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Concentration-Discharge Relationships Revisited: Overused But Underutilised?

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ABSTRACT

Over the past 50 years, concentration-discharge (cQ) relationships have been widely used to analyse water quality dynamics. Nowadays improved availability of concentration (*c*) and discharge (*Q*) data at different spatial and temporal scales have led to a high popularity of cQ applications. However, despite their widespread use, we see persistent challenges in the integration of cQ relationships across temporal scales, and in the identification of the encoded processes. In this commentary, we show that different catchment processes may lead to similar cQ responses resulting in a lack of clear causality. We emphasise that cQ relationships applied at different time scales integrate different parts of the catchment and may, therefore, convey different information. Finally, we advocate for the careful use of cQ relationship as one, but not the only, tool in addressing ecohydrological questions.

1 | Introduction

The variation of streamwater solute concentrations with discharge—so-called concentration (*c*) discharge (*Q*) relationships—provide insights into catchment-scale processes governing the mobilisation and transport of water and solutes and thus defining water quality. This cQ approach has been used extensively over the past 50 years to aggregate time series and their covariance into descriptive metrics beyond mean and standard deviation of *c* and *Q* alone, enabling comparisons of water quality dynamics across catchments and landscapes (e.g., Speir et al. 2024).

We begin by briefly outlining the history of cQ relationship applications and providing an overview of their diverse use. Building on this, we highlight two critical challenges in applying cQ relationships we perceive. We conclude by outlining a way forward that would allow us to advance our understanding of landscape-scale processes through the utilisation of cQ relationships.

2 | A Brief History and Overview of Applications of cQ Relationships

Concentration-discharge relationships were first proposed in the late 1960s and early 1970s (Likens et al. 1967; Hall 1970, 1971; Johnson 1979), and have gained in popularity ever since: A Web of Science search in August 2024 found 4821 articles on the topic "concentration AND discharge AND relationship," with 270 articles published in 2023 alone. In addition to this broad presence in journal articles and conference presentations nowadays, the topic received its own special issue in Water Resources Research (Chorover, Derry, and McDowell 2017) and was discussed in a recent review article (Speir et al. 2024).

cQ relationships are typically derived from concentration (*c*) and discharge (*Q*) measurements at the catchment outlet. Measurements at the outlet are assumed to integrate hydrological and biogeochemical processes across the entire catchment, and hence cQ relationships have been used extensively to understand the underlying controls of catchment-scale water quality dynamics. These relationships can be described mathematically in various ways (see e.g., Hall 1970, 1971), with power law relationships and ratios of coefficients of variations of concentration and discharge being the most common choices (Wymore et al. 2023). These simple metrics allow for a straightforward classification of concentration dynamics (e.g., dilution vs. enrichment pattern) when joint concentration and discharge time series are available, with the ease of application contributing to the popularity of these simple models.

cQ analyses are typically employed to discern the spatial distribution and availability of solute sources in catchments, supporting interpretations of source limitation and transport limitations: The slope of the cQ relationship allows, for example, distinguishing solute contributions from deeper geogenic sources (typically featuring a more negative cQ slope) and those from the shallow subsurface with a positive cQ slope, (e.g., Zhi and Li 2020; Stewart et al. 2022). cQ relationships also aid in the identification of lateral distribution of solute sources, distinguishing between sources near or far from the stream, or from upstream or downstream areas (Herndon et al. 2015), or a combination of vertical and lateral sources (Knapp, Li, and Musolff 2022). Hysteresis in cQ relationships stemming from concentration differences between the rising and falling limb of a flow event have been linked to temporal differences in the mixing of those different sources (Johnson and East 1982; Evans and Davies 1998). Recent methodological advancements in the analysis and quantification of event-scale hysteresis have improved our ability to extract process information from event-scale cQ relationships (Lloyd et al. 2016; Musolff et al. 2021). Additionally, cQ analysis can reveal the importance of legacy stores (Basu, Thompson, and Rao 2011), and help in understanding the interplay of solute mobilisation with biogeochemical processing for individual compounds (e.g., Creed et al. 2015, for dissolved organic matter; Ali et al. 2017, for total phosphorus Ebeling et al. 2021, for nitrate). Through the comparison and integration of cQ slopes of different compounds, their biogeochemically driven co-dependencies have been demonstrated (e.g., Shogren et al. 2020; Wymore, Fazekas, and McDowell 2021, for carbon vs. nitrogen dynamics). Finally, systematic relationships of c and Q can assist in interpolating and extrapolating concentration time series from sparse data, help to quantify loads exported from catchments (e.g., Hirsch, Moyer, and Archfield 2010; Appling, Leon, and McDowell 2015; Zhang and Ball 2017), and thus support the prioritisation of sampling efforts (Bieroza et al. 2018). More recently, cQ analyses across catchments have provided insights into landscape functioning (Basu et al. 2010; Thompson et al. 2011; Moatar et al. 2017; Zarnetske et al. 2018; Godsey, Hartmann, and Kirchner 2019; Lintern et al. 2021), and into changes in hydrological and biogeochemical processing along river networks (Creed et al. 2015). Analyses across time, for example, seasons or decades, highlight temporal evolutions and changes in source distribution, catchment functioning and land use/land cover (Dupas et al. 2016; Moatar et al. 2017; Ehrhardt et al. 2019). Recent advances have also been made in the mathematical description of cQ relationships, with breakpoint analysis identifying potential changes in processes across the discharge range (Moatar et al. 2017; D'Amario, Wilson, and Xenopoulos 2021).

3 | Remaining Challenges

The description of cQ relationships has undergone continuous improvement and adaptations since they were first proposed half a century ago, and—as demonstrated above—are applied widely. Extensive efforts in field data collection, along with technical advances in sensor development (Bieroza et al. 2023), have greatly increased data availability in recent years. This has resulted in longer time series of water quality in various biomes and landscape settings, often at sub-hourly frequency. Moreover, homogenised and quality controlled low-frequency, long-term water quality data from countries all over the globe are becoming more and more available to the scientific community (Sterle et al. 2022). These advances in the availability of c and Q data have spurred the usage of cQ relationships and enabled investigations of water quality dynamics at novel scales. However, in our perception this new data availability has also led to an uncritical overuse of cQ relationships. We think that cQ relationships are too often presented as the final outcome of an analysis rather than its starting point, and many studies conclude with the classification of transport- or source limitation, instead of using this as the basis for more in-depth analyses of the underlying processes. In our view, despite the abundance of scientific publications using cQ relationships, we have therefore made limited progress in understanding the processes that cQ relationships reveal. We, therefore, perceive that these relationships are 'over-used but under-utilised'. From our perspective, there are two key challenges that we need to address for a better utilisation of cQ relationships: The first one—integration of temporal scales—arise from today's possibilities to apply cQ to long-term low-frequency and short-term high-frequency data. The second one—causality and understanding of processes—addresses the ambiguity of cQ patterns in terms of their governing processes.

3.1 | Integration of Temporal Scales

Concentration-discharge relationships were first proposed for long-term low-frequency data, but recent developments in sensor technology have resulted in a wealth of new high-frequency data, which has revealed some stark differences in event-scale and low-frequency long-term cQ patterns that we are still struggling to fully explain (Minaudo et al. 2019; Knapp et al. 2020; Musolff et al. 2021; Winter et al. 2024). These differences can be so pronounced that they exemplify Simpson's paradox (Simpson 1951; Blyth 1972), which describes the effect of a trend appearing in separate groups of data, but reversing or disappearing when the groups are combined. In the case of cQ relationships, this means that cQ patterns observed on the event scale may completely reverse when event observations are combined for long-term analysis.

One key implication of Simpson's paradox is that we cannot infer event-scale cQ behaviour from long-term behaviour and vice versa (Knapp et al. 2020; Musolff et al. 2021). The paradox ultimately raises the question of what drives the variability in concentrations within and between events and what explains the stark contrast between cQ patterns across time scales. Recent work by Winter et al. (2024) suggests that different parts of the catchment actively contribute to water and solute export at different time scales and that the hydrologic connectivity of sources and the stream network plays a decisive role. Additionally, changes in soil biogeochemical processes between events will likely also impact solute mobilisation across events. Consequently, cQ patterns at different time scales will also provide insights into different processes contributing to solute mobilisation, transport, and fate.

Contrasting event- and long-term cQ patterns also have implications for cQ analyses of low-frequency water quality time series. We must recognise that low-frequency data are often based on grab samples, and therefore, may represent distinct parts of the hydrograph (e.g., the same discharge reading may belong to a summer event or winter baseflow, where processes are entirely different). Minaudo et al. (2019) demonstrated how this knowledge can be used in fitting cQ relationships, by separately accounting for low-flow and storm-flow components of long-term low-frequency timeseries. To overcome the challenges associated with the interpretation of cQ dynamics across timescales, we encourage more of these kinds of analyses that can ultimately help to develop a better framework that allows us to integrate across temporal scales. Such approaches allow us to acknowledge the contrast between dynamic antecedent conditions and long-term mean properties of a catchment in shaping concentration dynamics.

3.2 | Causality and Understanding of Processes

The discrepancy between event-scale and long-term cQ relationships also points to another, more fundamental problem in cQ analyses: An implicit assumption we seem to make when employing cQ relationships is that concentrations are causally and directly determined by discharge. While this is rarely expressed as such directly, the mathematical formulation with c and Q as the dependent and independent variable, respectively, often appears to drive interpretation and process understanding. However, our conceptual process understanding of how catchments store and release water and solutes does not support this direct, causal relationship between concentration and discharge. For example, Knapp, Li, and Musolff (2022) raised the question of whether changes in discharge are simply the result of the same, third process or condition that also affects concentration changes. The study suggests that this process may be hydrologic connectivity parameterised as antecedent precipitation. Similarly, the transmissivity feedback idea presented by Bishop et al. (2004) conceptualises discharge and solute export as a function of catchment wetness with groundwater heads controlling discharge, while at the same time riparian soil wetness controls solute mobilisation (e.g., Ledesma et al. 2022). Hence, water levels and soil wetness may jointly control discharge, solute concentrations, and, thus, emerging cQ patterns, but we relate concentrations to discharge in our analyses because discharge is typically easier to measure than catchment-averaged soil moisture content or groundwater table depth. But whatever the underlying processes may be, we argue that the strong focus on a (direct and potentially causal) relationship between discharge and concentration may hinder identification of the underlying catchment-scale processes. This does not mean that we should stop using cQ relationships in their current form, but we encourage all users to acknowledge and carefully consider the importance of other drivers in their analyses. What sounds like a small shift in perspective may have substantial consequences for process-level understanding of water quality drivers, turning cQ relationships into a much more powerful tool for the analysis of water quality dynamics.

Process understanding is further complicated by equifinality, that is, meaning that different processes may result in the same cQ patterns. While this ambiguity of processes is known (Godsey, Kirchner, and Clow 2009; Chorover, Derry, and McDowell 2017), most studies focus on using cQ analysis to confirm one specific hypothesis instead of trying to resolve this ambiguity. For example, soluble reactive phosphorus (SRP) commonly exhibits a dilution pattern, which is typically interpreted as indicating constant-load contribution from a point source (e.g., a wastewater treatment plant) that gets diluted in variable discharge. However, various studies (Musolff et al. 2017; Dupas et al. 2018; Rode et al. 2023) demonstrate that the same pattern can be obtained in catchments without wastewater sources as a result of groundwater contributions or mobilisation of SRP from the riparian zone under reducing conditions.

We suggest that more rigorous hypothesis testing is needed, such as that conducted by Wondzell and Ward (2022), who tested nine alternative hypotheses on observed hysteretic behaviour of DOC and ruled out many of them based on additional observations. We also recommend better integration of cQ analyses with contextual catchment data, such as soil moisture, groundwater levels or topography, which can provide valuable additional insights into the plausibility of mechanisms and processes. In a similar vein, modelled catchment processes like runoff generation or the creation of multi-constituent cQ relationships or a comparison with travel-time approaches (Druhan and Benettin 2023) can provide useful sense-checking of assumed processes. Essentially, we propose that cQ patterns should not be used in isolation, but that a better understanding of underlying processes can be gained from them if they are placed into context with, for example, topographical, geochemical, geological, and geophysical information.

4 | Conclusions

The joint analysis of concentration and discharge through concentration-discharge (cQ) relationships is a versatile approach with a straightforward application to data, allowing to characterise, classify, and ultimately compare water quality time series. However, in the light of today's increasing data availability, the simplicity and usability of cQ analyses also poses a significant risk: due to ambiguities regarding underlying processes, cQ relationships may not provide the simple answers to questions on underlying catchment processes we hope to find. We, therefore, recommend using cQ tools with caution and not relying on them as the sole method for analysing concentration and discharge time series. cQ is most effective when used in conjunction with other information, for example, on catchment setting and hydrological and (bio-)geochemical conditions. In the end, cQ relationships are a tool and should be considered as the hammer to hit our ecohydrological questions, rather than as the nail providing the answers.

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Data Availability Statement

Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

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