WATER CHEMISTRY IN THE CATCHMENT WITH HIGHEST RAINFALL AT GLOBAL SCALE AND INTENSIVE HUMAN ACTIVITY (NORTHEAST INDIA)

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ABSTRACT

The subtropics within the monsoonal range are distinguished by seasonal rainfall and intensive human activity affecting stream water chemistry. This paper aims to determine spatio-temporal variations of stream water chemical elements in anthropogenically modified catchment located in the area with highest annual rainfall at global scale. The study was conducted in the Umiew catchment (493.7 km²) on the southern slope of the Meghalaya Plateau in Northeast India. The area encompasses two typical landforms with different land use of the southern slope: the grass covered hilly plateau with high population density and the forested deep canyon. The upper part of the Umiew catchment is built up of crystalline rocks that are covered by horizontally bedded sandstones and limestones in the lower part. The water sampling was conducted along the Umiew river in six sites during winter (baseflow) and monsoon season (fastflow) in 2014-2015. Numerous physico-chemical parameters were measured, including temperature, pH, electrical conductivity (EC), dissolved organic carbon (DOC) and major ions. Chemical element concentrations were found to be low, with a total dissolved load (TDS) below 100 mg L⁻¹. The facies pattern change from Na-HCO₃⁻ in the upper part to Ca-HCO₃ at the catchment outlet. Naturally low concentrations of chemical elements and very small seasonal differences associated with weathered bedrock, leached soils as well as forest vegetation. Human activity increases the spatial and temporal variation in the concentrations of chemical elements. In effect, water chemistry exhibited strongest control of anthropogenic impact in densely populated built-up areas in the upper part of the catchment. Low ion concentrations in the middle part of the catchment with deep forested canyon are a result of the crystalline deep weathered bedrock, high rainfall and forest vegetation. High ion concentrations at the river outlet are effect of intensive carbonate rocks weathering.

Keywords: subtropics, high rainfall, anthropogenic impact, land use, population

INTRODUCTION

The subtropics are distinguished by the distinct rainfall seasonality and long-term human activity. The result of the anthropogenic impact is a shift from natural to humandominated landscapes through deforestation for agriculture and mineral extraction as well as settlement development [1], [2]. Recent decades of accelerated population growth in many subtropical areas have caused further intensification of agriculture and expansion of built-up areas [3], [4]. In effect, within a relatively small area, there are often significant contrasts in population density and mosaics of land use and land cover (LULC) types affecting stream water chemistry [5], [6]. However, the complexity of natural and anthropogenic interactions, such as nonlinear hydrological processes, the intensification of present-day human activities, or catchment scale, complicate the distinction between the natural and anthropogenic impact on water chemistry [7].

The densely settled subtropical uplands constitute an example of areas where human activity is superimposed on changes induced by natural forces [8]. The Meghalaya Plateau located in Northeast India where the present study was conducted, is one of the rainiest inhabited environments on Earth, with more than 11,000 mm of precipitation recorded annually in Cherrapunji and Mawsynram. High monsoonal rains and hills with steep slopes cause that any human intervention in such a fragile environment can lead to rapid and long lasting changes [9], [10], [11]. Over recent decades, the rapid increase in population has generated intensification of farming systems and settlements, which are mirroring similar tendencies throughout the tropics [12]. The implications of human impact for water chemistry in subtropical regions can therefore be investigated and predicted on the basis of observations from the Meghalaya Plateau in Northeast India.

The presented paper attempts to determine the relative importance of natural processes (high rainfall, geology) as compared to human activities (LULC, population density) in the spatial and temporal transformation of the water chemistry within subtropical catchment.

MATERIAL AND METHODS

Study area

The study was conducted in the Umiew catchment (493.7 km²) on the southern slope of the Meghalaya Plateau (the North-Eastern extension of the Indian Peninsular Shield) which is exposed to humid southwest monsoon winds from the Bay of Bengal (Figure 1). The area encompasses two typical landforms with different LULC of the southern slope: the grass covered hilly plateau and the forested deep canyons. The upper part of the Umiew catchment is built up of deep weathered gneisses and quartzites intruded by granites [13]. Crystalline basement is covered near Cherrapunji and Mawsynram by resistant to weathering sandstones as well as to a lesser extent limestones.

The climate is monsoonal with the warm rainy season spanning from June to September and the dry cool winter [14]. The mean annual air temperature varies between 24°C in the Umiew outlet to 16.6°C in Shillong. The mean annual rainfall is strongly modified by the relief and varies from 6000 mm in the foothills to 11,000–12,000 mm in Cherrapunji and Mawsynram that are located at the spurs. The rainfall decreases with the distance from the edge of plateau to 2200 mm in Shillong.

The soils are nutrient deficient, due to the leaching resulting from high rainfall. Finer textured soils are found in the upper part of catchment, where was preserved the thicker weathered deposits [15]. In this part of the catchment, rice and potatoes are important cultivation crops [16]. The soils of sedimentary complex around Cherrapunji and Mawsynram are severely degraded with an armoured layer on the surface. The soils in adjoining canyons are rich in humus but shallow resulting from mass movements.

About 92% of the population is concentrated within the hilly plateau where the average density reached 211 inhabitants km^{-2} in 2011 [17]. The rest of the inhabitants are spread on the steep slopes of the canyon, where the average density is only 24 inhabitants km^{-2} .



Figure 1: Location of the study area in the Meghalaya Plateau (A), geology and sampled sites (B), and LULC (C) in the Umiew catchment.

Data collection and analysis

The sampling was conducted in the Umiew catchment (493.7 km²) in five selected springs (S1–S5) and in five sites along the Umiew river (U1-U5) (Table 1). It was assumed that the inclusion of springs would help to explain the transformation of water chemistry downstream. Sampling, which consisted of measurements of physico-chemical parameters of water and collecting samples for chemical analysis, was conducted four times (i.e. twice during baseflow in the dry winter season (December 2014 and 2015) and twice during fastflow in the wet monsoon season (August 2014 and 2015).

Site	Site elevation	Area	Discharge winter- monsoon	Population density in 2011	Forest	Grassland	Cultivated land	Built up
No.	(m a.s.l.)	(km ²)	(L s ⁻¹)	(inhabitants km ⁻²)	(%)	(%)	(%)	(%)
S1-S5	1850	-	0.2-0.8	-	-	-	-	-
U1	1780	10.8	490-1200	1031	11	27	47	15
U2	1740	29.0	1100-2000	800	12	25	53	10
U3	1680	59.3	2950-5300	570	16	18	60	6
U4	1540	120.2	3000-50000	260	22	28	47	3
U5	60	493.7	8000-1000000	138	46	49	4	1

Table 1: General information on the sampling sites in the Umiew catchment, Meghalaya Plateau.	Umiew
catchment: $S1-S5$ – springs, $U1-U5$ – river.	

Water temperature (T), pH, and EC were measured in the field. Analyses of the main ions were conducted in a laboratory. Prior to analysis, samples were filtered through a Whatman glass microfiber GF/D with a filter size of 25 mm and pore size of 0.45 μ m. Cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) and anions (Cl⁻, SO4²⁻, NO3⁻) were determined by ion chromatography ICS3000 DIONEX. Limits of detection were: Ca²⁺ – 0.4 mg L⁻¹; Mg²⁺, Na⁺, SO4²⁻, NO3⁻, Cl⁻, and K⁺ – 0.1 mg L⁻¹. Bicarbonates (HCO3⁻) were determined using titration. Dissolved organic carbon was measured with the IL 550 TOC-TN by HACH. The limit of detection was 0.1 mg L⁻¹. Ionic (charge) balance error was expressed as the difference between cation and anion charges divided by their sum and multiplied by 100%, not exceeding 10%.

The LULC of the study catchment was prepared on the basis of a Landsat 8 multispectral satellite image with panchromatic sharpening, to spatial resolution of 15 m for 2015. The population data were collected at village level for 2011 [17].

RESULTS AND DISCUSSION

Role of natural factors and human activities in spatio-temporal changes of water chemistry in the Umiew catchment

Temperature was the lowest in the springs and forested canyon in winter, while it increased progressively downstream in the monsoon season in the Umiew catchment (Table 2, Figure 2). Stream water was found to be alkaline during winter and acidic during the monsoon season. The exception was the outlet of the Umiew where the pH was always above 7. Chemical element concentrations and stream discharge were usually negatively correlated, except NO₃⁻, SO₄²⁻, and DOC.

Concentrations of ions were low, as reflected in the EC and TDS, both of which ranged from 12 to 54 μ S cm⁻¹ and from 8 to 62 mg L⁻¹, respectively. Despite low concentrations, significant spatial differences between sampled sites were apparent in both seasons. The lowest EC and TDS values were observed in the springs. These values increased downstream, but irregularly and showed two peaks. The first, lower peak (U1-U2) appeared where the Umiew traverse the most densely populated and built up upper part of the Umiew catchment. The second higher peak (U5) was noted at the outlet of the Umiew river underlined by carbonate rocks. A similar pattern was exhibited by Ca²⁺, Mg²⁺ and HCO₃⁻ ions in both seasons. The remaining ions (K⁺, Na⁺, Cl⁻, NO₃⁻ and SO₄²⁻,) showed one concentrations maximum in the upper, most densely populated part of the catchment (U1-U2).

Winter	S1-S5	U1	U2	U3	U4	U5
T (°C)	13.1	14.7	16.8	14.6	14.1	19.7
pH	7.1	7.5	7.0	7.6	7.9	7.9
EC (μ S cm ⁻¹)	11.5	42.0	35.6	26.2	27.2	53.7
TDS (mg L^{-1})	10.78	31.91	27.92	21.79	24.3	62.32
Ca^{2+} (mg L ⁻¹)	0.86	3.26	2.81	2.17	2.12	11.19
$K^{+} (mg L^{-1})$	0.31	1.29	1.08	0.80	1.08	0.62
Mg^{2+} (mg L^{-1})	0.20	0.79	0.60	0.48	0.48	1.13
$Na^{+} (mg L^{-1})$	1.73	3.79	3.32	2.84	3.33	2.66
$Cl^{-} (mg L^{-1})$	0.98	3.78	1.70	1.93	2.25	1.45
$HCO_{3}^{-} (mg L^{-1})$	5.54	14.12	16.69	10.76	12.26	41.98
NO_3^{-} (mg L ⁻¹)	0.34	3.44	0.73	1.67	1.56	0.98
$SO_4^{2-} (mg L^{-1})$	0.65	1.00	0.55	0.74	0.72	2.28
DOC (mg L^{-1})	0.01	0.32	0.43	0.37	0.40	0.21
Monsoon	S1-S5	U1	U2	U3	U4	U5
Monsoon T (°C)	S1-S5 18.6	U1 20.3	U2 20.7	U3 20.9	U4 21.6	U5 23.7
Monsoon T (°C) pH	S1-S5 18.6 6.2	U1 20.3 6.5	U2 20.7 6.6	U3 20.9 6.4	U4 21.6 6.6	U5 23.7 7.3
Monsoon T (°C) pH EC (μS cm ⁻¹)	S1-S5 18.6 6.2 11.5	U1 20.3 6.5 36.0	U2 20.7 6.6 31.8	U3 20.9 6.4 25.4	U4 21.6 6.6 23.5	U5 23.7 7.3 49.8
Monsoon T (°C) pH EC (μS cm ⁻¹) TDS (mg L ⁻¹)	S1-S5 18.6 6.2 11.5 8.20	U1 20.3 6.5 36.0 23.84	U2 20.7 6.6 31.8 21.08	U3 20.9 6.4 25.4 19.09	U4 21.6 6.6 23.5 18.10	U5 23.7 7.3 49.8 45.96
$\begin{tabular}{ c c c c c } \hline Monsoon & \\ \hline T (^{\circ}C) & \\ \hline pH & \\ \hline EC (\mu S cm^{-1}) & \\ \hline TDS (mg L^{-1}) & \\ \hline Ca^{2+} (mg L^{-1}) & \\ \hline \end{tabular}$	S1-S5 18.6 6.2 11.5 8.20 0.77	U1 20.3 6.5 36.0 23.84 3.26	U2 20.7 6.6 31.8 21.08 2.77	U3 20.9 6.4 25.4 19.09 2.49	U4 21.6 6.6 23.5 18.10 2.22	U5 23.7 7.3 49.8 45.96 6.64
$\begin{tabular}{ c c c c c } \hline Monsoon & T (°C) \\ \hline pH & EC (μS cm$^{-1}$) \\ \hline TDS$ (mg L$^{-1}$) \\ \hline Ca$^{2+}$ (mg L$^{-1}$) \\ \hline K^{+}$ (mg L$^{-1}$) \\ \hline \end{tabular}$	S1-S5 18.6 6.2 11.5 8.20 0.77 0.14	U1 20.3 6.5 36.0 23.84 3.26 0.58	U2 20.7 6.6 31.8 21.08 2.77 0.70	U3 20.9 6.4 25.4 19.09 2.49 0.61	U4 21.6 6.6 23.5 18.10 2.22 0.48	U5 23.7 7.3 49.8 45.96 6.64 0.55
$\begin{tabular}{ c c c c c } \hline Monsoon & T (°C)$ \\ \hline pH$ \\ \hline EC (μS$ cm$^{-1}$)$ \\ \hline TDS (mg L$^{-1}$)$ \\ \hline Ca^{2+} (mg L$^{-1}$)$ \\ \hline K^{+} (mg L$^{-1}$)$ \\ \hline Mg^{2+} (mg L$^{-1}$)$ \\ \hline \end{tabular}$	S1-S5 18.6 6.2 11.5 8.20 0.77 0.14 0.19	U1 20.3 6.5 36.0 23.84 3.26 0.58 0.68	U2 20.7 6.6 31.8 21.08 2.77 0.70 0.47	U3 20.9 6.4 25.4 19.09 2.49 0.61 0.45	U4 21.6 6.6 23.5 18.10 2.22 0.48 0.41	U5 23.7 7.3 49.8 45.96 6.64 0.55 0.72
$\begin{tabular}{ c c c c c }\hline $Monsoon$ T (°C)$ pH $EC ($\mu$S cm$^{-1}$)$ $TDS ($mg L$^{-1}$)$ Ca^{2+} ($mg L$^{-1}$)$ $K^+ ($mg L$^{-1}$)$ Mg^{2+} ($mg L$^{-1}$)$ $Na^+ ($mg L$^{-1}$)$ $Na^+ ($mg L$^{-1}$)$ $\end{tabular}$	S1-S5 18.6 6.2 11.5 8.20 0.77 0.14 0.19 1.16	U1 20.3 6.5 36.0 23.84 3.26 0.58 0.68 1.96	U2 20.7 6.6 31.8 21.08 2.77 0.70 0.47 1.91	U3 20.9 6.4 25.4 19.09 2.49 0.61 0.45 1.76	U4 21.6 6.6 23.5 18.10 2.22 0.48 0.41 1.67	U5 23.7 7.3 49.8 45.96 6.64 0.55 0.72 1.82
$\begin{tabular}{ c c c c c } \hline Monsoon & T (°C$) \\ \hline pH & EC (μS cm^{-1}$) \\ \hline TDS$ (mg L^{-1}$) \\ \hline Ca^{2+}$ (mg L^{-1}$) \\ \hline K^{+}$ (mg L^{-1}$) \\ \hline Mg^{2+}$ (mg L^{-1}$) \\ \hline Na^{+}$ (mg L^{-1}$) \\ \hline Cl^{-}$ (mg L^{-1}$) \\ \hline \end{tabular}$	S1-S5 18.6 6.2 11.5 8.20 0.77 0.14 0.19 1.16 0.60	U1 20.3 6.5 36.0 23.84 3.26 0.58 0.68 1.96 2.06	U2 20.7 6.6 31.8 21.08 2.77 0.70 0.47 1.91 1.60	U3 20.9 6.4 25.4 19.09 2.49 0.61 0.45 1.76 1.56	U4 21.6 6.6 23.5 18.10 2.22 0.48 0.41 1.67 1.53	U5 23.7 7.3 49.8 45.96 6.64 0.55 0.72 1.82 1.55
$\begin{tabular}{ c c c c c } \hline Monsoon & T (°C$) \\ \hline pH & EC (μS cm^{-1}$) \\ \hline TDS$ (mg L^{-1}$) \\ \hline Ca^{2+}$ (mg L^{-1}$) \\ \hline K^{+}$ (mg L^{-1}$) \\ \hline Mg^{2+}$ (mg L^{-1}$) \\ \hline Na^{+}$ (mg L^{-1}$) \\ \hline Cl^{-}$ (mg L^{-1}$) \\ \hline HCO_3^{-}$ (mg L^{-1}$) \\ \hline \end{tabular}$	S1-S5 18.6 6.2 11.5 8.20 0.77 0.14 0.19 1.16 0.60 4.19	U1 20.3 6.5 36.0 23.84 3.26 0.58 0.68 1.96 2.06 5.85	U2 20.7 6.6 31.8 21.08 2.77 0.70 0.47 1.91 1.60 6.35	U3 20.9 6.4 25.4 19.09 2.49 0.61 0.45 1.76 1.56 5.01	U4 21.6 6.6 23.5 18.10 2.22 0.48 0.41 1.67 1.53 4.59	U5 23.7 7.3 49.8 45.96 6.64 0.55 0.72 1.82 1.55 29.45
$\begin{tabular}{ c c c c c } \hline Monsoon & T (°C$) \\ \hline pH & EC (μS cm^{-1}$) \\ \hline TDS$ (mg L^{-1}$) \\ \hline Ca^{2+}$ (mg L^{-1}$) \\ \hline K^{+}$ (mg L^{-1}$) \\ \hline Mg^{2+}$ (mg L^{-1}$) \\ \hline Mg^{2+}$ (mg L^{-1}$) \\ \hline Cl^{-}$ (mg L^{-1}$) \\ \hline HCO_3^{-}$ (mg L^{-1}$) \\ \hline NO_3^{-}$ (mg L^{-1}$) \\ \hline \end{tabular}$	S1-S5 18.6 6.2 11.5 8.20 0.77 0.14 0.19 1.16 0.60 4.19 0.22	U1 20.3 6.5 36.0 23.84 3.26 0.58 0.68 1.96 2.06 5.85 7.49	U2 20.7 6.6 31.8 21.08 2.77 0.70 0.47 1.91 1.60 6.35 5.63	U3 20.9 6.4 25.4 19.09 2.49 0.61 0.45 1.76 1.56 5.01 5.57	U4 21.6 6.6 23.5 18.10 2.22 0.48 0.41 1.67 1.53 4.59 4.58	U5 23.7 7.3 49.8 45.96 6.64 0.55 0.72 1.82 1.55 29.45 5.23
$\begin{tabular}{ c c c c c } \hline Monsoon & T (°C)$ \\ \hline pH$ \\ \hline EC (μS$ cm^{-1}$)$ \\ \hline TDS (mg L^{-1}$)$ \\ \hline Ca^{2+} (mg L^{-1}$)$ \\ \hline K^+ (mg L^{-1}$)$ \\ \hline Mg^{2+} (mg L^{-1}$)$ \\ \hline Mg^{2+} (mg L^{-1}$)$ \\ \hline Na^+ (mg L^{-1}$)$ \\ \hline Cl^- (mg L^{-1}$)$ \\ \hline HCO_3^- (mg L^{-1}$)$ \\ \hline NO_3^- (mg L^{-1}$)$ \\ \hline SO_4^{2-} (mg L^{-1}$)$ \\ \hline \end{tabular}$	S1-S5 18.6 6.2 11.5 8.20 0.77 0.14 0.19 1.16 0.60 4.19 0.22 0.44	U1 20.3 6.5 36.0 23.84 3.26 0.58 0.68 1.96 2.06 5.85 7.49 1.71	U2 20.7 6.6 31.8 21.08 2.77 0.70 0.47 1.91 1.60 6.35 5.63 1.39	U3 20.9 6.4 25.4 19.09 2.49 0.61 0.45 1.76 1.56 5.01 5.57 1.39	U4 21.6 6.6 23.5 18.10 2.22 0.48 0.41 1.67 1.53 4.59 4.58 1.32	U5 23.7 7.3 49.8 45.96 6.64 0.55 0.72 1.82 1.55 29.45 5.23 1.58

 Table 2: Mean values of the physico-chemical variables during winter and monsoon seasons within the Umiew catchment. T – temperature, EC – electrical conductivity, TDS – total dissolved solids, and DOC – dissolved organic carbon.

The increase of EC, TDS, and most of the major ions in the densely settled landscapes suggests the weathering of anthropogenic infrastructure, which is termed the 'urban stream syndrome' [18], [19]. It covers the dissolution of concrete reinforced embankments of channelized streams (bridgeheads, walls, gabions); concrete pipes and gutters, roofs, walls of buildings, bridges, and roads [20], [21]. Nitrate levels also suggest anthropogenic influences because they exceed 1.0 mg L^{-1} [22]. Elevated concentrations of NO_3^- and SO_4^{2-} may reflect the effects of domestic sewage supply [19]. In addition, some households presumably led to a higher NO_3^- and SO_4^{2-} input of farm manure from pigs, goats, and poultry kept by farmers, as observed in other tropical regions [23]. Concentrations of Cl⁻ and Na⁺ can rise due to a flushing effect of domestic sewage effluents [24]. Anthropogenic sources of Cl⁻ may also affect the polyvinyl chloride (PVC) gutters and pipes used as part of building infrastructure [25]. Study of water chemistry in this part of the catchment indicated that within grasslands, vegetation biomass with dense roots is sufficiently high to increase the ion pool in the topsoil and than in the surface water [26]. In contrast, cultivated land only moderately affected water chemistry, through mobilization of ions during soil tillage in the monsoon season. Despite a significant human impact, chemical concentrations in the studied part of the catchment did not exceed the desirable limits set by the WHO [27].



Figure 2: Comparison of surface water physico-chemical properties during winter and monsoon seasons for the Umiew catchment. Sites as in Table 1. T – temperature, EC – electrical conductivity, TDS – total dissolved solids, and DOC – dissolved organic carbon. The line within the box represents the median.

In the middle course of the Umiew river, in the forested canyon (U4), a decrease of concentrations of most ions, especially NO_3^- and SO_4^{2-} associated with anthropogenic sources, is visible. This is also reflected in low EC and TDS values. Forest soils of the Umiew catchment are poor in chemicals [16]. Fast litter decomposition and nutrient uptake lead to the ion stock being held mainly in living biomass. Self-cleaning of the river is additionally facilitated by very high rainfall and low population density.

Concentrations of DOC showed strong seasonality with highest values in all sampled sites (U1-U5) including springs (S1-S5) during the monsoon season. They are the effect of various processes in the Umiew catchment. The high DOC concentration in springs might be an effect of the water table rising in the rainy season, resulting from increasing macropore flow as soil moisture increases, giving rise to a hydrologic flushing of DOC

from the topsoil to springs [28]. Elevated values of DOC in the upper part of the catchment reflect cultivation practices that stimulate the mobilization of the organic C pool in the soil [4] as well as a lack of sanitation infrastructure in the built up areas [24]. The increase in DOC concentrations in forest catchments is related to high rainfall that generates runoff and already has been documented in numerous studies from the tropical zone [29], [30].

Hydrochemical facies and mechanisms controlling water chemistry in the Umiew catchment

The springs and outlet of the Umiew river showed Na⁺–HCO₃⁻ and Ca²⁺–HCO₃⁻ water type respectively in both seasons (Figure 3). All other sampled sites had the Na⁺–HCO₃⁻ water type in the winter. The facies pattern was more differentiated during the monsoon season. Anthropogenic activities and human infrastructure were additional sources of Ca²⁺, NO₃⁻ and to some extent SO₄²⁻ ions [21] that changed the water type to Ca²⁺–NO₃⁻ in the upper part of the catchment. The seasonal enrichment of sampled sites with Cl⁻ during the monsoon was also visible.



Figure 3: The water facies for the Umiew catchment.

A plot of Na⁺/(Na⁺+Ca²⁺) against TDS provides information about the relative importance of the major mechanisms controlling water chemistry in the Umiew catchment (Figure 4) [31]. The plot shows transition from the atmospheric precipitation to the rock dominance sectors from springs to the outlet of the Umiew river. Samples from the monsoon season fall at the margin of the region that encompasses most water of the earth's surface. These samples with very low TDS in the upper part of the catchment suggest that weathered cover is well leached and significant additional amount of Na⁺ and Ca²⁺ has been derived from anthropogenic sources and rainfall [21], [32]. In contrast, the main source of major ions at the Umiew outlet is carbonate rock weathering.



Figure 4: Gibbs diagram classification of the surface water in the Umiew catchment.

CONCLUSIONS

Water chemistry of subtropical catchment in monsoonal climate with highest rainfall at global scale characterized naturally low concentrations of chemical elements and very small seasonal differences associated with weathered bedrock, leached soils as well as forest vegetation. Human activity (population density, LULC) overlapped with the natural features (geology, high rainfall) of the environment and increased the spatial and temporal variation in the concentrations of chemical elements. In effect, water chemistry exhibited dominance of natural or anthropogenic features in different parts of the subtropical catchment. Moderate to high ion concentrations in the deforested upper part of the catchment indicates that densely populated built-up areas exhibited the strongest control on stream water chemistry in both seasons. Low ion concentrations in the middle part of the catchment with deep forested canyon are mainly a result of the underlying geochemistry associated with crystalline deep weathered bedrock, high rainfall and forest vegetation. Such an ion pattern is closely related to natural environmental conditions in the investigated subtropical region. High ion concentrations at the river outlet are effect of intensive carbonate rocks weathering.

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