



## Research papers

# Concentration-discharge patterns in a small urban headwater stream in a seasonally dry water-limited tropical environment



Willis Gwenzi<sup>a,\*</sup>, Shyleen R Chinyama<sup>a</sup>, Sydney Togarepi<sup>b</sup>

<sup>a</sup>Biosystems and Environmental Engineering Research Group, Department of Soil Science and Agricultural Engineering, University of Zimbabwe, P.O. Box MP167, Mt. Pleasant, Harare, Zimbabwe

<sup>b</sup>Department of Geoinformatics and Surveying, University of Zimbabwe, P.O. Box MP167, Mt. Pleasant, Harare, Zimbabwe

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## ABSTRACT

The simplicity of the hydrochemical stationarity concept renders it attractive for partitioning solutes between geogenic and anthropogenic sources. The current study used a small urban headwater stream in a seasonally dry environment to address two research questions: (1) What concentration (C)-discharge (Q) patterns exist in small urban headwater streams?; and (2) Do the C-Q patterns persist across C-Q metrics and temporal scales? Four C-Q metrics were tested: concentration-discharge (C-Q), concentration-cumulative discharge (C-ΣQ), load (L)-discharge (L-Q) and normalized concentration-normalized discharge (NC-NQ). C-Q and NC-NQ revealed discharge-invariant behaviour for Ca, two linear relationships with threshold-like transitions from negative to positive slopes for Mg, K and Na, and positive linear relationships for Fe, Pb and  $\text{PO}_4^{3-}$ . The threshold-like transitions with distinct breakpoints were more apparent in C-ΣQ patterns for all solutes. These patterns are consistent with three hypotheses: (1) negative linear to zero slope relationships indicate dilution followed by discharge-invariant behaviour (Ca); (2) negative to positive linear relationships (Mg, K and Na) point to dilution followed by solute enrichment or flushing; and (3) positive to negative linear relationships (Pb, Fe and  $\text{PO}_4^{3-}$ ) suggest initial solute mobilization followed by dilution. The three dominant behaviours were robust across weekly, fortnightly and monthly timescales. Significant linear L-Q relationships were observed for all solutes, suggesting that loads can be predicted from discharge. Our findings suggest that C-Q relationships are highly dynamic, and multiple processes control streamflow hydrochemistry at different times depending on antecedent discharge. The application of multiple C-Q metrics provided additional insights not apparent by using a single metric. The insights are critical to understanding of catchment hydrology and conceptual representation of hydrochemical processes in models.

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## 1. Introduction

Stream concentration-discharge relationships are crucial for understanding catchment water and solute budgets, partitioning of solutes between geogenic and anthropogenic sources, chemical weathering rates and biologic uptake rates (Liu et al., 2003). Concentration discharge-relationships are also critical for the design and operation of urban water systems. There is an increasing interest to understand catchment hydrological and hydrochemical functioning from interpretation of concentration discharge-relationships in both pristine and human-dominated catchments (Godsey et al., 2009; Basu et al., 2010). Some studies applied

dynamical systems approach to investigate emergent behaviour in catchment processes (e.g., Kirchner, 2009; McDonnell, 2013).

Concentration (C)-discharge (Q) relationships have been the subject of several field and modelling studies focussing at event (Weiler and McDonnell, 2006; Smethurst et al., 2013), seasonal (Poor and McDonnell, 2007) and annual (Thompson et al., 2011; Basu et al., 2011a,b) timescales. Studies conducted at event-scale have analysed hysteretic loops to improve the knowledge of hydrological and biogeochemical processes (e.g., Fovet et al., 2015; Lloyd et al., 2016; Zuecco et al., 2016). For example, hysteresis indices have been developed to evaluate the direction (clock-wise versus anti-clockwise), shape and extent/magnitude of relationships between discharge, and suspended sediments (e.g., Aich et al., 2014), solute concentrations (Bieroza and Heathwaite, 2015; Lloyd et al., 2016); and water storage in saturated and unsaturated zones (Fovet et al., 2015). Other studies reported clockwise and

\* Corresponding author.

E-mail addresses: [wgwenzi@yahoo.co.uk](mailto:wgwenzi@yahoo.co.uk), [wgwenzi@agric.uz.ac.zw](mailto:wgwenzi@agric.uz.ac.zw) (W. Gwenzi).

anti-clockwise hysteretic C-Q relationships and their origins (e.g., Evans and Davies, 1998; Butturini et al., 2005; Weiler and McDonnell, 2006; Holz, 2010; Smethurst et al., 2013). A few event-scale studies reported no C-Q correlation (e.g., Bernal et al., 2002), while others observed linear load (L)-Q relationships (Goolsby et al., 2000; Donner et al., 2002, 2004; Vogel et al., 2005). For example, in a small Mediterranean forested catchment in Spain, discharge was a poor predictor of both dissolved organic carbon (DOC) and nitrate (Bernal et al., 2002). Factor analysis showed that antecedent moisture conditions and the magnitude of the storm event were the most relevant factors accounting for 63% of the total variance (Bernal et al., 2002). Other studies have used virtual experiments and end-member mixing models to investigate the response of concentration-discharge relationships to biogeochemical interactions between stream and catchment (e.g., Butturini et al., 2005) and, surface water and groundwater (Weiler and McDonnell, 2006). Mixing models with two or three runoff components and constant solute concentration in the input components have been used to explain solute concentration-discharge hysteresis observed during storm events (Evans and Davies, 1998; Butturini et al., 2005). In summary, the nature of C-Q relationships varies among studies depending on land use, spatial scale of measurement, contaminant, magnitude of storms, timescales and catchment position (headwater versus tailwaters).

The bulk of the studies conducted at event-scale are largely drawn from Mediterranean and temperate climates where snow-melt plays a key role in regulating both streamflow and hydrochemistry (e.g., Inamdar et al., 2009), while those on tropical climates are relatively limited. Compared to rural, natural or forested catchments (e.g., Rusjan et al., 2008; Holz, 2010; Smethurst et al., 2013), few studies are available on C-Q relationships in urban catchments. Moreover, despite the simplicity and widespread application of C-Q relationships for inferring geogenic and anthropogenic sources of solutes, there is a paucity of literature on the subject in water-limited urban catchments in tropical Africa. The application of C-Q relationships for solute partitioning is particularly important where complete solute and water budgets cannot be derived (Walling, 1999). The lack of literature on C-Q relationships in Africa stems in part from lack of intensive hydro-metric and hydrochemical monitoring programs associated with limited technical and financial resources. The bulk of hydrological studies in Africa focus on agricultural rainwater harvesting systems (e.g., Ngigi et al., 2007; Makurira et al., 2010; Dile et al., 2013), measurement and modelling of field and catchment water balances (Kiptala et al., 2013), and a few on water chemistry and eutrophication of reservoirs (e.g., Nhapi et al., 2002).

The complex interactions among the climatic, geogenic and anthropogenic factors control catchment hydrology and biogeochemistry. Unlike urban catchments in developed countries in temperate regions, water-limited catchments in Africa have a unique geology, and climate characterized by distinct wet and dry seasons. Rainfall is highly variable and episodic, which may in turn trigger corresponding catchment hydrological and biogeochemical responses. In addition, diverse anthropogenic activities in urban catchments such as land use practices (e.g., agriculture, built-up areas, industries), poor waste management practices, and lack of properly designed stormwater and wastewater management systems act as sources of contaminants. However, the nature of concentration-discharge relationships, and how geogenic and anthropogenic drivers influence such relationships in tropical urban catchments in Africa remain largely unknown. Moreover, the persistence of C-Q relationships across C-Q metrics and timescales has received limited research attention.

The current study seeks to provide some early insights on the subject by addressing two key research questions pertaining to methodological and temporal scale issues in catchment hydrology:

(1) What concentration-discharge (C-Q) patterns exist in small urban headwater streams?; and (2) Do the C-Q patterns persist across C-Q metrics and temporal scales (weekly, fortnightly, monthly)? The null hypothesis was that, unlike in large pristine and intensively managed catchments, small urban catchments will exhibit unique concentration-discharge patterns that persist across C-Q metrics and timescales. This hypothesis was motivated by the fact that, in seasonally dry environments, highly episodic tropical storms coupled with highly impervious surfaces in small urban streams will lead to rapid catchment response or short travel times. This will in turn imply that the control of streamflow hydrochemical signature could reflect the rapid transition from baseflow (geogenic) to overland (anthropogenic) processes. The specific objectives were: (1) To determine the temporal variation of discharge and runoff hydrochemistry in a small urban stream, and (2) to identify temporal patterns of concentration-discharge relationships and determine their persistence across C-Q metrics and temporal scales.

## 2. Materials and methods

### 2.1. Description of study site

The study was conducted on a small headwater urban stream within the University of Zimbabwe Campus, Harare, the capital city of Zimbabwe (Fig. 1). The stream has its source within the University of Zimbabwe campus where it emerges from a spring. The catchment area for the stream consists of three dominant land uses/surface covers; (1) built-up suburban area consisting predominantly of impervious areas including the university campus, residential areas, pavements and roads network; (2) landscaped areas with grass surfaces including sports fields and lawns; and (3) a pristine wetland area dominated by grasses, sedges and isolated groundwater-dependent woody species. The total area under each land use is estimated to be 29.6 ha, 127.7 ha and 44.2 ha, respectively, giving a total of 201.5 ha. The stream has an approximate width ranging from one to two and half meters. The stream flows into the Marimba River to the west, which then discharges into Lake Chivero, a major water source for the city of Harare.

The geology of the area is predominantly mafic rocks weathering to give clay soils (Baldock et al., 1991). Field description of soil profiles along a typical catena consists of three soil series: (1) well-drained red clayey soils with predominant 2:1 non-expanding clays in the uplands, transitioning to; (2) moderately drained reddish brown soils over yellowish clayey soils with a mixture of 2:1 expanding and non-expanding clays in the midslope; and (3) dark grey to black soils consisting of 2:1 expanding clays with a predominance of montmorillonite with high shrink-swell capacity and gleyic properties evident of permanently reducing conditions in the wetland (Nyamapfene, 1991).

The climate is typically tropical with warm and wet summers (mean temperature: 27 °C) and cool dry winters (average temperature: 17 °C) and long-term average rainfall of about 800 mm confined to the warm summer seasons stretching from late October to early April. Rainfall is highly seasonal and characterized by frequent moderate (30 mm hr<sup>-1</sup>) to high (up to 260 mm hr<sup>-1</sup>) intensity storms (Nyamangara et al., 2003).

### 2.2. Discharge measurements

Discharge measurements and streamflow sampling for chemical analysis were conducted at a single point along the stream with measurable streamflow throughout the year (17°47'23.13"S; 31°02'48.18"E) (Fig. 1). The assumption was that while absolute concentration and discharge may vary spatially or along the stream

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