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A Systematic Approach to Understand Hydrogeochemical Dynamics in Large River Systems: Development and Application to the River Ganges (Ganga) in India

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Abstract

Large river systems, such as the River Ganges (Ganga), provide crucial water resources for the environment and society, yet often face significant challenges associated with cumulative impacts arising from upstream environmental and anthropogenic influences. Understanding the complex dynamics of such systems remains a major challenge, especially given accelerating environmental stressors including climate change and urbanization, and due to limitations in data and process understanding across scales. An integrated approach is required which robustly enables the hydrogeochemical dynamics and underpinning processes impacting water quality in large river systems to be explored. Here we develop a systematic approach for improving the understanding of hydrogeochemical dynamics and processes in large river systems, and apply this to a longitudinal survey (> 2500 km) of the River Ganges (Ganga) and key tributaries in the Indo-Gangetic basin. This framework enables us to succinctly interpret downstream water quality trends in response to the underpinning processes controlling major element hydrogeochemistry across the basin, based on conceptual water source signatures and dynamics. Informed by a 2019 post-monsoonal survey of 81 river bank-side sampling locations, the spatial distribution of a suite of selected physico-chemical and inorganic parameters, combined with segmented linear regression, reveals minor and major downstream hydrogeochemical transitions. We use this information to identify five major hydrogeochemical zones, characterized, in part, by the inputs of key tributaries, urban and agricultural areas, and estuarine inputs near the Bay of Bengal. Dominant trends are further explored by investigating geochemical relationships (*e.g.* Na:Cl, Ca:Na, Mg:Na, Sr:Ca and NO_3:Cl), and how water source signatures and dynamics are modified by key processes, to assess the relative importance of controls such as dilution, evaporation, water-rock interactions (including carbonate and silicate weathering) and anthropogenic inputs. Mixing/dilution between sources and water-rock interactions explain most regional trends in major ion chemistry, although localized controls plausibly linked to anthropogenic activities are also evident in some locations. Temporal and spatial representativeness of river bank-side sampling are considered by supplementary sampling across the river at selected locations and via comparison to historical records. Limitations of such large-scale longitudinal sampling programs are discussed, as well as approaches to address some of these inherent challenges. This approach brings new, systematic insight into the basin-wide controls on the dominant geochemistry of the River Ganga, and provides a framework for characterising dominant hydrogeochemical zones, processes and controls, with utility to be transferable to other large river systems.

Keywords: water quality, hydrogeochemical processes, Ganga River Basin, River Ganges, water-rock interaction, sampling design

1. Introduction

Understanding the dynamics of complex large river systems is a major environmental management challenge, with important implications for global water, food and energy security. Water quality in rivers is impacted by underpinning ‘natural’ hydrogeological and biogeochemical processes, as well as human-environment interactions that are accelerating stress on water resources at unprecedented rates (Best, 2019). Whilst remote sensing of major rivers offers increasing potential for large-scale monitoring (Junqueira et al., 2021; Piégay et al., 2020) ground-truthing field measurements remains essential to our understanding of hydrogeochemical trends and processes at appropriate scales, especially given system complexity and spatial and temporal variability (Poudel et al., 2013; Varol et al., 2012; Wilbers et al., 2014). Developing systematic approaches for field sampling of large river systems is a critical research need; however, this remains challenging due to complexities around coordination, logistics, resource constraints and monitoring fragmentation as well as conceptual challenges in defining adequate sample/sampling strategies to ensure representativeness of observations. Whilst a number of frameworks for water quality monitoring and management exist (viz. Australian Government, 2018; Belitz et al., 2003; European Environment Agency, 2018 and others), understanding longitudinal water quality patterns, particularly in large rivers, remains very challenging due to multiple inputs and interactions, and associated inherent system heterogeneities.

The River Ganges (known locally as the Ganga) represents one of the world's largest and most important river systems, spanning > 2500 km in length through one of the most densely populated areas of the world. As a major source of livelihood, the River Ganga is culturally very important and a central focus for many social and religious traditions in the Indian-subcontinent (Kumar, 2017; Lokgariwar et al., 2014). However, regardless of its importance, the River Ganga is facing increasing environmental challenges associated with rapid development, climate change and increasing urbanisation, population, water demand and agricultural intensity (Jain and Singh, 2020; Moors et al., 2011; Pandey et al., 2016; Trivedi, 2010; Whitehead et al., 2015). Indian Government initiatives, including the Ganga Action Plan and the National Mission for Clean Ganga (Namami Gange) Programme, have been established in an attempt to monitor, control and/or mitigate pollution in the River Ganga (Ministry of Jal Shakti, 2021; Narain, 2014).

Surface water pollution in the River Ganga and tributaries has been widely reported (Bowes et al., 2020; Central Pollution Control Board, 2019; Hamner et al., 2006; Khan et al., 2020; Lata et al., 2009;

Mariya et al., 2019; Paul, 2017; Satya and Narayan, 2018; Seth et al., 2013; Sharma et al., 2019; Sharma et al., 2016; Sinha and Loganathan, 2015; Trivedi, 2010). However, most previous studies report only a limited number of chemical parameters for specific smaller sub-sections of the Ganga, which prevents detailed interpretation of underpinning hydrogeochemical drivers and controls of pollution sources, transport and transformations. Government initiatives such as the National Water Quality Monitoring Programme (NWMP) provide extensive historical records from 2002 (Central Pollution Control Board, 2019). However, most of these records contain only summary statistics (*e.g.* annual minimum and maximum) for temperature, dissolved oxygen (DO), pH, electrical conductivity (EC), biochemical oxygen demand, nitrate, faecal coliform and total coliform (Central Pollution Control Board, 2019), parameters which are largely aligned with regulatory requirements, but do not necessarily allow for comprehensive evaluation of water quality or the underpinning hydrogeochemical processes. More detailed studies of particular stretches have evaluated, for example, nutrient and microbial water quality (Bowes et al., 2020), heavy metal pollution (Paul, 2017) or emerging organic contaminants (Sharma et al., 2019). Systematic evaluation of overall hydrogeochemical patterns and underpinning processes throughout the dynamic river system at the basin scale remains a major research gap.

An integrated, comprehensive and basin-wide approach is required to understand the highly complex nature of the River Ganga, arising both from natural environmental conditions and human-environment interactions. Here, our overall aim is to develop and demonstrate a systematic approach for advancing the understanding of hydrogeochemical dynamics in large river systems such as the River Ganga. This conceptual framework is a demonstration of a coordinated, comprehensive approach to large-scale sampling, analysis and data interpretation which could be applied to a wide variety of parameters and types of river systems for improved monitoring and/or process-based understanding and to provide relevant information for water quality management. Our approach brings new insight by: (i) improving the conceptual understanding of dominant longitudinal water quality patterns and the underpinning hydrogeochemical processes in the Indo-Gangetic basin and elsewhere, and (ii) addressing, in part, the inherent limitations of a large-scale longitudinal survey spanning 1000s of kilometres. Our specific objectives are to (i) develop and test a conceptual framework for the design and interpretation of large-scale river basin studies; (ii) determine the patterns and dynamics of a selected suite of dominant hydrogeochemical parameters across the Ganga Basin; (iii) interpret the dominant hydrogeochemical processes across the basin; (iv) identify key hydrogeochemical zones across the basin and (v) evaluate the temporal and spatial representativeness of longitudinal sampling. This systematic approach is adaptable, and could be applied more widely, to develop process understanding of other large river systems across the world.

2. Methods

2.1 Conceptual Framework and Overall Approach

Our overall conceptual approach (**Figure 1**) comprises a number of stages, from planning to implementation, analysis and data interpretation to improve the understanding of hydrogeochemical dynamics in the River Ganga, enabling scope for integration across parameter-types, scales and datasets. Here we describe how the key stages of this framework have been developed and applied to a large-scale survey of the River Ganga although the approach could be adapted to other river systems.

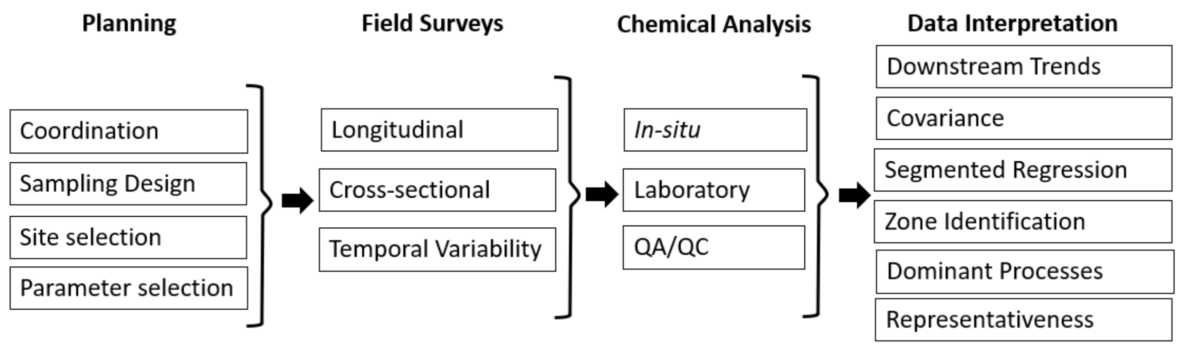

Figure 1. Conceptual summary of approach to sampling, analysis and interpretation for understanding hydrogeochemical dynamics and processes in large river systems.

2.2 Study Area

The study area spans the Indo-Gangetic Basin in India from Devprayag (Uttarakhand) in the foothills of the Himalayas to Noorpur (West Bengal) in the estuarine reaches south of Kolkata, covering a distance of > 2500 km (**Figure S1**, sites also shown on **Figure 5**). Substantial environmental and socioeconomic transitions occur along the course of the River Ganga (Bickle et al., 2003; Bickle et al., 2005; Dalai et al., 2003; Narain, 2014; Sharma et al., 2019; Tripathy and Singh, 2010); see **Supplementary Information**. Sampling sites (n = 81) were spread longitudinally along the main Ganga and Hooghly rivers (n = 64; noting the lower Ganga is known as the Hooghly downstream of approximately site G58) and key tributaries (n = 17). Sampling sites were selected to capture key potential influences (*e.g.* tributary inputs and a range of geological/agricultural/urban conditions) and to maintain regular sampling intervals (mean interval ~ 30 km) whilst balancing logistical constraints such as site access and driving distance. Sampling sites names are coded as XYY where X is G (Ganga or Hooghly) or T (tributary) and YY is a sequential number increasing with downstream distance. Approximate annual hydrological yields of the Ganga and key tributaries were obtained from the literature (Mariya et al., 2019); relative tributary contributions were estimated on the basis of total Ganga yield.

2.3 Water Sampling Approach and Conditions

Longitudinal water sampling, the dominant focus of this study, was undertaken by three teams (coordinated to align sampling conditions) working along the "upper" (Devprayaj to Varanasi), "middle" (Varanasi to Begusarai) and "lower" (Begusarai to Noorpur) segments. Transition areas were sampled by overlapping teams to compare data and ensure consistency. Surface water samples (n = 81) on the longitudinal survey were collected from accessible river bank-side locations (typically near ghats or shallow sloping banks), using a bucket (~ 20 L). All sampling occurred during a period of relatively stable conditions in the post-monsoon season in November 2019 (further details in **Supplementary Information** and **Figure S2**). The post-monsoon sampling period is expected to be a time of relatively high groundwater-surface water connectivity. Additional sampling was undertaken to assess the temporal and spatial representativeness of the main longitudinal survey (see **Supplementary Information**). A brief overview of our approach was previously presented (Richards and Team Saptanadi, 2020).

Water sub-samples for subsequent laboratory analysis of major and trace elements were filtered (0.45 µm, sterile ThermoFisher cellulose nitrate membrane filters) within ~ 5 minutes of sample collection and stored in acid-washed (20 % hydrochloric acid) Nalgene PTFE bottles (for primary analysis) and/or acid-washed (10 % nitric acid) and furnaced amber glass bottles (for limited secondary analysis). All re-useable sampling equipment was thoroughly rinsed between samples with sample water. Samples were stored in dark and cool conditions (as practicable under field conditions) prior to transport to the UK for further analysis.

2.4 Chemical Analysis

2.4.1 In-Situ Analysis

Measurements of pH, oxidation-reduction potential (ORP), temperature (T) and electrical conductivity (EC) were collected *in-situ* using a handheld meter (Myron L Ultrameter II, USA), and dissolved oxygen (DO) was measured using an optical DO meter (Hach HQ10, USA).

2.4.2. Inorganic Laboratory Analysis

Sub-samples for the analysis of Ca, Na, Mg, Sr and Si were acidified (1 % w:v using analytical grade HNO_3; J.T.Baker ULTREX II Reagent HNO_3) to pH < 2 upon return to laboratories in the UK (~ 2 – 14 days after collection), and stored dark and chilled (~ 4 °C) until analysis. Inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 5110 with software ICP Expert version 7.4.2 10790) was used for analysis of Ca, Na, Mg, Sr and Si at University of the West of England (Bristol, UK). Analysis of major anions (Cl, NO_3 and SO_4) was undertaken using ion chromatography (IC; Dionex AS50, Thermo Fisher Scientific) at the UK Centre for Ecology & Hydrology (CEH; Wallingford, UK). Inferred alkalinity as HCO_3^- was estimated on the basis of charge balance. Independent secondary analysis was undertaken for a subset of 24 samples using ICP-OES (Agilent 5800 for Ca, Na, Mg, Si, Sr) and IC (Dionex ICS5000 for Cl, NO_3 and SO_4) at the University of Manchester. See **Supplementary Information** and **Figure S3** for details on analytical quality assurance/quality control (QA/QC).

2.5 Data Interpretation: Software Packages and Analysis

OriginPro 2017 was used for linear regression, principal component analysis and data visualization. Correlation statistics based on ordinary least squares linear regression are reported as "t_{DF} = *t value; p = p value*", with a significance level of $\alpha = 0.05$ and where DF = degrees of freedom. Principal component analysis was undertaken on scaled and centred data. Segmented regression analysis was undertaken using R (version 4.0.5 with RStudio 1.4.1106) and the segmented package to test for threshold changes in the relationship between hydrogeochemical variables and distance downstream, conceptually analogous to the serial discontinuity approach (Ward and Stanford, 1995). A Davies test (Davies, 1987) was used to assess whether a significant breakpoint existed and segmented regression models of increasing complexity were then fitted (Muggeo, 2008) and ranked using the Akaike Information Criterion (AIC). Estimate(s) of the breakpoint(s) with a 95 % confidence interval and all associated slopes were then extracted for the top-ranking model; see **Supplementary Information** for further details on segmented regression. QGIS (version 3.12.2 București) was used to create maps with layer details provided in the associated captions. Elevation was estimated using Google Earth Pro (version 7.3.4.8248).

3. Results and Discussion

Following the structure of the interpretative stage of our framework, downstream patterns will be disentangled by firstly considering overall downstream trends and segmented regression to identify characteristic hydrogeochemical zones. Dominant hydrogeochemical processes will be identified using principal component analysis and bivariate relationships between key inorganic parameters. Finally, sampling representativeness and recommendations for future directions are discussed.

3.1 Overall downstream patterns in hydrogeochemical parameters

The downstream trends of a number of parameters indicate systematic shifts across the basin (**Figure 2**). A significant increase with downstream distance in the main Ganga/Hooghly river channel is apparent for T ($t_{62} = 12.7, p < 0.01$), pH ($t_{62} = 7.9, p < 0.01$), EC ($t_{62} = 2.5, p < 0.05$), and the concentrations of the dissolved ions Ca ($t_{61} = 5.1, t < 0.01$), Mg ($t_{61} = 2.4, p < 0.05$), Sr ($t_{61} = 2.6, p < 0.05$), and Si ($t_{61} = 8.7, p < 0.01$). The trends in concentrations of Cl ($t_{62} = 1.5; p = 0.14$), Na ($p_{61} = 1.7, p = 0.10$) and NO_3 ($t_{62} = 1.0, p = 0.31$) generally increase downstream, albeit not statistically significantly and concentrations are more variable than the other parameters. In contrast, there is a significant decrease downstream for DO ($t_{62} = -5.4, p < 0.01$) and SO_4 ($t_{62} = -3.6, p < 0.01$). In comparison to the upper reaches, the lower reaches of the basin are generally characterized by relatively low concentrations of DO and SO_4, and relatively high T, pH, EC, Ca, Mg, Sr, Si, Na, Cl and NO_3, consistent with the increasing cumulative inputs (*e.g.* urban centres, agricultural zones, tributary influences) present along the river continuum. In some cases there are clear localized inputs (*e.g.* site G14 at the city of Kanpur, Uttar Pradesh), near where previous studies have reported higher pollution concentrations (Bowes et al., 2020; Trivedi, 2010). However, the general significance of downstream trends indicates that regional rather than local controls are dominant for these selected parameters on a basin-wide scale. It is important to note that downstream distance is an analogue for covariables including elevation, temperature, flow velocity and discharge, and population density, and thus is not an independent explanatory variable. A limited comparison of selected parameters to Indian regulatory standards is in **Supplementary Information**.

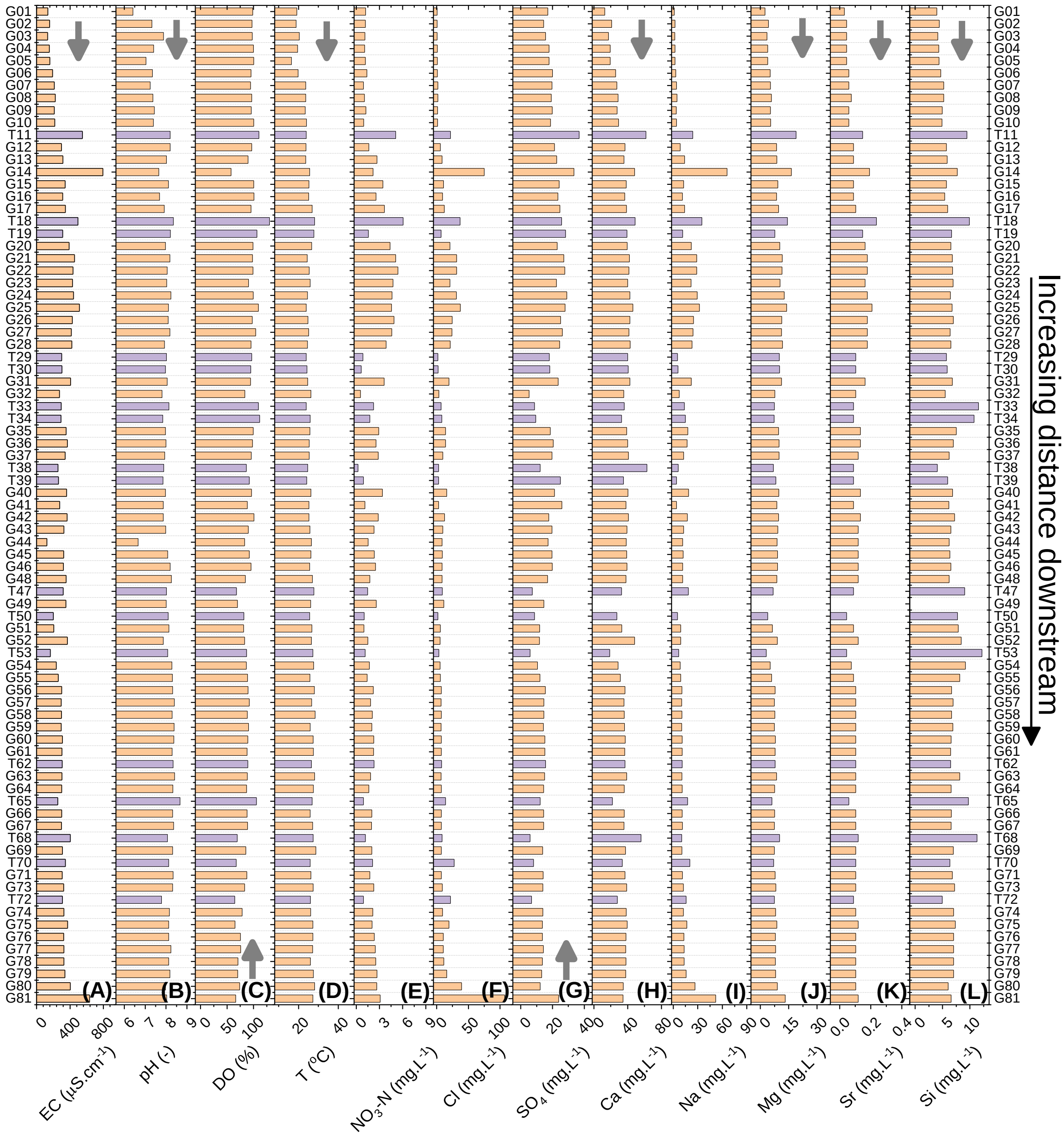

Figure 2. Basin-wide downstream trends represented as bar plots of measurements/concentrations of selected parameters: (A) electrical conductivity (EC); (B) pH; (C) dissolved oxygen (DO); (D) temperature (T); (E) NO_3-N; (F) Cl; (G) SO_4; (H) Ca; (I) Na; (J) Mg; (K) Sr and (L) Si. No Ca, Na, Mr, Sr, Si data available for site G49. Grey arrows indicate statistically significant (*p < 0.05*) downstream trends (tributaries excluded). Bar colour indicates Ganga/Hooghly (peach) and tributaries (purple). Y-axis represents sequential order and does not quantify downstream distance.

3.2 Characteristic Hydrogeochemical Zones & Impact of Key Tributaries

Segmented regression enables further interpretation of spatial trends and possible underpinning controls and processes across the River Ganga (**Figure 3**). Although patterns are distinct and parameter-specific, there is a dominant grouping of parameters (*e.g.* EC, NO_3, Cl, SO_4, Na, Mg, Sr) displaying similar trends characterized by: (1) an increase to ~ 1500 km downstream; (2) a decrease until the major tributary inputs at ~ 1800 km; (3) a region of relative stability (~ 1800 – 2700 km); and (4) a sharp increase ~ 2700 km downstream.

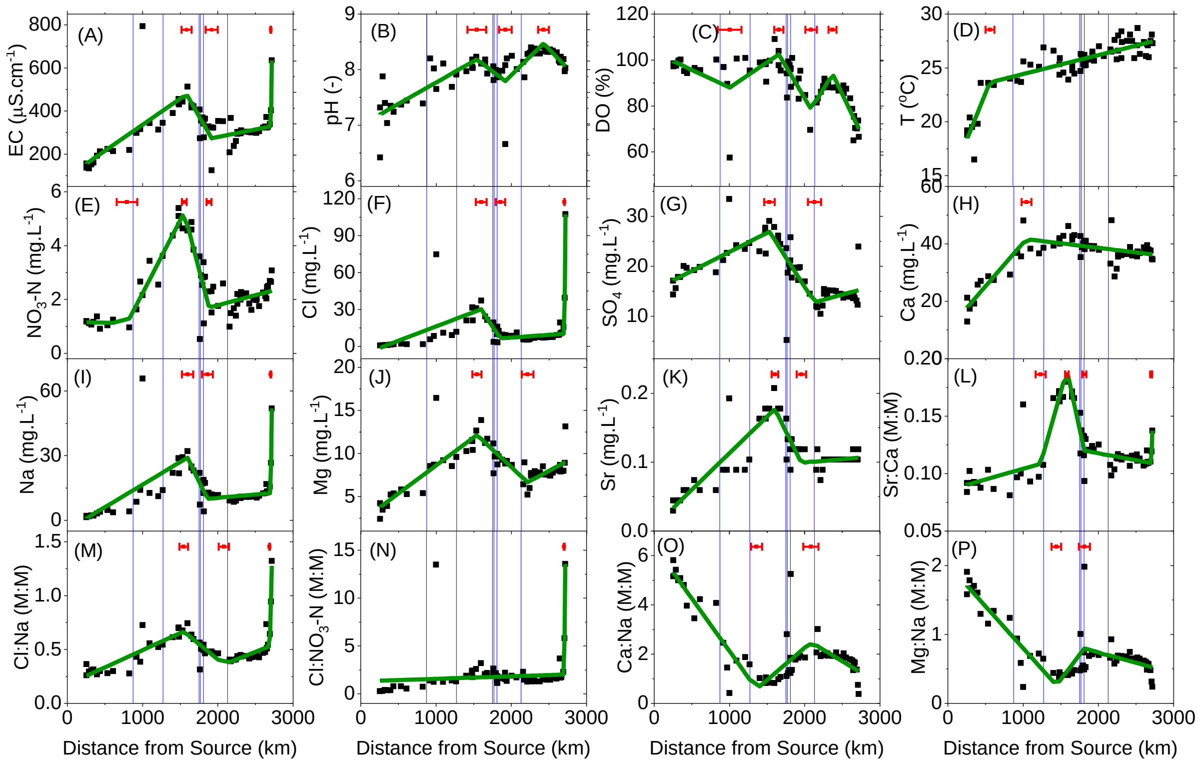

Figure 3. Selected physico-chemical/hydrogeochemical parameters against distance from source for the main Ganga/Hooghly samples (tributaries excluded). Blue lines indicate the intersection

points of major tributaries in increasing distance downstream: Ramganga (~ 875 km; yield ~ 15,300 $\cdot 10^6$ m^3), Yamuna (~ 1270 km; yield ~ 76,000 $\cdot 10^6$ m^3), Ghagara (~ 1750 km; yield ~ 94,400 $\cdot 10^6$ m^3), Sone (~ 1770 km; yield ~ 22,420 $\cdot 10^6$ m^3), Gandak (~ 1810 km; yield ~ 52,200 $\cdot 10^6$ m^3) and Kosi (~ 2130 km; yield ~ 61,560 $\cdot 10^6$ m^3). Parameters shown are: (A) electrical conductivity (EC); (B) pH; (C) dissolved oxygen (DO); (D) temperature (T); (E) NO_3-N; (F) Cl; (G) SO_4; (H) Ca; (I) Na; (J) Mg; (K) Sr; (L) Sr:Ca; (M) Cl:Na; (N) Cl:NO_3-N; (O) Ca:Na and (P) Mg:Na. Green lines are modelled segmented linear regression outputs; red dots and error bars (95 % confidence interval) are estimated breakpoints calculated from segmented linear regression. Mean annual yield of River Ganga is ~ 525,000 $\cdot 10^6$ m^3; all yields as reported elsewhere (Mariya et al., 2019).

The combination of breakpoints (*i.e.* approximate locations at which changes in trends are observed) across parameters (**Figure 4A**) enables identification of approximate locations of minor and major hydrogeochemical transitions which impact multiple parameters across the basin (**Table S1**). These breakpoint transitions (± 95 % confidence interval) can be described with regard to distance from source as follows: (i) ~ 530 ± 100 km (near G08) minor shift in T and ORP; (ii) ~ 790 ± 140 km (near G09/G10) shift in NO_3; (iii) ~ 1020 ± 110 km (near G14/G15) minor shift in DO and Ca; (iv) ~ 1230 ± 70 km (near G16/G17) shift in Sr:Ca; (v) ~ 1400 ± 70 km (near G20 and downstream River Yamuna tributary) minor shift in Ca:Na and Mg:Na; (vi) ~ 1570 ± 70 km (near G24/G25) major shift in ORP, NO_3, Sr:Ca, Cl:Na, Mg:Ca, pH, EC, Cl, SO_4, Mg, Na, Sr; (vii) ~ 1850 ± 50 km (downstream of River Gandak tributary and between G42/G43) major shift in ORP, NO_3, Sr:Ca, Mg:Na, Cl, Na; (viii) ~1930 ± 80 km (near G45/G46) minor shift in pH, EC, Sr; (ix) ~ 2120 ± 80 km (downstream of River Koshi tributary near G49/G51) major shift in DO, Ca:Na, Cl:Na, Mg:Ca, SO_4, Mg; (x) ~ 2380 ± 80 km (near Ganga/Hooghly transition and G61) minor shift in ORP, DO, pH; and (xi) ~ 2700 ± 5 km (downstream of Kolkata near estuary mouth and between G79/G80) major shift in Sr:Ca, Cl:Na, Mg:Ca, EC, Cl, Na and Cl:NO_3.

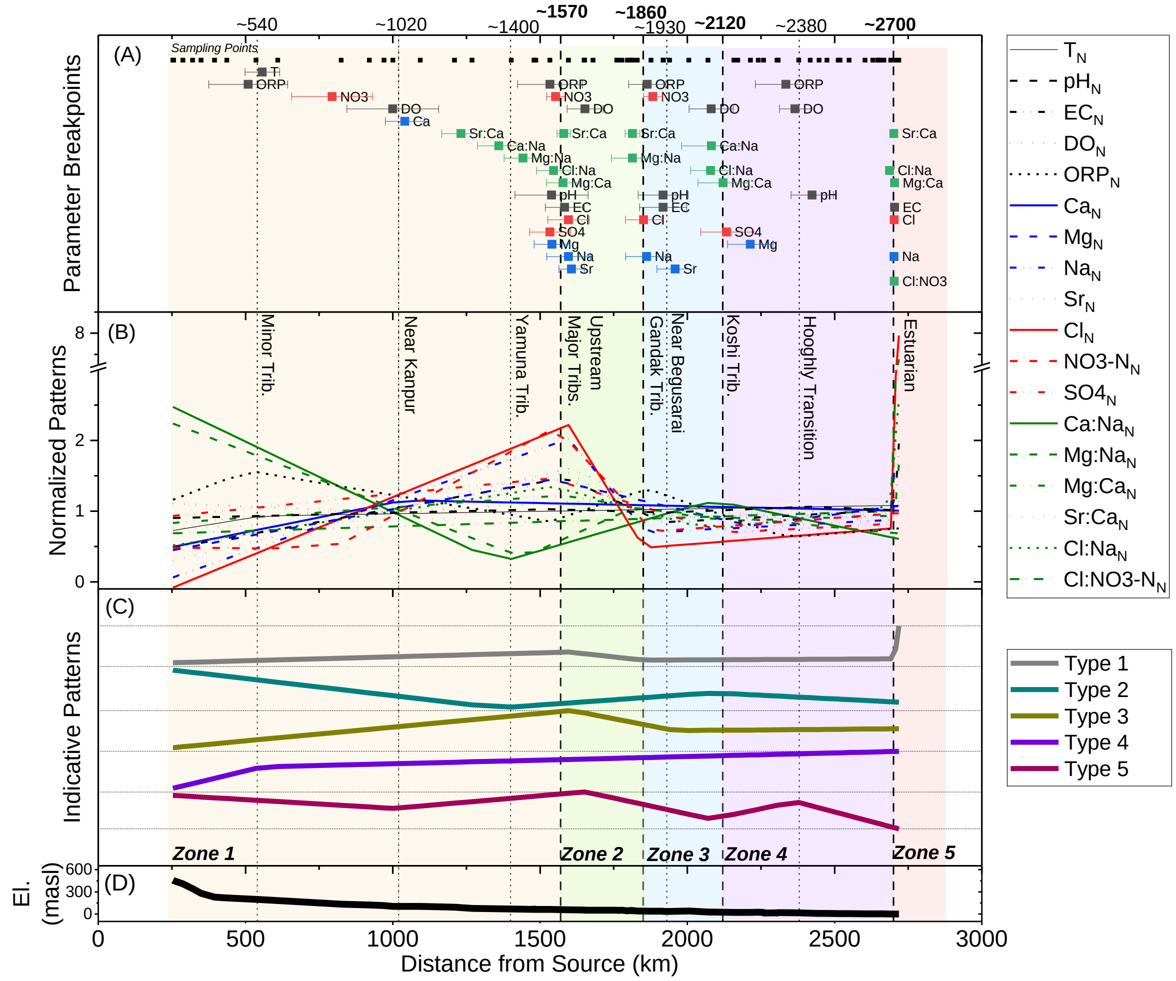

Figure 4. **(A)** Estimated breakpoints for selected physico-chemical/hydrogeochemical parameters as grouped by physico-chemical parameters (grey), anions (red), major/trace elements (blue) and elemental ratios (green). Small black dots represent sampling locations. **(B)** Modelled parameter trends based on segmented linear regression fits normalized to the mean value of each parameter. Line colours indicate the same groupings as shown on A. **(C)** Indicative patterns (no y-scale) of parameters with broadly similar behaviour, namely Type 1 (Cl, EC, Na, NO_3, Mg, Sr:Ca, Cl:Na, Cl:NO_3); Type 2 (Ca:Na, Mg:Na); Type 3 (Sr, SO_4); Type 4 (T, pH, Ca); and Type 5 (DO). **(D)** Elevation profile. Vertical dashed lines indicate modelled breakpoints of major hydrogeochemical transitions between zones (zones also correspond to background-coloured boxes and are defined as where there are overlapping breakpoints of ≥ 4 parameters) and vertical dotted lines indicate minor hydrogeochemical transitions (2 or more parameters). Single-parameter shifts are not shown as vertical indicators.

This analysis identifies five key zones across the basin defined based on areas bounded by the estimated major breakpoints (**Figure 5** and **Table S1**). Zone 1 stretches from the upper reaches of the River Ganga downstream for ~ 1500 km and is generally characterized by increasing T, NO_3, DO, Sr:Ca. Ca:Na and Mg:Na, consistent both with increased agricultural and urban inputs as well as carbonate weathering (Bickle et al., 2005). Zone 2 starts ~ 1570 ± 70 km downstream, near Ghazipur and downstream of the confluence with the River Yamuna tributary (annual yield ~ 76,000 · 10^6 m^3 or ~ 14 % of that of the total Ganga yield) (Mariya et al., 2019). Zone 2 is characterized by significant decreases of a number of parameters (EC, pH, DO, NO_3, Cl, SO_4, Mg, Na, Sr, Sr:Ca, Cl:Na and Mg:Ca) and an increase in ORP, consistent with mixing and dilution from the Yamuna. Zone 3 starts at ~ 1850 ± 50 km, downstream of Patna and the confluence of three key tributaries, the Rivers Ghagara, Sone and Gandak, of approximate annual yields of ~ 94,400 · 10^6 m^3, ~ 22,420 · 10^6 m^3 and ~ 52,200 · 10^6 m^3, or ~ 18 %, ~ 4 % and ~ 10 % of the yield of the Ganga, respectively (Mariya et al., 2019). Zone 3 is characterized by an initial increase in NO_3, Cl and Na concentrations, and a decrease in ORP, Sr:Ca and Mg:Na, likely reflecting combined contributions from both urban and tributary inputs. Continuing downstream, pH, EC and Sr shift from decreasing to increasing values, perhaps from urban inputs around Begusarai. Zone 4 begins ~ 2120 ± 80 km downstream, following the confluence with the Koshi tributary (annual yield 61,560 · 10^6 m^3 or ~ 12 % of that of the Ganga) (Mariya et al., 2019) and other urban areas including Bhagalpur. This is initially characterized by an increase in DO, SO_4, Mg, Cl:Na and Mg:Ca, and a decrease in Ca concentration. Within Zone 4, there is also a minor shift near the Ganga/Hooghly transition, where DO and pH decrease and ORP increases. Zone 5, commencing ~ 2700 ± 5 km along the river and downstream of Kolkata, is strongly consistent with an estuariane signature, with substantial increases in EC, Cl, Na, Sr:Ca, Cl:Na, Mg:Ca and Cl:NO_3 near the coast. Characteristic trends across all zones are shown with normalized patterns for selected parameters and for types/grouping of parameters which behave similarly (**Figure 4B & C**).

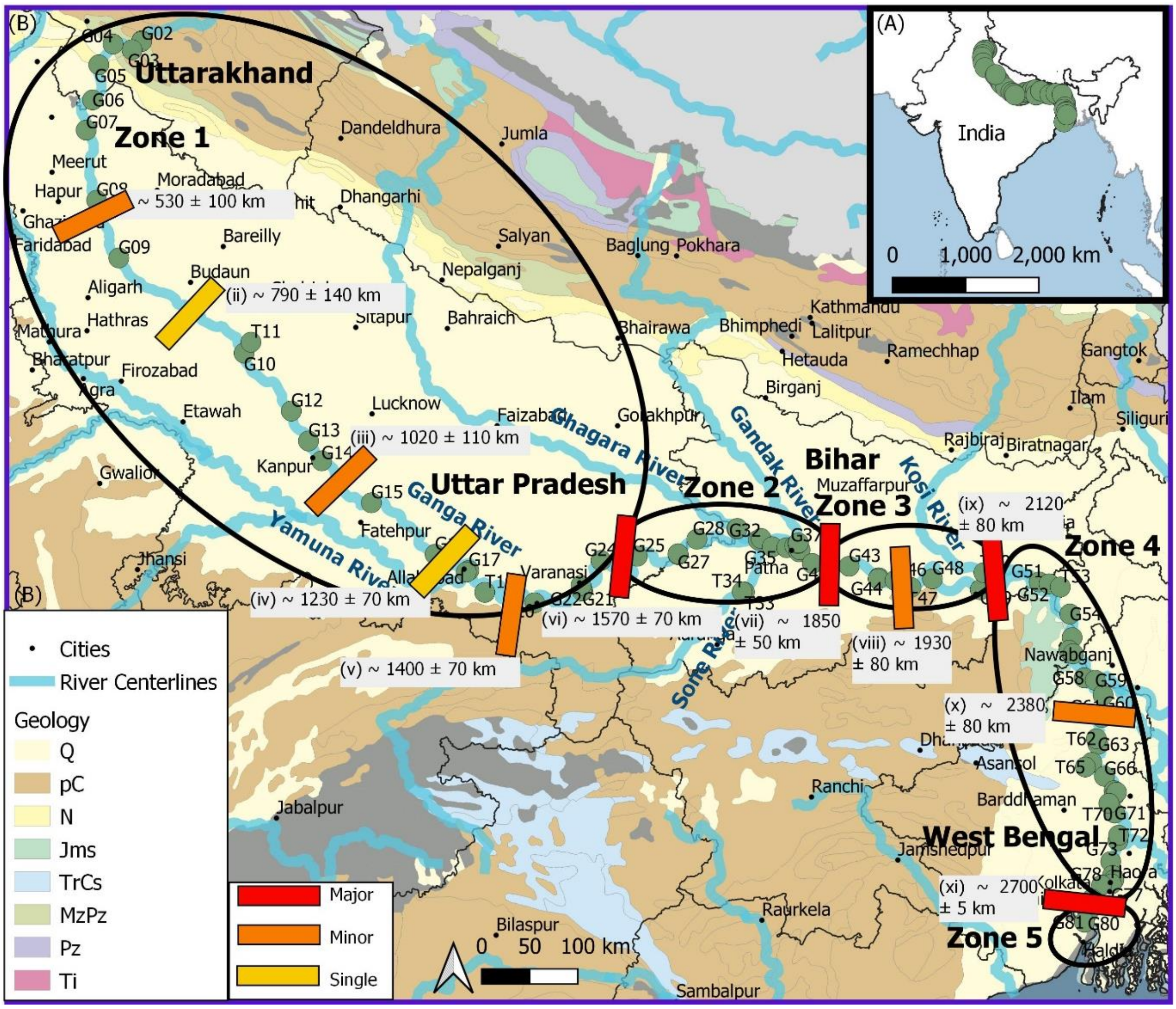

Figure 5. Map with indicative zones as divided by major hydrogeochemical transition (red bars; overlapping confidence intervals of estimated breakpoints of ≥ 4 hydrogeochemical parameters), minor hydrogeochemical transition (orange bars; overlapping confidence intervals of estimated breakpoints of 2 – 3 hydrogeochemical parameters) and single parameter shift (yellow bars); see **Table S1** for details. Estimated breakpoints are calculated from segmented linear regression. Zones 1 – 5 are split by major hydrogeochemical transitions. Sites G01 and G02 are overlapping within symbol sizes shown. Underpinning geology (Wandrey and Law, 1998) with Q = Quaternary sediments; pC = undivided Precambrian rocks; N = Neogene sedimentary rocks; Jms = Jurassic metamorphic and sedimentary rocks; TrCs = Lower Triassic to Upper Carboniferous sedimentary rocks; MzPz = Mesozoic and Paleozoic intrusive and metamorphic rocks; Pz = undivided Paleozoic rocks; Ti = Tertiary igneous rocks; dark grey = other; light grey = no data. Cities and exaggerated river centrelines (which do not represent river width) are from Natural Earth (https://www.naturalearthdata.com/). Sample IDs are XYY where X is G (Ganga or Hooghly) or T (tributary) and YY is a sequential downstream number.

3.3 Dominant Hydrogeochemical Controls

3.3.1 Principal Component Analysis

Principal component (PC) analysis was undertaken to initially screen the hydrogeochemical processes most likely to be dominant across the basin (**Figure S4** and **Table S2**). Four components explained ~ 94 % of the variance, with PC1 (63.4 % of variance) strongly positively influenced by Mg, EC, Sr, Na, Ca, NO_3, Cl, SO_4, pH and Si, consistent with dilution and mixing as major regional hydrogeochemical controls. A number of samples, especially from Zones 1 and 2 are strongly dominated by PC1. PC2 (17.9 % of variance) instead has strong positive loadings for pH, Si and Ca, largely consistent with controls on silicate and carbonate weathering, and a negative loading for SO_4, which is indicative of sulfide weathering. Zone 1 samples trend towards the bottom left of the PC plot, consistent with the lower pH and Si of the upper reaches. Zone 4, in particularly, is characterized by higher loadings of PC2.

3.3.2 Mixing and Dilution

The relationship between Na and Cl (**Figure 6A**) is consistent with mixing and dilution as dominant hydrogeochemical controls across the basin. Fresh (low Na, low Cl) sources are observed in upstream reaches of Zone 1, consistent with Himalayan runoff (Bisht et al., 2018). Most samples are parallel to, or near, the equimolar line representing differing degrees of mixing between fresher sources (*e.g.* near G01) and high Na-Cl end-members (*e.g.* relatively polluted site G14 and estuarine site G81) and/or halite dissolution. The tributaries clearly have mixed inputs, with the Ghaghara, Sone, Gandak and Koshi characterized by relatively fresh sources, likely to influence mixing/dilution at the confluences, whereas the Yamuna has relatively high Na and Cl concentrations, potentially due to high sewage effluent inputs from the cities of New Delhi, Ghaziabad and Agra (Mandal et al., 2010).

Concentrations of Na in slight excess of what would be expected from halite dissolution, especially at the upstream reaches, are likely to derive from other water-rock interactions. The general trend towards higher Na and Cl downstream is consistent with evaporative concentration (especially given consistency across parameters noted in PC1) and/or cumulative inputs from halite dissolution. Halite dissolution has been observed to be an important process in other circum-Himalayan basins including the Three Rivers of Eastern Tibet (Noh et al., 2009). Although Cl is commonly used in hydrological studies as a relatively conservative tracer, competing processes (*e.g.* mineral dissolution, diffusion), can also influence Cl concentration, introducing uncertainty in in-depth interpretation (Horner et al., 2017; McArthur et al., 2012; McArthur et al., 1989).

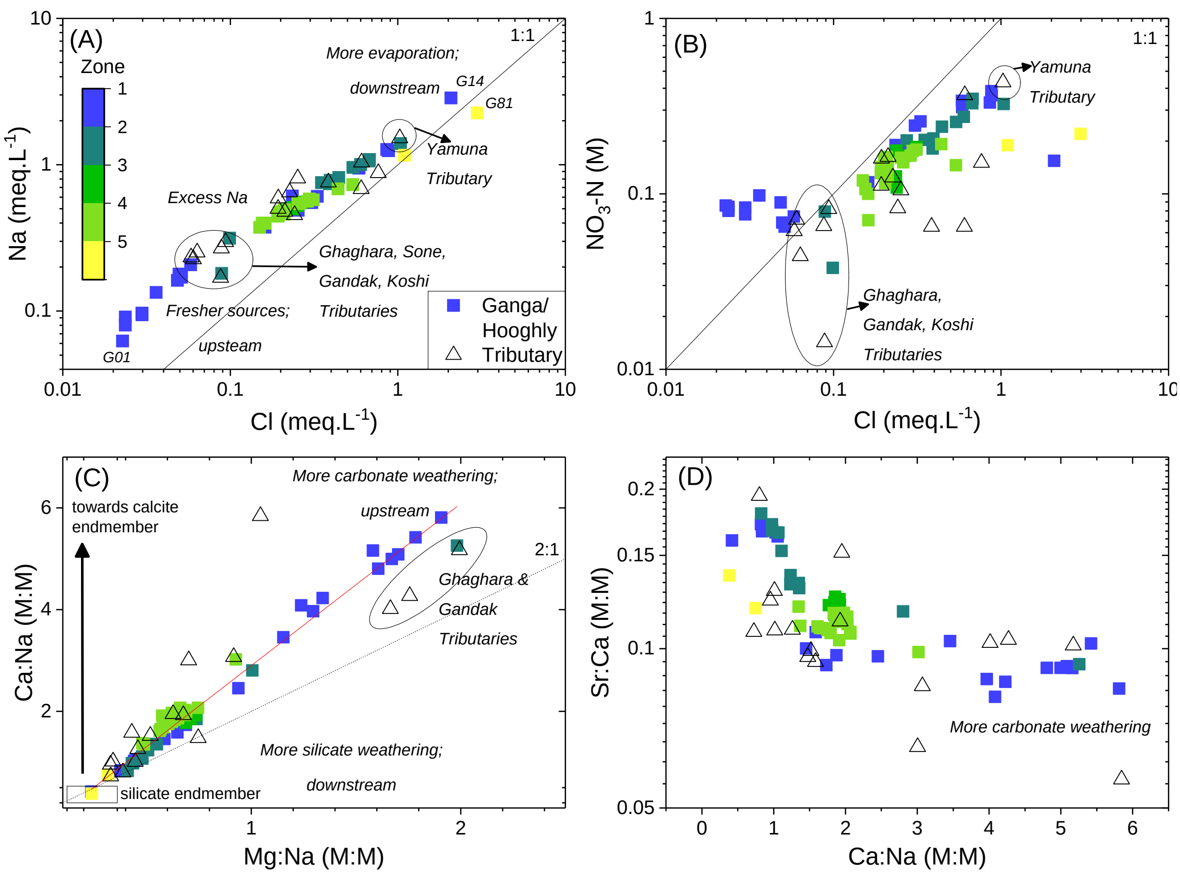

Figure 6. Basin-wide (A) Na versus Cl; (B) NO_3-N versus Cl; (C) Ca:Na versus Mg:Na (red dash line indicates linear regression); and (D) Sr:Ca versus Ca:Na all samples (n = 81). The silicate end-member indicated on (C) is defined as Ca:Na = 0.35 ± 0.15 and Mg:Na = 0.24 ± 0.12 (Gaillardet et al., 1999). Colour scale indicates downstream distance from source and symbol shape indicates Ganga/Hooghly (square) and tributaries (triangle); all data is on a molar basis.

3.3.3 Human-environment interactions

The relationship between NO_3 and Cl is more variable (**Figure 6B**). At upper reaches of Zone 1, Cl increases whereas NO_3 remains roughly constant, suggesting water-rock interactions (*e.g.* halite dissolution) increase the concentration of Cl. Throughout the rest of the catchment, NO_3 inputs increase, approximately following the 1:1 line with Cl. Elevated NO_3 concentrations are likely to arise from both urban and agricultural inputs, with Zone 2 and parts of Zone 1 generally having the highest NO_3:Cl ratios. Additional high concentrations of Cl in Zone 5 without a proportional increase in NO_3 are likely from estuarine inputs (Kaul and Froelich Jr, 1984). Detailed interpretation of sources and processing of nutrients in this system, including with regard to land use/land cover, is the subject of ongoing investigation by co-authors.

3.3.4 Water-rock interactions

The relationship between Ca:Na and Mg:Na (**Figure 6C**) suggests that there are substantial contributions associated with carbonate weathering particularly in Zone 1 as well as from the northerly Ghaghara and Gandak tributaries. These geological controls suggest that sources representing the end-member ratios of Ca:Na and Mg:Na are likely to be the dominant controls on overall major element water chemistry. Upstream reaches generally trend towards the calcite ($CaCO_3$) end-member whereas the estuarine samples approach the silicate end-member. The Ca:Na of Himalayan silicate rocks is always < 1 (Bickle et al., 2005 and references within), with an estimated granitic silicate end-member of Ca:Na = 0.35 ± 0.15 (Gaillardet et al., 1999), consistent with the furthest downstream samples. The slope of the linear regression between Ca:Na and Mg:Na is ~ 3.2 ± 0.1, slightly higher than previously reported (~ 1.1 ± 0.4) for the upper reaches of the basin (Bickle et al., 2005).

Sr:Ca values (**Figure 6D**) are dependent on rock type; with Sr:Ca ratios previously reported to be higher for limestones (~ 0.22 ± 0.02) than dolomites (~ 0.15 ± 0.02) in the Ganga headwaters (Bickle et al., 2005). The ratios of Sr:Ca to Ca:Na tend to be clustered particularly in Zone 2, 3 and 4 suggesting common rock types in those zones. Both of the cation plots Ca:Na to Mg:Na (**Figure 6C**) and Sr:Ca to to Ca:Na (**Figure 6D**) show reasonable approximations of two-component mixing of carbonate and silicate-derived components and are consistent with trends previously reported (Bickle et al., 2005). Deviations from dominant two-component mixing are likely to derive from additional water-rock interactions related to, for example, evaporites, phosphorites and siliceous lithologies (Bickle et al., 2005).

The downstream trends of Ca are strongly in agreement with inferred HCO_3^-, with very similar breakpoints identified ~ 1000 km downstream (**Figure S5**), consistent with trends expected from the weathering of carbonates and silicates. In the middle zones where many parameters decrease significantly, carbonate dissolution is likely to contribute to sustaining Ca and pH, resulting in the only slightly decreasing trends for these parameters. Sulfide weathering also appears to be an important process impacting concentrations of SO_4 and indeed sulfide minerals are very prevalent in the Ganges-Brahmaputra basin (Fendorf et al., 2010; Galy and France-Lanord, 1999). Interestingly, although the acidity produced by sulfide weathering may influence carbonate dissolution (Bufe et al., 2021), the relative importance and co-variation of these processes appears to be spatially-dependent as Ca appears to be continually produced within Zone 3 even when SO_4 is decreasing. Selected important chemical reactions expected to impact the hydrogeochemistry are shown in **Supplementary Information**.

3.3.5 Groundwater-surface water interactions

Groundwater has been demonstrated to substantially contribute to the water in the River Ganga, in addition to glacial melt and surface runoff (Mukherjee et al., 2018). Groundwater-surface water interactions are largely controlled by the relative difference between river stage and groundwater level as well as regional geology, with higher permeability sediments in the upper reaches of the Ganga Basin (Bonsor et al., 2017) leading to increased groundwater-surface water connectivity. During most of the year, the dominant groundwater flow direction is towards the River Ganga constituting its baseflow (Mukherjee et al., 2018), although this is expected to be strongly seasonally dependent as hydraulic gradients change with the monsoon (Lu et al., submitted). Relatively high degrees of groundwater-surface water connectivity are expected in the post-monsoon season, both for the Ganga and key tributaries. The observed chemical signatures are likely to thus inherently reflect this groundwater-surface water continuum, as well as the water-rock interactions which may have influenced the composition of the contributing groundwater. Particularly in zones with minimal influence from tributaries (*e.g.* Zone 1), a strong influence from groundwater is expected to be reflected in the observed surface water signatures. In particular, the observed freshening of river water (*e.g.* decreased EC, Na, Cl, NO_3, SO_4) at the transition to Zone 2 begins ~ 1570 km, which is upstream of the contributions from most of the major tributaries ~ 1700 – 1800 km. A further possible explanation for this is the release of stored fresh water (*e.g.* monsoonal flood water) from bank storage zones which are influenced both by the permeability of surrounding sediments (Bonsor et al., 2017) as well as the depositional patterns related to the energy of the river (Rhodes et al., 2017). The upper reaches of the Ganga have a steeper elevation gradient (**Figure 4D**) and are higher energy, which may lead to relatively high release of bank-stored water back to the river (Rhodes et al., 2017), as compared to lower energy zones further downstream. Localized biogeochemical processes in the hyporheic zone may also influence chemical signatures, although potential impacts are expected to be small because major patterns are reasonably explained by dominant processes including mixing, dilution, water-rock interactions and, to a lesser extent, human-environment interactions.

3.4. Representativeness of Longitudinal Sampling

Temporal and spatial representativeness can be inherent limitations in longitudinal sampling of large river systems. Here we have integrated a number of steps to assess and quantify sampling representativeness; specific recommendations follow in Section 3.5.

3.4.1 Short-term Variations

The extent of short-term variability (*e.g.* hourly to weekly time-scales) in hydrogeochemical conditions has been estimated using various approaches (see **Supplementary Information** and **Figure S6**). Substantial short term (*e.g.* hourly) shifts were observed over 15 minute sampling intervals (**Figure S6A - D**), indicating that short-term impacts can clearly be important. Variation in pH and T is broadly consistent with other studies of diurnal patterns in surface waters (Nimick et al., 2011; Pokrovsky and Shirokova, 2013) and likely reflects a combination of diurnal changes arising from natural daily shifts in temperature (and associated parameters), river metabolism (Cohen et al., 2013), shifting flow regimes of water within the river, and variable urban, anthropogenic and other upstream inputs. Although short-term variability may have significant impact on local biogeochemical processes, the extent of temporal variability on these timescales is much less than the spatial variability observed longitudinally.

3.4.2 Seasonal/Annual Variations & Comparison to Historical Data

The magnitude and spatial trends in our post-monsoon data show strong general agreement with historical records from India's National Water Quality Monitoring Programme (NWQM) (Central Pollution Control Board, 2019) (**Figure S8**). The relative similarity and consistency between T, pH and EC across years corroborates that the major hydrogeochemical controls (including concentrations of dominant inorganic ions) are likely largely controlled by regional factors including hydrogeological setting and climate. Importantly, however, temporal representativeness may be parameter-dependent, with wider variability expected particularly for parameters associated with localized anthropogenic activities (*e.g.* nutrients, microplastics).

3.4.3 Representativeness of Bank-side Sampling

River cross-sectional variability is discussed in **Supplementary Information** and **Figure S9.** In brief, the cross-sectional variability is generally less than the diurnal variations, and considerably less than the longitudinal variability observed.

3.5 Adaptability of Approach and Future Directions

Although we report here a hydrogeochemical investigation across the River Ganga in India, our approach could easily be adapted to improve the understanding of dynamics and processes of other large river systems and/or for systematic investigation of other types of parameters. In large river systems which span diverse environmental conditions (*e.g.* of varying geological, climatic, topographic and anthropogenic characteristics), it is imperative to identify the dominant drivers impacting regional water quality. In this case, statistical analysis including segmented regression and principal component analysis allows distinct zones and key hydrogeochemical controls (*e.g.* dilution, mixing, water-rock interactions) to be identified across the basin. Once a baseline study has been developed and implemented, such as is reported here, future studies could further expand the spatial and/or temporal resolution and/or types of parameters considered. Selection of appropriate methods for data analysis and interpretation are key design considerations for transferability and depend on the nature of specific research aims. To our knowledge, a systematic, coordinated basin-wide dataset for hydrogeochemical understanding of the River Ganga at this large scale has not been established in India. This approach creates a platform to investigate other parameters and to establish comparisons to other large river basins internationally in the future.

Whilst large-scale longitudinal surveys enable highly valuable spatial information to be obtained, the limitations inherent in longitudinal surveys (*e.g.* capturing complexities of localized inputs, diurnal hydrogeochemical controls or seasonal variability) must be considered. Recommendations to address, mitigate and/or quantify the impact of some of these inherent limitations whilst undertaking a large-scale longitudinal survey include: (i) conduct sampling ideally at the same time of day to mitigate the impact of diurnal variability (although this is not always feasible in studies across large river systems); (ii) undertake systematic time-series sampling throughout an entire day, ideally both at urban and rural locations, to quantify the extent of diurnal variability; (iii) undertake supplementary cross-sectional surveys at selected key locations, including near the extreme ends of longitudinal surveys, noting potential logistical constraints such as practicalities of small boat access in a busy shipping/transport hub such as Kolkata; (iv) compare data to historical records to assist in contextualizing annual representativeness; (v) repeat longitudinal sampling of all or selected sites in contrasting flow conditions (e.g. post- and pre-monsoonal conditions) to understand how underpinning hydrogeochemical processes may change throughout the year. Whilst many of these measures were integrated in our study here, it would be a recommended target for future work to repeat a similar longitudinal survey in the Ganga Basin under relatively low-flow conditions to expand temporal resolution of the dataset.

4. Conclusions

Here we develop and apply a systematic approach for advancing understanding of hydrogeochemical dynamics and processes in large river systems, as demonstrated via a longitudinal survey (> 2500 km) of the River Ganga and key tributaries from the Himalayas to the Bay of Bengal. The application of our framework evidences that overall, the lower reaches of the basin are characterized by higher T, pH, EC and concentrations of Ca, Mg, Sr, Si, Na, Cl and NO_3, and lower DO and SO_4, which is largely consistent with expected cumulative downstream inputs arising from both water-rock interactions and human-environment interactions over 1000s of kilometres. Although there are localized inputs in some cases, regional controls are likely dominant for most of these parameters on a basin-wide scale. Segmented regression enables the identification of estimated downstream breakpoints and five associated hydrogeochemical zones. The framework has been used to reveal that mixing and dilution are the most important hydrogeochemical controls across the basin, as well as carbonate and silicate weathering, strongly influencing the major element composition of surface water. The magnitude and spatial trends in our data are generally in strong agreement with historical governmental records. This agreement suggests that the major hydrogeochemical controls are largely controlled by regional factors (e.g. hydrogeological setting), although annual representativeness may not extend to all water quality parameters, especially those directly related to anthropogenic activities. The magnitude of short-term temporal variability in water quality parameters was found to be less than their longitudinal diversity. Selected cross-sectional surveys indicated some cross-channel variability, particularly near tributary inputs, likely attributed to differences in stream depth, flow and mixing. Rigorous interpretation of our results applying our framework to the River Ganga allows limitations of large-scale longitudinal sampling programs to be identified, including for instance challenges in assessing localized inputs and temporal/seasonal controls, along with some strategies to mitigate these impacts. In addition to providing new insight to the dominant hydrogeochemical processes impacting surface water composition in the River Ganga, our systematic approach is adaptable to other parameters and/or similar coordinated surveys of other large river systems across the world.

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Author Contributions

LAR: investigation, formal analysis, methodology, visualization, supervision, writing – original draft. **BGF**: investigation, methodology, data curation. **MJB**: investigation, conceptualization, methodology, funding acquisition, resources. **KK**: investigation; software, methodology. **AK**: investigation, methodology. **RK**: investigation. **SuK**: investigation, methodology. **MH**: investigation. **BH**: investigation, methodology. **RMST**: investigation, methodology, funding acquisition. **DSR:** methodology, resources. **HAN**: interpretation. **US**: interpretation. **LAK**: analysis, resources. **DJEN**: analysis, resources. **DM**: software, interpretation. **DMH**: interpretation, funding acquisition. **AG:** conceptualization, funding acquisition, methodology, resources. **BC:** funding acquisition. **HJ:** funding acquisition. **TKD:** funding acquisition. **DMR**: conceptualization, funding acquisition, resources. **StK:** conceptualization, funding acquisition. **DCG**: conceptualization, funding acquisition. **DAP**: conceptualization, funding acquisition, resources. All authors have contributed to manuscript reviewing and editing.

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