text{ such that } X_{chem.weath} = X_{primary} + X_{secondary} + X_{carb} \text{ -----(4)}$$

5 where rw, atm, anthro and chem.weath are river water, atmospheric input, anthropogenic input
6 and chemical weathering inputs respectively. Primary, secondary and carb are inputs from
7 primary minerals, secondary minerals and carbonate respectively.

8 **4.1 Atmospheric input**

9 Quantification of solute load from atmospheric processes to the river waters is
10 estimated using the equation (5), where chloride (Cl) is being used as the proxy due to its
11 conservative nature through hydrological cycle within the watershed^{1,49}.

$$12 X_{atm} = (X/Cl)_{rain} \times Cl_{ref} \text{----- (5)}$$

13 where X_{atm} is the molar concentrations of atmospheric input for a given element X (=Na, K,
14 Ca and Mg) and $(X/Cl)_{rain}$ is the X/Cl molar ratios of rainwater. Cl_{ref} is the critical chloride
15 concentration that accounts for evapo-transpiration, atmospheric wet and dry deposition
16 processes. In order to estimate the Cl_{ref} values, rainwater chloride concentration is multiplied
17 by 'F_{et}' to account for concentration effects of evapo-transpiration and 'F_{deposition}' to account
18 for interception deposition and effects of canopy such that, $Cl_{ref} = Cl_{rain} \times F_{et} \times F_{deposition}$. This
19 Cl_{ref} is used for further quantification purposes which results in providing the maximum¹
20 atmospheric input (upper limit) possible to the river waters rather than simply using the
21 rainwater chloride concentration alone. The factor 'F_{et}' calculated by using the rainfall and
22 runoff data is estimated to be 1.97 for CRB based on the study by Zade *et al.*⁵⁰. Rainwater
23 chemical composition obtained from the study of Rao *et al.*⁴¹ is used for quantification and
24 provided in Table S1. Rao *et al.*⁴¹ reported the rainwater and throughfall chemical composition

1 at Silent Valley (Nilgiri hills region within CRB) and concluded that ionic concentrations in
 2 throughfall are higher than the rainwater due to interception deposition as well as cycling of
 3 chemical species by canopy. Thus, the effects of deposition and canopy leaching are counted
 4 by the factor ‘ $F_{\text{deposition}}$ ’ and is taken as the ratio of Cl concentration in throughfall to rainfall
 5 (Table S1) which is about 1.88. The estimated values of atmospheric input to the total dissolved
 6 load (Fig. 6) vary from 21.5% at upstream (Kudige) to 6.5% at downstream (Musiri) regions
 7 with a discharge weighted average contribution of 13.5% for the whole basin. This indicates
 8 that solute load contribution from atmospheric processes to the total dissolved of CRB is minor.

9 **4.2 Anthropogenic input**

10 Anthropogenic input to the river load can be quantified using the values of Cl_{ref} assuming
 11 that there are no other sources such as evaporites for chloride except atmospheric and
 12 anthropogenic, which is indeed valid for CRB. If the chloride concentration measured in the
 13 river water is less than Cl_{ref} , then the whole chloride in river water is assigned to atmospheric
 14 origin and if it is more than Cl_{ref} , then the atmospheric input correction is applied with Cl_{ref}
 15 and the residual chloride (Cl_{res}) in the river water is attributed to anthropogenic input¹. This
 16 Cl_{res} is of anthropogenic origin and is balanced by the anthropogenic sodium (Na_{anthro}) in the
 17 dissolved load considering the presence of significant anthropogenic activities in the study area
 18 (section 3.1).

$$19 \quad Cl_{\text{res}} = Cl_{\text{anthro}} = Cl_{\text{riverwater}} - Cl_{\text{ref}} \text{-----} (6)$$

$$20 \quad Cl_{\text{anthro}} = Na_{\text{anthro}} \text{-----} (7)$$

21 The estimated values of anthropogenic input to the total dissolved load (Fig. 6) vary from 10%
 22 at upstream (Kudige) to 26% at downstream (Musiri) regions with a discharge weighted
 23 average contribution of 18.5% for the whole basin. This indicates that solute load contribution

1 from anthropogenic activities is significant and that about one-fifth of total solute load is from
 2 anthropogenic origin in the case of CRB.

3 **4.3 Silicate weathering input – primary minerals**

4 Solute load to the river water through chemical weathering of silicate rocks can be
 5 quantified using suitable proxies such as atmospheric input corrected Na (Na^*)⁵, atmospheric
 6 and anthropogenic input corrected Na (Na_{sil})^{46,51-52} or atmospheric input corrected Mg (Mg^*)¹²
 7 concentrations in river waters. Na in the Cauvery river waters is supplied from atmospheric
 8 input, anthropogenic activities and silicate weathering sources, contribution of Na from silicate
 9 weathering can be estimated after correcting Na river water concentrations (Na_{rw}) for
 10 atmospheric (Na_{atm}) and anthropogenic (Na_{anthro}) inputs by using the Cl_{ref} . To calculate the
 11 silicate contribution of K in the CRB, it is assumed that all the K in river waters are derived
 12 from atmospheric input and silicate weathering. The residual K in river waters after the
 13 correction of atmospheric inputs is assigned to silicate weathering. The silicate weathering
 14 contributions of Ca and Mg are estimated by using silicate component of Na (Na_{sil}) as the proxy
 15 based on two general assumptions^{5,53-54}. First, Ca_{sil} and Mg_{sil} are released in to the river waters
 16 in a fixed proportion relative to Na from the silicate minerals and the second, anthropogenic
 17 contributions of Ca and Mg are negligible. In this case, silicate weathering component budget
 18 equations are given by;

19 $Na_{sil} = Na_{rw} - Na_{atm} - Na_{anthro}$ ----- (8)

20 $K_{sil} = K_{rw} - K_{atm}$ ----- (9)

21 $Ca_{sil} = Na_{sil} \times (Ca/Na)_{rock}$ ----- (10)

22 $Mg_{sil} = Na_{sil} \times (Mg/Na)_{rock}$ ----- (11)

23 where the subscripts sil, rw, atm and anthro refers to silicate, river water, atmosphere and
 24 anthropogenic input respectively; $(Ca/Na)_{rock}$ and $(Mg/Na)_{rock}$ are the ratios of Ca and Mg with

1 which they released into river waters relative to Na from silicates. In the case of CRB, up to
2 the farthest downstream station Musiri, values of $(Ca/Na)_{rock}$ and $(Mg/Na)_{rock}$ are taken as 0.7
3 and 0.5 respectively, following the values of average silicate end-member (Fig. 5) based on the
4 mean rock composition. The estimated values of silicate weathering input (Fig. 6) to the total
5 dissolved load vary from 53% at upstream (Kudige) to 60% at the downstream (Kodumudi)
6 regions with a discharge weighted average contribution of 59% for the whole basin, which
7 indicate that the contribution of silicate weathering input is more pronounced.

8 **4.4 Chemical weathering input: Primary rock vs secondary soil minerals**

9 Dissolved solutes in Cauvery river waters are largely made up of water-rock/soil
10 interaction process (Fig. 4a and 4b) leading to the chemical weathering of drainage minerals
11 derived from primary rocks and secondary soils as discussed in section 3.1. However, solute
12 load contribution from chemical weathering of each source (primary vs secondary) is
13 characteristic to the basin and depends on degree of weathering of the drainage basin, i.e., how
14 well the terrain is drained. For example, intense weathering of rock associated with high
15 erosion rates leads to thin soil cover, rich in secondary minerals such as goethite and gibbsite.
16 The less intense/moderate weathering is associated with less erosion rates that results in thick
17 soils abundant in secondary mineral assemblages (chlorite/smectite/kaolinite) in the river
18 basin. Further, interaction between water and soil minerals occur in different ways such as
19 chemical weathering, cation exchange and adsorption⁵⁵, out of which chemical weathering of
20 the secondary soil minerals is the dominant process which depends on the residence time of
21 water on soil⁵⁶. As described in section 3.2, chemical weathering of secondary soil minerals is
22 influencing the dissolved load of Cauvery river along with primary rock minerals. In this
23 section, the contribution of primary and secondary minerals to the total dissolved load is
24 quantified assuming that all the Mg in Cauvery river waters is derived from rain input, silicate
25 weathering of both primary and secondary minerals and negligible contribution from carbonate

1 minerals. The following equations (12-15) are used to calculate the solute load contribution
2 from chemical weathering of secondary soil minerals.

3 $C_{a_{primary}} = C_{a_{sil}}$ ----- (12)

4 $Mg_{primary} = Mg_{sil}$ ----- (13)

5 $Mg_{secondary} = Mg_{river} - Mg_{rain} - Mg_{primary}$ ----- (14)

6 $C_{a_{secondary}} = Mg_{secondary} \times (Ca/Mg)_{soil}$ ----- (15)

7 where $C_{a_{primary}}$, $Mg_{primary}$, $C_{a_{secondary}}$ and $Mg_{secondary}$ are concentrations of Ca and Mg released
8 into the river waters during chemical weathering of silicate minerals present in rocks and soils
9 respectively. $(Ca/Mg)_{soil}$ is the ratio of Ca with which they are released into river waters
10 relative to Mg from silicate minerals present in soils. The computed values of solute load
11 contribution from the primary minerals (Fig. 7) to the total dissolved load vary from 15.5% at
12 upstream (Kudige) to 37.5% at middle (Biligundulu) regions with a discharge weighted average
13 contribution of 23.5% for the whole basin. Similarly, the estimated values of solute load
14 contribution from the secondary minerals to the total dissolved load varies from 37% at
15 upstream (Kudige) to 44% at the downstream (Urachikottai) regions with a discharge weighted
16 average contribution of 35.5% for the whole basin, indicating that the weathering contribution
17 of secondary minerals is significantly higher than the primary minerals. This shows that
18 chemical weathering of secondary minerals from soils is the dominant solute acquisition
19 mechanism for CRB.

20 **4.5 Carbonate weathering input**

21 It is found that the Ca concentrations in river waters ($C_{a_{rw}}$) are higher than the sum of
22 Ca contributed from atmospheric input (Ca^*) and silicate weathering ($C_{a_{sil}}$) estimated in the
23 sections 4.1 and 4.3. This indicates that, there are additional sources of Ca other than silicate
24 weathering as depicted from the Na-normalized mixing diagram (Fig. 5). Evaluating the study

1 area, the additional sources of Ca might be due to the trivial occurrence of carbonatites and
 2 calcretes in CRB. The residual excess of Ca in rivers waters after the correction of atmospheric
 3 input and silicate weathering is then allocated to carbonate weathering¹². Thus, solute load due
 4 to chemical weathering of scarcely present carbonates in CRB can be quantified using the
 5 silicate weathering yields of Ca (Ca_{sil}). Subsequently, the carbonate weathering component
 6 budget equation is given by;

$$7 \quad Ca_{carb} = Ca_{rw} - Ca_{atm} - Ca_{sil} \text{-----} (16)$$

8 where the subscripts carb, rw, atm and sil refers to carbonate, river water, atmosphere and
 9 silicate respectively. The quantified carbonate weathering input (Fig. 6) to the total dissolved
 10 load vary from 21% at upstream (Kollegal) to 10% at the downstream (Musiri) regions with a
 11 discharge weighted average contribution of 9% for the whole basin. This indicates that the
 12 contribution of carbonate weathering input is significantly lower than the silicate weathering
 13 input and shows overall control of silicate weathering on solute chemistry. Together, both the
 14 silicate and carbonate chemical weathering inputs represent 68% of the total dissolved load
 15 which imply that water-rock/soil interaction is the critical solute acquisition process for CRB.

16 **5. Chemical weathering and CO₂ consumption rates**

17 Chemical weathering rates depend on various factors; temperature, precipitation,
 18 composition of parent rock, biological effects etc. Though different methods are available to
 19 compute chemical weathering rates⁵⁷⁻⁵⁹, present study uses the river water hydrochemistry,
 20 drainage area and amount of discharge^{53,12} to compute them.

21 **5.1 Silicate and Carbonate weathering rates of CRB**

22 The silicate weathering rates (SWR) of the CRB are estimated by using the following
 23 equation^{5,12,47}.

$$24 \quad SWR = (Q/A) \cdot [(Na + K + Ca + Mg)_{sil} + SiO_2] \text{-----} (17)$$

1 where Q is the discharge in $\text{m}^3 \cdot \text{sec}^{-1}$, A is surface area of the basin in km^2 , $(\text{Na} + \text{K} + \text{Ca} + \text{Mg})_{\text{sil}}$
2 and SiO_2 are the silicate weathering derived total cation and silica concentrations (mg/L) of the
3 river water and the final values are reported in units of $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ with appropriate conversion
4 factors. The SWR of the CRB vary from 13 to 61 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ with a value of 13 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ at the
5 outlet of the basin (Musiri), which is slightly higher than the previously reported values of 9.5
6 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ by Pattanaik *et al.*¹⁴. This difference must be attributed to the modelling approach of
7 estimating the relative contributions from silicate and non-silicate sources to the dissolved load
8 of river water. Though, both studies use the elemental ratios mixing analysis approach, study
9 by Pattanaik *et al.*¹⁴ is based on Ca/Sr versus Mg/Sr ratios of primary minerals only while the
10 present study is based on Ca/Na versus Mg/Na ratios of primary minerals as well as secondary
11 minerals. Comparing the east and west flowing WG river systems, the average SWR reported
12 for west flowing rivers 53 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ ^{5,12} is several times (~ 4 times) higher than the SWR of the
13 east flowing Cauvery river. Similarly, SWR of other Peninsular rivers such as Krishna (14
14 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$)⁴⁵ are comparable to the CRB. Further, the Himalayan river systems such as Ganga
15 (10.2 - 15.2 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$),^{60,45-46} Brahmaputra (10.3 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$)⁴⁵ shows comparable SWR with
16 Cauvery while Yamuna (28 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$)⁴⁶ has higher and Indus (3.8 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$)⁴⁵ has lower SWR
17 than Cauvery. Comparing the SWR of Cauvery with world rivers, it is found that Cauvery has
18 higher SWR than the rivers draining in cratonic/shield area such as Mackenzie (1.8 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$),
19 Congo-Zaire (4.22 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$), Parana (5 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$)⁴⁵, Niger, Congo and Nyong (5.33 \pm 1.17
20 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$)⁶¹, Cameron (7 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$)⁶² and Toctatins (7.5 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$)⁴⁵, whereas Cauvery has
21 similar SWR values to Orinoco river (9.5 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$) and the Amazon river (13 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$)⁴⁵.

22 The carbonate weathering rates (CWR) of the CRB are estimated by using the following
23 equation^{12,47}.

24
$$\text{CWR} = \text{Q/A} \cdot [(\text{Ca} + \text{Mg})_{\text{carbo}}] \text{-----} (18)$$

1 where Q is the discharge in $\text{m}^3 \cdot \text{sec}^{-1}$, A is the surface area of the basin in km^2 and $(\text{Ca} + \text{Mg})_{\text{carbo}}$
 2 is the carbonate weathering derived concentrations (mg/L) of the dissolved Ca and Mg in river
 3 water and the final values are reported in units of $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ with appropriate conversion factors.
 4 The CWR of Cauvery river vary from 2 to $10.5 \text{ t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ with a value of $2 \text{ t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ at the
 5 outlet (Musiri) of the basin which is slightly higher than the previously reported values of 1.46
 6 $\text{t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ by Pattanaik *et al.*¹⁴. The estimated CWR of $2 \text{ t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ are several times lower than
 7 the corresponding SWR of $13 \text{ t} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$, suggests the limited contribution of carbonate minerals
 8 to the dissolved load and dominant role of silicate weathering in CRB.

9 **5.2 CO₂ consumption rates (CCR) of CRB**

10 The influence of rock/soil chemical weathering on atmospheric CO₂ must be understood
 11 with respect to the time frame. Chemical weathering of silicate rocks is considered as a
 12 regulating factor of CO₂ and hence the Earth's climate on long term (> 1Myr) evolution⁶³, but
 13 on shorter time scales (<1 kyr) chemical weathering of all lithologies are important for
 14 consumption of atmospheric CO₂. However, it seems that silicate weathering CO₂ consumption
 15 is highly sensitive to ongoing climatic variations⁶⁴. The CO₂ consumption rate (CCR)
 16 expressed in $\text{mole} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ during the chemical weathering of silicate minerals depend on the
 17 cation flux derived and is calculated using the equation (19),

$$18 \text{ CCR} = (Q/A) \cdot (\text{Na} + \text{K} + \text{Mg} + \text{Ca})_{\text{sil}} \text{-----} (19)$$

19 where Q is discharge in $\text{m}^3 \cdot \text{s}^{-1}$, A is surface area of watershed in km^2 and $(\text{Na} + \text{K} + \text{Mg} + \text{Ca})_{\text{sil}}$
 20 is the silicate weathering derived total cation concentration (mol/L) in the river water and the
 21 final values are reported in units of $\text{mole} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ with appropriate conversion factors. The CCR
 22 of CRB vary from 3.3×10^5 to $7.4 \times 10^5 \text{ mole} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ with a value of $3.3 \times 10^5 \text{ mole} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$
 23 at the outlet (Musiri) of the basin which is almost comparable to the range $(3.2 - 3.8 \times 10^5)$
 24 estimated by Pattanaik *et al.*¹⁴. Comparing the east and west flowing WG river systems, the
 25 average CCR of west flowing rivers $5.1 \times 10^5 \text{ mole} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ ^{15,12} is slightly higher than the average

1 CCR of the east flowing Cauvery river. Though the SWR of west flowing WG rivers are several
2 times (~4) higher than the east flowing Cauvery river (section 5.1), the CCR values are
3 comparable for both river systems. This contrary behavior must be attributed to difference in
4 degree of weathering i.e., intense weathering ($Re \sim 0$) of west flowing WG rivers result in
5 relatively high SiO_2 concentrations there by higher SWR than the moderate weathering ($Re \sim$
6 3) of east flowing Cauvery river with relatively less SiO_2 values. In addition, CCR of CRB is
7 slightly lower than the Peninsular river, Godavari ($5.8 \times 10^5 \text{ mole.km}^{-2}.\text{y}^{-1}$)⁶⁵, while it is
8 comparable to the CCR of other Peninsular river, Krishna ($3.6 \times 10^5 \text{ mole.km}^{-2}.\text{y}^{-1}$)¹². The CCR
9 of Himalayan river system such as Yamuna ($5 \times 10^5 \text{ mole.km}^{-2}.\text{y}^{-1}$)⁴⁶, Bhagirathi-Alaknanda
10 ($4 \times 10^5 \text{ mole.km}^{-2}.\text{y}^{-1}$)⁶⁰, Ganga ($6.92 \times 10^5 \text{ mole.km}^{-2}.\text{y}^{-1}$)⁴⁵ and Brahmaputra (4.93×10^5
11 $\text{mole.km}^{-2}.\text{y}^{-1}$)⁴⁵ are comparable to CRB while Indus ($0.6 \times 10^5 \text{ mole.km}^{-2}.\text{y}^{-1}$)⁶⁰ has lower and
12 Irrawady ($20 \times 10^5 \text{ mole.km}^{-2}.\text{y}^{-1}$)⁴⁵ has higher CCR than the CRB. Further, comparing the CCR
13 of Cauvery with world tropical rivers draining in cratonic/shield area such as the Amazon river
14 ($0.5 \times 10^5 \text{ mole.km}^{-2}.\text{y}^{-1}$), Orinoco river ($0.6 \times 10^5 \text{ mole.km}^{-2}.\text{y}^{-1}$), Congo-Zaire (0.5×10^5
15 $\text{mole.km}^{-2}.\text{y}^{-1}$) and Parana ($0.9 \times 10^5 \text{ mole.km}^{-2}.\text{y}^{-1}$) found to have lower values⁴⁵.

16 **6. Conclusions**

17 Multiannual hydrochemical data of the east flowing WG river, Cauvery is analyzed to
18 understand the dissolved load sources, solute acquisition mechanisms and their controlling
19 factors as well as to estimate the source-wise solute load, SWR and associated CCR. The salient
20 findings of the study are:

21 (i) The dominant solute acquisition mechanism for CRB is chemical weathering i.e., water-
22 rock/soil interaction with marginal influence of atmospheric processes at upstream followed
23 by significantly increasing anthropogenic activities towards downstream. Out of the chemical
24 weathering processes, silicate weathering is the major controlling mechanism for CRB with
25 marginal influence from carbonate weathering. Source-wise contributions (discharge

1 weighted) to the total dissolved load of CRB are estimated to be 13.5%, 18.5%, 59% and 9%
2 from atmospheric input, anthropogenic activities, silicate and carbonate weathering
3 respectively by using the chemical mass balance model.

4 (ii) The intensity of silicate chemical weathering occurring in the CRB is indicated by the index
5 (Re) > 3 suggests less intense weathering of primary minerals and formation of soils consisting
6 of secondary minerals. Understanding of chemical weathering mechanisms occurring in the
7 CRB using the Na-normalized mixing of elemental ratios reveal that weathering of secondary
8 minerals from soils is influencing the dissolved load of CRB besides the primary rock minerals.
9 The solute load contribution from secondary minerals (35.5%) is significantly higher than
10 primary minerals (23.5%) to the dissolved load of CRB.

11 (iii) The computed SWR and CCR of CRB vary markedly along the river with values of 13
12 $t.km^{-2}.y^{-1}$ and $3.3 \times 10^5 mole.km^{-2}.y^{-1}$ respectively at the outlet (Musiri). The estimated SWR
13 of east flowing WG river, CRB ($13 t.km^{-2}.y^{-1}$) are several times (~ 4) lower than the average
14 SWR of west flowing WG rivers ($53 t.km^{-2}.y^{-1}$) even though the silicate weathering associated
15 CCR are comparable for both east flowing Cauvery ($3.3 \times 10^5 mole.km^{-2}.y^{-1}$) and west flowing
16 ($5.1 \times 10^5 mole.km^{-2}.y^{-1}$) WG rivers.

17 (iv) The contrary behavior of east and west flowing WG rivers might be, due to differences in
18 degree of weathering intensity (Re). $Re > 3$ for CRB indicating the bisiallitzation phase of
19 incomplete weathering resulting in formation of secondary minerals in the drainage basin with
20 relatively less SiO_2 and high cation fluxes to the river waters, whereas west flowing WG rivers
21 have Re of 0.14, suggesting the allitization phase of complete weathering in the drainage basin
22 with relatively high silica and less cation fluxes to the river waters.

23

24

1 **Data availability statement**

2 The data that support the findings of this study are available from the India-WRIS with the
3 following link <https://indiawris.gov.in/wris/#/waterData>.

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28 **Author Contributions**

29 B.U and M.C contributed to design of the study, data preparation and manuscript writing. A.A,
30 V.V.D and G.S contributed in preparation of Maps, Figures and Tables. K.A.K contributed in
31 conceiving the ideas and reviewing the manuscript.

32 **Additional Information**

33 **Competing Interests:** The authors declare no competing interests.

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Figures

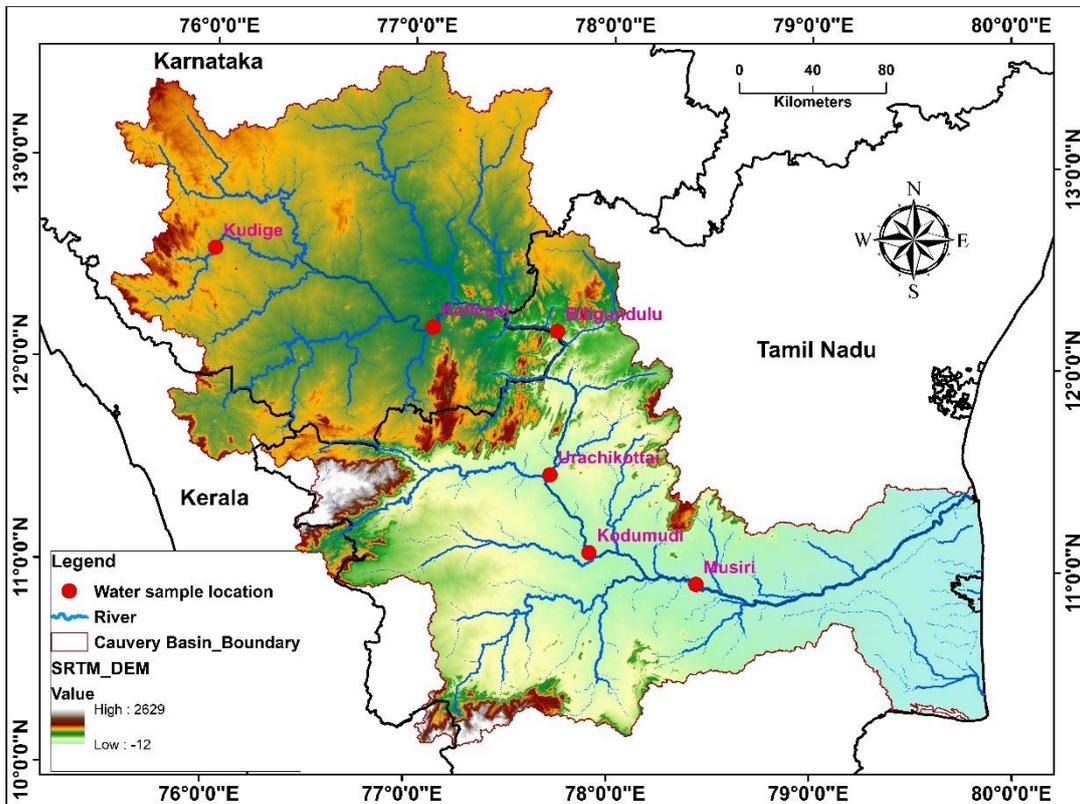
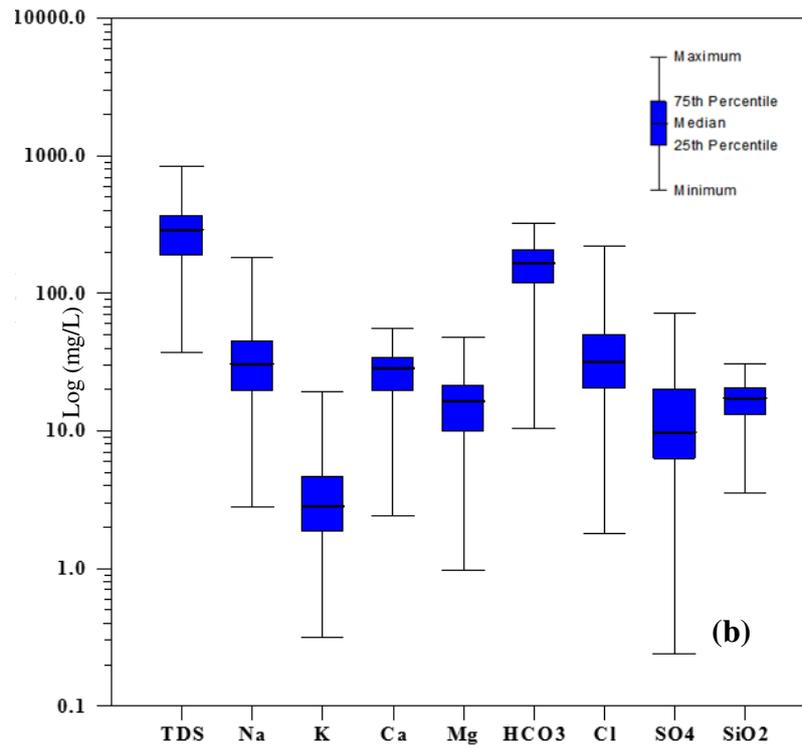
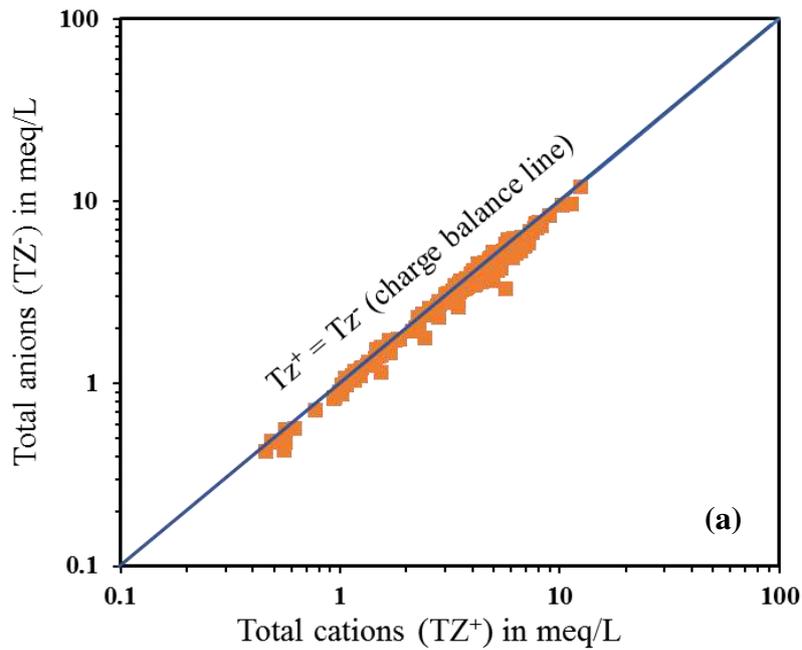


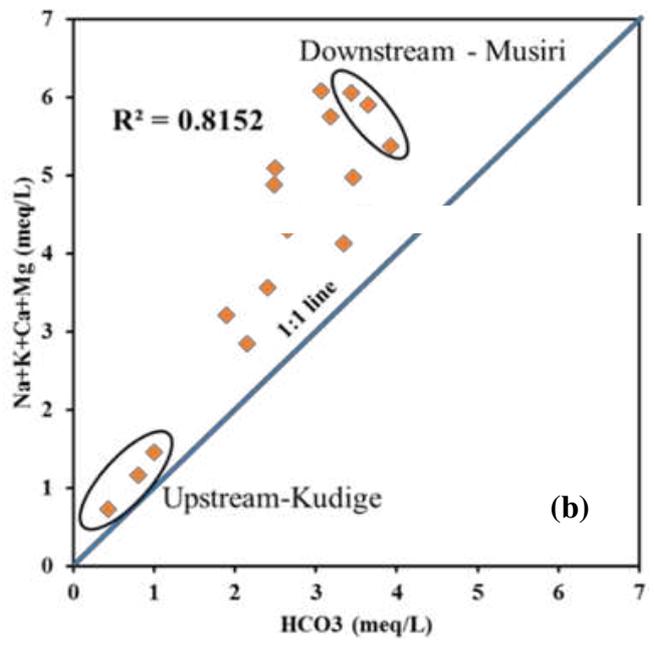
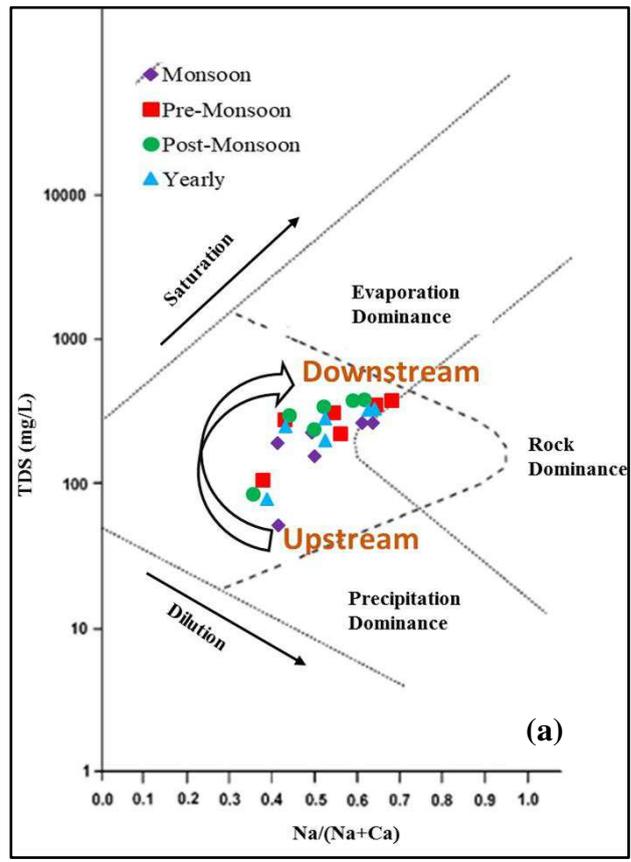
Figure 1. Cauvery River Basin (CRB) with drainage network, elevation and hydrological observatory (HO) stations;



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Figure 2. (a) Scatter plot between total cations (meq/L) and total anions (meq/L), indicating by and large the cations and anions are balanced, (b) Box plot of physio-chemical parameters, showing variation in the hydrochemical data of CRB.

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29 **Figure 3.** (a) Gibbs plot for CRB, specifying the overall dominance of water-rock/soil
 30 interaction over the hydrochemistry, though the data points are not clustered rather range
 31 from one end to other, (b) Scatter plot of HCO₃ vs Na+K+Ca+Mg with $R^2 = 0.81$, suggesting
 32 the common mechanism for all these ions i.e., chemical weathering of drainage minerals.

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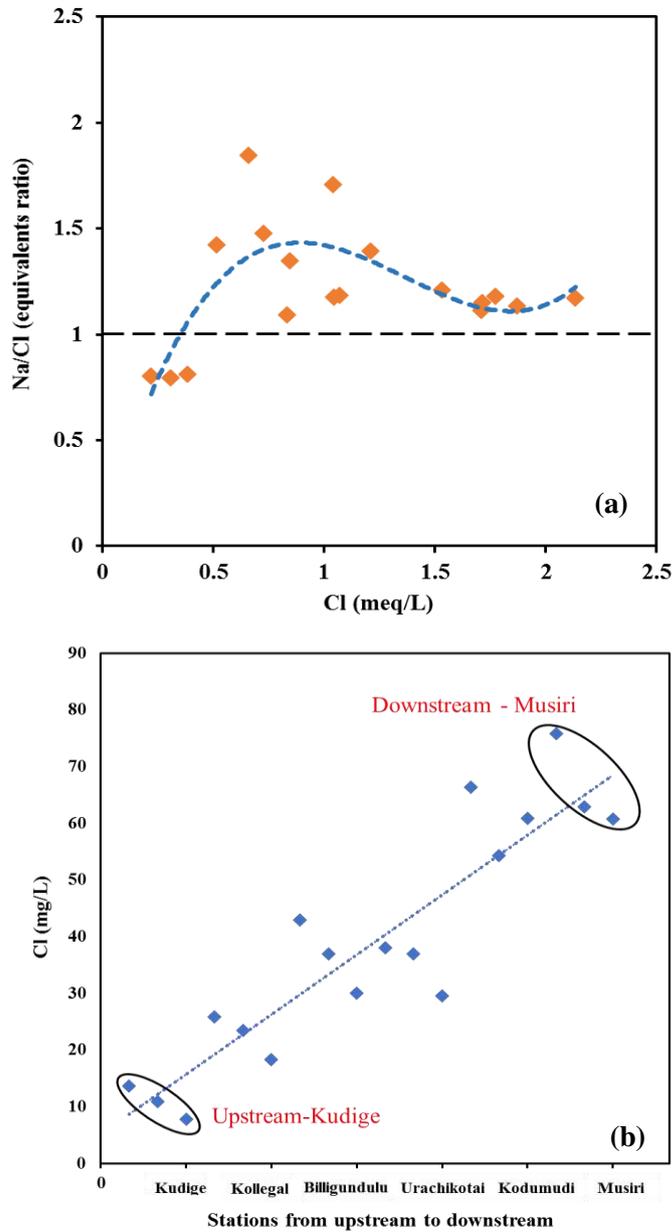


Figure 4. (a) Variation of chloride (Cl) concentration from upstream to downstream, (b) Scatter plot of Cl vs Na/Cl, indicating the addition of Na up to middle reaches due to the silicate weathering, then addition of both Na and Cl towards the downstream due the anthropogenic inputs

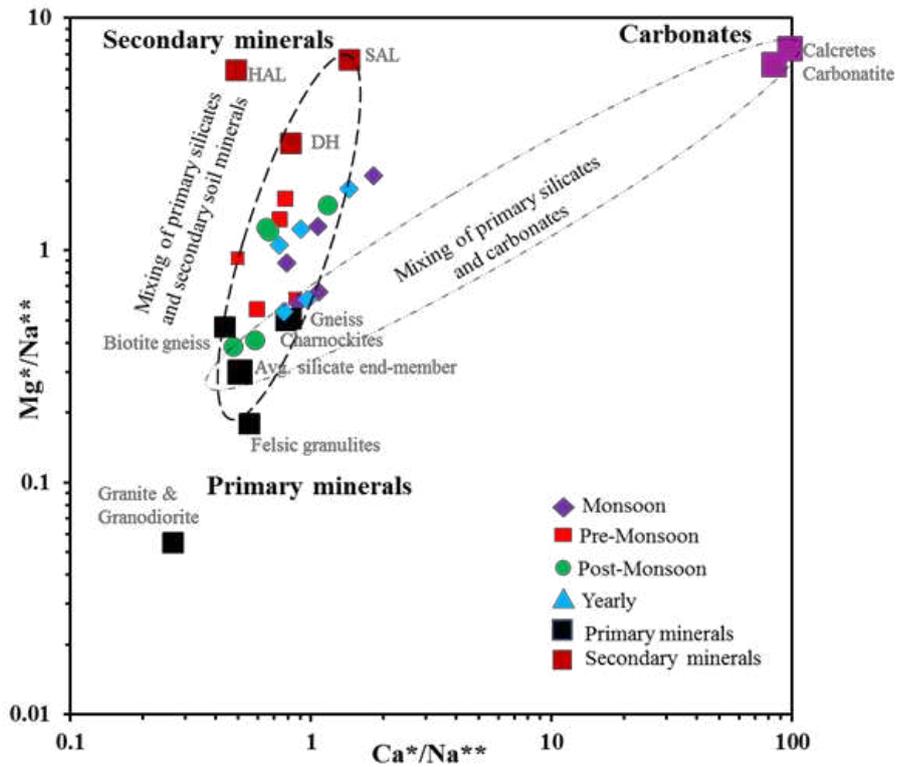


Figure 5. End-member mixing diagram for ‘3’ different end-members in terms of Ca/Na and Mg/Na ratios for CRB; primary silicate minerals from rocks, secondary silicate minerals in soils and sparsely available carbonate minerals, describing a mixing trend between primary minerals and secondary minerals for CRB water samples.

*HAL, SAL and DH refer to soil samples from Halguri, Salem and Dharmapuri respectively

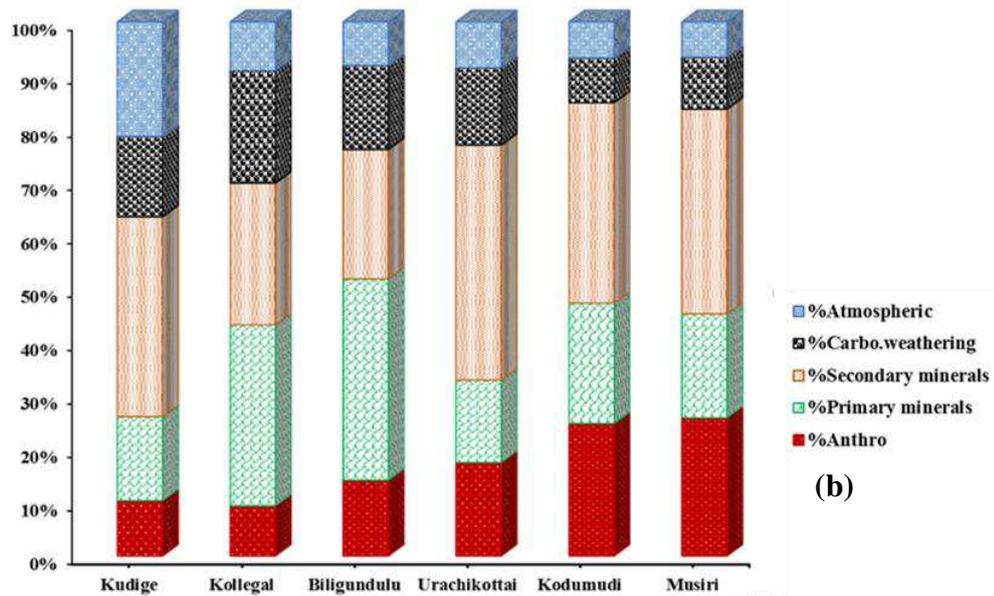
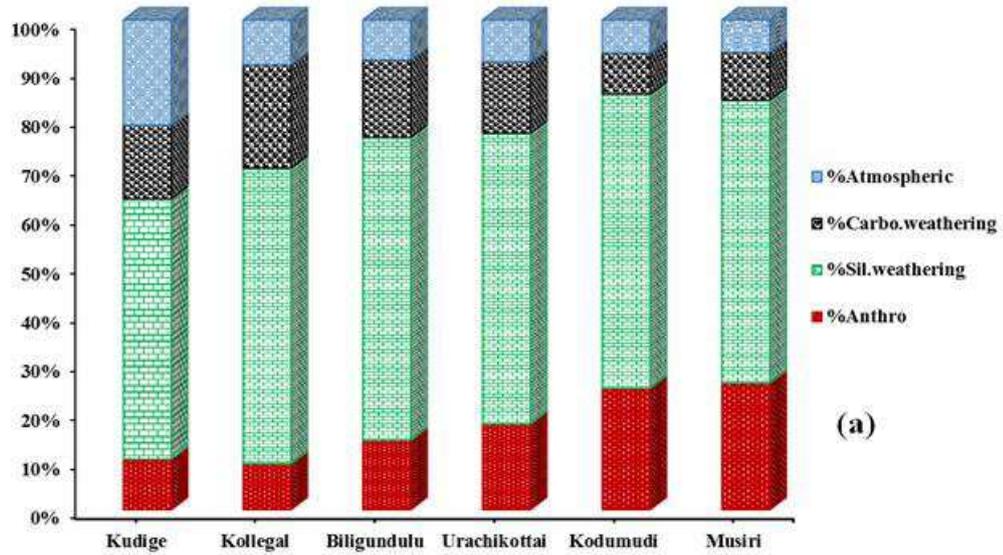


Figure 6. Source-wise solute load contributions (discharge weighted) to the total dissolved load of CRB from (a) atmospheric input, carbonate, silicate weathering and anthropogenic sources (b) atmospheric input, carbonate, secondary minerals, primary minerals weathering and anthropogenic sources, solute load of secondary minerals weathering (35.5%) is significantly higher than the primary minerals (23.5%), emphasizing the role of secondary soil minerals control over the CRB hydrochemistry.

HO-Station	Discharge (cumecs)	pH	EC (umho/cm)	TDS (mg/l)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Cl (mg/l)	SO ₄ (mg/l)	HCO ₃ (mg/l)	SiO ₂ (mg/l)
Pre-Monsoon season												
1.Kudige	4.15	7.33	147.10	117.68	7.14	2.17	12.16	5.93	13.60	3.24	60.68	15.63
2.Kollegal	23.36	7.83	397.89	308.76	24.74	2.66	34.13	15.44	25.84	8.46	203.10	10.53
3.Biligundulu	38.56	8.19	481.93	345.68	38.70	3.22	33.87	18.31	42.88	9.77	210.56	14.34
4.Urachikottai	81.40	8.07	379.35	246.50	29.18	3.48	23.93	21.21	38.01	17.14	161.01	18.23
5. Kodumudi	60.92	8.02	514.61	405.21	48.76	5.36	28.96	24.63	66.33	24.36	193.74	20.66
6.Musiri	25.63	8.16	535.09	421.20	57.53	5.88	28.35	24.21	75.76	27.65	186.15	18.52
Monsoon season												
1.Kudige	154.57	7.27	71.27	57.01	4.05	0.83	5.89	2.94	7.79	2.35	25.59	12.96
2.Kollegal	212.16	7.61	272.84	212.29	16.85	2.00	24.88	9.97	18.29	6.30	130.66	10.52
3.Biligundulu	272.29	7.96	341.60	252.24	26.19	2.62	27.86	11.77	29.99	8.97	146.03	12.90
4.Urachikottai	290.27	8.01	284.16	172.27	20.89	3.02	21.75	13.83	29.54	13.66	114.76	16.70
5.Kodumudi	300.67	7.97	448.87	294.10	45.36	5.23	27.06	17.19	60.88	22.24	150.84	17.27
6.Musiri	276.21	8.08	456.43	293.14	43.77	5.06	28.99	19.45	60.73	24.35	151.61	16.89
Post-monsoon season												
1.Kudige	22.21	7.49	117.80	94.24	5.60	1.29	10.56	4.47	10.86	2.52	48.12	12.69
2.Kollegal	52.14	7.98	418.54	334.21	28.07	4.03	37.17	15.78	23.46	6.94	221.20	11.95
3.Biligundulu	77.32	8.32	510.33	382.13	40.85	4.19	39.16	18.58	36.94	9.80	238.83	13.53
4.Urachikottai	210.06	8.08	390.91	264.37	28.17	3.24	29.48	19.74	37.00	17.81	166.77	17.91
5.Kodumudi	164.35	7.99	507.35	420.75	42.66	5.87	31.07	28.23	54.34	26.40	222.05	21.54
6.Musiri	139.29	8.07	523.20	426.27	48.16	5.59	31.36	27.14	62.91	28.94	208.79	16.93
Yearly weighted average												
1.Kudige	180.93	7.30	78.72	62.98	4.31	0.91	6.61	3.20	8.30	2.39	29.16	12.99
2.Kollegal	287.66	7.69	309.40	242.22	19.52	2.42	27.86	11.47	19.84	6.59	152.95	10.78
3.Biligundulu	388.18	8.05	389.15	287.40	30.35	3.00	30.71	6.01	32.65	9.21	170.92	13.17
4.Urachikottai	581.73	8.04	336.03	215.91	24.68	3.17	24.84	16.99	33.42	15.64	140.01	17.35
5Kodumudi	525.94	7.98	474.76	346.54	44.91	5.45	28.53	21.50	59.47	23.79	178.06	19.00
6.Musiri	441.13	8.08	482.08	342.62	45.96	5.27	29.70	22.16	62.29	25.99	171.67	17.00
Mean	400.93	7.91	377.74	280.45	30.93	3.65	26.48	16.60	38.62	14.49	157.81	15.54
SD	149.21	0.29	145.35	114.94	15.91	1.59	8.99	7.44	20.73	9.23	62.35	3.28
Min	180.93	7.27	71.27	57.01	4.05	0.83	5.89	2.94	7.79	2.35	25.59	10.52
Max	581.73	8.32	535.09	426.27	57.53	5.88	39.16	28.23	75.76	28.94	238.83	21.54
Krishna				360.00	30.00	2.40	29.00	8.00	38.00	49.00	178.00	24.00
Godavari				181.00	12.00	3.00	22.00	5.00	17.00	8.00	105.00	10.00
Mahanadi				224.00	14.00	8.30	24.00	13.00	23.00	3.00	122.00	17.00
Indus				122.00	1.00	2.10	27.00	1.00	9.00	15.00	64.00	5.00
Ganges	Maharana <i>et al.</i> ⁶⁸ and references therein			214.00	11.00	3.00	25.00	8.00	10.00	11.00	128.00	18.00
Brahmaputra				148.00	12.00	2.50	29.00	7.00	15.00	10.00	38.00	7.00
Narmada				322.00	27.00	2.00	14.00	20.00	20.00	5.00	225.00	9.00
Indian rivers-mean				159.00	12.00	3.00	30.00	7.00	15.00	13.00	74.00	7.00
Global mean				120.00	6.30	2.30	15.00	4.10	7.80	11.20	58.40	7.63

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2 **Table 1.** Surface water physio-chemical composition of Cauvery river & comparison with other rivers.

Description	Location	CaO	MgO	Na ₂ O	K ₂ O	Ca/Na	Mg/Na	End members	Avg. Ca/Na	Avg. Mg/Na	n	Reference
		(Wt.%)				(molar)						
Granite	Banglore	1.67	0.28	3.77	4	0.24	0.06	Granite & Granodiorite	0.23	0.058		M. Jayananda <i>et al.</i> , (2000)
Granite	Hoskote-Kolar area	1.44	0.27	3.53	4.92	0.23	0.06				4	M. Jayananda <i>et al.</i> , (2000)
Granite	Sankaridurg	1.3	0.6	4.2	3.68	0.17	0.11				1	A. Sharma and V. Rajamani (2000)
Granite	Satnur	1.1	0.15	3.4	7.32	0.18	0.03				1	A. Sharma and V. Rajamani (2000)
Granodiorite	Hoskote-Kolar area	2.64	0.2	4.55	2.92	0.32	0.03				2	M. Jayananda <i>et al.</i> , (2000)
Felsic Granulites	Tal-Cauvery region	4.3	1	4.3	0.7	0.55	0.18	Felsic Granulites	0.55	0.18	1	V. Rajamani <i>et al.</i> , (2009)
Charnockite	Cauvery Shear Zone	4.23	0.89	4.91	1.14	0.60	0.14	Charnockite	0.76	0.41	2	J.K. Tomson <i>et al.</i> , (2006)
Charnockite	Madurai Block	3.23	1.09	4.67	2.33	0.58	0.18				3	J.K. Tomson <i>et al.</i> , (2006)
Charnockite	South of CSZ and MB	4.35	2.95	3.62	1.81	0.78	0.63				4	J.K. Tomson <i>et al.</i> , (2006)
Charnockite	Dharmapuri	6.5	4.3	3.7	1.5	0.97	0.89				1	A. Sharma and V. Rajamani (2001)
Charnockite	Uttamalai	7.7	1.3	4.9	1	0.87	0.20				1	A. Sharma and V. Rajamani (2001)
Gneiss	Salem	7.5	3.3	4.4	0.13	0.94	0.58	Gneiss	0.63	0.49	1	A. Sharma and V. Rajamani (2000)
Gneiss	Halgur	4.7	2.1	3.7	3.37	0.70	0.44				1	A. Sharma and V. Rajamani (2000)
Gneiss	MuleHole	2.02	2.6	4.49	1.67	0.25	0.45				29	Braun <i>et al.</i> , (2009)
Biotite Gneiss	Sankaridurg	2.4	2	5.7	4	0.23	0.27	Biotite gneiss	0.44	0.47	1	A. Sharma and V. Rajamani (2000)
Biotite Gneiss	Satnur	4.3	3.2	3.7	3.45	0.64	0.66				1	A. Sharma and V. Rajamani (2000)
Carbonatite	Hogenakkal	47.70	3.51	0.84	0.75	85.77	6.24	Carbonatite	85.77	6.24	14	M.K Pandit <i>et al.</i> , (2016)
Calcretes	Mule Hole and Madur	-----	-----	-----	-----	99	7.32	Calcretes	99.00	7.32		Violette <i>et al.</i> , (2010)
Soils (after gneiss)	Salem	3.9	3.05	2.15	0.12	1.44	6.61	Soils	1.07	5.15	2	A. Sharma and V. Rajamani (2000)
Soils (after gneiss)	Halgur	0.85	1.27	1.1	1.75	0.48	5.96				1	A. Sharma and V. Rajamani (2000)
Soils (after biotite Charnockite)	Dharmapuri	1.15	0.87	1.1	0.65	1.3	2.88				2	A. Sharma and V. Rajamani (2001)

1

2 **Table 2.** Molar ratios of Ca/Na and Mg/Na values estimated for different dominant end-members using various rock types and soil (weathered)
3 profiles present in CRB

Figures

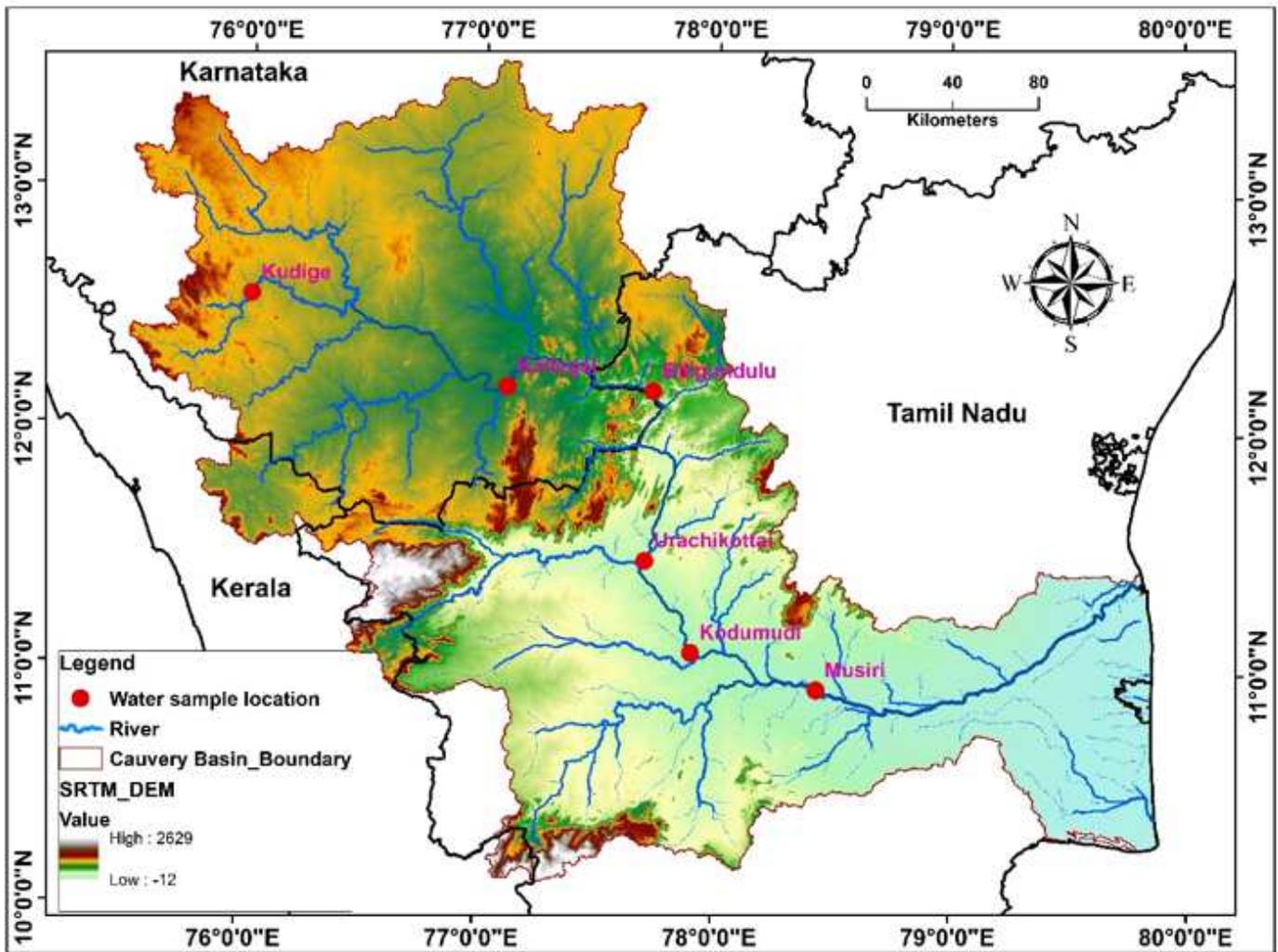


Figure 1

Cauvery River Basin (CRB) with drainage network, elevation and hydrological observatory (HO) stations; Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

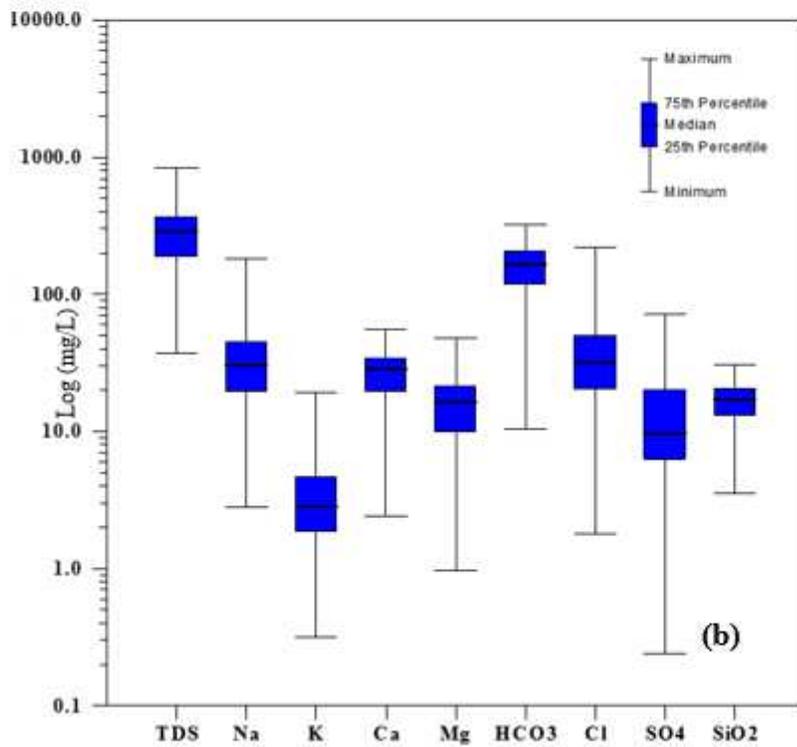
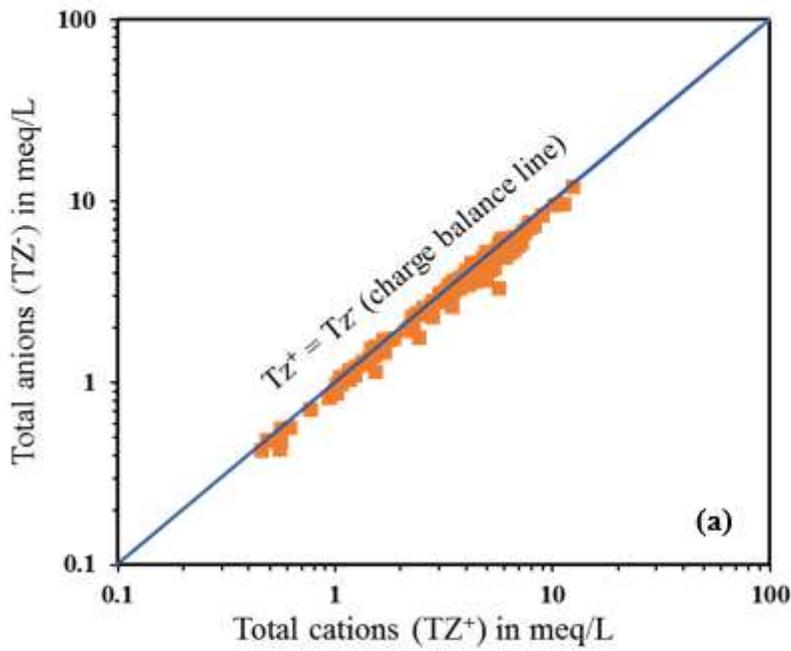


Figure 2

(a) Scatter plot between total cations (meq/L) and total anions (meq/L), indicating by and large the cations and anions are balanced, (b) Box plot of physio-chemical parameters, showing variation in the hydrochemical data of CRB.

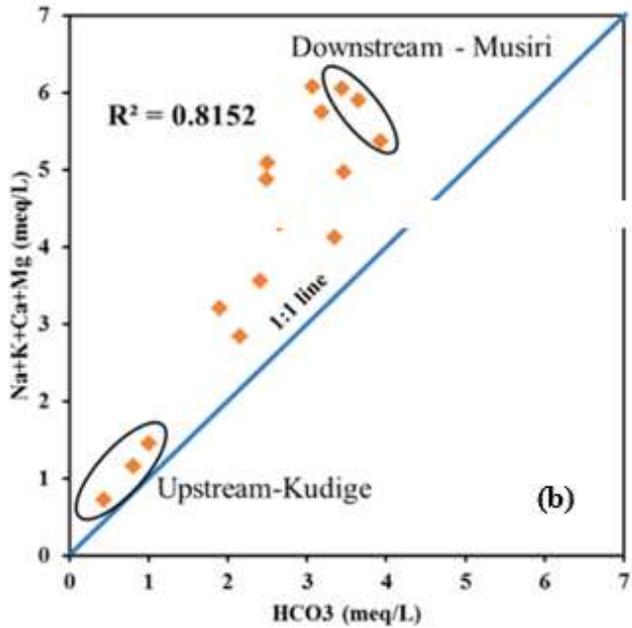
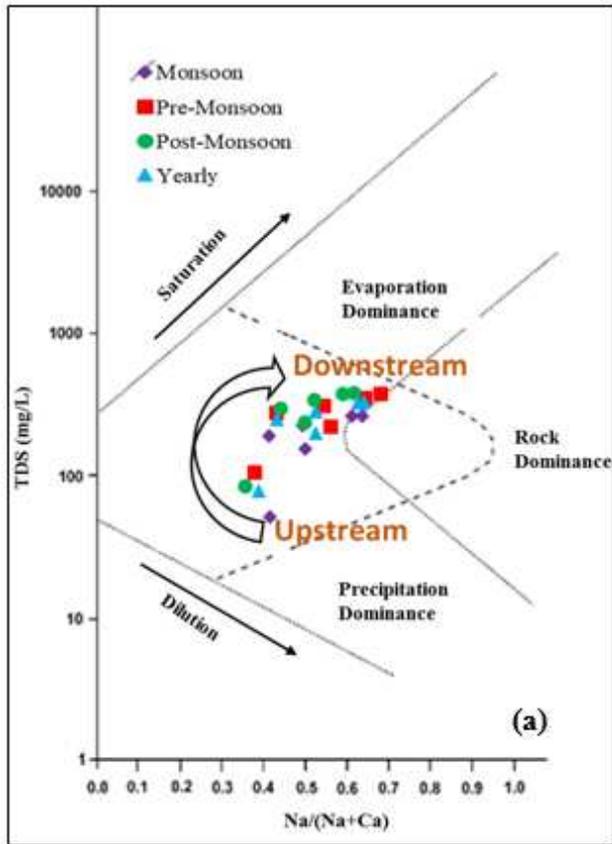


Figure 3

(a) Gibbs plot for CRB, specifying the overall dominance of water-rock/soil interaction over the hydrochemistry, though the data points are not clustered rather range from one end to other, (b) Scatter plot of HCO₃ vs Na+K+Ca+Mg with $R^2 = 0.81$, suggesting the common mechanism for all these ions i.e., chemical weathering of drainage minerals.

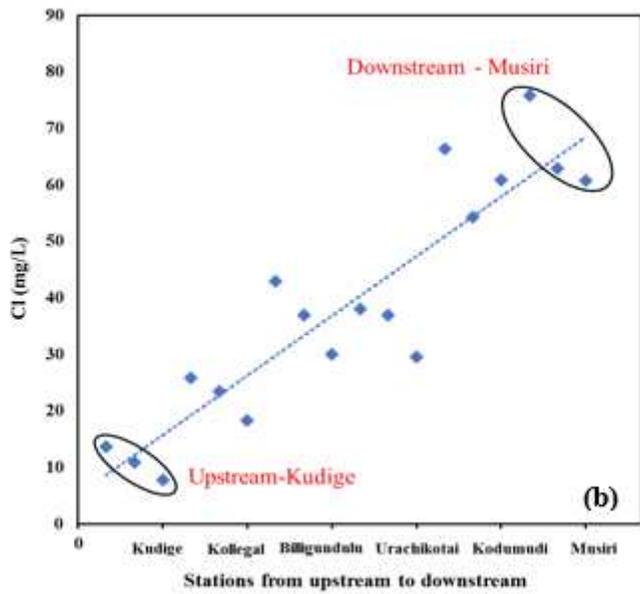
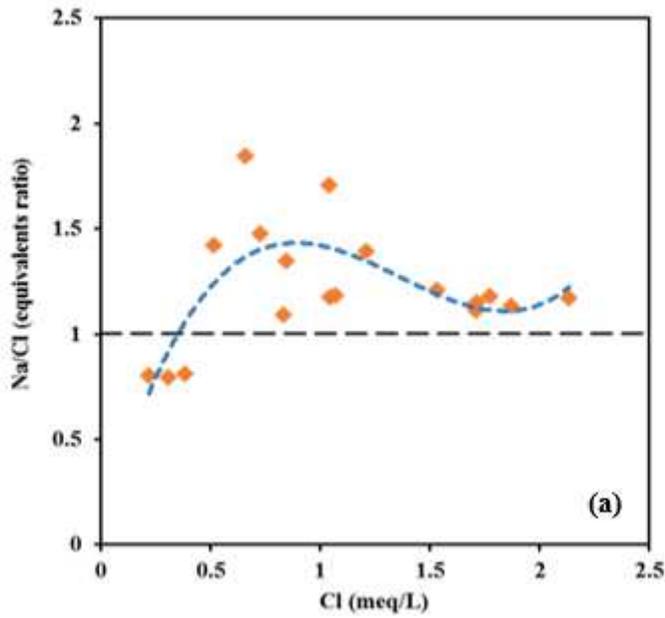


Figure 4

(a) Variation of chloride (Cl) concentration from upstream to downstream, (b) Scatter plot of Cl vs Na/Cl, indicating the addition of Na up to middle reaches due to the silicate weathering, then addition of both Na and Cl towards the downstream due the anthropogenic inputs

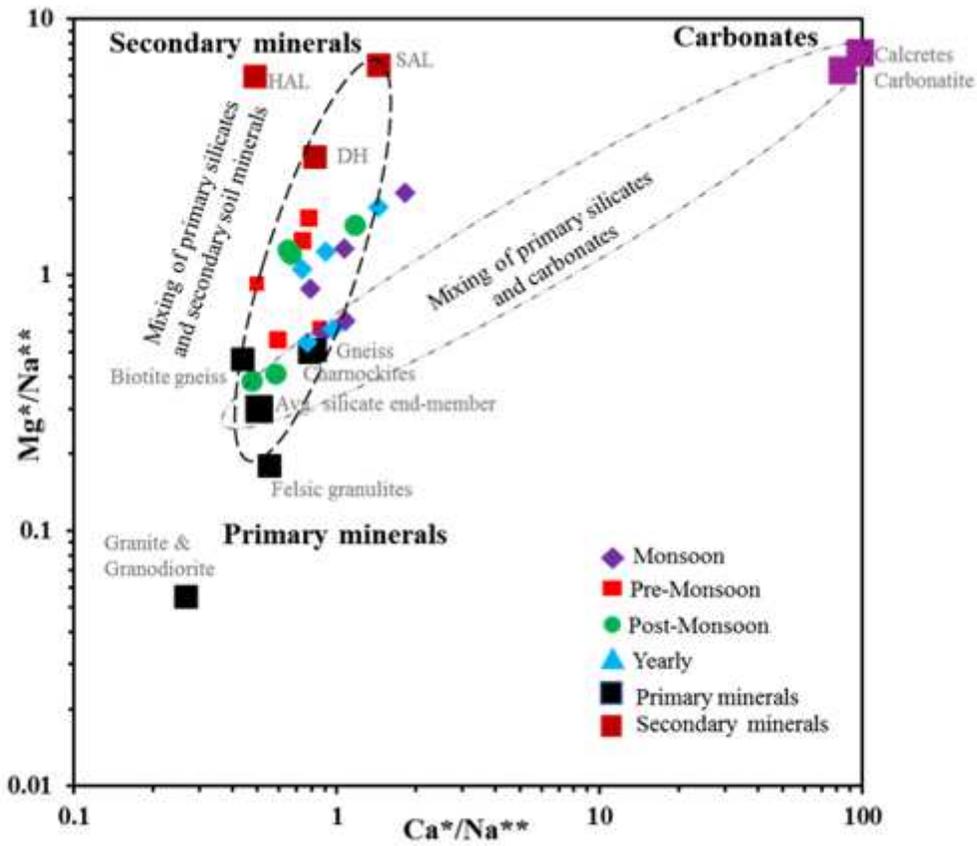


Figure 5

End-member mixing diagram for '3' different end-members in terms of Ca/Na and Mg/Na ratios for CRB; primary silicate minerals from rocks, secondary silicate minerals in soils and sparsely available carbonate minerals, describing a mixing trend between primary minerals and secondary minerals for CRB water samples. *HAL, SAL and DH refer to soil samples from Halgur, Salem and Dharmapuri respectively

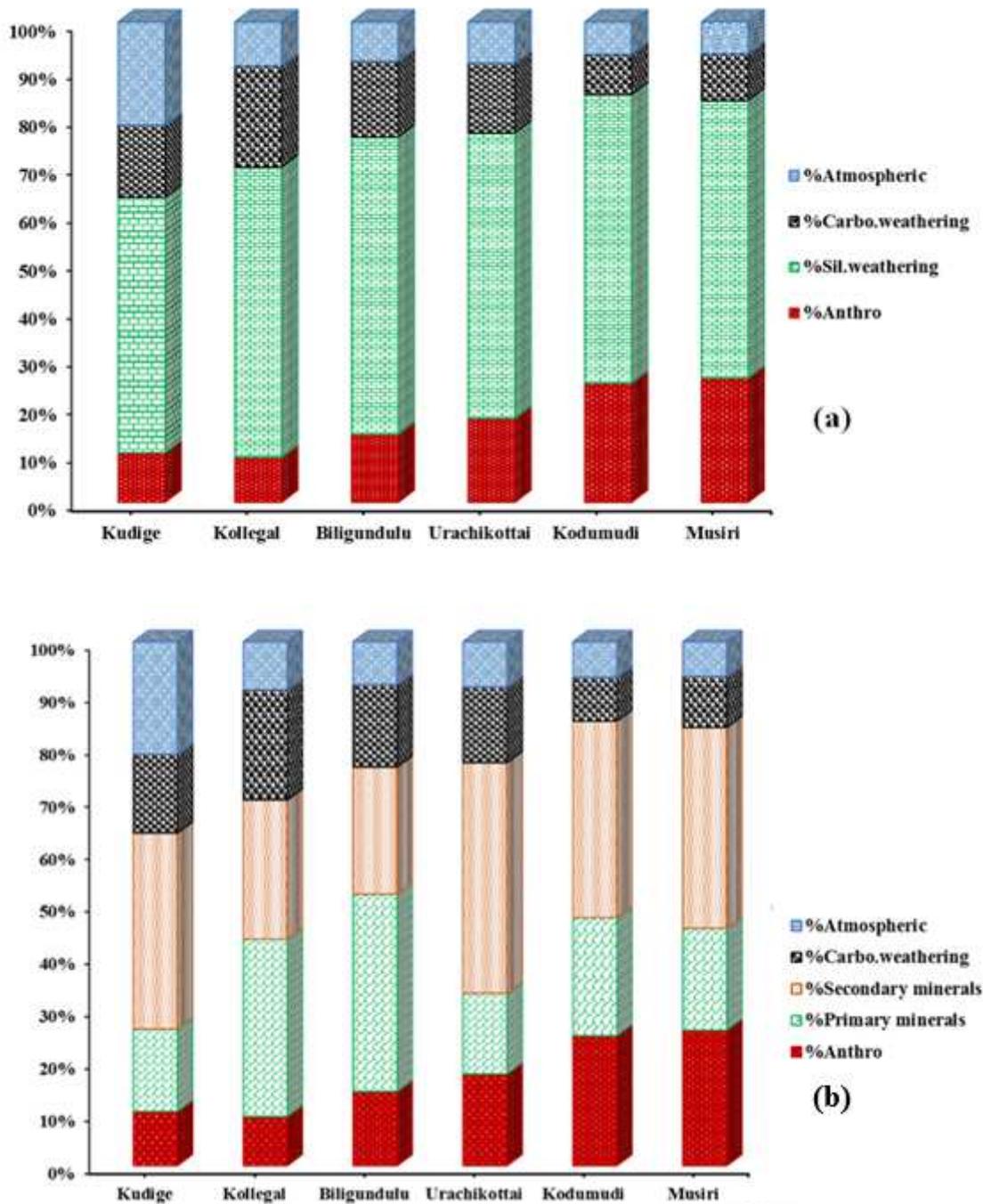


Figure 6

Source-wise solute load contributions (discharge weighted) to the total dissolved load of CRB from (a) atmospheric input, carbonate, silicate weathering and anthropogenic sources (b) atmospheric input, carbonate, secondary minerals, primary minerals weathering and anthropogenic sources, solute load of secondary minerals weathering (35.5%) is significantly higher than the primary minerals (23.5%), emphasizing the role of secondary soil minerals control over the CRB hydrochemistry.

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