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Dube, Y

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SHRINKING LABS ONTO MICROCHIPS:

THE RISE OF AUTOMATED WATER QUALITY OBSERVATION SYSTEMS

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Presented by:

Y DUBE

(Student number: 862087)

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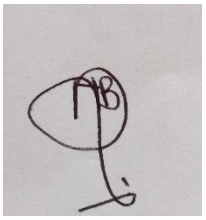
THE FACULTY OF SCIENCE, UNIVERSITY OF WITWATERSRAND, JOHANNESBURG

Supervisor: Professor RJ Scholes

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DECLARATION

I declare that this thesis has been composed solely by myself and that it has not been submitted, in whole or in part, in any previous application for a degree. Except where states otherwise by reference or acknowledgment, the work presented is entirely my own.



N.Y Dube

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ABSTRACT

South Africa is developing a research infrastructure called the Enhanced Freshwater and Terrestrial Ecological Observation Network (EFTEON). It is focused on a set of landscapes, where observations of climate, terrestrial ecology (land cover, phenology, and land-atmosphere fluxes), biodiversity (communities and populations), social-ecological circumstances (land use, livelihoods) and hydrology (soil water, river flows, aquifers and biogeochemistry) will be co-located and integrated. Automated instruments for river flow monitoring are well-established, but automated, continuous measurements of water chemistry for a comprehensive set of constituents is not yet fully operational anywhere in the world. A great deal of experimentation with different sensor systems is taking place. The pilot experiment in automated monitoring of water salinity at landscape scale described here is a technology testbed, to see if the sensors are sufficiently robust for long-term deployment, and if they can accurately quantify an important aspect of the stream chemistry. Deployment under field conditions for 14 months allowed robustness to be determined, both in terms of fraction of useful data collected and sensor drift. Accuracy was assessed by calibrations before, during and after deployment. Whether the achievable accuracy was sufficient for the landscape-scale biogeochemical questions posed by the network was assessed by seeing if it is possible to achieve a salt budget closure between several tributaries and the main stem of the river within + 10% error, based on data from a network of five sensors.

The successfully designed and implemented observation network consisted of five stations equipped with a Decagon Conductivity-Temperature-Depth device that integrates water depth over a weir (to get flow), electrical conductivity (to get salt content), and water temperature sensors connected to a Em50 Logger. Field robustness was at the lower limits of acceptability (65% of potential data flows were achieved) across a varying and challenging real-world conditions at the Sabi-Sand Catchment. The biggest component of data loss was theft of equipment, followed by unexplained logger failure. Nevertheless, the quantity of continuous data records obtained far exceeds the quantity of historical manual grab sample data records and has demonstrated the competency of automated water quality observation systems to capture hydrochemical events which are not presented in traditional manual water quality monitoring systems (for example, episodic events captured at observation station X3H015). The sensor arrangement was fit to capture riverine salt fluxes across time and space, but salt budget closure to within 10% was not possible. The achieved closure was within 30% error. The computation of catchment salt fluxes with existing monthly estimates derived from manual sampling is not adequate to represent the short-duration hydrological events that occur within a catchment. The implemented observation network has characterised the water quality status of clear mountain headwaters to slow moving rivers with varying land use changes influencing stream chemistry. This range is representative of many river systems in South Africa. Thus the methods developed in this study can be modified and used for the development of continuous water quality monitoring systems elsewhere in the country.

INTRODUCTION

Salt loading in South African rivers

Water quality problems such as salinization, the leaching of agricultural chemicals, eutrophication, elevated sediment loads, pathogens from untreated sewage, and leached acid, heavy metals or radioactive substances from mine operations are observed at over four-fifths of South Africa's freshwater monitoring sites (Department of Water and Sanitation, 2013; Donnenfeld *et al*., 2018; de Villiers *et al*., 2007). The pattern and variability of such issues over time and space is not well understood, since the current monitoring procedures based on manual grab samples followed by laboratory analysis are too sparse in terms of number of locations sampled, and too infrequent (typically monthly) to fully characterise the processes leading to the water quality issues.

The deterioration of water quality is a threat to the country's health, economy and biodiversity (Donnenfeld *et al*., 2018; Dabrowski *et al*., 2013; McLachlan *et al*., 2009; Claassen., 2013; Van der Merwe, 2009; Roux *et al*., 2010). The semi-arid catchments which characterise the areal extent of South African river systems have inherently highly variable water flow and chemistry. This is a constraint on understanding the dynamics of water quality in both natural and transformed landscapes: the signal is hard to distinguish from the noise. The existing monitoring networks do not sufficiently equip the country to deal with the water quality challenges it faces—either at a fundamental research level, or for purposes of water regulation.

Water quality in catchments, at both small and grand scales, are the result of the interaction of three broad sets of factors: the hydrological characteristics of the catchment (such as, its geology, soil, topography and climate), land cover and land use (including grazing, cropping and urbanisation) and water-use related activities (abstraction, impoundment and return flows) (Xu *et al*., 2019; Kiersch B *et al*., 2002; Uriarte *et al*., 2011). Agriculture uses nearly two thirds of the water in South Africa, municipalities a quarter, and mining, power generation and industry consuming the remainder. Consequentially, agricultural, and municipal effluents are important drivers of water quality deterioration. They contain high loadings of salts, nutrients and sediments, along with smaller but still potentially damaging levels of pesticides, endocrine disruptors and other chemicals (de Villiers *et al*., 2007).

The fraction of water used by agriculture for irrigation and livestock watering is likely to decrease in future, to make space for growing municipal and industrial use. As a result, agricultural water use will likely become more intensive, with implications from the salt, nutrient, pesticide and sediment loading in the return flows. Municipal water-use is expected to increase due to increasing urbanization (Donnenfeld *et al*., 2018). The main contemporary threat to water quality resulting from municipal use is from untreated or incompletely-treated sewage, which results in pathogens and elevated nutrient levels and biological oxygen demand. Even where sewage treatment is more effective, such as the larger metropolitan areas, the result is rising concentrations of total dissolved salts, especially where water is re-used several times. In rural areas, water supply infrastructure is often dysfunctional, therefore, people rely on stream water, boreholes and wells for basic domestic water needs.

The need for continuous monitoring of salinity

Natural hydrological processes, land use and stream-water use activities alter catchment water chemistry at both high frequency (hours to days) and low frequency (years to decades) and all timescales in-between. The degree of alteration is intensified by episodic events. As a result, water quality changes require a near-continuous monitoring procedure to be detected and diagnosed (MacKella *et al*., 2014; WWF-SA, 2016; Kruger *et al.*, 2017; de Villiers *et al*., 2007; Compagnucci *et al*., 2018). The intensification of the hydrological cycle as a result of climate change further threatens the availability and quality of freshwater resources (Huntington, 2006). The frequency at which both natural conditions and human-caused perturbations occur does not match the traditional weekly or monthly monitoring (Pule *et al*., 2019; Ryberg, 2006; Wanger *et al*., 2006; Hasenmueller., 2011). Other problems associated with traditional manual water quality sampling are high sampling costs (mostly due to travel and personnel costs), data gaps resulting from sample loss, the missing of episodic events, and high 'latency' (the delay between the taking of the sample and the availability of the data). Such factors limit the knowledge and transfer of research outcomes to decision makers. (Chappell *et al*., 2017 ;Campbell *et al.*, 2013a; Blaen *et al*., 2016; Viviano *et al*., 2014).

South Africa has had some form of water quality monitoring system for close to a century. Since 1972, the national government department currently known as 'Water and Sanitation' (previously Water Affairs) has monitored the country's water quality and quantity status, as guided by the Water Services Act (1997), National Water Act (1998) and the National Water Resource Strategy (2004). These acts gave rise to water quality management policies such as the Integrated Water Resource Management (IWRM) which is supported by the Resource Quality Information Service (RQIS)—a web-based, open-access database system. The web page is mainly a water quality data exploration tool that allows for easy access of data, consist of maps outlining the monitoring stations, different water management areas and surface water drainage patterns. Although the page is an extremely useful tool, for planners, regulators and the public, it has a disadvantage of the data lagging behind by several months and periodic web connection failure.

The South African Department of Science and Technology (DST) in 2016 launched a series of research infrastructures, whose purpose is to support next-generation research, which will in turn inform the decision-making needs of an increasingly complex environment. One of these infrastructures is the Expanded Freshwater and Terrestrial Environmental Observation Network (ETFEON) (Scholes *et al*., 2016). EFTEON is conceived as both a large scale ('landscapes' of tens to hundreds of square kilometres) and long term (decades) observation platform, which integrates all the elements needed to understand coupled ecological-social systems in South Africa (Scholes *et al*., 2016). One such element is water quality.

As a pilot study for automated water quality measurement under EFTEON, a relatively simple automated water quality observation system was established by the project described in this dissertation in the Sabi-Sand Catchment, in the north-east of South Africa. In this study, flow (calculated from calibrated depth over weir), temperature and electrical conductivity were logged on a continuous basis (recording the time-integral at 30 minutes intervals) at five locations.

The sample locations were selected to allow processes within the catchment to be represented and to take advantage of existing flow-gauging weirs. The parameters collected – date and time-stamp, depth (+ 2.5 mm), water temperature (+0.1 ⍰C) and electroconductivity (+ 0.01 dS m-1)—were selected because sensors for their detection are already available, at relatively low-cost, and with a reasonable record of reliability under field conditions (Panguluri *et al.*, 2009; Blaen *et al.*, 2016; Ryberg, 2006). The Sabie-Sand catchment was chosen as the testbed because of the co-deployment of many other systems relating to the terrestrial and social processes, and because the issue of increasing salinity is likely to be prominent in the area, due to its geology, climate and increasing development. Many studies have demonstrated the resultant freshwater salinization in hydrological systems due to development (as an example, see the works of: Uriarte *et al.*, 2011; Xu *et al.*, 2019; Kaushal *et al.*, 2018; Smedema, 2000; Cañedo-Argüelles *et al.*, 2016; Dabrowski *et al.*, 2013; Griffin *et al.*, 2014; Segerson *et al.*, 2002). Accurately detecting salinity across time and space advises scholars and decision makers on salinity sources (such as, saline soils, groundwater intrusion, out of standards runoff), antagonistic & synergistic interactions, estimating riverine loads (e.g. water chemistry), water allocation/availability for agricultural-, municipal- & industrial use, required treatment methods for water treatment plants, perturbs form freshwater- to salt tolerant plants as well as riverine ecosystems (Paine, 2003; Nthunya *et al.*, 2018).

Trial deployment of the sensors and data loggers for an automated in-stream water flow and quality monitoring system was intended to test the robustness of automated measuring instruments for long term deployment under real-world conditions, before more expensive and less stable sensors are deployed (Snyder *et al.*, 2018; Blaen *et al.*, 2016).

LITERATURE REVIEW

Salt loading in catchments

What is freshwater salinization?

An important threat to water quality is the freshwater salinization syndrome. This is a growing worldwide concern that constrains economic and social development, particularly in water-scarce arid and semiarid countries (Turton, 2019; Cañedo-Argüelles *et al.*, 2013; Mateo-Sagasta *et al.*, 2018; Van der Merwe, 2009). Freshwater salinization is the accumulation of salt in a water body beyond acceptable water quality standards—this occurs as a result of: 1). solute addition (that is, salt accumulation resulting from salts released during weathering processes and inflows from anthropogenic activities), and 2). salt concentrating processes associated with open-water evaporation (Harris *et al.*, 2009; Van der Merwe,2009; Walton, 1989). Salinization is typically measured either by electroconductivity (EC), or by total dissolved solids (TDS) (Yilmaz *et al.*, 2014; Hayashi, 2004). Electroconductivity (EC, µS/cm) is the ability of water to conduct electrical current due to ion activity, whereas Total Dissolved Solids (TDS, g/litre) refers to the mass fraction of all solids (particularly mineral salts) dissolved in water (Kumar *et al.*, 2014; Walton, 1989).

Natural salinization occurs due to accumulation of salts released during weathering processes and/or deposition by climatic processes such as rainfall or aeolian deposition as a result of proximity to the coast (Greene *et al*., 2016; Mateo-Sagasta *et al*., 2018). The rate of salt accumulation due to natural processes is dependent on climate and the type of geology. During weathering processes (particularly, chemical weathering), dissolved ions are released from minerals. For example, weathering of limestone or dolomite releases carbonate ions, while weathering of sedimentary rocks such as sandstone releases sodium, calcium, potassium and magnesium ions (Siegesmund *et al*., 2002; Day *et al*., 1995).

Human-induced salinization occurs through agricultural, municipal and industrial or mining effluent, surface runoff from urban settlements and seepage from wastewater disposal sites (Mateo-Sagasta *et al*., 2018; Kaushal *et al*., 2018; Williams, 2001; Department of Water and Sanitation, 2016). Prominent drivers of human induced freshwater salinization are municipal, industrial and agricultural return-flows. *Table 1* is a summary of municipal (i.e. human settlement), industrial and agricultural activities and associated contribution to freshwater salinization. Effluents from human settlement containing faeces, urine, detergents, food scraps, soil residues, seepage from pit latrines and surface runoff show elevated concentrations of dissolved salts, nitrogen, phosphorus, chlorides, toxic metals (such as chromium and copper) and other compounds (such as cyanide) (CSIR, 2010; Department of Water and Sanitation, 2016). In North America, mining activities, particularly hydraulic fracturing and coal bed methane production have all been associated with increases of salinity in rivers, due to surface runoff from, for example, coal stockpiles and dumps (Pond *et al*., 2008; Akabzaa *et al*., 2007) In South Africa, salinity originating from mining activity includes acid mine drainage from coal mines and sulphate ore bodies, but particularly from mine slurry dams (CSIR, 2010; Selebalo *et al.*, 2021).

Table 1: Agricultural, municipal & industrial activities constituents and their impact on the increase of salt loads in catchments (Zia et al., 2013; Barnes, 2003; Kenward *et al.*, 2013).

Activities	Constituents	Impact
	Agriculture	
Cultivation/till Deforestation	Sediments and solutes that result in an increase in TSS (Total Suspended solids) and TDS (Total Dissolved Solids) in rivers.	Increase in river salinity due to sediments and solutes transported by runoff (caused by rain or irrigation).
Excess Irrigation	Salts and nutrients (chloride, calcium, magnesium).	Return flows from irrigation water increases in-stream salt loads.
Plantation forestry	Overland flow, particularly from road infrastructure, and changed subsurface flow	Increased evapotranspiration resulting into runoff that has increased amounts of TDS (Webb *et al.*, 2007)

Animal waste in rangelands reaching aquatic system (e.g. river), & soil erosion	Bacteria, virus, heavy metals, cryptosporidium, Legionella. Increases in sediment load due to soil erosion	Runoff carrying animal faeces and urine containing pathogens into a river increases the amount of dissolved salts, erosion adds sediments.
Municipality		
Domestic waste water (reticulated)	Sewage water mainly consisting of dissolved salts, nitrogen, phosphorus, chlorides, toxic metals and compounds (such as, chromium, copper, cyanide).	Health hazard to human & animal health (e.g. emergence of water borne diseases, growth of toxin producing cyanobacteria, high mobilization of stream salts).
Urban or rural settlement, non-reticulated	Increase of point & non-point faecal contamination (via e.g., pit latrine and overland flow from surface defaecation and urination).	Constitutes are a health hazard to humans and animals, contributes to salt mobilization into rivers due to impervious surface coverage by, for example, roadways allowing increased in concentrated surface runoff.
Industries and mining		
Removing native vegetation (e.g., during construction or expansion phases)	Promote soil erosion that results in increased stream sediments with high TDS.	Contaminated soils increase overall stream salinity.
Unsustainable water resource withdrawals, spillage and runoff	Increased chemical concentration, e.g. heavy metals, TDS, AMD.	Coupled with decreased stream dilution, degrades aquatic species health, and may result in water borne diseases.

Numerous studies have publicized the escalation of freshwater salinization issues due to the ongoing release of flows that are highly concentrated in pollutants, as a result of human activities (e.g. unsustainable farming methods and improper mine waste disposal). These studies demonstrate that the rate of pollutant release exceeds the rate of natural dilution or salt immobilisation. The study by van Niekerk *et al*., 2007 on long-term salinity changes in selected South African rivers illustrates a gradual increase in electroconductivity for over 25 years in rivers such as the lower Orange River, Blyde River (at the confluence with the Olifants River, adjacent to the Sabi-Sand catchment studied here), Breë River and the Berg River. The deterioration of freshwater resources poses a threat to, among other things, human health, stream biodiversity, water security and economic development due to costs associated with water treatment facilities (CSIR, 2010; Van der Merwe, 2009; McLachlan *et al*., 2009; Department of Water and Sanitation, 2016; Williams, 2001; Roux *et al*., 2010).

Measuring salt concentration in rivers

Electrical conductivity and total dissolved solids are two of the main measurable bulk indicators of the amount of salts in water bodies, including rivers (Yilmaz *et al.*, 2014; Hayashi, 2004). The concentration of individual cations and anions can also be quantified, using a variety of techniques including specific ion electrodes and spectrophotometry. Electroconductivity of freshwater bodies is a physical property describing a water body's ability to conduct an electric current due to dissolved ion activity (Walton., 1989). Although it does not quantify the concentration of the individual contributing ions directly, there is a close relationship between EC, total dissolved salts and individual ion concentration. Therefore, it is justifiable to obtain one variable from the other through mathematical relationships (see: Equation 1). There are several methods, of varying complexity, to determine these relationships. The most accurate methods are those that consider infinite dilution equivalent conductivity, which can be related to measured electroconductivity. Even so, these methods are subject to an error of 1-2% (and even higher at electroconductivity values greater than those encountered in this study, that is, electroconductivity greater than 0.3 dS/m). The errors arise due to uncertainties concerning the activity of ions in uncontrolled environments, that is, outside the laboratory setting (Day *et al.*, 1984; Day *et al.*, 1995; Hubert *et al.*, 2015; Appelo *et al.*, 2004; Rusydi, 2018; McNeil *et al.*, 2000; Pawlowicz, 2008; Hem, 1985; Kumar *et al.*, 2014).

Nevertheless, it is universally assumed in water quality studies that almost all the conductivity is accounted for by the dissolved salts ion activity (Day *et al.*, 2004). Therefore, EC and TDS are assumed to be directly proportional.

$$TDS = f * EC$$

Equation 1

Where "f" is the conversion factor—a constant that allows for the estimation of TDS from a precisely measured EC (Singh *et al.*, 1975).This conversion factor is commonly used in all situations where TDS needs to be established (for example, agriculture, industry, water supply, resource management and mining (van Niekerk *et al.*, 2014) without laboratory procedures. The factor differs for different types of waters, depending on the ratios of various ions present. This varies between water bodies, sampling locations and seasons. Nevertheless, predefined conversion factors without site-specific validation are commonly applied (Niekerk *et al.*, 2014; Hubert *et al.*, 2015). A predefined range of 0.54 to 0.94 mg/l per µS/cm conversion factor is generally used in water quality studies. The higher values are characteristic of water bodies rich in sulphate and non-ionized silica, and the lower values are characteristic of water bodies with high free acid, sodium, chlorine and alkalinity (such as the Sabi-Sand system). While these general standards provide a good indication of the values to expect, accuracy is improved by using locally-calculated conversion factors. (Hem, 1985; McNeil *et al.*, 2000; Hubert *et al.*, 2015; Rainwater *et al.*, 1960). In South Africa, the DWS water quality guidelines make use of 0.65 mg/l per µS/cm as a standard EC:TDS conversion factor, applied across all fields, including domestic, industrial and agricultural (Hubert *et al.*, 2015; Niekerk *et al.*, 2014).

Balancing the salt budget

The budget approach in its simplest form assumes that the volume of water and total salt content flowing in a river are 'conserved', that is, the totals are constant over some period of time, and need to add up (Friebertshauser *et al.*, 1972). This means that water from all sources flowing into a river must be compensated for by an outflow of equal magnitude or a change in storage. At equilibrium, the salt flux carried in by one flow must equal the salt flux carried out by another (Friebertshauser *et al.*, 1972). Salt flux can be defined as by well-known Fick's Law, that is, the net difference between the salt concentrations on either side of the active layer interfaces of the draw and feed solutions, $C_{D,m} - C_{F,m}$ (Koseoglu *et al*., 2018). However, rivers are seldom at equilibrium, so the difference usually expresses as changes in the size of the salt stocks at various points in the system. The salt output: input ratio from a catchment can be used as an indicator for land and surface water salinization (Peck *et al*., 2010). There are several processes that can increase the amount of salt in a catchment and associated quantifying measures.

For example, Sandspruit Catchment (Berg River, South Africa) has demonstrated an increase in stream salinity due to the manifestation of dryland salinity—an accumulation of salt loads due to changes in land-use, that is, transforming indigenous vegetation to agriculture (Bugan *et al*., 2015). In this catchment, it was reported that in addition to natural salinization, changes in land-use from indigenous vegetation to agriculture altered water balance processes such as evapotranspiration and infiltration/recharge, resulting to the mobilization of stored salts to soil, stream and groundwater. The Bugan *et al*., 2015 study on quantifying the Sandspruit Catchment salt balance concluded that changes in catchment hydrology due to agricultural and/or any other development activities can result into a significant increase in catchment salt exports. In addition, salt balance computations are an efficient measure through which various processes contributing to stream salinity can be identified.

Another detailed study on quantifying catchment salt balance was conducted at the Fitzroy Basin (north-eastern Australia) by Jones *et al*., 2013. In this study, they used the salt budget approach to quantify the contribution of transformed land-use (e.g. coal-mining, irrigated cropping and grazing) activities to the annual salt loading in the catchment. These studies demonstrated how unsustainable land transformation results into the increase of salt mobilization and the impact it has on ecosystem health.

Effects of increased salt concentration on aquatic life

Department of Water Affairs and Forestry (2003) categorized salinity as a non-toxic inorganic constituent. These are constituents that may cause harm at extreme concentrations but their generally system characteristic and natural concentrations depend on local physical, geochemical and hydrological processes. Due to this, the general national standard for South African rivers state that TDS concentrations should not be altered by more than 15% from the natural cycle and amplitude; in addition, the frequency of natural cycles of TDS must not be altered, as the alteration may have undesirable effects on both aquatic and terrestrial life (Day *et al*., 1995; Department of Water and Sanitation (DWS),

2016). The indicative natural salinity of most rivers other than in their coastal reaches is approximately 1000 ppm of salts on a mass basis (i.e., one part per thousand, or 0.1%). Extreme deviation from this average may have undesired consequences. Alteration of the natural riverine salt concentration will affect aquatic species physiological mechanisms and morphological adaptations, which serve to balance internal salts concentrations of an organism against those found in their external environment (Department of Water and Sanitation (DWS), 2016; Department of Water Affairs and Forestry,2003; Stenseth *et al.*, 2009).

Freshwater species generally survive by balancing their internal osmic pressure with the media they live in. This means that their internal salinity concentration must be greater than that of the water they reside in (Day *et al*., 2004; Stenseth *et al.*, 2009). In the event of a water body having higher salinity concentrations, freshwater species will either adapt (through osmoregulation) to the new higher concentrations, spend energy expelling ions and keeping water or die as a result of the species being unable to cope at high salinity concentration (Day *et al*., 2004; Stenseth *et al.*, 2009). For those freshwater species that can adapt to higher salinity concentrations, natural selection may take its toll on the species genetic-diversity or community numbers, as there are genetic costs associated with adaptation (Stenseth *et al.*, 2009).

For example, elevated river salinity has been reported to reduce growth and reproduction of some freshwater species (e.g. cladocerans, Daphnia dentifera), amphibian, macroinvertebrate and in some cases lead to a generic drift in invertebrate communities (Williams, 2001; Cañedo-Argüelles *et al*., 2012; Cañedo-Argüelles *et al*., 2016; Hintz *et al*., 2019). Salt concentrations vary across rivers (both in time and space) and will determine the community and diversity of species that reside in an area. Variations in salt concentrations may increase one population in a community of species while simultaneously resulting in the decline of another. Dallas (1992) has shown evidence of this when they compared invertebrate fauna of the Berg River (located south of the Western Cape, South Africa) with those found during the early 1950s (Clark *et al*., 2009). Their findings concluded that due to salinity increases, *Afrochiltonia capensis* (a salt-tolerant species), had increased in numbers on the lower reaches of the river, while mayfly *Baetis bellus* had been replaced by *Baetis latus* (Day *et al*., 2004; Stenseth *et al.*, 2009; Clark *et al*., 2009).

Many studies suggest that juvenile stages of aquatic species are more sensitive to increased river salinity (Day *et al*., 2004; Cañedo-Argüelles *et al*., 2016; Kaushal *et al*., 2018). Harrison (1966) illustrated that the rate of egg-lying in freshwater snails (*Biomphalaria pfeifferi*) was reduced due to high Mg:Ca ratios in some streams in Zimbabwe. Hart *et al*., 1991 argued that while numerous freshwater bacteria can readily adapt to salinity variations, increase in salinity is linked with a decline in species richness. In addition, the adaptation of some bacteria (for example cyanobacterium *Microcystis aeruginosa*) can result in a decline in cell density and chlorophyll contents.

Increase in riverine salts can be either beneficial or detrimental on aquatic organisms due to synergistic or antagonistic processes (Cañedo-Argüelles *et al.,* 2019). These are processes by which a combination of substances serves to protect (antagonists) or sensitize (synergism) aquatic organisms to various water pollutants (Day *et al*., 2004). For instance, due to synergism, organophosphate insecticides (e.g., Atrazine) are toxic to *Daphnia carinata* and *Hyalella azteca* at high

salinity concentrations, but not significantly toxic at low salinity (Lizotte *et al.*, 2012; Hall *et al*., 1995). Antagonistic processes decrease the toxicity of some toxic metals (such as copper, cadmium, mercury, nickel, zinc and chromium) at elevated salinity concentrations (Hall *et al*., 1995).

Climate change impacts on freshwater salinization

South Africa is more vulnerable to climate change than many other countries (Niang *et al*., 2014; Department of Environmental Affairs, 2018a; Kusangaya *et al*., 2014; WWF-SA, 2016b; WWF-SA, 2017). Changes in climate, such as increasing temperatures and changing rainfall patterns, greatly alter hydrological responses in space and time. In general, for the summer rainfall parts of the interior of South Africa (including the Sabi-Sand catchment) stream-flow decreases are projected as a result of temperature increases driving an increase in evaporation, in combination with a projected general decrease in rainfall (Department of Environmental Affairs, 2018b). In addition, the pattern of flow is projected to change as a result of changes in episodic events, such as droughts and floods (Nkhonjera, 2017; Kusangaya *et al*., 2013; Yilmaz *et al*., 2011; Heritage *et al*., 1995).

Worldwide, data from observation networks suggest an ongoing intensification of the water cycle. This intensification threatens the availability and quality of water resources (Huntington, 2006). Rising temperatures, intense precipitation and prolonged periods of low stream-flows will exacerbate numerous existing water quality problems, such as increases in nutrient loads, pathogens, salinity, pesticides, decrease in pollutant dilution and thermal pollution (Day *et al*., 2019; Lane-Visser *et al*., 2014; Huntington, 2006; Kusangaya *et al*., 2013; Nkhonjera, 2017). This will, in turn, affect human health, stream biodiversity, water security and costs of cleaning and supplying water (Kusangaya *et al*., 2013; Nkhonjera, 2017). Intensive rainfall introduces floods and increase in runoff, which results in an enhanced transportation of sediments, pathogens, nutrients, and dissolved pollutants (such as salts and heavy metals) into freshwater systems (e.g. river catchments and lakes). More intense rainfall (even if the rainfall events are overall less frequent) leads to spillages in sewer systems and off-stream wastewater storage facilities, contributing to deteriorating freshwater quality status. In a semi-arid regions, prolonged periods of low stream-flow will promote salinity increases in both surface-water and shallow groundwater (Donnenfeld *et al*., 2018).

Climate change impacts will be more severe in the water sector than many other natural resource sectors (Nkhonjera, 2017; Kusangaya *et al*., 2013; Yilmaz *et al*., 2011). Developing countries, including South Africa, often do not have adequate data on water quality and quality, which hinders the understanding of the impact of climate change on natural resources. These threats highlight the need for improvement of current water quality monitoring systems to ensure future water security.

Water security concerns

Many scholars have defined the term "water security" (Pahl-Wostl *et al*., 2013; Vörösmarty *et al.*, 2010; *Warburton et al.*, 2012). Some of these definitions are inadequate, as they fail to consider the cross-scale interactions amongst surface water, groundwater, economic strength and human activities (Pahl-Wostl *et al.*, 2013). Water systems are altered across space and time through land cover changes, industrialization, urbanization and engineering schemes (e.g. irrigation schemes)—thus any strategy towards water security must incorporate these alterations, as well as consider local conditions (Vörösmarty *et al*., 2010; Warburton *et al*., 2012; James *et al.*, 2017). A more inclusive definition is: *water security is the capacity of a population to safeguard sustainable access to adequate quantities of acceptable quality water for sustaining livelihoods, human well-being, and socio-economic development, for ensuring protection against water-borne pollution and water-related disasters, and for preserving ecosystems in a climate of peace and political stability* (United Nations, 2013). In this way, water security is viewed as an umbrella term linking several human security concerns, such as water resource availability, human and ecosystem health as well as social and economic growth (UN-Water, 2013; UNESCO, 2019).

The acceleration of existing water quality problems due to climate change and other factors threatens water security in most water-scarce countries, such as South Africa (DWS, 2017; Muller, 2008). Water security is a dynamic concept for such countries, with many different elements defining the challenge: Water insecurity may be due to local hydrology, lack of appropriate infrastructure, lack of governance or historical indifference (van Koppen *et al*., 2014; Grey *et al*., 2013). In the long history of approaches to addressing water security, the basic logic has been to determine standards on how much water is required to meet both human and environmental needs (Srinivasa *et al*., 201; Van der Merwe *et al.*, 2009; Pahl-Wostl *et al.*, 2013; James *et al.*, 2017). These standards build on existing knowledge and are adjusted accordingly, but are not one-size-fit all. What may be applicable to one area may be inadequate for another. For example, the Falkenmark Index that captures hydrological constrains on water supply applies best to well-developed countries where water scarcity is largely due to local environmental factors (e.g., rainfall). It is less applicable to much of Sub-Saharan Africa, which may be highly populated by rain-fed cultivators, but lacks basic water infrastructure (Srinivasa *et al*., 2017).

There is confusion in what defines water security in agricultural, industrial and municipal undertakings (Meissner *et al.*, 2018). For instance, a study conducted at the Greater Sekhukhune District Municipality and the eThekwini Metropolitan Municipality (South Africa) revealed that water security at municipal level is based on an individual's perspective. For example, some individuals considered drought as a water security issue only if it interfered with daily household activities. At local government level, water security is only a state of emergency if it threatens their immediate surroundings. Perspectives are influenced by local lifestyles: thus, for example, the Great Sekhukhune District Municipality comprehension of water security, insecurity or non-security may be quite different to the comprehension in the eThekwini Metropolitan Municipality due to the rural versus city based lifestyles of these areas (Meissner *et al.*, 2018).

In South Africa, out of nineteen water management areas (WMAs), nine encounter water deficit while the remaining six face severe water shortage (DWS, 2017; DWS, 2018; Thopil *et al*., 2016). In addition, over 60% of South African rivers are overexploited and most future scenarios project an increase in withdrawals to facilitate agricultural, industrial and municipal increased water supply requirements (Donnenfeld *et al.*, 2018; Solomon *et al*., 2000; Muller *et al*., 2015; Heyns *et al.*, 2008; Turton, 2005). The majority of South African rivers are characterised by a very low to normal flow, only a small percentage is considered to range from normal to very high flows. Prolonged over abstraction of river systems at unsustainable levels decreases the overall dilution capacity of a river, resulting in water temperature increases, an increase in the concentration of undesired chemical (e.g. dissolved salts), limits river ecosystem absorption capacity for pollutants, decreases dissolved oxygen. These factors may promote outbreaks of waterborne diseases and water insecurity due to poor governance (WHO, 2003; Department of Water and Sanitation (DWS), 2016; Donnenfeld *et al.*, 2018; Hedden, 2016).

Water quality monitoring systems

Water quality monitoring is the repeated collection and analysis of the physical chemical and biological characteristics of water at fixed locations (Cloete *et al*., 2016). Traditional manual water quality monitoring systems are based on 'grab' samples (an approximately 500 ml clean and sterile, non-reactive bottle is filled beneath the water surface, and then sealed) followed by laboratory analysis. Continuous monitoring systems involve the automatic measurement of water quality indicators using sensors, recording systems and analysis software (Wanger *et al*., 2006; Tuna *et al*., 2013).

The usability of freshwater resources for drinking water, energy production, irrigation, fishery etc is determined by its water quality status. Decline in water quality status by both anthropogenic and natural processes is one of the factors controlling human and environmental health. John Snow (1854) was the first to illustrate the detrimental effects of poor water quality monitoring on human health when he traced a cholera epidemic outbreak in London to a drinking water outlet that had been polluted by sewage. Over time, scientific knowledge on how water quality influences human and environmental health has matured. Many scholars have identified a close relationship between water quality deterioration and land use transformation (see the works of: Zamani *et al.*, 2013; Goldstein *et al*., 2016; Zia *et al*., 2013; Williams, 2001; Pond *et al*., 2008b; Roux *et al*., 2010; Huntington, 2006; Akabzaa *et al.*, 2007; Ullah *et al*., 2018; Chauhan *et al*, 2015; Vörösmarty *et al*., 2010).

Nutrient loads, dissolved organic matter, phosphorus, acidity, pharmaceutical residues and microorganisms in freshwater systems (e.g. river or lakes) are sensitive to episodic events (such as floods or extreme low flows) and land-use water related activities in the catchment area (Gaetan *et al*., 2014; Blaen *et al*., 2016; Fauvel *et al.*, 2016; Ockenden *et al*., 2016; Chappell *et al*., 2017; Kruse, 2018;Samsudin *et al*., 2018). Traditionally, determinations of water quality are based on the collection and analysis of periodic manual samples (usually 'low frequency', in other words, monthly) in combination with instantaneous estimates of discharge at the time of sampling. The frequency and regularity of such sampling methods may not provide a good representation of in-stream water quality status (Gaetano *et al*., 2014; Blaen

*et a*l., 2016; Leigh *et al*., 2019). This is because stream water chemistry is highly variable in time, as a result, for instance, of brief rainfall events and short duration land-use activities or industrial or municipal discharges. Therefore traditional manual water quality sampling presents does not allow the detection of short-duration variations in stream-water chemistry (Blaen *et al*., 2016; Chappell *et al.*, 2017). This limit knowledge of hydrological system behaviour as well as the transfer of research outcomes to decision makers (Tuna *et al*., 2013; Chappell *et al.*, 2017; Blaen *et al*., 2016a; Viviano *et al*., 2014; Leigh *et al*., 2019).

The biggest challenge in water quality monitoring is the collection of sufficiently large data sets to ensure accurate and reliable analysis (Tuna *et al*., 2013). Though manual sample collection is reproducible, the amount of data collected and the procedure in which it is collected is inadequate to fully advise about the sensitivity of the hydrologic system to external inputs (such as, flood peaks, urban-, agricultural- and industrial effluents) (Ryberg, 2006; Chung *et al*., 2015; Blaen *et al*., 2016; Kruse, 2018; Tuna *et al*., 2013). Hence, there has been a gradual and ongoing shift, worldwide, from traditional manual sample collection to continuous (or automated) water quality monitoring systems.

The use of continuous water quality monitoring systems is in some ways analogous to the revolution in Earth observations resulting from the introduction of satellite remote sensing during the 1970s. The extent to which these systems work relies on a combined understanding of technology and science (Leigh *et al*., 2019; Martinez *et al*., 2004). As a result, the design and implementation of such systems are situation-specific: they depend on both the physical and social environment and the sensor network being deployed. (Hart *et al*., 2006; Chong *et al.*, 2003; Martinez *et al*., 2004; Blaen *et al*., 2016; Ryberg, 2006; Tuna *et al*., 2013; Snyder *et al.*, 2018). Automatic water quality measurements have grown from simple analogue loggers that require paper plotters, to modern-day intelligent sensor networks, which can produce large data sets for multiple environmental factors (Hart *et al*., 2006; Chong *et al*., 2003; Samsudin *et al*., 2018). The use of these systems has presented modern researchers with an unprecedented ability to comprehend environmental patterns (Chong *et al*., 2003; Samsudin *et al*., 2018). A typical simple continuous water quality monitoring system consists of sensor probes, data loggers and operating software. The system can grow in complexity depending on the objectives of the monitoring system (Martinez *et al*., 2004; Horsburgh *et al*., 2010; Samsudin *et al.*, 2018). Well-designed sensor systems can be integrated with several types of computer software, operating systems and communications hardware for optimum data assessment (Chong *et al.*, 2003).

Description of the technology of sensor systems is beyond the scope of this study, and is in any case subject to rapid and ongoing change. Current areas in which water quality sensors are rapidly advancing include, for example, fluorescence-based optical sensors, whose operational success has been tested in different environments to provide a relatively inexpensive high resolution proxy for dissolved organic carbon (DOC) (Snyder *et al.*, 2018). Particular ions can be measured using specific-ion probes (an example is the pH sensor, which measures H+). Continuous stream-sampling spectrophotometric systems may be required for particular chemicals, for which ion-specific electrodes are not available (such as phosphate). In some cases, hybrid systems are deployed – a high frequency automated water sampler, creating a collection of samples that are then analysed as a batch in the laboratory (Park *et al.*, 2020).

Deployment of high frequency (that is, hourly to sub-hourly monitored) sensors of stream water chemistry for variables such as electrical conductivity (EC), pH, temperature, turbidity, dissolved oxygen and fluorescence has increased in recent years and have demonstrated the competence of continuous water quality monitoring systems to detect hydrological system changes (see the works of: Tran Khac *et al.*, 2018; Cloete *et al*., 2016; Panguluri *et al*., 2009; Blaen *et al*., 2016; Snyder *et al*., 2018; Philadelphia Water Department and CH2M HILL, 2013). Successful operation of these systems allows for: a). Large data sets at high-resolution to improve monitoring system accuracy and precision, b). Data that are available in near or real-time, thereby creating early warning systems and close the gap of knowledge transfer between researchers and decision makers, and c). Reduction in cost associated with water quality monitoring systems due to comparably cheaper installation and minimum maintenance requirements, as instrumentations (that is, sensor probes, data loggers etc.) that are equipped with low-power consumption devices and multiple parameter detection ability. (Leigh *et al*., 2019; Chappell *et al*., 2017; Blaen *et al.*, 2016; Philadelphia Water Department and CH2M HILL, 2013; Martinez *et al*., 2004).

Automated water quality monitoring systems offer promising infrastructure for effective water quality monitoring. However, operational success is challenged by technical issues, including vulnerability to cyber-attacks (Leigh *et al*., 2019; Pule *et al*., 2019). Field-deployed instrumentation (e.g. sensors) is vulnerable to:

- Damage from extreme weather events (e.g. floods) and animals.
- Vandalism or theft by humans
- Sensor drift, i.e. a gradual change of the output while the input remains constant. This may occur due to temperature instability, bio-fouling (build-up of biological coatings on the sensor element), and electronic sensor degradation (Kalantar-zadeh, 2013). A drift can be determined by comparing initially calibration values with current measurements, and resultant changes can be corrected by applying appropriate calibration measures.

Another impediment to continuous water quality monitoring is the production of very high volumes of data. Dealing with such large data volumes requires an integrated approach to data processing, as well as advanced infrastructure for data storage and software programmes. The main data processing challenge with high-frequency data is to preserve quality control and assurance, since manual checking, labelling and correction of these datasets is unfeasible (Leigh et al., 2019; Horsburgh et al., 2015; Hill et al., 2009). Various data processing methods (e.g. programming models in RStudio, Python, or Matlab) that facilitate the needs of high-frequency data processing have been developed. Each method presents a unique data processing strategy based on the objectives of the monitoring system deployed (see the works of: Hasenmueller, 2011; Leigh et al., 2019; Horsburgh et al., 2015; Hill et al., 2009; Viviano et al., 2014; Wanger et al., 2001). Table 2 presents common errors in continuous water quality monitoring systems and associated data correction measures.

Table 2. Some commonly-encountered issues with continuous automated water quality systems

Problem Type	Description and commonly applied correction
Sensor drift (including fouling)	Erroneous sensor readings due to electronic drift, residue built-up, and biological growth. Variable data correction is applied via calibration curves.
Exceedance of detection limit	Data records with a range outside plausible values for that particular water quality parameter being measured. Erroneous values due to a sensor reporting limit, for example, sensor will record their programmed maximum or minimum instead of the actual measurement. Data correction is applied by deletion or flagging of known erroneous data points.
Power or sensor failure	Erroneous or missed data recordings due to battery and/or sensor failure. Data correction is applied via interpolation of missing data and deletion or flagging of known erroneous data points.

Water quality monitoring in South Africa

Water flow monitoring has been undertaken in South Africa since the early part of the 20th Century, initially using manually-read river gauges, and later paper-based recording instruments associated with gauging weirs. Grab samples for water quality have been taken and analysed, on an increasingly systematic basis, since about the 1920s. Since 1972, the national government department currently known as 'Water and Sanitation' (previously Water Affairs) has monitored the county's water quality and quantity status, as guided by the Water Services Act (1997), National Water Act (1998) and the National Water Resource Strategy (2004). These acts gave rise to water quality management policies such as the Integrated Water Resource Management (IWRM) which is supported by the Resource Quality Information Service (RQIS), a web-based, open-access database system. The RQIS provides national water resource managers with aquatic resource data, technical information, guidelines and procedures that support the strategic and operational requirements for assessment and protection of water resource quality/quantity. The department monitors "raw" surface water quality in rivers and dams and periodically issue long-term trend reports (Department of Water and Sanitation - South Africa, 2018). Water quality monitoring systems are based on a weekly to monthly manual grab samples at remote locations (such as gauge stations). Some physical constituents (such as pH, EC and turbidity) are recorded in the field at the time of sampling. Thereafter, bottled samples are sent for further chemical analysis at a centralised laboratory (Department of Water and Sanitation, 2017).

The Department of Water and Sanitation monitoring stations

DWS monitors both flow and quality in South African water bodies, since the two sorts of data are commonly used together. Flow measurements in South African rivers are complicated by the high variability of water discharges, heavy sediment, and debris loads. To manage these challenges the Department of Water and Sanitation(DWS) has modified the gauging station designs (Wessels *et al.*, 2009). The main idea behind gauging structures is to create an artificial control in the river with a known relationship between stage and discharge. A gauging station is a site on a river which has been selected, equipped and operated to provide the basic data from which systematic records of water-level ('stage' or 'water-level', also here referred to as water-depth) and discharge may be derived using a set of equations to ensure accuracy (Wessels *et al.*, 2009). Even so, common practical problems such as sediment build-up above the weir, downstream submergence, and accumulation of debris on weir crests often occur, and may result in inaccurate estimates of stream discharge. Therefore, it is recommended that these structures are surveyed and recalibrated on a regular basis to deliver discharge values with an accuracy within 2 - 5% (El Hattab *et al.*, 2019; Adeogun *et al.*, 2019; Wessels *et al., 2009)*.

The main purpose of these gauging stations is estimation of stream discharge, but they can also serve as fixed locations for manual sample collection or the installation of automated equipment. They essentially consists of a weir (which is an overflow structure designed perpendicular to the flow of a river) where a continuous record of stage can be obtained and where a relation between stage and discharge can be determined (El Hattab *et al.*, 2019).

Currently, the DWA operates a separate web page to provide access to data from their monitoring sites. The Resource Quality Information Services (RQIS) website provides national water resource managers with aquatic resource data, technical information, guidelines, and procedures that support the strategic and operational requirements for assessment and protection of water resource quality/quantity. This separate data system is accessible via the DWS Resource Quality Information Services webpage but not integrated with it, is maintained for water quality/quantity data exploration that allows for easy access of data (Department of Water and Sanitation, 2020). It consists of maps locating the monitoring stations, periodic (months) water quality status, different water management areas and surface water drainage patterns. Although the page is an excellent tool, it has a disadvantage of lagging behind by several months and periodic web connection failure.

Testing and integrating the evolving technology for water quality monitoring

There is a need for the integration of technology and different science disciplines towards ensuring natural resource sustainability. This need extends to many research fields, and to private institutions as well as government departments. The gap that exists between what is possible, and what is operational practice means that knowledge is lost—thereby resulting into the vulnerability of our understanding of natural resources and systems. Scholes (2016), in motivating for a national research infrastructure for ecology under the South African Research Infrastructure Roadmap (SARIR) initiative, suggested that an integration between research fields, private institutions, government departments and

citizen science can contribute to a better understanding of natural resources and their sustainable management, while keeping South Africa at the forefront of ecological research.

According to Scholes (2016), information and communication technologies as well as data management services are a fundamental part of every type of research infrastructure (RI), but the construction phase of a new RI will require the development and testing of new systems, such as the automation of scientific instruments, or the deployment of a distributed network of specialized sensors in a wide range of RIs. This study, a pilot exploration of continuous water quality monitoring systems, was established to explore some of these ideas and their practical feasibility.

The resulting funded RI, called the Enhanced Freshwater and Terrestrial Ecological Observation Network (EFTEON) is designed to connect biogeochemistry, biodiversity, hydrology, sociology, and mathematical sciences. The hydrological element of this will include continuous measurements of water quantity and quality in catchments. This initiative is not aimed at creating an operational monitoring network for management or regulatory purposes, but rather a research infrastructure to grow knowledge and capacity in the domain. It may also, incidentally, be fit to aid in measurements required by both national and international laws. It will build on the strong track-record of South African water quality measurements and provide guidance to regarding its future evolution. The launch of continuous measuring systems will reduce uncertainties associated with environmental changes due to, for example, land and water use activities and empower South African scientist to produce a world-class ecological research status.(Scholes *et al.*, 2015; Scholes, 2016).

Aim of this research

The aim was to *implement and test an operational water quality observing system for EFTEON, which is cost effective and fit for continuous monitoring of the aquatic salt content and riverine salt flux of a catchment.*

The test of operational accuracy and fitness-for-purpose of the designed system was the ability to achieve salt budget closure within + 10%, between two main tributaries of the catchment and its main stem. The salt budget was quantified using an equation based on the conservation of mass: the salt flux at a downstream point is the sum of the salt flux at contribution upstream points plus loses and gains between upstream and downstream conditions, which for the purposes of this study are assumed to be less than the 10% threshold set.

System sensitivity is tested by the ability to detect differences in salinity over time and space and especially to detect short-duration events, in order to identify various sources (that is, land-use-water related activities) contributing to river salinization.

Research objectives

The objectives were to:

- Determine the robustness, under field conditions, of a commercially-available salinity monitoring sensor, coupled to a datalogger and flow measurement device. Field condition, quality assurance (QA) and quality control (QC) measures included pre- and post-calibration measures to control system operational accuracy, and periodic data-downloads to assess data completeness and associated data errors.
- Quantify the aquatic salt content and riverine salt flux of a catchment. Catchment salt fluxes were calculated by converting the measured electroconductivity into a salt concentration, assuming a particular composition of cations and anions, based on prior manual chemistry monitoring. Then the concentrations were multiplied by the observed flow rates to obtain a flux over a period of a month and summed to a year. Salt-budget balance was tested by seeing if downstream salt fluxes were approximately equal to the sum of upstream fluxes. Source apportionment was done by relating the observed salt fluxes to known land use features of the landscape with catchment area. Overall system accuracy and precision was evaluated by salt budget closure.

METHODS

Study area description

Inkomati-Usuthu Water Management Agency (IUWMA) is one of the country's nine water management areas. The IUWMA covers three catchments: the Sabi-Sand, the Crocodile, and the Inkomati. The Sabi-Sand catchment (see Figure 2) drains the high altitudes and steep slopes of the Mpumalanga escarpment, and then flows eastward through the Lowveld, including the Kruger National Park (KNP), before entering Mozambique at an altitude of 59 masl, via the Corumano Dam. The whole catchment covers an area of approximately 7 096 km^2. There are two sub-catchments, the Sabi and the Sand River, each of which has a number of perennial and seasonal tributaries, with the Marite and the Mac Mac River being the most significant with respect to water quality and quantity (Department of Water Affairs and Forestry, 2013) . The Mac Mac tributary has a source at 1502 masl near the town Graskop and flows in a south-eastern direction, joining the Sabie River (rising near the town of Sabie) at 518 masl. About 87% of the the catchment area of the upper Sabie and Mac Mac rivers is covered by commercial forestry estates of pine and eucalyptus trees, though the actual fraction planted varies slightly year-to year, depending on the rotation. The Marite branch, further north, has the tributaries Ngwempisi, Maritsana and Motisti rivers, which all rise in areas of commercial forestry. The Ngwempisi and the Maritsana Rivers flow into the Inyaka Dam, below which they are called the Maritsana River, which joins the Motisti River at 511 masl to become the Marite River, which then joins the Sabie River at 450 masl (Inkomati-Usuthu Catchment, 2017). The Mutlumuvi River is a combination of the Mohlomobe and Tswafeng rivers draining from an elevation of 1640 masl. Together with the Klein Sand River (draining from 1658 masl), they make up the main sources of the Sand River. Both the Mutlumuvi and the Klein Sand rivers flow in an easterly direction towards their confluence with the Sand River

at an altitude of 427 masl and 519 masl respectively. Land use along these rivers is predominantly commercial forestry and rural/semi-urban settlements. The Sand River then confluence with the Sabie River at 231 masl to form the Sabie-Sand Catchment.

The variation in relief, altitude and geology has given rise to various microclimates, natural vegetation cover and land-use activities within the sub-catchments. Those are summarised in terms of zones (Figure 3):

- ZONE 1 & 2: Upper catchments

This region includes the sources of the main rivers. It is characterised by high-gradient streams flowing over bedrock resulting in waterfalls and plunge pools (Kleynhans, 2007). The topography consists of moderate to high relief closed hills and mountains. Important land use activities include large-scale pine and eucalyptus plantation forestry, resulting in 17 to 45% stream-flow reduction in the Sabie, and 31% flow reduction in the Sand Rivers' tributaries (Maitrea *et al.*, 2001; Du Toit, *et al.*, 2003; Inkomati-Usuthu Catchment, 2017). Observation stations X3H002 (25.089° S 30.777°) and Casteel (24.707°S 31.026°E) are located in these zones.

- ZONE 3 & 4: Mid-catchment

The upper end of zone 3 marks the transitional zone between the Escarpment and the Lowveld, approximately 10 km east of the steepest mountainous slopes. The hills give rise to low, medium and medium-high gradient streams flowing over bedrock and boulders, forming frequent but scattered riffle pools in confined or semi-confined valley floor with a narrow flood plain characterised by sand, gravel and cobble. Downstream, towards zone 4, the catchment is characterised by low to medium flows, pool-rapid systems with sand bars in the pools and a much broader flood plain. The headwaters of the Sand River are affected by high soil loss, resulting from poor vegetation management, town infrastructure and road construction, as well as high loading of municipal wastewater (Inkomati-Usuthu Catchment, 2017; Kleynhans, 2007; Du Toit *et al.*, 2003; Riddell *et al.*, 2019)

Zones 3 and 4 are dominated by horticulture (particularly tropical fruit plantations), densely populated rural and semi-urban settlements, minor mining and industrial activities, and wildlife-based tourism enterprises. The discharge of effluents (that is, domestic waste, waste water treatment plant spills, drainage from old mines, pollution from industrial factories etc.) from towns such as Hazyview, Bushbuckridge, Simile, Harmony Hills and Skukuza have resulted into a decline in environmental health due to poor wastewater management, worsened by the rapidly-increasing population (Inkomati-Usuthu Catchment, 2017; Kleynhans, 2007; Du Toit *et al.*, 2003). Observation station X3H023 is located within this region at 25.030° S 31.020°E.

- ZONE 5: Lower catchment

This zone includes the Kruger National Park and private protected wildlife areas adjacent to its western boundary. Nearly a third of the total catchment lies within this zone. The drainage is characterised by a well-developed meandering

pattern with a wide flood plain, low gradient channels over large bedrock boulders and randomly occurring alluvial sand bars. Human-caused water-quality degrading activities in this area are limited, but the water quality is frequently low due to the effect of up-stream activities Observation stations X3H008 (24.769°S 31.390°E and X0H015 (25.149°S 31.940°E), are located in this region. (Inkomati-Usuthu Catchment, 2017; Kleynhans, 2007; Du Toit *et al*., 2003).

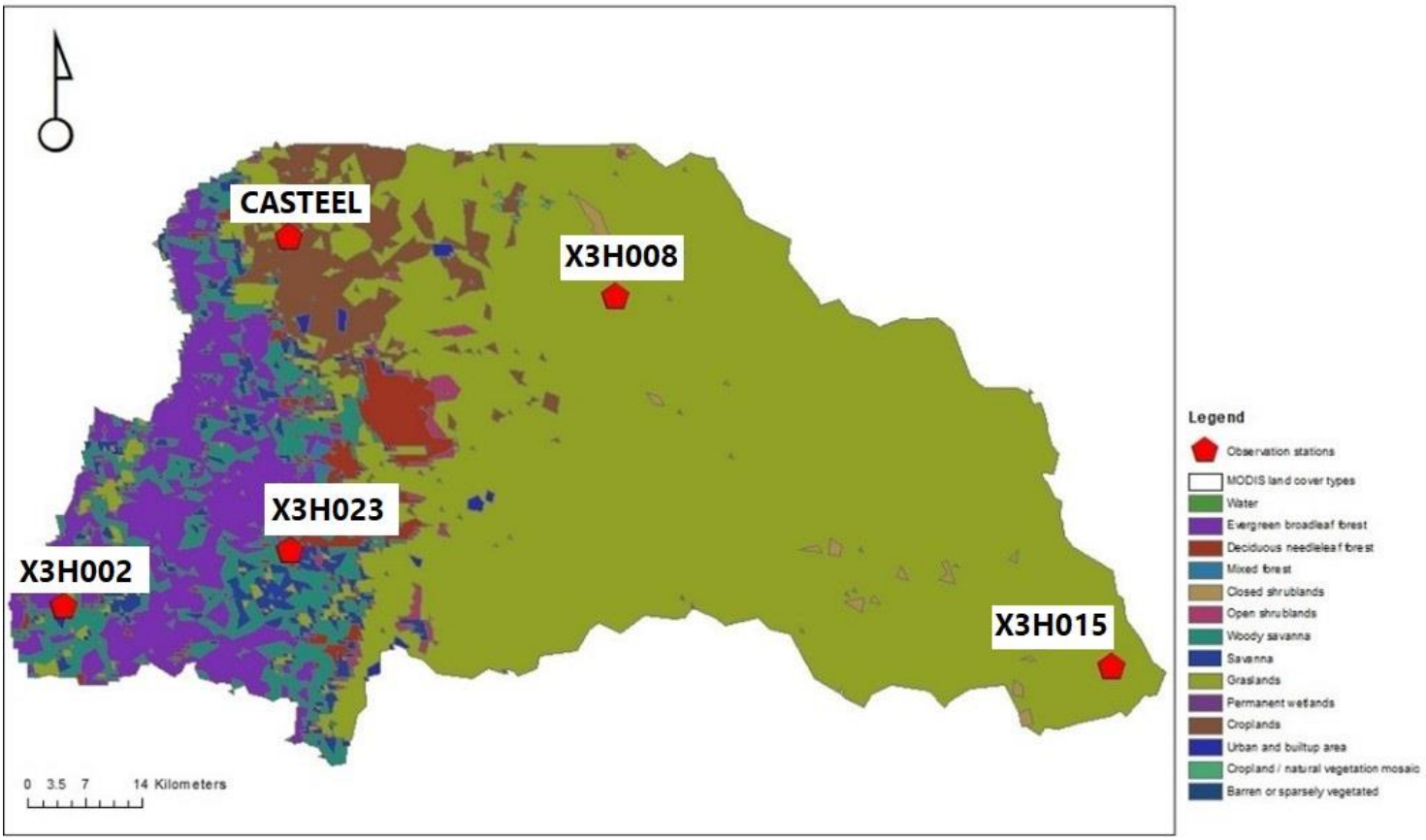


Figure 1: Land-use-land-cover types classification map of the Sabi-Sand Catchment.

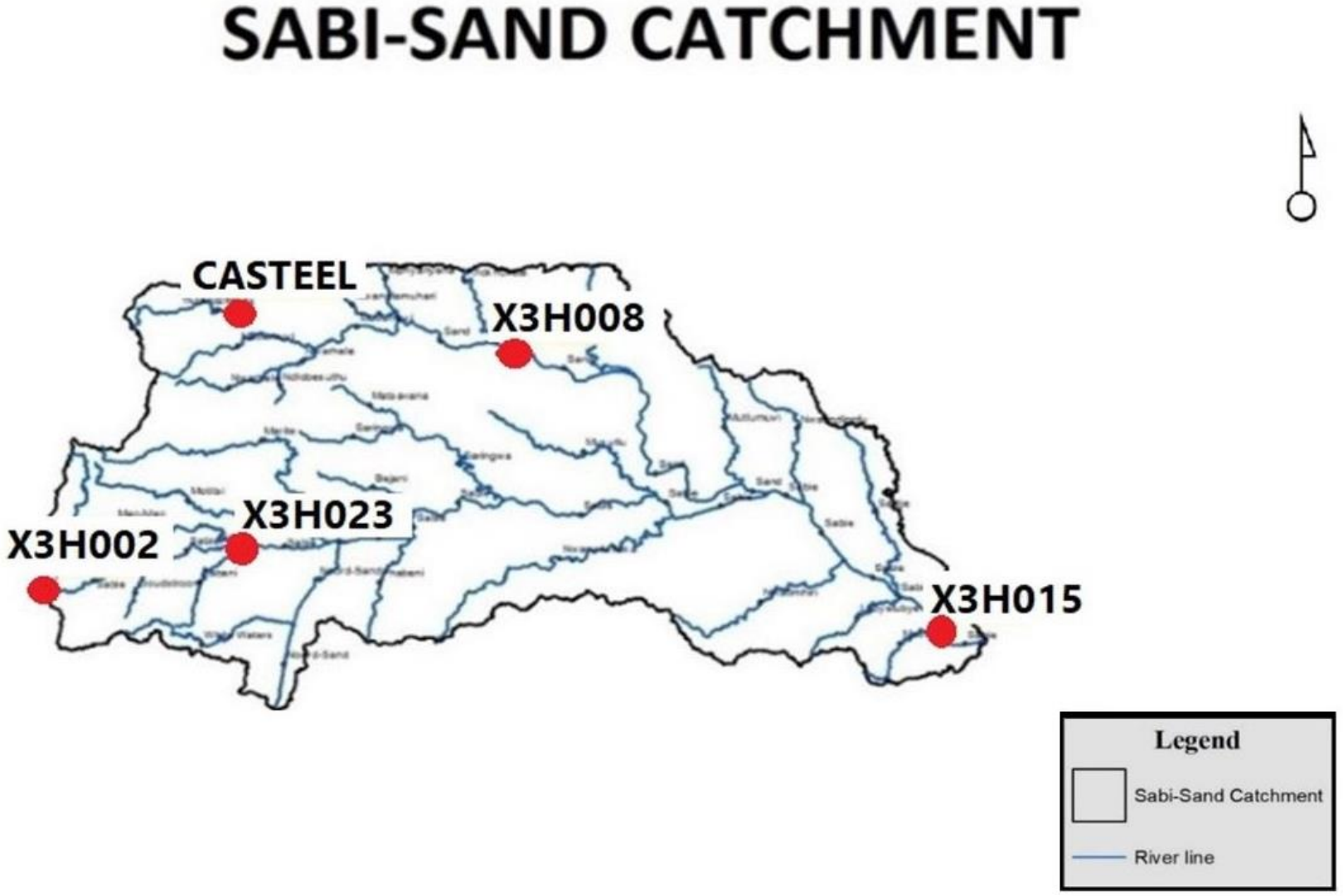


Figure 2: Map of the Sabi-Sand Catchment and observation stations.

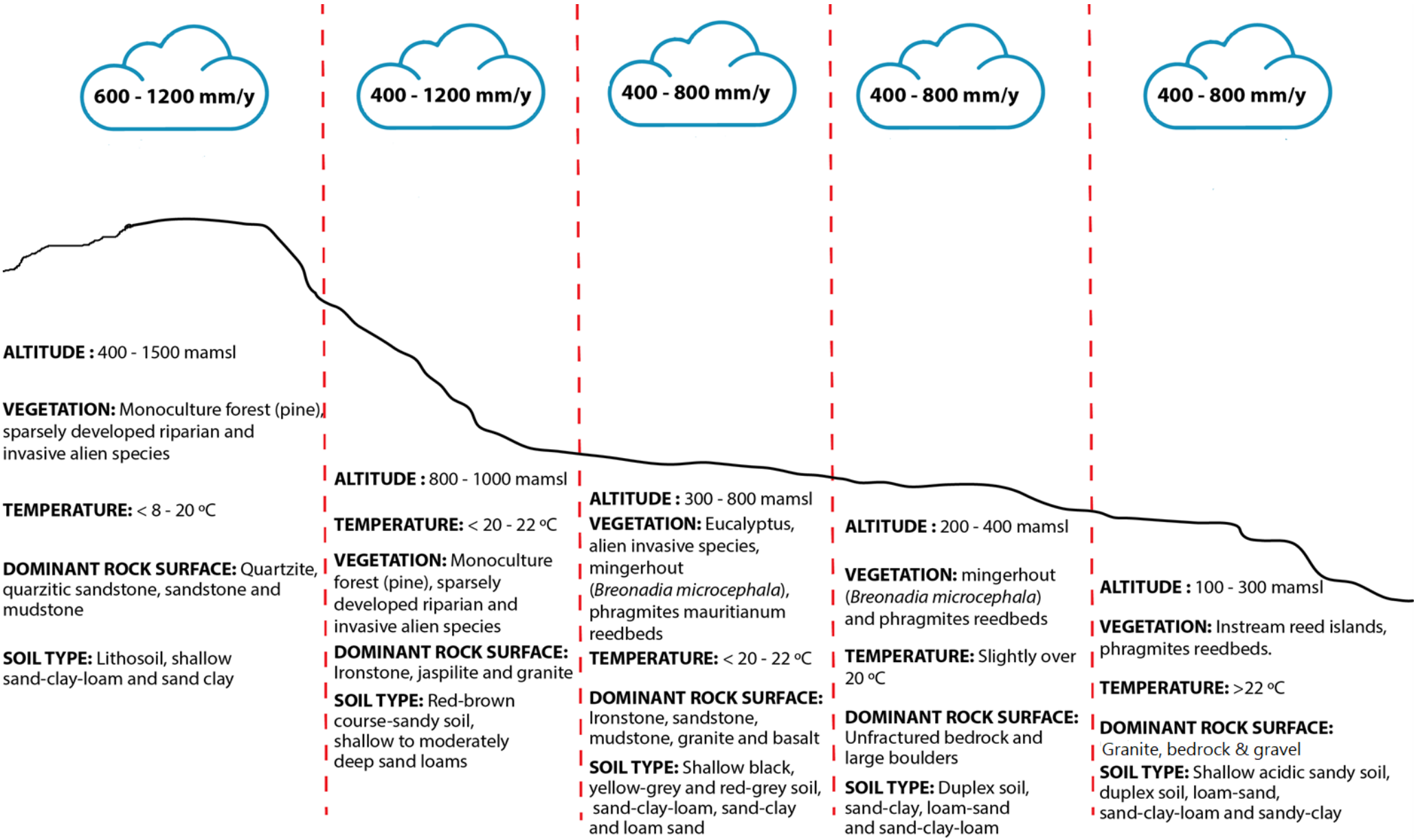


Figure 3: Sabi-Sand Catchment (cross-section view)(Modified from *Du Toit J.T. et al.. 2003)*

Network design and instrumentation

Five continuous monitoring stations were established, four in association with existing gauge stations belonging to the Department of Water and Sanitation, and one at a small ungauged weir designed for furrow irrigation. The stations were chosen based on their strategic locations relative to the drainage zones, and because they have reasonably long and complete flow and manual water quality records: There was no suitable gauging station at Casteel, so I used the irrigation-diversion weir.

Equipment selection, installation and maintenance

Each station was equipped with a Decagon CTD device that integrates Water Depth, Electrical Conductivity (EC), and Temperature sensors (CTD10/HYDROS 21), connected to a Em50 Logger (Em50G) (see Figure 4). This set will be collectively referred to as 'equipment' from this point-on. The logger (100x50x30 mm, in a water-resistant box) was housed in the gauge station structure, and connected to the sensor head via a 5 m submersible cable (see Figure 5). The cable was is enclosed within a PVC pipe to further protect from damage by UV radiation, flood-debris and vandalism.

This package was selected after a desktop review of about five different devices available in 2018 in South Africa. The factors considered were:

1. Accuracy, as given on the specification sheet

2. Cost, based on quotations from suppliers

3. Ease of installation, maintenance and data retrieval.

The decision was taken (prior to the commencement of this MSc project) to select five sets of a single type, rather than to buy one each of five different sensors. Comparing sensors is also a valid research question, but the key question to be addressed by this pilot projects was a different one: Can a specific number of sensors be deployed, e.g. 5, in their current pre-existing configuration adequately represent a catchment of 7 096 km^2?

The sensor system uses a vented differential pressure transducer to measure the pressure from the water column to determine water depth. The version we used has a measurement range of 0-5 m, with a resolution of 2.5 mm. A thermistor in thermal contact with the probe provides water temperature in the range -11 to 49°C with a resolution of 0.1° C. The electroconductivity (EC) sensor consists of four stainless-steel screws forming a four-electrode array, a design considered to be less sensitive to fouling than a two-electrode sensor. The EC sensor has a range of 0 to 120 dS/m, with a resolution of 0.001 dS/m and an accuracy of +/-0.01 dS/m. This range accommodates the typical range of salinity in various natural waters. The sensor head has a stainless-steel cover over all the sensors, which improves field durability, and a plug compatible with the inputs to the Em50 data logger (this simple 'plug-and-play' capability is important for field installation). The logger memory is nonvolatile flash and can accommodate 36,800 data scans. Thus if set to record the three parameters at half hourly intervals, it can capture data for about one year between downloads (Decagon Devices, 2012), and the AA batteries (also important, because they can be easily procured, even in the field) last about

two years. The memory is 'circular'; in other words, if it is full the logger overwrites the first records. Data are retrieved via a connection cable to the logger from a laptop, using manufacturer-provided software. Equipment maintenance for quality assurance (QA) and quality control (QC) incorporated periodic site visit for: tracking equipment robustness and functionality, performing pre- and post-calibration checks for verification of sensor drift, cleaning of equipment fouling, tracking battery performance and downloading data.



Figure 4: Equipment deployed for automated water quality observation network at the Sabi-Sand catchment. ***Panel A*** *is the Em50 data logger powered with AA alkaline batteries and connected to a red 5 m submersible cable.* ***Panel B*** *is the Water Depth, Electrical Conductivity (EC), and Temperature CTD sensors—demonstrating the sensor's full view, close-up view with the slight view of the inner electrodes and the front-top view as an inlet (stainless steel plate).*

Pre-testing and installation of equipment

All equipment underwent laboratory testing before and after field installation, and calibration twice during deployment, using a protocol modified from Wanger *et al*., 2006; Ryberg, 2006; Rasmussen *et al*., 2014; Horsburgh *et al*., 2010, and as suggested in the manual by Campbell et al. (2013). The data logger was programmed to record half-hourly (the actual measurements are continuous and are averaged over this period). This time-resolution was judged sufficient to capture the catchment's salt fluxes without overloading the logger memory, while being consistent with the resolution of the sensors. The CTD sensor was calibrated in the lab prior to installation, twice during its field operation, and finally in the

lab after removal at the end of the project, to track sensor drift. A two-point calibration was applied for EC (see: Hasenmueller, 2011). Temperature was simultaneously observed to evaluate any variations that may influence electroconductivity measurements. Water level data records were calibrated in the field against the installed depth gauge, and against continuous DWS water depth sensors.



*Figure 5: The installation design of the equipment in the field. **A**. Is a weir with the CTD sensor mounted inside the stainless steel pipe by the wall and the sensor cable covered by a PVC black pipe, **B** & **C** is the interior of a logging hart located next to the weir above flood level—the data logger was housed here and **D** is illustration of data is downloaded in the field.*

Data processing

Data completeness

Data completeness is a measure of the fraction of usable data recovered relative to the maximum that could be collected given the recording interval. The adequacy of completeness is judged relative to the aims of a particular study. Absolute completeness is desirable (100%), but most field installations do not meet this standard.

Data corrections

Automated water quality observation systems provide relatively large amounts of data, but the datasets do not lend themselves to traditional visual or manual methods of data analysis, quality control and quality assurance. They demand an integrated and automated approach that is compatible with the time at which datum is collected as well as its volume (Campbell *et al.*, 2013; Rasmussen *et al.*, 2014; Hallock, 2009; Morello *et al.*, 2014; Horsburgh *et al.*, 2010). Therefore, the datasets collected in this study were subjected to quality control (QC) and quality assurance (QA) measures as specified in Campbell *et al.*, 2013; Rasmussen *et al.*, 2014; Hasenmueller, 2011. Data correction measures included: data interpolation for periods of equipment failure, sensor drift correction and flagging of known erroneous values. The data were then plotted out for inspection for outliers and anomalies, and described using basic statistics such as means, ranges and standard deviations (Hem, 1985; Ryberg, 2006 and Harrison, 2007). Once the mean, range and standard deviation are broadly established (either for the whole record, or for seasonal segments), automated screening for outliers can be implemented.

Determination of salt concentration

A conversion factor for EC to TDS of 0.54 to 0.94 mg/l per µS/cm is widely used in water quality studies (Walton, 1988). A customised conversion factor (see **Equation 4**), dependent on ionic composition (see **Equation 2** and **Equation 3**) of the particular river, can substantially improve accuracy. The calculation of the conversion factor is based on calculating total ion concentration (see **Equation 3**)) from measured electroconductivity using (Walton, 1988):

$$\Lambda = 1000\frac{EC_{25}}{C}$$

Equation 2

$$\therefore C = \frac{1000EC_{25}}{\Lambda}$$

Equation 3

Where:

- Λ is molar conductance,
- C is ion concentration in mol per litre &
- EC_{25} is electroconductivity.
- t^0 temperature correction (1.9 °C)

Thereafter, using that calculated total ion concentration, the EC:TDS conversion factor (f) is computed (Hubert *et al*., 2015):

$$f = \sum C_l * \Lambda * t^0$$

Equation 4

Table 4 in the results & discussion chapter presents the EC to TDS conversion factors calculated for each station (Walton, 1989), based on the long term manual samples of ion concentration in the catchment, as collected and analysed by DWS (Department of Water and Sanitation, 2020). Further analysis of the concentration of major ions shows high dominance of sulphates and bicarbonates over other anions, at all observation stations in the catchment (see Department of Water and Sanitation, 2020).

Calculating flow from water-depth at the weir

This is a well-established hydrological procedure (El Hattab *et al.*, 2019; Adeogun *et al.*, 2019; Wessels *et al., 2009)*. Each of the DWS weirs has a unique design. Depth-discharge tables are established periodically for each weir using a sophisticated simulation package informed by a survey of the reach stretching several hundred meters above the gauge (Wessels *et al.*, 2009) (Figure 6). Even so, the gauging accuracy ranges from 2 – 5 %, and is substantially worse for flood

flows (Wessels *et al.*, 2009). The uncelebrated weir at Casteel did not, in the end, require calibration since the water quality sensor was vandalised and no data were available for analysis.



Figure 6: A weir is a flow measurement structure that spans across the width of a river—it consists of a low impoundment which has a flow gauging section and a data capture house/hart located in the highest flood level. In this image is an example of South African rivers weir station design—at observation stations X3H008 on the left and X3H002 on the right.

Observed and modelled salt flux calculation

The concentration of total dissolved salts is directly proportional to electroconductivity of water, provided the ionic composition is reasonably consistent over the concentration range. For this study, estimates of TDS were computed from 30-minute averages of EC multiplied by the conversion factors and then multiplied by the estimated flows over the same period to calculate a salt flux (Figure 7A) at each observation station. In addition, a monthly salt flux was computed based on accumulated flows and the monthly manually-sampled salt concentration (TDS) for each station, as per Figure 7BFigure 7Figure 7. This would be how salt balance would be calculated in the absence of automated measurement (see Figure 7AFigure 7Figure 7).

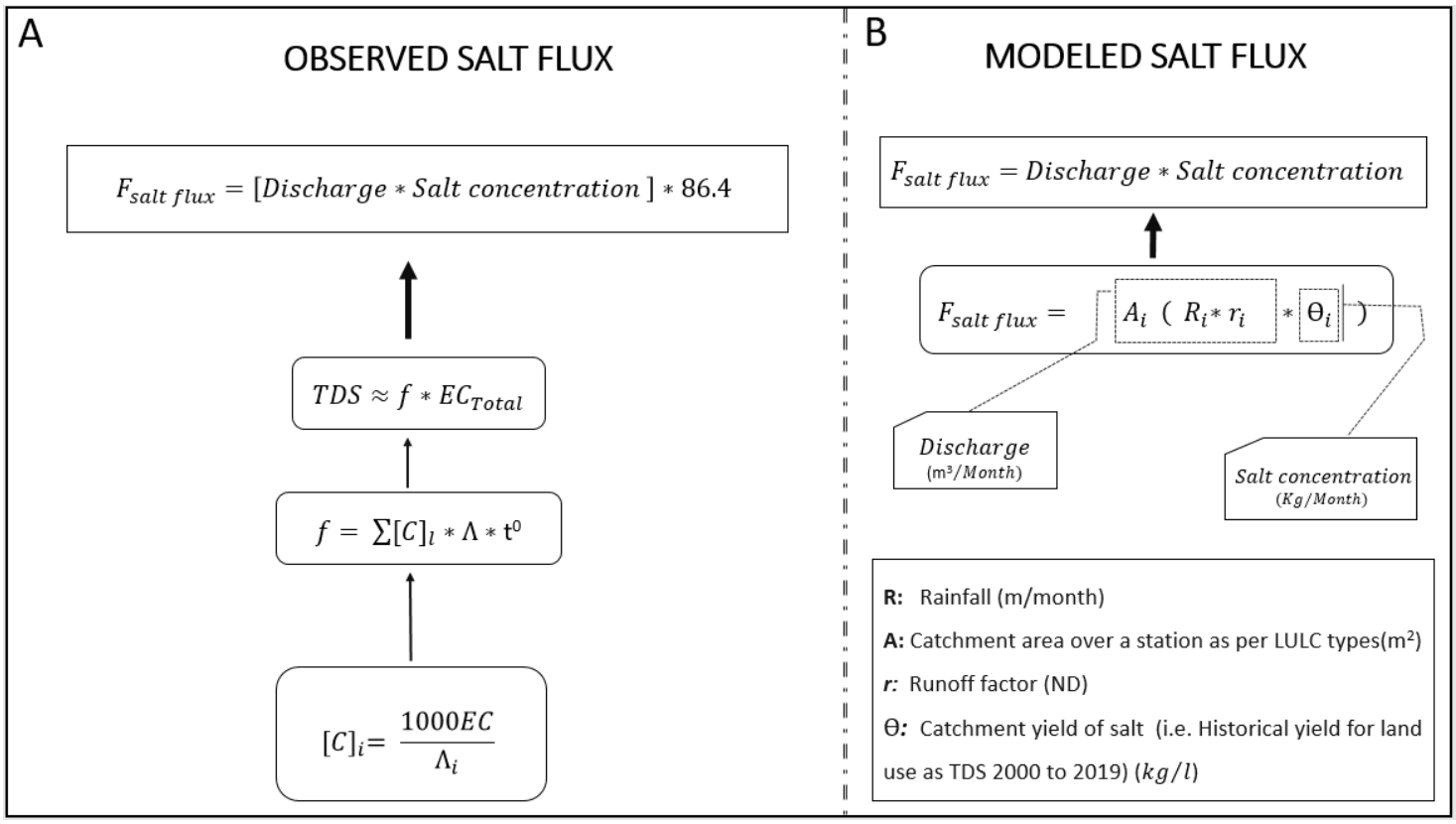


Figure 7: Computation of the observed and the modelled salt flux (Hem, 1985; Walton, 1989; Day et al., 1984; Horsburgh et al., 2010; Pawlowicz, 2008).([C] in meq/l). EC is from continuous measurements, molar conductance (Λ) from Walton, 1989, rainfall data by SA Weather Services, catchment areas as per LULC estimated via ArcGIS using EARTHDATA, runoff & catchment yield of salts by DWS historical data/reports (van der Spruy., 2018).

RESULTS

Data reliability

Sensor performance

Table 3 presents a summary of records obtained from the system after its deployment for approximately 14 months. In the end, the deployed system produced 66% complete data records with 34% failure rate. Observation stations X3H002, X3H023 and X3H015 were successful in collecting all data for the entire deployment duration, and the data were usable after only minor sensor drift correction. Large data loss was experienced at observation station X3H008. All data from the Casteel station was lost due to vandalism early in the deployment. The factors that can contribute to data loss include, among others: electronic failures (often due to moisture ingress to the sensor head, or to the logger box); signal interferences, for instance resulting from lightning strikes; sensor drift beyond the required accuracy due to biofouling; power supply failure; damage by flood debris; cable deterioration through exposure; vandalism and theft. Amongst these possible causes of data capture failure, the largest was due to the loss of one entire station due to theft and vandalism, which accounted for 18.5% data loss alone. This station that was vandalised is not a long-established DWS weir, and had no secure instrument box in which to place the logger, nor a solidly-engineered structure in which to lodge and protect the cable and sensor head. Installations at the four official DWS weirs did not experience theft or vandalism, although this is acknowledged to be a problem nationally with deployed automatic data collection systems. The next most important factor was intermittent electronic failure at X3H008. There were unexplainable periods of equipment switch-off, amounting to three-quarters of the potential data for this station, but only 15.5% overall system data loss (see Table 3). Table 4 consists of a statistical summary depicting system accuracy and precision evaluated by means of regression analysis of the measured and modelled salt flux at each observation station as well as site specific calculated EC:TDS conversion factor.

Data gap-filling

In order to perform the salt-budget closure test it was necessary to fill gaps in the downloaded records. A linear interpolation was performed to compute missing data periods at observation station X3H008. In other words, straight line was drawn from the last value before failure, to the first value after failure. This is clearly not realistic, but is the simplest assumption, and one that does not contaminate the analysis with artifacts resulting from a more complex, but unconstrained interpolation model. The station at Casteel was simply dropped from the analysis.

Table 3: Summary of data completeness

System	Date and time deployed	Date and time recovered	Number of installation days	Number of records per day (Temperature, Water level & EC)	Theoretical number of records possible for installation days	Data downloaded	% Useful data (Temperature, Water level & EC)	% Data loss
CASTEEL_A	2018/09/19 18:00	2019/06/13 8:35	430	144	61920	2877	04.60	95.40
X3H008_B	2018/09/19 14:00	2019/11/20 9:00	427	144	61488	16179	26.30	73.70
X3H002_C	2018/09/18 11:30	2019/11/20 14:30	428	144	61632	61608	99.97	00.04
X3H023_D	2018/09/18 14:30	2019/11/19 10:00	427	144	61488	61404	99.98	00.14
X3H015_E	2018/09/20 12:25	2019/11/21 10:30	429	144	61776	61428	99.49	00.57
All sensors	Data Completeness				308304	203496	66.0	33.99

Table 4: Validation of observed vs modelled salt flux (µS/cm) computation approaches and site specific calculated EC:TDS conversion factor (see Equation 4). (read together with Figure 15—the graphic presentation)

SITE NAME	Slope	Intercept	R^2	Residual Standard Error	Percentage error	EC to TDS Conversion factor (CF)
X3H008	1.026	2.18	0.63	0.277	12.71	0.60
X3H002	0.525	0.26	0.62	0.210	80.77	0.34
X3H023	1.875	5.36	0.67	2.876	53.66	0.21
X3H015	0.397	1.05	0.77	0.314	29.91	0.74

Sensor drift correction

Once the field-collected data is downloaded, it is still not ready for immediate use. A two-point calibration (0 and 1413 µS/cm) was applied on EC data records after every download, water level data records were calibrated with DWS continuous water quantity data and temperature was observed with EC calibration. Four calibration checks were performed—each time, downloaded data was corrected to account for the sensor drift experienced (see Table 5). Furthermore, calibration results and field measurements data records were used to verify as well as correct systematic drift on continuous data records (see Table 5 & Figure 8). Linear adjustment were performed to correct sensor drift. Manufacturer's accuracy is reported +/- 0.01 dS/m (equal to: 10 µS/cm). A summary of actual sensor drift and accuracy is reported in Table 5. Sensor accuracy is the the slope of the relationship between sensor measured EC and standard solution EC, while sensor drift is the difference in this slope between different calibration dates. Overall sensor drift at each station had a range of 0.4 – 0.65 % below manufacturer's given value (see Table 5).

*Table 5: Relationship of standard solution EC (µS/cm) vs sensor measured EC (µS/cm) (read with **Figure 8**) and overall sensor drift at each observation station.*

	Pre-installation	First calibration after installation	Second calibration after installation	Post-installation	Overall sensor drift during deployment period	% sensor drift
	(µS/cm)	(µS/cm)	(µS/cm)	(µS/cm)	(µS/cm)	
X3H008: Slope	0.982	1.002	1.026	1.026		0.4
Intercept		14.1	15.5	15.8	0.04	
R^2	1.00	0.99	0.99	0.99		
X3H002: Slope	1.006	1.015	1.060	1.059		0.53
Intercept			12.6	12.9	0.053	
R^2	0.99	0.99	1.00	1.00		
X3H023: Slope	0.974	1.105	1.034	1.039		0.65
Intercept		7.4	12.7	12.9	0.065	
R^2	0.99	0.99	0.99	0.99		
X3H015: Slope	0.982	1.012	1.016	1.018		0.36
Intercept		2.8	12.4	12.4	0.036	
R^2	1.00	0.99	0.99	0.99		

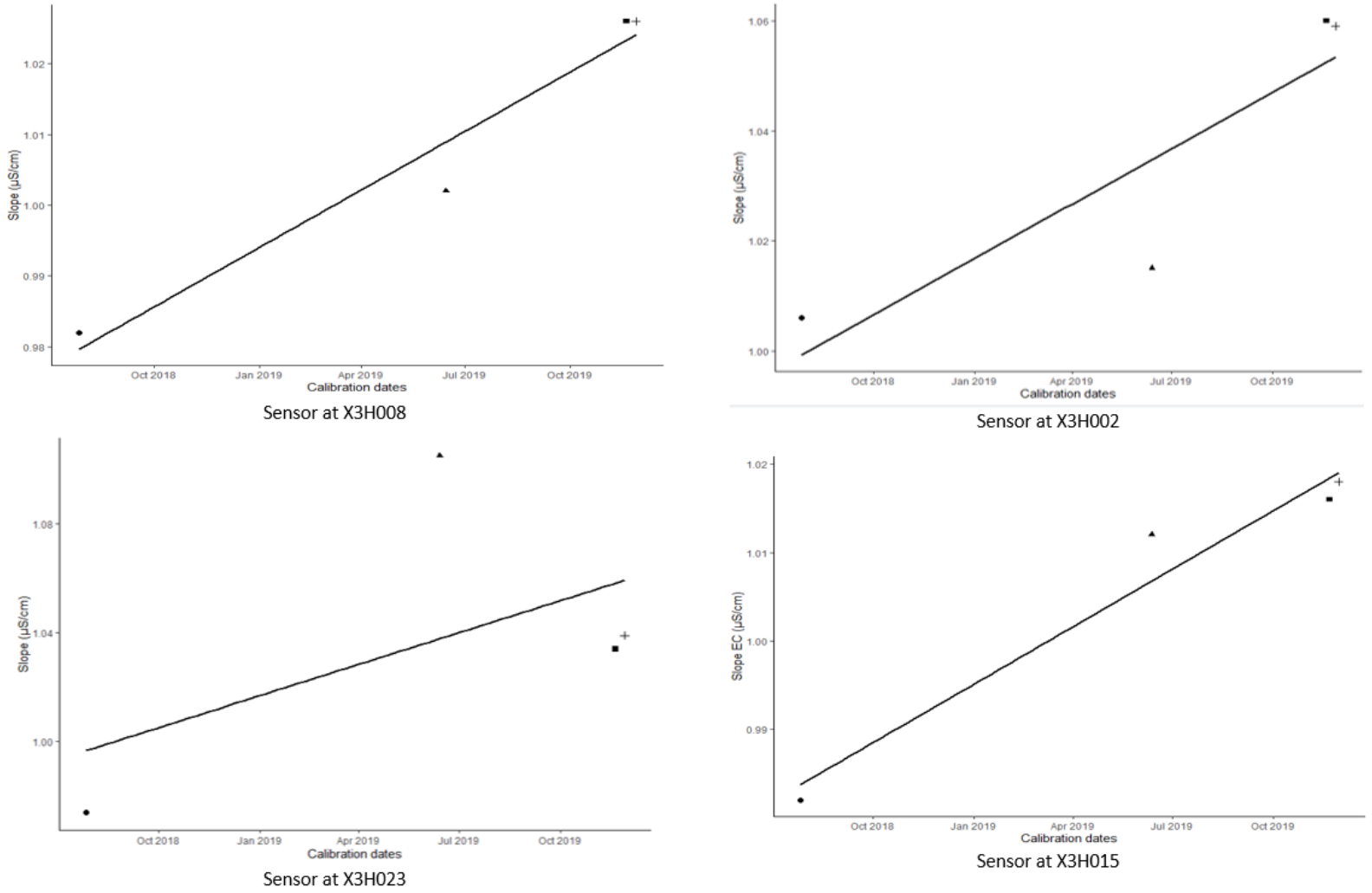


Figure 8: Relationship of standard solution EC vs sensor measured EC. Legend: ●*: **Pre-installation**,* ▲*: **First calibration after installation**,* ■*: **Second calibration after installation**,* +*: **Post-installation** (read with **Table 5**).*

Data records from individual stations

Here presented is TDS, stream flow and the salt flux at each observation station (with the exception to Casteel). The period reported is 18-19 Sept 2018 to 10-11 June 2019—the initially expected period of 18-19 Sept 2018 to 18-19 Sept 2019 was not possible due to limitations in the availability of DWS hydrological data for July, August and September.

Observation station X3H008 (Figure 9)

Data logger failure was experienced from 24 October 2018 to 14 June 2019, and again 30 August 2019 to 19 September 2019 (here not reported, due to lack of DWS hydrological data). The reported equipment operational period—19 September- to 24 October 2018 depicts a salt flux with a range of 2.60- to 7.89 kg/day. A straight line was drawn from the last value before failure, to the first value after failure for the period 24 October 2018 to 14 June 2019—this resulted in a salt flux with a range of 1 - to 100.0 kg/day, with significant events occurring 1 – 3 January 2019 (85.90- to 100.10 kg/day), 27 - 28 January 2019 (53.30- to 38.20 kg/day), 4 - 5 February 2019 (43.80- to 48.60 kg/day), and 14 February 2019 (69.60 kg/day). Due to equipment failure—15.5% observation network data loss resulted from this station.



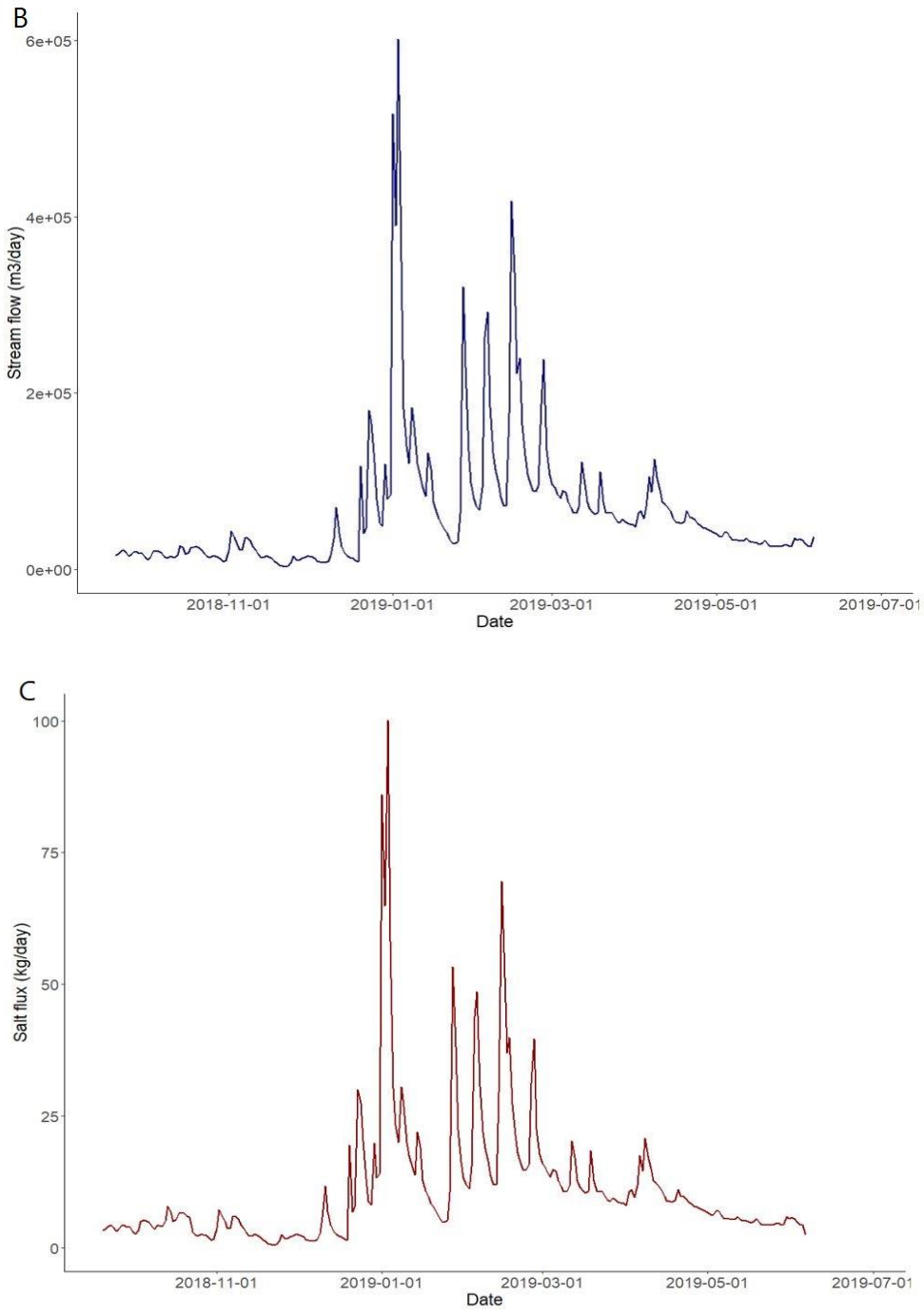
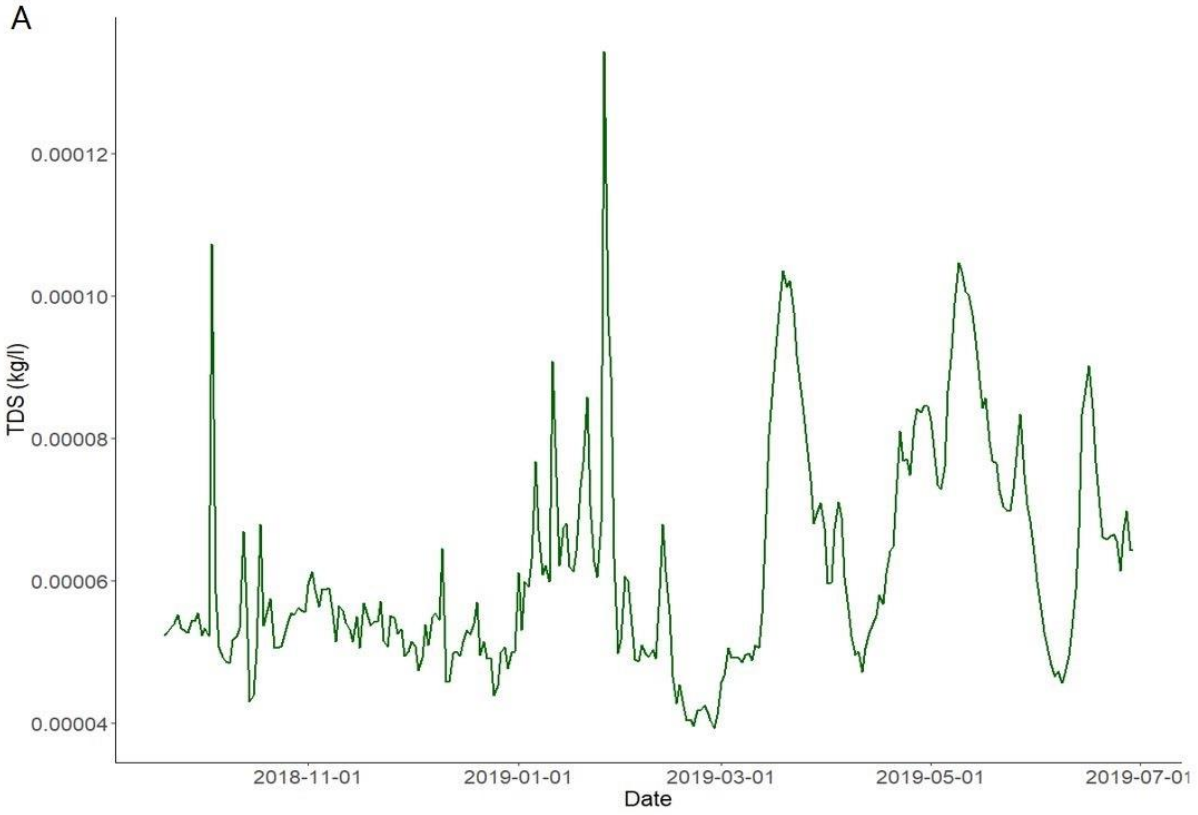


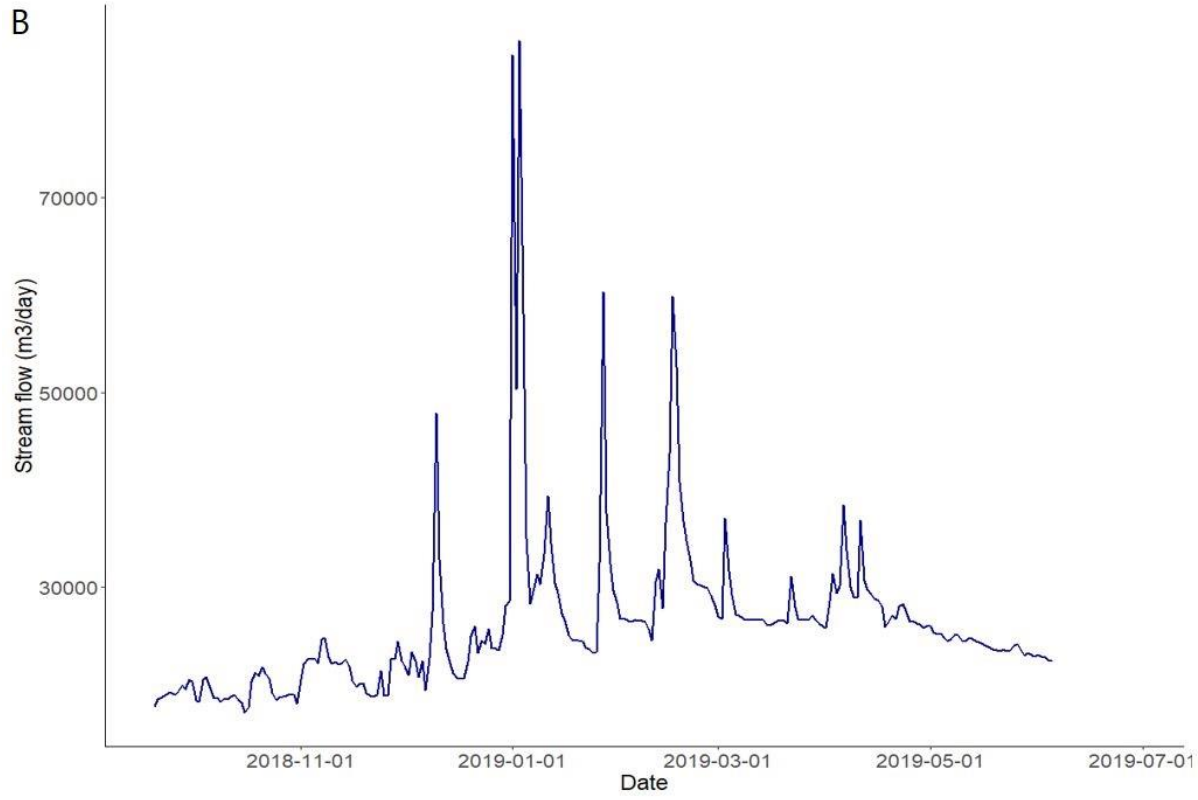
*Figure 9: Data records from observation station X3H008, where, **A**: TDS, **B**: Stream Flow, & **C**: Salt Fluxes*

Observation station X3H002 (Figure 10)

There is a range of salt fluxes 1.00 kg/day to 4.07 kg/day, with a significant salt flux events occurring on 1-5 January 2019 and 24-30 January 2019. During these days, the salt fluxes increased from 1.42- to 4.57 kg/day and 2.22- to 8.11 kg/day respectively. There are notable periods of decrease and increase in the salt fluxes with an increase in stream flow and/or TDS concentrations. These are, 06 October 2018, salt flux increased with TDS; 1-5 and 24-30 January 2019,

salt fluxes increase simultaneously with the increase of TDS and stream flow; the period of 28 February- to 06 June 2019—salt fluxes remain on the lower ranges while TDS and stream flow fluctuate with notable increases corresponding with those depicted in the salt fluxes, and lastly, the small increase in the salt flux on 23- to 26 March 2019 corresponds with an increase in stream flow while TDS predominantly decrease.





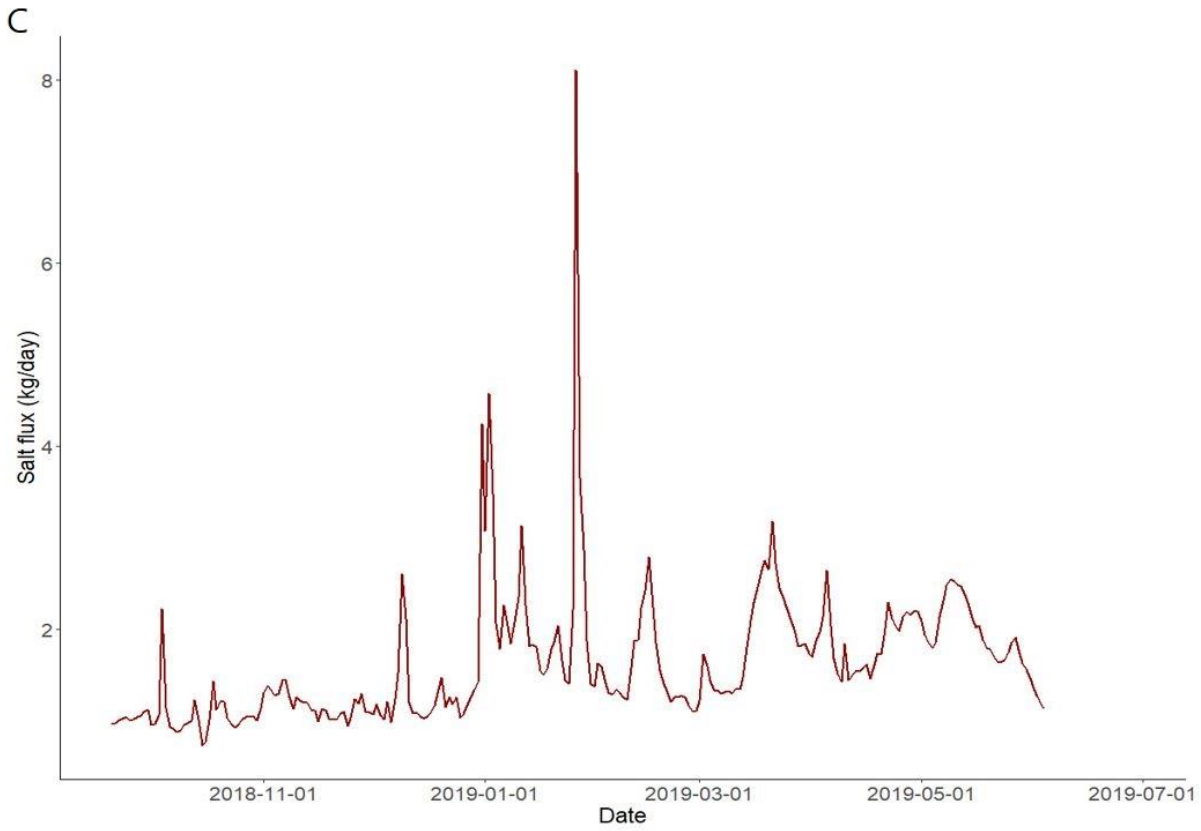
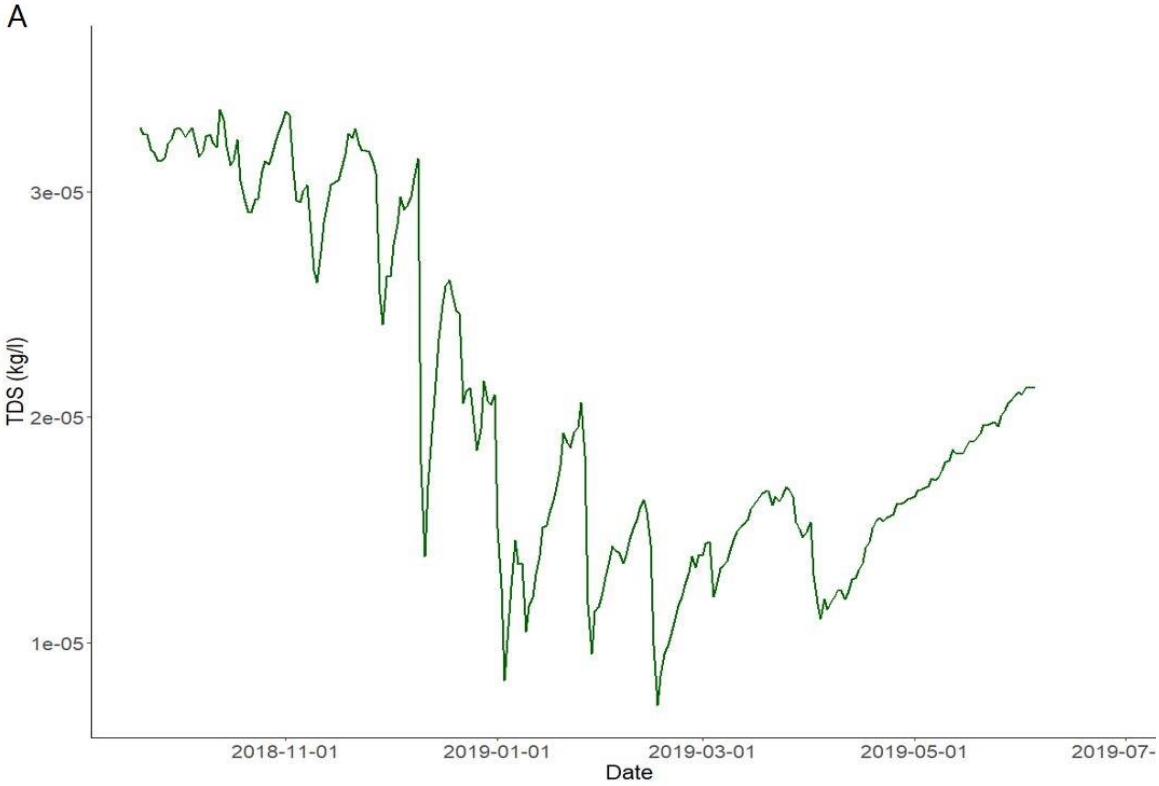


*Figure 10: Data records from observation station X3H002, where, **A**: TDS, **B**: Stream Flow, & **C**: Salt Fluxes*

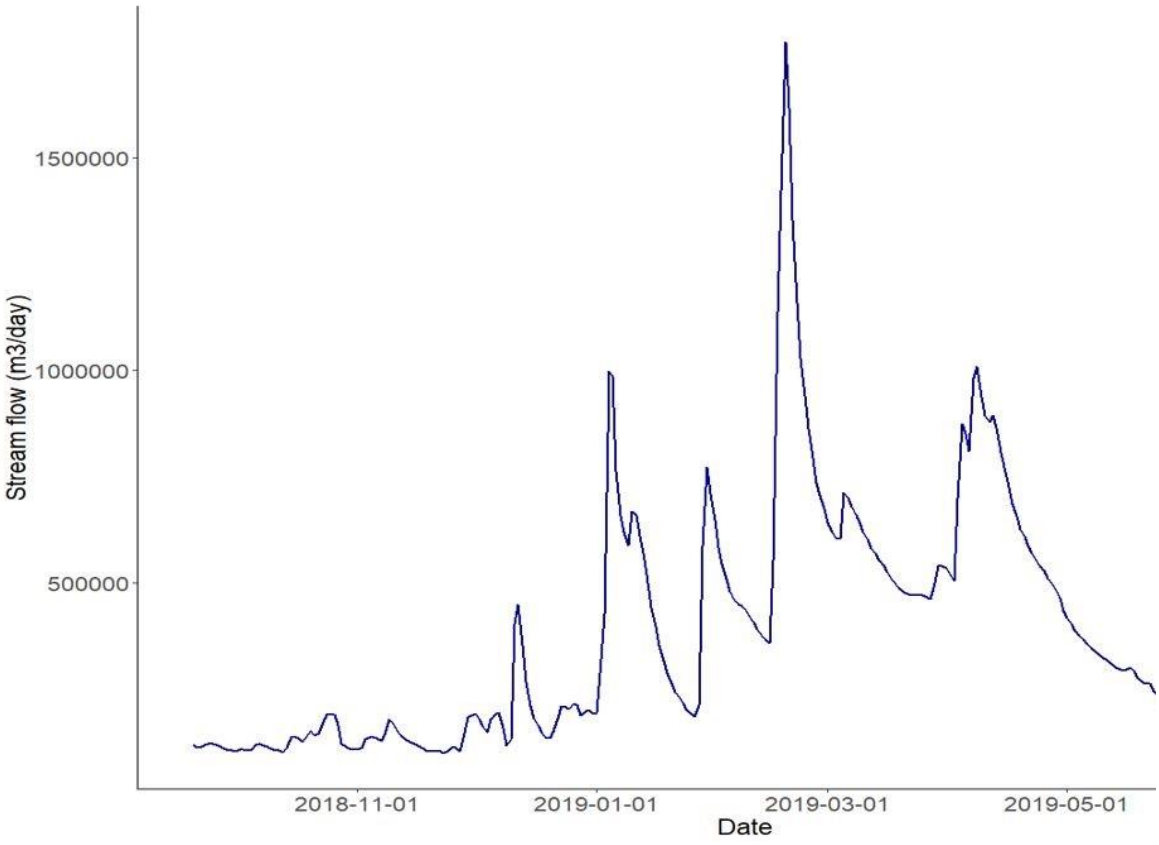
Observation station X3H023 (Figure 11)

The salt flux observed at this station can be separated (by eye) into three distinctly different periods: 19 September- to 08 December 2018 with a range of 3.21- to 5.91 kg/day; 08 December 2018 to 06 April 2019 with a range of 3.62- to 15.38 kg/day and 25 April- to 06 June 2019 with a range of 3.64- to 8.027 kg/day. The period of interest with significant events is 08 December 2018 to 06 April 2019. During this period: a). Salt fluxes increased with an increase in stream flow and a decrease in TDS on 08-11 Dec 2018, 20 December 2018 to 04 January 2019, 25-28 January 2019, 12-18 February 2019, and 1-6 April 2019, b). The salt fluxes decrease with stream flow while TDS increase on 03- to 25 January 2019 and 28 January- to 12 February 2019, and lastly, d). Salt fluxes decrease while stream flow increases and TDS prominently increase on 11- to 20 December 2018, 18 February- 26 March 2019 and 29 March- to 1 April 2019.

A


3e-05
2e-05
1e-05
TDS (kg/l)
2018-11-01
2019-01-01
2019-03-01
2019-05-01
2019-07-
Date

B


1500000
1000000
500000
Stream flow (m3/day)
2018-11-01
2019-01-01
2019-03-01
2019-05-01
Date

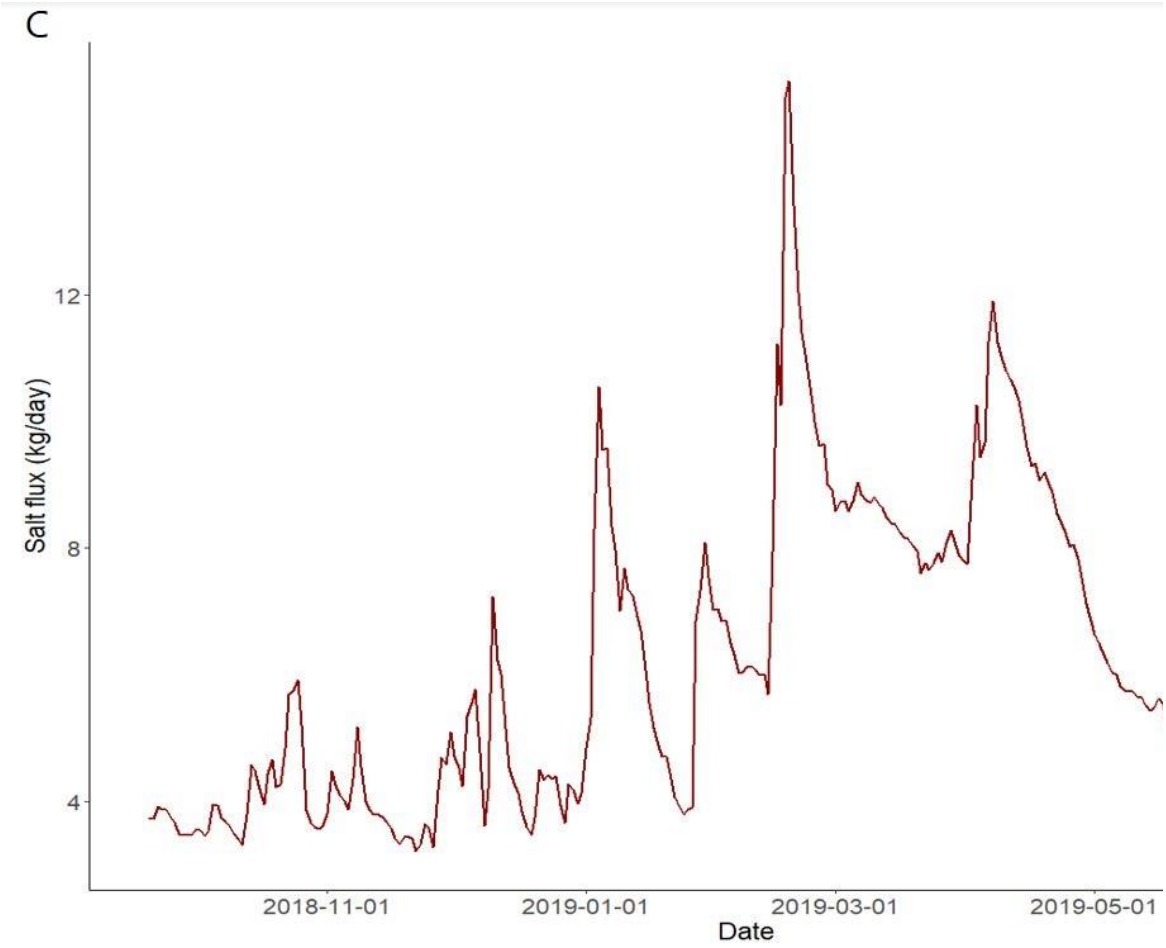
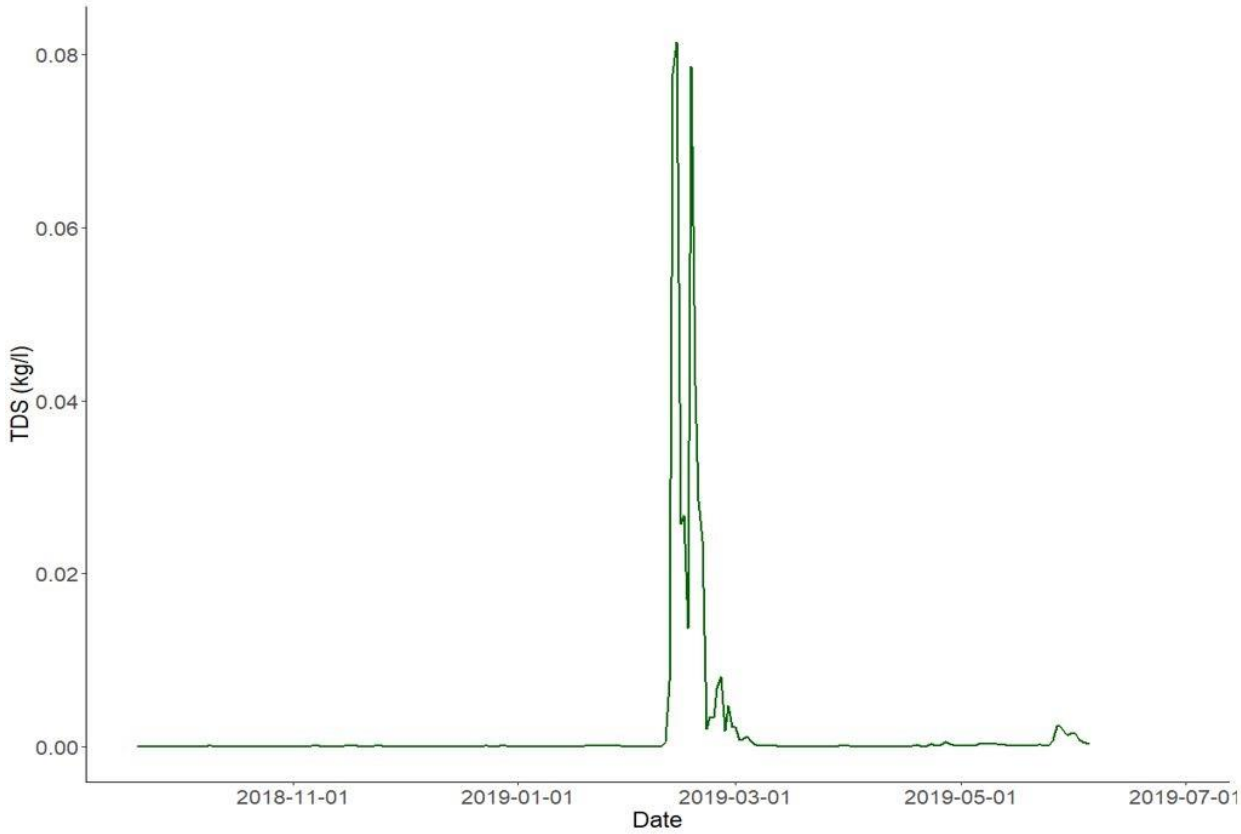


*Figure 11: Data records from observation station X3H023, where **A**: TDS, **B**: Stream Flow, & **C**: Salt Fluxes*

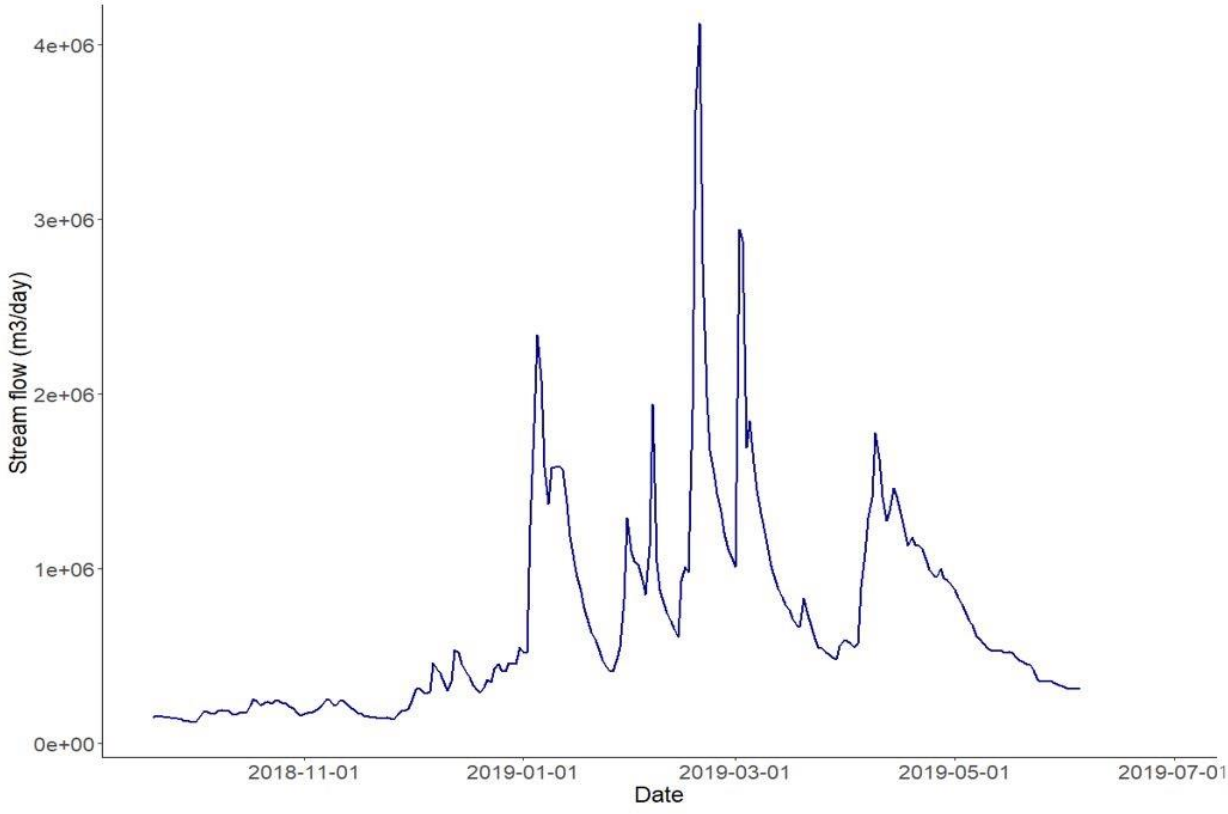
Observation station X3H015 (Figure 12)

The majority of the salt export from this catchment occurred in a brief period, 11-27 February 2019. During this period, maximum salt fluxes occurred on 12-13 February with 50805.03- and 49443751 kg/day, respectively; 17-18 February 2019 with 149831.029- and 151577.83 kg/day, respectively; 24-25 February 2019 with 9768.29- to 10802.38 kg/day and lastly, on 27 February 2019 with 5269.72 kg/day. The periods of highest salt fluxes correspond with the simultaneous increase in TDS while stream flow decreases, with the exception of 17-18 February 2019—where all variables of interest increase on 17 February 2019 and only TDS declined on 18 February 2019.

A


0.08
0.06
0.04
0.02
0.00
TDS (kg/l)
2018-11-01
2019-01-01
2019-03-01
2019-05-01
2019-07-01
Date

B


4e+06
3e+06
2e+06
1e+06
0e+00
Stream flow (m3/day)
2018-11-01
2019-01-01
2019-03-01
2019-05-01
2019-07-01
Date

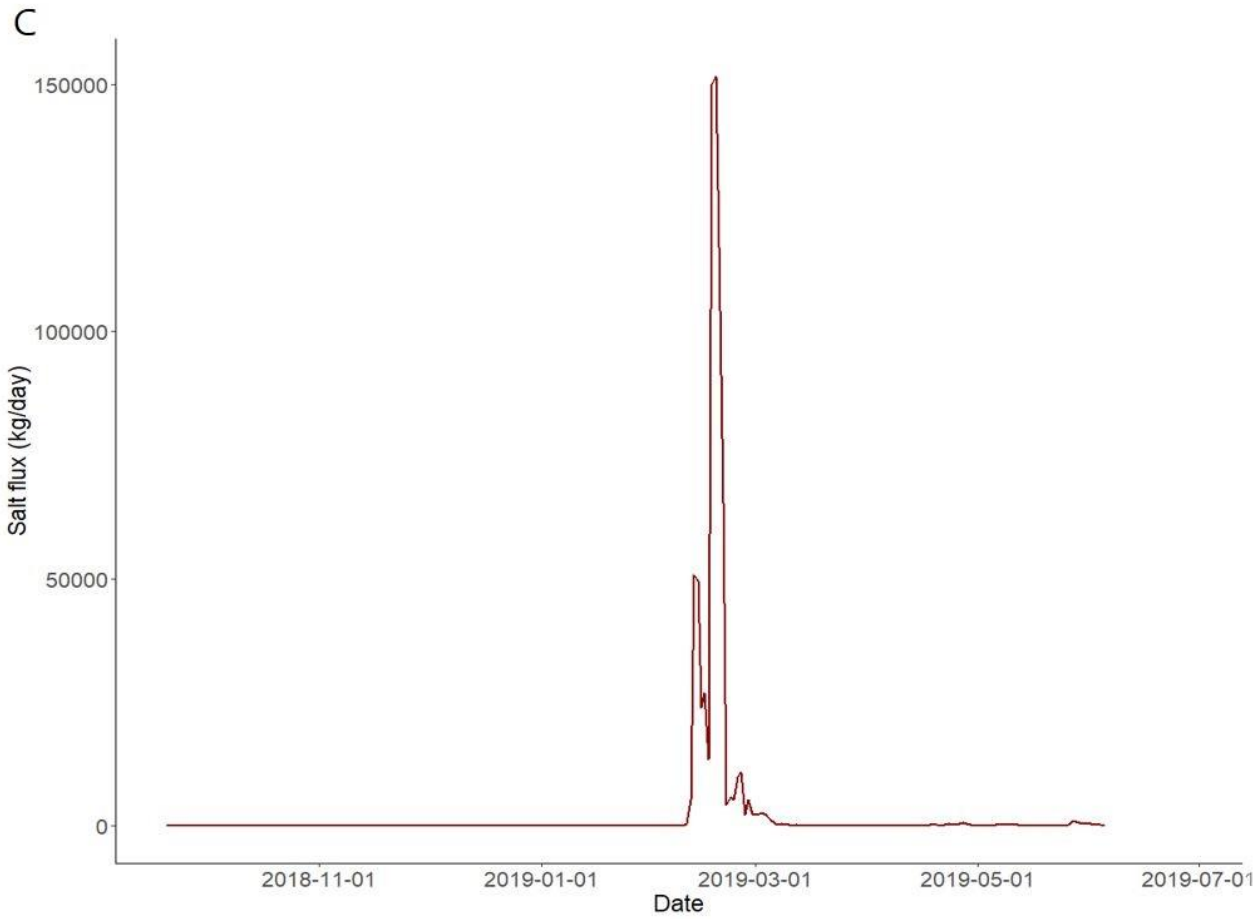


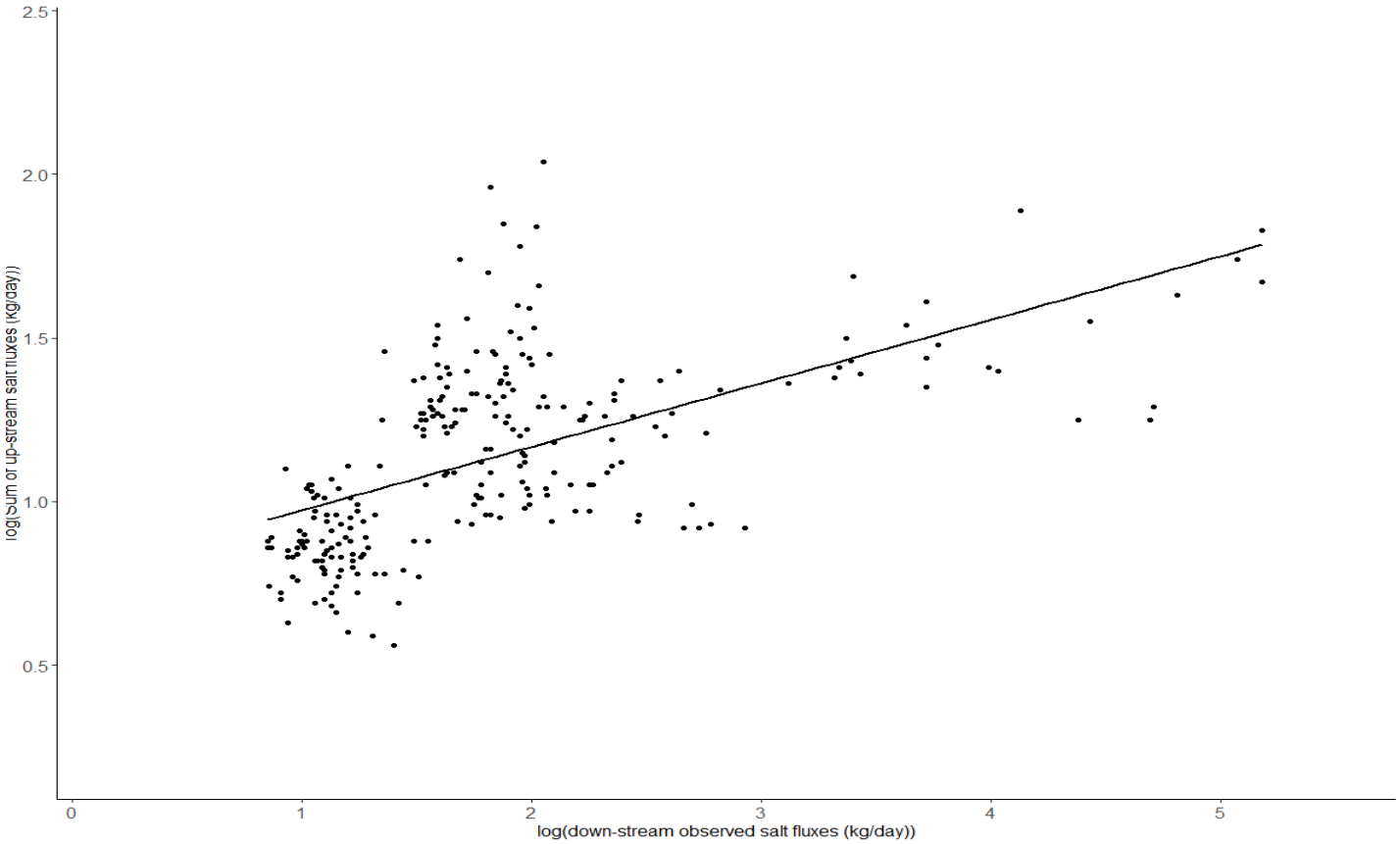
*Figure 12: Data records from observation station X3H015, where **A**: TDS, **B**: Stream Flow, & **C**: Salt Fluxes*

Catchment salt budget closure

Salt budget closure means that the salt flux at a downstream point is the sum of the salt flux at upstream points plus loses and gains between upstream and downstream conditions. To test the hypothesis, in Table 8 (stored in data archives), we evaluate if the sum of salt fluxes up-stream points (X3H008 plus X3H023) is approximately the same with the salt fluxes down-stream (X3H015) and Figure 13 is the regression results of the downstream salt fluxes vs the sum of salt fluxes up-stream. Results show that for the deployed observation network, the salt budget closure was in the order of 30%, which is about 20% more than the pre-defined error of + 10% (that is, achieved salt budget closure error minus pre-defined salt budget closure error (see: Equation 5)).

$$30\% - 10\% = 20\%$$

Equation 5

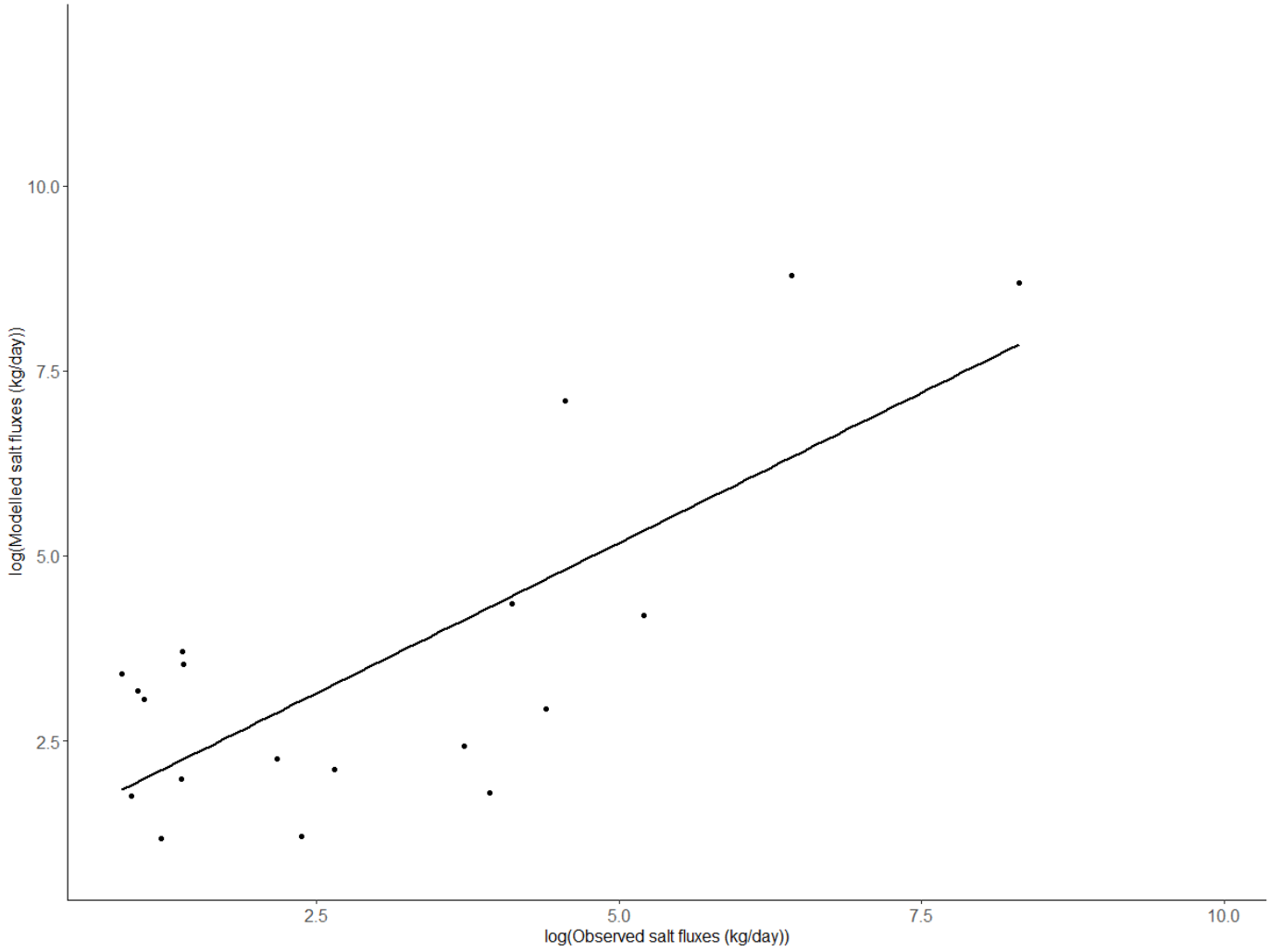


Slope	Intercept	R^2	RSE	% error
0.194	0.779	0.35	0.233	29.9

Figure 13: Salt budget closure (the values are expressed as their natural logarithm to accommodate the range).

Continuously-observed vs monthly modelled catchment salt flux

Salt flux is a result of salt concentration multiplied by stream-flow. In the absence of continuous data records obtained in this observation network, the salt flux is computed as per Figure 7—where historical DWS TDS data is the salt concentration and stream-flow is computed by catchment area, rainfall, and runoff coefficient. Table 6 reveals the modelled salt flux calculations, while Figure 14 and Table 4 presents regression results of observed vs modelled salt fluxes in all observation stations. The modelled salt flux was computed as to illustrate salt flux computations in the absence of continuous data records. Evidently, the computation of hydrochemical systems (that is, catchment salt fluxes) with existing estimates of manual sampling (and other data records of estimate) are not adequate to represent the true hydrological events that occur within a catchment. The modelling approaches either extremely over- or under-estimate catchment salt fluxes.



Slope	Intercept	R^2	MSE	% error
0.827	0.83	0.51	1.58	189.7

Figure 14: Linear regression results of observed vs modelled salt flux for all observation stations (the values are expressed as their natural logarithm to accommodate the range).

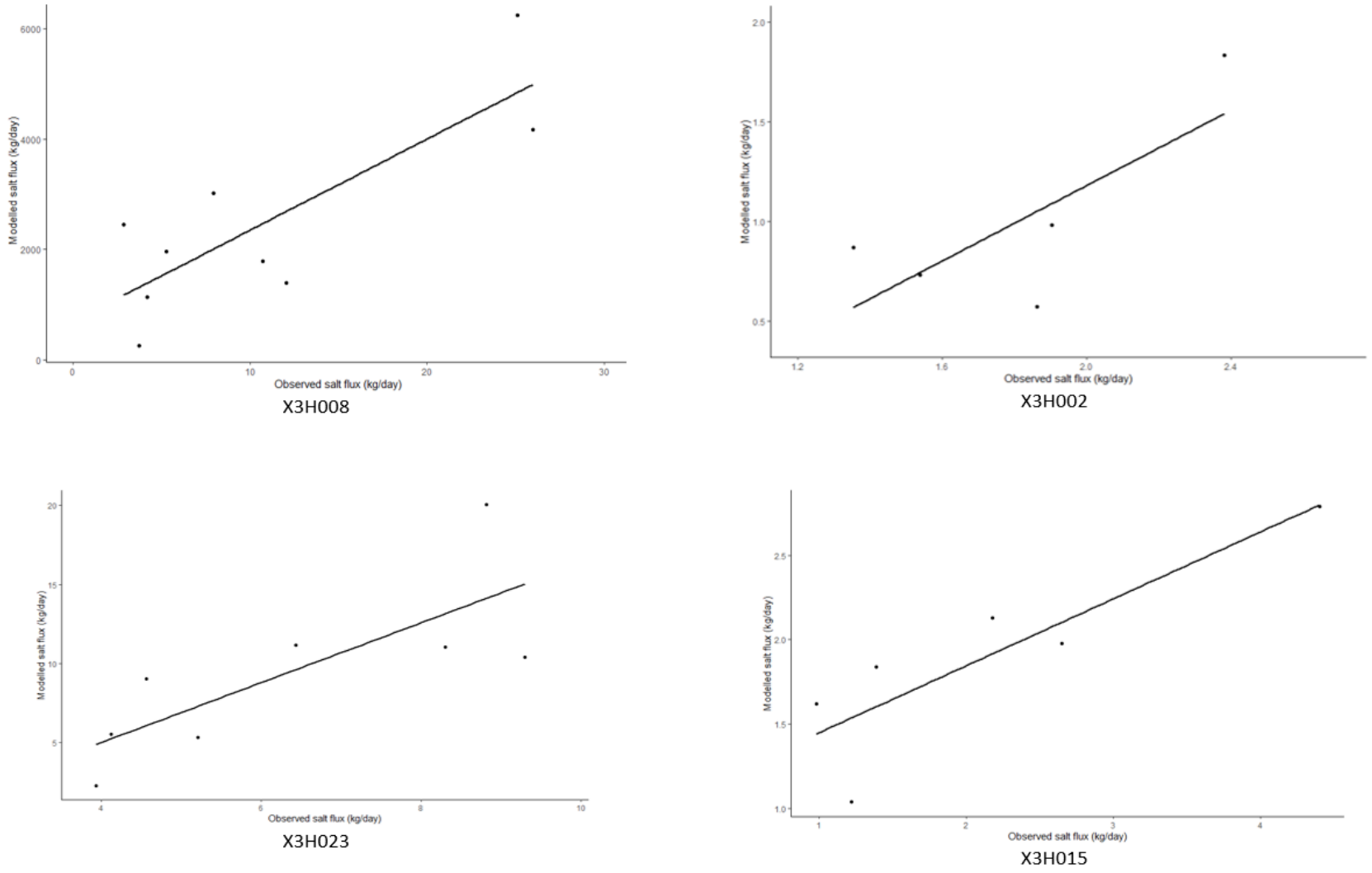


Figure 15: Linear regression analysis showing a positive and significant relationship between the observed vs modelled salt flux (read with Table 4 for the slope, R^2 and intercepts)

*Table 6 Modelled salt flux calculations: Salt flux is defined by flow * concentration—in the modelled salt flux. a monthly salt flux was computed based on catchment area accumulated flows and the DWS monthly manually sampled salt concentration (TDS) for each station as per Figure 7B calculation Figure. This would be how salt balance would be calculated in the absence of automated measurement (see Figure 7B for model calculation steps).*

X3H008	Area	*	Rainfall	*	Run off coefficient	*	TDS	=	Modelled salt flux
	(m^2)		(m/day)		ND		(kg/l)		(kg/day)
September			$1,4x10^{-3}$				$1,7x10^{-4}$		211.88
October			$6,0x10^{-3}$				$1,8x10^{-4}$		940.92
November			$2,1x10^{-2}$				$1,1x10^{-4}$		2027.39
December			$2,2x10^{-2}$				$1,3x10^{-4}$		2490.12
January	$4,6x10^{+9}$		$5,3x10^{-2}$		0.19		$1,1x10^{-4}$		5160.06
February			$3,9x10^{-2}$				$1,0x10^{-4}$		3447.16
March			$1,2x10^{-2}$				$1,1x10^{-4}$		1151.98
April			$1,5x10^{-2}$				$1,1x10^{-4}$		1480.73
May			$1,5x10^{-2}$				$1,2x10^{-4}$		1620.23

X3H002	Area	*	Rainfall	*	Run off coefficient	*	TDS	=	Modelled salt flux
	(m^2)		(m/day)		ND		(kg/l)		(kg/day)
September			$3,8x10^{-3}$				$9,8x10^{-5}$		0.17
October			$5,6x10^{-3}$				$1,0x10^{-4}$		0.26
November			$1,4x10^{-2}$				$1,0x10^{-4}$		0.61
December			$1,4x10^{-2}$				$9,1x10^{-5}$		0.57
January	$1,8x10^{+6}$		$3,0x10^{-2}$		0.25		$8,8x10^{-5}$		1.21
February			$1,1x10^{-2}$				$9,9x10^{-5}$		0.48
March			$1,4x10^{-2}$				$1,0x10^{-4}$		0.65
April			$1,0x10^{-2}$				$8,2x10^{-5}$		0.38
May			$0,0x10^{0}$				$9,0x10^{-5}$		0.17

X3H023	Area	*	Rainfall	*	Run off coefficient	*	TDS	=	Modelled salt flux
	(m^2)		(m/day)		ND		(kg/l)		(kg/day)
September			$3,8x10^{-3}$				$1,1x10^{-4}$		2.43
October			$6,3x10^{-3}$				$1,1x10^{-4}$		4.35
November			$4,3x10^{-3}$				$6,9x10^{-5}$		1.80
December			$1,6x10^{-2}$				$7,1x10^{-5}$		7.09
January	$2,8x10^{+7}$		$1,6x10^{-2}$		0.22		$9,2x10^{-5}$		8.79
February			$2,8x10^{-2}$				$9,2x10^{-5}$		15.76
March			$1,6x10^{-2}$				$9,1x10^{-5}$		8.69
April			$1,3x10^{-2}$				$1,0x10^{-4}$		8.16
May			$3,7x10^{-3}$				$1,9x10^{-4}$		4.20

X3H015	Area	*	Rainfall	*	Run off coefficient	*	TDS	=	Modelled salt flux
	(m^2)		(m/day)		ND		(kg/l)		(kg/day)
September			$5,0x10^{-4}$				$1,7x10^{-4}$		57.19
October			$0,0x10^{0}$				$1,9x10^{-4}$		0.00
November			$1,5x10^{-4}$				$1,5x10^{-4}$		15.07
December			$1,0x10^{-3}$				$1,3x10^{-4}$		94.47
January	$4,6x10^{+9}$		$0,0x10^{0}$		0.15		$1,3x10^{-4}$		0.00
February			$3,9x10^{-3}$				$3,2x10^{-4}$		849.77
March			$1,8x10^{-3}$				$1,1x10^{-4}$		129.48
April			$1,6x10^{-3}$				$1,7x10^{-4}$		182.17
May			$0,0x10^{0}$				$1,6x10^{-4}$		0.00

Table 7: Evaluating the extent of over- or under-estimation of modelled vs observed salt flux computation approaches for all observation stations (B – E) in the Sabi Sand catchment for the viable deployment period (18-19 Sept 2018 to 10-11 June 2019).

Interpretation note: Calculation of salt flux over/under estimation by Tofallis., 2009. Empty cells (ND = No Data) reflect the absence of original data from Department of Water & Sanitation (DWS) (for modelled salt fluxes)

Observation station	Observed salt fluxes	Modelled salt fluxes	Difference between Observed and Modelled salt fluxes	% percentage over/under-estimation
	kg/day	kg/day	kg/day	kg/day
X3H008 (B)	0.57	2.33	-1.76	-308.77
	0.62	2.97	-2.35	-379.03
	0.46	3.31	-2.85	-619.57
	0.90	3.40	-2.50	-277.78
	1.40	3.71	-2.31	-165.00
	1.41	3.54	-2.13	-151.06
	1.08	3.06	-1.98	-183.33
	1.03	3.17	-2.14	-207.77
	0.72	3.21	-2.49	-345.83
X3H002 (C)	1.03	0.17	0.86	83.50
	1.06	0.26	0.80	75.47
	1.17	0.61	0.56	47.86
	1.35	0.57	0.78	57.78
	2.38	1.21	1.17	49.16
	1.54	0.48	1.06	68.83
	1.90	0.65	1.25	65.79
	1.86	0.38	1.48	79.57
	1.98		1.98	100.00
X3H023 (D)	3.72	2.43	1.29	34.68
	4.12	4.35	-0.23	-5.58
	3.93	1.80	2.13	54.20
	4.56	7.09	-2.53	-55.48
	6.43	8.79	-2.36	-36.70
			0.00	
	8.30	8.69	-0.39	-4.70
	5.21	4.20	1.01	19.39
	4.12		4.12	100.00
X3H015 (E)	3.93		3.93	100.00
	4.56		4.56	100.00
	0.98	1.76	-0.78	-79.59
	1.08		1.08	100.00
	1.22	1.18	0.04	3.28
	1.39	1.98	-0.59	-42.45
	1.86		1.86	100.00
	4.40	2.93	1.47	33.41
	2.65	2.11	0.54	20.38
	2.18	2.26	-0.08	-3.67
	2.33		2.33	100.00

DISCUSSION

The observed low per unit catchment area salt fluxes at observation station X3H002 (and at Casteel, for the limited period of data availability) were expected, since these are upper-catchment sites with little land-use change that would be expected to yield significant salt loading. The salt content of the water increased in absolute terms downstream, as would be expected, and the salt fluxes, due to flow accumulation. The down-stream area-adjusted salt fluxes (to remove the effects of flow accumulation), showing the effect of land cover change, are revealed in the high range salt fluxes at observation station X3H008 (Sand River) when compared to X3H023 (Sabi River). In between is a landscape dominated by agricultural activities, large water abstraction & irrigation return flow for the Sabi River and one that is dominated by urbanization, water abstraction & returns of wastewater for the Sand River. The Sand River (X3H008) has higher salt concentrations, possibly attributable to direct stream discharge from the Thulamahashe wastewater treatment plant (WWTP) located upstream from the monitoring point. The river also collects effluents (resulting from poorly managed engineered drainage) from residential areas such as Dumphries, Thulamahashe, Edinburgh, Hluvukani, Athole, Allandale, there are also high levels of land degradation in the area. In addition, the site specific calculated EC:TDS conversion factor (see Table 4) falls in the higher range of those that are predefined by Hem, 1985. This is characteristic of water bodies rich in sulphate and non-ionized silica. Data logger failure (24/10/18 to 14/06/19 at X3H008) limit the analysis of the salt fluxes trend behaviour during this time as the patterns mostly result from stream flow variation, since the salt concentration in the water had to be assumed to be constant in the periods where data were missing.

At observation station X3H023, the salt flux varied simultaneously with stream flow increases and decreases in TDS due to dilution. There were few periods of interest where the salt fluxes decrease while TDS increased (e.g., on 03- to 25 January 2019 and 28 January- to 12 February 2019). The reason for increase in TDS with decrease in stream flow is thought to be stream water abstraction by activities such as agricultural irrigation schemes, water supply for tourism activities, reducing the dilution of a fairly steady flow of salt into the river (Dallas *et al*., 2004; Helmer *et al.*, 1997). Periods of high evaporation could have a similar effect. The conversion factor calculated for observation station X3H023 falls below the pre-defined range of converting electroconductivity into TDS. However, it is has a strong relation to the findings of a study by Hubert *et al*., 2015, which suggest an application of a conversion factor with the range of 0.25 to 1.34 (mg/l per µS/cm) for South Africa's mine water related water quality analysis. It is possible that the resultant conversion factor is due to stream water chemistry being influenced by effluents from old mines located within the catchment area (see Selebalo *et al.*, 2021).

At observation station X3H015 there are no Land use or cover types that would yield significant quantities of salt in the reaches between it, and the next upstream observation station. This station is located within Kruger National Park (KNP), which is a non-transformed nature conservation projected area with little water abstraction. It does include treated sewage effluent from the resting/research camp Skukuza, and minor drainage inputs from small tourist camps in the catchment. It also has no perennial river inputs, but subsurface drainage and ephemeral flows from several rivers, which all drain a granitic semi-arid area, which would be expected to deliver continuous background flows of salt from

weathering processes such as: rock weathering—a weathering process releasing dissolved ions such as sodium & sulphate (Vázquez *et al*., 2013; Alves *et al*., 2021). The brief period of high salt flux has a sensor reported electroconductivity of 2039.029- to 6440.103 µS/cm (151577.83 kg/day). According to the Revision of general authorisations in terms of section 39 of the National Water Act, 1998 (Act No. 36 of 1998) conductivity in effluent discharged into receiving water bodies should not exceed 70 - 150 mS/m (REPUBLIC OF SOUTH AFRICA NATIONAL WATER ACT, 2013). Therefore, based on this guideline, the sensor-measured peak electroconductivity exceeds acceptable limits for EC found in water bodies. These measured electroconductivity are similar to those found in untreated water from wastewater treatment plants or raw sewage (Samie *et al*., 2010; Iloms *et al*., 2020; Osuolale *et al*., 2015). World Health organisation water quality standard state that electroconductivity of surface water should not exceeded 400 µS/cm. The EC recorded by our sensors at the downstream observation stations does not comply to this standard. Such high EC values results into aesthetic effects in drinking water (e.g. change in taste/colour). In the case of agricultural and industrial activities, high conductivity may result in the decrease of crop productivity and for industrial water, in corrosion of metal surface equipment (Kaushal et al., 2021).In surface water bodies, food-plant and habitat-forming plant species are eradicated by high salinity (Rahmanian *et al*., 2015).

In general, salt fluxes trend depicts a patterns of lower fluxes from April to August and higher fluxes during September to March.

Salt budget closure

Operational accuracy and fitness-for-purpose of the designed observation network was tested by its ability to achieve salt budget closure within + 10% error. Salt budget closure was quantified using an equation based on the conservation of mass, that is, the salt flux at a downstream point (at station X3H015) should be the sum of the salt flux at contributing upstream points (stations X3H008 plus X3H023) plus loses and gains between the upstream and downstream measurement stations. My results show that for the deployed observation network, the salt budget closure was in the order of 30%, which is about 20% more than the pre-defined error (see Equation 5).

I conclude that the achievement of salt budget closure would need a much denser sensor network and presumably one less vulnerable to vandalism and theft. The sensors themselves are relatively accurate (see Table 5Error! Reference source not found.), and the flow values have a reported error of around 5%, therefore their combined error is within the 10% target. Thus, the big catchment-level deviations must be because of salt entering the drainage system between the upstream and downstream monitoring stations. Therefore, I strongly recommend building redundancy in the sensor network—where having more sensors will eliminate monitoring challenges such as: equipment failure, equipment theft (and resultant data loss until this can be remedied), as well as to minimize the distance between monitoring points, as to capture additional catchment response to return flows from LULC activities.

For example (see *Table 7*), the highest percentage error of observed- vs modelled salt flux was depicted at station X3H008 (B; give % error here so the examiner doesn't have to go look it up) as the monitoring station that experienced data lost due to equipment connection interference. I believe the is opportunity to minimize system error with redundancy of monitoring equipment.

Network performance

The overall functionality and long-term performance of the CTD sensor connected to Em50 data logger was admirable as indicated by the overall percentage of system data loss (excluding vandalism), and the relatively high accuracy and low drift (see Table 3). With the exception to of the Casteel station where data was lost due site vandalism and the performed gap-filling at X3H008 due to equipment failure, a nearly complete system data set was possible for the deployment period. This system has demonstrated the competency of automated water quality observation systems to capture hydrochemical events which are not presented in traditional manual water quality monitoring (for example, episodic events captured at X3H015). These captured events create a platform for researchers to study coupled ecological-social systems processes and their links. For example, sensor measured electroconductivity values at X3H008 and X3H015 during episodic events are similar to those found in in wastewater effluents and it can be inferred that stream-water chemistry during this time was influenced by WWTP stream-discharge or failures in the engineered drainage system (Iloms *et al.*, 2020).

Despite experienced limitations—the applied continuous observation systems have captured hydrochemical phenomenon as they occur within this catchment. The use of a system system such as this, suitably modified to accommodate many more sensors, would allow monitoring of stream hydrochemical events as they occur at an increasingly complex environment across time and space. The quantity and quality of data records obtained in this observation network has potential to aid in numerous hydrochemical studies (for instance, modelling hydrochemical systems) facilitating decision-making (such as, water use allocation, adjustments of water management policies and water quality standards) especially for a rapidly transforming landscape with significant ecological importance, such as the Sabi-Sand catchment (Stolz, 2018; de Mendiguren *et al.*, 2001). Equipment field robustness was satisfactory. One out of five sensors failure, for unknown reasons, in a 14-months deployment under field conditions. Vandalism and theft are a bigger issue, which could be addressed by 1) locating sensors in secure sites 2) community engagement and education (Storey *et al*., 2016; Epstein *et al.*, 2002).

The system experienced approximately 1% sensor drift in the 14 month period. To ensure that accurate data records are captured by the sensor network, frequent (quarterly) system maintenance and sensor drift correction is necessary. The overall sensor drift was below the manufacturer's given value (see Table 3). The inconsistency in calibration results (Figure 8) demonstrates the difficulty of conducting a good calibration in the field and the necessity of laboratory calibration checks prior and post deployment when using sensor technology.

The biggest advantage of continuous observation systems is that they eradicate the main challenge in stream water quality monitoring, that is, the collection of sufficiently large data sets that accurately describe environmental phenomena (Tuna *et al*., 2013). However, these systems require careful management. Of highest importance is the

identification of all quality assurance factors limiting system accuracy for specified objectives. As a first of its kind in the EFTEON context, the deployed continuous water quality observation network in the Sabi-Sand Catchment performance was good when compared to traditional methods (that is, grab sample followed by laboratory analysis) of monitoring stream water quality. During the deployment period, the observation network presented episodic events reporting extremely high amounts of electroconductivity (6440.103 µS/cm) which has never been captured in manual grab samples data records. The quantity of continuous data records obtained exceeds the quantity of historical manual grab samples data records by orders of magnitude. For example, continuous data records (see: *Summary of data completeness table, column data downloaded (203496 records))* available for the deployment period far exceed those captured with grab sample (see: *Table 6 monthly TDS* (36 records)) monitoring. Particularly EC & TDS.

In the comparison of observed continuous vs monthly estimated salt fluxes we further realize the importance of high frequency data. Table 4 indicates that estimating the fluxes using monthly accumulated flows and single gad samples is poorer than anticipated in terms of representing the true hydrological events that occur within a catchment. Theoretically, we would expect a stronger correlation between the observed & modelled salt flux—where results depict small standard error, an R^2 approaching 1 and a mean slope of 1 (for every step increase in the observed-, there will be an equal step increase in the modelled salt flux). These expectations mainly because: water quality monitoring data (continuous & grab samples) were from the same locations/station. For example, consider the result slope of station X3H015 (Table 4), for one unit increase in observed salt flux—there is 0.397 kg/month of modelled salt flux, indicating how poorly modelled approaches/grab samples represent catchment hydrochemical behaviours at this station. This is also realised in the over/under estimation in Table 7, as well as in the daily data records which showed EC records not present in grab-sample data. Although poorer than anticipated, the resultant R^2 indicates a positive, linear relationship of moderate to strong strength between observed- & modelled salt flux. Evidently, Modelling approaches either extremely over- or under-estimate catchment salt fluxes (see Table 7). The biggest contribution to this is low frequency water quality data associated with manual grab sampling, since the flow records are already continuous and automated.

CONCLUSION

The implemented continuous observation system for EFTEON was considered to be appropriately successful for the deployed period. Despite specified limitations, the network was fit for continuous monitoring of the aquatic salt content and riverine salt flux of a catchment.

The pilot design consisted of five stations equipped with a Decagon CTD device that integrates Water Depth, Electrical Conductivity (EC), and Temperature sensors (CTD10/HYDROS 21) connected to a Em50 Logger (Em50G) in association with existing hydrological gauging stations. Although the calibrated accuracy of the sensors was adequate for the task, the station density was insufficient to achieve a salt budget closure of within 10% in a catchment of this size (7096 km^2). A rough estimate is that the station density be that a required density is three times higher, i.e. about 15 stations, or one per 500 km^2. Ideally, more stations will provide more data and accommodate any data losses as a result of sensor failures. Thus, we propose two sensors at one station will be appropriate for back-up measures. As the authors, we feel that accuracy was compromised by station density and loss of data for some periods. Further testing to decide on a specific number & configuration of sensors—we suggest building redundancy in the system to eliminate data loss. From the collected data and impact of data loss from the over & under estimation results of the model—we suggest building equipment redundancy in the system.

Performance of the sensing and logging equipment was fairly good across a varying field conditions at the Sabi-Sand Catchment, and it can be expected to last for up to five years in field conditions before replacement is necessary (Decagon Devices, 2012). I strongly recommend building redundancy in the sensor network—where having more sensors will eliminate monitoring challenges such as: equipment failure, equipment theft, to minimize the distance between monitoring points, as to capture additional catchment response to return flows from LULC activities

The accuracy and drift of the sensors was fit to capture aquatic salt content over time, across the range from clear mountain catchment waters to salt-contaminated lowland reaches. The desired accuracy can only be assured with in-field calibration checks approximately quarterly, and removal of the sensors (and replacement with a spare set while the original is cleaned and recalibrated) about annually for the CTD sensors. The frequent visits may not reduce vandalism, but would allow it to be detected early. The equipment as deployed is relatively cheap (R15 000 per set in 2017) so the most cost-effective strategy may be to simply plan for an acceptable level of attrition.

The amount of usable high-frequency data and captured short duration hydrochemical events advocates for the efficiency of continuous monitoring systems when compared to low-frequency data obtained via traditional manual monitoring. This trial deployment of the sensors and data loggers for an automated in-stream water flow and quality monitoring system, was intended to test field robustness of automated-measuring instruments for long term deployment before more expensive sensors are deployed. The insights gained from this pilot study support the use of continuous monitoring devices for electroconductivity (and at a later stage, once the technology stabilises, possibly for other variables as well), provided it is done within a well-managed framework, and with nationally-collected monthly

samples as a cross-check. Hydrochemical parameters such as electroconductivity are fairly easy to measure and form a basis for riverine salt content calculations, used as an early indicator of change in water-quality status. In addition, measured electroconductivity works well as a proxy for identifying the influence of various hydrogeochemical processes in water quality studies (se studies: Cano-Paoli *et al.*, 2019; Loock *et al.*, 2015). The implemented observation network has characterised the water quality status of clear mountain headwaters to slow moving rivers with varying land use changes influencing stream chemistry. This range is representative of many river systems in South Africa. Thus the methods developed in this study can be adapted and used for the development of continuous water quality monitoring systems elsewhere in the country.

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